

378. *Selective Poisoning of the Catalyst in the Rosenmund Reaction.*

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A range of sulphur-containing poisons increased the yield of benzaldehyde produced by the hydrogenation of benzoyl chloride over palladium-barium sulphate in toluene at 110°. Tetramethylthiourea was the most effective in preventing hydrogenation beyond the aldehyde stage. No correlation was found between size of molecule and efficiency as a selective poison. From studies of (a) the ratio of hydrogen consumed to hydrogen chloride evolved, (b) the fate of [ $\alpha$ - $^{14}\text{C}$ ]benzaldehyde in a Rosenmund reaction, and (c) the effect of poison on hydrogenation of benzaldehyde, it has been deduced that this Rosenmund hydrogenation is consecutive rather than simultaneous, and a detailed selective-poisoning mechanism is proposed.

ALTHOUGH the effect of small amounts of poisons on surface catalytic reactions is well known, the detailed mechanism of the poisoning process is obscure in most cases. In this paper we report on the mechanism of poisons in the Rosenmund reaction,<sup>1,2</sup> in which acid

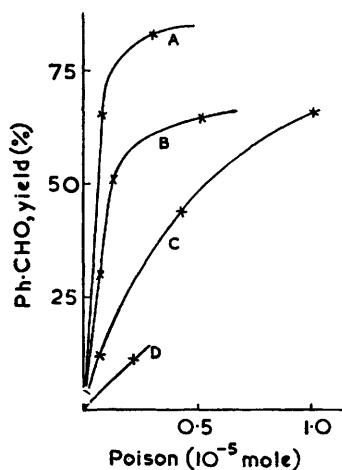


FIG. 1. The effect of varying the nature and quantity of poison on yields of benzaldehyde: 5% Pd-BaSO<sub>4</sub>, 1 atm., 110°.

Poisons: A, tetramethylthiourea; B, thiourea; C, thiophen; D, dibenzothiophen.

chlorides are catalytically reduced only as far as the aldehyde stage, further hydrogenation being inhibited by selective poisons such as quinoline-sulphur, thiourea, etc.

The acid chloride used in the present study was benzoyl chloride, with palladium on barium sulphate as catalyst and toluene as solvent. The reagents used were taken to be pure when a hydrogenation in the absence of a poison failed to produce any benzaldehyde.

*Effect of Variation in Nature and Quantity of Poison.*—Increasing the amount of poison present in a reaction mixture increased the yield of aldehyde, as shown in Fig. 1. To find out whether this was simply the result of poisons blocking the surface geometrically, large and small poison molecules were investigated. It is seen in Fig. 1 that tetramethylthiourea was a better poison than thiourea, but that the small thiophen molecule was a better poison than the larger dibenzothiophen. Thus no clear correlation seems to exist between the size of a poison molecule and its effectiveness. This conclusion is true only if the poison molecules were adsorbed intact to the same extent, and it was for this reason that partition of poison between liquid and catalyst was examined. A typical Rosenmund reaction with 0.040 mg. of thiourea as the poison was stopped after 20 min. and the

<sup>1</sup> Rosenmund, *Ber.*, 1918, **51**, 585.

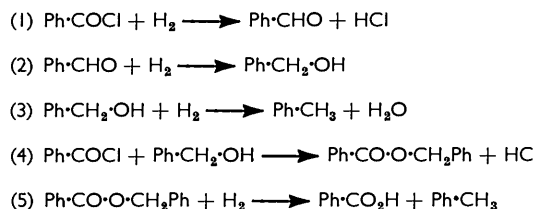
<sup>2</sup> Mosettig and Mozingo, *Organic Reactions*, 1948, **4**, 362.

thiourea separated off into water: only 0.002 mg. was detected colorimetrically by the Grote reagent.<sup>3</sup> Practically all the thiourea appeared to be on the catalyst. A later investigation of the adsorption of tetramethyl[<sup>35</sup>S]thiourea, by means of a liquid scintillation counter, showed that tetramethylthiourea was strongly adsorbed. At 20°, with 0.5 g. of 1% palladium-barium sulphate and 1.5 ml. of toluene, the partition of acid was: in toluene, 0.08, 0.71, 1.19 mg.; adsorbed, 0.15, 0.22, 0.20 mg. Colorimetric tests with thiophen (ninhydrin<sup>4</sup> used for detection) showed that it was also adsorbed completely on the catalyst.

Doubts were, however, cast upon these results when the chemical stabilities of the poisons were examined. When large amounts of thiourea (100 mg.) were hydrogenated, evolved hydrogen sulphide was detected and free sulphur remained in the reaction vessel. Tetramethylthiourea likewise decomposed. Thiophen was not detectably decomposed but it was probably hydrogenated to the tetrahydro-derivative.

Thus the study of compound poisons is complicated by their breakdown or hydrogenation, but it leads to the idea that elementary sulphur might be a poison. It was found that use of 0.08 mg. of sulphur resulted in an aldehyde yield of 27%; use of 0.48 mg. led to a 45% yield. Thus sulphur is not as effective a poison as tetramethylthiourea in equivalent amounts. Again, however, sulphur was lost from the system as hydrogen sulphide. Sulphur could be made an effective poison (0.16 mg. of S, yield 67%) if it was added to the reaction mixture only when this was at its working temperature. This suggested that palladium sulphide was being formed and that this was the real Rosenmund catalyst. Trials with palladium sulphide (PdS) on barium sulphate (5% of Pd) as catalyst gave 40% yields, but when the palladium sulphide was poisoned with tetramethylthiourea (0.3 g. of catalyst with 0.4–0.8 mg. of poison) yields rose to about 80%. Examination of the palladium sulphide showed that it was unstable under the conditions used, and this explained the need for the subsequent addition of poison.

*The Reaction Mechanism.*—Probable stoichiometric reaction steps are:



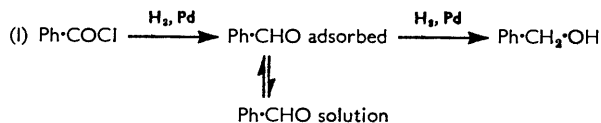
In each step except (4), hydrogen is consumed; in (1) and (4), hydrogen chloride is evolved. Thus examination of the ratio of hydrogen consumed to hydrogen chloride evolved might lead to the formulation of a reaction mechanism; *e.g.*, if the reaction is described by (1)–(3), then three moles of hydrogen will be absorbed for one hydrogen chloride evolved.

A closed system was constructed in which the reaction could proceed whilst hydrogen uptake and hydrogen chloride evolution were measured. Typical results for an unpoisoned and a poisoned reaction are shown in Fig. 2. In some 60 experiments at 110° the 1 : 1 correlation between hydrogen absorbed and hydrogen chloride evolved was always observed. This leads us to postulate that the reaction is described by (1), (2), and (4) at 110°. This was substantiated by a large-scale experiment in which ester was isolated. At room temperature different hydrogen to hydrogen chloride ratios are observed and at high temperatures (200°) decomposition of the ester was observed giving benzoic acid and presumably toluene.

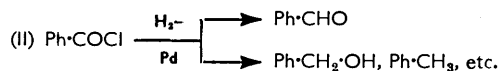
<sup>3</sup> Grote, *J. Biol. Chem.*, 1931, **93**, 25.

<sup>4</sup> Feigl, "Spot Tests in Organic Analysis," Elsevier Publ. Co., Amsterdam, 1960, p 473.

*Consecutive or Simultaneous Reaction Mechanism.*—In scheme (I) the adsorbed aldehyde might be in equilibrium with aldehyde in solution.



In scheme (II) benzoyl chloride molecules, on a catalyst surface, form benzaldehyde, which does not undergo further hydrogenation, whilst other benzoyl chloride molecules are hydrogenated directly to alcohol, etc. The role of a poison would be to influence the proportion of molecules reacting by either route.



We have distinguished between these mechanisms by studying the fate of [ $\alpha$ - $^{14}\text{C}$ ]-benzaldehyde added to an unpoisoned Rosenmund reaction. Total recovery of labelled aldehyde, after the reaction was complete, would support mechanism (II), whereas partial recovery would favour the consecutive scheme (I).

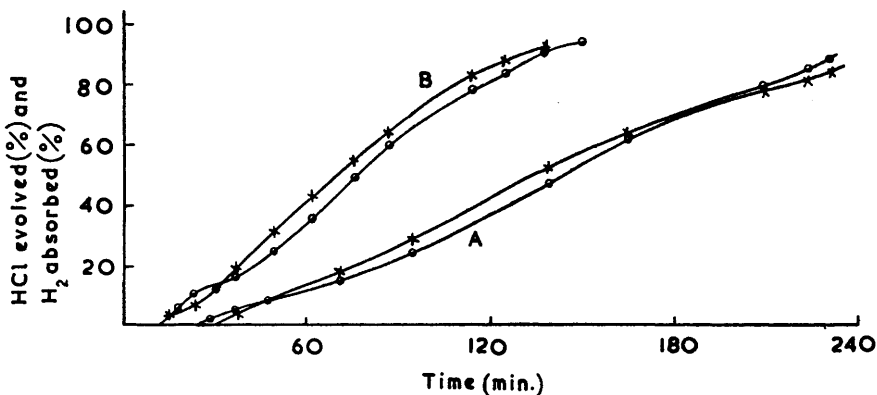


FIG. 2. Hydrogen uptake (○) and hydrogen chloride evolution (×) during poisoned (A) and unpoisoned (B) Rosenmund reactions. 10% Pd-BaSO<sub>4</sub>, 1 atm., 110°, in toluene.

[ $^{14}\text{C}$ ]Benzaldehyde was prepared from barium [ $^{14}\text{C}$ ]carbonate through benzoic acid<sup>5</sup> and benzoyl chloride. The chloride was hydrogenated by a Rosenmund reaction. This aldehyde was divided into two equal parts. The first sample was converted into a 2,4-dinitrophenylhydrazone whose radioactivity was determined, under "infinite thickness" conditions, by means of an end-window Geiger-Müller counter (activity 1135 counts/min.). The second portion was added to an unpoisoned Rosenmund reaction, which was stopped at 66% completion, as measured by hydrogen chloride evolution. This precaution was taken to avoid hydrogenation of aldehyde, which might have occurred when all the benzoyl chloride was consumed. The aldehyde was recovered and counted as before as the dinitrophenylhydrazone: its activity was 362 counts/min. If none of the added [ $^{14}\text{C}$ ]aldehyde had been hydrogenated in this reaction, the expected count would have been 684 per min. Thus 57% of the added aldehyde had been hydrogenated. The evidence suggests that the steps involved in a Rosenmund reaction are consecutive.

Corroboration for the consecutive mechanism comes from a study of removal of aldehyde from an unpoisoned reaction mixture immediately it was formed. Two reaction systems were compared: (a) Aldehyde was not removed from an unpoisoned reaction.

<sup>5</sup> Dauben, Reid, and Yankwich, *Analyt. Chem.*, 1947, **19**, 828.

The vessel in which the reaction took place was heated to  $159^{\circ}$  with the vapour of boiling *n*-propylbenzene. No distillation of product out of the vessel was allowed. The yield of aldehyde was 28% from this static reaction system. (b) Aldehyde was removed continuously from an unpoisoned reaction in a flow system: on this occasion the reaction vessel was heated to  $179^{\circ}$  by the vapour of boiling benzaldehyde, and the aldehyde

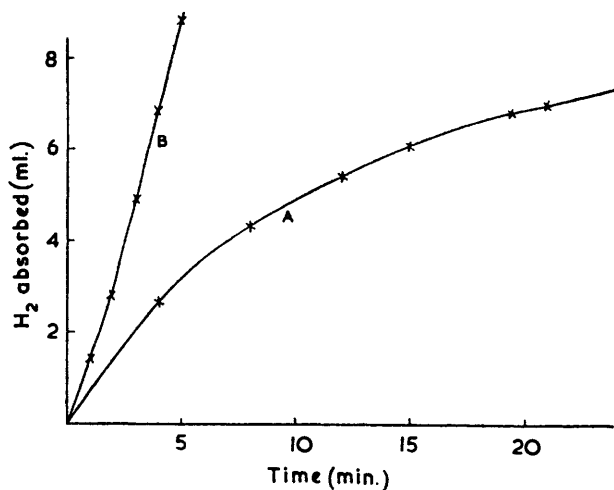


FIG. 3. Rate of absorption of hydrogen by benzoyl chloride (30 mg.) (A) alone and (B) mixed with benzaldehyde (20 mg.) in toluene (5 ml.) in presence of 10% Pd-BaSO<sub>4</sub> at  $20^{\circ}$ /1 atm.

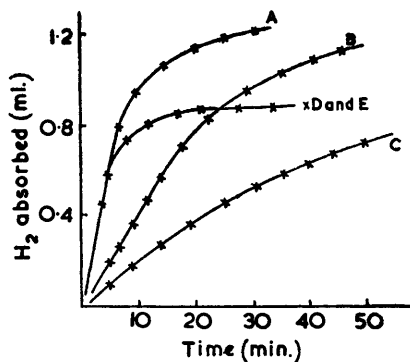


FIG. 4. The effect of varying the nature and quantity of poison on yields of benzaldehyde. 10% Pd-BaSO<sub>4</sub> (0.05 g.) in toluene at  $20^{\circ}$ /1 atm.

A, Unpoisoned; B, thiophen 0.2 mg.; C, thiophen 0.3 mg.; D, tetramethylthiourea 0.05 mg.; E, tetramethylthiourea 0.10 mg.

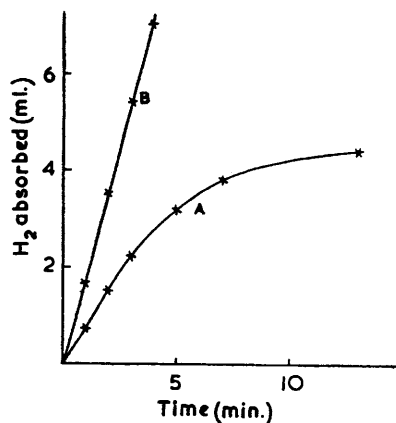


FIG. 5. The effect of pretreatment of a palladium catalyst by benzoyl chloride before hydrogenation of benzaldehyde:  $20^{\circ}$ /1 atm.

A, Unpromoted; B, promoted.

produced was removed by the hydrogen stream into a condenser. Since benzoyl chloride was rapidly distilled out of the system, it was added in portions to the reaction vessel throughout the hydrogenation. The high-boiling solvent used in this case was benzyl benzoate. The yield of aldehyde rose to 58%. This also indicates that a consecutive mechanism is likely for the Rosenmund reaction.

A third piece of evidence came from a study of the rate of hydrogenation of benzoyl chloride in the presence of added aldehyde. The results (Fig. 3) show that, at low concentration, the rate of hydrogen uptake is greater when aldehyde is present and thus it seems that benzaldehyde can be hydrogenated even in the presence of benzoyl chloride.

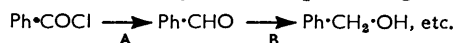
*Mode of Action of the Poison.*—Since it has been established that the Rosenmund reaction proceeds by consecutive steps, it is permissible next to examine the effect of poisons on the rate of aldehyde hydrogenation. Diminution of rates would correspond to an increase in Rosenmund reaction yields.

The effects of various amounts of tetramethylthiourea and thiophen were studied at room temperature, in a hydrogenation apparatus in which rate of hydrogen uptake could be measured. The results (Fig. 4) show a clearly visible reduction in rate with added poison.

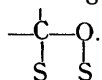
It should be noted that tetramethylthiourea is not a poison for aldehyde hydrogenation at room temperature, though it does prevent hydrogenation proceeding past the alcohol stage. The diverse behaviour of tetramethylthiourea may be analogous to that of elementary sulphur, reported above. At room temperature the tetramethylthiourea breaks down, but the sulphur-containing fragment does not combine firmly with the catalyst and therefore no poisoning is observed. At high temperatures the sulphur atom is probably attached to the catalyst by a stronger bond and poisoning takes place.

It was observed (Fig. 5) that the rate of hydrogenation of aldehyde was increased if the catalyst was treated first with benzoyl chloride. An analogous case of the promotion of palladium catalysts by the action of hydrogen chloride has been reported.<sup>6</sup> Even in the absence of hydrogen, benzoyl chloride reacted with the catalyst and after leaching with water, palladium ions were detected by means of *NN*-dimethyl-*p*-nitrosoaniline.<sup>7</sup>

*Discussion.*—Since (a) the reaction is consecutive, (b) small amounts of poison considerably increase the yield of aldehyde, and (c) the rate of aldehyde hydrogenation is affected by poisons, poison must adversely affect step B to a greater extent than step A.



Poison molecules could interfere with step B in the following way: Stoddart and Kembell<sup>8</sup> investigated the behaviour of the C=O group in acetone deuteration and exchange, and concluded that attachment of the C=O group to the catalyst was as



If benzaldehyde is adsorbed on the catalyst by this mechanism, then hydrogenation would require two hydrogen atoms, presumably adsorbed on neighbouring sites. Four sites would be required for each hydrogenation event, and the number available on a uniform surface rapidly diminishes as poison molecules are added to a surface, as Herington and Rideal<sup>9</sup> demonstrated by stochastic calculations.

If we apply the same concepts to the hydrogenation of benzoyl chloride, then the rate of this hydrogenation should be similarly diminished by poison molecules.

However, the carbonyl group in benzoyl chloride differs from that in benzaldehyde because of the chlorine attached to carbon. In acetaldehyde<sup>10</sup> the C=O distance is 1.22 Å, whereas in acetyl chloride<sup>11</sup> it is 1.19 Å. Thus the C=O group in benzoyl chloride has a stronger bond than that in aldehyde, and is less likely to be opened on a catalyst surface.

Attack can take place on the carbon atom of this group in a variety of circumstances,<sup>12</sup> and we suggest that a likely mode of chlorine removal from benzoyl chloride would be replacement of chlorine by active hydrogen from the catalyst surface, without adsorption of benzoyl chloride on the surface. Thus only dual sites are necessary on the catalyst for the supply of activated hydrogen. The rate at which dual sites diminish on a surface when poison molecules are added is much smaller than that for the disappearance of quadruple sites,<sup>9</sup> and hence the hydrogenation rate is affected to a smaller extent by poisons.

<sup>6</sup> Sato and Ishizuba, *J. Res. Inst. Catalysis, Hokkaido*, 1958, **6**, 138.

<sup>7</sup> Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publ., Inc., New York, 1944, p. 353.

<sup>8</sup> Stoddart and Kembell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 208.

<sup>9</sup> Herington and Rideal, *Trans. Faraday Soc.*, 1944, **40**, 505.

<sup>10</sup> Stevenson, Burnham, and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2922.

<sup>11</sup> Sinnott, *J. Chem. Phys.*, 1961, **34**, 860.

<sup>12</sup> Gould, "Mechanism and Structure in Organic Chemistry," Holt-Dryden, New York, 1960.

## EXPERIMENTAL

*Typical Rosenmund Reaction.*—To the catalyst (0.3 g.) in solvent (25 ml.), were added the poison, in a standard toluene solution, and freshly distilled benzoyl chloride. Hydrogen was passed through the mixture, which was then heated to 110° and stirred, and the hydrogen chloride liberated was collected and titrated as a measure of the rate of destruction of benzoyl chloride. When the rate diminished, at about 90% of the theoretical amount of hydrogen chloride evolved, the catalyst was removed and aldehyde yield measured by preparing the 2,4-dinitrophenylhydrazone.

*Preparation and Purification of Materials.*—*Benzoyl chloride.* The thionyl chloride method<sup>13</sup> of preparation was chosen rather than that involving phosphorus pentachloride, since traces of phosphorus might have interfered with the catalytic reaction.<sup>14</sup> The first portion of the benzoyl chloride in the distillation was always discarded. Otherwise, sulphur compounds in the initial distillation fractions were hydrogenated to an unshielded form which slowed down the subsequent hydrogenations.

*Solvent.* The criterion for purity adopted was that a solvent was pure when, used in a Rosenmund reaction without the presence of added poison, hydrogenation proceeded, but no yield of aldehyde was obtained. Distillation of solvents, usually toluene, twice over aluminium chloride,<sup>15</sup> followed by dehydration over potassium carbonate, then by sodium, gave satisfactory results.

*Hydrogen.* Cylinder hydrogen was found to be satisfactory without further purification.

*Glassware.* Before each hydrogenation, a mixture of toluene with aluminium chloride was refluxed in the apparatus. Comparison of kinetic results, however, is best restricted to reactions examined in the same glass vessel.

*Catalyst.* 1—10% Palladium on barium sulphate was used. Traces of iron in the catalyst acted as a promoter.

*Poisons.* Thiourea,<sup>16</sup> thiophen, tetramethylthiourea, etc., were used as poisons rather than the indeterminate poison sulphur-quinoline used by Rosenmund and Zetsche.<sup>17</sup>

*Impurities.*—Likely substances which might still be present in the purified reaction mixtures were alkali from the catalyst preparation, aluminium salts, and iron. Tests showed that aluminium chloride or sodium hydroxide, added in small amounts, did not substantially alter the reaction rate or products. Ferric chloride decreased the aldehyde yield, possibly because it formed complexes with the selective poisons.

*Preparation of Active Benzaldehyde.*—A Grignard reagent was prepared from bromobenzene (0.05 mole) and magnesium (0.054 g.-atom). A slight excess of Grignard reagent was treated with [<sup>14</sup>C]carbon dioxide prepared by the action of lead chloride (10 g.) on barium carbonate (0.99 g.), containing 1 mc of barium [<sup>14</sup>C]carbonate of specific activity 24.75 mc/mole. The complex was decomposed with dilute hydrochloric acid and extracted with ether and then with aqueous sodium hydroxide. Acidification of the alkaline layer precipitated benzoic acid (yield 85%), m. p. 121°. The benzoic acid was diluted to 2 g. with inactive acid and heated on a water-bath for 1 hr. with thionyl chloride (1.5 ml.), and the active benzoyl chloride (1.33 g.), b. p. 196°, was distilled off.

The active aldehyde was prepared by a Rosenmund reduction by using 5% palladium-barium sulphate (0.6 g.), tetramethylthiourea (0.1 mg.), toluene (25 ml.), and active benzoyl chloride (1.33 g.). The final mixture was made up to 50 ml. with pure toluene, and divided into two equal portions. The total aldehyde produced was shown to be 0.51 g. It was not necessary to separate the aldehyde before it was added to a further Rosenmund hydrogenation, as the small amount of poison used in the preparation would have been mostly removed by the catalyst, leaving an unpoisoned mixture favouring loss of aldehyde. The other reaction product, benzyl benzoate, does not interfere with the reaction.

We gratefully acknowledge useful discussion with Drs. J. D. Loudon and G. Buchanan. We also thank the D.S.I.R. for a grant (to S. A.) and for assistance in the purchase of equipment.

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[Received, October 20th, 1961.]

<sup>13</sup> Vogel, "Textbook of Practical Organic Chemistry," Longmans Green, London, 1956, p. 792.

<sup>14</sup> Zetsche and Arnd, *Helv. Chim. Acta*, 1925, **8**, 591.

<sup>15</sup> Zetsche and Arnd, *Helv. Chim. Acta*, 1926, **9**, 173.

<sup>16</sup> Weygand and Meusel, *Ber.*, 1943, **76**, 498.

<sup>17</sup> Rosenmund and Zetsche, *Ber.*, 1921, **54**, 425.