coe. We do not check, however, the high value for the California sample. It is possible, of course, that some variation in the isotopic content of boron may occur within the California deposits. This possibility is being investigated.

## Discussion

The boron samples investigated to date are all from secondary geological deposits with the possible exception of the boric acid vapors from Tuscany, which are of volcanic origin. Even in this case fractionation may occur in the vaporization process. Laboratory experiments are being carried out to determine the isotope fractionation, if any, in the steam distillation of boric acid. Other samples of boron from primary geological deposits are being collected. These include Tourmaline which contains 1–2% of boron and is a volcanic mineral. Finally, further secondary samples will be investigated to determine the variation in isotopic content of boron in different layers and at different depths in various California deposits.

**Acknowledgments.**—We wish to thank W. J. Whitehouse who first suggested this investigation and collected the samples, and M. Lounsbury who assisted with some of the mass spectrometer measurements. Further, we wish to thank the American Potash and Chemical Company, the Pacific Coast Borax Company, and Consolidated Borax, Limited, for their information regarding the mineral and geological deposits of boric acid samples. Finally we wish to acknowledge financial assistance from the National Research Council of Canada.

## Summary

A mass spectrometer investigation has been made of the isotopic constitution of boron obtained from various mineral deposits in the earth's crust. This investigation involved the use of boron trifluoride gas which was prepared from boric acid. Both the $BF_2^+$ and $B^+$ ions were considered in the determination of the $B^{11}/B^{10}$ ratios. Automatic recording equipment used with the mass spectrometers made it possible to determine the relative ratios of $B^{11}/B^{10}$ for the different samples with a precision of ±0.1%, and an absolute accuracy of ±0.5% or better.

The ratio of $B^{11}/B^{10}$ was found to vary from 4.27 to 4.42, or about 3.5%, depending on the source of the boron. Corresponding variations in the chemical atomic weights have been calculated using the latest mass data for the isotopes.

HAMILTON, ONTARIO, CANADA RECEIVED MARCH 19, 1948

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Photolysis of Persulfate. II. The Quantum Yield in Water and the Effect of Sodium Chloride in Dilute Alkaline Solution

BY LAWRENCE J. HEIDT, JOSEPH B. MANN AND HILDA R. SCHNEIDER

The persulfate ion, $S_2O_8^=$, in water absorbs ultraviolet light and is photochemically reduced to sulfate ions.[1,2,3] The over-all reaction is $S_2O_8^= + h\nu + H_2O = 2SO_4^= + {}^1/_2O_2 + 2H^+$. It is not known whether the oxygen produced in the reaction was originally part of the water, persulfate or hydroxyl ion. Hydrogen peroxide has not been found in any of the photolyzed solutions[3] so it is probably not an intermediate product in the photochemical reaction although it is made by the thermal hydrolysis of persulfates. The photochemical oxidation of the oxygen, therefore, appears to be the transfer of two electrons from divalent oxygen to the photon-activated persulfate anion.

The quantum yield, $\phi$, of the reaction has been measured by R. H. Crist[2] and by L. J. Heidt[3] over a wide range of conditions. The value of $\phi$ is a maximum in neutral solution; it decreases rapidly as the acidity is increased but alkali has a smaller depressing effect. Maximum quantum yields of unity[2] and six-tenths[3] have been reported for the reaction produced by light of $\lambda$ 254 m$\mu$.

The value of unity reported by Crist[2] was obtained by measuring the sulfate produced in the reaction by precipitating and weighing it as barium sulfate. His quantum yields would be larger than the real values if other material came down with the barium sulfate.

The value of six-tenths reported by Heidt[3] was obtained by measuring the change in the concentration of persulfate. This was done by reducing the persulfate in a mixture of sulfuric and phosphoric acids with excess ferrous iron followed by titration of the excess ferrous with permanganate solution. His quantum yields would be smaller than the real values if any product of the reaction oxidized ferrous iron. This product was not hydrogen peroxide because separate tests[3] showed it to be absent; neither was it oxygen because it was shown that air[1] and oxygen[3] did not affect the quantum yields obtained by this method. However, if chloride ions contaminated the solutions, hypochlorite is a possible product of the reaction and would oxidize the ferrous iron thereby lowering the quantum yields. The laboratory supply of

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[1] J. L. R. Morgan and R. H. Crist, THIS JOURNAL, **49**, 960 (1927).

[2] R. H. Crist, *ibid.*, **54**, 3939 (1932).

[3] L. J. Heidt, *J. Chem. Phys.*, **10**, 297 (1942).

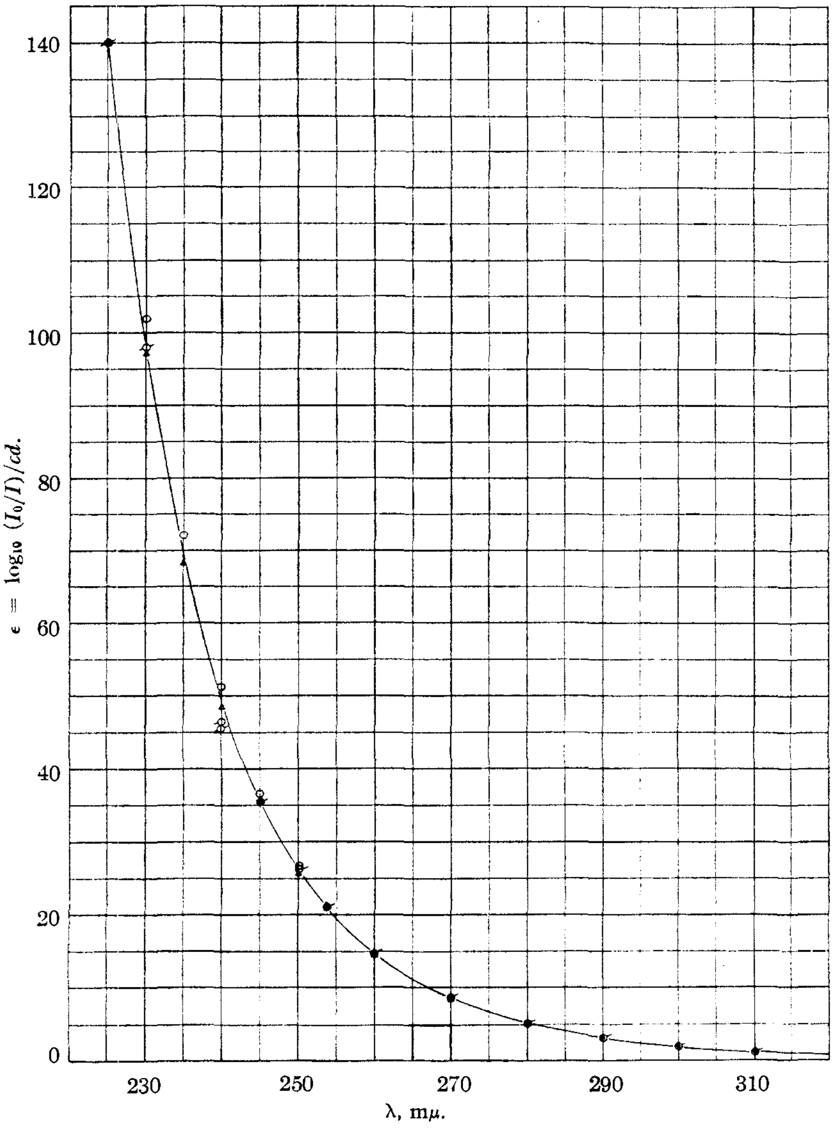

Fig. 1.— -O-, 0.003 *M* $Na_2S_2O_8$ in 0.1 *M* NaOH; O, 0.015 *M* $Na_2S_2O_8$ in 0.1 *M* NaOH; O-, 0.045 *M* $Na_2S_2O_8$ in 0.1 *M* NaOH; △, 0.015 *M* $Na_2S_2O_8$ in 0.1 *M* NaOH + 4 *N* NaCl; *c*, moles of $Na_2S_2O_8$ per liter of solution at 25 ± 2°; *d*, path length (in cm.) of light in the solution.

distilled water sometimes contains small amounts of chloride.

The measurements of the light fluxes in both researches employed methods based on calibrations in terms of light sources standardized by the U. S. Bureau of Standards.

The present study was made in order to determine the effect of chloride ions upon the quantum yield of the reaction in dilute alkaline solution. The study was made with monochromatic light of λ 254 mμ.

H. R. Schneider[4] was unable to obtain consistent values of $\phi$ when the persulfate was "purified" by precipitating it from dilute alkaline solution with ethyl alcohol. It was found later that the alcohol had not been completely removed from the persulfate although the masticated crystals had been repeatedly washed with distilled water.

In the present research and in the earlier work[3] no organic material of any kind was allowed to contact the persulfate or its solutions in the course of the purification or thereafter. The sodium persulfate was purified by recrystallizing it thrice from chloride-free distilled water made slightly alkaline with chloride-free sodium hydroxide. Only the middle fraction of the crystals was retained. This was masticated in distilled water and then washed on a sintered glass filter until the wash water was neutral to brom thymol blue. The final crop of purified crystals was air dried. Analysis for persulfate showed that the material was at least 99.9% pure sodium persulfate. The material was stored in the dark in glass stoppered bottles.

The apparatus and experimental procedures were essentially the same as in the earlier work.[3] Repeated successive photolyses of the uranyl oxalate actinometer in the three cylindrical 11-ml. clear fused quartz reaction cells showed that the cells had the same transparency to light of λ 254 mμ within ±0.5%. It was also found that when the cell was surrounded with a Pyrex test-tube, the latter absorbed more than 99% of the actinic light that produced photolysis in either the actinometer or persulfate solutions.

The analytical methods were entirely volumetric. Corrections were made for differences between the volumes delivered at room temperature and 20°.

The persulfate was determined by Schwicker's[5] method which employs excess ferrocyanide to reduce the persulfate. In the earlier work[3] excess ferrous sulfate was employed for this purpose. The excess ferrocyanide was determined at room temperature by titration in dilute sulfuric acid

(4) Hilda Rose Schneider, Master's Thesis, 1942, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

(5) Schwicker, *Z. anal. Chem.*, **74**, 433 (1928).

TABLE I

QUANTUM YIELDS, $\phi$, OF THE REACTION: $S_2O_8^{=} + H_2O + h\nu = 2SO_4^{=} + 0.5\,O_2 + 2H^+$ IN 0.0817 *N* NaOH AND VARYING AMOUNTS OF SODIUM CHLORIDE: $\phi = 0.011,\ \Delta(S_2O_8^{=})/E$

*E* equals the einsteins of light of λ 254 mμ absorbed by the persulfate solution at 25 ± 2°. Eleven-ml. samples were irradiated. The initial concentration of persulfate was between 0.180 and 0.186 mole per liter. An average of 9.86% of the persulfate was destroyed by photolysis. Concentrations are in moles per liter of solution at 25°.

| Run | (NaCl) | Minutes irradiated | $10^6E$/min. | $10^2 \times \Delta(S_2O_8^{=})$ | $\phi$(obs.) | $\phi_{\text{calcd.}}$ |
|---|---|---|---|---|---|---|
| 1(7) | 0.000 | 40 | 9.64 ± 1.05 | 1.91 ± 0.15 | 0.550 ± 0.020 | 0.558 |
| 2(1) | .000 | 40 | 15.22 | 3.14 | .566 | .558 |
| 3(1) | .0005 | 43 | 12.51 | 2.80 | .574 | .558 |
| 4(3) | .0010 | 30 | 13.16 ± 0.00 | 2.16 ± .02 | .602 ± .006 | .558 |
| 5(3) | .010 | 46.7 | 4.00 ± 0.26 | 1.01 ± .21 | .592 ± .022 | .558 |
| 6(2) | .100 | 50 | 3.62 ± 0.36 | .88 ± .11 | .539 ± .024 | .556 |
| [a]7(1) | 1.00 | 60 | 2.72 | .764 | .517 | .536 |
| [a]8(3) | 1.00 | 33.7 | 12.81 ± .00 | 2.05 ± .27 | .523 ± .003 | .536 |
| 9(5) | 4.00 | 30.0 | 13.18 ± .73 | 1.74 ± .26 | .484 ± .020 | .477 |

$$1/\phi_{(\text{obs.})} = (1.777 \pm 0.015) + (0.076 \pm 0.008)\,(\text{NaCl})$$

[a] These experiments confirm the earlier observation[3] that $\phi$ is independent of the light intensity.

with permanganate solution. The presence of sodium chloride in the solutions did not interfere with our analyses for persulfate.

The oxalate content of the actinometer was determined at 80° by titration, also in dilute sulfuric acid, with permanganate solution.

End-points were determined by the differential electrometric method as formerly[3]; they were reproduced to one drop of titer equivalent at best to $\pm 1.5 \times 10^{-8}$ mole of potassium permanganate.

Extinction coefficients, $\epsilon$, were obtained with a Beckman Spectrophotometer which had been previously calibrated.[6] The values of $\epsilon$ are given in Fig. 1. The term $I_0$ in the equation for $\epsilon$ attached to Fig. 1 is the intensity of the light beam transmitted by an equal depth *d* in cm. of the solvent in an absorption cell like the cell holding the solution.

The value of $\epsilon$ at λ 254 mμ for sodium persulfate is 21.2 ± 0.4; it is independent of the concentration of persulfate and it is not affected by either sodium hydroxide or chloride. Heidt[3] reported a value of 22 and Morgan and Crist[1] reported a value of 18 for $\epsilon$ at this wave length. Sulfuric acid also does not affect the value of $\epsilon$ for persulfate down to λ 230 mμ[1,3] and $\epsilon$ is the same for sodium, potassium and ammonium persulfates.[3] Thus the energy levels involved in the absorption of ultraviolet light by the persulfate ion are not perturbed by changes in the ionic strength of the solution or by hydrogen ions.

The quantum yields, $\phi$, and pertinent data are given in Table I. The data given are average values based on the number of expts. given in parentheses following the number of the run. The actinometer was 0.0017 *M* in uranyl oxalate and 0.004 *M* in oxalic acid; its quantum yield is 0.63 at 25° and increases 1.03-fold per ten degree rise in temperature.[7,8,9]

All of the photolyzed solutions absorbed at least 95% of the light of λ 254 mμ incident upon them before the light reached the stirrer, and less than 1% of this light emerged from the reaction vessel. The stirrer was a transparent fused quartz ribbon that was rotated on the axis of the cell.

The values of $1/\phi$ depend linearly upon the concentration of sodium chloride as shown in Fig. 2 by line A. The line was obtained from the data by the method of least squares. The equation for the line is given at the bottom of Table I. The probable deviation of any observed value of $1/\phi$ from the line is ±0.066.

The effect of sodium hydroxide upon $\phi$ was measured in the earlier work[3] from this Laboratory.

TABLE II

OBSERVED AND CALCULATED EFFECTS OF $OH^-$, $SO_4^{=}$, $CO_3^{=}$, $HPO_4^{=}$ AND $H^+$ UPON THE QUANTUM YIELD OF THE PHOTOLYSIS OF AQUEOUS SOLUTIONS OF PERSULFATE AT 26 ± 1° BY LIGHT OF λ 254 mμ

| Run[a] | Wt. | (NaOH) | $\phi$(obs.) | $\phi$(calcd.) |
|---|---|---|---|---|
| 7de | 2 | 0.0014 | 0.54 | 0.563 |
| 7abc | 3 | .0102 | .58 | .562 |
| 8b | 1 | .0782 | .55 | .559 |
| 8a | 1 | .0907 | .53 | .558 |
| 10 | 3 | .975 | .51 | .512 |

$$1/\phi_{(\text{obs.})} = (1.790 \pm 0.015) + (0.181 \pm 0.009)\,(\text{NaOH})$$

| Run | Wt. | (NaOH) | $(A^{--})$ | $\phi$(obs.) | $\phi$(calcd.) |
|---|---|---|---|---|---|
| 11 | 2 | 0.0892 | $0.9(SO_4^{=})$ | 0.38 | 0.385 |
| 16 | 2 |  | $1.0(CO_3^{=})$ | .42 | .373 |
| 14 | 3 |  | $0.8(HPO_4^{=})$ | .37 | .401 |
| 15 | 3 |  | $1.0(HPO_4^{=})$ | .38 | .374 |

$$1/\phi_{(\text{obs.})} = 1.78 + 0.9\,(A^{--})$$

| Run | Wt. | $(H^+) + (HSO_4^-)$ | $(H^+)$ | $\phi$(obs.) | $\phi$(calcd.) |
|---|---|---|---|---|---|
| 18 | 3 | 0.0332 | 0.028 | 0.31 | 0.266 |
| 22 | 3 | .0538 | .045 | .26 | .203 |
| 19 | 3 | .1089 | .075 | .12 | .142 |
| 20 | 3 | .2212 | .127 | .09 | .0940 |
| 21 | 3 | 1.0105 | .338 | .04 | .0393 |

$$1/\phi_{(\text{obs.})} = (1.75 \pm 0.40) + (70 \pm 2)\,(H^+)$$

[a] Run numbers are those of the earlier work.[3]

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(6) J. L. Crandall, Ph.D. Thesis, 1948, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

(7) W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930).

(8) F. P. Brackett and G. S. Forbes, *ibid.*, **55**, 4459 (1933).

(9) L. J. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

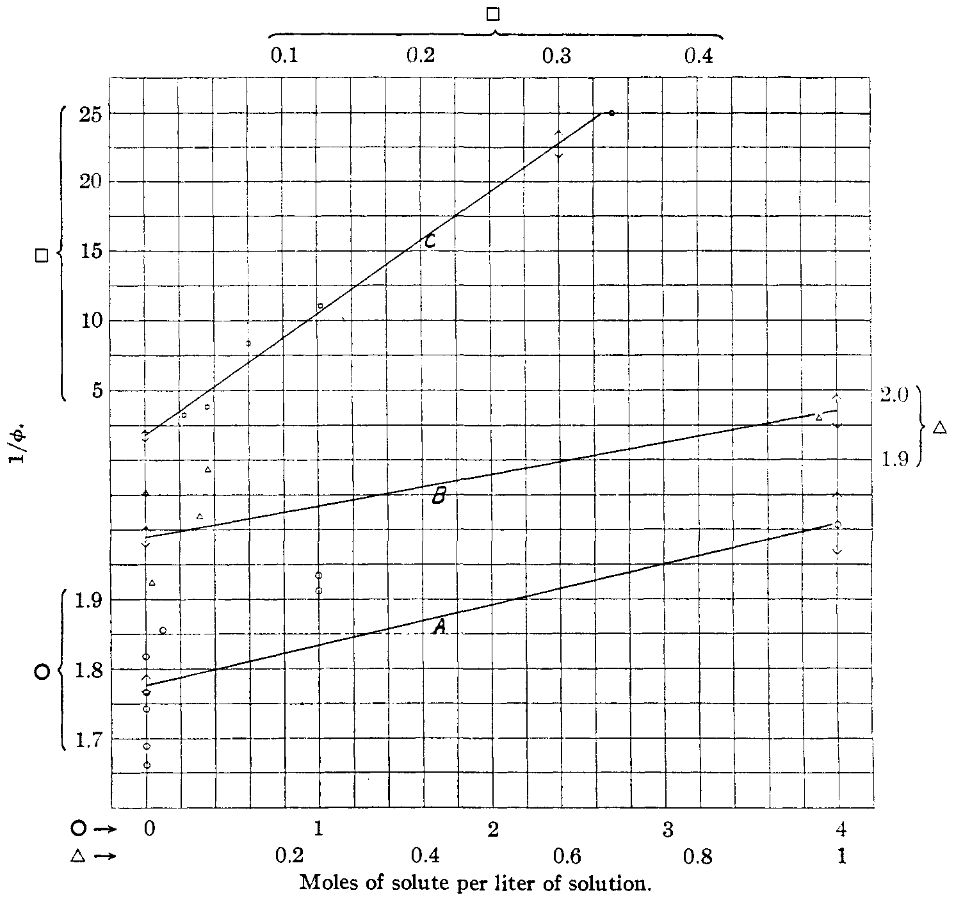

Fig. 2.—○, NaCl; △, NaOH; □, $H^+$.

The data are summarized in Table II. Again $1/\phi$ depends linearly upon the concentration of the added electrolyte as shown in Fig. 2 by line B. The equation for line B is given immediately under the data it represents. The probable deviation of any observed value of $1/\phi$ from the line is ±0.039.

The value of $1/\phi$ in 0.0815 *N* sodium hydroxide obtained in the present research by treating the data by the method of least squares is 1.777 ± 0.015 compared to 1.805 ± 0.016 in the earlier work.[3] These values agree within the limits of error and assign to $1/\phi$ a value of 1.791 in 0.0815 *N* sodium hydroxide free from chloride. This value reduced by $0.181 \times 0.0815$ or 0.015 gives a value for $1/\phi$ of 1.776, and for $\phi$ a value of 0.563 ± 0.005 rather than unity[2] in water free from all solutes except the sodium persulfate.

The effect of hydrogen ions upon $\phi$ also shows that $1/\phi$ depends linearly upon their concentration as shown in Fig. 2 by line C. The equation for line C is given under the data in Table II. The value of 1.75 ± 0.4 for $1/\phi$ when the concentration of hydrogen ion is negligible agrees within the limits of error with the corresponding value of $1/\phi$, 1.776 ± 0.015, based on the data obtained in solutions of sodium chloride and hydroxide. The concentrations of hydrogen ion, that is, $H_3O^+$, in the acid sulfate solutions were calculated from the e.m.f. data of W. J. Hamer.[10]

The effects of sulfate, carbonate and the acid phosphate anions, $A^{--}$, upon $\phi$ can be estimated roughly from the appropriate data in Table II. The problem is complicated by the hydrolysis of the anions. The quantum yields, however, for the sulfate, which is hydrolyzed to a negligible extent above *p*H 7, and the other divalent anions do not differ significantly at the same anion concentration when hydrolysis is ignored. The data give $1/\phi = 1.78 + 0.9\,(A^{--})$ when $1/\phi$ is taken as 1.78 in pure water.

The effects of all of the above species upon $\phi$ at 25 ± 2° can be brought together in one equation, namely

$$1/\phi = 1.776 + 0.076\,(\mathrm{NaCl}) + 0.18\,(\mathrm{NaOH}) + 0.9\,(A^{-2}) + 70\,(H^+)$$

Parentheses indicate moles of solute per liter of solution at 25 ± 2°. The values given in the tables for $\phi$ (calcd.) were calculated from this equation and agree with the observed values of $\phi$ within the limits of error.

In the earlier work[3] the depressing effect of hydrogen ions upon $\phi$ was attributed to deactivation

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[10] W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

of the photon-activated persulfate. Conductivity measurements gave no evidence for the formation of any weak electrolyte involving the persulfate and hydrogen ions in these solutions. The data obtained in the present research as well as the previous data can be represented by the following reactions

$$\begin{array}{ll} I & S_2O_8^= + h\nu = {}^*S_2O_8^= \\ k_1 & {}^*S_2O_8^= + H_2O = 2SO_4^= + {}^1/_2O_2 + 2H^+ \\ k_i & {}^*S_2O_8^= + M_i = S_2O_8^= + M_i + \text{heat} \end{array}$$

The equation for $\phi$ given by the above reactions is

$$1/\phi = 1 + a_2(\text{NaCl}) + a_3(\text{NaOH}) + a_4(\text{A}^{-2}) + a_5(\text{H}^+) + a_mM_m$$

The relationships between the rate constants, $k$, are $a_2 = k_2/k_1$, $a_3 = k_3/k_1$, etc. The numerical values of $a_i$ are given by the corresponding coefficients of the concentrations in the equation for $1/\phi$ derived from the data. The value of $1 + a_mM_m$ is 1.776.

Hydrogen ions deactivate the photon activated persulfate anions 55.5 $k_5/k_1$ or four thousand times more efficiently than the measured reaction utilizes the absorbed light if the above mechanism is correct.

Sodium ions do not perceptibly deactivate photon activated persulfate because $\phi$ remained constant when the concentration of sodium persulfate (hence sodium ions) was increased about fivefold.[3] The value of 0.776 for $a_mM_m$ therefore, equals $k_w/k_1$; so water is at most 0.776 as efficient in deactivating ${}^*S_2O_8^=$ as in bringing about the measured reaction.

Other mechanisms might be found which would also fit the data, but those that we have considered in which $S_2O_8^=$ is photo-dissociated into $SO_4^-$ ions or the OH radical is produced would have $\phi$ depend upon the light intensity or produce hydrogen peroxide, or both, contrary to the experimental facts. The chief objection to our mechanism is the long half life required for the photon activated persulfate ion in order to account for the large deactivating effect of hydrogen ions.

In the second reaction oxygen atoms rather than molecules would be produced initially but the mechanism of the subsequent formation of oxygen molecules would not affect the quantum yield which is based on the observed change in the concentration of the persulfate.

## Summary

1. The true value of the quantum yield for the photolysis of persulfate in water is found to be 0.567 ± 0.005 mole of $S_2O_8^=$ decomposed per einstein (6 × $10^{23}$ quanta) of light of λ 254 mμ absorbed by the persulfate in water at 25°.

2. Chloride and other ions deactivate photon activated persulfate anions. The efficiency of the deactivation decreases in the order $H_3O^+$, $A^=$, $OH^-$ and $Cl^-$. $A^=$ is $SO_4^=$, $CO_3^=$ or $HPO_4^=$. The deactivation accounts quantitatively for the depressing effects of these ions upon the quantum yields.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 15, 1948

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# Kinetics of the Thermal Chlorination of Benzal Chloride

BY HAROLD A. SCHERAGA[1] AND MARCUS E. HOBBS

The halogenation of hydrocarbons is of considerable interest from both the theoretical and practical points of view and has been the subject of many kinetic investigations. The thermal chlorination of methane[2a] and chloroform[2b] have been investigated kinetically and have given an insight into the nature of the mechanisms of these reactions. It was thought to be of interest to extend this work to aromatic substituted methanes by investigation of the chlorination of the alkyl side chain of toluene. In order to minimize the number of successive reactions that might take place in the chlorination process it seemed desirable to study the chlorination of benzal chloride, for, in this manner, it appeared that rather unambiguous information might be obtained about the ease of replacement of the last hydrogen atom of the side chain —$CHCl_2$ group.

Even in this relatively simple case there is the possibility of ring substitution, addition and/or side chain reaction. If one considers the factors determining whether a reaction will involve the side chain or the ring,[3] and the fact that the ring in benzal chloride is significantly less reactive than it is in toluene, it appears that chlorination at high temperatures, in the absence of catalysts, carriers and activating radiation, would result in a reaction that took place primarily, if not exclusively, in the side chain of an aromatic compound. That this expectation is in large measure fulfilled will be shown by the results obtained in this investigation. It might be pointed out that Mason and co-workers[4] have found that toluene may be con-

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[1] Part of a Thesis submitted by Harold A. Scheraga in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University, October, 1946. Present address: Department of Chemistry, Cornell University, Ithaca, N. Y.

[2] (a) R. N. Pease and G. F. Walz, THIS JOURNAL, **53**, 3728 (1931); (b) H. A. Taylor and W. E. Hanson, *J. Chem. Phys.*, **7**, 418 (1939).

[3] P. H. Groggins, "Unit Processes in Organic Synthesis," 3rd ed., McGraw-Hill Book Co., Inc., New York, N. Y., (1947) Chap. IV.

[4] J. Mason, *et al.*, *J. Chem. Soc.*, 3150 (1931).