I. The Efficiency of the Primary Photochemical Process for Halogens in Water. The Photochemical Reaction of Mn(II) and Cl₂[1]

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This paper presents the results of some experiments undertaken to establish the efficiency of production of chemically active species on the absorption of light by chlorine in solution. The method applied was a chemical one: reducing agents were added to the system and the quantum yield of the photo-oxidation of these substances by chlorine was measured. The reducing agents were selected to satisfy the conditions that they react efficiently with the products generated by the action of light on chlorine, and that these reactions be simple non-chain processes. Two reducing agents were used: Mn(II) in the presence of pyrophosphate ion, and Ce(III) in the presence of sulfate ion. Other observations suggest,[2] and internal evidence obtained in this study shows, that these reagents fulfill the conditions required to make the chemical method of establishing primary efficiency directly applicable. An important factor contributing to the successful use of these particular reducing agents is that the net reaction on oxidation involves a one-electron change. The products of reaction are Mn(III) as the pyrophosphate complex[3] and Ce(IV) as the sulfate complex.

transferred in part to the photoreaction cell. To follow the spontaneous reaction, a second portion was kept in a blackened cell at the temperature of the photoreaction. All manipulations of light-sensitive solutions were made in the dark or by red light.

In the experiments with Mn(II) the extent of reaction was determined by measuring the amount of Mn(III) developed. This was done iodimetrically after the chlorine was removed by reducing with Br⁻, and removing the Br₂ by extraction with carbon tetrachloride. Under the conditions of the analysis, bromine does not oxidize Mn(II), nor does Mn(III) oxidize Br⁻. In the experiments with hypochlorous acid, Mn(III) was determined spectrophotometrically using the wave length λ 7500 Å. The progress of the photoreaction of cerous ion and chlorine was followed by determining Ce(IV) iodimetrically.

The intensity of the light source was measured using the uranyl sulfate–oxalic acid actinometer.[5] The light beam was calibrated from time to time since its intensity was observed to decrease gradually as the lamp aged.

Results of Measurements of Extinction Coefficients.—Some values for the extinction coefficients of chlorine under various conditions, and for HOCl, are presented in Table I.

The values of α for chlorine at 0.6 M HClO₄ and 0.3 M NaCl agree closely with published values.[6] The absorption under these conditions can be attributed almost entirely to Cl₂, since the hydrolysis is negligible, and Cl₃⁻ represents only

TABLE I

VALUES OF THE DECADIC EXTINCTION COEFFICIENTS α(L. MOLE⁻¹ CM.⁻¹) FOR CHLORINE AND FOR HYPOCHLOROUS ACID

Conditions	NaCl, M	3200	3400	3650	3800	4000	4200	4400	4600
					Values of α at various λ's				
Cl₂, 0.6 M HClO₄, 25°	0.3	83	66.5	26.5	12.5	4.90	2.36	1.16	0.48
Cl₂, 0.6 M HClO₄, 25°	2.9	131.5	106.5	41.5	19.0	6.60	2.68	1.20	0.48
α_{Cl_2} at 25°/α_{Cl_2} at 0°	0.3		1.00	1.025	1.06	1.07	1.03		
HOCl at 25°	None	12.5	4.30	0.841	0.358	0.154	0.071		

Experimental

Apparatus.—A 100-watt G. E. A-H4 mercury arc lamp, operated at constant voltage was used as the source of light. The light beam was well defined and slightly convergent, and covered about one-third of the area of the front face of the reaction cell. The rear window of the cell was blackened to minimize back reflection. All experiments were performed at controlled temperature, with stirring of the cell contents.

The measurements of light absorption were made with a Beckman spectrophotometer. For the measurements which required a constant temperature, a thermostated cell compartment[4] was used.

Procedure.—For each experiment appropriate amounts of A. R. Na₄P₂O₇·10H₂O and NaCl were weighed out and dissolved in dilute perchloric acid. Mn(ClO₄)₂ was then added and more acid and water as needed to adjust to the desired pH and final volume. Chlorine was bubbled into the solution and the completed reaction mixture was

about 5% of the total chlorine. The increase in absorption coefficient as the concentration of chloride ion is raised shows that Cl₃⁻ is more strongly absorbing than is Cl₂. At 2.9 M NaCl, about 36% of the total chlorine is calculated to be present as Cl₃⁻, if the value of 0.19 is used for the quotient[7]

$$k_{Cl_3^-} = (Cl_3^-)/(Cl_2)_{aq}(Cl^-)$$

Some data on the variations of the extinction coefficient of $\Sigma(Cl_2)$ with (NaCl) at λ 3650 Å. are presented in Table II. The values of $\alpha_{Cl_3^-}$ were calculated from the data setting $\alpha_{Cl_2} = 24.3$, using the value 0.19 for the Cl₂–Cl₃⁻ equilibrium quotient. The rough constancy of the values of $\alpha_{Cl_3^-}$ thus calculated shows that our spectrophotometric data are consistent with the data of Sherrill and Izard; however, they are not

(1) Described in part at the Symposium on Elementary Processes in Reaction Mechanisms, April, 1949, San Francisco, Calif.

(2) Taube, THIS JOURNAL, 65, 1876 (1943); ibid., 68, 611 (1946); ibid., 69, 1418 (1947).

(3) Watters and Kolthoff, ibid., 70, 2455 (1948).

(4) Bell and Stryker, Science, 108, 415 (1947).

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

(6) Fergusson, Slotin and Style, Trans. Faraday Soc., 32, 956 (1936).

(7) Sherrill and Izard, THIS JOURNAL, 53, 1667 (1931).

TABLE II

VARIATION OF THE DECADIC EXTINCTION COEFFICIENT OF CHLORINE WITH SODIUM CHLORIDE CONCENTRATION AT λ 3650 Å., TEMP.. 25, $(HClO_4) = 0.5\ M$

(NaCl)	0.15	0.655	1.106	2.40	4.0
$\alpha_{\Sigma Cl_2}$ (exp.)	25.6	28.6	30.3	39.6	43.8
$\alpha_{Cl_3^-}$ (calc.)	69	64	59	70	69

precise or extensive enough to be considered as an independent check of $K_{Cl_3^-}$. An effort was made to fix the value of $\alpha_{Cl_3^-}$ more precisely by examining solutions at very high chloride concentration. $\alpha_{\Sigma Cl_2}$ in concentrated HCl was observed to be 46 ± 2, and in 12 M LiCl, 58 ± 5. It is evident from these data, and from an additional observation that LiCl but not HCl exerts a strong salting out effect on chlorine, that specific salt effects are very important in these concentrated solutions.

The molar extinction coefficients for Mn(III) in various solutions at λ 3650 Å. and 25° are as follows: at 0.1 M Na$_4$P$_2$O$_7$, pH of 2, 21.1; at 0.2 M Na$_4$P$_2$O$_7$, pH of 2, 24.2; at 0.1 M Na$_2$P$_2$O$_7$, pH of 2, 2.4 M NaCl, 26.5; in concentrated HCl, 2350.

Calculation of the Quantum Yield.—The quantum yield, ϕ, is defined as the number of molecules of chlorine reacting per quantum of light absorbed. In this section, only the corrections applied for various complicating factors are discussed, since the remainder of the quantum yield calculations follow in an obvious manner from the data.

A correction for the thermal change was made by subtracting the effect due to it, from the total change. The thermal and photochemical changes[8] appear to be independent, since the thermal rate, but not the photochemical rate, was observed to be sensitive to trace impurities. Duplicate experiments, which differed only in the source of pyrophosphate, showed thermal rates differing almost by a factor of 2. It should be noted (cf. Table III) that in all but four of the experiments, the thermal change was less than 12% of the total change.

A correction was applied for the internal filter effect of Mn(III). This correction amounted to only 2% for the most extreme case at λ 3650 Å. (Expt. 11) but was 20% in the most extreme case at λ 4360 Å. (Expt. 23). A special experiment with Mn(III) in concentrated HCl (and without added pyrophosphate) showed that absorption of light by the manganichloride complex produced no appreciable chemical effect.

Finally, corrections were applied for the effects produced by hydrolysis of chlorine. These are significant only in the experiments at low (Cl$^-$). The distribution of the absorbed light between Cl$_2$ and HOCl can readily be taken into

(8) Some observations on catalysis of the reaction of Cl$_2$ and Mn-(II) were reported by Ibers and Davidson, THIS JOURNAL, 72, 4744 (1950).

TABLE III

QUANTUM EFFICIENCY OF THE REACTION OF CHLORINE AND MANGANOUS ION

pH adjusted to 1.85, except in experiments 8 and 19

No.	Temp., °C.	(Cl$^-$)	(Pyroph.)	Av. (Mn^{++}) × 10^3	Σ(Cl$_2$) × 10^2	% hyd.[a]	Dark. % total	ϕ
				At λ 3650 Å.				
1	25.5	0.150	0.200	4.74	4.01	26.4	8.3	0.188
2	24.5	.300	.200	5.42	3.78	14.6	11.0	.202
3	24.4	.655	.100	2.63	3.79	7.0	12.4	.258
4	24.4	1.116	.100	2.63	3.22	3.5	9.6	.298
5	26.8	2.40	.100	2.28	3.41		2.9	.392
6	24.4	2.40	.100	2.28	2.75		3.6	.385
7	24.9	4.00	.050	2.23	2.61		1.5	.451
8	24.4	HCl[d]	None	3.30	6.04		0	.62
9	2.8	0.150	0.200	4.64	6.51	12.0	4.5	.124[b]
10[c]	2.8	.150	.200	4.66	2.93	11.0	5.0	.123
11	2.3	.150	.200	4.67	2.14	12.9	2.2	.134
12	2.8	.300	.200	4.63	7.59	5.1	4.0	.142
13	2.9	.655	.200	4.55	5.91	2.8	5.2	.183
14	3.1	1.11	.200	4.49	3.87		5.8	.223
15	2.4	1.11	.050	4.45	8.65		1.0	.225
16	2.6	1.55	.200	4.48	5.90		2.9	.247
17	2.4	2.40	.100	2.27	5.98		1.8	.325
18	2.4	3.50	.050	2.23	5.42		1.6	.393
19	2.8	HCl[d]	None	3.19	11.25		0	.54
				At λ 4360 Å.				
20	24.5	0.186	0.200	5.4	4.55	22	10.6	.119
21	24.5	.186	.200	5.4	4.78	22	10.1	.113
22	24.5	.186	.200	2.29	5.43	22	7.4	.120
23	24.3	.745	.200	5.4	3.58	5.7	20.8	.162
24	24.5	.745	.200	5.3	4.14	5.7	38.6	.155
25	3	.186	.200	5.53	6.52	10.6	3.8	.071
26	2	.745	.200	5.36	5.75	2.3	5.6	.104
27	3	1.216	.200	5.54	2.76		20.2	.143

[a] The % hydrolysis has been entered only for experiments in which it exceeds 2%. [b] In this experiment, the stirrer stopped for a time. Other experiments have shown that the quantum yield is reduced if the solutions are not stirred. The effect is probably due to the high concentration of manganic ion built up near the front window of the cell, much of the light then being absorbed by manganic ion and consequently wasted. [c] 0.78 M NaClO$_4$ added. [d] Concentrated HCl used.

account since the corresponding extinction coefficients were measured, and the equilibrium constant for hydrolysis is sufficiently well known. The contribution to the total change by the photoreaction of HOCl with the reducing agent was also allowed for. The correction was always small, amounting to only 2% of the total in the most extreme case.

The results proved, at worst, to be reproducible to within 5% of the mean. The data obtained at λ 3650 Å. are estimated to be accurate to within 5 to 10%. The data obtained at 4360 Å. are considered to be accurate to about 15%; both precision and accuracy are less at this wave length since most of the corrections to ϕ were relatively greater.

Results and Conclusions

Cl$_2$ and Cl$_3^-$ as Absorbing Species.—The results obtained for the photoreaction with Mn(II) as the reducing agent are presented in Table III. The conclusions about the rate law for the reaction which follow from the data are:

ϕ a, is independent of (Mn(II))—*cf.* No. 20–22

b, is independent of (Cl$_2$)—*cf.* No. 9 and 11

c, is independent of (Σ pyrophosphate)—*cf.* No. 14 and 15

d, is independent of light intensity[9]

e, decreases slightly as ionic strength increases— *cf.* No. 10 and 11

f, but increases as the concentration of chloride ion increases.

The data obtained with cerous ion as the reducing agent are presented in Table IV. It is evident that in this system also the quantum yield is independent of the concentration of the reducing agent, and that it increases as the chloride ion concentration increases.

TABLE IV

QUANTUM EFFICIENCY OF THE REACTION OF CHLORINE WITH CEROUS ION AT λ 3650 Å.; TEMP., 2.5°; (H$_2$SO$_4$), 0.16 M; (MgSO$_4$) = 0.481 M

No.	(Cl$^-$)	Av. (Ce^{+++}) $\times 10^2$	(Cl$_2$) $\times 10^2$	ϕ
1	0.150	11.47	5.87	0.129
2	0.150	2.44	4.45	.126
3	1.106	11.47	6.62	.207

In Fig. 1 the quantum yields for both systems are shown plotted against the concentration of chloride ion. A significant observation is that the quantum yield for the photoreaction with Ce-(III) as the reducing agent agrees within experimental error with that measured in the Mn(II) system. This observation, together with the fact that ϕ is independent of the concentration of reducing agent, proves that the chemically active species generated by the action of light on Cl$_{2aq}$ are completely consumed by the reducing agents, and that secondary thermal processes are not rate determining. It therefore appears fairly certain that the efficiency of the primary photochemical act is measured by the observed quantum yields.

The primary efficiencies for Cl$_{2aq}$ under various conditions as indicated by these experiments are as follows: at λ 3650 Å., 0.17 and 0.12 at 25 and 3°, respectively; at λ 4360 Å., 0.10 and 0.055 for the same respective temperatures. An interesting observation is the increase in primary efficiency with the concentration of chloride ion. However, even at the highest chloride concentrations attainable in aqueous solution (*cf.* No. 19, Table III), the primary efficiency is considerably below unity. The increase in ϕ with concentration of chloride ion can be ascribed in part at least to a higher primary efficiency for the species Cl$_3^-$ which develops as chloride is added. This interpre-

(9) This conclusion may be inferred by comparing the results obtained in No. 9 and 11. In No. 11, 90% of the light was absorbed in 1.85 cm. of path length; in No. 9, the same number of quanta were absorbed in 0.6 cm. of path. Despite this difference in average rate of absorption of quanta per unit volume, ϕ for both experiments is the same within experimental error. The conclusion is supported by the fact that in the analogous but more manageable system containing Br$_2$ instead of Cl$_2$, ϕ has been shown to be independent of intensity by direct variation of the light flux.
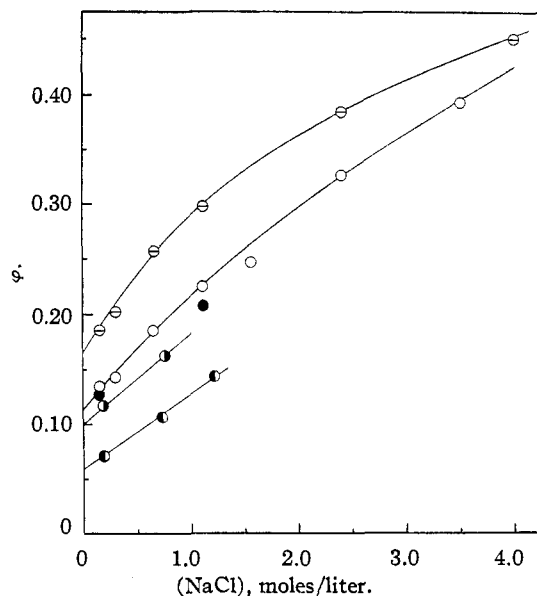

Fig. 1.—Variation of quantum yield with concentration of sodium chloride. Data presented are for the photoreaction of chlorine with Mn(II) and Ce(III):

Symbol	Reducing agent	λ, Å.	Temp., °C.
⊖	Mn(II)	3650	24.5
O	Mn(II)	3650	2.5
◑	Mn(II)	4360	24.5
◖	Mn(II)	4360	3
●	Ce(III)	3650	2.5

tation is supported also by the results of photochemical studies with iodine[10] and bromine[11] which show that the complexes I$_3^-$ and Br$_3^-$ utilize light more efficiently than do the corresponding halogens. Interpreting the data in this way yields for the primary efficiency for Cl$_3^-$ at 25° and λ 3650 Å. the following values: 0.50 at 1.11 M NaCl, 0.55 at 2.4 M NaCl and 0.58 at 4 M NaCl.

The values of the primary efficiency for Cl$_3^-$ calculated as above reveal a trend. This trend would presumably be more striking were it not for decrease in ϕ produced by the increase in ionic strength. A similar trend is much more strikingly displayed by data obtained in analogous systems containing Br$_2$ or I$_2$ instead of chlorine. In these systems absorption of light by the complexes Br$_3^-$ and I$_3^-$ is complete at relatively low concentrations of halide ions; however, the quantum yields continue to increase with halide ion concentration even beyond the concentration region in which Br$_3^-$ and I$_3^-$ absorb essentially all the light. Further discussion of the effect of Cl$^-$ and discussion of the effect of changes in wave length and temperature on the primary efficiency for chlorine will be deferred until the results for the analogous systems are presented.

(10) Durrant, Griffith and McKeown, *Trans. Faraday Soc.*, **34**, 389 (1938).

(11) Griffith, McKeown and Winn, *ibid.*, **29**, 386 (1933).

Hypochlorous Acid as the Absorbing Species.

—A few experiments (*cf.* Table V) were performed with hypochlorous acid as the absorbing species and Mn(II) as the reducing agent. These results were useful in correcting for the contribution by this path to the change observed in the chlorine experiments.

TABLE V

QUANTUM YIELD OF THE PHOTOCHEMICAL REACTION OF HYPOCHLOROUS ACID AND MANGANOUS ION

λ 3650 Å.; pyrophosphate concn., 0.200 M; pH 2

No.	Temp.	Av. (Mn^{++}) $\times 10^3$	(HOCl)	Dark, % total	ϕ
1	24.6	4.57	0.1263	31.0	0.246
2	24.6	4.56	.0954	26.1	.242
3	2.5	4.54	.1519	22.5	.160

Although the data are much less complete than the chlorine system, it seems fairly safe to interpret the values of ϕ observed as measuring the primary efficiency for HOCl + $h\nu$. The value of 0.25 suggested by the data for 25° and λ 3650 Å. may be compared with the values obtained by Young and Allmand[12] for the quantum yield of the photodecomposition of HOCl under the same conditions. The variation of the quantum yield for the photodecomposition with concentration, and the fact that the quantum yield can rise above unity shows that secondary thermal processes are to some extent rate determining. At 37 × 10⁻³ M HOCl, $\phi_{decomp.}$ was observed to be 1.9. This value compared to the value of 0.25 suggested by our data for the primary efficiency,

leads to the conclusion that the chain length for the photodecomposition is 8 under the indicated conditions.

Summary

The photochemical reactions: chlorine with manganous ion in the presence of pyrophosphate, chlorine with cerous ion, hypochlorous acid with manganous ion in the presence of pyrophosphate, have been studied in water solution and their quantum yields measured under a variety of conditions.

The quantum yield of the reaction of chlorine and manganous ion is independent, over a considerable range, of the concentration of manganous ion, chlorine, pyrophosphate ion and of the rate of light absorption. It increases as the chloride concentration increases, as the temperature increases, and as the energy per quantum increases. The quantum yield for the reaction of chlorine and cerous ion is within experimental error the same as that observed for the Cl₂–Mn(II) system.

The conclusion is reached that the observed quantum yields measure the primary efficiency for the production of chemically active species by the interaction of chlorine with a light quantum. This primary efficiency at λ 3650 Å. and 25° increases from 0.17 at low chloride to 0.62 in concentrated hydrochloric acid. At 3°, the values increase from 0.12 to 0.54 over the same range of chloride concentration.

For hypochlorous acid, a primary efficiency of 0.25 at 25° and λ 3650 Å. is indicated by the data.

(12) Young and Allmand, *Can. J. Research*, **27B**, 318 (1949).

Diphenylgermane and Dihalodiphenylgermane

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The usual procedure for preparing halogen-substituted alkylgermanes has been to prepare the tetraalkyl compound and halogenate it under conditions that would yield the maximum amount of the particular halogermane desired. The resulting mixture of mono-, di-, tri- and tetra-halogermanes is then fractionated.

The separation of dibromodiphenylgermane from tribromophenylgermane by fractionation is difficult due to the similarity of their physical properties. The halogermanes are easily reduced and since triphenylgermane and diphenylgermane differ markedly in their boiling points it was decided to subject the mixture obtained after halogenation to a general reduction reducing

all of the various alkyl halogermanes to the corresponding alkylgermanes which then should be easily fractionated. The procedure was surprisingly successful. Reduction was accomplished by the use of lithium aluminum hydride.[2] When the mixture was subjected to fractionation, it was found that almost pure diphenylgermane could be obtained from a single distillation by the use of a short fractionating column.

Since the diphenylgermane is readily converted to dibromodiphenylgermane by simple bromination, a relatively easy laboratory method for the preparation of this useful compound is now available.

Diphenylgermane has not been described in the literature. Kraus and Brown[3] attempted to prepare the compound by treatment of Ph₃GeNa