TABLE IV

THE HEATS OF EVAPORATION OF ACETONE

Temp., °C.	−60.00	−40.00	−20.00	0.00	20.00
ΔH_L calcd., cal./g.	155.46	149.68	143.92	138.05	132.14
ΔH_L observed cal./g.				140.50[19] 139.90[20]	
Temp., °C.	40.00	55.51	56.32	56.60	60.00
ΔH_L calcd., cal./g.	126.45	121.81	121.58	121.50	120.48
ΔH_L observed, cal./g.		124.00[21]	125.00[20]	123.30[22]	128.80[23]

Summary

1. The vapor pressures and densities of pure, anhydrous acetone have been measured over a large temperature range.

2. The solubility of carbon dioxide in acetone has been determined over the range +20° to −75°.

3. The latent heats of evaporation of acetone have been calculated by means of the Clausius-Clapeyron relation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

A STUDY OF NEGATIVE CATALYSIS IN THE OXIDATION OF BENZALDEHYDE

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An explanation for the mechanism of negative catalysis in homogeneous chemical reactions has been sought in the well-known theories of Titoff,[2] Taylor[3] and Christiansen;[4] on the other hand, negative catalysis in heterogeneous chemical reactions has been plausibly explained by the assumption of adsorption of the inhibitor on the positive catalyst surface.

Moureu and Dufraisse[5] have pointed out the high inhibitory power of phenolic substances in a variety of so-called auto-oxidations, such as the oxidation of benzaldehyde and acrolein and the oxidation of sodium sulfite; inhibitors added one part in one million were shown to give appreciable retardation.

In order to explain this high inhibitory power in homogeneous solution

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[19] Regnault, *Relat. exp. mach. feu*, **2**, 813 (1862).

[20] Winklemann, *Wied. Ann.*, **9**, 364 (1880).

[21] Tyres, *J. Chem. Soc.*, **181**, 1105 (1912).

[22] Wirtz, *Wied. Ann.*, **40**, 446 (1890).

[23] Young, *Dublin Proc.*, (N. S.) **12**, 374 (1910).

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[2] Titoff, *Z. physik. Chem.*, **45**, 641 (1903).

[3] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

[4] Christiansen, *ibid.*, **28**, 145 (1924).

[5] Moureu and Dufraisse, *Compt. rend.*, **174**, 258; **175**, 127 (1922).

by the hypothesis of molecular-compound formation between the inhibitor and one of the reactants, Taylor[3] has emphasized anew the fact that the active mass of a substance may be but a small fraction of the total mass. From this point of view, the concentration of inhibitor required to retard a reaction should be an approximate measure of the active mass of the reacting substance. The hypothesis of molecular-compound formation has received considerable support from the fact that in some cases such compounds have been isolated; phenolic substances, trichloroacetic acid and stannic chloride, which are inhibitors in the oxidation of benzaldehyde, also form isolable double compounds with it.

In opposition to the theory of Titoff, Taylor has observed that concentrations of positive catalysts produce accelerations of a lower order of magnitude than the retardation produced by equal concentrations of inhibitors. Thus, 0.001 *M* copper benzoate, partly in solution, partly suspended in benzaldehyde, causes a measurable acceleration of the oxidation, but to an extent which is a mere fraction of the retarding effect of 0.001 *M* hydroquinol. Similar observations were made with iron and manganese oxides as accelerants in the oxidation of benzaldehyde.

In the present study of the problem of negative catalysis, the oxidation of benzaldehyde has been investigated with the point of view that high inhibitory power produced by minute amounts of added substances might find explanation on the basis of surface catalysis. The idea of the nature of a catalytic surface, recently advanced by Taylor,[6] suggests that only a small fraction of the total surface area is catalytically active, together with the view that surface activity may be neutralized by a single layer of adsorbed molecules; only minute amounts of inhibitors should therefore be required to poison the active surface and thereby cause negative catalysis.

Experimental Part

The oxidation of benzaldehyde was studied in the dark room in the presence of light from a ruby lamp, for not only is the reaction catalyzed by light of short wave length such as the ultraviolet, but it is catalyzed remarkably by visible light from the incandescent light bulb.

The benzaldehyde, of Kahlbaum grade, was freshly redistilled in a vacuum and kept in the presence of nitrogen. The oxygen, made from liquid air, was not further purified.

Velocity rates were measured at 25° in a thermostat. Bulbs of silica, Pyrex and soft glass, and paraffin-lined bulbs, of 50cc. volume, served as reaction vessels, into which the benzaldehyde was either distilled directly or added by means of a pipet. The rate of reaction was observed from the volume of oxygen absorbed, the oxygen being measured over mercury in a gas buret at atmospheric pressure. Experiments were made both by

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[6] Taylor, *Proc. Roy. Soc.*, **108A**, 105 (1925).

shaking the solutions and by allowing them to stand. Two reaction vessels were mounted on the shaking device so that different solutions or different reaction vessels could be compared at exactly the same rate of shaking.

The rate of oxidation of benzaldehyde was found to be catalyzed remarkably by the addition of silica sand or broken glass; roughly, the reaction velocity of a 10cc. sample on shaking is doubled by the introduction of 1 cc. of sand. This makes it appear that we are concerned with a heterogeneous chemical reaction. On the other hand, the use of dust-free benzaldehyde gave no noticeable decrease in rate, differing in this from the *thermal decomposition of hydrogen peroxide*,[7] a heterogeneous reaction highly catalyzed by atmospheric dust.

The rate of oxidation of benzaldehyde is influenced by the entrance of a diffusion factor. That we are dealing with a diffusion factor is evident from a comparison of Curves 1 and 5, Fig. 1. Curve 1 represents the rate of oxidation of a freshly distilled solution, of 10cc. volume, on standing; Curve 5 gives the rate upon shaking. The rate of oxidation is found to be dependent upon the rate of shaking; apparently, when a solution is allowed to stand, the oxidation rate depends upon the rate of diffusion of oxygen to the active wall surface.

To give assurance that the high acceleration caused by the addition of silica sand to shaken solutions is a true phenomenon of surface catalysis, and is not due simply to a greater diffusion of oxygen caused by the agitation with sand, experiments were made without shaking as given in Fig. 1, Curves 1, 2 and 3. Curve 1 was obtained with 10 cc. of benzaldehyde, Curve 2 with 5 cc. of benzaldehyde plus 5 cc. of silica sand, and Curve 3 with 2 cc. of benzaldehyde plus 5 cc. of sand. It was made certain that no sand floated or remained partially uncovered so as to offer a larger exposed surface. Curve 3 indicates that the less the layer of benzaldehyde through which the oxygen had to diffuse to reach the active surface, the greater was the velocity of oxidation.

The diffusion factor is further indicated by a study of the temperature coefficient. For the range 15° to 25° the temperature coefficient has a maximum value of 1.3, which is within the range of diffusion coefficients. When the solution is shaken the temperature coefficient has a higher value but can be found only approximately because of an abnormal decrease in the rate of oxidation upon shaking, as will be understood in a following consideration of water catalysis.

In the study of catalysis by different wall surfaces, vessels of silica, Pyrex, soft glass and paraffin (A. H. Thomas paraffin) were found to give nearly equal velocity rates. Curves 4 and 5, Fig. 1, were obtained with reaction vessels of paraffin and glass, respectively. It is observed that the

[7] Dissertation by O. M. Reiff, under the direction of Dr. F. O. Rice, Johns Hopkins University, 1925.

velocity rates are initially equal; this result would be in opposition to the work of Norrish[8] and others on the polarity of surfaces. An explanation was sought in the removal of water vapor from the reaction, since a layer of polar water molecules adsorbed on the wall of the reaction vessel would be expected to form a more catalytic surface.

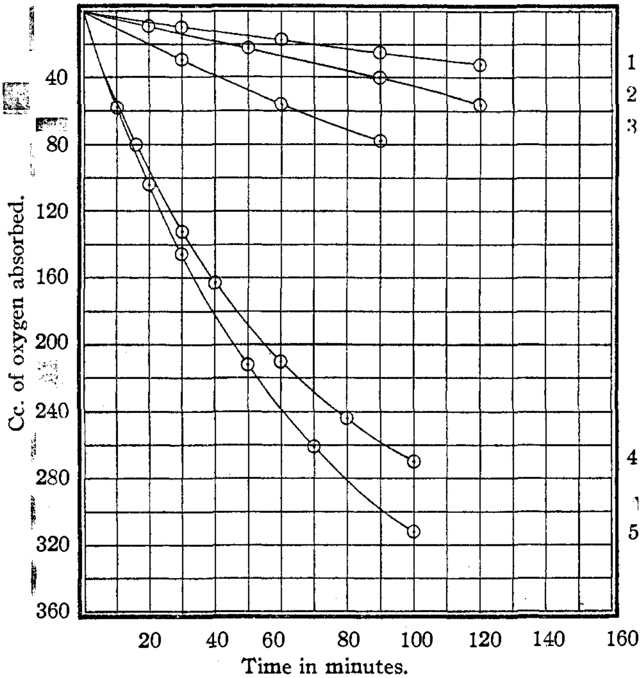

Fig. 1.

The drying process was effected by baking the entire distillation apparatus and reaction tubes at 400° for four hours in a high vacuum. The apparatus consisted of a drying tube and distillation vessel connected directly to two reaction tubes as a single unit, the whole having been made of Pyrex glass. The benzaldehyde was dried by distilling the vapors through the drying tube, containing anhydrous copper sulfate, into the distillation vessel, from which it was redistilled and condensed directly into the reaction tubes. Calcium chloride was also employed as drying agent; phosphorus pentoxide, unfortunately, reacts with benzaldehyde vapors. In determining the reaction velocities, oxygen dried over phosphorus pentoxide was passed into the one dry solution, while either moist oxygen was run into the second tube or its contents were transferred to another vessel not previously dried.

Curve 1, Fig. 2, shows the result of drying with anhydrous copper sul-

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[8] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923); **127**, 2316, 2793 (1925); **129**, 55 (1926).

fate, Curve 3 shows the effect of passing moist oxygen directly into a dry solution, while Curve 4 was obtained by transferring dry benzaldehyde to a fresh, moist tube. On the other hand, Curve 2 was obtained by passing *dry* oxygen into freshly distilled benzaldehyde, no precautions having been taken to dry the solution; Curve 5 shows the effect of passing moist oxygen into freshly distilled benzaldehyde which was not previously dried. The volume of benzaldehyde used in each case was 10 cc.

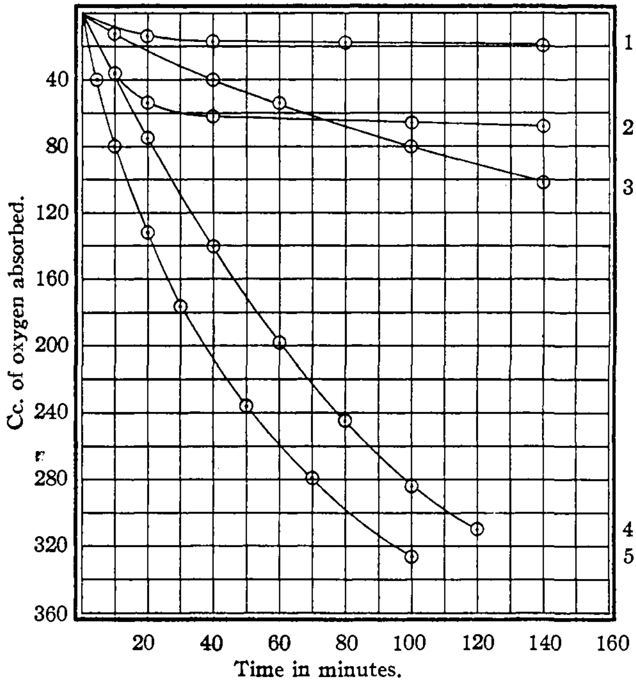

Fig. 2.

Each curve is characterized by an initial fast period with a following decrease in rate that is much greater than can be accounted for by the decrease in the concentration of benzaldehyde. It is observed from Curves 1 and 2 that an appreciable absorption of oxygen continues for a very short period when dry oxygen gas is passed into the solution; the presence of water vapor, on the other hand, is shown by Curves 3, 4 and 5 to cause reaction of much longer duration. Water vapor appears to be the dominant catalyst in the oxidation of benzaldehyde; however, adsorption of a film of water vapor on the wall surface seems to be a necessary criterion, since the introduction of water vapor directly into a dry solution does not give a velocity so great as that obtained by transference of a dry solution into another moist reaction vessel, the walls of which hold an adsorbed water layer. Apparently, catalysis by the dry wall surface is very slight.

The abnormal decrease observed in the rate of oxidation of benzaldehyde, as the reaction continues, has been previously accounted for on the basis of the intermediate reaction theory.

$$C_6H_5CHO + O_2 = C_6H_5COOOH \qquad (1)$$

$$C_6H_5COOOH + C_6H_5CHO = 2\ C_6H_5COOH \qquad (2)$$

Thus, a large amount of oxygen would be required for the formation of perbenzoic acid while the second change to benzoic acid would take place without the absorption of gaseous oxygen. On the assumption that Reaction 1 takes place more rapidly than Reaction 2 it is possible to account theoretically for the rapid fall in the slope of the curve representing the rate of oxidation. Furthermore, benzaldehyde has been previously considered an auto-oxidizable substance. Initial induction periods have been observed in certain cases; the fast period following the induction has pointed to catalysis by some oxidation product. On the other hand, the following considerations indicate the oxidation of benzaldehyde to be an auto-inhibited reaction, thereby offering an explanation for the abnormal decrease observed in the velocity rate.

It is important that freshly distilled benzaldehyde kept in an atmosphere of nitrogen does not show initial induction periods when oxidized later in an atmosphere of oxygen. When a solution is allowed initially to stand in contact with benzoic acid, however, short induction periods occur in the oxidation. This inhibiting effect is greater at higher temperatures. Thus, when benzaldehyde is initially heated in contact with benzoic acid in the presence of nitrogen for one hour at 150°, the reaction may be inhibited for several hours or even inhibited completely when carried out in an atmosphere of oxygen. Similarly, benzaldehyde distilled at atmospheric pressure in a current of nitrogen shows this inhibiting effect. Greater inhibitions at higher temperatures may be due to formation of a condensation product of benzaldehyde. In this connection, it is known that saturation of benzaldehyde with hydrogen chloride gas will stop further oxidation completely, possibly due in part to its high power as a condensation agent but chiefly to its strong affinity for water vapor.

This inhibiting action is also shown by the oxidation of benzaldehyde in paraffin vessels. The reaction velocity is high during the first run, Curve 4, Fig. 1; however, by pouring out the benzaldehyde and repeating with a fresh sample in the same vessel a velocity rate is obtained that is very nearly zero. This inhibiting action is not noticeable in glass vessels when fresh benzaldehyde is added to previously used, unwashed vessels. Possibly the negative catalyst adheres more strongly to the paraffin surface.

Last, when benzaldehyde is allowed to stand in an open bottle the rate of oxidation is rapid at first, crystals of benzoic acid separating in about an hour; however, the solution may stand for several months without complete oxidation having taken place.

The above examples point clearly to a poisoning action on the wall surface and principally the adsorbed polar water layer by the condensation and oxidation products of benzaldehyde. On this basis, the abnormal decrease in the rate of oxidation of benzaldehyde is readily explained without the use of the idea of the formation of perbenzoic acid.

The writer is indebted to Dr. F. O. Rice for suggesting the problem of the oxidation of benzaldehyde for investigation. He is grateful for the Grafflin Scholarship in chemistry awarded to him by Johns Hopkins University.

Summary

When benzaldehyde is allowed to stand in an atmosphere of oxygen, the rate of oxidation is dependent upon the rate of diffusion of oxygen to the active wall surface; the true reaction rate can be reached only by shaking or stirring the solution.

The formation of an active surface by the adsorption of a polar water layer on the wall of the reaction vessel, has been pointed out as the chief factor in the oxidation of benzaldehyde. Removal of water vapor as completely as possible has resulted in practically zero oxidation.

The oxidation of benzaldehyde appears to be an auto-inhibited reaction. The abnormal fall observed in the slope of the curve representing the rate of oxidation may be due to a poisoning action on the adsorbed polar water layer by the condensation and oxidation products of benzaldehyde. Negative catalysis caused by the addition of various inhibitors is explained by a similar poisoning action on the active surface by the inhibitor.

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