XIX.—*The Inhibition of Chemical Reactions. Part III. The Inhibition by Sulphur of the Atmospheric Oxidation of Benzaldehyde.*

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IT has long been known that benzaldehyde is oxidised rapidly by oxygen or by air, and it has been shown that the velocity of oxidation may be greatly reduced by the presence of *very* small traces of " anti-oxygens," *i.e.*, negative catalysts which are themselves oxidisable (see Moureu and Dufraisse, *Chem. and Ind.*, 1928, **47**, 819, 848, for a summary of many previous papers); for instance, one part of sulphur in 100,000 parts reduces it to about one-third (*idem, ibid.*, p. 822).

The following additional facts are of importance to the understanding of the present research. (1) The reaction is a chain reaction, in which several thousand molecules are oxidised for each

quantum absorbed, as proved by Bäckström (*J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, 15 and 16), in amplification of Christiansen's theory. (2) In at least some cases of anti-oxygen action the negative catalyst is itself oxidised; this has been clearly proved for the inhibition by alcohols of the oxidation of sodium sulphite (Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, **51**, 90). (3) The velocity of oxidation of benzaldehyde is increased by the addition of sand (Reiff, *ibid.*, 1926, **48**, 2893) or pumice (Brunner, *Helv. Chim. Acta*, 1927, **10**, 707). (4) The reaction certainly takes place in stages (Bäckström, *loc. cit.*), and is retarded by intensive drying (Reiff, *loc. cit.*). It has recently been suggested that pure benzaldehyde does not undergo oxidation (Kuhn and Meyer, *Naturwiss.*, 1928, **16**, 1028). (5) Benzoic acid, produced in the reaction, itself acts as a feeble inhibitor.

Most theories of anti-oxygenic action suppose that the negative catalyst detaches oxygen from its preliminary loose combination with the autoxidisable substance (*e.g.*, benzaldehyde), although there is a difference of opinion as to whether the oxygen is eventually liberated again as such (Moureu and Dufraisse, *loc. cit.*), or is fixed by reaction with the negative catalyst, as in the experiments of Alyea and Bäckström. In the latter case, inhibition must depend on the fact that the oxidation of the inhibitor is incapable of setting up or carrying on a chain of further oxidations.

The part of the problem which seems to have been least satisfactorily dealt with is that mentioned in the first paragraph. The explanation of the inhibitory effect of such minute traces must depend to a large extent on a demonstration of the site of reaction.

Moureu and Dufraisse (*loc. cit.*) and Bäckström (*loc. cit.*) believe the reaction to take place homogeneously in the liquid phase. The first two authors suggest that, as very few of the benzaldehyde molecules are at a sufficiently high energy level to react with oxygen, it is possible for a small number of inhibitor molecules to deal with these activated molecules, an explanation which demands for the original complex of benzaldehyde and oxygen the ability to survive 10^5 collisions (if the inhibitor is present in the proportion of one part in 10^5 parts) without further reacting with a benzaldehyde molecule to give stable benzoic acid. Bäckström depends on the high quantum yield of the reaction for an explanation of the efficiency of the negative catalyst.

The alternative is that offered by Reiff (*loc. cit.*) and Brunner (*loc. cit.*), and accepted by Rideal (*Trans. Faraday Soc.*, 1928, **24**, 571—574), *viz.*, that the reaction takes place, or is initiated, at the surface of the containing vessel, and is inhibited by the negative catalyst, adsorbed in high concentration on this surface. That

reactions are sometimes thus initiated and inhibited is unquestionable, a case in point being the inhibition of esterification by alkaline catalysts, investigated by the writer (J., 1928, 1204, 3256).

Reiff showed that the velocity of oxidation of 10 c.c. of benzaldehyde, standing without being shaken, was doubled by the introduction of 10 c.c. of sand, the activity of which in promoting the reaction would then be approximately equal to that of the original surface of the vessel. He further showed that 5 c.c. of benzaldehyde with 5 c.c. of sand absorbed oxygen $1\frac{1}{2}$ times as quickly as 10 c.c. of benzaldehyde alone, and that 2 c.c. of benzaldehyde and 5 c.c. of sand absorbed oxygen three times as quickly. This latter result Reiff interpreted as showing that here the oxygen had to diffuse through a much thinner layer of benzaldehyde to reach the sand and the oxidation rate therefore increased.   The rate was greatly increased by shaking, and this was attributed to the increased rate of diffusion of oxygen to the active solid surface.

These experiments, however, only *prove* that oxidation can take place on the surface of the sand.   It is *assumed* that the velocity in the absence of added sand depends on the walls of the container. It seems unlikely that the smooth walls of a 50-c.c. vessel could have an activity comparable with that of 10 c.c. of finely-divided sand, and scepticism on this point is increased by the fact that almost identical speeds of reaction were obtained by Reiff with vessels of silica, Pyrex glass, and soft glass, and with vessels lined with paraffin wax.   The use of dust-free benzaldehyde caused no decrease in the rate of oxidation.   These experiments suggest that the velocity of reaction is appreciably affected only by the introduction of a *large* amount of extra surface.   Experiments on paraffin-lined vessels and on the effect of sand are described later.

Brunner performed experiments in a shaking machine, and showed that the velocity of oxidation was increased in direct proportion to the amount of powdered pumice added.   Here too it is assumed that the original reaction, in the absence of pumice, is due to the walls of the vessel.

The possibility that the reaction takes place in the vapour phase is rejected by Moureu and Dufraisse (*Chem. Reviews*, 1926, **3**, 134, 129), who believe that crystals of benzoic acid appear on the upper portion of the vessel only where benzaldehyde has first condensed as a liquid.   The appearance of the vessel in some experiments which were carried on for several days by the writer does not accord with this, for fine needle crystals were formed which projected for a considerable distance into the gaseous phase.   In any event, however, the amount of reaction in the gaseous phase is small and, although estimations of the benzoic acid on the vessel wall above

the surface of the liquid were made in many cases, the amount, even where the reaction had proceeded until all the oxygen had been absorbed, never exceeded 4% of the total benzoic acid formed.

The evidence offered in the present paper tends to show that the choice lies, not between a reaction initiated at the solid–liquid interface and one taking place homogeneously in the liquid phase, but between the latter and a reaction initiated at the liquid–gas interface and capable of being inhibited there by a catalyst adsorbed preferentially at that interface.

EXPERIMENTAL.

The investigation concerns mainly the oxidation of benzaldehyde by atmospheric air, when standing quietly in an unshaken vessel. Experiments were made with pure oxygen also, but the results were of the same general type as when air was used.

In these experiments the benzaldehyde, unless otherwise specified, was Kahlbaum's pure material, freshly distilled in an atmosphere of nitrogen, and stored under that gas. The velocity of reaction was followed by noting the absorption of oxygen, and no attempt was made to distinguish between the first stage of the reaction (formation of perbenzoic acid) and the final conversion into benzoic acid. The specimen under examination was placed in a vessel connected to a differential manometer, the other arm of which was attached to a vessel of the same size. By reading the difference in height between the two columns of liquid, volume errors due to small variations of temperature were eliminated. In the earlier experiments (Series I—IV) mercury was used as manometric liquid, but in the remainder greater delicacy was obtained by the use of water, and the benz-aldehyde was throughout assumed to be moist. [It has already been shown by Brunner (*loc. cit.*) that small variations in moisture content have little effect on velocity of oxidation.]

Series I.—The velocity of oxidation of pure benzaldehyde in plain glass vessels was compared with that in vessels to which had been added solid glass rods whose total geometrical surface was approxim-ately equal to that of the portion of the containing vessel in contact with the liquid. The results were not very consistent. Sometimes the vessel with added surface showed a slightly higher velocity than the other, sometimes slightly lower. In no case was the speed of reaction increased by more than 15%.

Series II.—Experiments were carried out with the same amount of pure benzaldehyde in flasks and tubes of different shapes but approximately the same volume. The rate of absorption over a period of 2 hours was roughly proportional to the area of the liquid–gas interface. For example, when this interface was increased in

the ratio 7·8, the velocity increased in the ratio 7·2, and with an area ratio of 3·2 the velocity ratio was 2·6.

Series III.—In all vessels the benzaldehyde is drawn up on the glass wall by capillary action to some little height above the liquid surface, and it seemed possible that reaction might be very intense in these places where liquid–gas and liquid–solid interfaces are close together.   Experiments were performed in which were introduced glass rods of such a length as to project slightly above the surface of the liquid and thus increase the area of this liquid film. The velocity of reaction was found to be diminished rather than accelerated.

Series IV.—When benzaldehyde is shaken in air, the velocity of oxidation is greater than when the liquid stands quietly. It has already been pointed out that shaking increases the diffusion of oxygen to the solid surfaces. It is also true, however, that it increases diffusion into the homogeneous phase, and again, that it increases greatly the area of the liquid–gas interface, which cannot be neglected as a possible site of reaction.

Brunner's experiments, already quoted, employed a relatively enormous increase of surface (pumice). It was desirable to try a surface comparable with that of the original flask.   For obvious reasons, it is impossible to agitate violently a glass flask containing a number of loose solid glass rods.   An extra surface was therefore added by fixing a spiral of solid glass of known surface area into the stopper of the flask.   The flask employed had a capacity of 155 c.c., and a surface area of 130 sq. cm. to the highest point to which the benzaldehyde splashed during shaking at 160 revolutions per min. The solid coil had a surface area, exposed to the shaken benzaldehyde, of 31 sq. cm., or 24% of the area of the original surface.   The volume of the coil was 6 c.c., and this was taken into account in calculating the absorption of oxygen.

The experiments A were performed in sunlight at 5°, and B in the dark at 12·4°. The solid coil was omitted in A1 and B1, and included in A2 and B2 ; t is the time interval from the start (in minutes) and R the average rate of absorption of oxygen (c.mm./min.).

	R.				*R.*	
t.	A1.	A2.		*t.*	B1.	B2.
0—3	730	640		0—5	445	380
4—6	570	550		6—14	156	154
7—9	530	450		15—24	116	120
10—12	400	410		25—35	114	107
13—15	430	380		36—44	110	107
16—18	330	290		45—56	100	111
19—21	330	320		57—70	114	105
22—24	330	290				
25—27	300	290				
28—30	270	210				
0—30	422	383		0—70	140	135

In experiments A the oxygen consumption declined by 9·2% when extra surface was included, and in B by 3·6%, whereas an increase of about 24% was to be anticipated if the reaction took place solely on the solid surface. Two other pairs of experiments were performed in the dark, at temperatures of 10·5° and 11·0°, and in each case a diminution of speed of about 4% on inclusion of the extra surface was noted.

Series V.—In these experiments cylindrical glass bottles of about 330 c.c. capacity and 5·2 cm. diameter were used. In bottle B the circular bottom was almost flat, in A it was slightly convex; otherwise the bottles were similar. A differential water manometer, with a bottle of the same size containing only air saturated with water vapour, was used in each case. In those experiments where it was used, the light was supplied by a single electric bulb. For A, the distance of the bottle from the light was 88 cm., and for B, 44 cm. In all cases there was an initial rapid absorption which declined rapidly to an almost constant rate. The initial absorption was difficult to measure accurately and the irregularities are probably largely due to experimental error. The average rate of absorption over the period 14—104 minutes was taken as the significant rate for each experiment.

Three types of experiment were made with each bottle. In the first, 12 c.c. of benzaldehyde were employed, in the second 12 c.c. of benzaldehyde and eight glass rods (of total surface approximately equivalent to the submerged surface of the containing bottle), and in the third 5 c.c. of benzaldehyde. The temperature of experiment throughout was 15·3°. In most experiments the first reading of the manometer was taken $\frac{1}{2}$ minute after the benzaldehyde began to be run into the bottle.

Bottle B. Light at 44 cm.

Conditions.	(1) 12 c.c. Ph·CHO.		(2) 12 c.c. Ph·CHO + rods.		(3) 5 c.c. Ph·CHO.	
	t.	*R.*	*t.*	*R.*	*t.*	*R.*
	$\frac{1}{2}$—1	345	$\frac{1}{2}$—1	462	$\frac{1}{2}$—1	473
	1—3	273	1—3	274	1—3	293
	3—5	208	3—5	228	3—5	211
	5—10	172	5—10	149	5—8	173
	10—14	137	10—14	112	8—14	126
	14—24	120	14—24	109	14—24	92
	24—42	120	24—36	99	24—34	88
	42—62	120	36—47	99	34—43	82
	62—85	114	47—60	106	43—53	85
	85—104	114	60—72	99	53—67	76
			72—91	92	67—78	72
			91—104	89	78—88	63
					88—104	
	14—104	117·2	14—104	98·2	14—104	76·5

A repetition of the above experiments, and experiments under

the same three sets of conditions with B in the dark, and with A in the dark and the light, followed a similar course, and the following summary gives only the steady rates (values of R for 14—104 mins.).

			Values of R under conditions		
			(1).	(2).	(3).
Bottle B.	Light	....	117·2, 106·7	98·2, 96·8	76·5, 84·3
,,	Dark	....	48·0	41·6	48·3
Bottle A.	Light	....	62·7	67·4	55·7
,,	Dark	....	40·1	45·7	47·8

These results show that the effect of doubling the solid–liquid interface is small. In A, it results in a slight increase in velocity, and in B in a reduction (a result confirmed in Series IX). The experiments of Reiff and Brunner make it probable that some portion, at least, of the reaction takes place on the solid surface. We may have here the net result of two opposite effects, an acceleration due to an increase in solid surface, and a diminution in velocity explainable in some other way. The fact that, in all experiments performed in the light, the velocity with a shallow layer of benzaldehyde is markedly less than with a deep layer suggests that the diminution in velocity is due to earlier interruption of the reaction chain postulated by Christiansen and Bäckström.

The fact that 5 c.c. of benzaldehyde absorb oxygen more slowly than 12 c.c. in a similar vessel can hardly be due to the greater proportional accumulation of benzoic acid, as the percentage of this acid formed in these experiments is always low and quite insufficient to explain the results. The latter appear to contradict Reiff's experiments in which 2 c.c. of benzaldehyde over 5 c.c. of sand absorbed oxygen twice as quickly as 5 c.c. of benzaldehyde over 5 c.c. of sand. The difference is probably due to the fact that the particular sand used had a much more active, as well as more extensive, surface than the glass vessel, and the acceleration here outweighed the diminution in velocity due to earlier interruption of the reaction chain. On this theory, the fact that addition of extra surface to A results in a small increase in velocity, in contrast to the result in B, may be due to the different distribution of liquid and solid resulting from the slight convexity of the bottom of A. The relative importance of the two opposite effects may, therefore, be different in the two bottles.

Series VI.—These experiments were performed with three tubes of 34 c.c. capacity and 1·4 cm. diameter, prepared from uniform soft-glass tubing. One tube (T) was left in its original condition. Another (N) was narrowed slightly, and in the third (W) a small bulb was blown, in positions such that 6 c.c. of benzaldehyde filled the

tube to the centre of the narrowing or the bulb respectively. Allowance being made for the liquid creeping on the glass to the extent of 0·3 cm., the total liquid surfaces in T, N, and W, respectively, were 3·1, 2·5, and 5·9 sq. cm., or in the ratio 1·0 : 0·81 : 1·90. (If the creep surface is neglected the ratio is 1·0 : 0·69 : 2·20.) We have, therefore, three similar vessels, containing the same amounts of air (28 c.c.) and benzaldehyde (6 c.c.), and with almost identical solid surfaces (submerged area = 22 sq. cm.), but differing in the area of the liquid–gas interface.

Experiments with the light at 44 cm., at 15·3°, showed that the relative steady velocities in T, N, and W for the period 14—104 minutes were 1·0, 0·84, and 2·03, or roughly in the ratio of the areas of the liquid–gas interface.

Series VII.—It was thought desirable to repeat Reiff's experiments in which contact of benzaldehyde with the glass surface was prevented by coating the glass with paraffin wax. Experiments were made simultaneously with two similar bottles, one of plain glass, the other lined with paraffin wax. After the subsidence of the short initial period of rapid oxidation (14 mins.), the velocity of reaction in the glass vessel remained almost constant for over an hour. The velocity in the wax-lined vessel, which, at the end of the 14 minutes, was little less than that in the glass vessel, fell off continuously.

An examination of Reiff's curves showed that this happened in his experiment also, although to a less extent. As melted paraffin wax and benzaldehyde are freely miscible, it seemed likely that benzaldehyde would dissolve some solid paraffin wax. It was found that benzaldehyde which had been left over-night under nitrogen in contact with paraffin wax at 15° did not oxidise appreciably for at least an hour when placed in contact with air. Paraffin wax is therefore dissolved, and is a remarkably good inhibitor. The wax used melted at 71° and may have dissolved in benzaldehyde more rapidly than that employed by Reiff.

These experiments make it clear that paraffin wax is not a suitable substance for covering the glass walls of the vessel. The possibility was next considered of floating the benzaldehyde on the surface of an inorganic liquid of higher density. Contact with the solid surface would thus be greatly reduced, and the surface of a liquid can hardly present " active points " for heterogeneous catalysis, such as are believed to be present in a solid catalytic surface. Water is not sufficiently dense, and it was found that benzaldehyde which had been left in contact with a concentrated solution of sodium chloride oxidised much less rapidly than normally, having suffered partial inhibition; a concentrated solution of calcium chloride,

however, proved satisfactory, for benzaldehyde which had been thoroughly shaken with it still oxidised almost as rapidly as before.

A glass-stoppered vessel was filled completely with equal volumes of benzaldehyde and calcium chloride solution and shaken vigorously for $\frac{1}{2}$ hour. Three cylindrical glass bottles of 290 c.c. capacity and 5·8 cm. diameter were connected to the same water manometer. One was used as a control; into the second (A) were put 10 c.c. of the calcium chloride solution, and 10 c.c. of benzaldehyde previously shaken with calcium chloride were carefully floated on top of it; and into the third (B) were put 10 c.c. of the shaken benzaldehyde, in direct contact with the glass.

Allowing for the rise of liquid on the walls due to surface tension, the ratio of glass surface in contact with benzaldehyde in A and B was 1·0 : 3·4. The following results were obtained.

A $\begin{cases} t \\ R \end{cases}$	$\frac{1}{2}$—1	1—3	3—5	5—7	7—10	10—15	15—25	25—48	48—61	5—61	
	120	135	141	141	126	132	126	123	117	123	
B $\begin{cases} t \\ R \end{cases}$	$\frac{1}{2}$—2	2—4	4—5	5—7	7—9	9—12	12—17	17—27	27—50	50—63	5—63
	84	75	120	120	120	120	126	134	135	132	132

The velocity of oxidation in A was about 7% less than in B, instead of 70% less, as would be expected if the reaction were entirely initiated at the glass surfaces. It is noteworthy that these experiments are the only ones performed by the author in which the initial rapid absorption, subsiding after the first few minutes, was absent. The explanation of this phenomenon is still far from clear.

Experiments similar to those of Reiff with sand (already quoted) were also performed, but the geometrical surface area of the silver sand used was evaluated. 1,000 Grains of sand weighed 0·0081 g. The density was 2·6, from which it was calculated (on the assumption that the grains were spherical) that 275 grains have a surface area of 1 sq. cm.

The bottles used for the experiment were similar to those employed in Series V, and the area of glass covered by 10 c.c. of benzaldehyde was about 35 sq. cm. The weight of sand having approximately the same surface area is only 0·08 g. The following results (mean of several experiments) were obtained at 12·7°.

	R (14—74 minutes).
10 c.c. Benzaldehyde	50
(a) 10 c.c. Benzaldehyde + 0·08 g. sand	46·5
(b) 5 c.c. Benzaldehyde + 10 g. sand	33
(c) 11 c.c. Benzaldehyde + 10 g. sand	54

These results are quite unlike those of Reiff, but resemble closely those of Series V, in that addition of a sand surface comparable in area with that of the original glass (a) has little effect, while reduction

in the depth of liquid (b) diminishes the oxidation. When the original depth of liquid is restored (c) (1 c.c. of benzaldehyde extra being allowed for soakage between the grains of sand), the velocity is restored to a value only a little faster than the original. The difference between these results and Reiff's is probably due to the fact that his sand had a surface of much greater specific activity than the silver sand used in these experiments.

Series VIII.—The following experiments on benzaldehyde which contained sulphur as an inhibitor were made with the light at 44 cm., and with tubes T and W (see Series VI). The temperature was 15·3°. Since in many of the experiments, the reaction velocity did not become constant as quickly as in the experiments with large bottles (Series V), the mean velocity for the period 34—104 minutes was considered the significant velocity. The following is a summary of the results :

Sulphur, parts per 10^6.	R (34—104).		Ratio, W/T.	Velocity as % of original.		Diminution % for each part of sulphur per 10^6.	
	T.	W.		T.	W.	T.	W.
Nil	1·866	3·475	1·86	100	100		
3·3	1·582	2·927	1·85	84·8	84·2	4·61	4·79
10	0·612	1·028	1·68	32·8	29·6	7·76	8·15
20	0·555	0·920	1·66	29·8	26·5	0·30	0·31
100	0·280	0·434	1·55	15·0	12·5	0·19	0·18
1000	0·124	0·124	1·00	6·6	3·6	0·009	0·010

From these results the following facts emerge.

(1) The ratio of velocities in W and T remains fairly constant as long as the amount of inhibitor present is small.

(2) The effect of each part of sulphur per million appears to be less for the first 3·3 parts than for the next 6·7 parts. That this phenomenon is due to adsorption of sulphur on the solid surface is shown by Series IX. Proportionately more of the first sulphur added is removed from solution, for the solid surface probably becomes rapidly saturated with sulphur. This result is the opposite of what would be expected if the reaction were wholly initiated on the solid surface.

(3) The addition of sulphur causes a very rapid diminution in reaction velocity until the velocity has been reduced to about 30% of the original. After that, further addition of sulphur has a much· smaller effect. This suggests that about 70% of the reaction takes place in ways readily affected by inhibitors, and about 30% (in vessels of the shape employed) in ways not readily affected.

Series IX.—A few experiments were made with tubes W and T, to which had been added glass rods of 10 sq. cm. surface area (about 45% of the submerged surface of the tube) and volume 1·15 c.c. Only 4·85 c.c. of benzaldehyde were used, so that the liquid level

stood at the same points as before. The other conditions were as in Series VIII.

Sulphur, parts per 10^6.	R (34—104).		Velocity as % of original.		Diminution % for each part of sulphur per 10^6.	
	T.	W.	T.	W.	T.	W.
Nil	1·704	3·135	100	100		
10	1·184	2·246	69·5	71·6	3·05	2·84
20	0·523	0·868	30·7	27·7	3·88	4·39

These results confirm the fact already noted, that the addition of extra glass surface to benzaldehyde containing no inhibitor is accompanied by a reduction rather than an acceleration in velocity. The further reduction due to the addition of 10 parts of sulphur per million parts is only about 30% instead of 70%, as in the case of benzaldehyde containing no extra glass surface, but 20 parts of sulphur cause a total reduction of about 71%, as against 72% in Series VIII. There is here more solid surface for adsorption of inhibitor, and therefore, with small amounts of inhibitor added, the amount of inhibitor actually available is much less than one would expect.

Discussion.

It is clear from Series II, VI, and VIII that the velocity of oxidation in unshaken vessels is approximately proportional to the area of the liquid–gas interface. This fact could be reconciled with any of the three following theories : (1) that the reaction is initiated at this interface, (2) that we are measuring a diffusion rate, the reaction taking place in the homogeneous phase, (3) that we are measuring a diffusion rate, the reaction taking place at the solid–liquid interface.

Let us first consider theory (3). It is shown in Series I, III, and IX, that addition of extra glass surface is accompanied by no increase in velocity. This can be reconciled with theory (3) only if we assume that the surface of the containing vessel is so catalytically " active " that it is already more than sufficient for all the oxygen that reaches it, and that the addition of extra surface merely means the substitution of new " active points " for some of the original.

The results of Series IV show that we must further assume an ability to cope with the much greater quantity of oxygen which would diffuse to the solid surface when the vessel is shaken at 160 revolutions per minute.

The writer has also performed experiments which show that the velocity of oxidation increases with rate of shaking (and therefore rate of diffusion of oxygen) up to the maximum velocity employed (160 r.p.m.).

The experiment performed in Series VII, with benzaldehyde

floated on calcium chloride solution, seems to prove definitely that the reaction is not, in the main, a solid surface phenomenon, for the glass–benzaldehyde interface in the vessel A is only to be found round the edges of the vessel, and is not likely to be reached at all by most of the molecules of oxygen which diffuse into the benzaldehyde near the centre of the liquid surface.

The experiments with sand in Series VII showed that the substitution for glass of an enormously greater surface of silver sand increases very little the velocity of reaction, and these experiments, as well as those in Series V, indicate that when the solid surface is brought nearer to the oxygen by diminishing the depth of liquid, the result (in experiments in the light) is a diminution of speed rather than an increase.

The sand experiments suggest that the results obtained by Reiff are exceptional and must be due to the fact that the sand used by him acted as a decided positive catalyst. This theory, however, conflicts with the idea that we are measuring a diffusion rate to the glass surface where reaction takes place practically instantaneously, for, if this be the case, the substitution of a more active solid surface can make no appreciable change in velocity.

The results quoted in Series VIII, and discussed in (2) under that series, also militate against a solid-surface theory.

The experiments described in this paper afford no means of discriminating with certainty between a homogeneous reaction in which a minute proportion of inhibitor acts by interrupting a chain which would otherwise be much longer, and a reaction initiated at the liquid surface and checked by an inhibitor adsorbed at this surface in high concentration. There are several points, however, which incline the author towards the view that the latter type of reaction is the more important.

The experiments of Series VIII show that the velocity of oxidation is reduced by 70% by the addition of 10 parts of sulphur per million parts, while the addition of further sulphur has a very much smaller effect on the velocity. If these results are plotted, a curve is obtained very similar to that obtained for the effect of pyridine on the esterification of ethyl alcohol and acetic acid (J., 1928, 1204). In the latter case, the portion of the reaction which is readily affected by small amounts of inhibitor was shown to be a surface reaction, while the portion not readily affected is probably a homogeneous reaction. It is at least possible that the similarity of curve is due to a similarity of cause.

In the second place, the idea that the reaction is largely initiated in the surface layer seems reasonable of itself. The concentration of oxygen in the surface layer is clearly higher than in the body of the

liquid, unless we assume that no reaction takes place until the solid surface is reached, an assumption which the author has given reasons for rejecting.

The higher concentration of oxygen in the surface layer should mean more reaction in that layer, but the percentage of inhibition will not be greater there than elsewhere unless there is a preferential concentration of inhibitor at the liquid–gas interface. This hypothesis is so far untested in this case, but experiments on the problem are projected. The possibility that they may yield positive results is increased by the results of experiments by McBain and Davies (*J. Amer. Chem. Soc.*, 1927, **49**, 2230) and Laing, McBain, and Harrison. (*Colloid Symposium Monograph*, 1928, **6**, 63), who have shown that, in the case of aqueous solutions of such diverse substances as *p*-toluidine, camphor, amyl alcohol, and sodium oleate, the surface concentration of the solute is high even in dilute solutions, and that, when the bulk concentration reaches 1—5 g. per litre, a surface layer more than one molecule thick is composed almost entirely of solute molecules.

A theory that the reaction is initiated to a considerable extent at the liquid surface does not necessarily conflict with the belief that the reaction is a chain reaction. It merely modifies it by suggesting that the reaction chain usually begins at the liquid surface, where it is more readily interrupted by an inhibitor concentrated there than when it begins in the homogeneous phase where the concentration of inhibitor is lower. The reduction in velocity when the depth of liquid is reduced (Series V and VII) may be due to earlier interruption of the reaction chain by collision with the solid surface. The diminution of reaction in Series III has probably a similar explanation.

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