THE APPLICATION OF RADIOCHEMICAL TECHNIQUES TO THE STUDY OF SURFACE REACTIONS.

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Stanley Affrossman.

Abstract

The aim of the investigation was to find the mechanism of selective catalysis in the Rosenmund reaction, i.e. the catalytic hydrogenation of acid chlorides to aldehydes under such conditions that no further hydrogenation takes place. Benzoyl chloride was chosen as the primary reactant in all the experiments. A detailed examination was made of the purity of the reagents. The reaction conditions were investigated to find the procedure necessary in order to give an optimum yield of aldehyde. The effect of controlled amounts of added impurities in the reaction mixture and in the synthesis of the catalyst was also examined.

A range of selective poisons for the reaction was investigated and it was found that the most powerful poison, i.e. the one which gave the largest yield of aldehyde with the minimum amount of poison added, was tetramethylthiourea. It was shown that decomposition or hydrogenation of all the poisons took place during the reaction. Elementary sulphur was found to be an efficient poison if added under the correct conditions. Palladium sulphide (PdS) catalysts decomposed with loss of sulphur under the reaction conditions and required addition of a sulphur poison in order to give a yield of aldehyde.

The effect of temperature on the reaction was also studied and it was found that the reaction products varied with the temperature.

To distinguish between consecutive and simultaneous reaction mechanisms, C^{14} labelled aldehyde was added to a hydrogenation. A loss of activity showed that the reaction proceeded in a stepwise manner, i.e. the primary reaction product could react further by being readsorbed on the catalyst surface.

As an aid to the elucidation of the mechanism, the adsorption of reactants on the catalyst surface was investigated by means of a liquid scintillation counter. An accurate method of determining the partition ratio of a reactant, between solvent and catalyst, in the presence of scintillation quenching effects was discovered. The adsorption of aldehyde was examined and there was shown to be a correlation between the amount of aldehyde on the catalyst surface and the rate of reaction at the corresponding concentration.

A mechanism for the selective action of the poison in the Rosenmund reaction was postulated to explain these results.

CHAPTER 1.

THE INTRODUCTION.

INTRODUCTION

The effect of small amounts of poisons in surface catalytic reaction systems is well known. Among the reviews in the literature on this topic may be mentioned those of Berkman, Morrell and Egloff(1), Emmett(2) and Maxted(3). The large number of examples quoted in these sources illustrates the importance of this field in catalysis. The detailed mechanism of poisoning is, however, still obscure in most cases, but the results of many experiments on poisoned reactions have given us a partial insight into the nature of poisons. This is especially true in the case of the electronic constitution of poisoning atoms or molecules and the poisoning of metal catalysts by alloy formation. It has become clear that the poisoning properties of an atom or molecule are associated with its electronic configuration(3). "Free" electrons are evidently necessary to give a poison to catalyst bond. Evidence of such a coordinate link between a sulphur poison, methyl sulphide, and palladium has been obtained directly by magnetic susceptibility(4). Consistent with this view is the fact that a shielded compound has no poisoning properties(3) and most detoxification techniques involve the conversion of an "unshielded" compound e.g. thiophene, into a "shielded" one, e.g. thiophane sulphone(5).

It is also possible to poison catalytic reactions by changing the electronic structure of the metal catalyst. A very elegant study of electronic effects has been made by Couper and Eley(6), who showed that palladium could be poisoned by absorption of hydrogen. Catalytic activity falls as hydrogen is dissolved in the palladium. Alloying palladium with gold has the same result. These effects are ascribed to the filling of the d-band of the palladium, which has to have vacancies in order to function as a catalyst.

There have been many discussions on the heterogeneity or homogeneity of catalyst surfaces with respect to catalysis. This arises from the postulate that specific sites are involved in catalysis and the hypothesis of active sites is often invoked to explain examples of selective catalysis. An example of this is the discovery by Vavon and Husson(7) that carbon disulphide poisoned platinum, first for hydrogenation of acetophenone, then cinnamic acid, nitrobenzene and finally benzene. This was taken as evidence of heterogeneity of surface sites. However, Herington and Rideal(8) showed that the surface could be considered homogeneous and the progressive poisoning explained as due to decreasing accessibility of the surface the larger molecules being poisoned first. The geometrical aspects of poisoning are not so well understood as the electronic effects. The importance of these aspects however led Balandin to formulate his theory of multiplets(9). In the multiplet theory it is postulated that catalytic activity is determined by the surface geometry of the catalyst. The catalytic units or multiplets assist the breaking of chemical bonds by exerting forces on atoms of molecules adsorbed on the catalyst surface. The multiplet theory has had its greatest success in the explanation of the dehydrogenation of saturated six membered rings. In these rings the shape of the molecule is rigidly fixed and the geometry of the catalyst plays a large part in the reaction as the rings have to lie flat on the surface of the catalyst to be dehydrogenated. The spacing of the atoms in the catalyst is critical, as the hydrogen atoms have to be attracted away from the ring, yet the carbon atoms of the ring must be held firmly. Only the octahedral faces of certain metals fit these requirements and it was found that only in these cases did dehydrogenation take place. With reactions having less well-defined geometry the multiplet theory does not always predict a result.

Maxted and Evans(10) examined the relationship between poison size and toxicity for a series of thiols and sulphides. The poisoning effect was shown to increase with increasing size of the poisoning molecule. In order to confirm that the increase in molecular size of the poison is responsible for the increase in poisoning effect, it is necessary to know the amount of poison actually on the catalyst surface. The partition of poison between solvent and catalyst was not measured for these poisons, and their results are based on the hypothesis that the poisons are all adsorbed to the same extent. Maxted and Evans(10) did attempt to measure partitions of poison between solvent and catalyst for other poisons, and they found little difference between apparent and true toxicity curves. To determine the partition ratio they used a kinetic method, as very small amounts of poison had to be measured. A more direct method of measuring the amount of poison on a catalyst surface was used by Minachev et al(11) who used active thiophene to determine the amount of poison taken up by platinum on alumina, used for the dehydrogenation of cyclohexane. He found that the sulphur content and the catalytic activity were related linearly. The use of a radioactive isotope overcomes the difficulty of measuring very small quantities of poison.

To elucidate properly the mechanism of poisoning of catalytic reactions we require a correlation between adsorption of the reactants and catalytic activity. While considerable efforts are being made to investigate this relationship in the gas/solid phases, relatively little has been done in the liquid/solid phases. The apparent lack of interest in the liquid/solid phases is due to the experimental difficulties involved. In the gaseous phase, it is possible to measure extremely small pressures and therefore measure directly changes of concentration produced by adsorption. The problem of adsorption measurements in the liquid phase cannot be solved so simply, and measurements of concentration have to be undertaken by chemical or physical analysis. The difficulties of measuring small quantities by analysis explains the lack of knowledge of liquid/solid adsorptions. Modern analytical methods are, however, overcoming the difficulties involved. The use of radio isotopes as an analytical tool has made the task much easier and radiochemical procedures are being developed rapidly.

The first approach to the determination of the adsorption of reactants on a catalyst surface is usually the measurement of surface areas. The determination of surface areas by adsorption from the liquid phase is progressing, as the following examples illustrate. The adsorption of aliphatic alcohols and acids, from aqueous solution onto non-porous carbons, has been studied by Hansen and Craig(12). The adsorption of various dyes on graphite has been studied by Giles et al.(13), whilst Kipling and Wilson(14) have shown that methylene blue is unsuitable as a standard adsorber as its mode of adsorption varies. Finally mention must be made of the use of C^{14} labelled acids by Ryan, Kunz and Shepard(15) to measure adsorption. The C^{14} was counted both in a gas counter and a liquid scintillation counter.

It was our intention to examine the mechanism of a selectively poisoned surface reaction, and to examine the distribution of reactants on a catalyst surface. The system chosen for investigation was the reaction discovered by Rosenmund(16). If we hydrogenate an acid chloride the products can be represented by,

$$R.COCl \rightarrow R.CHO, R.CH_2OH, R.CH_3.$$

Rosenmund found that addition of a "poison" to the system prevented the hydrogenation proceeding past the aldehyde stage. The Rosenmund reaction is therefore an example of selective catalysis. Much use has been made of the Rosenmund reaction in preparative organic chemistry and there is an excellent review by Mosettig and Mozingo(17) of the reaction conditions and compounds hydrogenated. The early work of Rosenmund and Zetzsche(18) showed that impurities, in the solvents used, were a controlling factor in stopping the reaction at the aldehyde stage, and they developed a "regulator", quinoline/sulphur, to make this control accessible. Weygand and Meusel(19) confirmed Rosenmund's results and suggested thiourea as a more quantitative regulator.

The Rosenmund reaction has been carried out under a variety of conditions, even as a gaseous phase hydrogenation(20,21). A number of solvents have been used(22), toluene and xylene are however the most common. The reaction has been carried out with and without poisons(23). Both aromatic and aliphatic acid chlorides have been successfully hydrogenated. Only the chlorides of the dibasic acids(24), and triphenylacetyl chloride(25), give no aldehyde; these acid chlorides being apparently unstable under the reaction conditions.

There is no general agreement in the literature on the reaction conditions to be chosen for any particular Rosenmund reaction. Sometimes poisons have been added, sometimes they have not. It is possible that they have often been present in the reagents.

As the object of the research was to discover a detailed reaction mechanism for the Rosenmund reaction, the first stage was to investigate the reaction in great detail to determine the correct reaction conditions. To eliminate any possible complications, e.g. steric or electronic effects, which would have arisen from the use of various reactants the reaction was carried out with a single acid chloride, benzoyl chloride, in a toluene solvent with palladium/barium sulphate as the catalyst.

After the reaction had been made reproducible the action of the poison on the hydrogenation was investigated. This was attempted by using various related poisons and examining their effect.

A study of the relative amounts of hydrogen absorbed during the reaction and the hydrogen chloride evolved at the same time, indicated which reaction steps were taking place and led to two stoicheiometric mechanisms.

The behaviour of active aldehyde, added during a Rosenmund reaction, eliminated one of these mechanisms and indicated the mechanism of poisoning.

The hydrogenation of aldehyde was then investigated and an attempt was made to correlate the catalytic activity with adsorption experiments carried out on active aldehyde. The last part of the thesis concerned the perfection of techniques for measuring adsorptions.

CHAPTER 2.

PREPARATION OF REACTANTS.

2. PREPARATION OF REACTANTS.

The first stage in the investigation was the purification of the reactants. This was necessary in order to obtain reproducible results and because the intention was to study the effects of added poison without accidental interference from contamination. In the following we consider the reaction components separately.

2.1. THE ACID CHLORIDE.

As stated in the introduction, the investigation would cover a single system intensively. It was therefore decided to use only one acid chloride so keeping this component of the reaction unchanged i.e. free from change in electronic or steric effects introduced by using various acid chlorides and so influencing the course of the reaction and its poisoning.

The acid chloride chosen was benzoyl chloride, the simplest member of the aromatic series used originally by Rosenmund(16).

The acid chloride was prepared by the action of a chloride on the corresponding acid. The two chlorides most commonly used are thionyl chloride and phosphorous pentachloride. The phosphorous chloride is unsuitable for the Rosenmund reduction as traces of phosphorous are difficult to remove from the acid chloride and may prevent the reaction taking place(26).

THE THIONYL CHLORIDE METHOD(27).

0.25 mole Benzoic acid and 0.30 mole thionyl chloride were refluxed for one hour on a water bath at 100°C. Unchanged thionyl chloride was then distilled off. The benzoyl chloride was distilled using a condenser with a calcium chloride guard tube to prevent entry of moisture. The boiling point of the acid chloride was 196°C. The nominal yield was 0.20 mole, but it was found that in order to remove all traces of sulphur compounds from the benzoyl chloride, quite a large initial amount of benzoyl chloride had to be rejected, so reducing the yield to 0.10-0.15 mole. If this was not done properly, then during a Rosenmund reduction, the reaction would start normally at a reasonable rate and then slow down. This was ascribed to sulphur compounds in the acid chloride which would rapidly hydrogenate to an unshielded structure and the rate would slow to a value too low for practical use.

If it was attempted to prepare small amounts of acid chloride, e.g. 1.0 g, then the fraction which had to be rejected, during distillation, resulted in a low yield. It was, therefore, always advisable to make large scale preparations as it was very difficult to remove sulphur compounds from small quantities of benzoyl chloride.

An alternative method of preparation using oxalyl chloride has been reported(28). Oxalyl chloride contains no sulphur or phosphorous poisoning atoms and the residual reaction products can be removed by vacuum distillation in many cases.

2.2. THE SOLVENT

At this stage we shall have to consider precisely what we mean by purity. When we add a suitable poison in a Rosenmund hydrogenation and stop the reaction after 1.0 mole of hydrochloric acid has been evolved, we find that the yield of aldehyde increases from zero to over 80% depending on the amount and type of poison. The criterion which was taken, therefore, was that a reactant was pure when, on added in a Rosenmund reaction, it produced no yield. This applies to all the reaction components but especially the solvent. Due to the great difficulties in removing all sulphur sources, complete purity was not always obtained and a small yield of aldehyde was often found even without adding poison.

The most commonly used solvents are hydrocarbons, e.g. toluene, xylene, decalin etc. These hydrocarbons contain sulphur compounds in varying amounts. As the Rosenmund reaction is very sensitive to certain sulphur compounds, e.g. 0.1 mg tetramethylthiourea with 0.3 g 5% Pd/$BaSO_4$ raises the yield of aldehyde from zero to 65%, the purification has to be very thorough. Ordinary distillation is inadequate, for the sulphur compounds distil over with the hydrocarbon. The method used throughout the following work was that reported by Zetzsche and Arnd(29), namely the use of aluminium chloride to remove the sulphur compounds. The aluminium chloride first forms an addition compound with the sulphur then eliminates it as H_2S(30). The solvent was distilled twice over aluminium chloride, shaken intermittantly with water for one hour, dried over potassium carbonate and finally over sodium. As traces of water stop the reaction all solvents must be thoroughly dried.

Other methods which have been used are washing the solvent repeatedly with concentrated sulphuric acid(29) or distillation over Raney nickel catalyst(31). As the washing procedure has to be carried out 25 times, the method was regarded as too laborious and wasteful of solvent for normal use. The distillation method is wasteful of catalyst. The purification of solvent by passage down a palladium catalyst column was investigated. Removal of sulphur compounds did take place, but like the distillation method a large amount of catalyst was wasted. The aluminium chloride method has been found to give pure solvents with the minimum trouble.

Solvents other than hydocarbons have been used, e.g. ethers(22), and we have found the reaction to proceed equally well in an ester (see later). In most of the reactions described in the following work, toluene has been used. It was found that even AnalaR toluene had to be purified in order to give zero yield of aldehyde in an unpoisoned Rosenmund reaction.

2.3. CLEANING OF APPARATUS.

The apparatus had to be free from traces of sulphur compounds. New apparatus could be cleaned ordinarily by being washed with water, then acetone. If an apparatus had been used for hydrogenations it was very difficult to remove small amounts of catalyst adhering to the vessel walls, frequently in inaccessible places. We found that apparatus could be cleaned effectively by refluxing therein a mixture of toluene and aluminium chloride for 30 mins. It was then washed with water and finally with acetone. This procedure was followed before every hydrogenation.

2.4. THE HYDROGEN.

The hydrogen was obtained from a cylinder. No purification or drying of the hydrogen was attempted nor was it found necessary.

Heterocyclic aldehydes are unstable in the presence of traces of oxygen. In preparations involving heterocyclic acid chlorides, traces of oxygen in the hydrogen can be removed by passage of the hydrogen over hot copper turnings(32).

2.5. THE CATALYST.

The catalyst used for the Rosenmund reaction is palladium deposited on a substrate such as barium sulphate(33), calcium carbonate(34) or charcoal(24). We restricted our choice to palladium om barium sulphate. The proportion of palladium can vary from 1.0 to 10.0 per cent.

Preparation of 5.0% Palladium/Barium Sulphate(17)

1.7 g Palladium chloride were dissolved in 100 ml. distilled water containing 1 ml. concentrated hydrochloric acid. A solution of 15 g anhydrous sodium sulphate in 200 ml. distilled water was added in the course of five minutes to a mechanically stirred solution of 21 g barium chloride dihydrate in 200 ml. distilled water at 70°C. The precipitate was washed, by decantation, with hot distilled water, till no more chloride was detectable in the washings. The barium sulphate was then suspended in 300 ml. distilled water containing 1 ml. 40% aqueous formaldehyde, the palladium chloride was added and the mixture was heated to 80°C and stirred continuously. I N Sodium hydroxide was then added over 15-30 mins till the solution was weakly alkaline to litmus. The heating and stirring was then contimued for 20 mins. The precipitate was washed by decantation with distilled water till chloride free. The precipitate was centrifuged and dried over silica gel in a vacuum desicator. The use of distilled water throughout should be noted.

It was found, that different catalysts of the same percentage palladium gave different reaction rates. A yield was obtained with all catalysts in spite of this variation. The difference in rates was probably caused by impurities giving a promotion effect. There have been many cases cited of this type of promotion, a typical example of which is the promotion of palladium on silica by silver, reported by Alchudzhyan and Mantikyan(35). The catalytic activity for the hydrogenation of benzene increases at first with increasing amount silver and then decreases. Promotion of this type may be related to the discovery of Wagner(36) that silver or boron in small amounts increases considerably the ability of palladium to absorb hydrogen. Adams and Carothers(37) promoted platinum catalysts with iron salts for the hydrogenation of benzaldehyde and as iron is a likely impurity in catalyst preparation a catalyst was made as above, but 5.0 mg ferric chloride were added to the palladium chloride/barium sulphate mixture before reduction; this gave approximately 0.01% Fe in the catalyst. This catalyst was compared with a commercial catalyst supplied by Johnson,Matthey & Co. Ltd., im which the iron content was known from spectrographic analysis to be 0.001%. The results are shown in the following table which gives the time of hydrogenation for unpoisoned Rosenmund reactions using 0.3 g 5% catalyst. The yields for hydrogenations poisoned with 0.1 mg thiourea are also given to show that the aldehyde obtained depends on the amount of poison used and not on the rate of hydrogenation.

Iron	Hydrogenation time, unpoisoned	Yield, poisoned
0.001%	120 mins	42%
0.01%	75 mins	51%

2.6. THE POISONS.

The original poison used by Rosenmund was quinoline/sulphur(18). Quinoline/sulphur is prepared by refluxing quinoline and sulphur together for five hours. The mixture obtained is of indeterminate composition and contains unchanged quinoline and sulphur. In order to study adsorption effects, a quantitative poison was required, i.e. which was reproducible and of known composition. The use of thiourea(19) was found to give reproducible results and it gave good yields. Thiourea was therefore used in the first stages of the investigation.

A variety of other poisons were also tried, including thiophene. The yields varied considerably from poison to poison. The subject will be discussed later in detail.

2.7. ADDITIONS.

The effect of various likely impurities, which

TABLE 1

ADDITION	NONE	5 mg NaOH	5mg $AlCl_3$	5 mg $FeCl_3$
Time, mins, unpoisoned	100	120	107	150
Time, mins, 0.1 mg thiourea	150	130	140	175 (170)
Yield Ph.CHO, unpoisoned	18%	24%	32%	15%
Yield Ph.CHO, 0.1 mg thiourea	54%	55%	59%	25% (24%).

might still have been present in the reaction components, was examined. Expected impurities would be aluminium salts from the purification of the solvent and alkali from the preparation of the catalyst.

As iron salts increased the rate of reaction when added during the preparation of the catalyst (see section 5 above), the effect of iron salts added during the reaction was investigated. The results are shown in table 1.

It is seen that sodium hydroxide and aluminium chloride had little effect on the reaction. Ferric chloride had the surprising effect of decreasing the yield and showed no promotion effect, as in paragraph 5. A possible explanation of this is the formation of a complex between the selective poison and the iron, when the iron is added at such a late stage.

2.8. INFLUENCE OF REACTION VESSEL.

In spite of the above precautions, it was found at times that, on using the same components in different flasks, different rates of reaction were observed, though both vessels were cleaned with aluminium chloride and toluene. This was judged to be due to arsenic which is present in pyrex glass.

For consistent results, therefore, rate data is only comparable in the same reaction vessel unless tests show no difference with the same components in other vessels.

2.9. STIRRING.

It has been reported(38) that rapid stirring is necessary to make the reaction proceed at a reasonable rate. With the small quantities used, e.g. 0.3 g catalyst, moderate stirring sufficed and no difference in rate was observed on increasing the speed of the stirrer.

If the precautions given above were adhered to closely then the reaction was found to be reproducible.

CHAPTER 3.

TYPICAL ROSENMUND REACTION.

3. TYPICAL ROSENMUND REACTION

3.1. APPARATUS AND PROCEDURE.

The usual apparatus for Rosenmund reductions consists of a three necked flask equipped with a stirrer, condenser and hydrogen inlet. The stirrer was made with a stirring gland fitted with 1 cm of polythene tubing over the end, the polythene tubing overlapping onto the glass stirring rod. Vaseline was applied to the point of contact of the stirring rod and polythene tubing. A tube was led from the top of the condenser into a beaker containing water and two drops phenolphthalein. The hydrochloric acid produced was titrated with I N caustic soda.

The reaction was taken as complete when hydrochloric acid had ceased to be evolved. If hydrogenation was continued after all the acid chloride had reacted then aldehyde hydrogenated and the yield was decreased.

The reaction can also be followed by measuring the absorption of hydrogen. In this case it is difficult to know when to stop the hydrogenation, e.g. if the reaction is,

$$R.COCl + 2H_2 \rightarrow R.CH_2OH + HCl,$$

then stopping the reaction at 1.0 mole hydrogen absorbed will only correspond to 50% of the acid chloride being used.

To start the reaction the catalyst, 0.3 g, was placed in the reaction vessel, and the solvent, 25 ml., added. The poison a standard solution in toluene, and benzoyl chloride, which was distilled immediately before use, were then pipetted into the flask and the hydrogen flow was started. The catalyst was completely covered with solvent at this stage and the hydrogen was bubbled gently through the solution till all the air had been flushed from the apparatus. Otherwise water was produced by the combination of oxygen and hydrogen on the catalyst. Water, as mentioned previously, slowed the reaction to a negligible rate. When the apparatus had been flushed with hydrogen, the stirrer was started and the heater, an electric mantle controlled by a Simmerstat, was switched on. The reaction was carried out at the boiling point of the solvent, 110°C in the case of toluene. The amount of hydrogen chloride liberated was measured by titration and graphed against the time of reaction. The reaction was stopped when the rate of liberation of hydrogen chloride fell to a negligible value, at about 92% of the theoretical amount. The mixture was allowed to cool while hydrogen was still being passed through the apparatus. The catalyst was then removed by filtration and the aldehyde produced determined by the formation of a derivative of 2,4-dinitrophenylhydrazine.

3.2. ESTIMATION OF ALDEHYDE.

The reagent for estimation of aldehyde was a saturated solution of 2,4-dinitrphenylhydrazine in ethanol and concentrated hydrochloric acid. The derivative was filtered by suction, washed with a small amount of ethanol, dried between filter papers and weighed. Tests on samples of benzaldehyde of known concentration showed that this method of estimation gave accurate, reliable results over a wide range. It should be noticed that the melting point of the unpurified derivative above, 243°C, is higher than that of the recrystallised product, 237°C, as reported in the literature(39).

A method of extraction of the aldehyde which would have permitted recovery, was the conversion to a bisulphite derivative(40). This procedure would have been particularly useful in the preparation of C^{14} labelled aldehydes. It was found, however, that when the aldehyde was in a toluene solution, as in the Rosenmund reaction, and present in small amounts, e.g. 500 mg, then the bisulphite method was inaccurate and unreliable.

CHAPTER 4.

EFFECT OF SULPHUR POISONS ON THE REACTION.

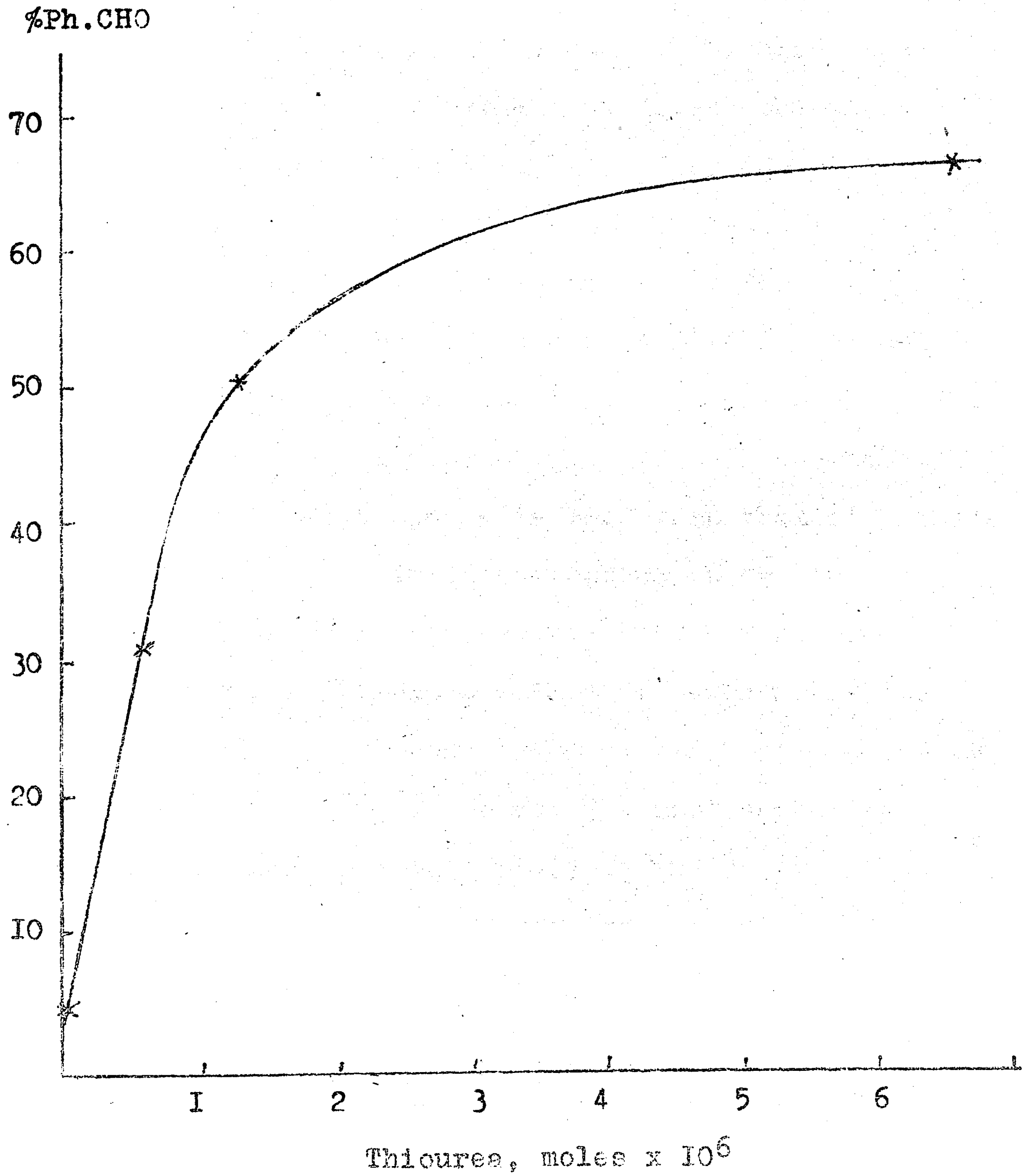
4. EFFECT OF SULPHUR POISONS ON THE REACTION

4.1. EFFECT OF VARIOUS POISONS.

After the reaction had been made reproducible, the next stage was to examine the effect of different poisons and different amounts of poison on the yield. If the amount of poison in the Rosenmund was increased, then the yield increased and eventually leveled off as in graph 1. If the mechanism is a simple blocking of the surface i.e. poison prevents aldehyde adsorption on the surface and thus prevents it being hydrogenated, then we may find a correlation between the size of the poison and the slope of the poisoning graph. Related poisons were therefore investigated to see if there was a correlation between size of poison and poisoning effect in the reaction. As thiourea had already been used, graph 1, and because it resulted in a good yield of aldehyde, tetramethylthiourea was investigated.

As noted previously, the solvent has to be purified very carefully in order to reduce the yield of aldehyde to zero. The most likely impurity in hydrocarbons is thiophene. This suggests that thiophene acts as a poison in the Rosenmund reaction. Accordingly, thiophene and

GRAPH I



dibenzothiophene were tried to establish a connection between poisoning effect and size of the poison molecule. The results are summarized in graph 2.

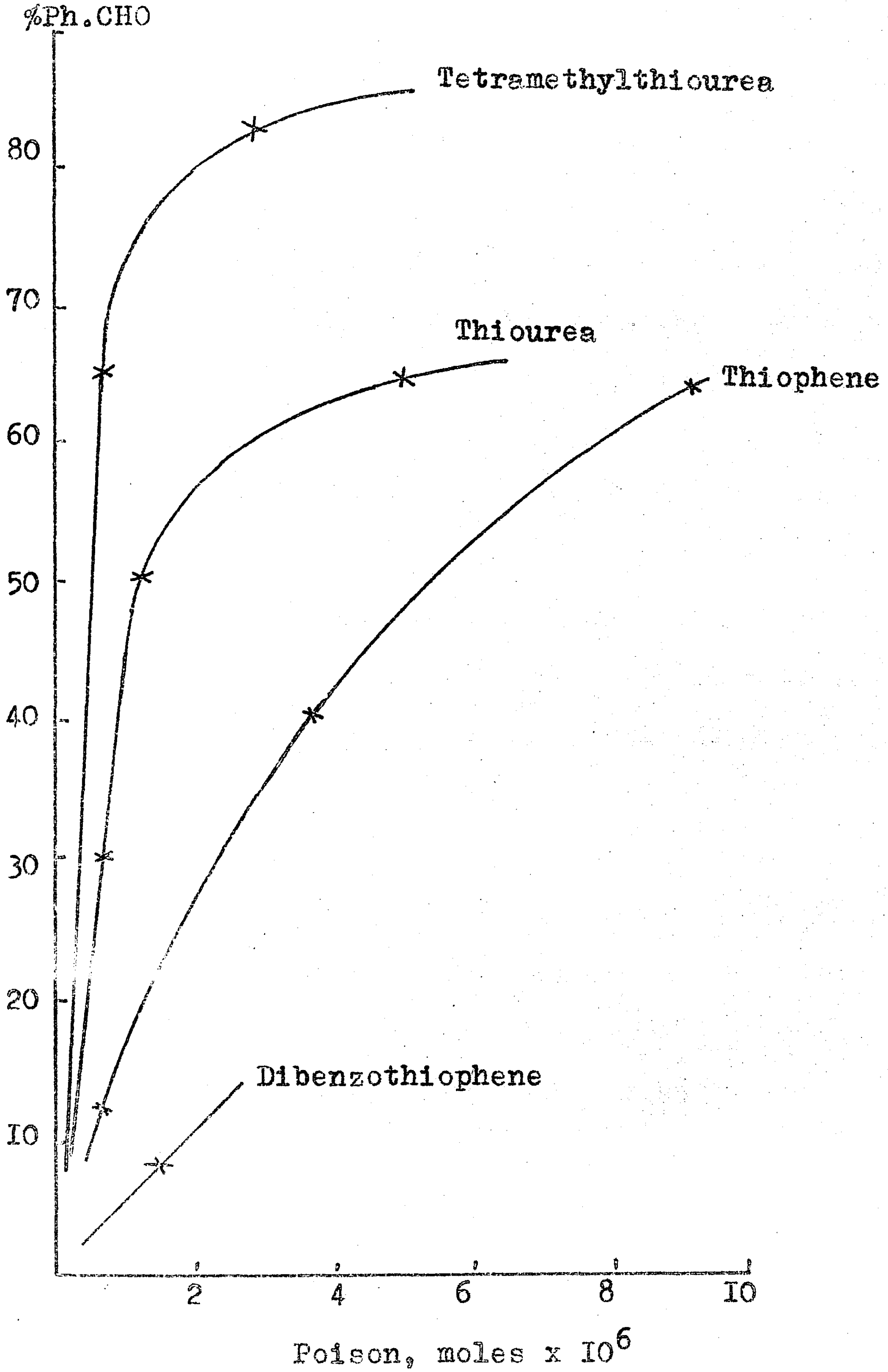
There is seen to be considerable difference in poisoning power of different sulphur compounds. No correlation is found between size of the molecule and poisoning effect, as tetramethylthiourea is a better poison than thiourea, but dibenzothiophene is less poisonous than thiophene. This does not necessarily mean that the above hypothesis of the poison keeping the aldehyde off the surface is incorrect. The extent of poisoning will depend on the quantity of poison actually adsorbed on the catalyst surface. It is possible that the partition ratio of dibenzothiophene is less than that of thiophene, i.e. there is less dibenzothiophene on the surface than thiophene although equivalent amounts were added to the solution. A method of determining the actual amount of poison on the catalyst was therefore required. One of the simplest and most sensitive methods is colourimetric analysis and colour tests were sought for the above poisons.

4.2. PARTITION OF POISON BETWEEN LIQUID AND CATALYST

a. Thioureas.

A sensitive colour test for thioketones is

GRAPH 2


%Ph.CHO
80
70
60
50
40
30
20
IO
Tetramethylthiourea
Thiourea
Thiophene
Dibenzothiophene
2
4
6
8
IO
Poison, moles x IO6

given by the Grote reagent. The test also applies to thioalcohols.

Grote Reagent(41)

A solution of 0.5 g sodium nitroprusside in 10 ml. water was made. 0.5 g Hydroxylamine hydrochloride was added and then 1.0 g sodium bicarbonate. When evolution of gas had ceased, two drops of bromine were added. Excess bromine was removed by bubbling air through the mixture which was then filtered. The solution was made up to 25 ml. To apply the test, the sulphur compound was dissolved in 2-3 ml. water and solid sodium bicarbonate added to excess. 0.5 ml. Grote reagent was added and the colour which developed, was compared with a series of standards freshly made up. The limit of sensitivity is approximately 2 γ.

A series of tests were carried out with probable reaction mixtures. These included toluene, aldehyde, acid chloride and ester (see later). Aldehyde and ester interfered with the colour test. As thiourea is soluble in water the above mixtures were shaken with water and filtered through a filter paper previously wetted with water. The toluene layer containing the aldehyde etc. was left behind in the filter, This procedure gave a solution free from interference. When tested, the standard solutions gave a colour density corresponding with the content of thiourea.

A typical Rosenmund reaction mixture was prepared with 0.040 mg thiourea as poison. The reaction was stopped after 20 mins, the reaction mixture shaken with water and the water layer separated as above. On testing for thiourea, 0.002 mg was detected. Practically all the thiourea appeared to be on the catalyst. The experiment was repeated using 0.30 mg thiourea. After 20 mins only 0.01 mg was left. It therefore appeared that all the poison went onto the catalyst.

b. Thiophenes.

Reagent for thiophene(42).

The reagent for thiophene is freshly prepared 0.01% ninhydrin in concentrated sulphuric acid. One drop of the reagent was added to the reaction mixture to be tested. The limit of identification is 0.2γ. Aldehyde and acid chloride did not interfere. The reagent is specific for thiophene and does not detect dibenzothiophene.

The partition of thiophene between the solvent and the catalyst was examined in a typical Rosenmund reaction mixture as with the thiourea. The results showed a negligible amount of thiophene was present in the solvent after a reaction.

4.3. STABILITY OF POISONS.

It might reasonably be expected that a partition of the poison between solvent and catalyst would take place. It was therefore necessary to investigate the loss of poison more thoroughly. A possible cause of the apparent loss of poison was decomposition of the poisoning molecule, the tests being specific no poison would therefore be detected.

A large amount of thiourea, 100 mg, was placed in a flask with catalyst and toluene. Hydrogen was passed and the effluent gas was examined for hydrogen sulphide by means of lead chloride paper. None was detected. But when Benzoyl chloride was added hydrogen sulphide was then evolved. On examining the contents of the flask after the reaction, free sulphur could be detected. The experiment was repeated with tetramethylthiourea and decomposition was observed here also. Thiophene gave no detectable decomposition. However it is possible that the benzoyl chloride reacts with thiophene to form a compound such as 2-benzoylthiophene(43) or 2,5-dibenzoylthiophene(44). As the colour test is specific for thiophene, then no sulphur compound would be detected after the reaction.

Further investigation showed that even in the cold tetramethylthiourea broke down in the presence of catalyst and hydrogen to give an amine, detected by its odour, and an unknown sulphur compound. Thiophene also hydrogenates in the cold with catalyst and hydrogen to give thiophane.

From these results it was seen that the poison in the Rosenmund reaction is not stable and poisoning curves cannot be directly correlated with the quantites or shapes of the substance added.

4.4. ELEMENTARY SULPHUR AS A POISON.

As thiourea and tetramethylthiourea both broke down to elementary sulphur, it was decided to find the effect of elementary sulphur as a poison. The results are shown in the table.

Poison	0	0.08 mg S	0.32 mg S	0.48 mg S
Yield	6%	27%	34%	45%

From the table it is seen that for Rosenmund reactions carried out with the normal procedure, elementary sulphur is a mild poison.

An equivalent amount of tetramethylthiourea to 0.08 mg elementary sulphur gives a yield of 80%. This result suggests that again loss of sulphur is taking place.

The effluent gas in a run similar to the above was examined for hydrogen sulphide. For a time, whilst the heater was warming up, hydrogen sulphide was evolved rapidly. After some minutes evolution ceased. Addition of more sulphur to the hot reaction mixture did not produce more hydrogen sulphide. This suggested that, at the lower temperatures, the sulphur was being converted to hydrogen sulphide before it was able to combine firmly with the catalyst. Accordingly another Rosenmund reaction was attempted, this time with 0.16 mg sulphur, added after the reaction mixture was at 110°C. After a few minutes when the sulphur had reacted, the benzoyl chloride was added. From the table shown above the yield should be approximately 30%; the yield found was 67%.

It is therefore seen that elementary sulphur suffices as a Rosenmund poison and in the case of elementary sulphur at least, a "compound" is formed between the palladium and the sulphur. This suggests that the ideal Rosenmund catalyst would be a palladium sulphide.

4.5. PALLADIUM SULPHIDE CATALYSTS.

A survey of the literature on the palladium/sulphur system(45) showed that only the following palladium sulphides exist,

Pd_4S, $Pd_{2.8}S$, $Pd_{2.2}S$, PdS and PdS_2.

Of these, $Pd_{2.8}S$ only occurs in quenched systems and PdS_2 requires prolonged reaction at high temperature in its preparation. They are therefore unlikely to occur under the present reaction conditions. It was therefore decided to prepare PdS, as this contained the largest proportion of sulphur, and as increasing the amount of sulphur added raised the yield, see graph 2, then it would be expected that PdS would give a good yield of aldehyde, if indeed it hydrogenated benzoyl chloride at all.

Preparation of palladium sulphide (PdS),I.

A solution of sodium sulphide was made up and standardised with arsenous oxide solution, the excess arsenous oxide being back-titrated with iodine. Barium sulphate was prepared as in section 5 on the preparation of reactants. The barium sulphate was suspended in water and 5 ml. concentrated hydrochloric acid were added. The palladium chloride was added and then an equivalent amount of sodium sulphide was added over 15-20 mins, in the cold while stirring. The solution was tested to ensure that it was acid after all the sulphide had been added. The precipitate was washed by decantation, filtered and washed with acetone. The catalyst contained 5% palladium.

A Rosenmund hydrogenation was then attempted with the sulphide catalyst, all other conditions being as usual and no poison being used. The yield of aldehyde was 40% and the time for the reaction was 215 mins.

Preparation of palladium sulphide (PdS),2.

Another sulphide catalyst was then made under different conditions. The barium sulphate was made as usual and suspended in dilute hydrochloric acid. Hydrogen sulphide from a Kipp generator was passed through the suspension which was heated to 70°C and stirred mechanically. The precipitate was washed by decantation, filtered and then washed with acetone. The catalyst contained 5% palladium.

A Rosenmund reduction was carried out as before. The yield was 40% and the time of reaction 220 mins.

The low yields are surprising in view of the large amount of sulphur present. To check the reaction two further trials were attempted on the palladium sulphide catalysts, this time with a poison added. To 0.3 g catalyst containing 3.5 mg sulphur as sulphide, were added 0.4 mg tetramethylthiourea in the first experiment and 0.8 mg tetramethylthiourea in the second. The yields were respectively 75% and 81%.

These results suggested that there was also a loss of sulphur with the palladium sulphide. The palladium sulphide was therefore examined for stability under the reaction conditions. Palladium sulphide and toluene were placed in a flask and hydrogen was passed through. Tests for hydrogen sulphide showed that none was evolved in the cold. When the reaction mixture was heated a large amount of hydrogen sulphide was evolved. When benzoyl chloride was added this ceased, and another reaction was coming into play. These results showed that palladium sulphide (PdS) is unstable under the reaction conditions. This does not necessarily mean that a surface layer of sulphide would be similarly unstable.

The necessity for having the sulphur poison in exactly the right form is shown by the loss of "sulphide" sulphur in spite of it being bound initially to the palladium. A much smaller amount of poison in the correct form has a far greater effect on the yield.

The above results could be accomodated in a reaction scheme as follows.

4.6. BENZOYL SULPHIDE MECHANISM.

1 $Ph.COCl + H_2S \rightarrow Ph.COSH + HCl$,

2 $Ph.COSH + PhCOCl \rightarrow Ph.CO.S.OC.Ph + HCl$,

3 $Ph.CO.S.OC.Ph + H_2 \rightarrow Ph.COSH + Ph.CHO$,

2 and 3 forming a cycle of events. Further products would be formed by hydrogenation of the aldehyde on the catalyst.

To test this reaction scheme, dibenzoyl sulphide was synthesised to use in a Rosenmund reaction.

4.7. PREPARATION OF DIBENZOYL SULPHIDE(46).

To a cold, concentrated aqueous solution containing one mole of sodium sulphide was added two moles benzoyl chloride and enough borax to absorb the hydrochloric acid produced and keep the pH greater than 6.0. The mixture was shaken by hand for 20 mins. The product was filtered, washed with water, extracted with sodium carbonate and washed with water again. The dibenzoyl sulphide was recrystallised from ether. The M.P. was 49°C.

4.8. HYDROGENATIONS WITH DIBENZOYL SULPHIDE.

Initially, a small amount, 1.0 mg, dibenzoyl sulphide was added in place of a poison in a normal run. No evolution of hydrochloric acid was observed in two hours. A check with tetramethylthiourea gave a normal yield. An attempt was then made to hydrogenate the dibenzoyl sulphide by itself. In order to do this an apparatus was used (it is described later) in which hydrogen absorption could be measured, the reaction still being carried out at the boiling point of toluene. 0.41 g Dibenzoyl sulphide was placed in the reaction tube together with 0.3 g 5% palladium catalyst and 5 ml. toluene. The volume change for the reaction,

$$Ph.CO.S.OC.Ph + H_2 \rightarrow Ph.COSH + Ph.CHO,$$

is 40 ml. which would have been easily detectible. No absorption of hydrogen was observed in four hours. It therefore appears that dibenzoyl sulphide does not hydrogenate under the given reaction conditions and the mechanism proposed above is therefore invalid.

4.9. CONCLUSION.

It is seen that the results of examining the action of poisons do not allow us to formulate a reaction mechanism. It was therefore decided to direct our attention to the reaction products obtained.

CHAPTER 5.

THE STOICHEIOMETRY OF THE REACTION.

5. THE STOICHEIOMETRY OF THE REACTION.

5.1. INTRODUCTION.

We must now consider just which reaction steps are taking place. There are a large number of possibilities, some of the more probable being,

$$Ph.COCl + H_2 \rightarrow Ph.CHO + HCl,$$

$$Ph.CHO + H_2 \rightarrow Ph.CH_2OH,$$

$$Ph.CH_2OH + H_2 \rightarrow PhCH_3 + H_2O$$

$$Ph.COCl + Ph.CH_2OH \rightarrow Ph.CO_2CH_2Ph + HCl,$$

$$Ph.CO_2CH_2Ph + H_2 \rightarrow Ph.CO_2H + Ph.CH_3.$$

It should be noted in each of the above steps, hydrogen is absorbed or hydrochloric acid is evolved or both take place. If, therefore, we can measure the ratio of hydrochloric acid evolved in a reaction to the amount of hydrogen absorbed we may obtain an idea of which steps are taking place, e.g. if we find three H_2 absorbed for each HCl evolved, the probable scheme would be,

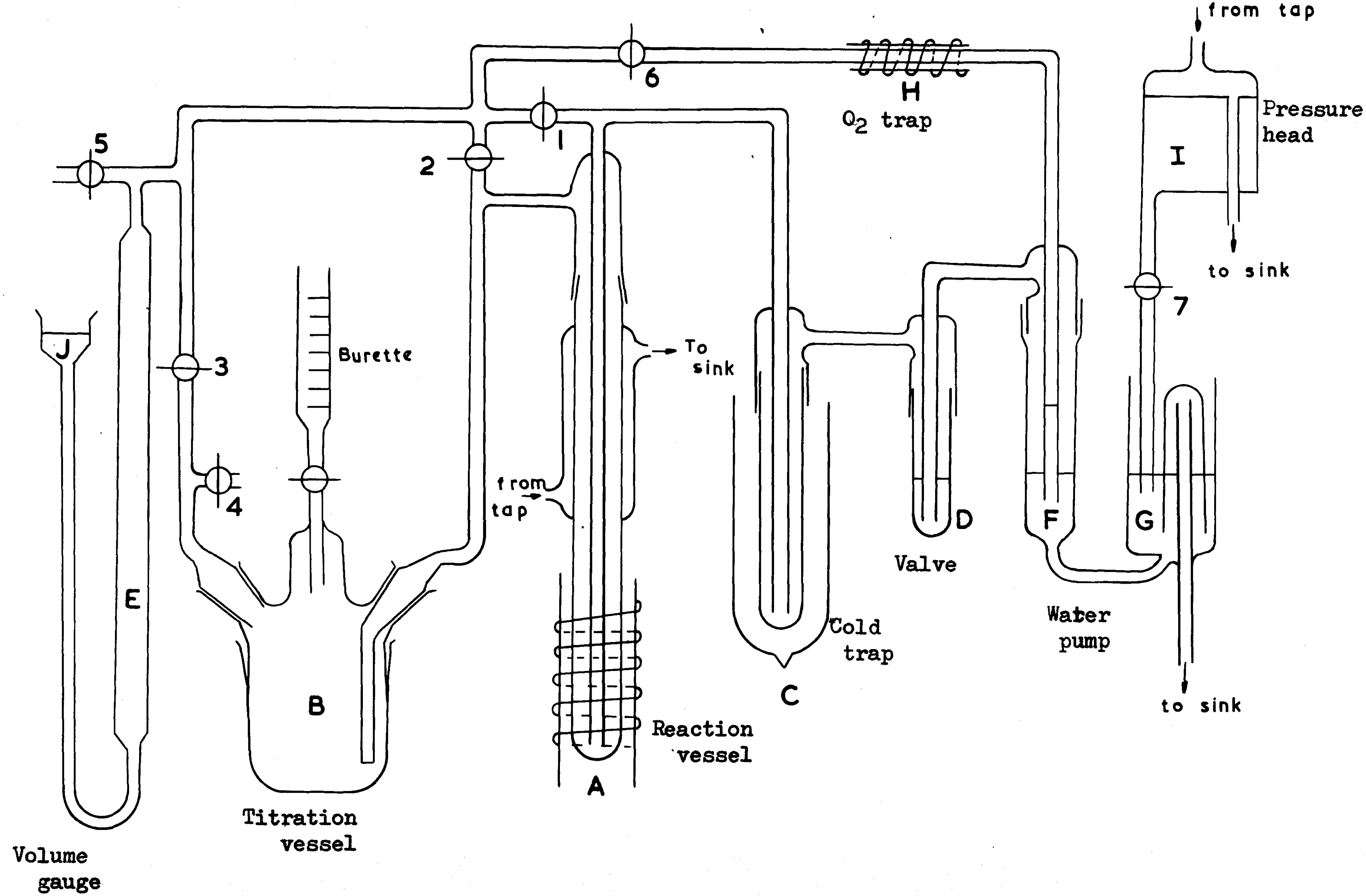
$$Ph.COCl + H_2 \rightarrow Ph.CHO + HCl,$$

$$Ph.CHO + H_2 \rightarrow Ph.CH_2OH,$$

$$Ph.CH_2OH + H_2 \rightarrow Ph.CH_3 + H_2O$$

An apparatus was therefore constructed which measured absorption of hydrogen and evolution of hydrochloric acid simultaneously.

Fig. 1.


from tap
6
H
O_2 trap
Pressure head
I
to sink
5
2
1
7
3
Burette
To sink
J
from tap
4
D
F
G
E
Valve
Water pump
Cold trap
B
C
to sink
Reaction vessel
A
Titration vessel
Volume gauge

5.2. DESCRIPTION OF APPARATUS (fig. 1).

The apparatus consists of a water circulating pump, F, described in appendix 1; a cold trap, C, as any water vapour carried over from the pump must be removed otherwise the reaction would be completely inhibited; a reaction vessel, A, including a heater and a condenser; a titration vessel, B, with a burette attached by a gas-tight joint; a gauge, E, for measuring hydrogen absorption and finally a trap, H, to remove any residual oxygen in the apparatus.

The level of liquid air in the water trap, C, must be kept constant or the gas in the apparatus will contract or expand due to the difference in effective cooling. Liquid nitrogen over an hour or so dissolves oxygen from the air and produces a slight temperature change. It is therefore best to use liquid air. As hydrogen and catalyst are present in the system, liquid oxygen is not recommended.

5.3. PROCEDURE.

To start the reaction, the components were placed in the reaction vessel, A. Water was circulated through the condenser integral with the reaction tube and the heater was slipped into position. The heater consisted of a piece of glass tubing, which just fitted over the reaction vessel, having an element wound round it and controlled by a Simmerstat. The titration vessel B was filled with water and two drops phenolphthalein. Taps 1, 2, and 3 were then closed and hydrogen was passed through the apparatus, in at tap 5 and out at tap 4. The flushing with hydrogen was assisted by raising and lowering the level in the calibrated tube, E. When flushing was complete, tap 6 was closed and tap 3 opened. Hydrogen was passed through the section between taps 3 and 4 so removing any oxygen trapped there. Tap 4 was then closed and the water in E was brought to a suitable level. Tap 5 was then closed and tap 6 opened. In order to remove any traces of oxygen which might still have been present, the oxygen trap, H, was switched on. The oxygen trap consisted of a tube packed with copper spirals and heated to 350°C. The apparatus was adjusted to atmospheric pressure by lowering J till the levels in J and E were equal. The level in F was adjusted so that it was below the end of the inlet tube and was made equal to that in G by letting water in through tap 7; taps 1 and 2 were opened to eliminate the pressure drop across A and B. The volume was then read on the gauge E. The pump was started with taps 1 and 2 closed. After a few cycles the pressure was again adjusted to atmospheric and the volume read. After repeating this several times the volume remained constant. The heater round the reaction vessel was then switched on and the volume read every few minutes till the rapid expansion had ceased. The hydrochloric acid evolved was determined by titration in vessel B and at the same time a reading was taken of the hydrogen volume at various times during the reaction. The hydrogen absorption and hydrochloric acid evolution were plotted against time.

5.4. RESULTS.

The results are shown in graph 3 for an unpoisoned Rosenmund reaction and graph 4 for a Rosenmund reaction poisoned with thiourea to give a 60% yield. In fact in some 60 runs, the 1:1 correlation between hydrogen and hydrochloric acid as shown in the graph was observed. This limited the possible reaction schemes to only one reasonable choice.

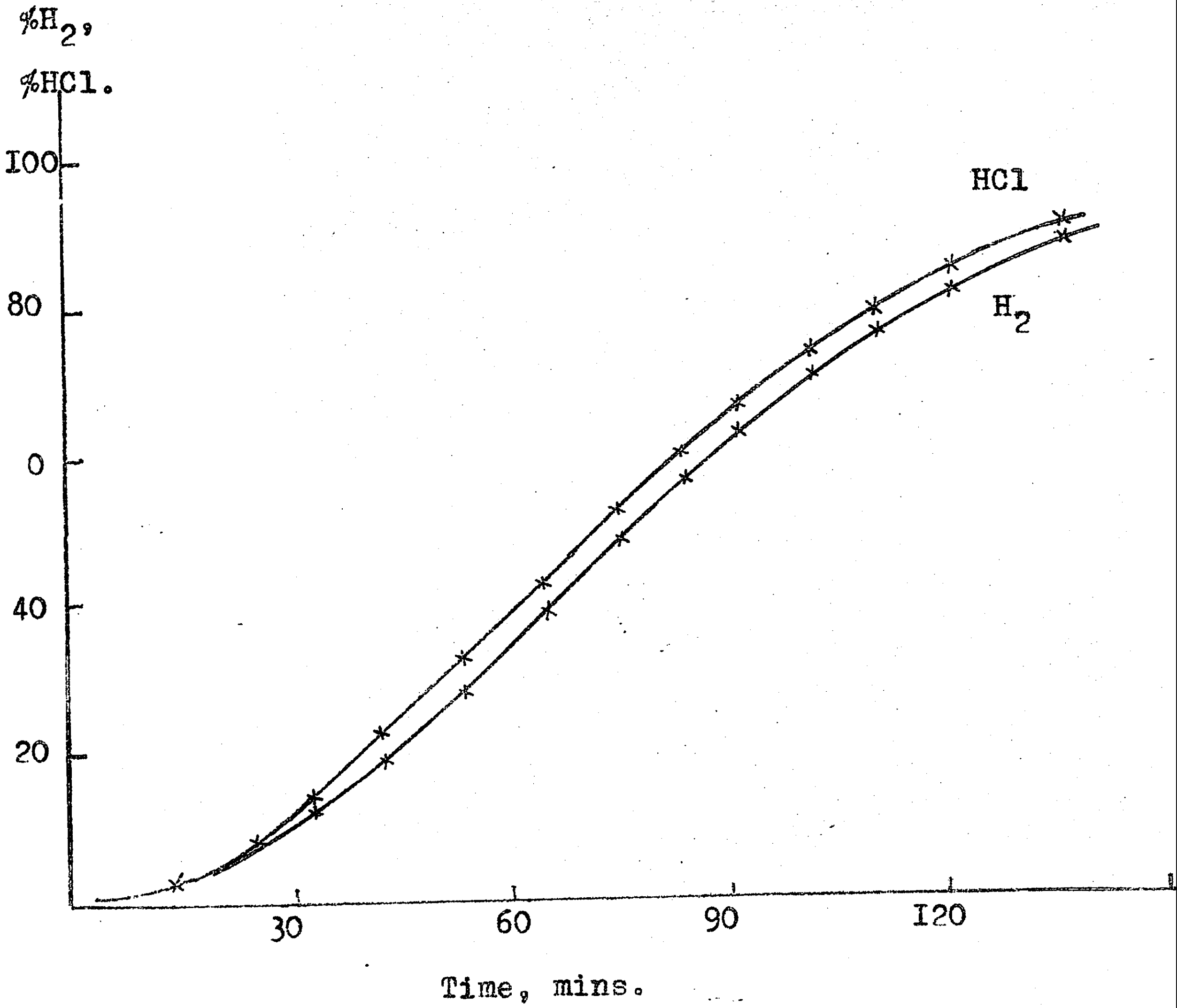
At the temperature and pressure used, i.e. 110°C and atmospheric pressure, the reaction scheme is,

1 $Ph.COCl + H_2 \rightarrow Ph.CHO + HCl$,

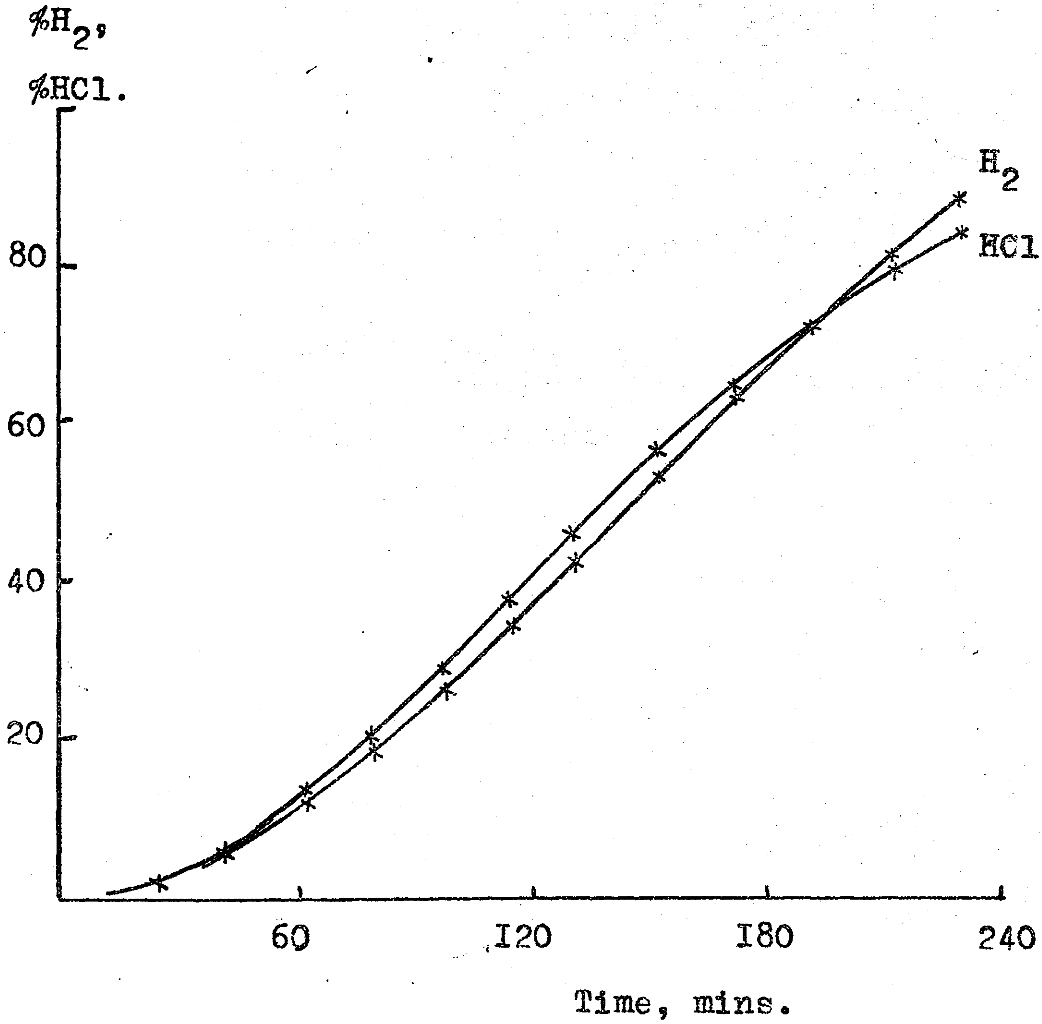
2 $Ph.CHO + H_2 \rightarrow Ph.CH_2OH$,

3 $Ph.CH_2OH + Ph.COCl \rightarrow Ph.CO_2CH_2Ph + HCl$ - fast.

GRAPH 3



GRAPH 4



It should be noted that the reaction steps given above are purely stoicheiometric and do not necessarily correspond to actual reaction stages. The validity of the reaction scheme was checked by isolating the ester.

5.5. ISOLATION OF ESTER.

A Rosenmund reaction was carried out on 5.0 ml. benzoyl chloride with 0.6 g 5% palladium/barium sulphate in 25 ml. toluene. No poison added. When the reaction was complete, the catalyst was removed by filtration. The ester was isolated by distillation; a yield of 47% ester was obtained with a boiling point of 320°C.

5.6. VARIATION OF REACTION SCHEME WITH TEMPERATURE.

At different temperatures we find different reaction schemes. At room temperature step 3 in the above scheme does not take place readily but the alcohol hydrogenates further and we have,

1 $Ph.COCl + H_2 \rightarrow Ph.CHO + HCl$,

2 $Ph.CHO + H_2 \rightarrow Ph.CH_2OH$,

3 $Ph.CH_2OH + H_2 \rightarrow Ph.CH_3 + H_2O$.

Examination of the hydrogenation of aldehyde at room temperature confirmed that 2.0 moles of hydrogen are absorbed giving the hydrocarbon.

At very high temperatures, i.e. 200°C, we have a different scheme. In this case we find that the ester hydrogenates and we obtain,

1 $Ph.COCl + H_2 \rightarrow Ph.CHO + HCl$,

2 $Ph.CHO + H_2 \rightarrow Ph.CH_2OH$,

3 $Ph.CH_2OH + Ph.COCl \rightarrow Ph.CO_2CH_2Ph.$,

4 $Ph.CO_2CH_2Ph + H_2 \rightarrow Ph.CO_2H + Ph.CH_3$.

The benzoic acid produced at 200°C could be detected by the appearance of white crystals in the condenser during the hydrogenation.

The formation of the ether,

$$2Ph.CH_2OH \rightarrow Ph.CH_2OCH_2.PH + H_2O,$$

has been reported by Rosenmund(47), and the acid anhydride,

$$Ph.CO_2H + Ph.COCl \rightarrow (Ph.CO)_2O + HCl,$$

is said to occur with heterocyclic acid chlorides under certain conditions (32).

Under normal Rosenmund conditions, i.e. 110°C and atmospheric pressure, the reaction scheme given in paragraph 4 is obtained. We are now in a position to discuss the detailed action of the poison.

CHAPTER 6.

DETAILED POISONING MECHANISM.

6. DETAILED POISONING MECHANISM.

6.1. INTRODUCTION.

The object of the research was to discover the mechanism of the poisoning of the Rosenmund reaction. The work described under stoicheiometry has shown the reaction conditions and has set a limit on the number of reaction steps which might take place. The major problem of great interest to catalyst chemists remains. Does the poison keep aldehyde off the catalyst surface, or does benzoyl chloride hydrogenate directly to the final product, aldehyde or alcohol? In other words, is the reaction simultaneous or consecutive or a combination of the two? The alternatives are as follows,

a - simultaneous,

$$\begin{array}{lcl} Ph.COCl & \rightarrow & Ph.CH_2OH, \\ \downarrow & & \\ Ph.CHO & & \end{array}$$

b - consecutive,

$$\begin{array}{lclcl} Ph.COCl & \rightarrow & Ph.CHO(adsorbed) & \rightarrow & Ph.CH_2OH \\ & & \upharpoonleft\downharpoonright & & \\ & & Ph.CHO(in\ solution) & & \end{array}$$

There are a number of ways of investigating this problem and we shall first consider what, superficially, appears to be the simplest.

6.2. PHYSICAL REMOVAL METHOD.

On looking closely at the consecutive and simultaneous mechanisms we observe that the difference

FIG. 2

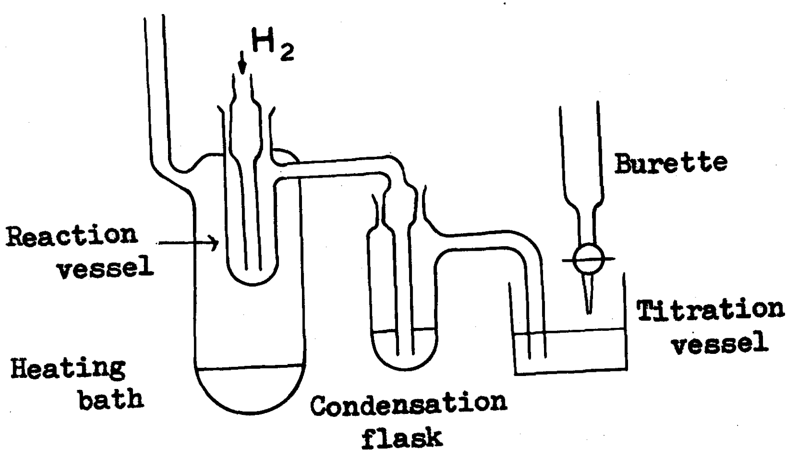
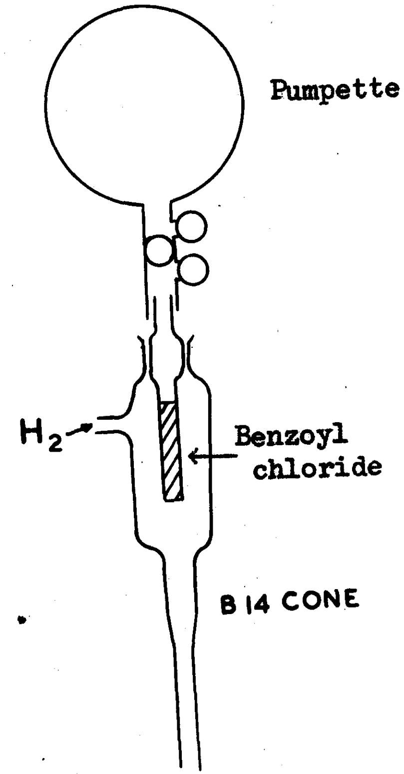

H2
Reaction vessel
Heating bath
Condensation flask
Burette
Titration vessel

FIG. 3

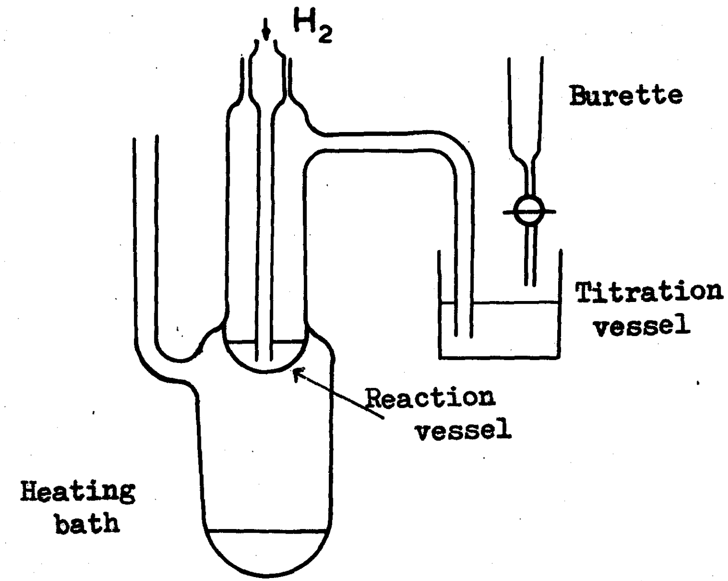

Pumpette
H2
Benzoyl chloride
B 14 CONE

between them is that in the consecutive mechanism the aldehyde produced leaves the catalyst and then returns to be hydrogenated, while in the simultaneous mechanism the aldehyde remains on the catalyst till it is hydrogenated to alcohol, or it leaves the catalyst and cannot be readsorbed. If, therefore, we remove the aldehyde from the system immediately it is produced, we shall have, in the case of a simultaneous reaction with no poison, no yield and in the case of a consecutive reaction with no poison, 100% yield. Unfortunately it is practically impossible to remove a reactant from the system immediately it is produced and the most we can hope for in the case of a consecutive reaction is a slight increase in the amount of aldehyde produced.

6.3. APPARATUS.

To examine the above hypothesis two apparatuses were constructed. The first apparatus, fig. 2, was designed so that aldehyde was removed immediately it was formed. The reaction vessel was totally immersed in a bath of boiling benzaldehyde. Any aldehyde produced during the reaction would therefore be removed in the stream of hydrogen passing through the vessel and would not condense till it reached the external condensation chamber. Toluene was placed in this chamber to assist condensation and

Fig. 4.



collection. The aldehyde was determined as a 2,4 - dinitrophenylhydrazine derivative. It was found that at the temperature used, 179°C, and with a flow of gas passing through the apparatus, benzoyl chloride, B.P. 196°C, was removed from the system quite rapidly. An additional piece of apparatus, fig. 3, was therefore added in place of the hydrogen inlet previously used, in order to add benzoyl chloride continuously during the run. This unit consisted of a hydrogen inlet with a dropper built in. In use the dropper was filled with benzoyl chloride by means of a pumpette and placed in position. Hydrogen was passed through the tube into the apparatus. It was found that a slight vacuum had to be kept in the pumpette otherwise drops of benzoyl chloride fell uncontrollably. To add benzoyl chloride during a run, the pumpette was filled with air and gently squeezed with the suction valve open. Benzoyl chloride dropped down the inlet tube and was forced through to the reaction mixture by the hydrogen. A small amount of benzoyl chloride was left in the tube to prevent entry of oxygen to the system.

The second apparatus, fig. 4, was designed to condense aldehyde, formed during the reaction, back into the reaction mixture. In order that the results should be comparable with those of the first apparatus, the temperature of the heating bath was kept only $20^{\circ}C$ lower than the boiling point of benzaldehyde. This was achieved by refluxing n - propyl benzene, B.P. $159^{\circ}C$, in the heating bath. Boiling benzaldehyde would have facilitated removal of aldehyde formed during the reaction. Condensation of aldehyde was aided by immersing only part of the reaction vessel in the heating bath.

Toluene could not of course be used as a solvent for the reaction as a high boiling solvent was required. A high boiling solvent, which was also free from sulphur compounds, was benzyl benzoate. This was known to be produced during the Rosenmund reaction. With this solvent it was found that after the reaction had been running for some time, crystals of benzoic acid condensed in the side arm of the apparatus. This is probably due to,

$$Ph.CO_2CH_2.Ph + H_2 \rightarrow Ph.CO_2H + Ph.CH_3.$$

6.4. RESULTS.

When the aldehyde was not removed from the reaction mixture the yield was found to be 28%. On removing the aldehyde continuously the yield increased to 58%. The reaction therefore appears to be consecutive.

The results are open to criticism for a number of reasons, particularly on account of the temperature difference between the two systems. The yield may increase on raising the temperature slightly, for the mechanism may be temperature dependent. Also benzyl benzoate hydrogenates at these temperatures, it may affect the reaction by adsorbing on the catalyst. Had this been the only method available to us in deciding whether the reaction was simultaneous or consecutive, further research would have been merited to design an apparatus in which aldehyde is efficiently returned to the reaction vessel, even at its boiling point and with gas streaming through, in order to eliminate temperature differences between the apparatuses. Another solvent, which was also free from poisons but which would not hydrogenate, would have been found to improve the experiment. As other methods existed however it was decided not to pursue the matter any further.

It should be mentioned that an attempt was made initially to design an apparatus working on the flow system, using liquid toluene as the carrier, to investigate the above. This proved to be extremely inefficient due to the small amount of acid chloride which reacted during the time of contact with the catalyst.

6.5. RADIOCHEMICAL TRACER METHOD.

If we again consider the detailed reaction mechanisms,

a simultaneous,

$$\begin{array}{c} Ph.COCl \rightarrow Ph.CH_2OH, \\ \downarrow \\ Ph.CHO \end{array}$$

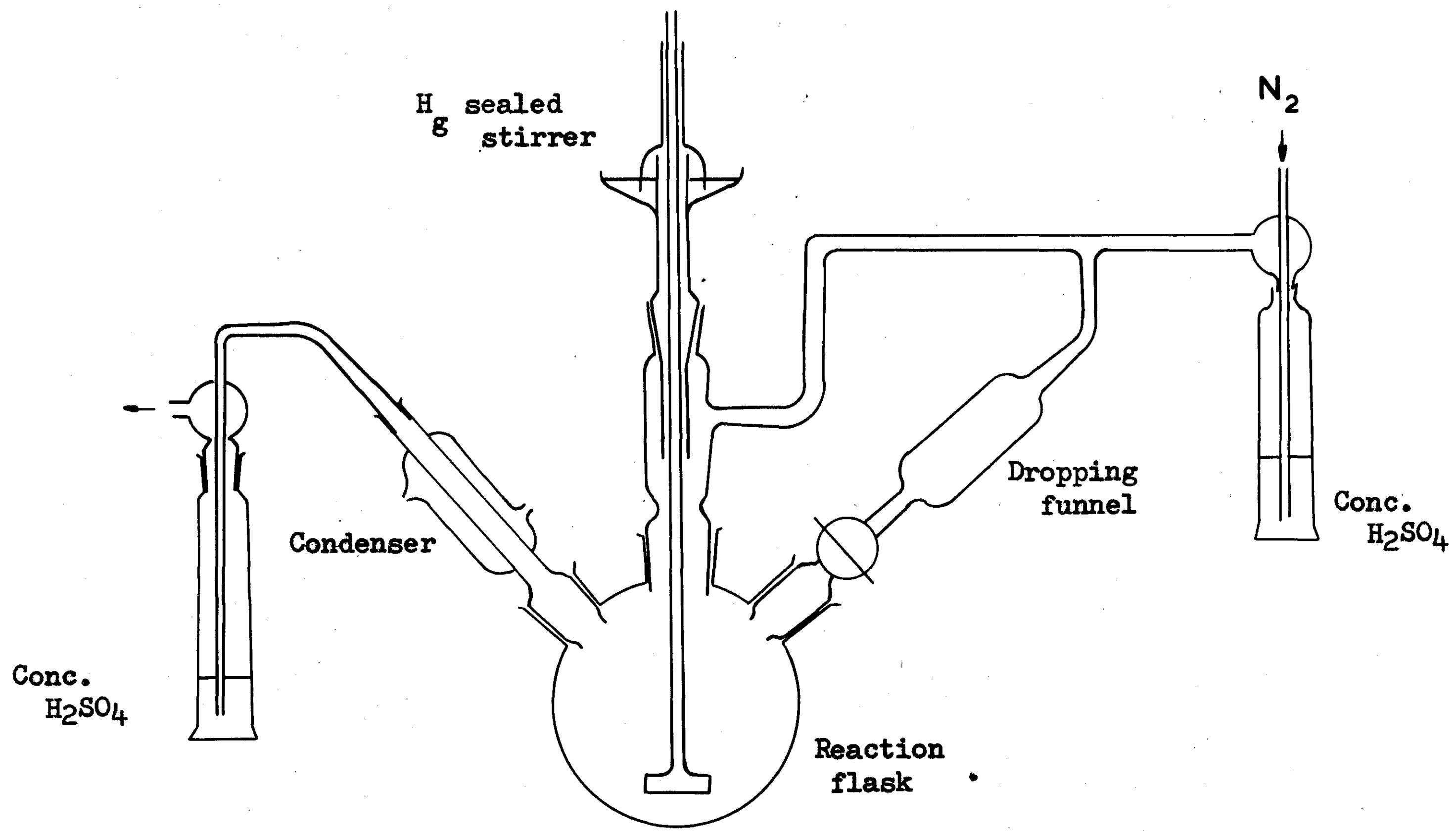
b consecutive,

$$\begin{array}{l} Ph.COCl \rightarrow Ph.CHO \text{ (adsorbed)} \rightarrow Ph.CH_2OH, \\ \qquad\qquad\quad \uparrow\downarrow \\ \qquad\qquad\quad Ph.CHO \text{ (in solution)}, \end{array}$$

we see that if we add C^{14} labelled aldehyde to the reaction mixture in the course of a Rosenmund hydrogenation, then, if a path exists to hydrogenate aldehyde from solution, we shall find a loss in total activity of the aldehyde. If the reaction, on the other hand, is completely simultaneous, i.e. aldehyde cannot return to the surface when acid chloride is present, then no loss in total activity will be found.

The necessity for using C^{14} labelled aldehyde in this method is explained as follows. It may be thought that inactive aldehyde, added during the course of a hydrogenation, would hydrogenate and be lost if the reaction was consecutive. Experimentally this was found not to be the case. On adding aldehyde to an unpoisoned hydrogenation, the aldehyde was recovered completely. At first it may appear that the reaction must therefore be

Fig. 5.



H
g sealed stirrer
N_2
Condenser
Dropping funnel
Conc. H_2SO_4
Conc. H_2SO_4
Reaction flask

simultaneous but the reaction can also be consecutive if the rate of aldehyde hydrogenation is at a maximum. Added aldehyde would not therefore hydrogenate appreciably faster and the difference in yield would not be detected with the derivative. Naturally aldehyde left at the end of a reaction would be hydrogenated, so this argument only applies in the presence of acid chloride.

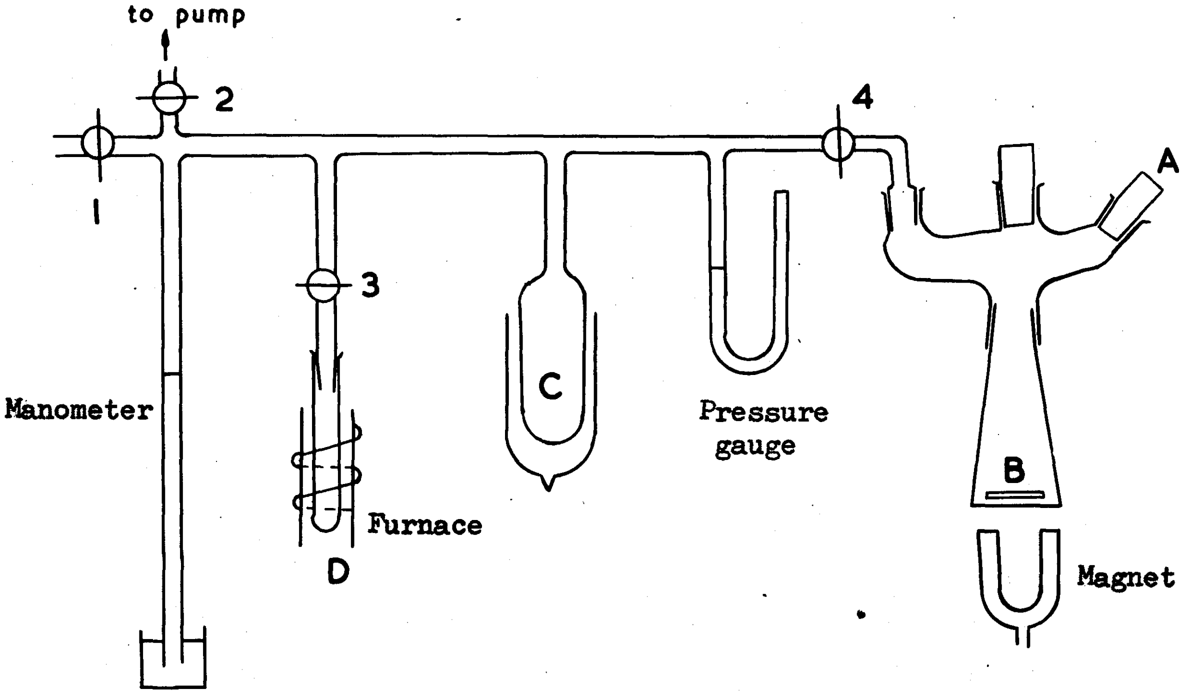
The C^{14} labelled aldehyde used was prepared by the Rosenmund reduction. The starting material was barium carbonate - C^{14} which was converted to benzoic - C^{14} acid then to aldehyde via the acid chloride.

6.6. PREPARATION OF BENZOIC - C^{14} ACID(48).

a Preparation of Grignard reagent(49).

An apparatus was prepared as in fig. 5. The apparatus was previously dried in an oven and assembled hot, 0.054 mole magnesium being placed in the flask. Nitrogen from a cylinder was then passed through it for 30 mins. 0.05 mole Bromobenzene was then placed in the dropping funnel,the stirrer was started,and 10 drops were allowed to fall onto the magnesium. 30 ml. Ether were then added to the halide and the mixture was stirred. Approximately half of this mixture was run into the flask. More solution was added from time to time to maintain the reaction.

Fig. 6.



A beaker of water was kept at hand to cool the flask, if the reaction became too vigorous. On completion of the reaction a water bath was placed round the flask and the ether was boiled gently for 30 mins whilst stirring. The flask was then cooled and a further 50 ml. ether were added to bring the solution to a suitable volume.

To determine the concentration of the Grignard reagent, portions were titrated against N/2 hydrochloric acid using phenolphthalein as an indicator. The equations are,

$$2\ Ph.MgBr + 2H_2O \rightarrow 2Ph.H + MgBr_2 + Mg(OH)_2,$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O,$$

$$\therefore\ HCl \equiv Ph.MgBr.$$

b <u>Carbonation of Grignard reagent</u>.

The carbonation of the Grignard reagent was carried out in the apparatus shown in fig. 6. The Grignard reagent was reacted with C^{14} labelled carbon dioxide. The complex formed was hydrolysed with acid to give the benzoic - C^{14} acid. The benzoic - C^{14} acid was extracted with ether and purified by forming the sodium salt and then precipitating the free acid by acidification with hydrochloric acid. To prevent loss of Grignard reagent by reaction with moisture in the apparatus, the carbon dioxide was prepared dry by the action of lead chloride on barium carbonate at 350°C rather than by acidification of the carbonate.

Procedure.

The flask, B, was dried in an oven and placed on the apparatus. Taps 2 and 3 were then closed and nitrogen was passed into the apparatus at tap 1 and out at stopper A, which was removed. 10 ml. Grignard reagent i.e. a slight excess, were pipetted into a flask B, using a dry pipette. Stopper A was then replaced and tap 1 closed. 0.005 mole barium carbonate (0.99), containing 1 mc. of barium carbonate - C^{14} of specific activity 24.75 mc./mM., and 10 g lead chloride were then placed in D. The furnace was replaced and then the contents of B were frozen out with liquid nitrogen. Taps 3, 4 and 2 were opened and the apparatus was evacuated then taps 2 and 4 were closed. The reading on the manometer was noted and then the furnace was switched on and adjusted to 350°C. The extent of carbon dioxide production was noted on the manometer. When evolution of carbon dioxide had ceased, a Dewar of liquid nitrogen was placed round vessel C and the carbon dioxide was frozen into it. Tap 3 was then closed. The carbon dioxide was taken off over a bath of acetone/dricold in order to retain any moisture which may have been present. The pressure was noted and compared with the value obtained during practice runs. Tap 4 was then opened and the carbon dioxide was frozen into flask B and tap 4 was closed again. The liquid nitrogen bath was then removed and an acetone/dricold bath at - 20°C put in its place. The stirrer was started as soon as the mixture melted. After 20 mins stirring the acetone bath was removed. To ensure complete absorption of carbon dioxide the apparatus was left overnight. The solution was acidified with dilute hydrochloric acid at 0°C. The acid was extracted with ether, the ether was in turn extracted exhaustively with a small volume of sodium hydroxide solution. The hot alkali solution was acidified and cooled; the benzoic acid then precipitated. The yield of crude benzoic - C^{14} acid was 85%, M.P.121°C.

It should be noted that the furnace vessel, D, should not be used more than once as the lead chloride attacks the glass at 350°C weakening it and under vacuum a leak can develop. Also Grignard reagent should only be present in a small excess otherwise further condensation takes place to give triphenylmethylcarbinol.

6.7. PREPARATION OF BENZALDEHYDE - C^{14}.

Benzoyl - C^{14} chloride was prepared by the thionyl chloride method previously described. The weight of benzoyl chloride obtained was 1.33 g. The acid chloride was hydrogenated by the Rosenmund procedure described in section 3.1.; the quantities used were 25 ml. toluene, 0.6 g 5% catalyst, 1.33 g benzoyl - C^{14} chloride and 0.1 mg tetramethylthiourea. On completion of the reaction, the catalyst was removed by filtration, and the solution was made up to 50 ml. with pure toluene. The solution was then divided into two 25 ml. portions. One of the portions was used to determine the yield and 2,4 - dinitrophenylhydrazine showed that a total of 0.51 g aldehyde had been produced. The activity of the aldehyde produced was determined from the derivative. The other portion was retained to be added to a further Rosenmund hydrogenation.

6.8. ADDITION OF ACTIVE ALDEHYDE DURING A ROSENMUND, HYDROGENATION.

There was no need to separate the aldehyde produced above before it was added to a Rosenmund reaction mixture. The other product, benzyl benzoate, does not interfere with the reaction. As we wished to produce conditions which were favourable for the hydrogenation of aldehyde, little or no poison had to be present. This requirement was fulfilled as the poison used in the preparation described above, 0.1 mg, would be mostly removed by the catalyst during the aldehyde preparation.

A further Rosenmund hydrogenation was performed, to which was added the second portion of active aldehyde produced in the preceding section. 0.6 g 5% Catalyst was used and 1.0 ml. benzoyl chloride was added to the mixture. The reaction was stopped at 66% completion to prevent aldehyde being hydrogenated after all the acid chloride had reacted. The 2,4 - dinitrophenylhydrazine showed that a total of 0.423 g aldehyde was present in the mixture.

6.9. COUNTING OF ALDEHYDE DERIVATIVE.

The 2,4 - dinitrophenylhydrazone was counted by the method of infinite thickness described in appendix 2. The derivative was made into a slurry with a small amount of acetone, placed on a counting tray by means of a dropper, and tapped carefully to give a smooth surface. The acetone was driven off slowly under an infra-red lamp, the tray being rotated to equalise the heat distribution. With care, a flat surface free from cracks could be obtained. When a larger quantity of derivative was required it was deposited on top of the material already present. The results are tabulated below.

Sample 1,

Weight derivative (mg)	Counts/min(-background)
100	965
112	1014
124	1071
142	1102
182	1135 ± 14
Sample 2, 84	354
137	361
174	362 ± 9

In sample 2, the aldehyde has been diluted with inactive aldehyde produced during the reaction. we shall compare the results as follows.

The total yield of active aldehyde produced in the first hydrogenation = 0.51 g,
therefore, that quantity of active aldehyde added in the second hydrogenation = 0.5 x 0.51 = 0.255 g,
therefore, the total counts per minute of aldehyde added to the reaction = 0.255 x 1135 x F,
where F is a standard factor required to convert the measured counts per minute per tray, at infinite thickness into counts per minute per gram of aldehyde.
The weight of aldehyde recovered in the second hydrogenation = 0.423 g.
Let this have a count rate of C counts per tray, counted under the same conditions as before. Them if we assume that no active aldehyde was lost during the second hydrogenation,

$$C \times F \times 0.423 = 0.255 \times 1135 \times F$$

$$\text{i.e.} \quad C = \frac{0.255 \times 1135}{0.423} \quad 684 \text{ c.p.m.}$$

Let the fraction of active aldehyde which was unchanged be f. Then the fraction of the total counts remaining in the second hydrogenation = f x 0.255 x 1135 x F. But the observed count rate was 362 counts per minute. Thus the total number of counts present in the second hydrogenation = 362 x F x 0.423.

Therefore, $f \times 0.255 \times 1135 \times F = 362 \times F \times 0.423$.

Therefore, $f = \dfrac{362 \times 0.423}{0.255 \times 1135} = 0.53$.

Therefore 47% of the active aldehyde had been hydrogenated when the reaction was 66% complete as measured by hydrogen chloride evolution.

6.10. CONCLUSION.

The results imply that a reaction path exists in the Rosenmund hydrogenation whereby aldehyde, produced during the reaction, can leave the catalyst surface and can then return and be hydrogenated further. The Rosenmund reaction therefore appears to be consecutive, i.e. the mechanism is,

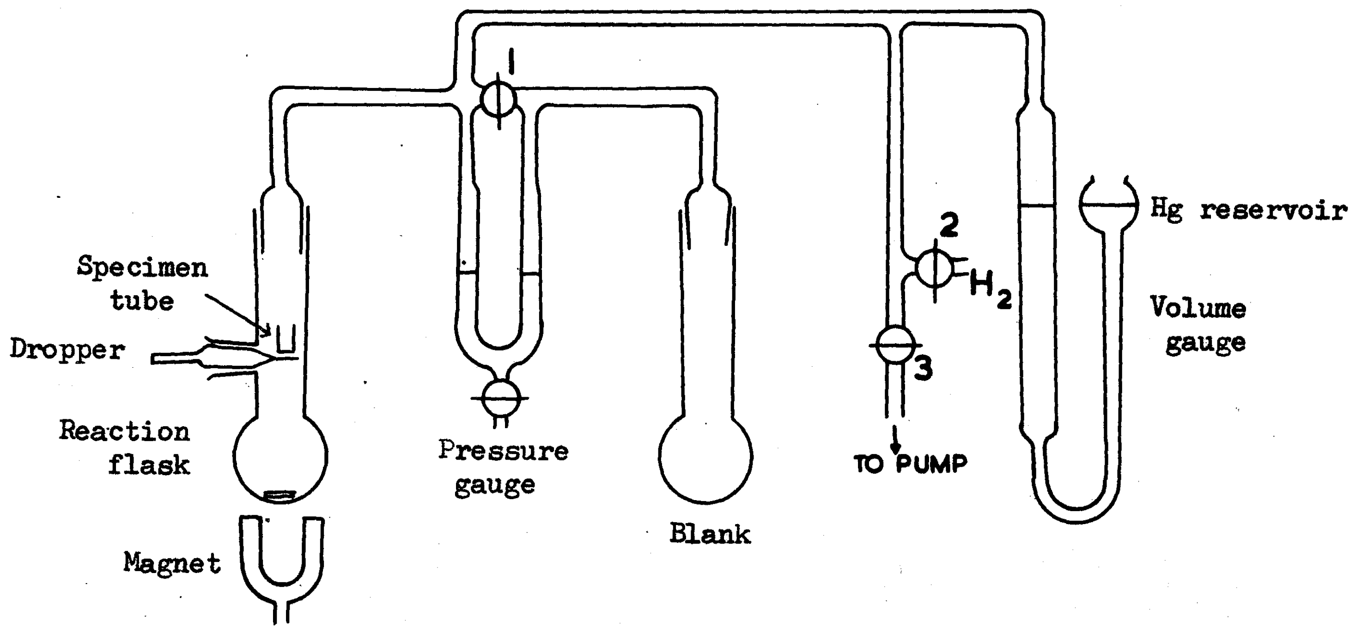
$$\begin{array}{l} \text{Ph.COCl} \longrightarrow \text{Ph.CHO(adsorbed)} \longrightarrow \text{Ph.CH}_2\text{OH.} \\ \qquad\qquad\qquad\quad \upharpoonleft\!\downharpoonright \\ \qquad\qquad\qquad \text{Ph.CHO(in solution)} \end{array}$$

Since it has now been established that the Rosenmund reaction proceeds by a consecutive mechanism, it is now permissible to examine the effect of poisons on the rate of aldehyde hydrogenation. Diminution of this rate would correspond to an increase in Rosenmund reaction yields.

CHAPTER 7.

HYDROGENATION OF ALDEHYDE.

Fig. 7.


1
2
3
H_2
Hg reservoir
Specimen tube
Dropper
Reaction flask
Magnet
Pressure gauge
Blank
TO PUMP
Volume gauge

7. HYDROGENATION OF ALDEHYDE.

As it was desired to compare the hydrogenation data with later adsorption studies, it was decided to investigate the hydrogenation of aldehyde at room temperature. The measurement of adsorptions at high temperatures is too complicated for a preliminary investigation.

7.1. APPARATUS AND PROCEDURE.

In order to study hydrogenation of aldehyde at room temperature an apparatus was built, as shown in fig. 7, to measure absorption of hydrogen.

PROCEDURE.

The catalyst was weighed into the flask and the solvent added. If poison was used, it was added at this stage. The dropper, which consisted of an air lead flattened and sealed at one end, was placed in position and the aldehyde solution was pipetted into a sample tube and carefully lowered onto the dropper. The reaction flask was then placed on the apparatus. The blank consisted of a flask containing toluene in an equal amount to that in the reaction flask. The two flasks were mounted close together on the apparatus so that each was under exactly the same conditions. Any change in temperature during the experiment resulted in the same change in vapour pressure of the toluene in the two flasks and was thus cancelled out on the differential pressure gauge. The pressure gauge was filled with vacuum oil as this was more sensitive to pressure change than mercury. The mercury reservoir was adjusted to its lowest position. A hydrogen cylinder was then connected to tap 2 and a vacuum pump to tap 3. Tap 1 was left open and tap 3 was opemed to the pump position. The apparatus was thereby evacuated, and when a reasonable vacuum had been attained, shown by the level of mercury in the volume gauge, tap 3 was closed and tap 2 opened to admit hydrogen, till atmospheric pressure was reached again. Tap 2 was then closed and the process repeated four times to ensure complete replacement of air by hydrogen. The apparatus was then evacuated and hydrogen admitted slowly till the mercury levels in the graduated tube and the reservoir, which was positioned opposite the bottom of the graduated tube, were equal. The apparatus was now exactly at atmospheric pressure. Taps 1 and 2 were then closed and the hydrogen cylinder and pump were disconnected. Adjustment of the levels in the differential pressure gauge to the marker line therefore indicated atmospheric pressure throughout the experiment. The magnetic stirrer was switched on and hydrogen absorption commenced. Readings were taken by adjusting the mercury reservoir, which was connected to a fine control for ease of manipulation, till the levels in the pressure gauge were equal. The volume was then read on the graduated tube. After the absorption had ceased, the dropper was rotated and the sample tube fell into the mixture. Readings were then taken every minute till absorption ceased.

7.2. EFFECT OF POISON ON ALDEHYDE HYDROGENATION.

The effect of poison on aldehyde reduction is shown in graph 5. Thiophene poisons the reaction as was expected. Tetramethylthiourea has the surprising result of stopping the reaction at the alcohol stage, but not slowing the rate of reduction when used in "normal" amounts. It is seen, therefore, that at room temperature, thiophene poisons the hydrogenation of aldehyde. Tetramethylthiourea is not a poison for aldehyde hydrogenation at this temperature and is not therefore suitable as a poison in the investigation of adsorption isotherms at room temperature.

7.3. THE EFFECT OF CONCENTRATION ON REACTION RATES.

If adsorption bears any relation to catalysis then we may expect a correlation between the amount of aldehyde adsorbed on the catalyst and the rate of hydrogenation at any given concentration. It was

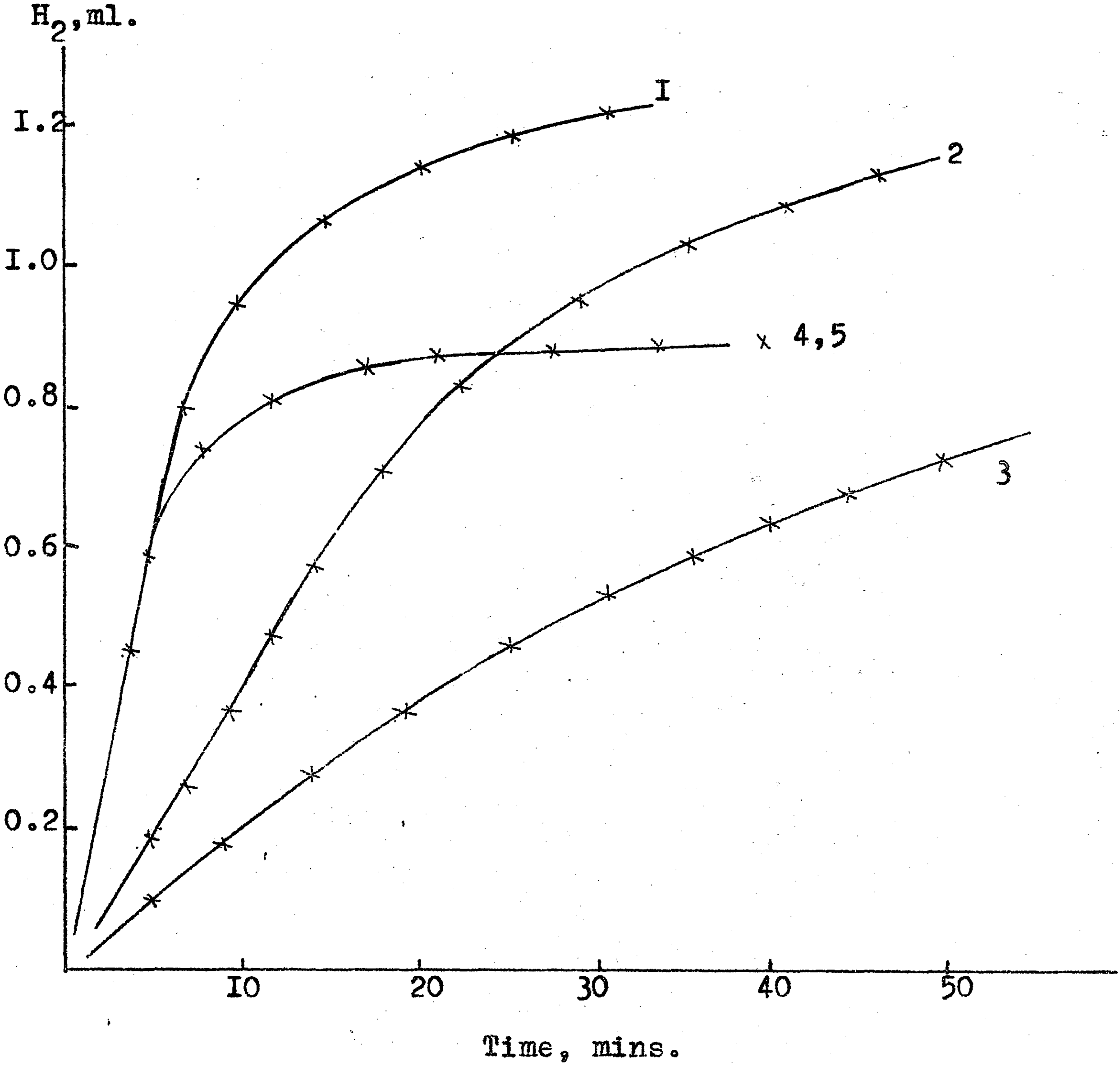
GRAPH 5

Aldehyde hydrogenation.

I-unpoisoned,

2- 0.2 mg thiophene, 4- 0.05 mg tetramethylthiourea,

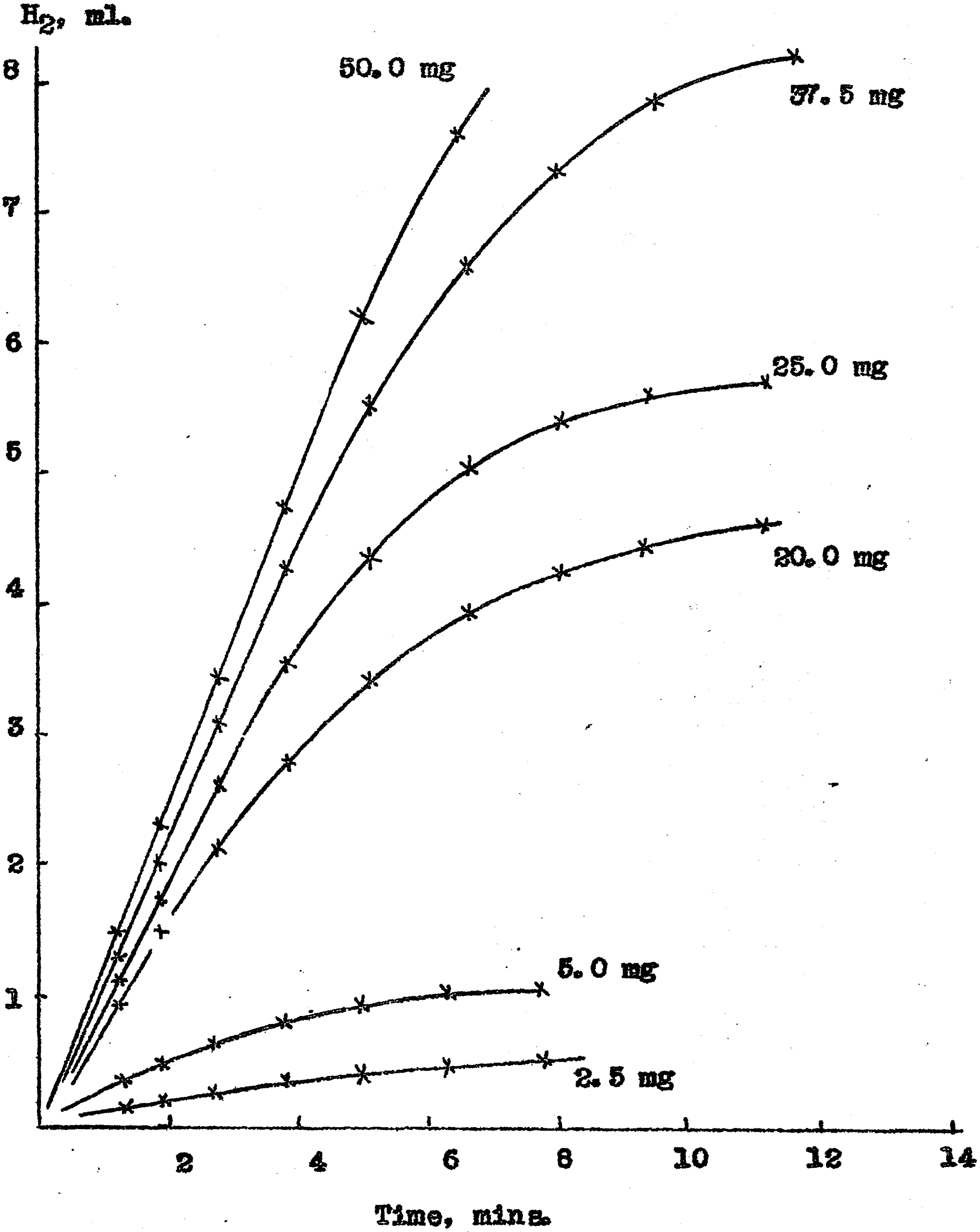
3- 0.3 mg " 5- 0.10 mg "



therefore decided to examine the hydrogenation rates of aldehyde at various concentrations. The hydrogenations were carried out on 0.05 g 10% catalyst (the same catalyst being used in the adsorption studies) in a total volume of 5 ml. toluene. The results are shown in graph 6. The initial rate of reaction was taken from the curves, for each amount of aldehyde added, and plotted against the concentration as in graph 7. It should be noticed that there is a definate break in the graph at about 5.0 mg aldehyde per ml.

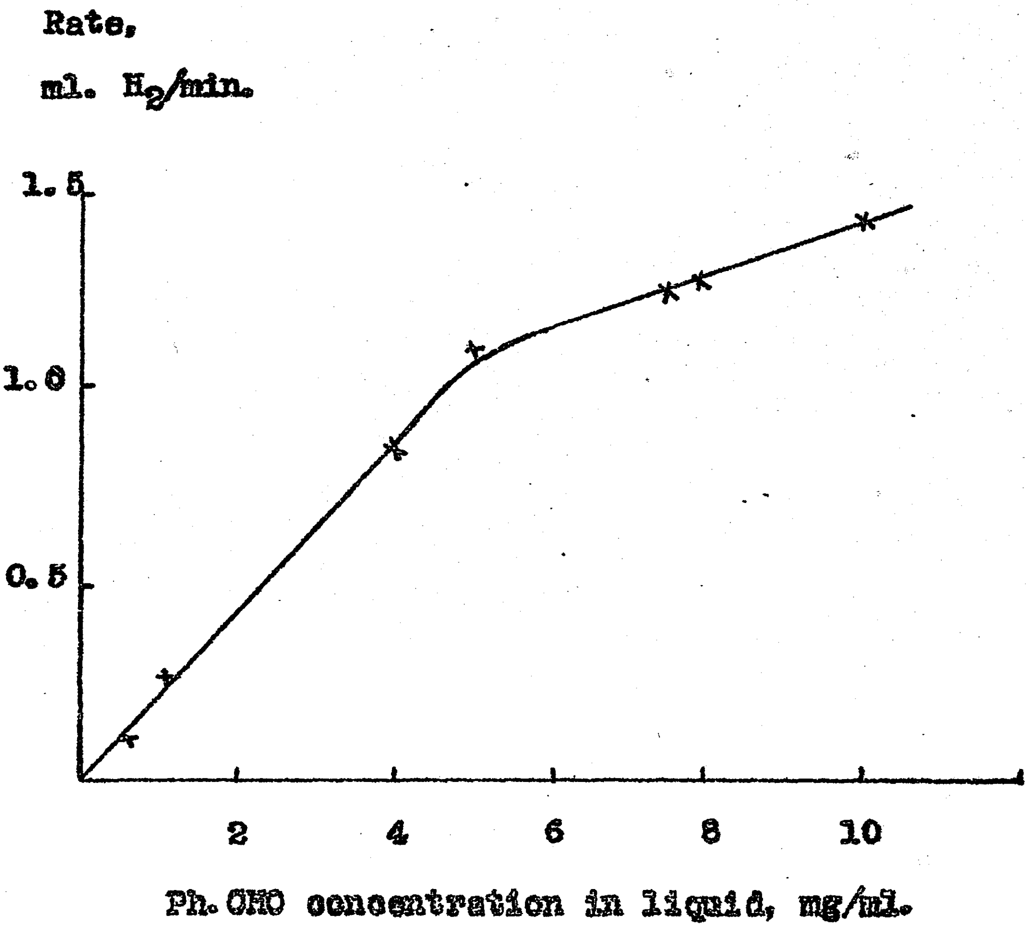
GRAPH 6

Aldehyde hydrogenation



GRAPH 7

Aldehyde hydrogenation rate



CHAPTER 8.

HYDROGENATION OF BENZOYL CHLORIDE AT ROOM TEMPERATURE.

8. HYDROGENATION OF BENZOYL CHLORIDE AT ROOM TEMPERATURE

As the Rosenmund reaction has been shown to be consecutive (section 6.10), then any substance which slows aldehyde hydrogenation is a potential selective poison. Our prime interest, therefore, lies with the hydrogenation of aldehyde. However, in view of the difference in poisoning with tetramethylthiourea at high and low temperatures, it was decided to investigate the hydrogenation of benzoyl chloride at room temperature.

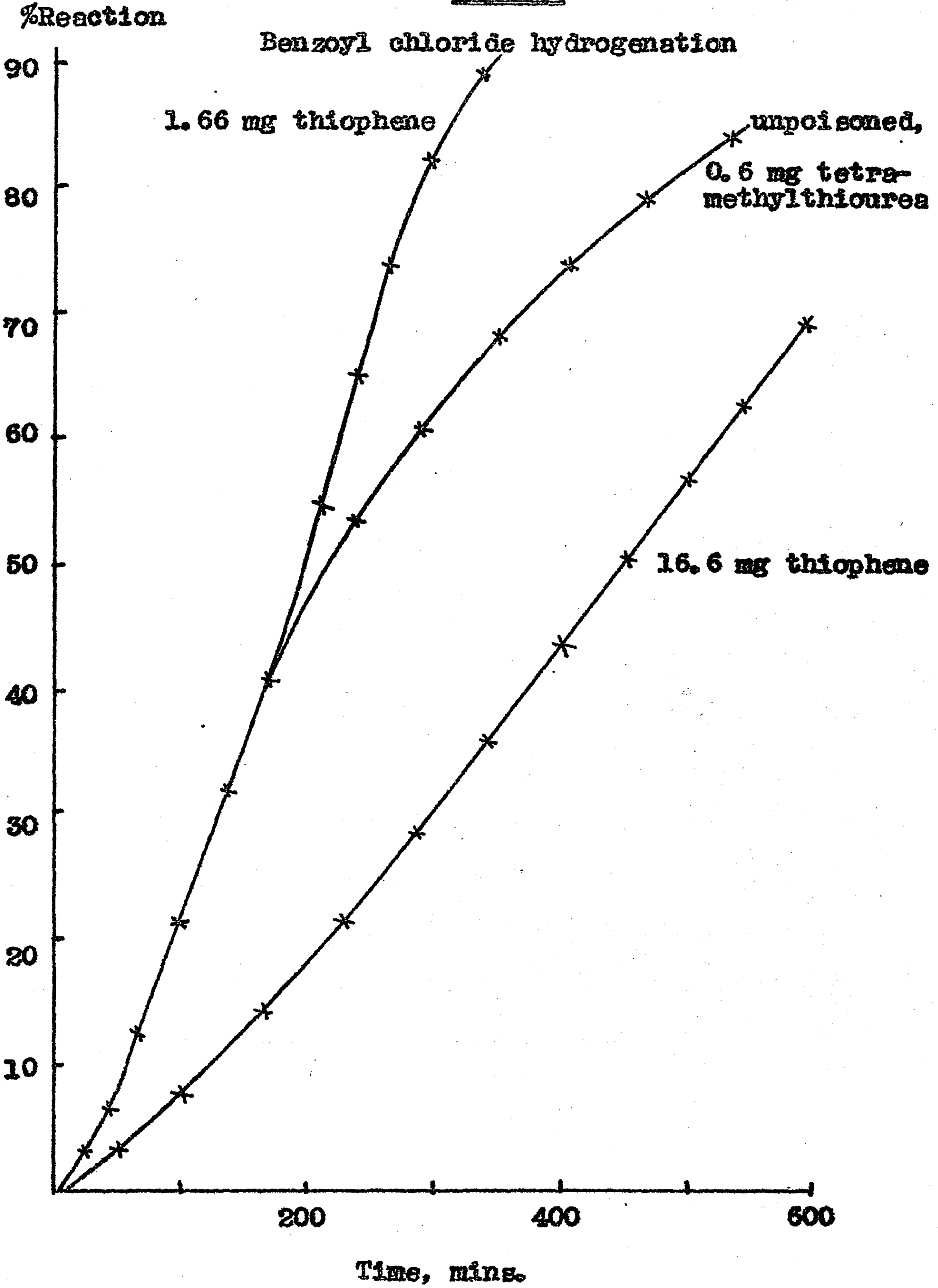
8.1. APPARATUS AND PROCEDURE.

The apparatus consisted of a flask equipped with a hydrogen inlet, almost touching the bottom of the flask, and an outlet led under water in a beaker to trap hydrogen chloride evolved. The acid was titrated with caustic soda using phenolphthalein as indicator. Because of the slow rate of reaction, only small amounts of benzoyl chloride were used. The rate of reaction is shown in graph 8 for 0.6 g 10% catalyst and 60.0 mg benzoyl chloride in 10 ml. toluene.

8.2. RESULTS.

The experiment was repeated using thiophene and tetramethylthiourea as poisons, graph 8. Tetramethylthiourea did not affect the rate, small amounts of thiophene increased the rate in the later

GRAPH 8

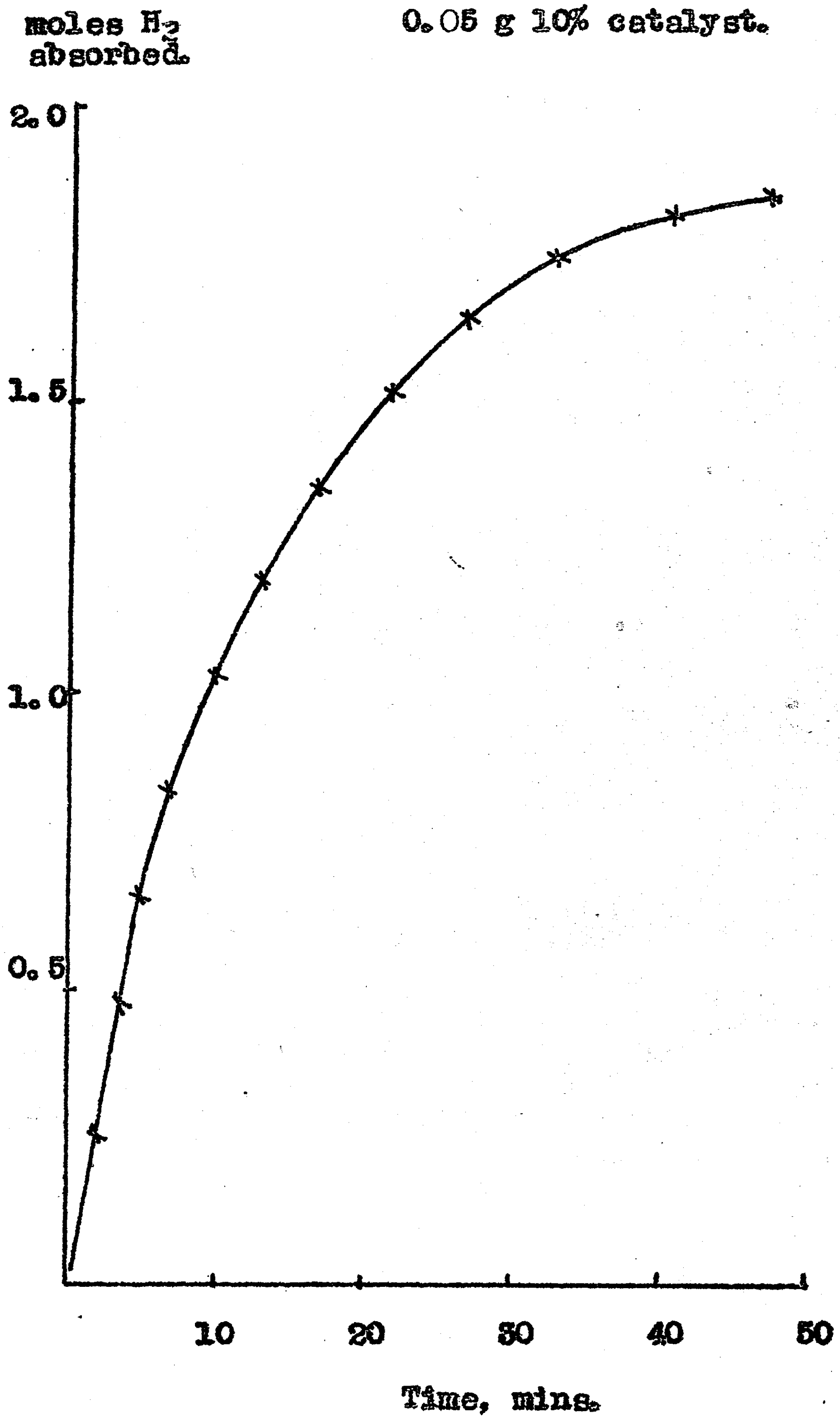

%Reaction
Benzoyl chloride hydrogenation
1.66 mg thiophene
unpoisoned,
0.6 mg tetramethylthiourea
16.6 mg thiophene
90
80
70
60
50
40
30
20
10
200
400
600
Time, mins.

stages of the reaction while very large amounts, e.g. 16 mg on 0.6 g 10% catalyst, decreased the rate by about half. No yield of aldehyde was obtained with thiophene or tetramethylthiourea. These strange results merited further investigation. The hydrogenation of benzoyl chloride was examined on the hydrogen absorption apparatus described above, fig. 7. This apparatus was not used initially, as the hydrogenation of benzoyl chloride produced hydrogen chloride which might have masked the absorption of hydrogen. With small amounts of benzoyl chloride, the hydrogen chloride produced probably remained dissolved in the toluene. The same applies to the initial stages of reduction of larger amounts of benzoyl chloride. The rate of reaction is shown in graph 9 for 0.05 g 10% catalyst and 30.0 mg benzoyl chloride in 5 ml. toluene. The reaction is therefore much faster than when measured by evolution of hydrochloric acid, see graph 10, 0.2 g 10% catalyst and 30.0 mg benzoyl chloride in 5 ml. toluene. The probable reason for this is the formation of palladium chloride with the hydrochloric acid (50). The rate measured at room temperature by evolution of hydrochloric acid is the rate of hydrogenation of palladium chloride. At high temperatures we did not have this delay between hydrogen absorption and hydrochloric acid

GRAPH 9

Benzoyl chloride hydrogenation

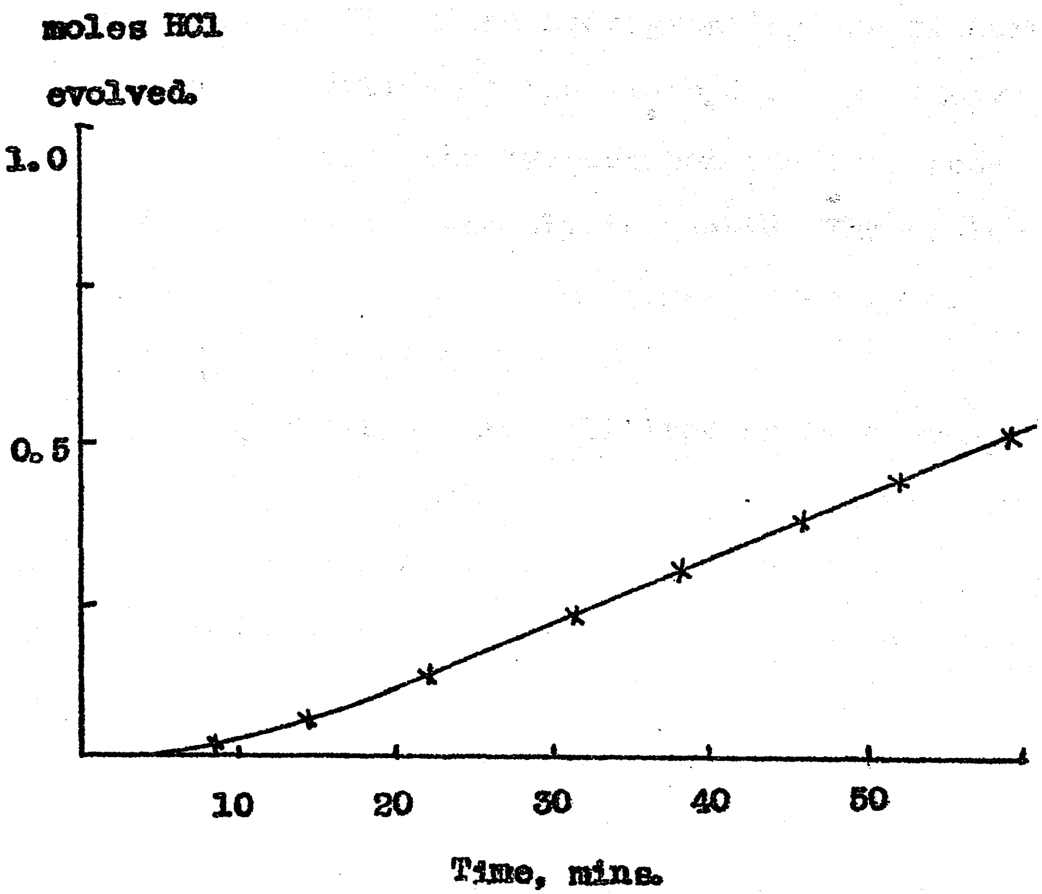
0.05 g 10% catalyst.



GRAPH 10

Benzoyl chloride hydrogenation

0.2 g 10% catalyst.



evolution, see graphs 3 and 4. Any palladium chloride formed at high temperatures must therefore be hydrogenated rapidly.

In view of the above results the hydrogenation of aldehyde at room temperature was re-examined, this time in the presence of benzoyl chloride.

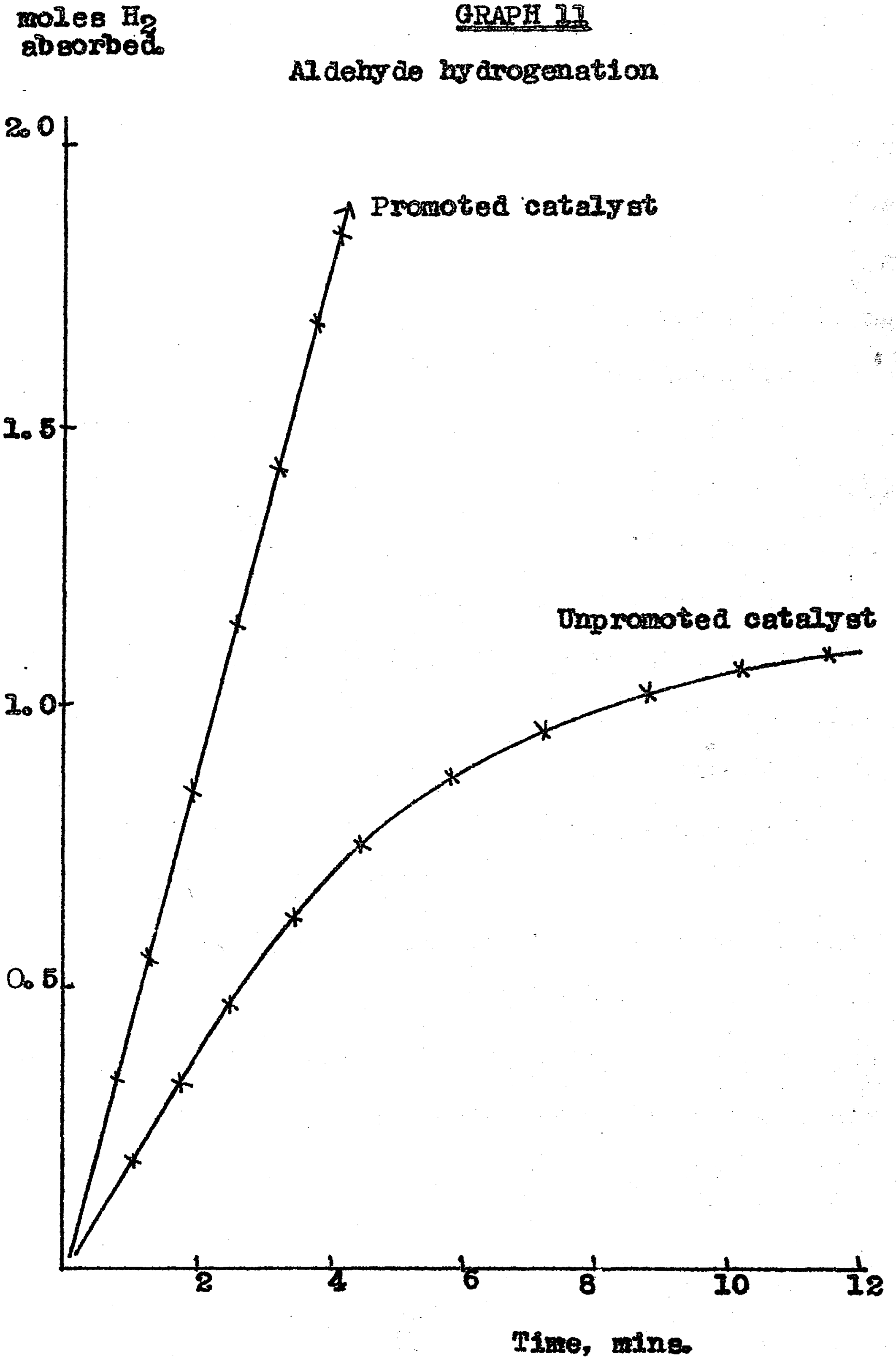
8.3. HYDROGENATION OF ALDEHYDE ON PRE-TREATED CATALYSTS

Graph 11 shows the effect of pre-treating the catalyst with benzoyl chloride before hydrogenation of the aldehyde. These experiments were carried out by adding benzoyl chloride to the catalyst and toluene in the reaction flask and hydrogenating the mixture fully before addition of the aldehyde. The aldehyde was hydrogenated to the hydrocarbon and the speed of hydrogenation was greatly increased. The action of benzoyl chloride on the catalyst, therefore, promotes the hydrogenation of aldehyde.

As the catalyst has a limited surface area, then when we hydrogenate large concentrations of benzoyl chloride or aldehyde, the rate of hydrogenation will be at a maximum. We see therefore, that with "normal" quantities of reactants, if we hydrogenate aldehyde and acid chloride together we will not increase the rate of hydrogen absorption over that for acid chloride alone. When the rate of hydrogenation is still concentration dependent however, i.e. at low

GRAPH 11

Aldehyde hydrogenation



concentrations, then if the reaction is consecutive, we may expect that the overall rate of hydrogen absorption of aldehyde and acid chloride would be greater than that for acid chloride alone. This was observed, and the results are shown in graph 12 for 30 mg benzoyl chloride in 5 ml. toluene with 0.05 g 10% catalyst, and 30 mg benzoyl chloride plus 20 mg benzaldehyde under the same reaction conditions. It is seen that aldehyde and acid chloride hydrogenate at the same time suggesting a consecutive mechanism.

It should be noticed that there is a slight delay in attaining maximum rate when aldehyde and acid chloride are hydrogenated together. This delay is not observed when aldehyde is hydrogenated on a pre-treated catalyst, graph 11 and is therefore probably due to formation of the palladium chloride.

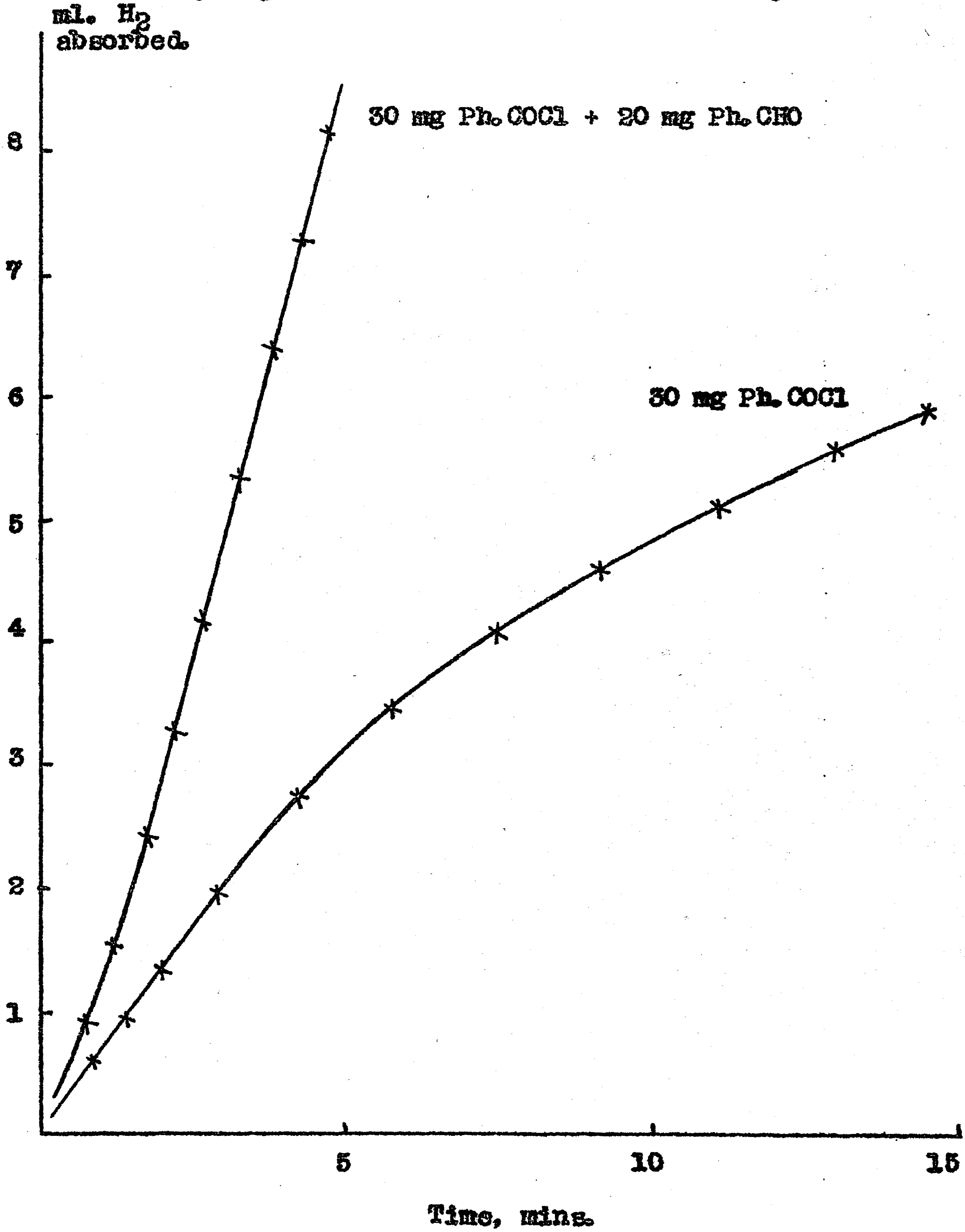
8.4. CONCLUSION.

The results obtained in this section showed that the action of benzoyl chloride changed the nature of the catalyst for aldehyde reduction. The first stage in the Rosenmund hydrogenation can now be thought of as a chemical reaction between the benzoyl chloride and the palladium, e.g.

$$\mathrm{Ph.COCl} + \mathrm{Pd} + \tfrac{1}{2}H_2 \longrightarrow \mathrm{Ph.CHO} + \mathrm{PdCl}.$$

GRAPH 12

Hydrogenation of acid chloride + aldehyde



CHAPTER 9.

MEASUREMENTS OF ADSORPTION.

9. MEASUREMENTS OF ADSORPTION.

9.1. INTRODUCTION.

The fundamental question in catalysis is, which of the reactants are actually on the catalyst surface? An answer to this can be obtained from the measurement of adsorption isotherms. The importance of the adsorption isotherm in our problem can be seen from the mechanism. The previous results have enabled us to reduce possible reaction paths to one probable mechanism,

$$\begin{array}{lll} \text{Ph.COCl} \rightarrow & \text{Ph.CHO (adsorbed)} & \rightarrow \text{Ph.CH}_2\text{OH.} \\ & \quad\;\; \upharpoonleft\downharpoonright & \\ & \text{Ph.CHO (in solution)} & \end{array}$$

The poison can act purely as a surface blocking agent or it can act electronically e.g. by modifying the electronic nature of the hydrogen, or catalyst, or adsorbed aldehyde. In the first case poison could block the readsorption of aldehyde from the solution and thereby increase the yield. In the second case, though aldehyde could readsorb, it would not be hydrogenated further. We therefore see that by examining the adsorption isotherms of aldehyde with and without poison present we would be able to determine the detailed action of the poison.

9.2. MEASUREMENTS OF ADSORPTION.

In essence the determination of adsorption isotherms for a compound depends on the following sequence of operations. The substance, in a standard solution, is brought into contact with a weighed amount of catalyst for a standard time. The solution is then removed and the new concentration is determined. The amount of the substance adsorbed on the catalyst can therefore be calculated. As, for reasonable quantities of catalyst, the amounts of the substance adsorbed are very small, e.g. microgram or milligram quantities, we see, therefore, that the determination of adsorption isotherms depends on the quantitative analysis of very small quantities.

The methods used previously have been mainly colourimetric, spectrometric, or interferometric in order to attain the high degree of sensitivity required. An example of the colourimetric method is shown in section 4.2. The spectrometric method is similar and there are many examples of its application, particularly to the adsorption of dyes(14). Interferometric methods have been used successfully to measure adsorptions of fatty acids (51,52).

These methods have severe limitations. They are applicable only to those compounds which have the necessary molecular properties, e.g. in the case of colourimetric methods only those compounds for which suitable colour tests exist can be studied. They are also usually only applicable to simple systems, the presence of other compounds interfering with or nullifying the method. A further limitation is that the molecule being studied may be altered structurally during the investigation and so render the methods inapplicable. This is especially true in the case of adsorption studies connected with catalysis, where hydrogenation or complete breakdown of the molecule may take place. A solution to all these difficulties is to use a sensitive radiochemical method. These methods can be applied to complicated systems and are independent of change in molecular structure. If, for example, we consider the estimation of thiourea attempted in section 4.2., we see that none of the initial methods can be applied as the molecule breaks down to elementary sulphur. As, however, radioactivity is a property of the atom and is independent of the molecular structure, it is seen that by labelling the thiourea with active sulphur we could follow the change in concentration of the sulphur at any time independently of the state of the rest of the molecule.

9.3. PROBLEM OF RADIOACTIVE COUNTING IN ADSORPTION SYSTEMS.

There are three main methods of counting radioactive isotopes.

End-Window Counting

The isotopes required for our purpose, C^{14}

and S^{35}, are low energy β - emitters. As end-window counting is extremely inefficient, of the order of 1%, then, if we wish to employ this method, high activities must be used. The use of high activities introduces experimental difficulties. Self-destruction of the compounds containing the active isotope may take place. Manipulation of the samples becomes much more hazardous, especially where volatile, active compounds are being used in a number of determinations. The expense of the radio-isotope also rises considerably.

The actual samples themselves are not easily made reproducible in view of the self-absorption and other corrections required. For an adsorption curve determination, a large number of samples has to be accurately compared and so a more convenient method was devised.

Gas Counting.

A very efficient method of estimating radio-activity makes use of gas counting. In this procedure the substance being examined is converted to a gas, e.g. C^{14} labelled compound converted by combustion to carbon dioxide - C^{14}. The active gas is then introduced into a gas counter. This method overcomes difficulties due to self - absorption or the geometry of the active source.

A very high efficiency of counting is obtained as all the activity introduced into the Geiger-Müller tube is counted. However the method is very time consuming and is therefore unsuitable for the determination of adsorption isotherms in which a large number of samples have to be counted.

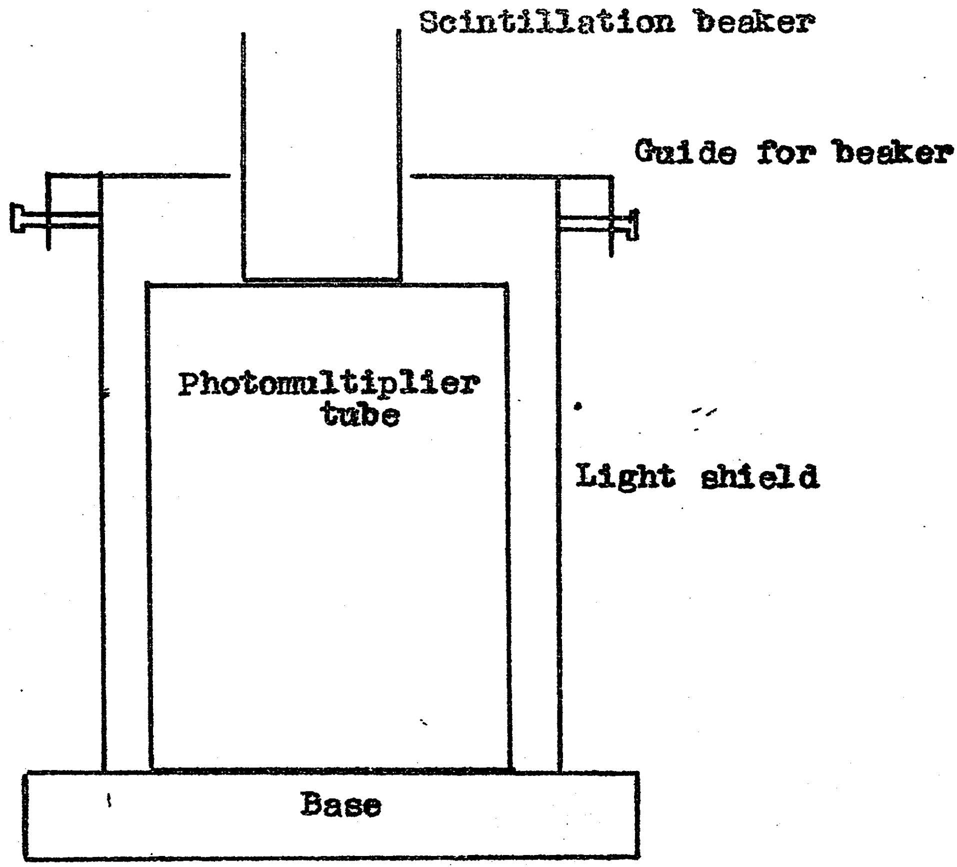
Liquid Scintillation Counting.

Liquid scintillation counting is the most useful method for our purpose. In the determination of adsorption curves, it was noted that a solution was contacted with a catalyst; the catalyst was then removed and the problem concerned the determination of the concentration (activity) of the solution remaining. With the liquid scintillation counter the solution obtained after centrifuging is transferred directly into the scintillation liquid in many cases, as there is often no preparation or conversion required of the compound to be counted. The efficiency of the liquid scintillation counter is about 60% and there is no correction needed for self-absorption or for the geometry of the active source. Speedy and accurate operation can readily be obtained.

CHAPTER 10.

THE SCINTILLATION COUNTER.

Fig. 8


Scintillation beaker
Guide for beaker
Photomultiplier tube
Light shield
Base

10. THE SCINTILLATION COUNTER.

10.1. INTRODUCTION.

The scintillation counter, fig 8, unlike the other counters mentioned, is not based on gas ionisation. When a β-emitter is dissolved in the scintillation liquid, the radiation is converted into light. There are many types of scintillator, solid and liquid, organic and inorganic. They all have the property that the action of radiation on the scintillator molecules produces an excited state. This excited state loses energy in the form of visible or uv photons. As the adsorption isotherms were required for compounds dissolved in toluene, the scintillator chosen for our use was toluene based. It was therefore possible to transfer the solution to be examined directly into the scintillator without further treatment so increasing the accuracy and convenience of the determinations. The scintillation compounds are specially chosen for good characteristics, i.e. good light yields and short light decay times.

The light, generated in the scintillator, falls on the photocathode of a photomultiplier tube. The photoelectrons produced fall on a secondary electrode or dynode. Each photoelectron produces several secondary electrons, at this dynode, which are in turn multiplied at further dynodes. If the intial number of photoelectrons is n, then the amplification is n^x, where x is the number of dynodes. The gain of a photomultiplier can be over one million times. The signal from the photomultiplier is amplified and counted on a scaler or ratemeter.

10.2. FIRST COUNTING APPARATUS.

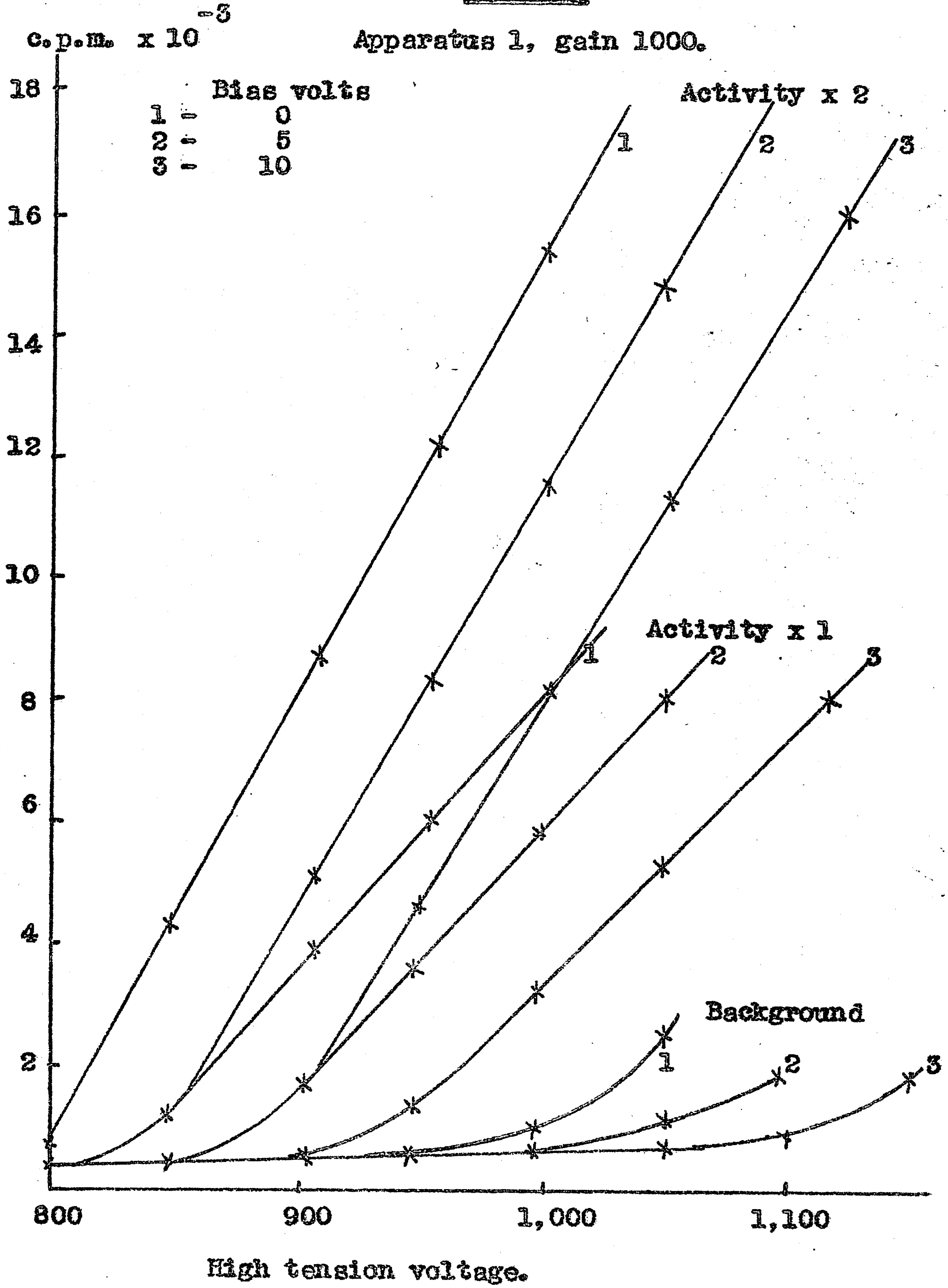
In the first counting apparatus, a scintillation beaker, 7cm high and 2.8cm in diameter, was used. The scintillation beaker is specially constructed from glass having a very low content of natural radioisotopes, e.g. K^{40}, to reduce background. The outside of the beaker is coated with metal in order to reflect light back into the counter and thus minimise light loss. The scintillation beaker has a flat base and is placed on the face of a photomultiplier tube, fig 8. To ensure good optical contact a drop of silicone oil was smeared over the face of the photomultiplier tube before placing the beaker in position and when the beaker was not on the apparatus, it was stood on a Petri dish containing silicone oil. In order to obtain reproducible results, the scintillation beaker has to be placed always in the same position on the photomultiplier tube. To achieve this, a metal guide, having a hole just wider than the diameter of the beaker was fixed over the photomultiplier tube. The photomultiplier tube was kept in a light-tight box which was only opened when the illumination was provided solely by a weak red light. The scintillation liquid was also kept in darkness till it was required, to reduce the possibility of phosphorescence which would give an apparently increased count rate.

The output from the photomultiplier tube, E.M.I. 6097 S, was fed into an Ekco amplifier, type N640A, and thence to an Ekco scaler, type N529B. A power pack in the scaler provided the high tension for the photomultiplier tube.

The characteristic counting curves for the apparatus were obtained using 20 ml. scintillator, Nuclear Enterprises type N.E. 213. The background, with the scintillator in the beaker, was determined for different settings of the bias control in the scaler and the gain control on the amplifier. 0.1 ml. Cyclohexane - C^{14}, specific activity approximately 0.3 microcuries per ml., was then added to the scintillation liquid and the mixture was stirred to ensure a homogeneous solution. The change in volume of the solution in the scintillation beaker is not critical as its own volume of solvent can be added to the scintillation liquid, producing only 2-3% difference in the count rate. The count rate of the cyclohexane - C^{14} was determined for various positions of the controls as for the background. The results are shown in graphs 13 and 14.

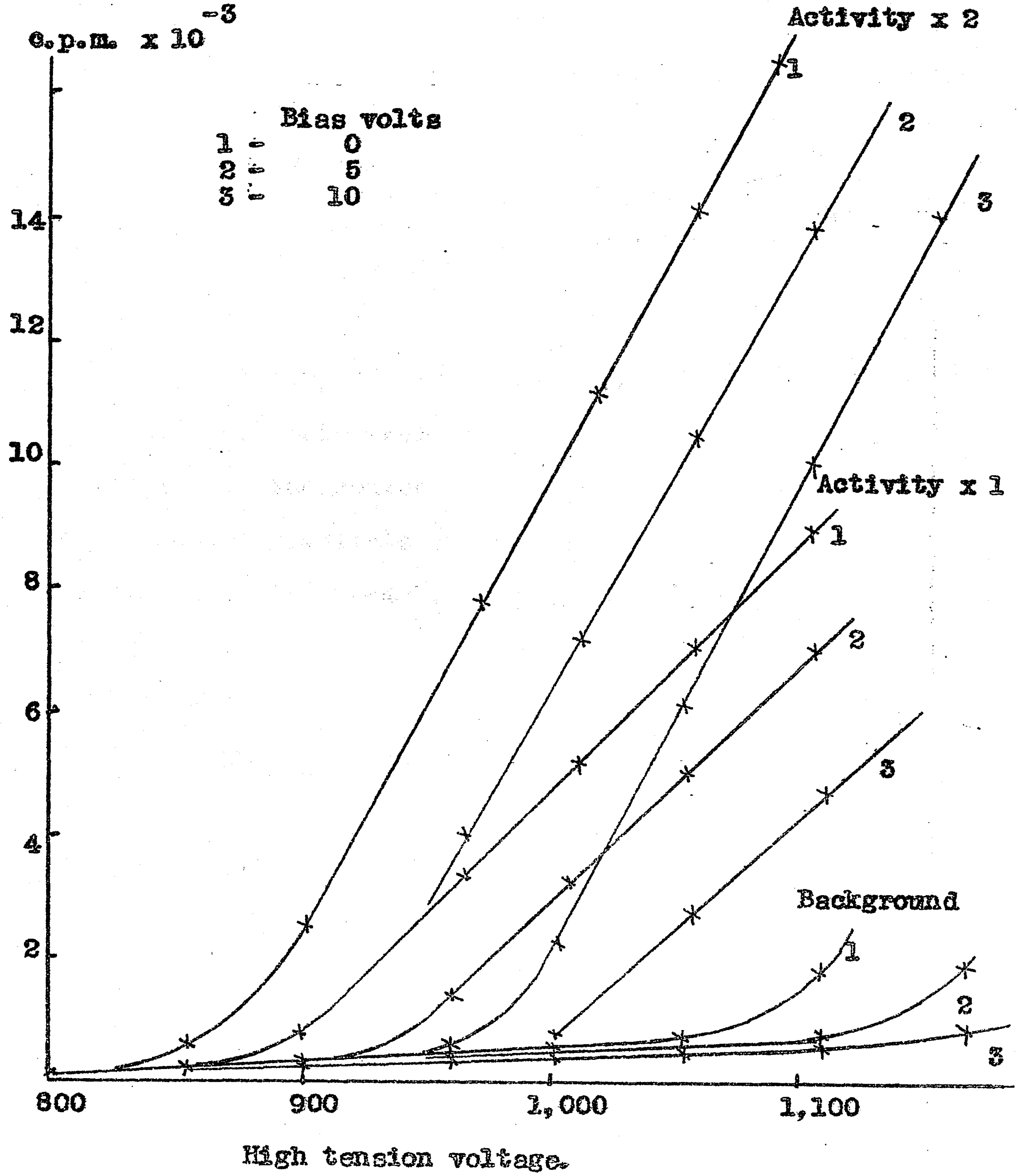
It is seen from the graphs that increasing the voltage on the photomultiplier tube increases the observed count rate. This is a result of the increase in the strength of the output pulses from the photomultiplier tube produced by increasing the voltage on the dynodes. As the strength of the output pulses also depends on the energy of the radiation, which is not constant but follows a distribution pattern, then a distribution in height of the output pulses is obtained. Increasing the voltage on the photomultiplier tube therefore increases the number of pulses which are large enough to surmount the barrier set by the discriminator bias on the scaler and so results in an increase in count rate. Conversely raising the barrier in the discriminator, by increasing the bias voltage reduces the count rate. The background and the active source both show these effects. It is seen, graph. 13, that with the gain control on the amplifier at 1000 and the bias at zero, the background is reasonably low up to 1000 volts high tension after which it rises rapidly. Increasing the bias delays the rise in background to higher voltages. The count rate of the source increases linearly over a large range of high tension voltage. Increasing

GRAPH 13


c.p.m. x 10^{-3}
Apparatus 1, gain 1000.
Bias volts
1 - 0
2 - 5
3 - 10
Activity x 2
Activity x 1
Background
1
2
3
18
16
14
12
10
8
6
4
2
800
900
1,000
1,100
High tension voltage.

GRAPH 14

Apparatus 1, gain 500.



the bias decreases the count rate and displaces the curve towards higher voltages, the gradient of the linear portion of the curve remaining the same, e.g.

BIAS	GRADIENT, c.p.m./V	
volts.	Approx. 0.1 ml. cyclohexane-C^{14}.	Approx. 0.2 ml. cyclohexane-C^{14}.
0	4.5	7.3
5	4.5	7.3
10	4.5	7.3.

The gradient of the background is 0.2 c.p.m./V. If we subtract this from the gradients found for the activities of the sources including the background, we obtain the gradients of the activities of the sources, i.e. 4.3, and 7.1 c.p.m./V respectively. The ratio of these gradients gives us the ratio of the activities of the sources, i.e. 1.65. At any given voltage, the count rates obtained for different active sources will be related to the activities of the sources. The characteristic counting curves for the apparatus, with the amplifier gain control set at 500, are shown in graph 14.

The determination of adsorption isotherms was carried out with the amplifier gain control at 1000 and with zero bias voltage on the discriminator of the scaler. Maximum amplification was thereby obtained enabling small activities, corresponding to small amounts of aldehyde, to be measured. As the background rises rapidly when the voltage on the photomultiplier tube is increased beyond 1000V, the high tension was fixed at 900V to ensure a low background.

The results obtained (discussed later) by using this apparatus showed that a very small amount of aldehyde was adsorbed by the catalyst, i.e. the percentage loss of aldehyde, from the solution, was very low. The reproducability of measurement by the apparatus was therefore of great importance. It was decided to assemble a more accurate apparatus having improved stability.

10.3. SECOND COUNTING APPARATUS.

The larger the energy of the radiation of an active source above the background, the easier it is to measure accurately the activity of the source. As we are restricted to one isotope, C^{14}, we cannot alter the energy of the radiation of the source. However we can alter the background. A large proportion of the background from a photomultiplier tube originates in the thermal emission of electrons from the photocathode. It is possible to reduce this

Fig. 9

Photomultiplier —— Power pack

Cathode follower

Amplifier

Pulse analyser

Scaler — Ratemeter

thermal emission by cooling the photomultiplier tube. The use of liquid nitrogen as a coolent gives very good reduction of backgrounds(53), but as it may have led to trouble with moisture condensation problems it was not considered worthwhile to employ it. Therefore, in order to keep the background constant, the photomultiplier tube was cooled with tap water. The photomultiplier tube from the previous apparatus was also used in this apparatus. Polythene tubing was wrapped round the light shield, shown in fig. 8, and tap water at about 13°C was passed through continuously.

The arrangement of the apparatus is shown in fig. 9. The high tension for the photomultiplier tube was obtained from a stabalised power supply, Dynatron type N103. The output from the photomultiplier tube was taken to a cathode follower, Dynatron type 1430A, in the light-tight box using as short a lead as possible to minimize stray capacitance. The cathode follower was connected to a matching amplifier, Dynatron type 1430A, which was stabalised and had linear amplification. A pulse analyser, Dynatron type N101, was connected after the amplifier in order to be able to select from the spectrum of pulses by means of a gate. Two outputs were provided from the pulse analyser. In order to aid scanning of the spectrum of pulses, one of the output connections was taken to a ratemeter. Ekco type N522C; the other was taken to a scaler, Ekco type N529C.

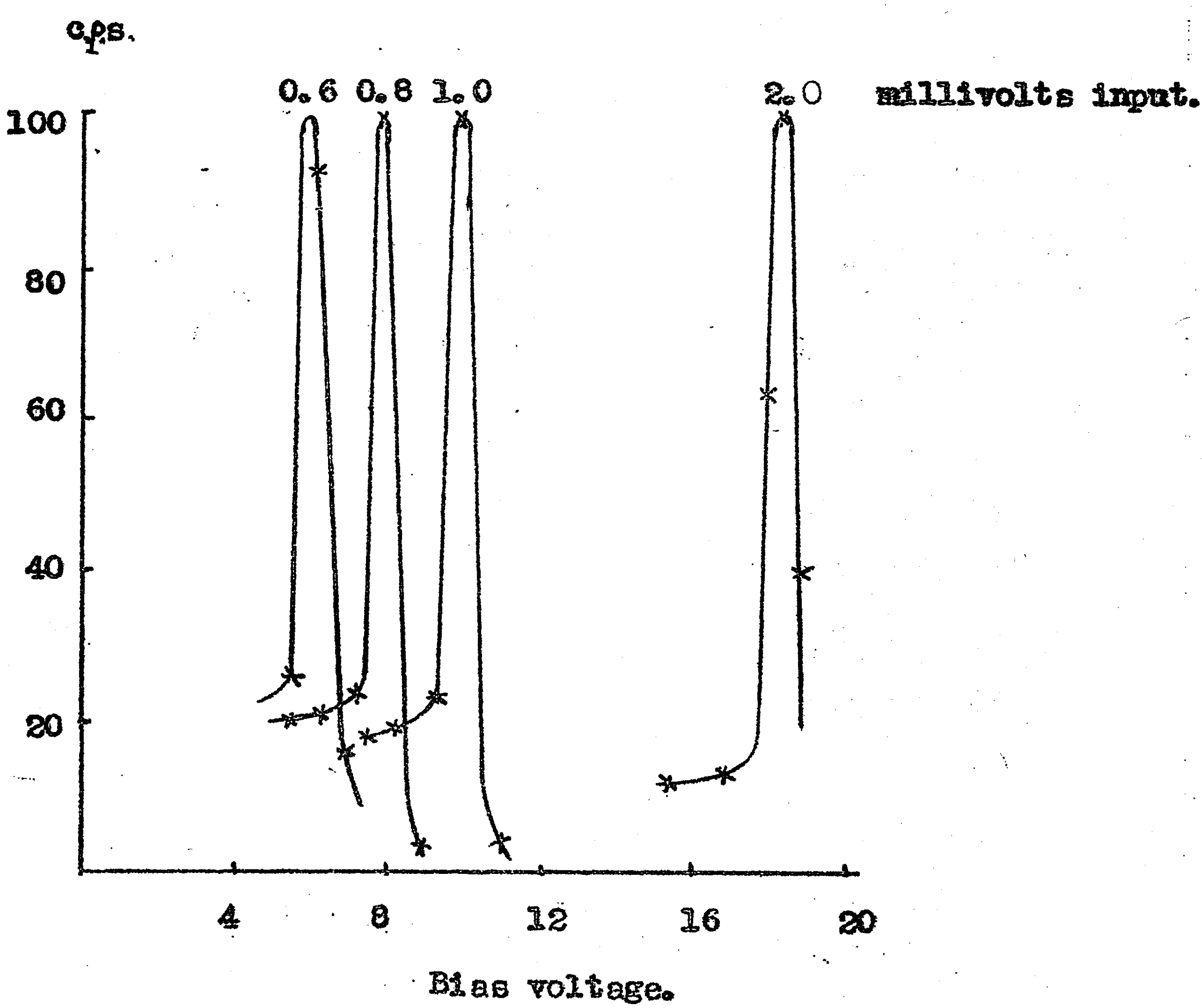
The effect of the gate in selecting pulses is shown in graph 15. This graph was obtained by connecting a signal generator to the amplifier. The signal generator was adjusted to give a square wave of 100 c/s. The graph shows the spectrum for a 1.0V channel width on the pulse analyser with varying input voltages from the signal generator. The amplification of the input signal is 10,000 times as 1.0 mV from the generator produces a 10V output from the amplifier.

The most accurate results are obtained if it is possible to sepérate a peak, in the spectrum of pulses, for C^{14}. An attempt was therefore made to locate such a peak. 0.1 ml. Cyclohexane-C^{14}, specific activity approximately 0.3 microcuries per ml., was mixed thoroughly with 15 ml. scintillator in the scintillation beaker and the active source obtained was then placed in the counter. The spectrum of pulses obtained from the C^{14}, at various settings of the controls, was scanned on the ratemeter. It was found impossible to separate a peak for the C^{14} due to the thermal noise issuing from the photomultiplier tube at the temperature used ($13^{\circ}C$). As stated previously

GRAPH 15

Apparatus 2,

Attenuation zero, channel width 1.0V,
differentiation time constant 250 microseconds,
integration time constant 0.08 microseconds,
signal generator 100 c/s.

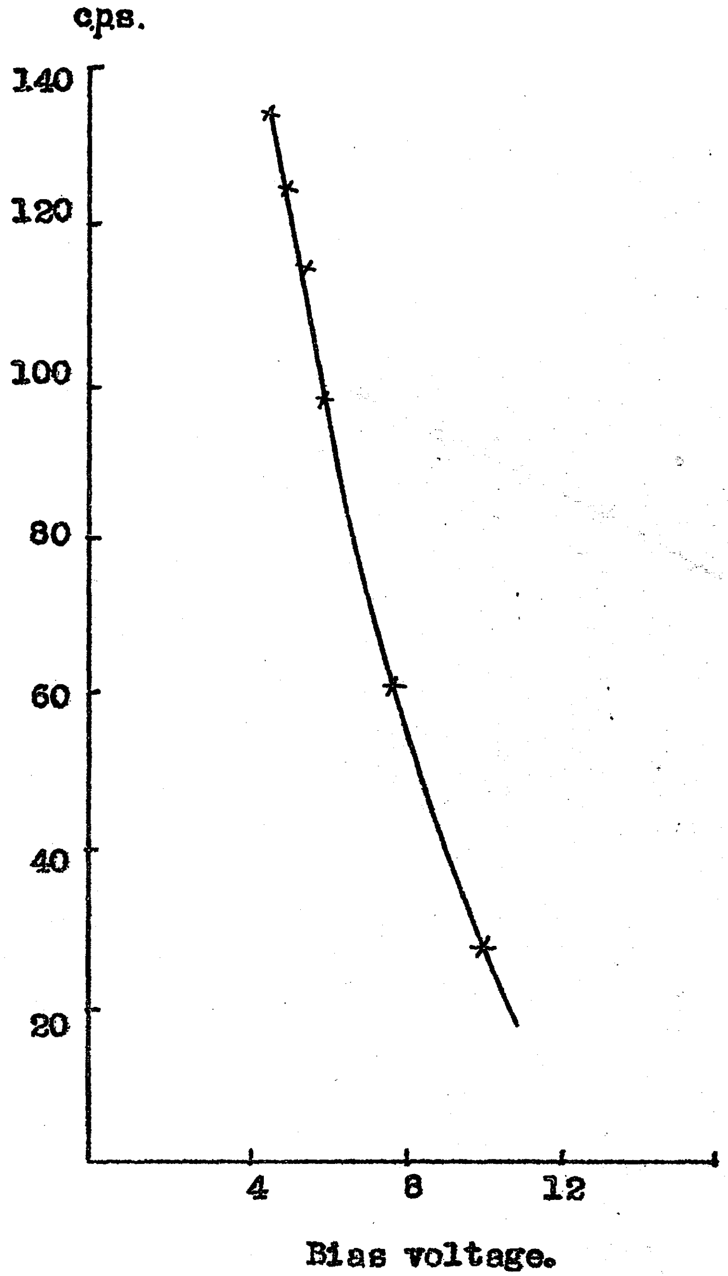


further cooling of the photomultiplier tube may have resulted in moisture problems. It was therefore decided to select the most favourable spectrum obtained and to examine the count rates observed for reproducibility. A spectrum, such as that shown in graph 16, would not give the accuracy required as a slight change in voltage in the apparatus would produce a large change in the count rate, due to the steep slope of the graph. We therefore require a spectrum with a small gradient. A favourable spectrum is shown in graph 17. To obtain this spectrum the controls were adjusted to zero attenuation on the amplifier, with the differentiation time constant at 250 microseconds and the integration time constant at 0.8 microsecond. The high tension voltage on the photomultiplier tube was fixed at 800V. The channel width on the pulse analyser was adjusted to 1.0V. Graph 18 shows the reproducability of a series of counts obtained at these settings with the exception of the channel width which was adjusted to give a 5.0V channel at 10.0V bias, i.e. the curve is being examined between 10.0 and 15.0V. The count rate was increased by increasing channel width, and therefore the time required for each reading was decreased. The statistical error of the readings is indicated in the graph. It is seen that with the controls indicated the readings fall within

GRAPH 16

Apparatus 2,

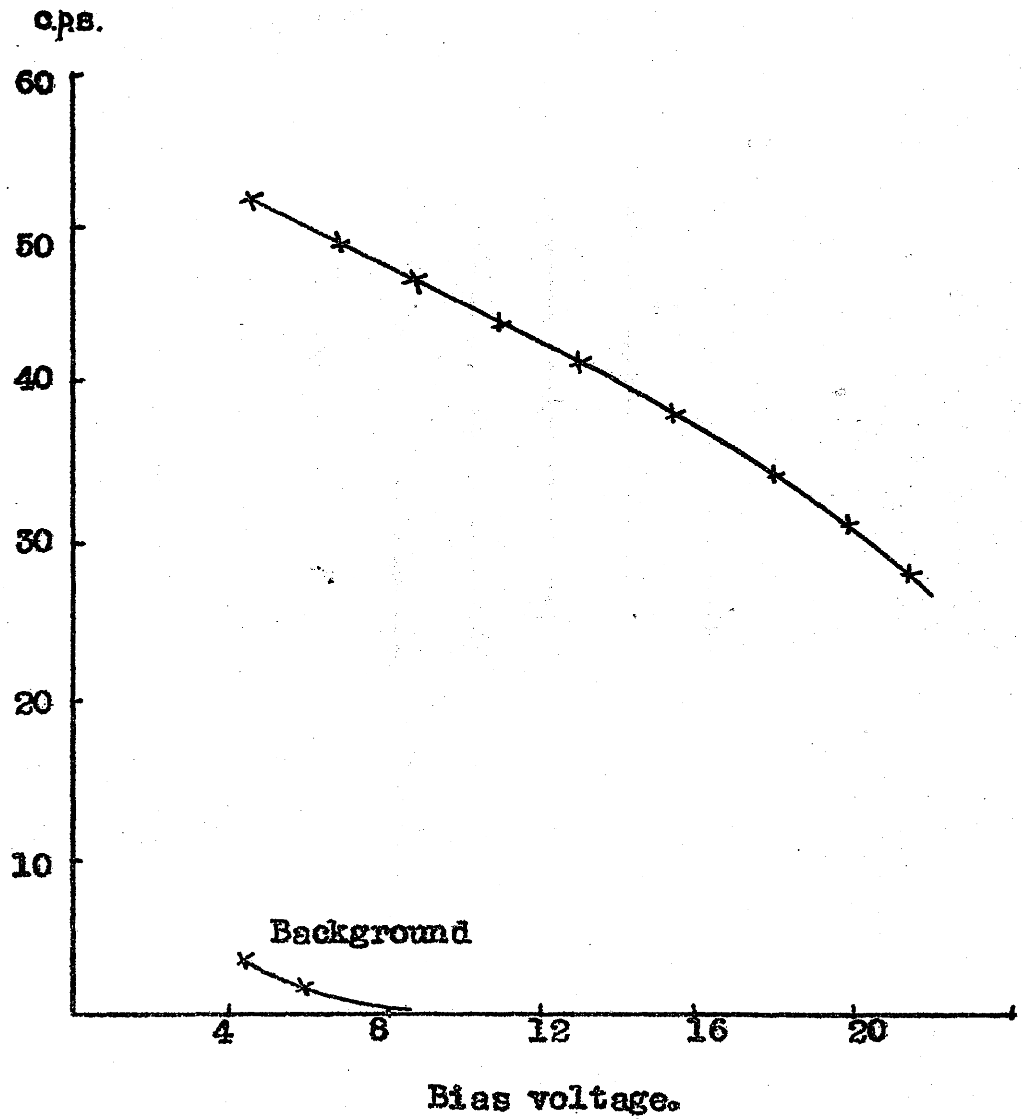
Attenuation 40 db., channel width 1.0 V, differentiation time constant 250 microseconds, integration time constant 0.08 microseconds, high tension voltage 600, cyclohexane-C^{14} source.



GRAPH 17

Apparatus 2,

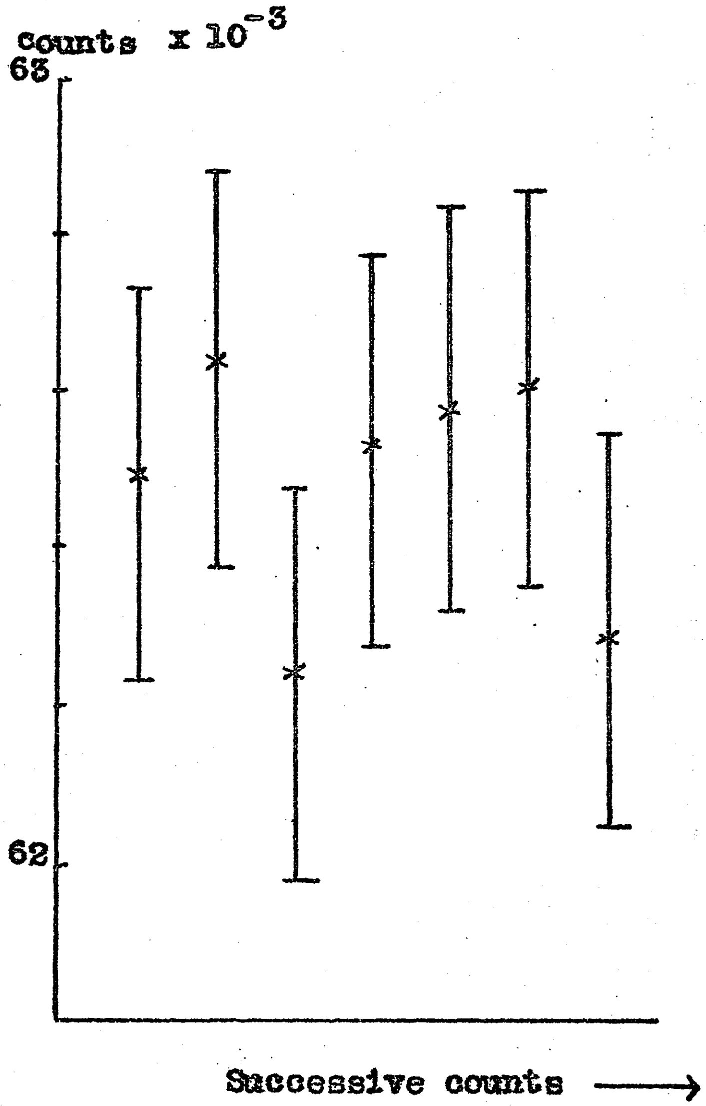
Attenuation zero, channel width 1.0 V, differentiation time constant 250 microseconds, integration time constant 0.8 microseconds, high tension voltage 800, cyclohexane-C^{14} source.



GRAPH 18

Apparatus 2,

Attenuation zero, channel width 5.0 V, differentiation time constant 250 microseconds, integration time constant 0.8 microseconds, high tension voltage 800, bias voltage 10.0, cyclohexane-C^{14} source. 5 minute counts.



the statistical error and are therefore of the required accuracy.

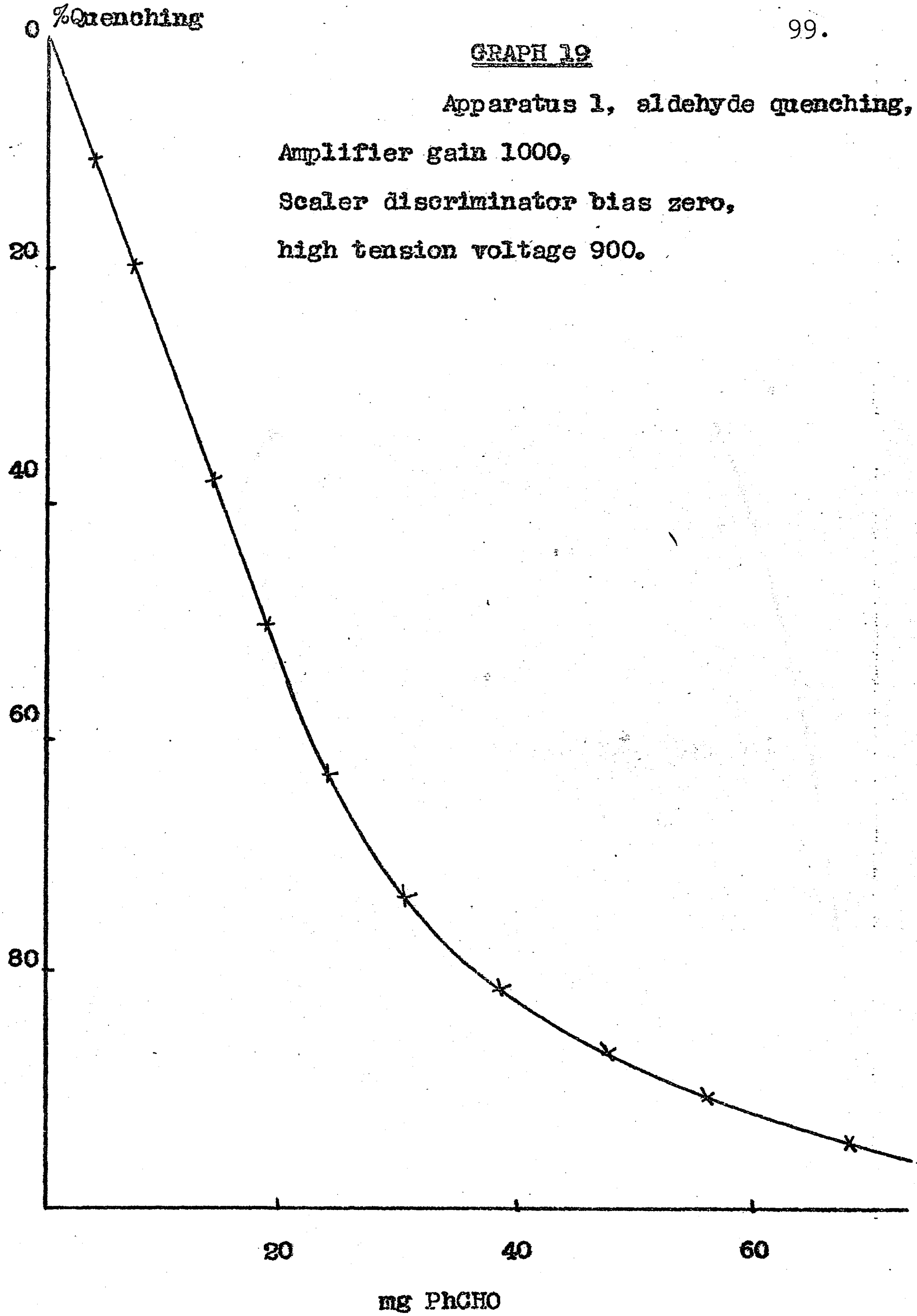
10.4. THE PROBLEM OF QUENCHING AND PROMOTION.

Certain substances, when added to a scintillator, alter the count rate of the active source present. The quenching or promotion is a function of the concentration of the added substance. For a fixed setting of the controls on a given apparatus the alteration is reproducible. An example of a quenching curve is shown in graph 19. The graph was obtained by preparing an active source with cyclohexane-C^{14}, as in the previous section, and adding aliquots of an aldehyde solution of known concentration. It is found that altering the equipment or the position of the controls alters the shape of the quenching curve(54). Graphs 20 and 21 show other quenching curves obtained, for aldehyde, by altering the equipment and controls.

Of the compounds which concern us, aldehydes, acid chlorides and thioketones are strong quenchers, while organic acids, esters, alcohols, thiophene and toluene have slight or negligible quenching effect(55). The quenching and promotion effects complicate the comparison of activities, as, if the molecule is altered during the determination of adsorption, e.g. by hydrogenation, then its quenching properties may

GRAPH 19

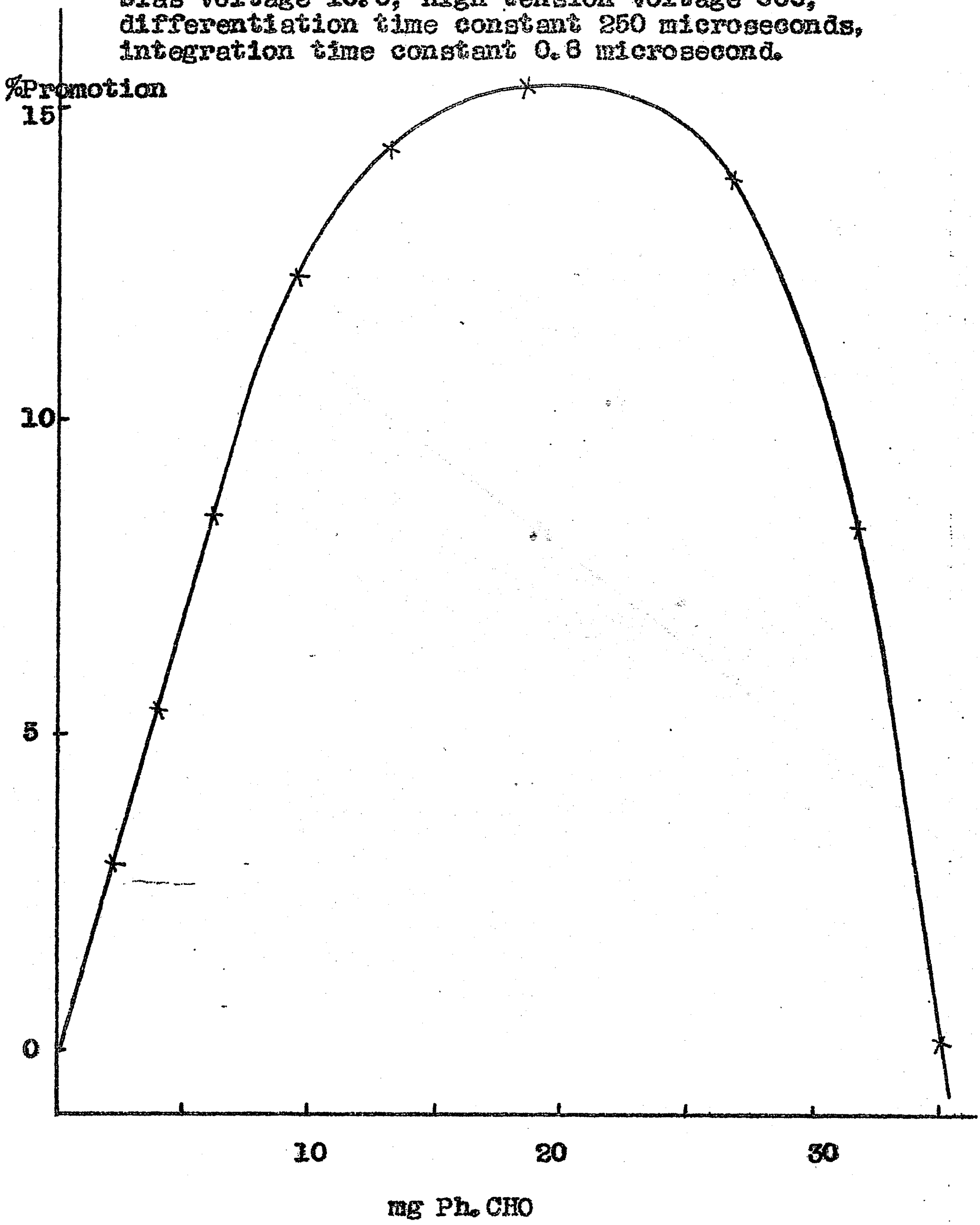
Apparatus 1, aldehyde quenching,
Amplifier gain 1000,
Scaler discriminator bias zero,
high tension voltage 900.



GRAPH 20

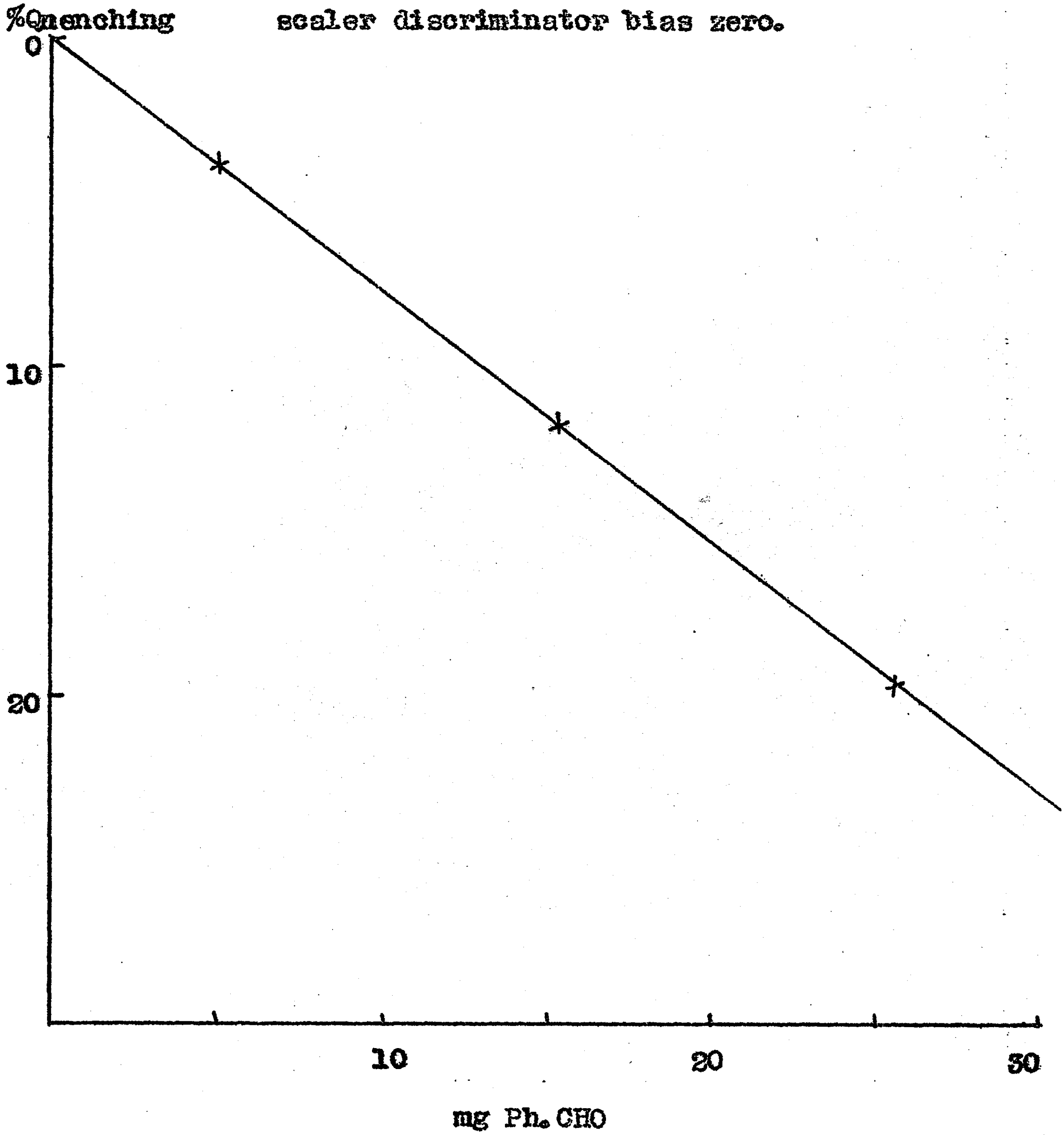
Apparatus 2, aldehyde quenching,

Attenuation zero, channel width 5.0 V,
bias voltage 10.0, high tension voltage 800,
differentiation time constant 250 microseconds,
integration time constant 0.8 microsecond.



GRAPH 21

Apparatus 2 (without pulse analyser), aldehyde quenching,
Attenuation zero, high tension 800 V,
differentiation time constant 250 microseconds,
integration time constant 0.08 microseconds,
scaler discriminator bias zero.



change, making a calibration curve, of activity versus concentration, invalid.

CHAPTER 11.

DETERMINATION OF ADSORPTION ISOTHERMS.

11. DETERMINATION OF ADSORPTION ISOTHERMS.

A preliminary investigation concerned the adsorption of tetramethylthiourea on a catalyst surface. To investigate this adsorption it was necessary to prepare active tetramethylthiourea.

11.1 PREPARATION OF TETRAMETHYLTHIOUREA – S^{35}

The active tetramethylthiourea was prepared by exchange between tetramethylthiourea and active sulphur. Exchange had been shown to take place betweem thiourea and sulphur (56). 2.0 g Tetramethylthiourea was dissolved in 25 ml. AnalaR toluene and 11.8 mg active sulphur, specific activity approximately 65 microcuries per gram, was added. The molar ratio of the sulphur to tetramethylthiourea was 0.022:1. If we presume that the exchange would be complete, then the ratio of activity in the sulphur to the activity in the tetramethylthiourea would be 0.022:1, i.e. most of the activity would be transferred to the tetramethylthiourea. To ensure that exchange was as near equilibrium as possible, the mixture was refluxed at 110°C for approximately 100 hours. When the mixture was cooled, crystals of tetramethylthiourea separated out. The melting point was 79°C; the literature gives a value of 82°C. A mixed melting point with inactive tetramethylthiourea confirmed the identity of the compound. Most of the elemental sulphur remained dissolved in the toluene. Any elemental sulphur coming through would have little activity because of the distribution described above.

11.2. DETERMINATION OF ADSORPTION ISOTHERMS - METHOD 1.

Isotherms calculated by this method were carried out on the first counting apparatus(section 10.2.). The simplest method of determining adsorption isotherms is to mix thoroughly the radioactive compound, dissolved in solvent, with the catalyst; centrifuge to separate the catalyst from the solvent, and to pour the supernatent liquid into the scintillator, where the concentration can be determined. This method neglects the loss of solution by retention on the walls of the vessel and by the catalyst. For compounds having a large partition ratio, catalyst: solvent, the retention is not important, and the method suffices for a preliminary study of adsorption.

11.3. ADSORPTION OF TETRAMETHYLTHIOUREA.

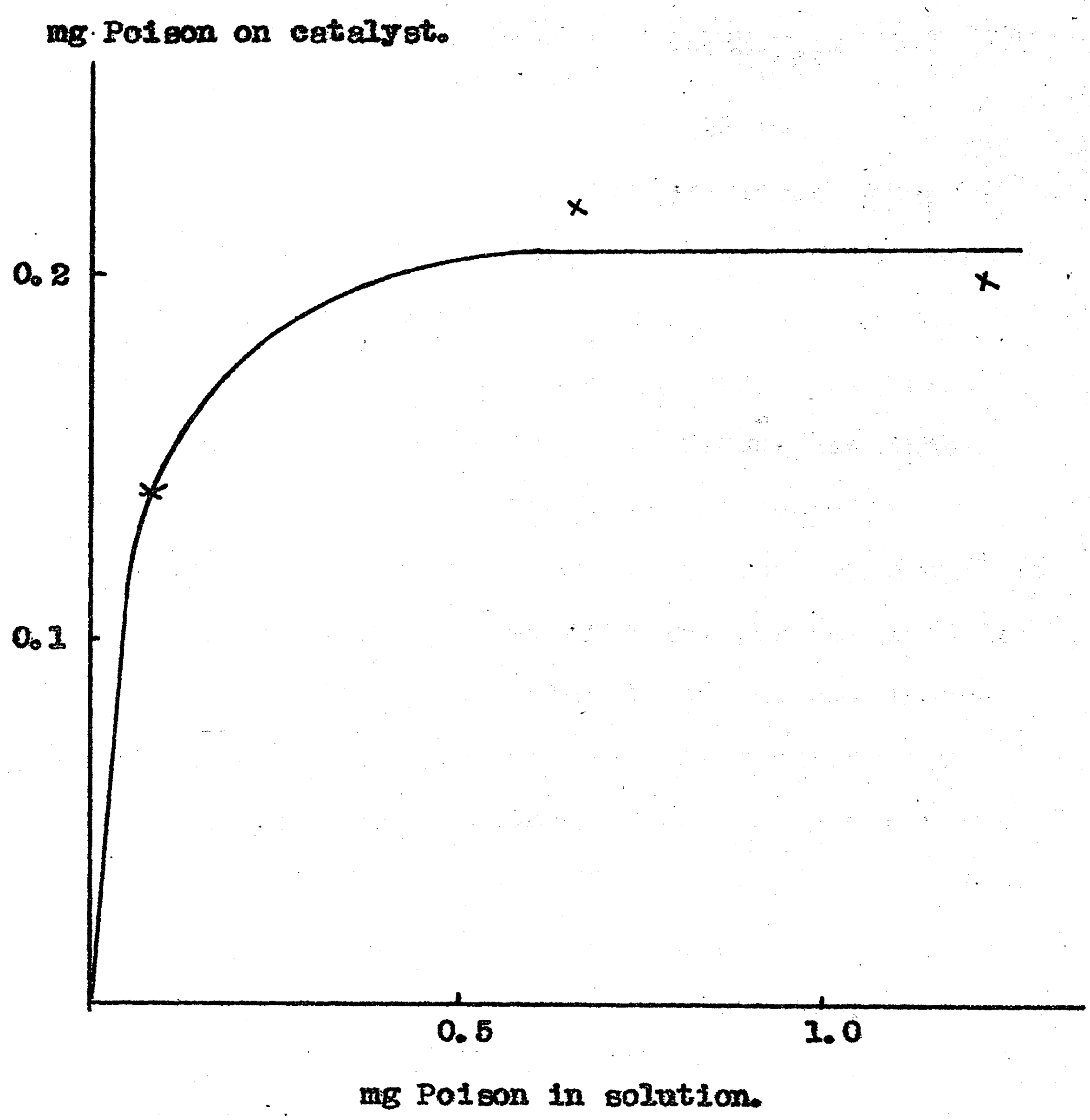
In a 3" x $\frac{3}{8}$" test-tube was placed 0.1 g 5% catalyst. Active tetramethylthiourea, 0.22-1.20 mg, was added as a toluene solution. The total volume of the solution was then made up to 1.5 ml. with pure toluene. The mixture was agitated with a thin stirring-rod for one minute, centrifuged, and the supernatent liquid poured carefully into the scintillator. The mixture was stirred to ensure a homogeneous solution and the beaker was then transferred to the counter. The count rate obtained was converted to the weight of tetramethylthiourea by comparison with a calibration graph which showed that the specific activity of the tetramethylthiourea was 488c.p.m./mg over the range used, quenching being neglected. The adsorption curve obtained is shown in graph 22. It is seen that the tetramethylthiourea is strongly adsorbed and the adsorption reached saturation at 0.2 mg tetramethylthiourea on the catalyst. With the high partition ratio in favour of the catalyst, the adsorption isotherm obtained is probably reasonably accurate. This simple method therefore suffices for the adsorption of tetramethylthiourea.

11.4. ADSORPTION OF ALDEHYDE.

Similar experiments to those in the previous section were carried out for aldehyde. As initial runs showed that the partition ratio was less favourable than with tetramethylthiourea, a larger quantity of catalyst, 0.5 g 1% catalyst, was used with the same volume, 1.5 ml., solution. The specific activity of the aldehyde used was 9,380c.p.m./mg. Quenching was neglected as before. Aldehyde was added over the range 0.7-7.0 mg. A sample calculation is shown below,

GRAPH 22

Adsorption of tetramethylthiourea



0.70 mg active Ph.CHO in 1.5ml. toluene was mixed with 0.5 g 1% catalyst and agitated frequently over 10 minutes.

The expected count rate for total added aldehyde =
0.7 x 9,380 = 6,566 c.p.m.

The count rate obtained minus the background =
5,086 ± 53 c.p.m.

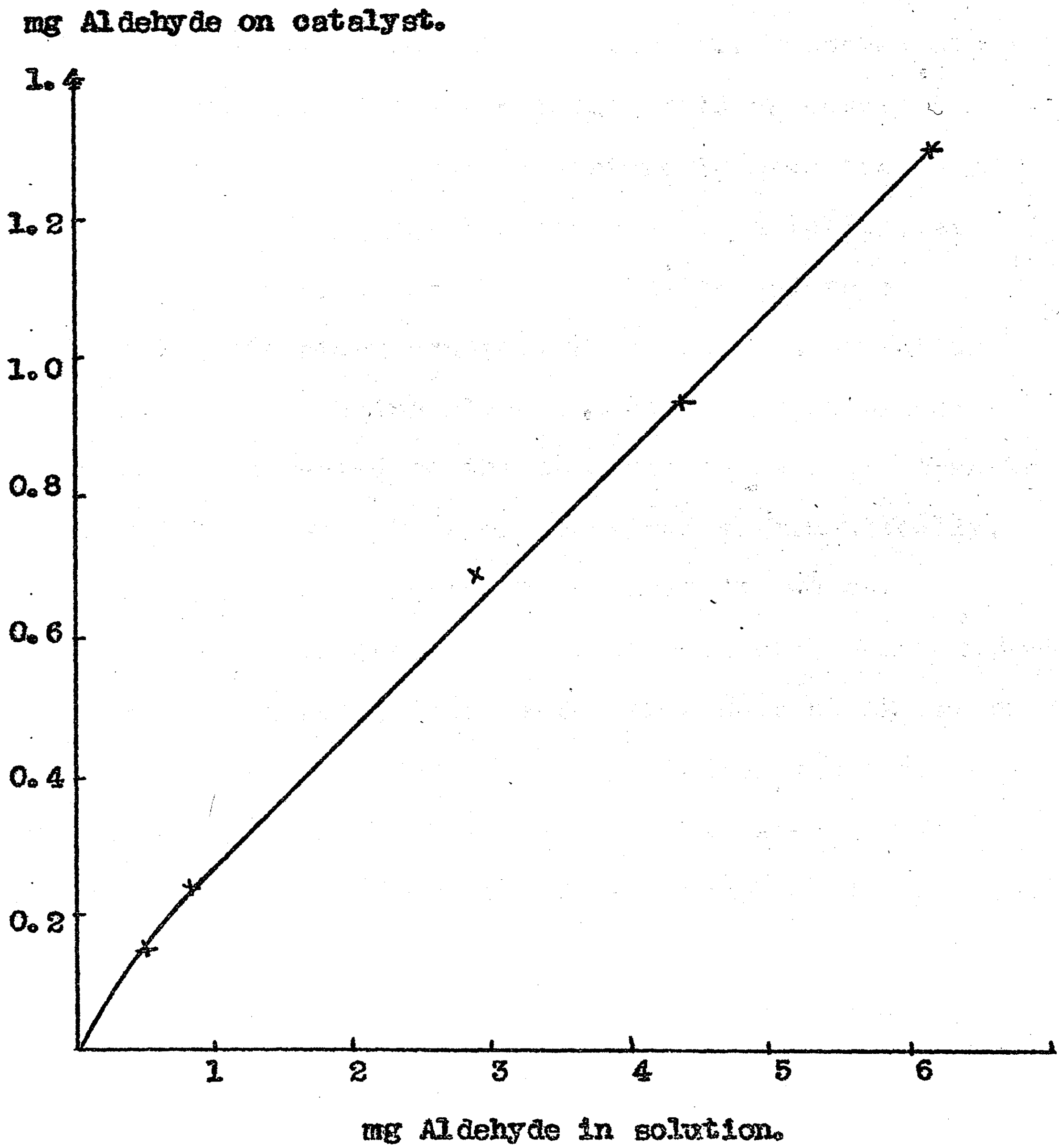
Therefore, Ph.CHO on catalyst $= \frac{6,566 - 5,086}{6,566} \times 0.70$

$= 0.16$ mg.

For amounts of added aldehyde larger than 1.0 mg, the active aldehyde was diluted with inactive aldehyde and the specific activity redetermined. The isotherm obtained is shown in graph 23. The partition is seen to be far less favourable than with the tetramethylthiourea. We can therefore expect that a large fraction of the loss in count rate on contacting the aldehyde and the catalyst is due to retention of the solution by the catalyst, or on the wall of the test-tube. It was therefore necessary to devise a method of obtaining adsorption isotherms without including retention. Also in order to improve the accuracy of counting, the second counting apparatus (section 10.3.) was used in all subsequent determinations.

GRAPH 23

Adsorption of aldehyde 1



11.5. DETERMINATION OF ADSORPTION ISOTHERMS - METHOD 2

The obvious way to avoid losses of active material, other than by adsorption was to count only an aliquot of the solution after the contact period. In principle this method would give perfect results. However to obtain the most favourable transfer of compound from the solution into the adsorbed state it was necessary to use a large ratio of catalyst to volume solution. The largest ratio practical was found to be 1.0 g catalyst to 2.0 ml. solution, as a reasonable fraction of the solution had to be pipetted off after contact. Any errors in pipetting reagents or removing aliquots would be multiplied on being corrected to the original volume. All transfer of solutions was therefore measured gravimetrically, to 0.1 mg. Each experiment involved the weighing of three quantities, aldehyde added, total solution & solution removed, and hence there were three sources of error. Also only half the activity in solution was counted, as the maximum volume which could be removed, after the mixture had been centrifuged, was 1.0 ml. In order to correct for self-quenching of the aldehyde, an amount of aldehyde, as nearly equal as possible to the final amount, was weighed out similarly and counted, i.e. the count rate given by the aldehyde was not linear with concentration due to quenching. This calibration was done separately for each experiment. These complications resulted in a very time-consuming procedure and great care was required to reduce all errors to an acceptable level.

A sample calculation is shown below.

Weight active aldehyde solution added, (1.0 ml.), containing 15.0 mg/ml., = 0.8494 g.

Weight of total solution = 1.7260 g

Weight of solution removed = 0.9161 g

Contact time = 20 mins.

Count rate observed minus background = 4,841 ± 18c.p.m.

Therefore the count rate for the total solution =

$$\frac{4,841 \times 1.726}{0.9161} = 9,121 \text{ c.p.m.}$$

<u>Calibration</u>.

Weight active aldehyde solution = 0.4432 g

Count rate observed minus background = 5,165 ± 18 c.p.m.

Expected count rate for the total solution =

$$\frac{5,165 \times 0.8494}{0.4432} = 9,899 \text{ c.p.m.}$$

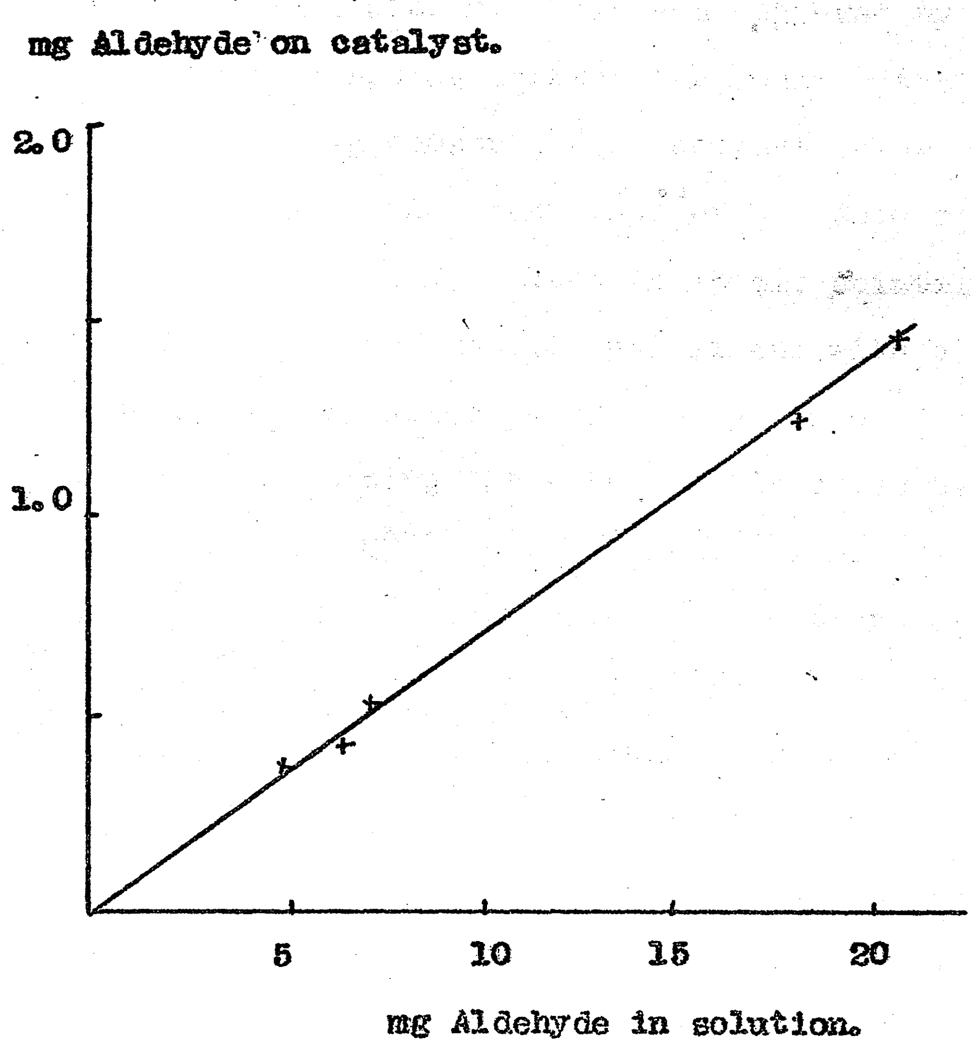
Therefore the counts "lost" = 9,899-9,121 = 778 c.p.m.

Therefore, aldehyde on catalyst $= \frac{778 \times 15.0}{9,899} = 1.2$ mg

The results are shown in graph <u>24</u>. Later work showed that the radiochemical purity of the aldehyde was very doubtful and it is probable that the curve represents the adsorption of benzoic acid in the

GRAPH 24

Adsorption of aldehyde, 2.



presence of aldehyde.

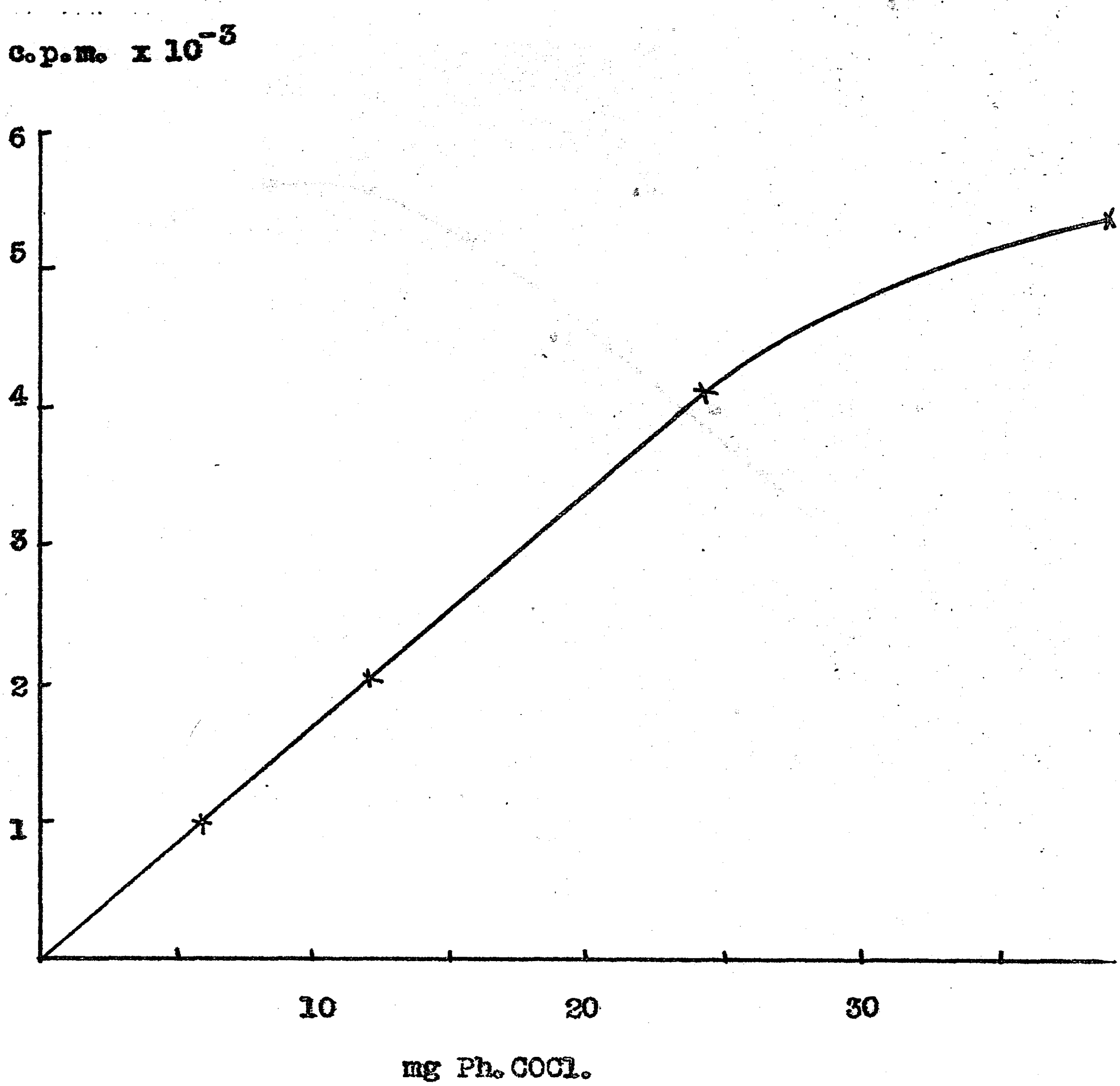
This method of determining adsorption curves was rejected because, if quenching poisons were to be introduced into the system then the extent of quenching would be unknown and the results would be meaningless.

11.6. DETERMINATION OF ADSORPTION ISOTHERMS - METHOD 3.

A method of measuring adsorption isotherms was required, which would enable quenching effects to be taken into account. This was achieved by a variation of method 1. Let us examine the count rates given by a quenching compound e.g. benzoyl chloride. Graph 25 shows the count rate of 0 - 40.0 mg active benzoyl chloride dissolved in 15 ml. scintillator liquid. The count rate is not linear with concentration. The extent of quenching of benzoyl chloride can be found by examining the effect of inactive benzoyl chloride on a C^{14} active source. 0.1 ml. Cyclohexane-C^{14}, specific activity approximately 0.3 microcuries per ml., was dissolved in 15 ml. scintillator and the count rate determined for the addition of 0 - 40.0 mg inactive benzoyl chloride. The results are shown in graph 26. If we combine graphs 25 and 26, then we obtain a corrected calibration curve showing the true relationship between count rate and active

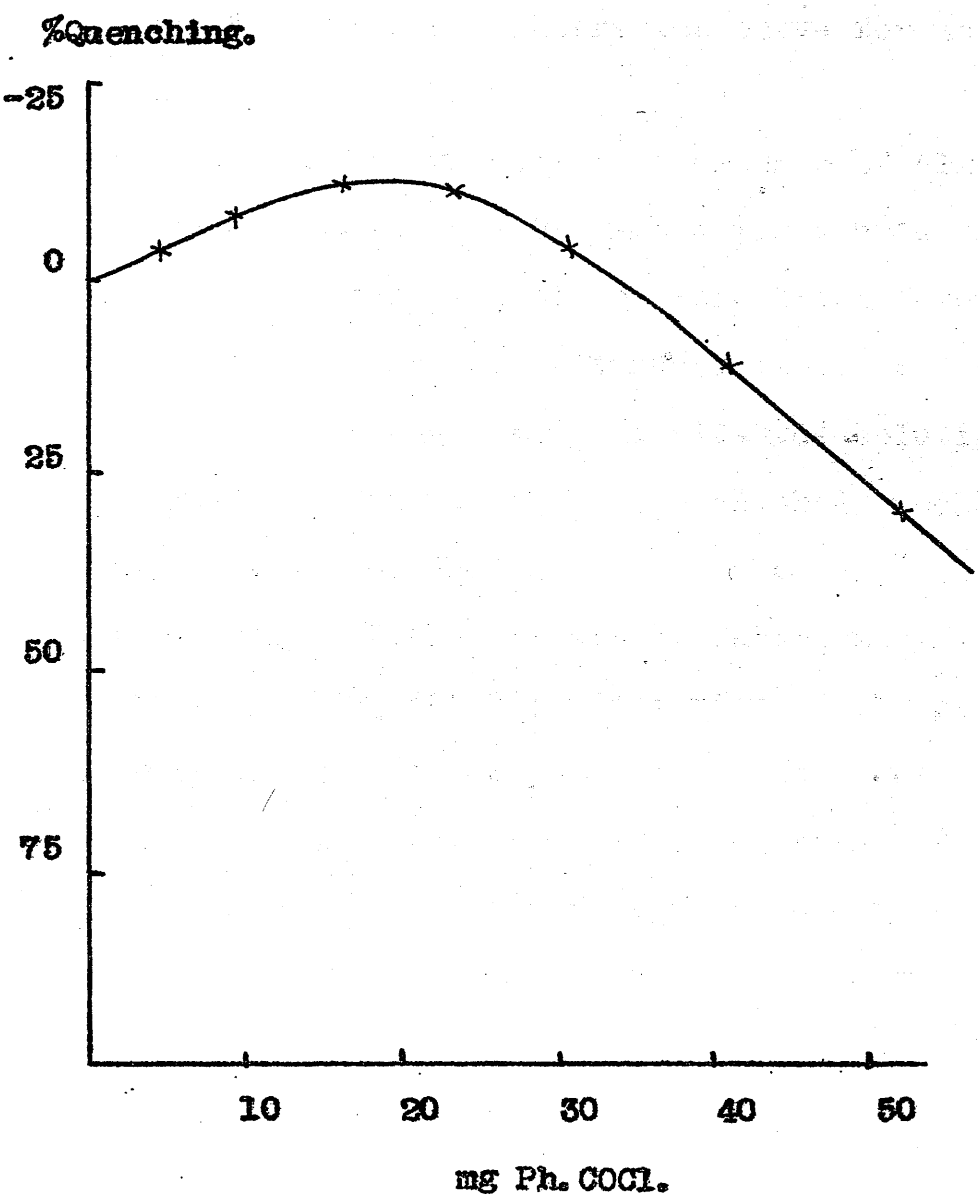
GRAPH 25

Count rate of active benzoyl chloride.



GRAPH 26

Benzoyl chloride quenching.



benzoyl chloride concentration, graph 27, which is seen to be linear.

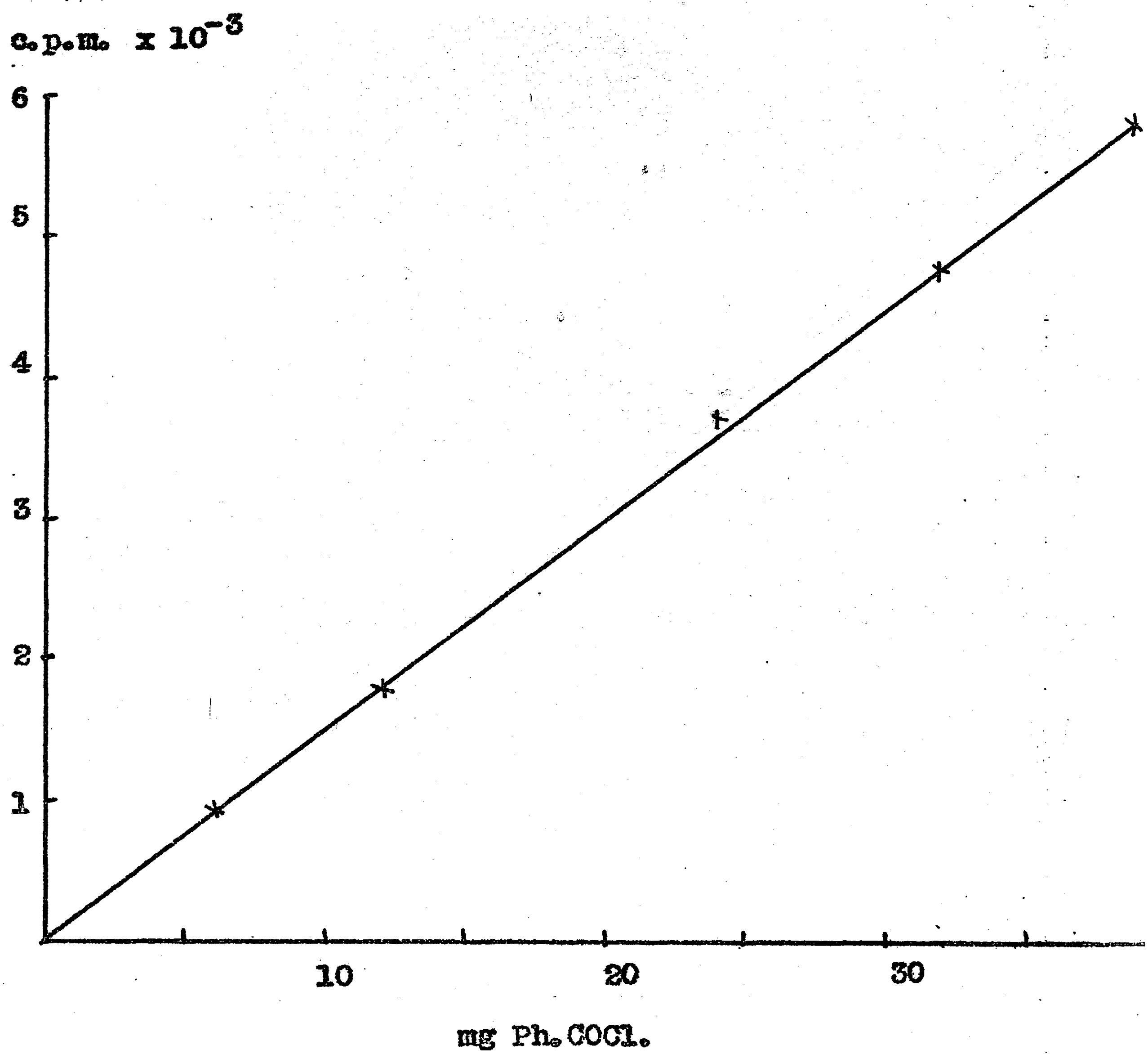
These experiments were repeated using aldehyde in place of benzoyl chloride. The count rate versus concentration of active aldehyde is shown in graph 28 and the effect of quenching by inactive aldehyde on cyclohexane - C^{14} is shown in graph 29. Graph 30 shows the corrected calibration curve for active aldehyde.

In the determination of amounts of aldehyde adsorbed on catalysts by method 1, aliquots of C^{14} labelled aldehyde in toluene were brought into contact with the catalyst for a standard time. The suspension was then centrifuged and the aldehyde solution decanted. In this process some aldehyde would have been retained mechanically by the catalyst, and on the walls of the container. Furthermore if we wished to carry out the adsorption in the presence of hydrogen and with a quenching poison, small chemical changes in the system, e.g. hydrogenation of aldehyde or poison, might have affected the quenching properties of the solution and hence the observed count rate. Thus direct determination of aldehyde concentration from observed count rate was not possible.

These factors can, however, be allowed for

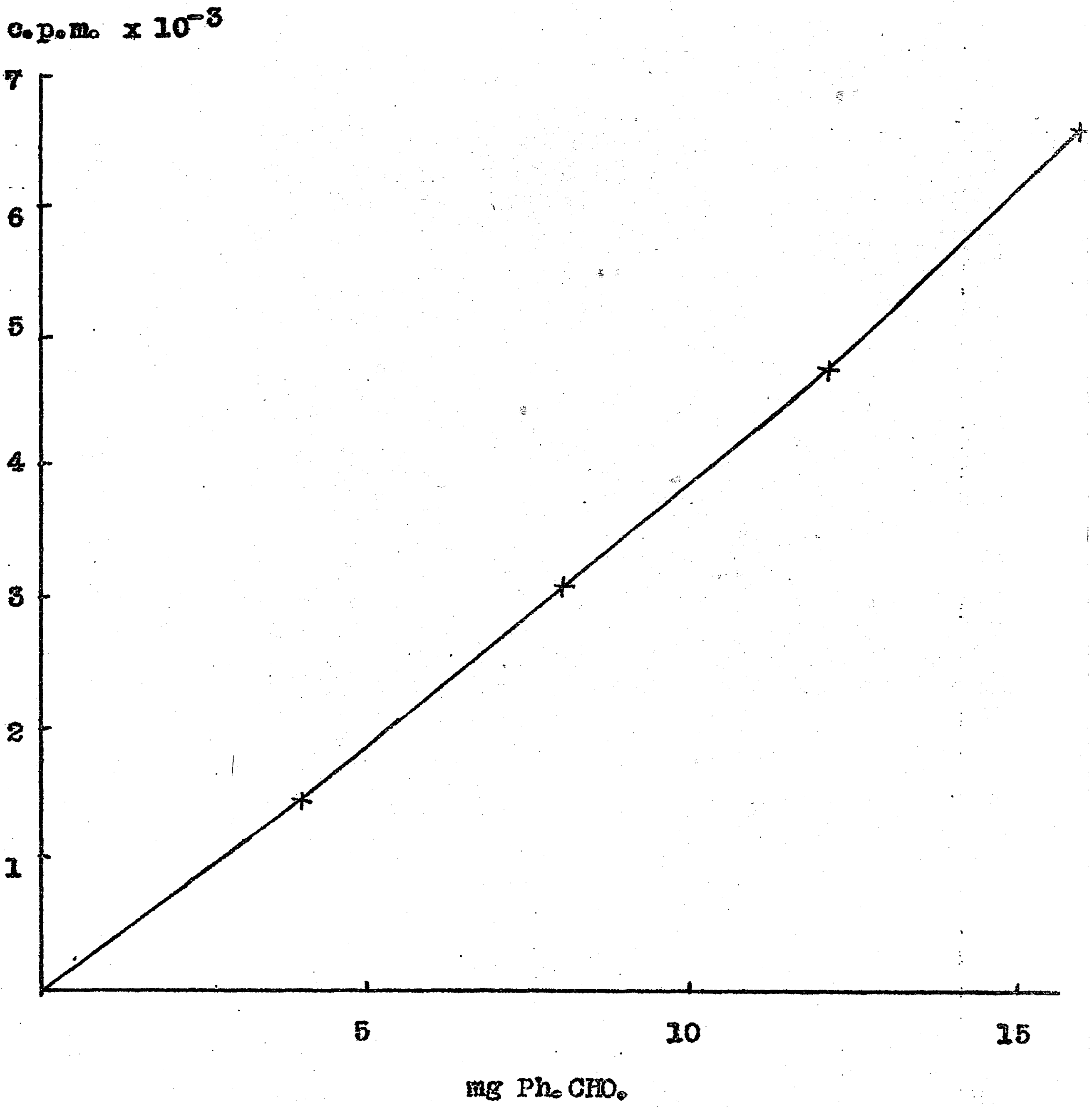
GRAPH 27

Count rate for active benzoyl chloride corrected for quenching.



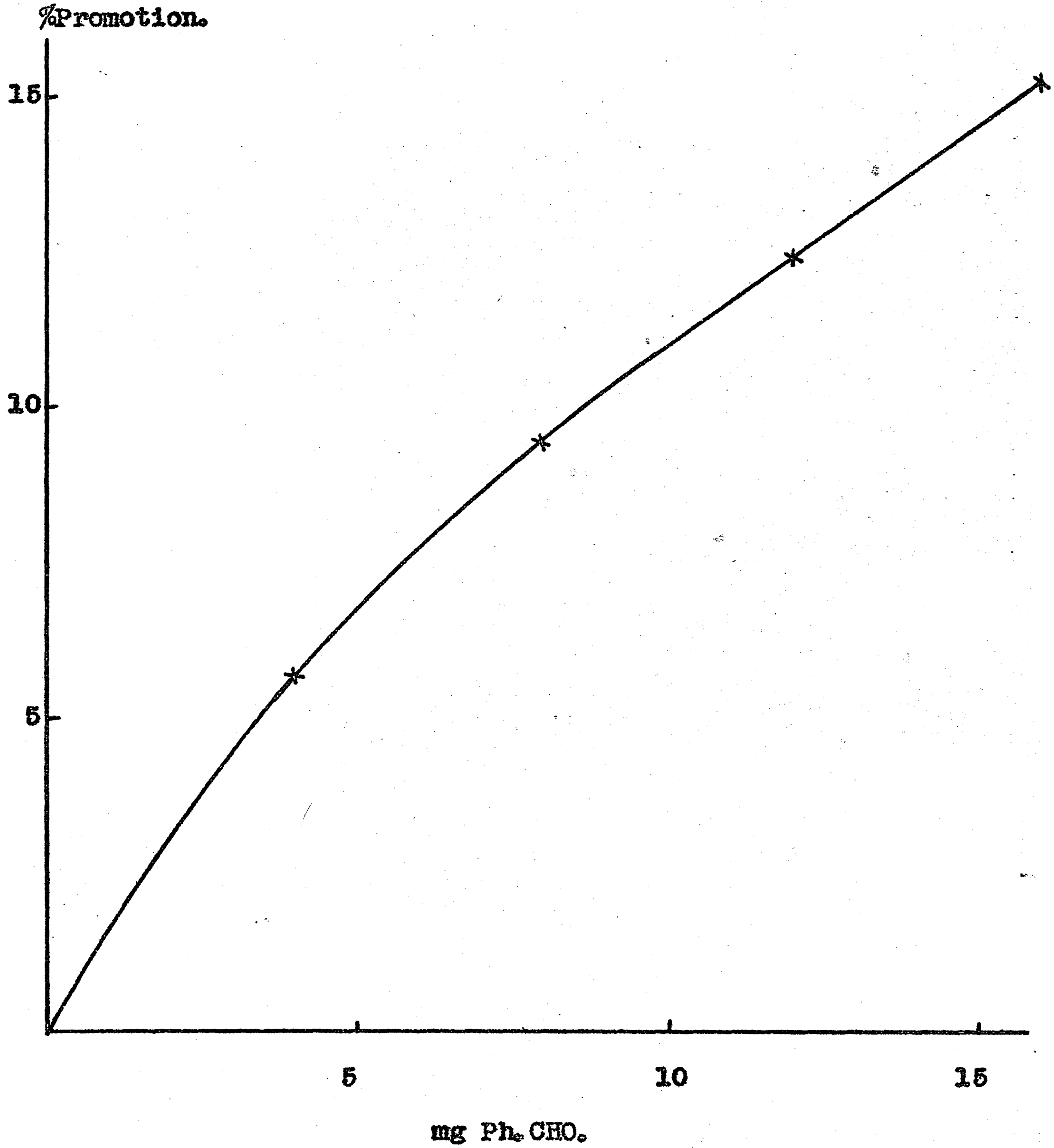
GRAPH 28

Count rate of active aldehyde.



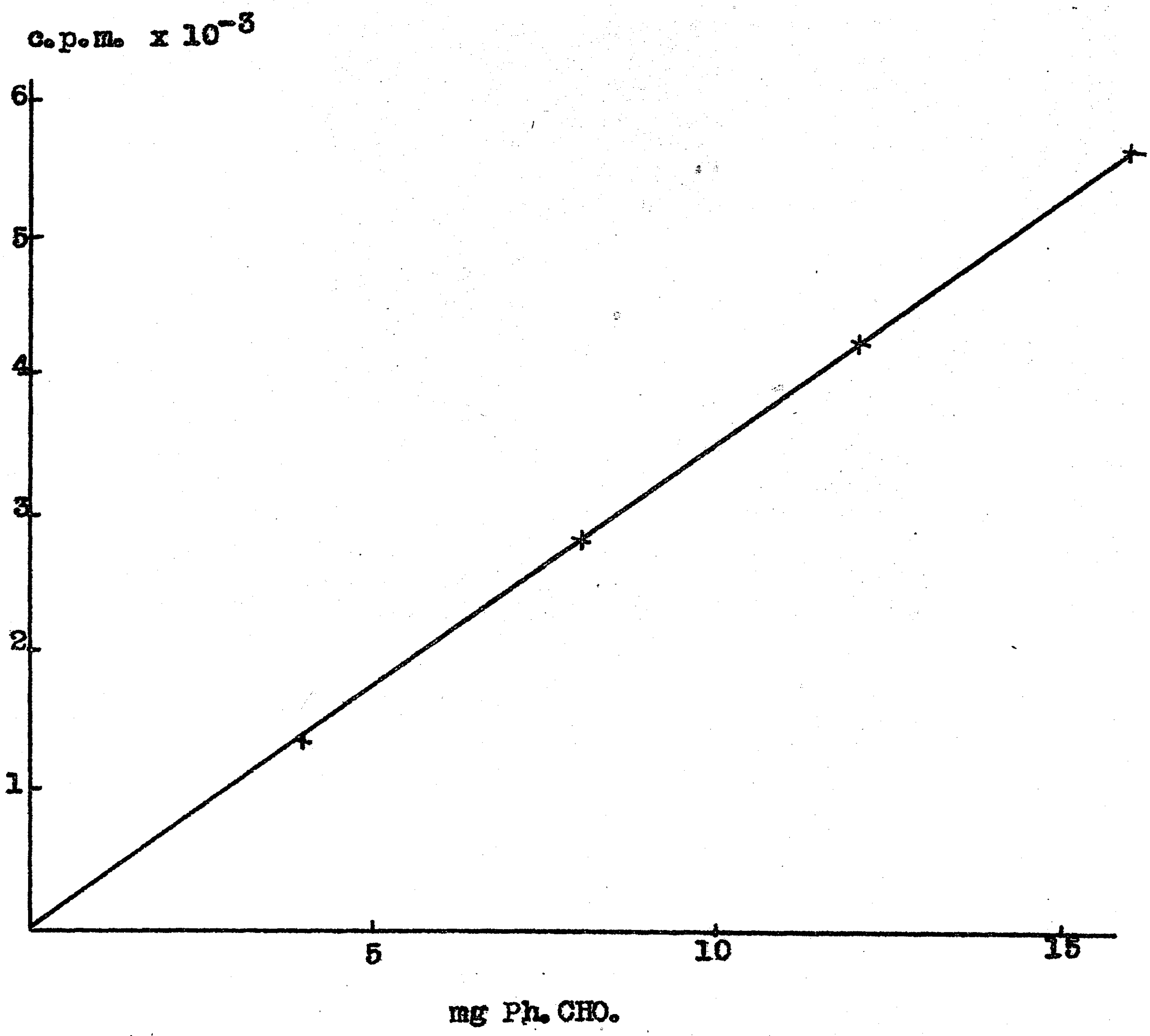
GRAPH 29

Aldehyde quenching.



GRAPH 30

Count rate of active aldehyde corrected for quenching.



as follows. A blank experiment was carried out using an active solvent (non-quenching) and inactive aldehyde. The experimental conditions were exactly the same as in the determination with active aldehyde. Any counting losses which occured could only have been the result of mechanical or quenching losses. Loss of the active solvent by adsorption was negligible on a percentage basis due to the large amount present. The losses in this blank experiment were used as a measure of the mechanical and quenching losses in the experiment with active aldehyde.

For example in a blank experiment, 0.5 g 10% catalyst and 0.77 ml. toluene were contacted for 60 secs. with hydrogen. 6.0 mg Aldehyde in 0.23 ml. toluene and 0.5 ml. active cyclohexane – C^{14}, specific activity approximately 0.06 microcuries per ml., were then added and mixed with stirring for 60 secs. As no active toluene was available active cyclohexane – C^{14} was used instead. The mixture was centrifuged and the supernatent liquid poured into 15 ml. scintillator.

The aldehyde was not added before hydrogen was passed as rapid hydrogenation would have taken place leaving no aldehyde present.

0.5 ml. Active cyclohexane should give 3,429c.p.m.

This was previously determined.

Activity observed = 3,166 c.p.m.

Therefore loss = 7.7%

In the partition experiment,

0.5 g 10% catalyst and 1.20 ml. toluene were contacted 60 secs. with hydrogen. 6.0 mg Active aldehyde in 0.3 ml. toluene were then added and equilibrated 60 secs. with stirring. The mixture was centrifuged and the supernatent liquid poured into 15 ml. scintillator. The corrected activity of 6.0 mg active aldehyde, from the calibration curve = 2,100 c.p.m.

Activity observed = 1,890 c.p.m.

Therefore loss = 10.0%

Therefore loss due to adsorption = 10.0 - 7.7 = 2.3%.

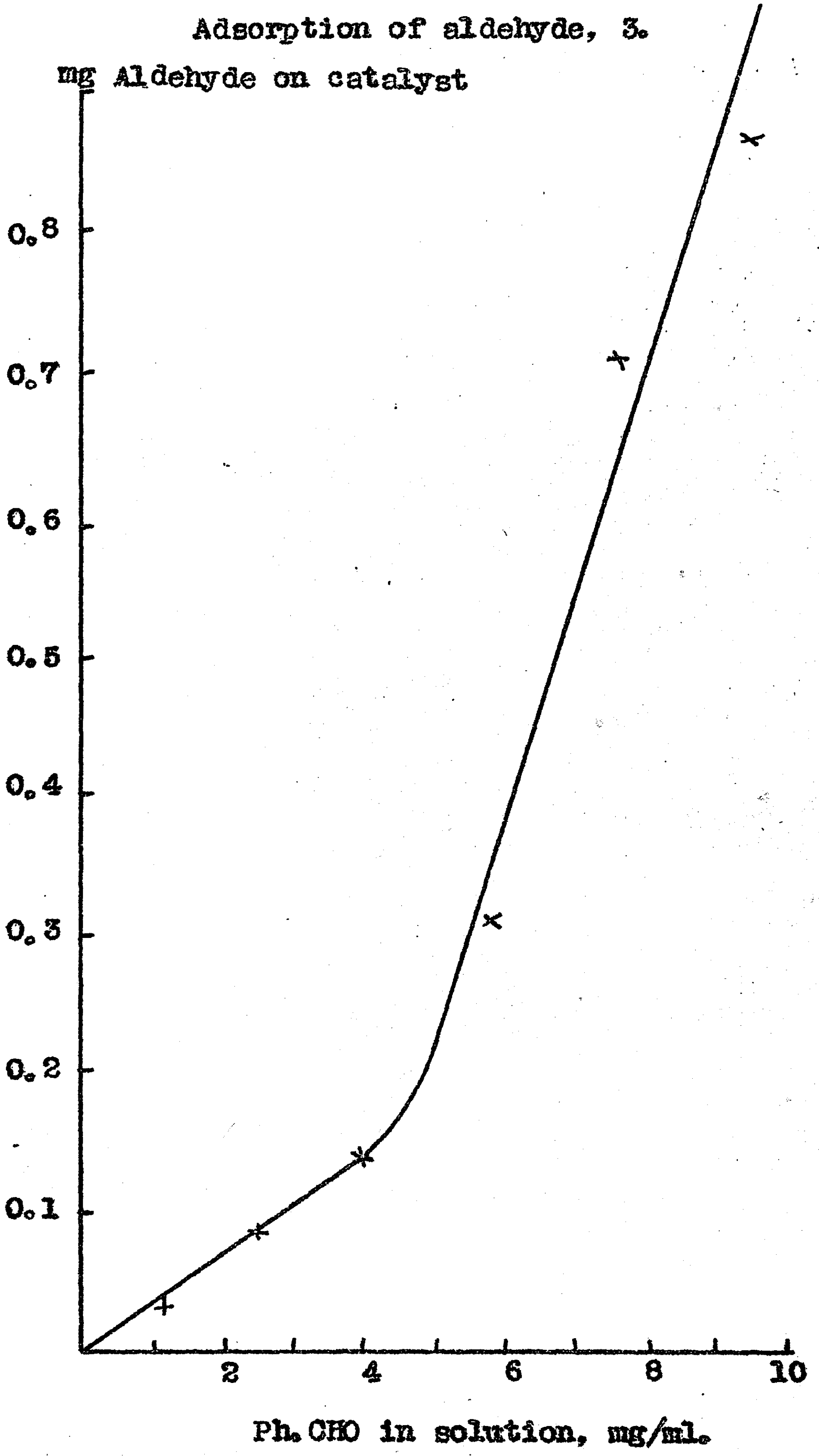
Therefore aldehyde on catalyst = $\frac{2.3 \times 6.0}{100}$ = 0.14 mg.

The adsorption isotherm obtained for aldehyde is shown in graph 31. The break at 5.0 mg aldehyde per ml. should be noted.

The method is seen to give accurate results. All solutions can be pipetted and no further weighing of solutions is required. A point which requires particular attention is the stability of the aldehyde. The active aldehyde was kept in an atmosphere of inert gas. When aldehyde had to be removed, the solution was pipetted out as quickly as possible to avoid entrance

GRAPH 31

Adsorption of aldehyde, 3.



of air. In spite of these precautions a slight difference could be detected in specific activity after one week, due to change in quenching effect by oxidation of aldehyde. Aldehyde used in the blank was made up daily as unprotected aldehyde oxidised to a large extent in two days.

The result obtained will be discussed in the next section.

CHAPTER 12.

DISCUSSION - ADSORPTION CURVES.

12 DISCUSSION - ADSORPTION CURVES.

12.1 DETERMINATION OF ADSORPTION CURVES.

The first method used to find adsorption curves is detailed in section 11.2. The results on tetramethylthiourea show the affinity of this type of compound for a palladium catalyst. The simple method employed suffices for strong adsorptions, and an adsorption curve can be speedily obtained with a reasonable degree of accuracy. The results on aldehyde however indicate the need for a more accurate method. The low adsorption ratio of aldehyde on the catalyst, to aldehyde in the solution, makes retention of active material by the catalyst and on the walls of the test-tube, the major source of loss. Changes in the quenching properties of any of the substances present may also decrease or increase the count rate of the solution by similar amounts to that produced by adsorption.

The second method, described in section 11.5, overcomes the difficulties due to retention. Quenching is still, however, an unknown factor. The long contact times of solution and catalyst (necessary as the reaction tube has to be at the temperature of the balance room before it is weighed) may result in an unstable substance, such as aldehyde, being altered structurally before the activity of the solution can be measured. The procedure is also time-consuming. The method is not therefore suitable for the study of aldehyde adsorption. If however quenching is not important in a system, and the substances being investigated are stable, then the highest accuracy is possible with this procedure.

The final method used, section 11.6, gave the best results for aldehyde. It is possible, by this method, to allow for quenching and retention in each experiment, and the procedure is suitable for complex systems. Even coloured solutions can be introduced provided the density of colour is reproducible. The limitation of the method arises because the results are calculated by measuring percentage losses of the active material added. The overall experimental errors, introduced by transfer of solution from the reaction tube into the scintillator and pipetting the reagents, are about 1.0%. The adsorption isotherm of aldehyde, graph 31, shows that only 2.0% of the aldehyde goes onto the catalyst in the initial stages. This curve, therefore, probably represents the limiting case of the method. If more accuracy is required, a different procedure is necessary.

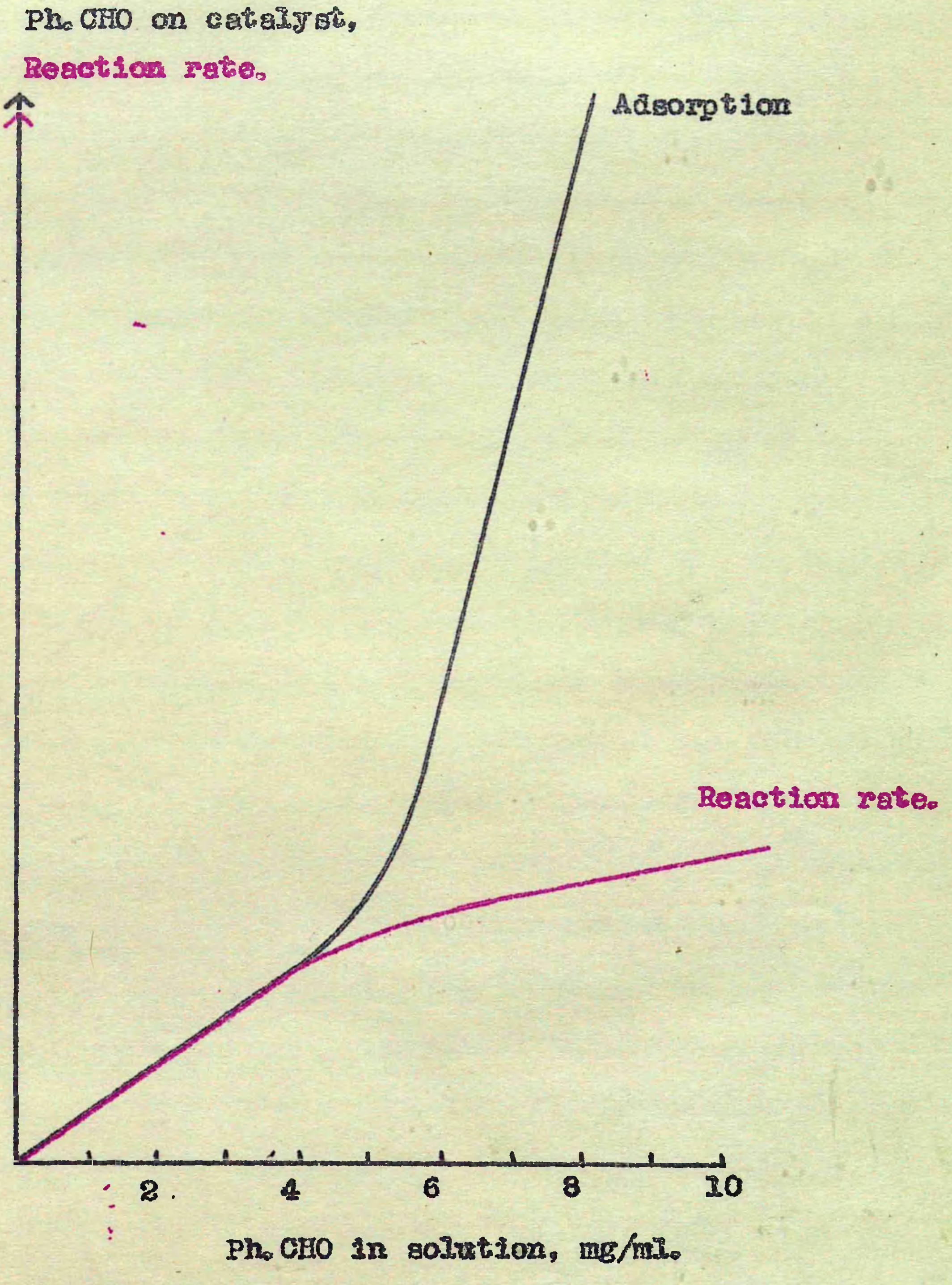
12.2 CORRELATION BETWEEN ADSORPTION AND CATALYSIS.

The aim of measuring adsorption isotherms is to find a correlation betweem adsorption and catalysis. As stated previously if adsorption bears any relation to catalysis then we may expect a relation between the amount of an adsorbed species on a catalyst and the rate of reaction. The rate of reaction for various concentrations of aldehyde is shown in graph 7. If we compare the curve obtained for the unpoisoned reaction with the adsorption curve for the same catalyst, graph 32, we see that both curves show an inflexion at 5.0mg/ml. of aldehyde in solution. The sudden rise in adsorption at 5.0 mg/ml. aldehyde is probably due to the onset of the formation of multilayers. The hydrogenation curve follows the adsorption curve during the formation of the monolayer. The rate then falls off as saturation of the surface is approached.

These results, if corroborated, are of great significance. The number of active sites on the catalyst which are being used must be proportional to the amount of aldehyde on the catalyst, in order to give the correlation obtained. If the number of active sites is a reasonable fraction of the total sites then it ought to be possible to examine the

GRAPH 32

Correlation between adsorption and reaction rate.

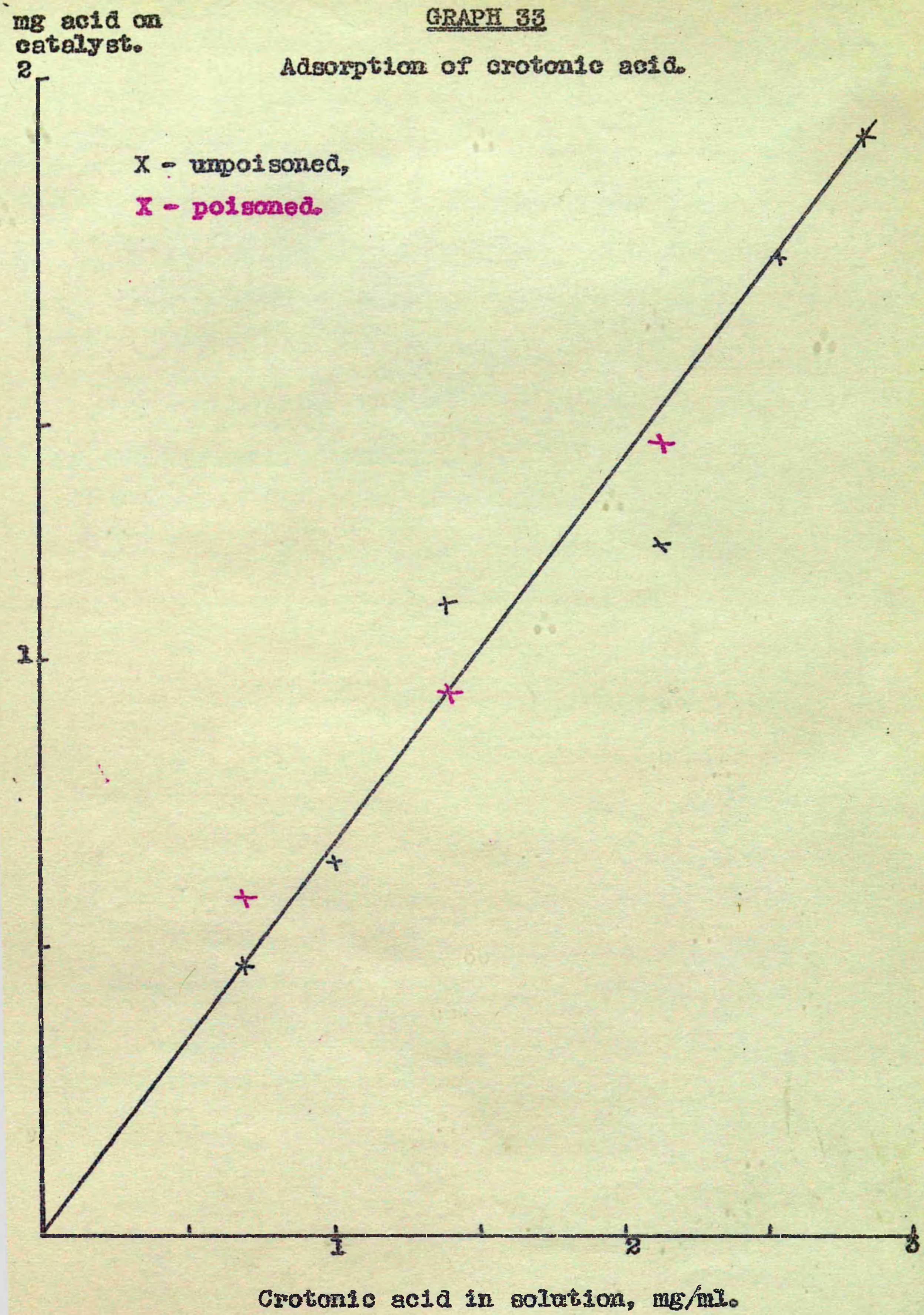


effect of a poison directly by measuring the change in aldehyde adsorption. It is possible however that the number of active sites is only a very small fraction of the total sites. It has, for example, been shown by Wishlade(57) that only about 20% of the total sites are active for the hydrogenation of ethylene on nickel. In this case it would be impossible to detect a change in adsorption, on the addition of poison, with available methods for the determination of adsorption curves. A probable example of this type of adsorption is given by crotonic acid on palladium/barium sulphate with a toluene solvent. (This investigation was carried out by D. Cormack, B.Sc. under the supervision of the authors.) Graph 33 shows the adsorption curves for 1.0-4.0 mg crotonic acid in 1.5 ml. toluene with 0.05 g 5% palladium/barium sulphate catalyst. The adsorption curve in the presence of 0.2 mg thiophene, which slows the hydrogenation rate to half the unpoisoned value, is also shown. It is seen that poison produces no measurable decrease in adsorption.

The adsorption curve for aldehyde shows that the aldehyde molecule is on the surface of the catalyst. A mechanism for the Rosenmund reaction therefore, will have to include this fact.

GRAPH 33

Adsorption of crotonic acid.



The adsorption of tetramethylthiourea was shown to be very strong. It is a reasonable hypothesis that the adsorption in this case is due to the sulphur atom, and in spite of the breakdown of the molecule when hydrogen is introduced into the system, the sulphur atom probably remains adsorbed on the catalyst.

12.3. CATALYST POISONS.

The outstanding feature of the Rosenmund reaction is the dependence of the yield obtained on the amount of poison present in the system. The first section of the thesis has shown the great care which must be exercised in obtaining pure reagents. It is our opinion that the trouble many workers experience in carrying out the Rosenmund reaction, and the differing views in the literature on the necessity for poisons, is largely due to the unknowing use of sulphur containing solvents, or the fortuitous introduction of sulphur poisons into the system.

The extent of poisoning has been shown to depend on the chemical structure of the poison introduced (graph 2). The problem of interpreting the different behaviour of poisons is complicated by the alteration of the poisons themselves during the reaction. It is also true that the extent of adsorption is unknown, especially for unstable poison molecules. It is therefore unlikely that useful information on the Rosenmund reaction could be obtained from this source.

Elementary sulphur can act as a poison, but it should be noted that this does not exclude the possibility that the rest of the poison molecule may play a part in the poisoning by geometrical blocking of the surface or changing the electronic nature of the catalyst-sulphur link. This will be discussed later.

When elementary sulphur was added to the catalyst in the presence of hydrogen, and the mixture was then heated, the evolution of hydrogen sulphide was detected (section 4.4).,This removal of sulphur did not take place when the sulphur was added after the reactants were hot. We see therefore that sulphur can be removed from the system readily unless the reaction conditions are such that a stable "compound" is formed. Chemical binding of the sulphur and the palladium as palladium sulphide did not aid the formation of a poisoned catalyst, as palladium sulphide was also unstable under the reaction conditions (section 4.5).

Gronvold and Rost(45) have shown that the solubility of sulphur in palladium is negligibile It therefore appears that the sulphur in the system is present as a surface layer on the palladium. We then have to consider the difference between a stable surface layer of sulphur and an unstable layer. As the stable layer is formed at high temperatures 110°C, and the unstable layer occurs at low temperatures, about 40°C, perhaps the difference is that in the unstable layer only physical adsorption of the sulphur on the palladium takes place, whereas the stable layer is chemically bound. The instability of palladium sulphide does not invalidate this hypothesis as bulk properties are frequently different from those of a surface layer.

At room temperature, poisons such as thiophene do not break down completely, but hydrogenate to the saturated compound. Maxted and Ball(58) illustrated the reversibility of adsorption of poisons at these temperatures. As the poison molecule must be more strongly bound than the reacting species, then the substance being hydrogenated must be held on the catalyst by weak bonds.

12.4 PRODUCTS OF THE ROSENMUND REACTION.

The various products obtained from the Rosenmund reaction at various temperatures are detailed in section 5. This versatility can be put to good use in synthesis, but, unless the reaction conditions are fully understood and properly controlled, it is more likely to be a hinderance in obtaining the correct compound. The possible reaction products and the reaction conditions for benzoyl chloride are as follows,

1 room temperature, no poison - gives the hydrocarbon,

2 110°C, no poison - " " ester,

3 110°C, poison - " " aldehyde.

Further, a possible synthetic route to the alcohol is to carry out the reaction at 110°C with tetramethylthiourea to give the aldehyde and then hydrogenate further with fresh catalyst and tetramethylthiourea at room temperature (section 7.2).

If benzoyl chloride is present during the room temperature hydrogenation, the final product will be the hydrocarbon. This is possibly because the actual poison at this temperature may be the amine produced by hydrogenation of the tetramethylthiourea, and benzoyl chloride would give,

$$Me_2NH + Ph.COCl \longrightarrow Ph.CO.NMe_2 + HCl.$$

12.5 MECHANISM OF THE ROSENMUND REACTION

The possible mechanisms for the Rosenmund reaction were shown to be (section 6.1),

1 consecutive,

$$\begin{array}{l} Ph.COCl \longrightarrow Ph.CHO \text{ (adsorbed)} \longrightarrow Ph.CH_2OH, \\ \qquad\qquad\quad\ \ \downarrow\uparrow \\ \qquad\qquad\quad Ph.CHO \text{ (in solution)} \end{array}$$

2 simultaneous,

$$\begin{array}{l} Ph.COCl \longrightarrow Ph.CH_2OH \\ \quad\ \ \downarrow \\ Ph.CHO. \end{array}$$

The addition of active aldehyde to a Rosenmund hydrogenation mixture has shown the reaction to be consecutive. This result is confirmed by the physical removal method (section 6.2) and the fact that aldehyde and acid chloride hydrogenate simultaneously at low concentrations (graph <u>12</u>).

The promotion of the catalyst by the acid chloride indicates the nature of the initial stage in the reaction. We therefore arrive at a mechanism as follows,

<u>1</u> $R.COCl + Pd + \frac{1}{2}H_2 \longrightarrow R.CHO + PdCl$,

<u>2</u> $R.CHO + H_2 \longrightarrow R.CH_2OH$,

As the reaction is consecutive the action of the poison must be to reduce the rate of stage <u>2</u>, in the above mechanism, to a greater extent than stage <u>1</u>. We are therefore led to consider the mechanism of reduction of the rate of aldehyde hydrogenation, as any substance which slows this rate may increase the yield in the Rosenmund reaction.

It has been shown that aldehyde adsorbs on the catalyst. The probable manner of adsorption can be inferred from the investigation of Stoddart and Kemball(59) on the deuteration and exchange of acetone. They concluded that their results could be explained on the basis of attachment of the $>C=O$ group to the catalyst thus,

```
   |
 - C - O
   |   |
   S   S.
```

If benzaldehyde is adsorbed on the catalyst in this manner, then hydrogenation would require two hydrogen atoms, presumably adsorbed on neighbouring sites. A total of four sites would be required therefore, for the hydrogenation of an aldehyde molecule. The number of these groups of sites available on a uniform surface rapidly diminishes as poison molecules are added. This blocking of the surface has been examined quantitatively by Herington and Rideal (8) by stochastic calculations.

We must now consider why this poisoning does not take place to the same extent with benzoyl chloride. We are forced to the conclusion that benzoyl chloride does not hydrogenate by the same mechanism as benzaldehyde.

The carbonyl group in benzoyl chloride differs from that in benzaldehyde because of the chlorine atom attached to the carbon atom. The effect of this chlorine atom is to increase the strength of the carbonyl group, as the overlap of orbitals between the chlorine, the oxygen and the carbon atoms, results in π- bonding between them. Thus the carbonyl bonding in benzoyl chloride is stronger and less likely to be broken on a catalyst surface than in aldehyde.

It is probable therefore that benzoyl chloride does not adsorb on the catalyst by opening of the carbonyl bond. The benzoyl chloride possibly adsorbs on a single site or reacts from the liquid phase. In either case fewer sites are needed for hydrogenation than with aldehyde. Therefore the poison molecules will diminish the number of these groups of sites to a lesser extent than the number of aldehyde hydrogenation groups.

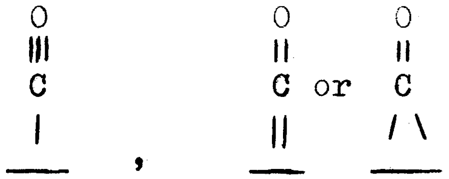
We see therefore that the Rosenmund reaction can be explained by a consecutive mechanism,

$$\begin{array}{ccccc} Ph.COCl & \longrightarrow & Ph.CHO \text{ (adsorbed)} & \longrightarrow & Ph.CH_2OH \\ & & \updownarrows & & \\ & & Ph.CHO \text{ (in solution)} & & \end{array}$$

The yield of aldehyde is increased by poison molecules blocking the surface of the catalyst and so reducing considerably the number of quadruple sites required for aldehyde hydrogenation, whilst still allowing benzoyl chloride to hydrogenate on the sites remaining.

12.6 ELECTRONIC POISONS.

The poison has been considered on a purely geometrical basis. Though a reasonable mechanism for the Rosenmund reaction has been advanced, the possibility of the poison acting electronically has to be considered. By electronic action we mean that poison does not displace a reactant but influences it by some other mechanism. An example is the adsorption of carbon monoxide on metal surfaces investigated by Eischens(60). Carbon monoxide can adsorb on metals by a single or a double bond attachment,



(10 electrons) (12 electrons).

Eischens found that hydrogen dissolved in the metal increased the proportion of double bond structures by donating electrons to the metal. Oxygen had the opposite effect, as it extracted electrons from the metal.

Campbell and Thomson(61) found that there were two modes of hydrogen adsorption on nickel when oxygen was present. From experiments on the displacement of hydrogen by mercury they concluded that hydrogen is normally present as $H^{\delta-}$, but in the presence of oxygen the hydrogen is converted to $H^{\delta+}$.

These examples show the importance of electronic effects in surface chemistry. Attempts to produce an electronic poisoning mechanism for the Rosenmund reaction met with little success and the geometric mechanism, described previously, remains the most feasible.

12.7 POSSIBLE CAUSES OF FAILURE OF THE ROSENMUND REACTION

The yield of aldehyde in the Rosenmund reaction is increased by blocking quadruple sites, necessary for aldehyde hydrogenation, whilst leaving smaller groups of sites available for the hydrogenation of the acid chloride. It is therefore necessary to have the correct quantity of poison in the system, i.e. small enough not to stop the reaction completely, yet large enough to ensure blocking of most of the aldehyde hydrogenation sites. This critical concentration of poison, required for a good yield of aldehyde, is the probable cause of lack of success with the Rosenmund reaction.

It is to be expected that the ratio of the rates of hydrogenation of an acid chloride and the corresponding aldehyde would vary considerably with different substances. The quantity of poison necessary for a good yield of aldehyde will therefore also vary according to the acid chloride being hydrogenated. A case may even arise where an aldehyde is hydrogenated so much faster than the corresponding acid chloride that it is practically impossible to obtain a yield from the reaction.

These features explain the wide variation in yields of aldehyde reported in the literature for various acid chlorides.

12.8 FUTURE WORK.

Future work will be directed to improving techniques for measuring adsorption curves. If it is found that the number of active sites for aldehyde hydrogenation is a reasonable fraction of the total sites, then it will be possible to measure directly the effect of various poisons on the adsorption of aldehyde.

Another prospect is the production of a standard poisoned catalyst. This could be made by blocking the surface of the catalyst, before the hydrogenation, by contact with a standard solution of metal ions. Surface blocking by the evaporation of mercury onto the catalyst was attempted, but was unsuccessful. The probable reason for this is that mercury, palladium and hydrogen form an alloy(62). A mercury poisoned nickel catalyst would be possible as no alloy is formed in this case.

THE APPENDIX.

13. APPENDIX 1

Water Pump.

The water pump, F, fig 1, was of very simple construction it consisted of a 10 cm. tube coaxial with a 50 mm. tube. The water level was raised and lowered by an automatic siphon, G. The drain tube being much wider than the inlet tube, the siphon emptied almost completely each cycle. The siphon was best fed from a constant water head, I. When the water level in F was raised it cut off the inlet tube; then the water level in the inlet tube rose till it equalled the sum of the difference in heights between all the liquid levels and inlet tubes, which were all going in the other direction, in the system. The two levels, in the inlet tube and in the outer tube in F, then rose together, and as, for the same height, i.e. pressure, the outer tube displaces more gas than the inner tube, then gas was pushed through the valve, D, and through the apparatus. When the water level in F fell, gas was sucked through the inlet tube, the water level in the valve rising in its inlet tube. The pump was simple and reliable but required some care in construction as the lengths of the various tubes was critical in order to obtain maximum effect.

14. APPENDIX 2

Count Rates At Infinite Thickness.

When we wish to compare the activity of two samples which are β-emitters, we must take into account the self-absorption of the material being counted. If we consider a sample of thickness g mg/cm^2 having a total activity a_g per unit thickness in the absence of absorption losses, then the observed activity from a layer of thickness dx at a distance x below the surface is approximately,

$$da = a_g e^{-\mu x}.dx,$$

μ being the absorption coefficient.

The observed activity is therefore,

$$a = a_g \int_0^g e^{-\mu x}.dx = a_g/\mu\,(1-e^{-\mu g}),$$

The absorption being presumed exponential and scattering being neglected(63). When the source is very thick or the energy of the β-emitter is low, it is possible to regard the sample as infinitely thick. From the above equation, if $g \rightarrow \infty$,

$$a_\infty \rightarrow a_g/\mu \quad ,$$

and as μ is the same for both our samples,

$$a_{g1}/a_{g2} = a_{\infty 1}/a_{\infty 2} \quad ,$$

the subscripts 1 and 2 denoting samples 1 and 2 respectively.

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