LVII.—*The Inhibition of Chemical Reactions. Part IV. The Site of Anti-oxygenic Action. The Oxidation of Sodium Sulphite and Benzaldehyde.*

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IN Part III of this series (J., 1930, 115) it was suggested that the spontaneous oxidation of benzaldehyde is initiated to a considerable extent (about 70%) at the liquid–gas interface, from which reaction chains are propagated into the liquid, the large inhibiting effect of very small amounts of sulphur and other substances being attributed to their preferential concentration at the interface. It was admitted that the data given in that paper afforded no means of discriminating with certainty between this mechanism and one by which the inhibitor acted by interrupting the reaction chain in the body of the liquid, although the shape of the inhibition curve was deemed to favour the former hypothesis.

To establish this hypothesis, it was desirable to investigate the actual concentration of an anti-oxygen at the surface of the liquid concerned, and show a connexion between the surface concentration and the magnitude of anti-oxygenic action.

The method adopted for investigating the surface concentration of the inhibitor was that used by McBain and Davies (*J. Amer. Chem. Soc.*, 1927, **49**, 2230), Laing, McBain, and Harrison (*Colloid Symposium Monographs*, 1928, **6**, 63), and McBain and Du Bois (*J. Amer. Chem. Soc.*, 1929, **51**, 3534), in which the films from a large number of bubbles, formed by passing an inert gas through the solution in question, are collected and analysed.

The practical difficulty of performing such experiments with a solution of sulphur in benzaldehyde was too great, owing to the ease with which this liquid oxidises, and to the analytical complications which would arise from its contamination with an uncertain amount of oxidation products. It was decided, therefore, to examine the inhibition by *iso*propyl and *sec.*-butyl alcohols of the oxidation of sodium sulphite, investigated by Bäckström (*ibid.*, 1927, **49**, 1460), Alyea and Bäckström (*ibid.*, 1929, **51**, 90), and others.

EXPERIMENTAL.

Measurements of Adsorption at the Air–Liquid Interface.—The apparatus and experimental procedure were similar to those of McBain and his collaborators (*loc. cit.*). A stream of bubbles of air, previously saturated with the vapours of the solution to be employed, was passed up an inclined tube (A), 134 cm. long, containing an aqueous solution of the required alcohol, with which the bubbles remained in contact long enough for an equilibrium surface to be established. (Equilibrium is complete after 4 secs., according to McBain: the time of contact in these experiments was about 9 secs.) The bubbles passed thence into a vertical tube of smaller diameter which was bent twice at right angles into a swan-neck at a height of 8 cm.: while the bubbles passed up this tube, most of the adherent solution drained away. The bubble films in continuous procession passed over the bend at the top of the vertical tube and collapsed into a receiver. Each experiment lasted for 60—80 mins. The collected solution was then ready for analysis. A bubble-former (as described by McBain) was made, and the rest of the apparatus was adjusted so as to give a stream of bubbles moving with suitable velocity and forming a continuous series of films in the vertical tube. The apparatus was cleaned before each series of experiments with hot chromic acid, and washed with distilled water and the solution to be used. The slightest trace of grease causes premature breaking of the bubbles.

If the surface layer surrounding each bubble has a concentration of alcohol different from the original solution, this should be revealed by analysis. As, however, the film carried over by each bubble is not one or two molecules thick but many, the increase of concentration (if any) of the surface layer is diluted by admixture with many molecular layers of the original solution, and the percentage change is likely to be very small.

An examination of the analytical possibilities showed that the interferometer method used by McBain was the only one likely to be satisfactory.

As no Rayleigh interference refractometer was available, one was constructed locally by one of us (V. H. ff.), using as source of light a motor headlight run off a 200-volt circuit reduced by a suitable resistance to about 12 volts. The light was focused by a lens on an adjustable slit from which it passed through the two halves of a glass cell with accurately planed parallel ends, and divided down the centre by a glass slide. From each cell the light passed through one of two parallel slits and a long-focus lens. The bands produced were viewed with a microscope fitted with an internal scale and an external micrometer screw. The block bearing the cell, slit, and lens was fixed inside the innermost of a series of three boxes, the spaces between which were filled with cotton wool and wood shavings. The solutions to be examined were left for several hours in the box before analysis to attain temperature equilibrium, and transferred to the cells (without the boxes being opened) by delivery tubes with rubber tubing attached. Precautions were taken against evaporation.

Dimensions of the Refractometer :—

Distance from light to lens	88 cm.
Distance from lens to slit	24 cm.
Distance from slit to parallel slits	184 cm.
Distance from parallel slits to objective of telescope ...	72 cm.
Total length	368 cm.
Height of beam above bench	28 cm.
Length of cell	8·675 cm.
Distance apart of slits	0·65 cm.

The original solution was placed in the right-hand half of the cell, and the film solution or the solution remaining in the long tube (A) in the left-hand half.

The instrument was calibrated by measuring the shift produced in the interference bands by the introduction into the left-hand half of solutions differing in concentration by a known amount from a standard solution in the right-hand half. It was possible to read the shift to approximately 0·001 S.D. (scale division). The following is an example of the figures obtained with *iso*propyl alcohol :

Left-hand side (g. per litre).	Right-hand side (g. per litre).	Reading (S.D.).	Diff.
4·35	4·35	23·166	0·014
4·2925	4·35	23·152	
4·35	4·35	23·164	0·012
4·2925	4·35	23·152	

A change of 0·0575 g./litre in concentration therefore causes a mean difference of 0·013 scale division. Calibration curves were drawn for both alcohols.

The highest change in concentration obtained during the experiments only gave a shift of about 0·1 S.D., and a very high degree of accuracy cannot be claimed for the individual results, of which the general trend is nevertheless quite clear. The symbols used are :

V = volume of collapsed film collected.

A = total surface area of bubbles collected (calculated on the assumption that each bubble has a cylindrical body with spherical ends).

c_f, c_o, c_r = concentration of film, original, and remaining solution respectively (in g. per litre).

Γ = increased concentration of solute in the surface layer (in g. per sq. cm.).

As an example of the method of calculation, the following experiment with *sec.*-butyl alcohol is given :

Volume of film solution, ml.	125	
Duration of experiment, mins.	77	
Time for 30 bubbles, secs.	7·74	
Length of bubble, cm.	0·617	
Readings of interferometer (mean of 3)	0·0170	Mean 0·0166
,, ,, ,, ,, ,,	0·0163	
Reading corrected for change of concentration during the experiment [so as to give directly a value for $c_f - \frac{1}{2}(c_o + c_r)$]	0·0156	

(A reading of 0·005 S.D. corresponds to $7{\cdot}12 \times 10^{-6}$ g./ml.)

$$\Gamma = \frac{V}{A}\left(c_f - \frac{c_o + c_r}{2}\right)$$

$$= \frac{125 \times 7{\cdot}74}{30 \times 60 \times 77 \times 1{\cdot}6537} \times \frac{7{\cdot}12 \times 10^{-6} \times 0{\cdot}0156}{0{\cdot}005}$$

(where 1·6537 sq. cm. is the calculated area of one bubble)

$$= 9{\cdot}4 \times 10^{-8} \text{ g. per sq. cm.}$$

The following results were obtained :

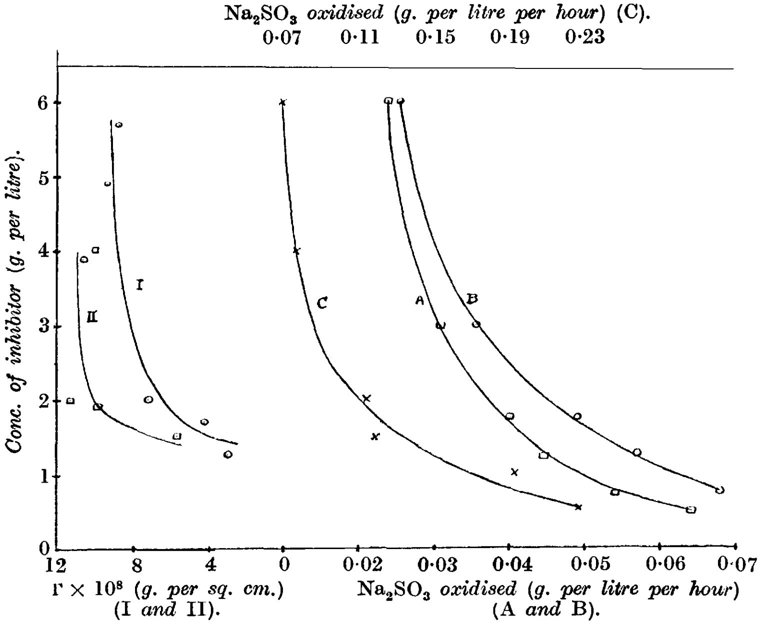
*iso*Propyl alcohol
(Fig. 1, Curve I).

Original soln. (g./litre).	$\Gamma \times 10^8$ (g./sq. cm.).	Mean.
5·7	8·7	8·7
4·9	7·3 6·7 14·0	9·3
4·6	7·3	7·3
3·9	10·5	10·5
2·0	7·7 6·8	7·2
1·7	3·4 5·1	4·2
1·24	2·5	2·5
0·6	Shift not detectable.	
0·5	,, ,, ,,	

sec.-Butyl alcohol
(Fig. 1, Curve II).

Original soln. (g./litre).	$\Gamma \times 10^8$ (g./sq. cm.).	Mean.
4·0	9·4 10·4 10·0	9·9
2·0	9·8 12·6 11·4	11·3
1·9	8·0 10·3 11·0	9·8
1·5	5·7	5·7
1·0	Shift not detectable.	

FIG. 1.



The rather wide variation between individual results is certainly due to the limitation of the home-made refractometer. The general results are nevertheless clear, that for concentrations higher than 2 g. per litre, Γ has a mean value of about $8{\cdot}6 \times 10^{-8}$ g. per sq. cm. for *iso*propyl and about $10{\cdot}3 \times 10^{-8}$ g. per sq. cm. for *sec.*-butyl alcohol and varies very little with change in concentration. This agrees substantially with the results obtained by McBain for *iso*amyl alcohol, for which $\Gamma = 16 \times 10^{-8}$ g. per sq. cm. for concentrations higher than 2 g. per litre.

If 22×10^{-16} sq. cm. be taken as the area of an alcohol molecule (*J. Amer. Chem. Soc.*, 1927, **49**, 2251) the figures quoted above suggest that, for concentrations higher than 2 g. per litre, a surface layer of solute molecules two or more deep is formed.

The values of Γ required for a unimolecular layer are :

*iso*Propyl alcohol	$4{\cdot}5 \times 10^{-8}$ g. per sq. cm.
sec.-Butyl alcohol	$5{\cdot}5 \times 10^{-8}$,, ,, ,,

Although the exact concentration at which these values are attained is left in doubt, the results quoted make it clear that there is an abrupt change in Γ between 2 and 1 g. per litre, and the unimolecular layer is probably formed in each case at a concentration of about 1·5 g. per litre.

It has been suggested (Harkins, *Colloid Symposium Monographs*, 1928, **6**, 37) that, owing to oscillation, the true area of a bubble is greater than that determined by measurement. If adsorption becomes complete when the area is a maximum, then when the surface diminishes, the concentration of dissolved substance at the bubble surface will be abnormally high. It seems unlikely that the concentration could thus be affected to any great extent, but, even if we suppose the maximum area to be twice as great as that calculated in this paper, a unimolecular layer of solute will have been formed in all solutions whose concentrations is 2 g. per litre and upwards.

It was observed that, although with solutions of concentration exceeding about 1·5 g. per litre, the bubbles, in favourable circumstances, ascended the vertical tube with ease, yet when the concentration fell below 1·5 g. per litre it became increasingly difficult to secure the passing of the bubbles over the bend without collapse. This marked decrease in the stability of the bubbles thus appeared to coincide with the point at which a complete unimolecular layer ceased to be formed.

The presence of sodium sulphite as well as alcohol in the aqueous solution is not likely to interfere very greatly with the establishment of a surface layer of alcohol, for the concentration of sodium sulphite in the surface layer is, no doubt, lower than in the bulk of the solution, as is the case with inorganic salts in general.

Measurements of the Velocity of Oxidation.—The velocity of oxidation was now measured of solutions of sodium sulphite containing various amounts of *iso*propyl or of *sec.*-butyl alcohol. 50 Ml. of a solution containing 20 g. of sodium sulphite per litre and a suitable amount of alcohol were placed in an unshaken cylindrical bottle, with free access to the air (area of exposed liquid surface = 22 sq. cm.). Four bottles were used for each dilution, and one was taken for titration at intervals. The rate of oxidation was at first fairly constant, and the value given is the average rate for the first 7 hours.

The concentration of the sulphite solution was determined by titration with 0·05*N*-sulphuric acid to p_H 4·3, methyl-orange being used as indicator, and the standard being the colour obtained with an equal volume of a buffer solution made by diluting 50 ml. of *N*/5-potassium hydrogen phthalate solution and 5·53 ml. of *N*/5-sodium hydroxide solution (free from carbonate) to 200 ml. (Dodge *et al.*, *J. Amer. Chem. Soc.*, 1920, **42**, 724, 1655).

The following results are typical of numerous experiments :

	Inhibitor, g./l.	Na_2SO_3 oxidised, g./l./hr.
sec.-Butyl alcohol. Temp., 12·8°. (Curve A)	0·5	0·064
	0·75	0·054
	1·25	0·0445
	1·75	0·040
	3·0	0·031
	6·0	0·024
*iso*Propyl alcohol. Temp., 13·1°. (Curve B)	0·75	0·068
	1·25	0·057
	1·75	0·049
	3·0	0·0355
	6·0	0·0255
sec.-Butyl alcohol. Temp., 25°. (Curve C)	0·5	0·227
	1·0	0·192
	1·5	0·118
	2·0	0·113
	4·0	0·078
	6·0	0·071

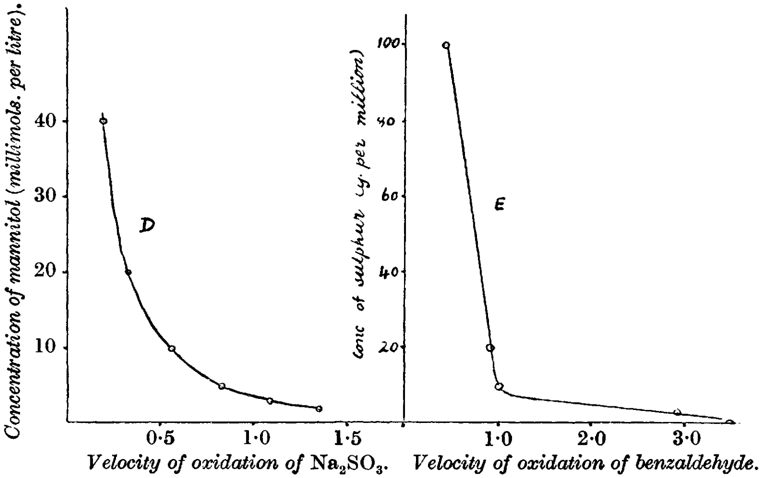
Discussion.

To make it probable that anti-oxygenic activity in a given case is due to the concentration of the inhibitor at the air–liquid interface, where it interferes with a reaction initiated at or near that interface, at least three conditions should be fulfilled : (1) the rate of the uninhibited reaction should be proportional to the area of the interface, (2) the inhibitor should be preferentially adsorbed at the interface, (3) when reaction velocity is plotted against inhibitor concentration, the curve should show a discontinuity, which might be expected to occur at the inhibitor concentration corresponding with the formation of a unimolecular layer of inhibitor at the interface.

It was shown by Bailey in Part III of this series that, for benzaldehyde autoxidation, conditions (1) and (3) hold. Curve E (Fig. 2), constructed from data given in that paper (*loc. cit.*, p. 113), shows the relationship between inhibitor (sulphur) concentration and velocity of benzaldehyde oxidation, and exhibits a marked discontinuity at an inhibitor concentration of about 10 g. per million. To test condition (2) for this particular case has not been possible. Ordinary analytical methods are not sufficiently delicate to measure the very small concentration changes involved, and, in the interferometer method employed in the present paper, the errors due to accidental oxidation would almost certainly render worthless any results that might be obtained.

It is now shown that condition (2) holds for aqueous solutions of alcohols which inhibit the oxidation of aqueous sodium sulphite solutions, but condition (3) no longer obtains.

FIG. 2.



Curve D (Fig. 2) is constructed from Bäckström's data for the inhibition by mannitol of the oxidation of sodium sulphite, the solution being shaken throughout the experiment. The curve is smooth, and similar in appearance to Curves A, B, and C obtained from experiments performed without shaking. The mechanism in both cases appears to be the same, and no explanation has yet been offered more probable than that proposed by Bäckström (*loc. cit.*), *viz.*, that reaction chains are interrupted by inhibitor molecules.

The extent of this interruption in homogeneous solution must be a function of the concentration of inhibitor, and of the number of reaction chains commenced per unit time. The curve obtained by plotting velocity against concentration of an inhibitor acting in this way should be free from discontinuity. If this is so, reaction-chain interruption in homogeneous solution cannot furnish a complete explanation of Curve E (autoxidation of benzaldehyde.).

It has been demonstrated by one of us (*loc. cit.*) that the inhibition of benzaldehyde autoxidation cannot be attributed to the arrest of a solid-surface reaction, and the comparison of Curve E with Curves A, B, C, and D makes it unlikely that chain interruption in homogeneous solution can be responsible. It remains possible that, in the case of benzaldehyde, accumulation of inhibitor at the gas–liquid interface may be the deciding factor, even although the present research has failed to demonstrate its importance in the case of sodium sulphite oxidation. The effectiveness of an inhibitor concentrated at the surface may be due to inactivation of a reaction complex which, if not interfered with, might initiate a lengthy chain, or, as has been suggested to us, its action may be due to a diminution in the velocity with which oxygen diffuses into the liquid. This effect, if it exists, would probably be due to the lower solubility of oxygen in the inhibitor layer, and it might be expected to increase in intensity until a complete layer of inhibitor had been adsorbed at the gas–liquid interface, and to change abruptly when that point has been reached.

The suggestion that, in certain cases, the reaction between oxygen and a liquid may take place, or be initiated, largely in the surface layer, is strengthened by the work of Davis and Schuler (*J. Amer. Chem. Soc.*, 1930, **52**, 721) and of Davis and Crandall (*ibid.*, pp. 3757, 3769) on the absorption of gaseous olefins by sulphuric acid, in which they show that the bulk of this reaction between a gas and a liquid takes place in a thin film on the surface of the liquid.

Summary.

(1) When *iso*propyl or *sec.*-butyl alcohol is dissolved in water, a layer of solute 1—2 molecules deep is formed at the surface of the solution when the concentration of solute reaches about 1·5—2 g. per litre.

(2) When oxidation velocity of sodium sulphite solution is plotted against concentration of alcohol (inhibitor), the curve obtained shows no discontinuity at this concentration of inhibitor.

(3) The inhibitor–velocity curves suggest that the mechanism of the autoxidation of benzaldehyde cannot be identical with that of sodium sulphite in aqueous solution. Possible explanations are discussed.

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