

semiquinone formation and semiquinone autoxidation are identical for hydroquinone and for the various methyl hydroquinones. In analogy with the findings for 2,5-dimethylhydroquinone, the extrapolated values for the length of the autocatalytic period for toluhydroquinone and for hydroquinone may therefore be too high.

Summary

1. The autoxidation of pseudo-cumohydroquinone, 2,5-dimethylhydroquinone, toluhydro-

quinone and hydroquinone is investigated further.

2. The saturation of the quinone catalysis in the autoxidation of pseudo-cumohydroquinone is explained.

3. The suggestion is corroborated that the apparent indifference of the autoxidation of hydroquinone and its lower homologs to the presence of the respective quinones is caused by the fact that the quinone catalysis reaches saturation at rather low concentrations of the quinones.

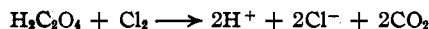
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The Direct and Sensitized Photochemically Induced Reaction of Chlorine and Oxalic Acid. Comparison with the Chemically Induced Reaction

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Previous studies of the reaction



have shown that the spontaneous reaction¹ proceeds slowly in 2*M* hydrochloric acid and that ferrous ion² acts as an inducing agent by the initiation of a chain reaction. While the extensive data on the ferrous ion induced reaction have been completely interpreted by a mechanism involving atomic chlorine and an oxalate free radical, it has appeared to us desirable to seek a more definite conclusion as to the identity of the active intermediates. In the work reported here, this has been attempted by studying the kinetics of the reaction above induced by light, and comparing for the chemically and photo induced reactions such properties of the reaction paths as specific rate, energy of activation and the effect of inhibitors. It has thus been established with reasonable certainty that the same intermediates operate in both systems; from a consideration of the methods of production and of the properties of the intermediaries, it likewise seems certain that they are, indeed, mainly atomic chlorine³ and the oxalate free radical.⁴

A principal goal in these investigations is to establish absolute values for the various specific reaction rate ratios of the intermediate substances (e. g., $k_2/k_5^{1/2}$, $k_6/k_5^{1/2}$, see Discussion) not only because the values themselves possess interest, but also because they may be regarded as properties of the intermediates useful in identifying them in other systems. It will be evident that to calculate the absolute values of such ratios from the experimental data, the actual rate of intermediate production must be known. This rate may

be considered as the product of two factors: the rate at which the inducing agent, light quanta or chemical substance, is introduced, and the efficiency of the primary intermediate production process. The first factor can easily be measured, the second can in special cases be inferred. If, for example, the effects produced by widely differing means for intermediate production, such as light and a reducing agent, agree quantitatively (*i. e.*, one quantum being equivalent in its effect to two ferrous ions) it would seem fairly safe to conclude that the efficiency is unity for each type of process. While the possibility of accidental agreement on a value of the efficiency less than unity exists, it seems remote, and can be eliminated almost completely if a third method of intermediate production gives quantitative agreement. These arguments have been applied in reaching some tentative conclusions about the efficiency of the three primary processes which have been compared.

Experimental

Apparatus.—As light source for most experiments, a C-H-1 Mazda a. c. mercury vapor lamp was used; for a few runs, a Hanovia 550W d. c. lamp was employed. The energy input was checked with a voltmeter and, in some series, the constancy of radiant output was checked by means of photronic cells. The variation in voltage never exceeded 3% during a continuous series of experiments. A lens and a round-bottom flask served to concentrate the beam on the reaction cell. Directly in front of the cell were placed light filters and a shutter. To obtain substantially monochromatic light, filters were used: 3650 Å. Corning Glass filter no. 584; 4047 Å., Wratten filter no. 36; 4360 Å., Corning Glass filters no. 585 and no. 038. The reaction cell was cylindrical in shape and was painted black, except for the front and back windows, which were made of

(1) Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518 (1932).

(2) Taube, *This Journal*, **68**, 611 (1946).

(3) *Cf. ref. 2*, footnote 2.

(4) The oxalate free radical will be represented as C_2O_4^- rather than HC_2O_4 . The assumption that HC_2O_4 is a strong acid seems reasonable from a consideration of its electronic configuration.

Corex D glass. The length of the cell was 3.5 cm. and the diameter of the windows 5.0 cm. A glass stirrer was inserted, the lower bearing of which was a reentrant glass tube sealed to the cell.

Method.—In an experiment, the reaction mixture was introduced into the cell, its temperature measured, and illuminated for a known length of time. A mean temperature was used in the calculations; it was established using a graph showing the variation of temperature with time in a typical experiment. The maximum rise during any experiment was 2.5°. The solutions, the method of handling them, and the methods of analysis were similar to those described in reference 2.

Absorption Measurements.—To determine absorption coefficients for chlorine and for ferric ion in 2 M hydrochloric acid, the photo system was adjusted to give a smaller, almost parallel, beam. One Weston Photronic Cell, Model 594, was placed as closely as possible against the back window of the reaction cell to measure the light transmitted, while a second one, on the other side of the lamp, served to compensate for fluctuations in the light source. They were connected to a potentiometric setup containing a Leeds and Northrop scale and lamp galvanometer. Stray light was eliminated as much as possible. The measurements of fractional absorption were tested as to their independence of light intensity and external resistance. A five-fold change in light intensity with no change in the measurements, was considered a good test for the validity of the results.

A further check was made, comparing the absorption coefficient values obtained for the actinometric solutions with those measured by Leighton and Forbes.⁵ The agreement was within 3% for wave lengths 3650 and 4350 Å., but our value was about 10% lower at 4047 Å.

In the following table are recorded values of α for chlorine and ferric ion solutions in 2M hydrochloric acid at several wave lengths. α is defined by the equation

$$\log \frac{I_0}{I_{tr}} = \frac{\alpha cd}{2.303}$$

c being expressed in moles per liter and d in cm. Errors in the final results due to inaccuracies in the values of the absorption coefficients are to a considerable extent eliminated because the light source was calibrated using the same experimental arrangements.

	At 3650 Å.	At 4047 Å.	At 4360 Å.
Cl ₂ in 2 M HCl	7.8	4.85	2.95
Fe ⁺⁺⁺ in 2 M HCl; H ₂ C ₂ O ₄			
0.01 to 0.07 M	2990	230	155

Beer's law was obeyed at every wave length. The absorption coefficients of ferric ion were found to be independent of the concentration of oxalic acid present in the range employed in the experiments, 0.01 to 0.07 M.

(5) Leighton and Forbes, *THIS JOURNAL*, **52**, 3139 (1930).

Calibration.—To calculate absolute specific rate constants, it was necessary to know the energy output of the light source. A uranyl oxalate actinometer was employed for this purpose according to the general procedure of Leighton and Forbes.⁵ Uranyl sulfate and oxalic acid solutions were made up without special purification. The cell described above served as the reaction vessel. A solution of 0.05 M oxalic acid and 0.01 M uranyl sulfate was illuminated for one and one-half to two and one-half hours, with continuous stirring. No temperature corrections were applied since the temperature coefficient was reported as approximately 1.⁵ Analyses of the initial and the final oxalic acid concentrations were carried out on aliquot portions using potassium permanganate and the procedure given in Kolthoff and Sandell.⁶

The quantum yields determined for the various wave lengths by Leighton and Forbes were used in the calculations of I_0 , the rate at which light is incident on the cell in mole quanta per minute. A typical experiment and results are given

Wave length, Å.	t , hours	ΔO_x	$(I/I_0)_{abs}$	γ	I_0
3650	1.92	8.4×10^{-4}	0.76	0.492	19.5×10^{-6}
		moles			

γ is the quantum yield, Δ the number of moles which reacted, and $(I/I_0)_{abs}$ the fraction of light absorbed by the reaction mixture.

Conditions, Definitions and Calculations

The concentration of hydrochloric acid was 2M in all experiments. The temperature was measured in every experiment, and the specific rates were corrected to 25° using the results of measurements on the temperature coefficient of the unsensitized reaction. The results obtained on applying the same correction to the ferric ion sensitized reaction are consistent, and it can be concluded that the temperature coefficients of the unsensitized and sensitized changes are very nearly the same.

Time, t , is expressed in minutes and the concentration in moles per liter throughout.

Δ represents the change in chlorine concentration; (\overline{Ox}) represents the average total oxalate concentration. I_{abs} is defined as twice the rate at which mole quanta are absorbed per liter per minute; this quantity, therefore, compares directly with R in the ferrous ion induced reaction.²

The fraction of the incident light absorbed in any experiment for the unsensitized reaction was calculated from the measured absorption coefficient and the average value of chlorine concentration in the experiment. When both chlorine and ferric ion were present in the system, the relation

(6) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1936.

$$\log \left[\frac{1}{1 - (I/I_0)_{\text{abs}}} \right] = \frac{d}{2.303} \left[\alpha_{\text{Fe}^{+++}}(\text{Fe}^{+++}) + \alpha_{\text{OCl}_2}(\overline{\text{Cl}_2}) \right]$$

was used. I_{abs} was calculated from I_0 (number of quanta falling on the face of the solution per minute) and the fractional absorption using the relation

$$I_{\text{abs}} = \frac{2I_0}{0.060} \left(\frac{I}{I_0} \right)_{\text{abs}}$$

0.060 is the volume of the cell solution, in liters.

The chain length, tabulated for some series, is defined as $\Delta/I_{\text{abs}}t$.

A correction was applied to the specific rates to allow for the change in the rate of free radical production along the direction of the light beam. The value of Δ obtained compares to the value Δ' which would be obtained if the same amount of light were absorbed uniformly, in the ratio: $2(1 - e^{-acd/2})/\sqrt{acd(1 - e^{-acd})}$, and this ratio was used in making the correction. The correction was usually negligible except at 3650 Å.

No allowance has been made for variation of the light intensity in a direction perpendicular to the beam. However, an effort was made to reduce error from this source to a minimum by finding a spot of light which was at least twice the diameter of the cell, and which did not change greatly in total cross-section throughout the length of the cell. The form of the expression above shows furthermore that the ratio Δ/Δ' is not very sensitive to gradual changes in intensity. Thus even for the extreme case in which the light intensity is reduced 20-fold throughout the cell length, Δ/Δ' is 0.93.

It is believed that the absolute values of the specific rates reported are accurate to within about 10%. Most of the conclusions are based on the forms of the rate laws, and on comparisons of specific rates, rather than on the absolute values of specific rate, and are unaffected by considerable variations in the absolute values.

The Unsensitized Reaction.—Experiments were performed at three wave lengths. Table I summarizes the data at 3650 Å. for comparatively high values of the ratio of chlorine to oxalic acid concentrations. The specific rate k' is defined by the rate law

$$-\frac{d(\text{Cl}_2)}{dt} = -\frac{d(\text{Ox})}{dt} = k(\text{Ox})I_{\text{abs}}^{1/2} \quad \text{I}$$

and was calculated using the integrated form:

$$k = \Delta/(\overline{\text{Ox}}) I_{\text{abs}}^{1/2}t \quad \text{II}$$

For one series of results the incident light was not calibrated, but since it was kept constant, the relative values of k for the series still serve to establish the rate law.

Rate law (I) is obeyed well over the thirty-fold variation in chlorine and the nineteen-fold change in oxalic acid concentration studied. Some of the scattering is due to the uncertainty caused by loss

of chlorine, particularly at high chlorine concentrations. The necessary corrections were determined by blanks, *i. e.*, experiments performed under the same conditions but in the absence of light, and amounted to as much as 20% in some cases. Where there was little loss of chlorine, the correction was due mainly to the spontaneous reaction, which is reproducible and very small under the conditions used.

TABLE I

THE PHOTOCHEMICAL REACTION AT RELATIVELY HIGH VALUES OF $(\overline{\text{Cl}_2})/(\text{Ox})$

(HCl) = 2 M; temp., 25.0°; $\lambda = 3650 \text{ \AA}$.

No.	$(\overline{\text{Cl}_2}) \times 10^3$	(Ox)	$t \times 10^3$	$\Delta \times 10^3$	$(I/I_0)_{\text{abs}}$	Chain length $\times 10^3$	k_r^a	k^b
1	0.654	0.1366	2	0.680	0.167		7.3	
2	0.773	.0342	4	.372	.194		7.5	
3	2.02	.0342	6	.840	.431		7.5	
4	2.13	.0342	6	.825	.449		7.1	
5	3.17	.0683	6	2.14	.587		7.9	
6	4.76	.0342	12	2.24	.735		7.4	
7	4.30	.0342	6	1.087	.699		7.2	
8	5.40	.0342	6	1.140	.780		7.8	
9	5.58	.0342	6	1.186	.790		7.8	
10	5.83	.0342	6	1.105	.804		7.0	
11	4.08	.0683	6	2.25	.680		7.6	
12	4.93	.1366	3	2.02	.747		7.5	
13	5.58	.0171	12	0.1038	.790		7.2	
14	4.05	.0683	6	1.863	.676		7.3	
15	8.82	.1708	3	2.54	.915		7.2	
16	11.56	.0342	12	2.19	.961		7.2	
17	12.14	.0342	7	1.417	.966		7.9	
18	0.388	.0343	2	0.205	.103	1.58		0.36
19	1.20	.0343	4	.667	.285	0.930		.35
20	3.31	.0343	13.6	2.93	.598	.573		.31
21	3.52	.0343	10	2.35	.625	.598		.33
22	6.95	.0688	6	3.22	.857	.997		.33
23	6.98	.1030	3	2.31	.858	1.43		.32
24	7.14	.0343	15	3.61	.865	0.442		.31
25	7.75	.0343	15	3.81	.885	.456		.31
							Av. 7.4	.33

^a Relative values $k_r = \Delta/(\overline{\text{Ox}})t(I/I_0)_{\text{abs}}^{1/2}$. ^b Absolute values $k = \Delta/(\overline{\text{Ox}})tI_{\text{abs}}^{1/2}$.

When the ratio $(\overline{\text{Cl}_2})/(\text{Ox})$ decreases, rate law I fails eventually (Table II, Nos. 4–13) and a new rate law becomes valid (Table II, Nos. 9–13)

$$-d(\text{Ox})/dt = k'[I_{\text{abs}}(\text{Cl}_2)(\text{Ox})]^{1/2} \quad \text{III}$$

TABLE II

THE PHOTOCHEMICAL REACTION AT RELATIVELY LOW VALUES OF $(\overline{\text{Cl}_2})/(\text{Ox})$

$\lambda = 3650 \text{ \AA}$.; temp. = 25.0°

No.	$(\overline{\text{Cl}_2}) \times 10^3$	(Ox)	$(\overline{\text{Cl}_2})/(\text{Ox}) \times 10^3$	$\Delta \times 10^3$	$t \times 10^3$	$(I/I_0)_{\text{abs}}$	$k_r^a \times 10^3$	$k_r'^a \times 10^3$
1	2.74	0.0692	50	1.67	10	0.534	3.3	
2	2.63	.0682	47	1.23	7.58	.520	3.3	
3	3.44	.104	43	2.21	8.25	.617	3.3	
4	3.29	.346	12.5	2.33	3	.600	2.9	
5	1.97	.380	6.1	0.790	1	.423	3.3	
6	0.917	.380	2.8	2.59	0.5	.234	2.8	5.2
7	.604	.380	2.0	.382	1	.155	2.6	6.5
8	.302	.380	1.05	.213	1	.081	1.95	7.1
9	.166	.278	0.99	.226	2	.046	1.9	8.5
10	.137	.278	.77	.157	1.5	.038	1.95	9.1
11	.194	.509	.51	.141	0.75	.053	1.6	8.4
12	.176	.509	.51	.177	1	.048	1.6	8.8
13	.171	.509	.49	.165	1	.047	1.1	8.5

^a These are relative values only, using $(I)/(I_0)_{\text{abs}}$ in place of I_{abs} .

Since the change in (Ox) is very small during an experiment, the integrated form of rate law III is

$$k' = \frac{2[(Cl)_0^{1/2} - (Cl)_t^{1/2}]}{(Ox)^{1/2}t(I_{abs})^{1/2}} \quad IV$$

The data contained in Table II show that the change in rate laws occurs in the region of $(\overline{Cl}_2)/(\text{Ox}) = 10^{-3}$ approximately.

To investigate the effect of change in wave length, experiments were performed also at 4047 and at 4360 Å. in the concentration range where rate law I is obeyed. Tables III and IV present these data.

TABLE III

THE PHOTOCHEMICAL REACTION AT 4047 Å.
(HCl) = 2 M; temp., = 25.0°

No.	$(\overline{Cl}_2) \times 10^3$	(Ox)	t	$\Delta \times 10^3$	$(I/I_0)_{abs}$	Chain length	k
1	4.23	0.0688	28.3	1.388	0.069	1.005	0.33
2	8.30	.0688	26.5	1.658	.131	0.674	.31
3	9.10	.0688	24	1.900	.143	.778	.34
4	23.5	.0688	25	2.545	.329	.437	.32
							Av. .33

TABLE IV

THE PHOTOCHEMICAL REACTION AT 4360 Å.

No.	$(\overline{Cl}_2) \times 10^3$	(Ox)	t	$\Delta \times 10^3$	$(I/I_0)_{abs}$	Chain length	k
1	3.83	0.0686	10	0.807	0.039	5.20	0.32
2	4.69	.0688	20.3	1.910	.047	5.05	.33
3	4.77	.0343	10	.497	.048	2.60	.34
4	9.33	.0686	15	1.024	.092	1.86	.34
5	2.16	.0344	16.5	3.24	.199	2.48	.32
6	2.74	.0344	20	2.11	.246	1.08	.33
7	2.51	.0343	20	1.99	.228	1.10	.33
8	2.96	.0343	15	1.72	.263	1.10	.33
							Av. .33

To expose the effect of variation in light intensity, the values of k , and I_0 , the rate at which mole quanta of light fall on the face of the cell per minute, are tabulated below for each wave length.

TABLE V

Wave length, Å.	$I_0 \times 10^6$	k
3650	18.9	0.33
4047	2.13	.33
4360	11.95	.33

The change in wave length produced a nine-fold variation in the parameter I_0 , with no resultant change in k . A more drastic change in this variable was effected also by the change in chlorine concentration. Although I_0 itself is not changed thereby, the amount of light absorbed, and hence the rate of production of free radicals, is varied, which is the quantity pertinent to the rate law. The variation in I_{abs} which was thus achieved with no significant change in k was 110-fold (compare expt. 25 of Table I and expt. 1 of Table III).

Temperature Coefficients.—In order to determine the activation energy of the photochemical reaction, the variation of the rate with tem-

perature was measured. Figures 1 and 2 present the data at high and at low values of $(\overline{Cl}_2)/(\text{Ox})$, respectively.

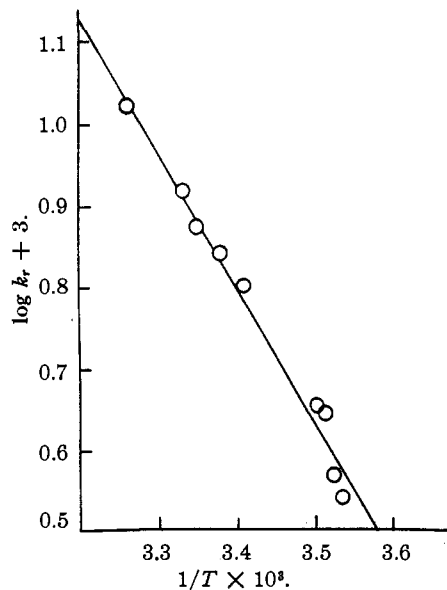


Fig. 1.—Temperature coefficient at high values of $(\overline{Cl}_2)/(\text{Ox})$. $\lambda = 3650$ Å.

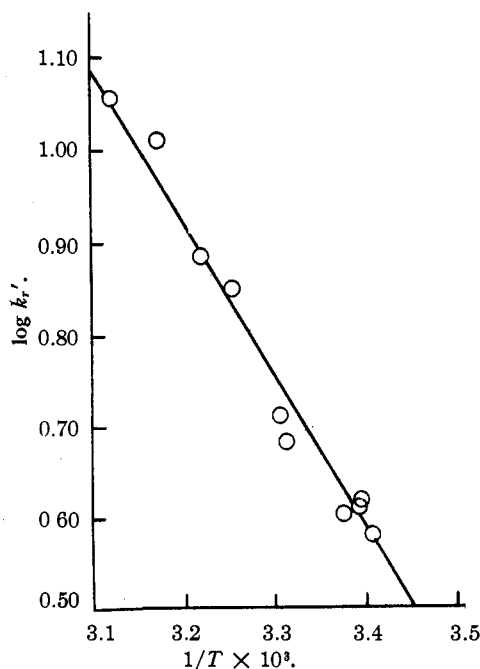


Fig. 2.—Temperature coefficient at low values of $(\overline{Cl}_2)/(\text{Ox})$. $\lambda = 3650$ Å.

Applying the integrated Arrhenius equation

$$\log k = -(E/2.303RT) + \log c$$

the activation energies were calculated to be 6900 \approx 200 cal. from Fig. 1, and 7300 \approx 500 cal. from Fig. 2. The latter value, as can be seen from the graph, is not as reliable, due to experimental dif-

faculties. The time interval, t , in the experiments at low values of concentration ratio was often small, causing uncertainty in the values of k' .

The Sensitized Reaction.—It was of interest to learn whether the reaction would be sensitized by a substance other than chlorine, which might produce radicals on absorption of light. Ferric ion and uranyl sulfate were tried as likely sensitizers, since both absorb strongly in the range of wave lengths used. The latter did not sensitize the reaction, but ferric ion was found suitable and its behavior was investigated further.

The main body of data was obtained at 4360 Å., because chlorine absorbs only a small fraction of light at this wave length so that most of the reaction is due to the sensitization. Other series of experiments were done at 3650 and 4047 Å. for the purpose of comparisons.

TABLE VI
THE FERRIC ION SENSITIZED REACTION AT 4360 Å.
(HCl) = 2M; temp. = 25.0°

No.	$(\bar{Cl}_2) \times 10^3$	$(Fe^{++}) \times 10^4$	(Ox)	t	$\Delta \times 10^3$	$(I/I_0)_{abs}$	k	k cor.
1	0.517	8.48	.0343	6	0.378	0.371	0.16	
2	1.08	8.48	.0343	5.5	.535	.375	.24	
3	2.21	8.48	.0343	9	1.198	.382	.33	
4	4.82	8.17	.0132	20	1.18	.389	.36	0.37
5	9.26	8.48	.0343	18	3.01	.425	.39	.41
6	9.65	8.17	.0343	15	2.48	.418	.37	.38
7	9.95	8.48	.0686	10	3.24	.429	.38	.39
8	10.17	8.17	.0343	15	2.52	.422	.38	.39
9	20.3	8.17	.0343	15	2.68	.479	.38	.40
10	20.4	8.17	.0686	17.5	6.41	.479	.39	.41
11	24.1	8.17	.0343	15	2.75	.499	.38	.41
12	0.585	3.39	.0343	6	0.337	.173	.21	
13	.813	3.26	.0344	11	0.770	.169	.25	
14	.633	3.26	.0344	8	0.497	.167	.22	
15	1.03	3.26	.0344	8	0.541	.171	.24	
16	1.07	3.39	.0343	8.09	0.606	.177	.27	
17	1.43	3.26	.0686	5	0.795	.174	.27	
18	2.31	3.26	.0688	5	0.988	.182	.34	.38
19	3.47	3.26	.0686	8	1.763	.202	.37	.38
20	4.63	3.26	.0343	8	0.890	.201	.36	.37
21	4.75	3.26	.0343	14	1.57	.192	.37	.37
22	9.86	3.39	.0686	13	3.17	.248	.38	.40
23	0.560	1.70	.0343	7.5	0.338	.093	.23	
24	1.02	1.70	.0343	8	0.478	.097	.30	

Table VI and Fig. 3 summarize the data at 4360 Å. It is to be noted that rate law I holds at high chlorine concentration, although a decrease is observed in k as the concentration of chlorine de-

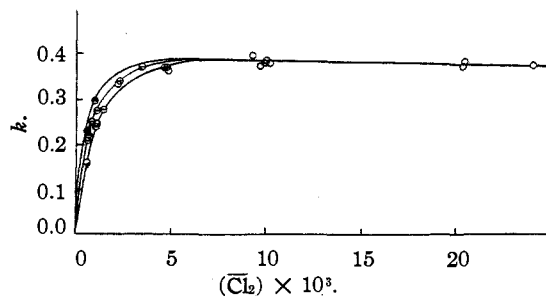


Fig. 3.—The ferric ion sensitized reaction at $\lambda = 4360$ Å.: O, 8.2×10^{-4} M Fe^{+++} ; \ominus , 3.3×10^{-4} M Fe^{+++} ; \bullet , 1.7×10^{-4} M Fe^{+++} .

creases to low values. The limiting value of k at high chlorine is about 0.38; when this is corrected for the contribution by the unsensitized reaction, the value of k for the sensitized change (corrected k in the table) becomes 0.40. The decrease in k at low values of (Cl_2) must be attributed to an influence of the ferric ion since it sets in at much higher values of $(Cl_2)/(Ox)$ than is the case for the unsensitized reaction. Not as apparent at 4360 Å., but quite evident at 4047 Å. is the effect of ferric ion at low chlorine concentration. Experiments in which 1, 2 and 5 ml. of ferric ion solution are used at constant chlorine concentration show a decrease in k as ferric ion is increased (*cf.* Fig. 3). This trend is not observed at high chlorine concentration.

Oxalic acid concentrations were varied five-fold with no apparent effect on the value of k .

TABLE VII
THE SENSITIZED REACTION AT 4047 Å.
(HCl) = 2M; temp. 25°

No.	$(\bar{Cl}_2) \times 10^3$	$(Fe^{++}) \times 10^4$	(Ox)	t	$\Delta \times 10^3$	$(I/I_0)_{abs}$	k	k cor.
1	0.788	8.17	0.0688	10	0.514	0.489	0.13	
2	1.382	8.17	.0688	10	0.730	.494	.18	
3	1.563	8.17	.0688	10	0.794	.495	.19	
4	3.66	8.17	.0688	20	2.31	.513	.28	
5	10.20	8.48	.0686	25	3.78	.575	.35	0.35
6	19.30	8.48	.0686	26	4.24	.636	.35	.37
7	21.7	8.17	.0688	25	4.38	.642	.38	.40
8	0.495	3.26	.0344	9	0.201	.237	.16	
9	0.997	3.26	.0688	10	0.614	.243	.22	
10	1.018	3.26	.0344	20	0.660	.244	.23	
11	2.79	3.26	.0688	15	1.42	.266	.32	
12	4.15	3.39	.0686	20	2.29	.291	.37	
13	4.83	3.39	.0686	20	2.20	.299	.35	
14	8.73	3.26	.0688	20	2.41	.337	.36	.37
15	8.86	3.26	.0688	20	2.27	.338	.34	.34
16	10.73	3.39	.0686	20	2.40	.366	.34	.35
17	0.413	1.70	.0343	19	0.251	.866	.13	
18	0.724	1.70	.0344	14	0.341	.138	.23	
19	1.445	1.70	.0343	17	0.290	.149	.31	
20	2.90	1.70	.0343	21	0.786	.170	.33	
21	5.43	1.70	.0686	20	1.86	.204	.36	

Table VII and Fig. 4 show the results obtained at 4047 Å. The same variations in k are observed here; there is a decrease in k at low chlorine, a dependence on ferric ion in that region, and no change with oxalic acid concentration.

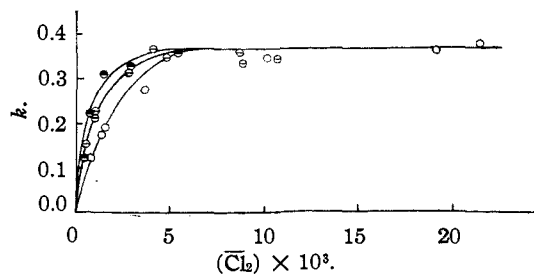


Fig. 4.—The ferric ion sensitized reaction at $\lambda = 4047$ Å.: O, 8.2×10^{-4} M Fe^{+++} ; \ominus , 3.3×10^{-4} M Fe^{+++} ; \bullet , 1.7×10^{-4} M Fe^{+++} .

The reproducibility at high chlorine is rather poor, but the maximum lies along k approximately

TABLE VIII
THE EFFECT OF VO⁺⁺ AND Mn⁺⁺ ON THE SENSITIZED AND UNSENSITIZED REACTION
3650 Å.

No.	In.	(In) × 10 ⁴	(Cl ₂) × 10 ³	(Fe ⁺⁺) × 10 ⁴	(Ox)	(I/I ₀) _{abs}	Δ × 10 ³	Temp., °C.	k ₆ ^a / √k ₅	
1	VO ⁺⁺	0.833	3.89	..	0.0688	0.663	2.33	8	23.3	97
2	VO ⁺⁺	.833	4.16	..	.0343	.687	1.76	12	22.8	101
3	VO ⁺⁺	.833	9.07	..	.0688	.920	2.75	8	22.4	114
4	VO ⁺⁺	1.667	3.92	..	.0688	.665	2.55	12	22.4	80
5	VO ⁺⁺	.833	3.88	2.51	.0343	.976	1.96	12	22.4	138
6	VO ⁺⁺	1.667	4.57	2.51	.0343	.980	1.49	12	22.6	111
7	VO ⁺⁺	.833	4.13	2.51	.0343	.978	1.97	12	23.9	138
8	VO ⁺⁺	2.50	4.22	2.51	.0343	.978	1.14	12	23.4	107
4360 Å.										
9	VO ⁺⁺ ^a	1.667	9.93	8.48	.0343	.517	0.826	13	21.1	95
10	VO ⁺⁺	1.667	8.63	8.48	.0343	.511	0.747	13.5	22.4	111
3650 Å.										
11	Mn ⁺⁺	.100	3.34	..	.0688	.610	3.40	10	25.8	440
12	Mn ⁺⁺	.100	3.92	..	.0343	.665	2.30	10	25.7	60
13	Mn ⁺⁺	.100	3.96	5.57	.0343	.998	2.07	10	24.3	640

^a Defined in the text.

0.36. Again correcting for the contribution by the unsensitized reaction (at $k = 0.33$), the maximum value of k is raised to 0.37.

A few experiments were done at 3650 Å. (not recorded here), but not enough to warrant any definite conclusions. The very high fractional absorptions of both chlorine and ferric ion at this wave length call for large corrections. This causes uncertainty in the determination of absolute values of k , but they were found to be of the same order of magnitude as reported above for other wave lengths.

Inhibitors.—Some substances were found to inhibit the photochemical reaction. Of these, vanadyl ion and manganous ion were studied further in the hope that their behavior would prove to be relatively simple and interpretable. Table VIII is a summary of experiments at two wave lengths.

The effect of vanadyl ion can be described successfully by the rate law

$$\frac{k_6}{\sqrt{k_5}} = \left[fI_{abs} - \left(\frac{\Delta}{(Ox)tk} \right)^2 \right] \frac{(Ox)tk}{\Delta^2(I_n)}$$

which was deduced for "ideal inhibitors" in connection with the chemically induced reaction.² The specific rate ratios $k_6/\sqrt{k_5}$ were calculated using for k the value of 0.40, and for f the efficiency of the primary process, a value of unity in the case of the sensitized reaction and of $(0.33/0.40)^2 = 0.68$ in the unsensitized reaction (see discussion).

Since the temperature coefficient was not measured for this system, the values of $k_6/\sqrt{k_5}$ could not be corrected to 25.0°. The large deviations are outside those expected from this source and are probably caused by small experimental errors. The form of the rate law tends to magnify inaccuracies due to uncertain blank corrections, etc.

In all but the first four experiments, sensitizer was added with no resultant effect on the values of $k_6/\sqrt{k_5}$.

The behavior of the system containing manganous ion cannot be described by the above rate law. The efficiency of this inhibitor increases as the concentration of oxalic acid increases for the range investigated, and is greater for the sensitized than for the unsensitized reaction at corresponding conditions.

Discussion

In the table below, some of the important results of the investigations of the ferrous ion induced, the unsensitized photo-induced, and the ferric ion sensitized photo-induced reactions are arrayed to facilitate comparison.

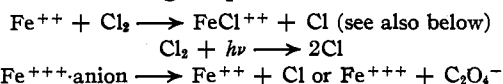
	Fe ⁺⁺ induced	Unsensitized photo- induced	Fe ⁺⁺⁺ sensitized photo- induced
At Relatively High Values of (Cl ₂)/Ox)			
Rate law,			
—d(Cl ₂)/dt =	$k(Ox)R^{1/2}$	$k(Ox)I_{abs}^{1/2}$	$k(Ox)I_{abs}^{1/2}$
Value of k	0.40	0.33	0.40
Activation energy	6,900	6,900 = 200	ca. 7,000
Efficiency of VO ⁺⁺			
as inhibitor	111 ^a	100	115
Effect of Mn ⁺⁺	inhibits	inhibits	inhibits
Effect of air	none	none	none
At Relatively Low Values of (Cl ₂)/(Ox)			
Rate law,			
—d(Cl ₂)/dt =	$k'[(Ox)(Cl_2)R]^{1/2}$	$k'[(Ox)(Cl_2)I_{abs}]^{1/2}$...
Rate law changes form at (Cl ₂)/(Ox) ratio of:	ca. 10 ⁻³	ca. 10 ⁻³	...
Activation energy	...	7300 = 500	...

^a See below.

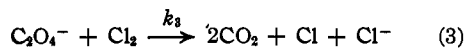
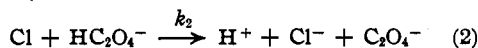
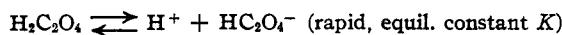
In the region of high values for the ratio (Cl₂)/(Ox) for the three systems investigated, the rate laws correspond exactly, the activation energies

and the effect produced by the inhibitor VO^{++} agree quantitatively, and the specific rates are very nearly the same. It therefore seems safe to conclude that the same intermediates operate in the three systems under these conditions. A consideration of the methods of productions and the properties observed for one of the intermediates^{2,7} makes it also seem safe to conclude that it is atomic chlorine. The second intermediate which is required to set up a chain path must be derived from the oxalate by a one-electron oxidation, and will be considered to be C_2O_4^- , (although CO_2^- (+ CO_2) is not excluded as a possibility). Thus, the general features of the mechanism which operates in these systems seem fairly well established and the mechanism is presented below.

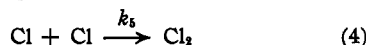
Chain Initiating Steps



Chain Carrying Steps



Chain Breaking



The agreement of the specific rate for the ferrous ion chemically induced reaction and the ferric ion sensitized photo-reaction suggests an efficiency of unity for the primary processes in these systems. This conclusion must still be regarded as tentative since the error in the values for the photo-reactions may be fairly great, and the agreement may be accidental. However, it is given some additional support by the observation that the specific rate for the unsensitized reaction also compares reasonably well.

The discrepancy between the values for the sensitized and unsensitized reaction, 0.40 as compared to 0.33, however, seems outside experimental error and may mean that the efficiency of the primary process in the latter case is only about 0.7.⁸ Alternatively, the primary efficiencies may be unity in all cases, the higher values observed when iron ions are present being due to an additional path for reaction provided by the alternation of iron between the two and four oxidation states. It is hoped that experiments now in progress, studying other inducing agents, both oxidizing and reducing, may lead to more definite conclusions on these points.

To determine the magnitude of the possible error in the values of k arising from the intensity fluctuations of the a. c. light source, two experi-

ments were carried out at 3650 Å. using the d. c. lamp. The results are shown in Table IX. On the basis of these data, it seems likely that any effect, if it does exist, is small.

TABLE IX

$(\text{Cl}_2) \times 10^4$	(Ox)	t	$\Delta \times 10^4$	k
4.73	0.0688	6	2.065	0.306
4.67	.0688	8	2.952	0.329

The composition of the complex ion formed by Fe^{+++} in the system is not known and alternative primary processes have been suggested for the ferric sensitized reaction, depending on whether a $\text{Fe}^{+++}\text{-Cl}^-$ or $\text{Fe}^{+++}\text{-C}_2\text{O}_4^-$ bond undergoes oxidoreductive rupture. It is of interest to note that an efficiency of unity for the primary process has been observed in the photo reduction of ferric ion by oxalic acid.⁹ In connection with the mechanisms written for the primary or chain initiating steps for the three types of processes, it should be emphasized that the experiments conducted, while they may serve to identify the chain carrying intermediates, and to establish the efficiency of the initiating processes, do not fix the exact mechanisms by which the intermediates are formed. Thus, the data on the ferrous induced reaction are equally well explained if it is assumed that Fe^{++} is oxidized to Fe(IV) by Cl_2 , and that Fe(IV) then reacts with oxalic acid to produce Fe^{+++} and the radical C_2O_4^- .

The unsensitized photo-reaction and ferrous induced reaction are at least in qualitative agreement, also at low ratios of $(\text{Cl}_2)/(\text{Ox})$. Thus in both systems, the rate law changes to form III, and in both, this transition takes place at about the same value of the ratio $(\text{Cl}_2)/(\text{Ox})$. The explanation for this type of change in rate law has been advanced elsewhere; as applied to the present system, the chain breaking step



is expected to predominate over (5) as the ratio $(\text{Cl})/(\text{C}_2\text{O}_4^-)$ is decreased by decrease in $(\text{Cl}_2)/(\text{Ox})$. Quantitatively the two systems do not agree at low values of $(\text{Cl}_2)/(\text{Ox})$; whereas the ratio k'/k is ca. 14 for the ferrous induced reaction, it is ca. 26 for the photo-reaction (data from Table II). At the present time it is not certain whether this difference is real or whether it is due to the experimental difficulties which arise as the ratio $(\text{Cl}_2)/(\text{Ox})$ is decreased to low values.

Some calculations which, although admittedly rough, nevertheless serve to show that the interpretations advanced are internally consistent, are presented below. The results of the ferrous ion induced experiments have been used in the calculations.

The equations

$$k = \frac{k_2 K}{\sqrt{k_6} K + (\text{H}^+)} = 0.40$$

(9) Livingston, *J. Phys. Chem.*, **44**, 601 (1940).

(7) Taube, *This Journal*, **65**, 1876 (1943).

(8) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 386 (1933).

and

$$k' = \left[\frac{k_2 k_3}{2k_4 K + (H^+)} \right]^{1/2} = 5.7$$

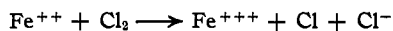
follow on comparing the derived rate laws with those experimentally established. The over-all activation energy of 7,000 measured for k can be associated almost completely with step 2. The over-all activation energy for k' was also measured as about 7,000, and since the activation energy for step (4) can be assumed to be small, that for step (3) will be about 7,000 cal. Since the activation energies for steps (2) and (3) are about the same, and since the p_z factors are not expected to differ widely, the specific rates k_2 and k_3 should be of the same order of magnitude. If for K the value of 0.06 is substituted, and for k_4 and k_5 the maximum specific rates expected on collision theory, about 10^{13} , k_2 and k_3 are calculated to be 4×10^7 and 50×10^7 , respectively.

These values for the specific rates of steps (2) and (3) and the assumptions made above fix the concentration ratio at which the transition in rate laws can be expected. In the region in which the transition takes place, the steps (4) and (5) will participate equally in chain breaking, *i. e.*, $k_4(\text{Cl})(\text{C}_2\text{O}_4^-) = k_5(\text{Cl})^2$. Making use of the assumption that k_4 and k_5 are equal, it follows that $(\text{Cl}) = (\text{C}_2\text{O}_4^-)$ at the critical region. Substituting this relation and the values calculated above for k_2 and k_3 in the equation for the steady state condition

$$k_2(\text{Cl})(\text{HC}_2\text{O}_4^-) = k_3(\text{Cl}_2)(\text{C}_2\text{O}_4^-)$$

the critical concentration ratio $(\text{Cl}_2)/(\text{Ox})$ is calculated to be 2.4×10^{-3} . The change is observed experimentally at $(\text{Cl}_2)/(\text{Ox})$ about 10^{-3} .

The deviations from rate law I observed for the ferric ion sensitized system must be due to effects arising from the presence of ferric ion at relatively high concentration, and implies some participation, direct or indirect, of ferric ion in the chain breaking step. The step: $\text{Fe}^{+++} + \text{C}_2\text{O}_4^- \rightarrow \text{Fe}^{++} + 2\text{CO}_2$ is eliminated as a possibility, for in this case the deviation should depend on the concentration of oxalic acid. An hypothesis which does fit the general observations made on the deviation, is that the reaction



is noticeably reversed at high ferric ion concentration, and the steady state concentration of ferrous ion is thereby increased so that chain breaking processes involving it, such as reaction with atomic chlorine become important.

VO^{++} behaves as an ideal inhibitor in the three systems investigated. A point of some interest is that the efficiency as inhibitor of a solution of VOSO_4 in 2 *M* hydrochloric acid changes with time. Thus, the solution used in the experiments on the ferrous induced reaction gave a value of 42^2 for $k_6/k_5^{1/2}$; when these experiments were repeated using the same solution of VO^{++} at the time of the photochemical work about one year later, this ratio was observed to be 111. The aging was demonstrated also by making up a new solution, and testing it from time to time.

The deviations from "ideal" inhibitor behavior observed for Mn^{++} (and other catalysts) have been explained elsewhere.² The higher efficiency observed for Mn^{++} in the ferric sensitized as compared to the direct photoreaction suggests that the step $\text{Fe}^{++} + \text{Mn}^{+++} \rightarrow \text{Fe}^{+++} + \text{Mn}^{++}$ plays an important part in regenerating the inhibitor, and thus enhances the rate of the chain breaking step involving Mn^{+++} over that of the chain continuing step.

Summary

The kinetics of the photochemical reaction of chlorine and oxalic acid, direct and ferric-ion sensitized, have been investigated. The rate laws, activation energies and the effects of inhibitors have been compared with those observed in the ferrous ion induced reaction.

The conclusion was reached that the same mechanism, a chain reaction involving atomic chlorine and an oxalate free radical, operates in both systems.

The following properties characterizing the intermediate atomic chlorine have been established. The value of $k_2/\sqrt{k_5}$ is 14, where k_2 is the specific rate constant for the reaction of atomic chlorine with binoxalate ion, and k_5 is the specific rate for recombination of atomic chlorine. The rate of reaction of atomic chlorine with vanadyl ion is about 8 times more rapid than it is with binoxalate ion. The activation energy of the reaction of atomic chlorine with binoxalate ion is about 7,000 calories, as it is for the complementary reaction of the oxalate radical with chlorine.

Values of about unity for the primary efficiencies in the ferrous ion induced reaction and the ferric ion sensitized photo reaction are indicated by the data; for the direct photo reaction, the primary efficiency probably lies in the range 0.7 to unity.

CHICAGO, ILLINOIS

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