[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE INHIBITIVE ACTION OF ALCOHOLS ON THE OXIDATION OF SODIUM SULFITE

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In a previous paper by Bäckström[3] it was shown that the photochemical oxidation of a sodium sulfite solution is a chain reaction, and that those substances which are known to inhibit the thermal reaction[4] have a similar effect on the photochemical reaction. The results obtained with alcohols as inhibitors were particularly striking, showing a quantitative agreement between light and dark reaction. It must be assumed, therefore, that the thermal reaction also is a chain reaction, and that the role of the inhibitor, in the thermal as well as in the photochemical oxidation, consists in the breaking of reaction chains.

In a later paper,[5] Bäckström discussed the different ways in which the inhibitor might act in this process and concluded that the mechanism by which the chains are broken is probably an induced reaction between the inhibitor and one of the reactants. In the particular case of the alcohols this is indicated by Bigelow's[4a] results on the inhibitory power of the four butyl alcohols in the oxidation of sulfite solutions. He found that the primary, the secondary and the *iso*butyl alcohols all acted as inhibitors, but that the tertiary had no effect. Since the first three alcohols can be oxidized easily to aldehydes and ketones, whereas the tertiary can only be oxidized with the simultaneous destruction of the molecule, there seems to be a direct relation between inhibitory power and oxidizability in this case;[6] and the logical conclusion seems to be that the alcohols are actually oxidized in the process of breaking the reaction chains. Without postulating any special mechanism of chain propagation, we may describe the reaction chain as a series of processes whereby the oxidation of one sulfite ion induces the oxidation of another, and so on. The assumption would be, then, that in the presence of the alcohol this sometimes leads, instead, to

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[3] Bäckström, THIS JOURNAL, **49**, 1460 (1927).

[4] (a) Bigelow, *Z. physik. Chem.*, **26**, 493 (1898); (b) Titoff, *ibid.*, **45**, 641 (1903), and others.

[5] Bäckström, *Medd. Kgl. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927).

[6] Compare the theories of Dhar, *Proc. Acad. Amsterdam*, **23**, 1074 (1921); *Z. anorg. Chem.*, **122**, 146 (1922), and Moureu and Dufraisse, *Compt. rend.*, **176**, 624 (1923), linking inhibitory power and oxidizability.

an induced oxidation of an alcohol molecule, and that this reaction is incapable of inducing further oxidations.[7]

In view of these considerations, it was decided to make a study of the oxidation of sulfite solutions in the presence of alcohols, in order to see whether the oxidation of the sulfite is accompanied by an induced oxidation of the alcohol, and, if so, whether the extent of this reaction is in accordance with the theory.

Theoretical

Bäckström found that his results on the rate of oxidation of sulfite solutions in the presence of alcohols could be expressed by the formulas

$$v_d = \frac{k_1}{kC + k_2} \qquad (1)$$

$$v_l = k_3\, v_d = \frac{k_3 k_1}{kC + k_2} \qquad (2)$$

where v_l = light rate; v_d = dark rate; C = concn. of alcohol and k_1, k_2, k_3 and k are constants. The value of k depends on the nature of the alcohol and is a measure of its relative inhibitory power. The formulas express the facts that under a given set of experimental conditions the ratio between the rates of light and dark reaction remains constant, independent of the nature and concentration of the alcohol present, and that both rates are inversely proportional to a sum of two quantities, one being a constant, k_2, and the other proportional to the concentration of the inhibitor. The form of the equations and the complete analogy between light and dark reactions which they reveal indicate that the presence of the alcohols does not affect the number of chains *started* per unit time, but that they act solely by *breaking* the reaction chains.[8]

The fact that the chain length is inversely proportional to the factor $(kC + k_2)$ shows that the chains may be broken in two ways: (1) by the alcohol, its activity in breaking the chains being proportional to its concentration, C, and its relative inhibitory power, k, or (2) due to some other cause represented by the constant k_2. In the present paper we are concerned only with the former of these two processes.

In view of what was said in the preceding section, we shall now make the assumptions (1) that the alcohol is oxidized in breaking the reaction chains, and (2) that this induced oxidation is completely incapable of carrying on (that is, always breaks) the reaction chains. Let us then consider what results we should expect under different experimental con-

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[7] Or, at least, less efficient than the corresponding reaction involving a sulfite ion.

[8] This is in agreement with the fact that they were present only in small concentrations and that, with one exception, they do not absorb the activating light. Consequently, in neither thermal nor photochemical reaction would they be expected to affect the primary process by which the reaction chains are started.

ditions. For convenience we shall assume that we are dealing with *iso*-propyl alcohol.

Every time a chain is broken by the alcohol, an acetone molecule will be formed. If we call the total number of chains started and broken per minute n, then the number of chains broken in that time by the alcohol will be $n[kC/(kC + k_2)]$, and this number of acetone molecules will be formed per minute. Since the velocity of sulfite oxidation V is expressed by the formula $V = k_1/(kC + k_2)$, it follows that the amount of acetone formed in a given time will always be proportional to CV, the product of velocity and inhibitor concentration.

At small inhibitor concentrations this product increases with increasing values of C, and the rate of acetone formation will increase in proportion.

At large inhibitor concentrations, on the other hand, where k_2 is negligibly small compared to kC, this product becomes virtually constant, independent of the alcohol concentration. In this region practically all the chains are broken by the alcohol. Increasing the alcohol concentration causes the chains to be broken sooner and, therefore, lowers the rate of sulfite oxidation, but the *number* of chains broken remains the same, and the amount of alcohol oxidized in a given time will therefore remain constant, independent of its concentration.

For the same reasons the number of alcohol molecules oxidized in a given time will be the same *for different alcohols*. The only difference will be that the amounts of these alcohols which have to be added in order to reach the region where k_2 can be neglected will vary inversely as their specific inhibitory powers, k.

This reasoning applies equally well to *mixtures of alcohols* in a given solution. They will be oxidized in proportion to their concentrations and relative inhibitory powers, but the total number of molecules oxidized in a given time will still be the same. All of this will, of course, be true only if the formula continues to be valid at high inhibitor concentrations; that it does is shown by our results.

The predictions above apply equally to the thermal and the photochemical reactions. In the case of the latter still another prediction may be made, namely, as to the number of alcohol molecules oxidized; in the region of constant CV it should be equal to the number of light quanta absorbed by the solution. This is assuming, however, that every absorbed light quantum starts a reaction chain, an assumption which is not necessarily correct, but which can be tested by experiments of this kind. If it is correct, that is, if the quantum efficiency actually evaluates the chain length of the photochemical reaction, then we should also expect it to measure the chain length of the thermal reaction. On this basis we may predict approximately the quantity of alcohol which should be oxidized, in the region of constant CV, by dividing the rate of oxidation of the pure sulfite solution by the value found by Bäckström for the quantum efficiency in the absence of inhibitors, namely, about 50,000 molecules of oxygen reacting per $h\nu$. The thermal oxidation rate of a pure sulfite solution under the conditions of our experiments was about 5 cc. of oxygen absorbed per minute per 10 cc. of solution, which leads to a value of about 0.000025 mole of alcohol oxidized per liter per hour.

These and other consequences of the theory were subjected to experimental test and were found to be completely verified except that the results indicate that two alcohol molecules, rather than one, are oxidized in the process of breaking a chain. This would, of course, not materially change the argument presented above. The inhibitors used were *iso*propyl, *sec.*-butyl and benzyl alcohols.

Materials

Water.—Tap water was distilled a few minutes before use into Pyrex flasks from a tin-lined still and block-tin condenser. Precautions were taken to use this water throughout all operations.

Sodium Sulfite.—Merck's c. p. crystals of $Na_2SO_3 \cdot 7H_2O$ were recrystallized from pure water four times. The third and fifth crystallizations gave identical oxidation rates, so there was no advantage in crystallizing any further.

Isopropyl Alcohol.—Standard Oil Company product. All the ordinary methods for removing acetone from *iso*propyl alcohol failed for this research. For example, with the usual bisulfite method,[9] it was extremely difficult to lower the acetone content of *iso*propyl alcohol below 0.001%, whereas it was necessary in this work to use alcohol containing less than 0.0001% of acetone. The following method therefore was developed and found to be a simple and direct method for removing very minute traces of ketones from the lower boiling alcohols. Several liters of the alcohol was refluxed with 2 g. of *p*-nitrophenylhydrazine per liter for several hours on a water-bath. Nitrogen bubbled through the solution during refluxing served both to stir the solution and to exclude oxygen. At the end of this time the alcohol was distilled over in a stream of nitrogen, using a 2-foot fractionating head. It contained less than 0.0001% of acetone; b. p. 81.9–82.9°.

Secondary Butyl Alcohol.—Standard Oil Company product. It received the same treatment as the *iso*propyl alcohol; b. p. 99.7–99.8°.

Benzyl Alcohol.—Merck's c. p. alcohol was used without further purification. It contained less than 0.0001 *M* benzaldehyde per liter as shown by Schiff's test.

Acetone.—Redistilled Merck's c. p. grade.

Methylethyl Ketone.—Eastman Kodak Company product. It was redistilled twice; shaken three times with equal volumes of a saturated solution of pure sodium chloride, in which it is insoluble, to remove acetone.[10] Subsequent distillation of the ketone layer yielded a pure methylethyl ketone, free from acetone.

Benzaldehyde.—Kahlbaum's DAB5 benzaldehyde was redistilled in an atmosphere of nitrogen. It contained less than 0.01% of benzoic acid, as determined by titration with sodium hydroxide in the presence of phenolphthalein.

Ethyl Alcohol.—It gave a coloration with Schiff's reagent corresponding to less than 0.001% of benzaldehyde.

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[9] Marshall, *J. Chem. Soc.*, **89**, 1375 (1906).

[10] Price, *J. Soc. Chem. Ind.*, **115**, 1118 (1919).

Experimental

The apparatus consisted of a shaker which turned a set of glass-stoppered, narrow-mouthed 125-cc. bottles end-over-end at about 180 revolutions per minute. Each of these was charged with 20 cc. of 0.6 *M* sodium sulfite solution, buffered by the addition of 0.01 equivalent per liter of sulfuric acid, and containing varying quantities of alcohol. These solutions had the same composition as in Bäckström's work. The bottles were then filled with oxygen and the glass stoppers sealed in with paraffin. Preliminary experiments showed that during the above operations, consuming about fifteen minutes for a set of six bottles, the oxidation was negligible.

The strength of the sulfite was determined by titration with *N*/2 sulfuric acid, using brom-cresol green as indicator, as in Bäckström's work. Extreme precautions were taken in order to obtain reproducible results by preparing the distilled water and all solutions immediately before use and by washing all glassware repeatedly with distilled water to remove all traces of impurities.

The length of the shaking period, generally from two to thirty-five hours, was regulated to be such that less than 1.5 millimoles per 10 cc. of sulfite was oxidized. At the end of this period, 5 cc. of the sulfite was titrated with *N*/2 sulfuric acid, as above, and the quantity of sulfite oxidized obtained from this value. Other samples were immediately removed from the bottles and tested colorimetrically for the aldehyde or ketone formed, using the methods given below.

Throughout the run the average temperature of the room was 21 ± 0.5°, orientation experiments on the temperature coefficients of the sulfite and alcohol oxidations showing that the maximum error from temperature fluctuation was about 2%.

Dependence of Oxidation Rate on Experimental Conditions.—Preliminary measurements were made in a specially constructed shaking apparatus which permitted a study of the dependence of the oxidation rate on shaking conditions, volume of solution, and oxygen pressure. It was found that as the "reactivity" of the solution is decreased, by removing positive catalysts or adding increasing quantities of inhibitor, the oxidation rate (in moles per unit volume per unit time) becomes virtually independent of all these factors, including oxygen pressure.[11] The oxidation rate of a strongly inhibited solution, as directly observed in cc. of oxygen absorbed per minute at the working pressure, is thus four times higher at $^1/_4$ atm. than it is at 1 atm.

As a result of these experiments it may be stated that (with very few exceptions) the values given in this paper represent true oxidation rates, in the sense that neither an increase in oxygen pressure nor an increased shaking efficiency would have raised the results.

These preliminary experiments also included a study of the oxidation rate as a function of the concentration of the solution. It was found that the oxidation of a pure sulfite solution proceeds more slowly the more concentrated the solution, a fact which has previously been observed by Milbauer and Pazourek.[12] In accordance with this the rate increases

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[11] This confirms an observation by Reinders and Vles, *Rec. trav. chim.*, **44**, 249 (1925).

[12] Milbauer and Pazourek, *Bull. soc. chim.*, **31**, 676 (1922).

steadily during a single run, as the sulfite concentration decreases, until a sudden drop occurs when the reaction is almost complete.

These facts are of great theoretical interest and will be investigated further in a more systematic study of sulfite oxidation.

Colorimetric Determinations

Since the quantity of alcohol oxidized in a run is of the order of 0.0005 millimole/10 cc./hour, the problem of measuring this change is of course the difficult feature of this research. The literature supplies tests only one-tenth as sensitive as are needed here. The following colorimetric methods were therefore developed, and if carried out as described will give accuracies of determinations as listed in Table II.

Acetone

Colorimetric Determinations in Concentrations of 0.00005 *M* to 0.002 *M*.—A development of the Kolthoff modification[13] of the Fabinyi-Frommer method[14] was found applicable. The test is specific for acetone, no color being given by methylethyl ketone or aromatic ketones.

Reagents.—The following solutions are employed: 10% vanillin in methyl alcohol, Merck's C. P. (not ethyl alcohol at these dilute acetone concentrations); should be made up fresh every few days; a potassium hydroxide solution, 100 g. of potassium hydroxide in 60 cc. of water; a series of standard acetone solutions made by dissolving 1 cc. of freshly distilled acetone in water and diluting to approximate concentrations of 0.004 *M*, 0.002 *M*, 0.0018 *M*, 0.0012 *M*, 0.0006 *M*, 0.0003 *M* and 0.00015 *M*, each solution containing 0.02 equivalent of sulfuric acid per liter.[15] The standards are then accurately determined by titration with *N*/100 thiosulfite and iodine, by the well-known Messinger method.[16] The strength of the standard acetone solutions fell less than 1% during two weeks, as shown by titrations.

Preparation of Standard and Unknown Test Solutions.—In a test the standard solution consists of 1 cc. of standard acetone solution, 1 cc. of 1.2 *M* sodium sulfite solution and the same quantity of alcohol as in the unknown. The latter is made up by diluting 2 cc. of solution to be tested to a volume equal to that of the standard solution. The media of unknown and standard will then be exactly alike, differing only in acetone content. The color test is not affected by the extent to which the sodium sulfite in the unknown has been oxidized.

The Test.—Three unknown samples falling between the limits of two standard solutions may be tested conveniently at a time. Run 2 cc. of potassium hydroxide from a 10-cc. graduated pipet into each of the five tubes to be tested and swirl momentarily. Then into each run 1 cc. of the vanillin solution from a 5-cc. graduated pipet, shake thoroughly and place the five test-tubes simultaneously in a water-bath at the

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[13] Kolthoff, *Pharm. Weekblad*, **55**, 1021 (1918); Csonka, *J. Biol. Chem.*, **27**, 209 (1916).

[14] Fabinyi, *Chem. Centr.*, **1900**, ii, 302; Frommer, *Ber. Klin. Woch.*, **42**, 1008 (1905); Bohrisch, *Pharm. Centr.*, **48**, 207 (1907).

[15] According to Folin and Denis, *J. Biol. Chem.*, **18**, 263 (1914), the sulfuric acid also helps to prevent polymerization of the acetone in the standards.

[16] J. Messinger, *Ber.*, **21**, 3366 (1888); *J. Biol. Chem.*, **43**, 43 (1920), and *J. Soc. Chem. Ind.*, 10, 166 (1891).

proper temperature. Allow to stand for exactly twenty minutes. In the meantime prepare five test-tubes each containing 10 cc. of water. Upon removing the acetone tubes from the water-bath immediately mix the water in the test tubes with the contents of the acetone tubes. The sulfates and sulfites which were precipitated by the concentrated potassium hydroxide will then redissolve, permitting a comparison of the reddish brown colors in a colorimeter. The above experimental procedure minimizes the time consumed between addition of reagents to the test solution and colorimeter readings, so that the colors in all five tubes will be strictly comparable. The readings are completed within fifteen minutes after removing the tubes from the bath.

The temperature of the water-bath is most important in obtaining reproducible results. A bath with thermoregulator attachment was used, giving the desired temperatures to within ±0.1°. For acetone concentrations within the range 0.00005 *M* to 0.0005 *M*, 65° was found to be the temperature at which the bath should be kept. For higher concentrations of acetone, between 0.0005 and 0.002 *M*, 50° should be used.

The colorimeter was of the standard DuBoscq type, Bausch and Lomb 1924 model. The colorimeter settings are plotted and the value of the unknown is determined graphically. Thus when the standards 0.0001 and 0.0002 *M* acetone give colorimeter readings of 50 and 30, respectively, a colorimeter setting of 40 would correspond to 0.00015 *M* acetone. While this method is not absolutely exact when the color does not vary directly with the acetone concentrations, the values it yields, nevertheless, fall well within the limits of error given in Tables I and II, where a typical set of colorimeter readings is presented.

TABLE I

TYPICAL COLORIMETER READING DATA

Acetone concn., *M*/l.	Colorimeter readings, *a*	Δa	*b*	Av. error in acetone detns. throughout the range, % (*c*)
0.002	26	24	±0.50	±1.3
.001	50			
.00030	31	19	±0.75	±2.6
.00015	50			
.000150	38	12	±1.00	±5.5
.000075	50			

Δa = difference between colorimeter readings; that is, the number of colorimeter units representing a change from $^2/_3$ to $^4/_3$ the average acetone concentration in each range.

b = error of reproducibility of lower colorimeter settings, expressed in colorimeter units. (Higher setting always at 50.0.)

c = $(2/3)(b/\Delta a) \times 100$.

TABLE II

TYPICAL COLORIMETER READING DATA

Molarity of aldehyde or ketone	Average exptl. error, *c* %		
	Acetone	Methylethyl ketone	Benzaldehyde
0.005 to 0.002	...	...	±1.1
.002 to .001	±1.3	...	±1.7
.001 to .0005	...	±1.4	±3.8
.0005 to .0002	±2.6	...	±7.0
.0002 to .0001	...	±4.6	...
.0001 to .00005	±5.5	±6.0	...

Tests conducted in the presence of 0.6 *M* Na_2SO_3.

Methylethyl Ketone

The same procedure was employed as for the acetone, with the following changes: the vanillin in methyl alcohol was replaced by a 10% solution of salicylaldehyde in ethyl alcohol. The temperature of the bath was kept at 40 ±1°, since at above 60° the accuracy of the determination fell off rapidly at these low concentrations. Upon removal from the bath, instead of diluting with 10 cc. of water as was done in the acetone test, 15 cc. of a 20% by volume ethyl alcohol solution in water was added. This concentration was sufficient to dissolve the sulfite and salicylaldehyde; other proportions of alcohol and water will precipitate one or the other of the ingredients.

The comparison of the greenish-yellow tints obtained with the standards is done exactly as in the case of acetone, standard solutions being 0.002, 0.001, 0.0005 and 0.0002 M/liter, respectively, each containing 0.02 equiv. of sulfuric acid per liter. They, too, were accurately standardized by titrating with N/100 thiosulfate and iodine by the Messinger method.[16]

See Table II for the accuracy of the determinations.

Benzaldehyde

The sensitivity of Schiff's reagent[17] has long been known, and was employed by Woodman and Lyford[18] in determining benzaldehyde in minute quantities. However the much smaller concentrations of benzaldehyde obtained in this work required a refinement of their method.

Reagents

Schiff's Reagent.—The less sulfur dioxide present in the Schiff's reagent, the more sensitive is the test, although some sulfur dioxide is necessary for the color reaction.[19] The following procedure was found to work satisfactorily down to 0.0002 M benzaldehyde solutions. Bubble sulfur dioxide into 100 cc. of water for about five minutes and determine the amount absorbed by measuring the increased weight of the solution. Add a volume of this solution corresponding to 0.60 g. of sulfur dioxide to 0.17 g. of rosaniline hydrochloride in 50 cc. of water in a 250-cc. glass-stoppered volumetric flask. Allow to stand for one hour, shaking at frequent intervals, by which time most of the color will have disappeared. Fill up to the mark and use immediately. Fresh solutions should be made up every six hours when testing benzaldehyde in the ranges 0.0001 to 0.0005 mole/liter, but the reagent is good for several days when testing higher concentrations.

Aldehyde-Free Ethyl Alcohol.[18,20]—By distilling alcohol from solid potassium hydroxide (80 g./liter) an alcohol was obtained which gave a negligible coloration with Schiff's reagent under the conditions employed below.

Standard benzaldehyde solutions were made by successively diluting 10.00 cc. of benzaldehyde with aldehyde-free alcohol to give 0.005 0.002, 0.001, 0.0005 and 0.0002 M benzaldehyde solutions. These solutions will keep several months when stored in amber bottles.

Separation from Sulfite.—Before applying the Schiff's test, the aldehyde was separated from the sulfite by distillation. It was found that if 10 cc. of the solution containing partially oxidized sulfite and traces of benzaldehyde was distilled, the first

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[17] Schiff, *Compt. rend.*, 61, 45 (1865).

[18] Woodman and Lyford, THIS JOURNAL, **30**, 1607 (1908).

[19] Wieland and Schiering, *Ber.*, **54**, 2527 (1921).

[20] See purification processes for ethyl alcohol in Tolman, THIS JOURNAL, **28**, 1625 (1906).

5 cc. of distillate contained all of the benzaldehyde. When the $P_{\rm H}$ of the solution was changed slightly from its original value[3] of $P_{\rm H} = 8.4$, the benzaldehyde still came over quantitatively, but at $P_{\rm H} = 4.3$, where all of the sulfite is present as the bisulfite, or at very high $P_{\rm H}$'s (13) only about 70% of the benzaldehyde was recovered, possibly due to the stability of the bisulfite–benzaldehyde compound in the one case or the Cannizzaro reaction in the other.

A number of test-tubes 18 × 150 mm. were constricted in the middle to about 7.0 mm. inside diameter and graduated to hold exactly 10 cc. up to a mark on the constriction. Into one of them 5 cc. of aldehyde-free alcohol was run, and a 10-cc. sample solution distilled over in an atmosphere of nitrogen into the alcohol until the mark on the constriction was reached; 5 cc. of distillate was thereby collected. The volume caught could be reproduced to within 1% by this method. The benzyl alcohol present in the sample also distilled over, but it neither oxidized nor introduced any error in the benzaldehyde determination, as shown by blank tests. The mixture was then shaken, and the tube placed in an ice-bath at 0° for one minute along with two tubes containing standard solutions. These latter were made by adding 5 cc. of standard benzaldehyde solutions to 5 cc. of water; 2.5 cc. of the special Schiff's reagent, similarly cooled, was added to each of the three tubes, and the contents thoroughly shaken and allowed to stand at 0° for thirty minutes. At the end of this time their reddish pink colors were compared in the colorimeter. The strengths of the unknowns were determined graphically as with acetone; the accuracy is given in Table II.

Results

At High Inhibitor Concentrations.—The results, summarized in Table III, verify the predictions made in the introduction. The detailed experimental data are given in Tables IV, V and VI.

TABLE III

SUMMARY OF RESULTS

Alcohol	*C*, concn. range of alc., where $CV = K \pm 15\%$ mole/l.	Incr. in alc. concn.	*CV* throughout range × 10^4 ±15%	Inhib. power *k* of alc. (from *CV*)	Oxid. prod., mole formed per liter per hour ±15%	
*Iso*propyl	0.05 to 1.5	30-fold	34	3.0	Acetone	0.000046
Sec.-butyl	0.150 to 1.8	12-fold	103	1	Methyl-ethyl-ketone	0.000049
Benzyl	0.0073 to 0.167	23-fold	2.8	37	Benzaldehyde	0.000048

TABLE IV

THE INDUCED OXIDATION OF *ISO*PROPYL ALCOHOL

		Observed values		Values calcd. to one hour		
Alc., *C*	Hours shaken	Sulfite ox.	Acetone formed × 10^4	*V* × 10^4	*CV* × 10^4	Acetone × 10^4
0.025	2.5	0.269	0.87	1080	27	0.35
.025	2.5	.237	.85	950	24	.34
.050	2.5	.154	1.04	616	31	.42
.050	2.5	.143	0.92	572	29	.37
.050	2.0	.115	.85	575	29	.42
.100	5.0	.165	2.4	330	33	.48
.100	5.0	.167	2.3	334	33	.47
.100	5.0	.180	2.5	360	36	.50

TABLE IV (*Concluded*)

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Acetone formed × 10^4	V × 10^4	CV × 10^4	Acetone × 10^4
.150	5.0	.131	2.4	262	39	.48
.150	5.0	.123	2.5	246	37	.50
.250	5.0	.072	2.4	144	36	.48
.250	5.0	.068	2.3	136	34	.46
.250	5.0	.083	2.2	166	41	.45
.250	10.0	.130	4.4	130	32	.44
.250	10.0	.139	4.4	139	35	.44
.250	10.0	.130	4.2	130	32	.42
.375	10.0	.089	4.3	89	33	.43
.375	10.0	.112	4.3	112	42	.43
.500	10.0	.056	4.2	56	28	.42
.500	10.0	.060	4.0	60	30	.40
.500	10.0	.075	4.5	75	37	.45
.500	21.0	.129	9.6	61	31	.45
.500	21.0	.127	10.2	60	30	.48
1.00	21.0	.069	11.2	33	33	.53
1.00	21.0	.069	11.7	33	33	.56
1.50	21.3	.056	10.6	26	39	.49
1.50	21.3	.059	11.2	28	42	.52
2.50	27.0	.050	18.3	19	46	.67
2.50	27.0	.048	17.8	18	44	.66
				Averages	34	.46

V = decrease in sulfite concentration per hour. In computing averages, the 2.5 M and 0.025 M values were omitted. All concentrations expressed as moles per liter.

TABLE V

THE INDUCED OXIDATION OF SECONDARY BUTYL ALCOHOL

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Ketone formed × 10^4	V × 10^4	CV × 10^4	Methylethyl ketone × 10^4
0.15	2.05	0.175	0.92	850	128	0.45
.25	4.0	.186	2.1	465	116	.53
.25	4.0	.196	2.1	490	122	.52
.30	4.0	.141	2.0	353	106	.49
.30	4.0	.121	1.6	303	91	.40
.45	4.0	.101	2.0	253	114	.50
.45	4.0	.106	1.8	265	119	.46
.45	6.0	.131	2.2	218	98	.37
.45	6.0	.141	2.5	235	106	.41
.60	6.0	.106	2.6	177	106	.43
.60	6.0	.106	2.7	177	106	.45
1.00	14.0	.123	7.8	88	88	.56
1.00	14.0	.128	7.3	91	91	.52
1.20	14.0	.111	7.8	79	95	.55
1.20	14.0	.118	8.3	84	101	.59

TABLE V (*Concluded*)

Alc. *C*	Hours shaken	Observed values Sulfite ox.	Ketone formed $\times 10^4$	Values calcd. to one hour *V* $\times 10^4$	*CV* $\times 10^4$	Methylethyl ketone $\times 10^4$
1.50	15.5	.088	7.8	57	85	.50
1.50	15.5	.103	8.5	66	100	.55
1.80	15.5	.088	8.4	57	102	.54
1.80	15.5	.080	8.1	52	93	.52
				Averages	103	.49

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

TABLE VI

THE INDUCED OXIDATION OF BENZYL ALCOHOL

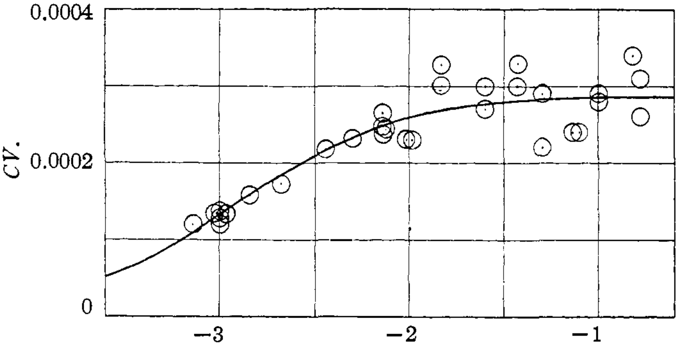
Alc., *C*	Hours shaken	Observed values Sulfite ox.	Benzaldehyde formed $\times 10^4$	Values calcd. to one hour *V* $\times 10^4$	*CV* $\times 10^4$	Benzaldehyde $\times 10^4$
0.00735	2.62	0.086	1.1	330	2.4	0.42
.00735	2.92	.096	1.1	330	2.4	.38
.0147	3.73	.076	1.6	200	3.0	.43
.0147	4.30	.096	2.0	220	3.3	.46
.025	10.25	.122	4.9	119	3.0	.48
.025	11.25	.120	6.3	107	2.7	.56
.037	12.90	.106	6.8	82	3.0	.53
.037	13.20	.116	8.4	88	3.3	.64
.050	18.10	.080	7.7	44	2.2	.43
.050	19.00	.110	10.4	58	2.9	.55
.075	22.15	.070	9.8	32	2.4	.44
.075	24.66	.080	13.0	32	2.4	.53
.10	31.00	.087	17.9	28	2.8	.58
.10	36.38	.107	15.1	29	2.9	.42
.15	37.50	.086	19.0	23	3.4	.51
.167	38.00	.071	18.0	19	3.1	.47
.167	61.00	.095	24.0	16	2.6	.39
				Averages	2.8	.48

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

In order to prove that the oxidation of the alcohol was definitely induced by the oxidation of the sulfite, 5-cc. samples of alcohol solutions were shaken with 15 cc. of (1) water, (2) *N*/2 KOH and (3) phosphate buffer of *P*H = 8.4, the initial *P*H of the sulfite solutions in Table IV. The alcohol solutions added were: benzyl, 0.04 *M*; *sec.*-butyl, 1.0 *M*; *iso*propyl, 1.0 *M*. In addition to these, 15-cc. samples of a previously oxidized 0.8 *M* sulfite solution were shaken with 5 cc. of 0.04 *M* benzyl, of 0.5 *M* *sec.*-butyl and of 0.25 *M* *iso*propyl alcohol. With a shaking time of seventy-two hours, less than the following quantities of alcohol were oxidized: benzyl alcohol, 0.0002 mole/liter; *sec.*-butyl alcohol, 0.00005 mole/liter;

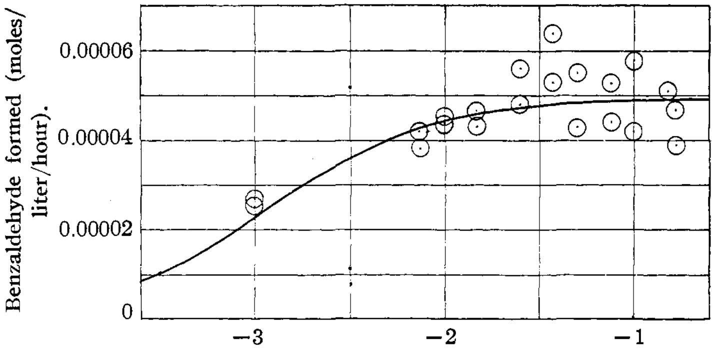
*iso*propyl alcohol, 0.00005 mole/liter, compared with the amount normally oxidized in seventy-two hours: (Table III) 0.00356 mole/liter.

At Low Inhibitor Concentrations.—In these experiments, which were made with benzyl alcohol, the shaking period was necessarily so short as to produce only a very minute quantity of benzaldehyde in the sulfite sample. By successive distillations of a 90-cc. sample (six 15-cc. samples from a set of bottles in a normal run), however, the benzaldehyde was obtained in concentrations sufficiently large to permit of accurate colorimetric analysis.



○, values observed; ——, values calculated from $V = 0.00029/(C + 0.0012)$.

Fig. 1A.



○, values observed; ——, values calculated from: Benzaldehyde formed = $CV \times 0.48/2.8$ (see Table VI).

Fig. 1B.

The results given in Table VII, and represented in the upper graph of Fig. 1, show that the rate of sulfite oxidation obeys a formula of the type discussed in the introduction, namely, $V = 0.00029/(C + 0.0012)$, throughout the entire range studied.

Table VIII establishes that the dropping off in CV at lower alcohol concentrations is accompanied by a corresponding decrease in benzaldehyde formed. This is demonstrated in Fig. 1, where the lower graph summarizes the results on the amount of benzaldehyde formed and shows that it is given within experimental error by the expression $(0.48/2.8) \times CV$ throughout the range of benzyl alcohol concentrations studied.

TABLE VII

INHIBITION BY BENZYL ALCOHOL OF SULFITE OXIDATION

Alcohol, C	Hours	Observed values Sulfite oxidized	Values calcd. to one hour $V \times 10^4$	$CV \times 10^4$
0.00072	0.33	0.055	1650	1.20
.00100	1.00	.130	1300	1.30
.00100	1.00	.120	1200	1.20
.00100	1.00	.135	1350	1.35
.00144	1.00	.110	1100	1.58
.0021	1.37	.113	825	1.73
.0036	2.00	.121	610	2.20
.0050	2.6	.120	460	2.30
.0072	2.85	.098	340	2.50
.0072	2.85	.105	370	2.65
.00735	2.62	.086	330	2.40
.00735	2.92	.096	330	2.40
.0147	3.73	.076	200	3.00
.0147	4.30	.096	220	3.30
		vs.		
.0147	3.73	.076	220	
to	to	to	to	2.8
.167	61.00	.120	16	

(Averages, see Table VI)

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

TABLE VIII

CV AND ALDEHYDE FORMED AT LOW CONCENTRATION

Benzyl alcohol concn. C	$CV \times 10^4$	Benzaldehyde formed $\times 10^4$	Ratio of $\frac{0.001\ M \text{ rate}}{0.01\ M \text{ rate}}$ for CV	for aldehyde
0.01	2.30	0.44		
.01	2.30	.45		
			$\frac{1.36}{2.30} = 0.59$	$\frac{0.26}{0.445} = 0.58$
.001	1.37	.25		
.001	1.35	.27		

Mixtures of Inhibitors

Benzyl Alcohol–*Iso*propyl Alcohol.—Experiments were made with sulfite solutions containing equal molal quantities of benzyl and *iso*propyl alcohols. Five cc. of the solutions shaken was titrated to determine sulfite oxidized, 2 cc. was removed and tested for acetone and, finally, a 10-cc. sample was tested for benzaldehyde. Preliminary measurements showed that the presence of as much as 0.01 *M* benzaldehyde or 0.02 *M* acetone had no effect on the accuracy of a colorimetric determination of acetone or of benzaldehyde, respectively, carried out as described above.

Tables IX and X show that the inhibitory power of a mixture is an additive property and confirm the prediction in the introduction as to the relative amounts oxidized of the two alcohols.

TABLE IX

*Iso*PROPYL ALCOHOL–BENZYL ALCOHOL MIXTURES

	Observed values				
Hours	Sulfite oxidized	Concn. of each alcohol	Benzaldehyde $\times 10^4$	Acetone $\times 10^4$	Ratio of benzaldehyde/acetone
16.05	0.165	0.025	7.6	0.56	14
16.05	.133	.025	6.7	.56	12
24.00	.146	.050	8.9	.72	12
40.20	.103	.100	17.0	1.17	15
40.20	.088	.100	14.4	1.08	13
				Average	13

TABLE X

VALUES CALCULATED TO ONE HOUR

Concn. of each alcohol	$\Sigma kC^a \times 10^4$	$V \times 10^4$	$\Sigma kCV^a \times 10^4$	Benzaldehyde $\times 10^4$	Acetone $\times 10^4$
0.025	0.338	103	35	0.47	0.035
.025	.338	83	28	.42	.035
.050	.675	61	41	.37	.030
.100	1.35	26	35	.42	.029
.100	1.35	22	30	.36	.027
		Averages	34	.41	.031
		Total inhibitor oxidized		0.44	

[a] *k*, the inhibitory power for *iso*propyl alcohol is here taken as unity, giving a value of 12.5 (Table III) for benzyl alcohol. Compare with the value of 13, obtained above, Table IX, from the relative amounts oxidized.

Benzyl Alcohol–Hydroquinone Mixtures.—In this case most of the chains are broken by the hydroquinone, as is shown by the fact that the CV value for hydroquinone is practically independent of the presence of benzyl alcohol (see Table XII). The quantity of benzaldehyde formed was less than one-twelfth of that which would have formed in the absence of hydroquinone. It is a duplication of the phenomena observed in the benzyl alcohol–*iso*propyl alcohol mixtures.

Attention should be directed toward the increasing CV values for hydroquinone with increasing concentration of the latter in Tables XI and XII. Bäckström[3] had previously observed that hydroquinone and some other substances behave differently from the alcohols, apparently inhibiting the light reaction much more strongly than the dark reaction. The fact that these substances are themselves capable of reacting with oxygen, especially in alkaline solution, suggests that in these cases the phenomena are complicated by a *direct* oxidation of the inhibitor. The rate of this reaction would naturally increase with the concentration[21] which would account for the increasing values of CV; and the increase in the observed "dark rate" caused by this direct oxidation of the inhibitor, which would probably not be accompanied by a corresponding increase in the light rate, would give the impression that the light reaction has been suppressed to an abnormal degree. Since, in the present case, the oxidation rate was determined by measuring the decrease in sulfite concentration, and not the oxygen consumption—as in Bäckström's experiments—the observed facts can only be accounted for on this basis if the oxidation of hydroquinone involves a reaction with sulfite. It might, for instance, lead to the for-

TABLE XI

HYDROQUINONE–BENZYL ALCOHOL MIXTURES

Hydroquinone concn., C	Benzyl alc. concn., C'	Hours	Sulfite oxidized	$V \times 10^4$	$CV \times 10^4$	Average CV
0.05	0.05	4.8	0.021	44	2.2	2.2
.025	.025	5.1	.016	31	0.8	
.025	.025	15.4	.031	20	.5	0.7
.025	.025	16.8	.061	36	.9	
.0125	.0125	5.3	.018	34	.4	
.0125	.0125	15.8	.041	26	.3	.3
.0125	.0125	31.0	.046	15	.2	
.05	0	11.0	.053	48	2.4	2.4
.025	0	10.7	.020	19	0.5	0.6
.025	0	18.6	.050	27	.7	
.0125	0	4.0	.013	32	.4	
.0125	0	22.4	.033	15	.2	.3
.0125	0	22.4	.037	17	.2	

TABLE XII

RESULTS OF EXPERIMENTS

Concn. of hydroquinone and of benz. alc.	CV, hydroquinone alone $\times 10^4$	CV, hydroquinone + benz. alc. $\times 10^4$	Benzaldehyde formed per hour $\times 10^4$	Ratio $\frac{\text{benzyl alcohol (Table 6)}}{\text{benz. alc. + hydroquinone}}$	
				for CV	for aldehyde
0.05	2.4	2.2	<0.04	1.3	>12
.025	0.6	0.7	$<.03$	4	>16
.0125	.3	.3	.04	9	12

V = decrease in sulfite concentration per hour. All concentrations expressed as moles per liter.

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[21] The true inhibitory power would therefore be more nearly given by the experiments at the low concentrations of inhibitor in Table XII. They indicate that the inhibitory power of hydroquinone is more than ten times that of benzyl alcohol.

mation of the hydroquinone sulfonates observed by Pinnow[22] in oxidized developer solutions.

Photochemical Measurements.—The applicability of the theory to the photochemical reaction was tested in a series of experiments with *iso*propyl alcohol. The apparatus consisted of a quartz shaker similar to that used in Bäckström's work, except that the tube was shaken horizontally. Conditions of shaking were such that, as shown by preliminary experiments, the oxidation rate of the sulfite was independent of volume of solution shaken, number of strokes per minute, length of stroke and oxygen pressure. The light from a Hanovia Quartz lamp, burning at 69 ± 0.5 volts and 3.5 ± 0.05 amperes was filtered through a chlorine–bromine filter, so that only wave lengths 2300 to 2800 Å. were transmitted, as shown by visual observation of the filtered light through a monochromator in the exit slit of which was placed a piece of uranium glass. This light illuminated about a 5-cm. length of the quartz shaker. Under these conditions the photochemical reaction was about fourteen times greater than the thermal reaction so that, within limits of error, the reaction measured could be considered entirely photochemical.

The results, given in Table XIII, are completely analogous to the ones previously obtained for the thermal reaction. Over a considerable range of high inhibitor concentrations, CV and alcohol oxidized remain constant. The ratio between CV and acetone formed (510/6.6 = 77) is the same as was found for the thermal reaction, Table IV (34/0.46 = 74); that is, in a solution of a given composition the chain length is the same whether the chains are started thermally or photochemically.

Table XIII

The Induced Oxidation of *Iso*propyl Alcohol: Photochemical Reaction

		Observed values		Values calcd. to one hour		
Alc., C	Hours shaken	Sulfite ox.	Acetone formed × 10^4	V × 10^4	CV × 10^4	Acetone × 10^4
0.05	0.166	0.155	1.03	9300	470	6.2
.05	.166	.169	0.98	10200	510	5.9
.10	.166	.089	1.17	5400	540	7.0
.10	.25	.120	1.75	4800	480	7.0
.10	.33	.167	2.27	5100	510	6.9
.50	1.166	.117	8.2	1000	500	7.0
.50	1.00	.108	7.0	1080	540	7.0
1.50	3.25	.102	19.5	314	470	6.0
1.50	3.00	.116	19.8	387	580	6.6
2.50	4.00	.108	26.5	270	675	6.6
				Averages	510	6.6

V = decrease in sulfite concentration per hour. In computing averages the 2.5 M values were omitted. All concentrations expressed as moles per liter.

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[22] Pinnow, *Z. Elektrochem.*, 19, 262 (1913).

Blank experiments in which there was no sulfite present in the solution showed that the direct photochemical oxidation of the alcohol was negligible (0.00001 in a blank against 0.00066 mole per liter per hour in a normal sulfite run).

Chain Length and Quantum Efficiency.—As was shown in Tables III to VI, the amount of alcohol oxidized, in the region of constant *CV*, is of the order of magnitude expected, being just about twice the predicted value of 0.000025 mole per liter per hour. This indicates the correctness of the assumption underlying the prediction, namely, that the chain length of the thermal reaction is equal to the photochemical quantum efficiency, but it does not constitute an accurate test since it is based on measurements on uninhibited sulfite solutions; these give high oxidation rates that are difficult to measure accurately and that vary considerably with shaking conditions. However, a more satisfactory comparison, utilizing the data for strongly inhibited solutions, gives the same result.[23] Bäckström's formula for the light rate,[3] when applied to a solution which is 0.1 *M* with respect to benzyl alcohol, gives a quantum yield of 64 molecules of oxygen or 128 of sulfite reacting per $h\nu$. On the other hand, the data in Table VI show that in a solution of this composition the number of sulfite molecules oxidized for every alcohol molecule oxidized is 28/0.48 = 58, a figure which is of the same order of magnitude but which again indicates that in the process of breaking a reaction chain, two molecules of the alcohol are oxidized rather than one: this would make the chain length equal to $2 \times 58 = 116$. The question whether 1 or 2 molecules are oxidized in this process is of no importance to the arguments presented in this paper, but it is obviously of great importance to a complete elucidation of the reaction mechanism. By a repetition of the quantum efficiency measurements it is hoped to decide this question more definitely.

Utilizing the result of the preceding section, namely, that the chain lengths of thermal and photochemical reaction are identical,[24] we may state the above result in a different way by saying that, in the photochemical reaction 128/58 = 2.2 molecules of benzaldehyde are formed for every quantum absorbed by the solution; that is, the induced oxidation of the benzyl alcohol obeys the Einstein photochemical equivalence law.

This is a result which is completely analogous to the one obtained by Cremer,[25] in a study of the photochemical hydrogen–chlorine combination in the presence of oxygen. Here oxygen acts as an inhibitor and

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[23] This throws an interesting light on Bäckström's results on the quantum efficiency of the photosensitized reaction (ref. 5, pp. 26–29).

[24] No measurements were made on the induced oxidation of benzyl alcohol in the photochemical reaction, since it was feared that the light absorption of the alcohol might introduce complications. Unlike the aliphatic alcohols, benzyl alcohol has an absorption spectrum extending farther toward the visible than that of the sulfite.

[25] Cremer, *Z. physik. Chem.*, **128**, 285 (1927).

the reaction is accompanied by an induced, or "photosensitized," formation of water. This induced reaction was found by Cremer to be independent of the oxygen pressure and to obey the equivalence law, two molecules of water being formed for every light quantum absorbed by the chlorine.

Copper Accelerated Solutions.—It is well known that copper ions tremendously accelerate the oxidation of pure sulfite solution.[26] If the effect of copper ions is merely one of starting more than the usual number of sulfite chains per unit time, both *CV* and the quantity of benzaldehyde formed would be proportionately higher, but otherwise the phenomena observed for pure sulfite solutions would be unchanged.

Table XIV gives some results in the presence of 2.5×10^{-6} mole/liter of copper sulfate.[27] It shows that *CV* and the rate of benzaldehyde formation, are constant, independent of alcohol concentration, and that both have been proportionately increased over the normal values.

TABLE XIV

COPPER ACCELERATED REACTION: THE INDUCED OXIDATION OF BENZYL ALCOHOL

Alc. concn., C	Hours	Observed values		Values calcd. to one hour			Increase over the normal value (Table VI)	
		Sulfite ox.	Benzaldehyde $\times 10^4$	$V \times 10^4$	$CV \times 10^4$	Benzaldehyde	$CV/2.8 \times 10^{-4}$	Benzaldehyde/ 0.48×10^{-4}
0.025	1.0	0.028	1.4	280	7.0	1.4	2.5	2.9
.025	2.0	.060	3.3	300	7.5	1.65	2.7	3.4
.050	7.88	.118	13.0	150	7.5	1.65	2.7	3.4
.050	8.20	.118	9.0	144	7.2	1.1	2.6	2.3
.100	14.65	.108	17.5	74	7.4	1.2	2.6	2.5
.100	14.00	.099	16.5	71	7.1	1.2	2.5	2.5
					Averages		2.6	2.8

At higher copper concentrations, however, the results are more complex, due probably to the deficiency of the shaker in supplying oxygen at these high reaction rates, and possibly also to the limited solubility of the copper (as $Cu(OH)_2$?).[28]

It should be emphasized at this point that it is quite possible, as first suggested by Titoff,[4b] that a sulfite solution which is perfectly free from positive catalysts such as copper salts would not react with oxygen in the dark; but no satisfactory evidence has been presented to substantiate the idea of Luther and Titoff that the inhibitors act by combining with, or in some way destroying, this positive catalyst. Moreover, it seems

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

[27] Blank tests on solutions of 5 cc. of 0.04 *M* benzyl alcohol with 15 cc. of water; of potassium hydroxide; of phosphate buffer, $P_H = 8.4$; or of oxidized 0.8 *N* sulfite, all in the presence of 2.5×10^{-6} mole per liter copper sulfate, gave no benzaldehyde after fifty hours of shaking.

[28] Reinders and Vles, *Rec. trav. chim.*, **44**, 249 (1925).

impossible to explain our results, as well as those of Bäckström, on this theory.[29]

Summary

It has previously been shown that the action of alcohols in inhibiting the oxidation of sulfite solutions must consist in the breaking of reaction chains, in the thermal as well as in the photochemical reaction. The present investigation leads to the conclusion that the mechanism of this process involves an induced oxidation of the alcohol, two molecules of the oxidation product (an aldehyde or ketone) being formed whenever a chain is broken.

The following experimental results, chiefly obtained for the thermal reaction, may be accounted for on this basis.

1. The oxidation of the sulfite induces an oxidation of the alcohols.
2. At low inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concentration.
3. At high inhibitor concentration the amount of alcohol oxidized per unit time is constant, independent of its concentration. This was shown to apply to the photochemical as well as to the thermal reaction.
4. In this concentration region the number of inhibitor molecules oxidized per unit time is quantitatively the same for different alcohols of widely different inhibitory powers.
5. Two alcohols present in the solution at the same time have an additive inhibitory effect. They are oxidized in proportion to their inhibitory powers, the total number of alcohol molecules oxidized being the same as when only one alcohol is present.
6. Copper sulfate accelerates the thermal reaction without altering the ratio of sulfite oxidized to alcohol oxidized.
7. The chain length is the same for the thermal and photochemical reaction and is equal to the photochemical quantum efficiency. This may also be expressed by saying that in the light reaction the induced oxidation obeys the Einstein equivalence law.

The alcohols used as inhibitors were *iso*propyl, *sec.*-butyl and benzyl alcohols. In order to determine quantitatively the minute traces of acetone, methylethyl ketone and benzaldehyde that were formed in the reaction, colorimetric tests were developed for concentrations to as low as 0.00005 mole per liter, about ten times as sensitive as those previously described in the literature.

Some experiments with hydroquinone gave results that suggest an ex-

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[29] A recent investigation by Mason and Mathews, *J. Phys. Chem.*, **30**, 414 (1926), gave a result which is not consistent with our views on the role of copper in this reaction; they stated that copper sulfate acted as an inhibitor to the photochemical reaction. We have found, however, by a series of experiments with copper sulfate, that this does not hold true under our experimental conditions.

planation for the anomalous behavior of this substance as an inhibitor to the oxidation of sulfite solutions.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 191]

MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

BY WARREN P. BAXTER AND ROSCOE G. DICKINSON

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Introduction

The photochemical decomposition of nitrogen pentoxide into nitrogen dioxide and oxygen was first studied by Daniels and Johnston.[1] Their method of experimentation was to illuminate, with sunlight or light from a tungsten lamp, a glass bulb containing nitrogen pentoxide crystals immersed in ice water and measure the pressure increase attending the illumination. By the use of light filters these authors were able to demonstrate that only light of wave length shorter than 4600 Å. was effective in producing decomposition. They also established the important result that, at least with radiations in the neighborhood of the violet part of the spectrum, the presence of nitrogen dioxide is necessary for the reaction, that is, this decomposition of colorless nitrogen pentoxide is photosensitized by the brown dioxide.

Two important suggestions have been made as to the mechanism of this reaction. Fazel and Karrer[2] have advanced the hypothesis that a light quantum is absorbed by a nitrogen dioxide molecule, which is thereby raised to a higher quantum state, and that this excited molecule, NO_2', then makes a collision of the second kind with a pentoxide molecule, transferring energy of activation to the pentoxide molecule. The activated nitrogen pentoxide molecules subsequently decompose. Norrish,[3] on the other hand, has shown that nitrogen dioxide is decomposed by light from a mercury arc into nitric oxide and oxygen. He has accordingly suggested that in the sensitized decomposition of the pentoxide, the first reaction is the decomposition of the dioxide, and that this is then followed by a dark reaction between nitric oxide and nitrogen pentoxide, $NO + N_2O_5 = 3NO_2$. For this mechanism to play an important part in the pentoxide decomposition, it is necessary that the thermal reaction between nitric oxide and nitrogen pentoxide have a rate at least comparable with the rate of recombination of nitric oxide and oxygen. Busse

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[1] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[2] Fazel and Karrer, *ibid.*, **48**, 2837 (1926).

[3] Norrish, *J. Chem. Soc.*, 761 (1927).