to be the most efficient, with manganese dioxide and nickelic oxide next in order. In general, mixtures of the oxides gave results corresponding to the proportion of each active material in the mixture. These data are presented in the form of a graph.

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

THE CHAIN-REACTION THEORY OF NEGATIVE CATALYSIS[1]

BY HANS L. J. BÄCKSTRÖM[2]

RECEIVED MARCH 25, 1927 PUBLISHED JUNE 7, 1927

In the fall of 1923 the author, at the suggestion of Professor Hugh S. Taylor, began an investigation of negative catalysis as exhibited in the reaction between benzaldehyde and oxygen. In the course of preliminary experiments, the reaction was soon found to be highly light-sensitive, and it was also discovered that a substance which had been found by Dr. Taylor to be an excellent inhibitor for the dark reaction, namely, the well-known anti-knock compound, lead tetra-ethyl, had marked retarding effect on the photochemical reaction, the addition of one drop of this liquid to 4 cc. of benzaldehyde lowering the reaction rate in the light of a mercury arc from 6.2cc./min. to 0.1cc./min. Thus, also, the photochemical reaction showed negative catalysis, a property often exhibited by those reactions that deviate from the Einstein photochemical equivalence law by giving abnormally high quantum yields, in other words, by photochemical chain reactions. At this stage of the investigation, our attention was called to a theory of negative catalysis, advanced by Christiansen,[3] which is based on the assumption that those thermal reactions which exhibit this phenomenon are *thermal chain reactions*. It was then apparent that a test of this hypothesis might be obtained by finding out, with quantum-efficiency measurements, whether, in the case under investigation, the photochemical reaction was actually a chain reaction, and whether the similarity between the thermal and the photochemical reactions in their behavior towards inhibitors, which was indicated by the experiments with lead tetra-ethyl, was sufficiently general to support the theory that the reaction mechanism is analogous in the two cases.

This has been done for the auto-oxidation of benzaldehyde, enanth-

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[1] A preliminary report of this investigation was presented before the April, 1924, meeting of the American Chemical Society at Washington, D. C., and abstracted in *Science*, **59**, 489 (1924).

[2] Charlotte Elizabeth Procter Fellow of Princeton University, 1923–1924.

[3] (a) Christiansen, *Dissertation*, Copenhagen, **1921**. (b) Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923). (c) Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

aldehyde and solutions of sodium sulfite. In all cases it has been found that a great number of molecules react for every light quantum absorbed, and since it has also been found that there is a general agreement between light and dark reaction as regards the action of different inhibitors, there seem to be good reasons for believing that these reactions actually represent instances of thermal chain reactions.

Christiansen's Theory

Christiansen's theory[3c] may be briefly stated as follows.

He points out that "the molecules of the reaction products just after the reaction, possess an available energy greatly in excess of the mean energy at the temperature considered. Not only do they contain the energy (usually denoted as the critical energy) which was necessary for the reaction to occur, but, as is well known, the reaction is very often accompanied by an evolution of heat which must appear in the resulting molecules from the reaction as kinetic energy or potential energy easily transformable into kinetic.

"Now these very 'hot' molecules have sufficient energy to activate molecules of the reactants at the first encounter, and when these react, the resultants in their turn are again able to act as activators and so on. Consequently, it is possible that the occurrence of one elementary reaction will give rise to a whole series of such reactions;" and he assumes that the negative catalysts are substances that have the power of breaking the reaction chains thus set up by "taking up the energy from the 'hot' molecules of the reaction products or reacting with them in some way or another."

Among the reactions mentioned by Christiansen as probable examples of thermal chain reactions are those dealt with in this paper. Reactions of this class have received considerable attention in recent years[4] and have been found to show negative catalysis to a high degree.

If the reaction mechanism is the one pictured above, it would seem to be a plausible consequence that when the primary activation is brought about, not by molecular collision but by the absorption of a light quantum, this should also cause a great number of molecules to react, and it is this consequence which has been tested in this paper.

Experimental Method

Four cc. of the aldehyde was shaken with oxygen in a quartz tube (Fig. 1) which consisted of a wider part (A), 10.3 cm. long and 2.4 cm. in diameter, and a narrower part (B), 10 × 1.0 cm., into which fitted a glass tube (C). The two tubes were joined together with a thick piece of rubber tubing (D) as shown in the figure. Tube B was connected

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[4] (a) Moureu and Dufraisse, *Compt. rend.*, **174**, 258 (1922); and a series of other papers, summarized in Reports of the Solvay International Council on Chemistry, Brussels, April, 1925, p. 524. (b) Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

to a Hulett gas buret[5] by means of a piece of vacuum tubing, 60 cm. in length. The tube was generally shaken at a rate of 240 complete strokes a minute, the length of the stroke being 8 cm. However, in the experiments on sulfite solution that were carried out with a greater volume of liquid (10 cc.), the stroke was only 6 cm. The tube was immersed in a water-bath, and could be illuminated through a quartz window, the light source being a mercury-vapor lamp. The intensity of the light was at first only estimated which, as shown by Bodenstein,[6] can be done with an accuracy which is sufficient for the purpose. In later experiments, however, carried out in monochromatic light obtained by means of a quartz monochromator,[7] the intensity was measured with a thermopile which was calibrated by means of a Hefner lamp. The experimental conditions making it impossible to measure the intensity of the transmitted light and the losses by reflection, the determinations were confined to the total energy carried by the beam of parallel monochromatic light emerging from the monochromator. The cross section of this beam was approximately circular and had a diameter of 0.9 cm. Since the diameter of the tube was as much as 2.4 cm., it follows from Fresnel's formula that the reflection losses at the curved surface of the tube were no greater than at a plane surface, and that consequently the quartz window in front of the thermopile, which was removed during measurements on the Hefner lamp, automatically corrects for the most important reflection losses, the loss at each of the two quartz-water interfaces amounting only to about 0.6%. The results of the intensity determinations should, therefore, give a true measure of the number of light quanta entering the reaction tube, so that in cases where the light is very strongly absorbed by the liquid in question, the figures obtained for the quantum efficiency should be correct, within the limits of error; in other cases they represent minimum values.

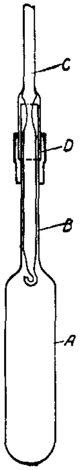

Fig. 1.

The results of the energy measurements are summarized in Table I.[8]

TABLE I

ENERGY MEASUREMENTS

Wave length, mμ	366	313	"294"	280	265	254
Relative intensities (ergs)	157.0	100	44.4	16.1	23.6	26.7
Relative intensities (quanta)	183.6	100	42	14.5	20.0	21.6

The absolute intensity of Line 313 was 199 ergs per second = 1.90 × 10^{15} quanta per minute, putting the radiation from the Hefner lamp

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[5] See Taylor and Burns, THIS JOURNAL, **43**, 1274 (1921).

[6] Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

[7] From the firm of Carl Leiss, Berlin-Steglitz.

[8] The author is indebted to Mr. Hubert N. Alyea for assistance in making these measurements.

(without diaphragm) = 1088 ergs per sq. cm. per second at 1 meter's distance.[9] Consequently, a reaction velocity in the light of this line amounting to 1 cc. of oxygen per minute at 20° corresponds to a quantum efficiency of 13,300 molecules per $h\nu$. Similarly, a rate of, for example, 0.26 cc. in Line 254 corresponds to $0.26 \times 13{,}300 \times 100/21.6 =$ 16,000 molecules per quantum. The accuracy claimed for these absolute values is ±10%; the relative values are considerably more accurate.

All of these figures were obtained with the lamp burning at 309 watts, which is the average wattage used throughout the investigation. Changes in this value of 5% or more did not measurably change the relative intensities, whereas the absolute intensities varied as the 2.6th power of the wattage. With the slit-widths used (entrance slit 1.0 mm., exit slit 1.2 mm.), all of the lines listed were monochromatic, except "294;" the light obtained with this setting consisted of several lines of wave lengths around 300mμ, but was free from the strong line 313.

It is well known that although quartz-mercury lamps are subject to aging, the rate of deterioration is mainly dependent on the electrical conditions under which the lamp is being used. Owing to the fact that, in the present instance, a 400-watt lamp was burned throughout at 309 watts, the light intensity stayed so constant that reaction-velocity figures could be reproduced within a few per cent. after the lapse of a whole year. It may be said, therefore, that although the energy measurements are strictly applicable only to the velocity data (given in the next section of this paper) which were obtained in connection with these measurements, they can actually be applied to all the data presented.

The materials used were the purest commercial preparations obtainable. The aldehydes were purified by fractional distillation under a pressure of 15–20 mm., but the inhibitors were generally used without further purification. The sodium sulfite was recrystallized thrice from water which had been redistilled, using a Jena flask and a block-tin condenser. The strength of the sulfite solutions was determined by titration with 1 N sulfuric acid to $P_{\text{H}} = 4.3$, using bromocresol green or bromophenol blue as an indicator; an equal volume of a buffer solution of the right P_{H}, and containing the same quantity of indicator, served as a color standard. This method may be shown to be capable of an accuracy of 0.5%.[10]

Unless otherwise stated, the temperature of the bath was 20.0° ± 0.1°. Reaction rates are expressed in cubic centimeters of oxygen per minute.

In order to avoid complications, the investigation has so far been limited to the initial stages of the oxidation process, where the influence

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[9] Coblentz, *U. S. Bur. Standards Bull.*, **11**, 87 (1914).

[10] See Bjerrum, "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," *Ahrens Sammlung*, **21**, 1 (1914).

of concentration changes and the effect of the oxidation products on the reaction rate can generally be neglected.

The Quantum Efficiency of the Light Reaction

Benzaldehyde.—Under the conditions of these experiments, pure benzaldehyde, unlike the other substances studied, shows a rather definite dark reaction; as soon as the shaking is started the aldehyde begins to absorb at a high rate, and this rate stays constant or increases only slightly during the run.

In the following experiment, two-minute periods of illumination alternated with three-minute periods of darkness. The lamp was burning at 305 watts.

Table II

Pure Benzaldehyde

Wave length, mμ	..	..	366	..	313	..	254	..	280	..	366
Rate, cc./min.	1.20	1.30	2.70	1.43	1.85	1.42	1.46	1.44	1.51	1.45	2.32
Light reaction	..	..	1.33	..	0.43	..	0.03	..	0.06	..	0.87
Molecules/$h\nu$			10,000		5900		1900		5700		6500

No weight can be given, in this case, to the figures for Lines 254 and 280, but the experiment may serve to show that we are dealing with a photochemical chain reaction. All the lines used are strongly absorbed by benzaldehyde.[11] The gradual decrease in the light reaction shown by the two values for Line 366, is characteristic of benzaldehyde, and is probably connected with the accumulation in the liquid of the oxidation products—the final product, benzoic acid, as well as the intermediate product, benzoperacid, which, as will be shown in a later paper, is relatively stable. In the presence of sufficient quantities of an inhibitor, this effect is not noticed.

Enanthaldehyde.—The rate of oxidation of enanthaldehyde in the dark does not seem to have any definite value inasmuch as, during the course of the oxidation, the velocity first increases, then reaches a maximum and finally begins to decrease again. The figures for the light reaction, on the other hand, obtained by subtracting the average of the rates before and after the illumination period from the rate observed during illumination, are quite reproducible. In Table III the rates are given in the order in which they were observed.

The absorption spectrum of enanthaldehyde has never been determined, but a glance at the absorption curves for the lower aliphatic aldehydes[12] shows convincingly that all of the lines used should be absorbed to more than 99% in a 1-mm. layer of the aldehyde, except 366, for which the absorption must be very small; this accounts for the low apparent

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[11] Henri, "Études de Photochimie," Gauthier-Villars and Co., Paris, **1919**, p. 145.

[12] Ref. 11, p. 85.

TABLE III

PURE ENANTHALDEHYDE

Wave length, mμ	313	294	313	265	254[a]	366	313	254	265
Rate during illumination	1.21	1.09	1.51	1.14	1.23	0.96	1.49	1.10	1.01
Dark rate	0.61	0.83	0.98	1.01	0.97	.88	0.90	0.84	0.83
Difference	.60	.26	.53	0.13	.26	.08	.59	.26	.18
Molecules/$h\nu$	8400	8500	6900	8100	15,700	560	7200	15,100	11,300

[a] Between this and the next determination the tube was left without shaking for seven minutes while the buret was being refilled with oxygen.

quantum efficiency obtained in the latter case, but not for the marked increase in quantum efficiency when passing from 313 and 294 to 254, which must, therefore, be due to some other cause.

Sodium Sulfite Solutions.—When a pure sulfite solution is shaken with oxygen in the dark the rate is quite high, and increases until practically all of the sulfite has been oxidized, when a sudden drop occurs. Under these conditions it is difficult to study the light reaction, since the correction for "dark rate" becomes rather arbitrary and makes the final result uncertain. The following experiment may serve as an illustration. The solution, 10 cc. in volume, contained 6 millimoles of sodium sulfite and 0.05 millimole of sulfuric acid. The rate of oxidation being very sensitive to the hydrogen-ion concentration, the addition of sulfuric acid serves the purpose of buffering the solution by transforming a definite proportion of the sulfite ions into bisulfite ions.[13] The first buret reading was taken one minute after starting the shaking.

TABLE IV

SODIUM SULFITE

Illumination	..	..	..	254	..	..	..	265	..	..	..
Time, min.	1	2	3	4	5	6	7	8	9	10	11
Rate	2.55	2.60	2.65	3.55	2.95	3.0	2.95	3.65	3.28	3.37	3.45
Average		2.60		2.79		2.97		3.17		3.37	
Molecules/$h\nu$				47,000				32,000			

For Line 254 the absorption should be practically complete, but not for 265; no other lines are appreciably absorbed by the solution.[14]

The dark reaction observed after an illumination period will be seen to be greater than would be expected from the rate of increase observed before illumination; in other words, there is a photochemical after-effect.

In the presence of inhibitors, the reaction takes a more regular course, the velocity decreasing slowly as the sulfite in the solution is being used. For instance, under the same conditions as in the foregoing experiment, except that the 10 cc. of solution also contained 0.02 millimole of mannite, the following rates were observed before, during and after illumination

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

[14] Baly and Bailey, *J. Chem. Soc.*, **121**, 1820 (1922).

with Line 254: 1.36, 2.18 and 1.34 cc./min.; light reaction 0.83 cc./min. at 305 watts = 53,000 molecules per quantum.

The Effect of Inhibitors of Light and Dark Reaction

The essential facts may be stated as follows. (1) The light reaction shows negative catalysis in a very marked degree, just as the dark reaction. (2) An inhibitor for the light reaction invariably acts as an inhibitor also for the dark reaction; so far no exception has been found to this rule. (3) In the case of benzaldehyde, the dark reaction is considerably more sensitive to inhibitors than the light reaction, in the sense that a concentration of inhibitor which is insufficient appreciably to affect the light reaction may have a considerable effect on the dark reaction. My present data do not entirely exclude the possibility that there may even be substances that act as inhibitors for the dark reaction but have no effect on the light reaction. In the case of enanthaldehyde, the parallelism is considerably more marked, whereas with sodium sulfite solutions this parallelism is practically complete with *one* class of inhibitors; inhibitors of another class, however, affect the photochemical reaction relatively more strongly than the thermal reaction.

The following examples may be given.

Benzaldehyde.—Light intensity and temperature were only approximately equal in different experiments. The mercury arc was used without the monochromator. The dilution is expressed in moles of aldehyde for 1 mole of inhibitor.

TABLE V

EFFECT OF INHIBITORS ON LIGHT AND DARK REACTION

Inhibitor	Dilution	Dark rate	Light rate
Pure aldehyde	....	1.28	1.18
Diphenylamine	10,000	immeasurably slow	0.003
Anthracene	10,000	0.01	.07
Phenol	1,000	.07	.84
Trichloro-acetic acid	1,000	.21	1.75

Enanthaldehyde.—The results contained in the following tables were obtained with the lamp burning at an average of 309 watts, the maximum deviations from this average amounting to ±4%; since the intensity varies as the 2.6th power of the wattage, this means that it was defined only to about ±10%. The tables give both the absolute values of the rates obtained in the light of the different mercury lines, and the relative

TABLE VI

PURE ENANTHALDEHYDE, TWO DIFFERENT SAMPLES

Dark reaction	Light reaction wave lengths, mμ					Ratios				
	366	313	294	265	254	366	313	294	265	254
0.35–0.75	...	0.50	0.19	0.12	0.18	..	100	38	24	36
.20– .50	0.09	.54	.25	.16	.27	16	100	46	30	50

TABLE VII

ENANTHALDEHYDE AND PICRIC ACID (1 MOLE IN 20,000)

Dark reaction	Light reaction wave lengths, mμ					Ratios				
	366	313	294	265	254	366	313	294	265	254
0.07–0.09	...	0.254	0.122	0.058	0.076	..	100	48	23	30

TABLE VIII

ENANTHALDEHYDE AND α-NAPHTHOL

Moles of aldehyde per mole of inhib.	Dark reaction	Light reaction wave lengths in mμ					Ratios				
		366	313	294	265	254	366	313	294	265	254
10,000	0.013	0.015	0.058	0.020	0.010	0.017	26	100	34	17	29
25,000	0.028–0.033	.030	.123	.054	.028	.036	24	100	44	23	29
50,000	.05 – .07	.050	.226	.093	.052	.070	22	100	41	23	31
100,000	.09 – .14	.047	.30	.131	.085	.112	16	100	44	28	37
500,000	.25 –1.0	...	.62	...	.13	.24	..	100	..	21	39
						Av.	22	100	41	22	33

values, putting the values for 313 mμ = 100. The dark rates given are the minimum and the maximum values observed during the run.

The product of dark reaction and concentration has the following values for the five dilutions studied.

Dilution	10,000	25,000	50,000	100,000	500,000
Product	1.3	1.1–1.3	1.0–1.4	0.9–1.4	$0.5\text{–}2.0 \times 10^{-6}$

The relation between the velocity of the light reaction (v) and the concentration of inhibitor (c) in moles per mole of aldehyde may be represented approximately by a formula of the type $v = A/(c + B)$. In Line 313, the constants are $A = 6.25 \times 10^{-6}$; $B = 9.06 \times 10^{-6}$.

Dilution	10,000	25,000	50,000	100,000	500,000
Obs. rate	0.058	0.123	0.226	0.30	0.62
Calcd. rate	.057	.128	.215	.33	.57

TABLE IX

ENANTHALDEHYDE AND β-NAPHTHOL

Moles of aldehyde per mole of inhib.	Dark reaction	Light reaction wave lengths in mμ					Ratios				
		366	313	294	265	254	366	313	294	265	254
5,000	0.024–0.040	0.030	0.081	0.035	0.022	0.023	37	100	43	27	28
10,000	.045– .073	.045	.132	.055	.033	.046	24	100	42	25	35
20,000	.115– .140	.060	.218	.095	.076	.086	28	100	44	35	39
40,000	.180– .210	.087	.368	.138	.102	.160	24	100	37	28	43
						Av.	28	100	42	29	36

PRODUCT OF DARK RATE AND CONCENTRATION

Dilution	5,000	10,000	20,000	40,000
Product	4.8–8.0	4.5–7.3	5.7–7.0	$4.5\text{–}5.2 \times 10^{-6}$

For the light rate in Line 313, the constants are $A = 18 \times 10^{-6}$; $B = 2.61 \times 10^{-5}$.

LIGHT RATE IN LINE 313

Dilution	5000	10,000	20,000	40,000
Obs. rate	0.081	0.132	0.218	0.368
Calcd. rate	.080	.143	.237	.352

The accuracy of these figures, although not very high, is sufficient to prove certain facts. First of all they indicate that the action of the inhibitor is independent of the wave length of the exciting light; the ratios between the velocities in the different lines remain essentially constant, irrespective of the nature and the concentration of the inhibitor added except, possibly, that there seems to be a trend in the values for 254mμ. The results for α- and β-naphthol should be seen in the light of the characteristic differences between the absorption spectra of these substances. Marchlewski and Moroz[15] give the following values for the extinction coefficients of 0.0001 *M* alcoholic solutions.

Wave length, mμ	365	315	295	265	255
α-Naphthol	0.0100	0.3000	0.6150	0.1350	0.2025
β-Naphthol	.0675	.2250	.0640	.6250	.4700
Ratio α/β	.15	1.3	9.6	.22	.43

A recent paper by de Laszlo[16] essentially confirms these results and shows, in addition, that the same relations are found in a non-polar solvent, hexane. The following approximate values for the ratio between the extinction coefficients for α- and β-naphthol were read from his curves.

Solvent	Wave lengths			
	313	294	265	254
Alcohol	1.3	6	0.3	0.2
Hexane	1.0	6	.6	.4

It will be seen that in the figures for the "ratios" in Tables VIII and IX, there is nothing to correspond to the difference in absorption coefficient for Lines 313 and 294, and that the deviations observed in Lines 265 and 254, if indeed they are outside the limits of error, are in the opposite direction from what should be expected if the action of the inhibitor were due to its absorption of the activating light or of some kind of "isochromatic resonance radiation." These experiments, therefore, fail to reveal any reasons against the theory that the mechanism of inhibition is the same in light and dark reaction.

As to the relation between inhibitor concentration and reaction velocity, the tables show that as the concentration increases, the rates of both light and dark reaction approach inverse proportionality; for the dark reac-

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[15] Marchlewski and Moroz, *Bull. soc. chim.*, **35**, 473 (1924).

[16] de Laszlo, *Proc. Roy. Soc.*, **A111**, 355 (1926).

tion this relation seems, indeed, to hold over a wide range of concentrations, as shown by the constancy of the values for the product of concentration and reaction velocity. This product, and the constant A in the above formulas, measure the effectiveness of the inhibitor for dark and light reaction, respectively; consequently, α-naphthol is approximately five times more effective than β-naphthol for the thermal reaction, but only 2.9 times more effective for the photochemical reaction. Thus, there is no quantitative agreement.

Sodium Sulfite Solutions.—In the case of sodium sulfite solutions, light and dark reaction show a parallelism in their behavior towards one class of inhibitors, namely, the alcohols, which is practically complete; whether this class includes other substances remains to be seen. Table X contains the results obtained with the alcohols. Besides the inhibitor, the solutions (10 cc.) contained 0.6 mole of sodium sulfite and 0.01 equivalent of sulfuric acid per liter. Table IV gives the results obtained in the absence of inhibitors.

TABLE X

INHIBITORY ACTION OF ALCOHOLS

Inhibitor	Concn., mole/liter	Dark rate Obs.	Dark rate Calcd.	Light rate in 254 mμ Obs.	Light rate in 254 mμ Calcd.
Mannite	0.04	0.200	0.197	0.136	0.136
Mannite	.02	.333	.346	.24	.24
Mannite	.01	.56	.56	.37	.39
Mannite	.005	.83	.81	.56	.56
Mannite	.003	1.085	.99	.68	.68
Mannite	.002	1.35	1.11	.83	.76
Methyl alcohol	.02	0.53	0.53	.37	.37
Methyl alcohol	.01	.82	.78	.49	.54
Ethyl alcohol	.02	.28	.28	.205	.195
Ethyl alcohol	.01	.46	.47	.32	.33
Benzyl alcohol	.001	.145	.137	.094	.095
Benzyl alcohol	.00025	.43	.43	.27	.30

These results can be summarized in the two formulas $v_d = 0.009084/(kc + 0.00622)$; $v_l = 0.692v_d$, where v_d is the dark rate, v_l the light rate in line 254, c the concentration in moles per liter, and k a constant expressing the relative efficiency of the inhibitor. Putting the inhibitory power (k) of mannite = 1, the values for methyl, ethyl and benzyl alcohol become 0.54, 1.30 and 60, respectively. According to the formulas, two parallel straight lines should result when the product kcv is plotted against v; this has been done in Fig. 2.

The formulas express the facts that, within the limits of their applicability, that is, up to velocities around 0.8 cc./min., the ratio between light and dark reaction is constant, and that both rates are inversely proportional to a sum of two quantities, one being a constant and the other proportional to the concentration of the inhibitor. Interpreted in terms of the chain-reaction theory, these results signify that the activity of the inhibitor in breaking the reaction chains is proportional to its concentration and independent of whether the primary activation is thermal or photochemical; in addition, however, the breaking of the chains is due not only to the action of the specific inhibitor, but also to some other constant cause similarly independent of the nature of the primary activation.

Another inhibitor which may belong to this class is potassium cyanide, although this substance seems to have a double effect, which may possibly be connected with the fact that the primary activations that cause the "dark rate" are probably due, at least in part, to the presence of traces of copper salts. A lower value is found for the dark rate if the determination is made some hours after mixing the solutions than if the rate is determined immediately after mixing; in the latter case the velocity decreases abnormally rapidly during the run. The values observed for the ratio between light and dark reaction range from 0.48 to 1.0. As an inhibitor for the light reaction, potassium cyanide is about 14 times stronger than mannite.

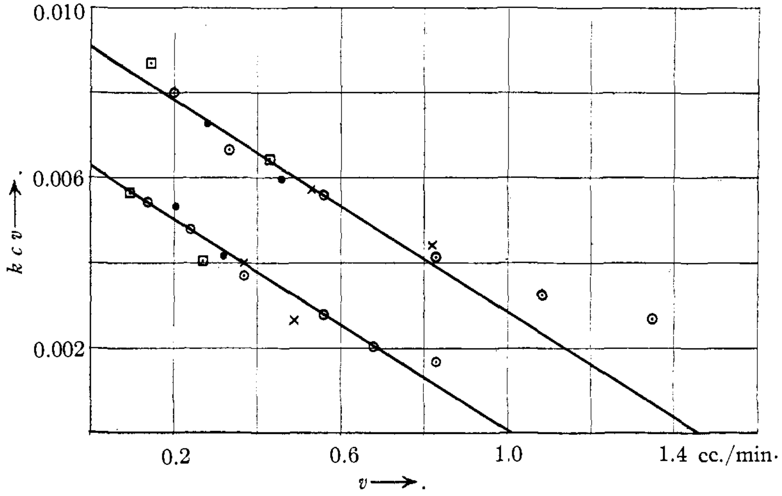

Fig. 2.—Upper curve, dark reaction; lower curve, light reaction; ⊙, mannite; ×, methyl alcohol; ●, ethyl alcohol; ⊡, benzyl alcohol.

There is, however, a second class of inhibitors that suppress the light reaction more strongly than the dark reaction, as shown by Table XI.

TABLE XI

Inhibitor	Concn., mole/liter	Light rate (254mμ)	Dark rate	Ratio
Sodium sulfide	0.0001	0.02	0.18	0.11
Sodium sulfide	.00002	.13	.675	.19
Hydroquinone	.0001	.034	.186	.18
Hydrazine sulfate	.001	.010	.136	.07

Since the PH of the solutions, as determined colorimetrically, was 8.4,[17] the inhibitors listed were present as sodium hydrogen sulfide, free hydroquinone and a mixture of hydrazine sulfate and free hydrazine, respectively. The fact that both hydroquinone[18] and sodium hydrogen sulfide[19] absorb light of the wave length employed seems to suggest that this case might be analogous to the photochemical decomposition of hydrogen peroxide solutions studied by Anderson and Taylor.[20] The same applies, however, to one of the substances in Table X, namely, benzyl alcohol;[21] on the other hand, it probably does not apply to hydrazine, although the absorption spectrum of this substance has never been determined. Further work, therefore, will be necessary to decide the reason for the deviating behavior of these inhibitors.

Conclusion

In judging the question whether the quantum efficiencies observed are sufficiently high to account for the enormous sensitivity towards some inhibitors, which is shown by these reactions, it should be remembered that the absorption of a light quantum does not, by necessity, always produce a chemically active molecule. Sometimes this condition is fulfilled, as shown by those reactions that obey the Einstein photochemical equivalence law but, on the other hand, a great number of reactions give a quantum efficiency of *less* than one molecule per quantum, and the same causes which produce this result may be operative also in the reactions studied in this paper. It is possible, therefore, that the actual "chain length" may be considerably greater than the experimental quantum efficiency.

Further discussion of these data will be presented in later papers, together with the publication of experiments bearing upon other phases of the problem. In these, the results of other investigators will also be taken up for discussion.

The author wishes to express his great indebtedness to Professor Hugh S. Taylor for suggesting the problem and for his powerful aid in this investigation.

Having returned to Sweden in June, 1924, the author has continued work on this problem in the Nobel Institute for Physical Chemistry. A second paper will soon appear in the "Communications from the Nobel Institute."

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[17] This gives 2.5×10^{-7} for the second dissociation constant of sulfurous acid, and this value was confirmed by two other determinations; Kolthoff [*Z. anorg. Chem.*, **109**, 69 (1920)] found 1×10^{-7} at 15°. The old value of 5.1×10^{-6}, found by Jellinek [*Z. physik. Chem.*, **76**, 257 (1911)] is undoubtedly in error.

[18] Hartley, *J. Chem. Soc.*, **53**, 641 (1888).

[19] Wright, *ibid.*, **103**, 528 (1913).

[20] Anderson and Taylor, THIS JOURNAL, **45**, 650 (1923).

[21] Baly and Tryhorn, *J. Chem. Soc.*, **107**, 1058 (1915).

Summary

The rates of oxidation of benzaldehyde, enanthaldehyde and solutions of sodium sulfite have been studied both in monochromatic light and in the dark. In every case the photochemical reaction is a chain reaction, the maximum yields obtained amounting to about 10,000, 15,000 and 50,000 molecules per quantum, respectively.

The photochemical reactions show negative catalysis as well as the thermal reactions, and there is a marked parallelism between them as regards the action of different inhibitors.

It is concluded that the mechanism of the thermal reactions is similar to that of the photochemical reactions and, consequently, that these reactions are examples of thermal chain reactions, in accordance with Christiansen's theory of negative catalysis.

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THE DETERMINATION OF FERROUS IRON IN SILICATES

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RECEIVED MARCH 28, 1927 PUBLISHED JUNE 7, 1927

Introduction

An excellent discussion of the determination of ferrous iron in silicates is given by Hillebrand in his "Analysis of Silicate and Carbonate Rocks,"[1] including a comparison of the merits of the sealed-tube and hydrofluoric acid methods of decomposition, the effects of fine grinding, sulfides and other factors, as well as the proper conditions for the titration. In addition to this, Barnebey[2] has given a thorough review of the literature up to his time, so it need not be repeated here.

The consensus of opinion has been that the hydrofluoric acid method of decomposition leaves nothing to be desired in the way of accuracy, and when carried out according to Pratt[3] with coarse powders, an analysis can be completed in a very short time. Until 1915 the end-point with permanganate was fleeting and unsatisfactory, and the results were high when much ferrous iron was present; however, in that year Barnebey[2] proposed the use of boric acid to secure a good and permanent end-point, the effect being to tie up the hydrofluoric acid as HBF_4, and thus prevent the oxidation of the bivalent manganese by the permanganate, and ferrous iron by the air during the titration. In a later paper Barnebey[4] suggested the use of potassium dichromate for standard solution, with boric acid

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[1] Hillebrand, *U. S. Geol. Survey Bull.* No. **700**, 189 (1919).

[2] Barnebey, THIS JOURNAL, **37**, 1481 (1915).

[3] Pratt, *Am. J. Sci.*, [3] **48**, 149 (1894).

[4] Barnebey, THIS JOURNAL, **37**, 1829 (1915).