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Citation: *J. Chem. Phys.* **16**, 886 (1948); doi: 10.1063/1.1747027

View online: <http://dx.doi.org/10.1063/1.1747027>

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that the coupling of a large number of CH_2 groups, which must occur in a hydrogen chain, may produce a change of dipole moment which has a component parallel to the chain axis.

If it were possible to produce planar orientation in addition to that produced by stretching, more information could be obtained about the directions of the various bonds in the crystallites. Since it is known that rolling produces planar orientation in Nylon-66, this seems a suitable material for future study, in order to develop the technique, and it is hoped to extend the treatment to other polymers. The use of completely crystalline substances also offers attractive possibilities, and here again Nylon-66 seems suitable for experiment, since crystals of it can be grown

by the controlled polymerization of hexamethylene diammonium adipate.²⁴ It is also important to re-investigate several of the polymers already described under the higher resolving power obtainable with a lithium fluoride prism, and work on these lines is now proceeding. Since this increase of resolving power is particularly marked in the 3- μ region, it is intended to make use of it to obtain more definite information about the orientation of methylene and methyl groups.

We wish to acknowledge our indebtedness to Dr. F. Happey, for taking the x-ray photographs, to Dr. C. H. Bamford, M. J. Crank and Dr. M. J. S. Dewar for helpful discussions, and to the Directors of Courtaulds Limited, for permission to publish this account.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 9 SEPTEMBER, 1948

On the Photo-Chemistry of Some Ions in Solution

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(Received April 28, 1948)

The absorption spectra of chlorate, bromate, iodate, and hypobromite ions and of hypobromous acid were measured.

The decomposition of bromate ion was investigated in the light of a mercury arc in the spectral region: 1900Å to 2600Å. The quantum yield of the decomposition is 0.19. The main decomposition reaction leads to the formation of hypobromite and molecular oxygen. The irradiation of hypobromite ions leads to the formation of bromide and bromate ions in a ratio of about 4 to 1 and to the evolution of oxygen. The decomposition of chlorate ion and iodate

ion is analogous to that of bromate. It is assumed that in all these cases the primary process of light absorption consists of the transfer of an electron to the hydration layer. In the case of halate ions, the photo-chemical reaction can be formulated as a decomposition of the complex $(\text{XO}_3^- \cdot \text{H}_2\text{O})$ to $\text{XO}^- + \text{H}_2\text{O} + \text{O}_2$; in the case of the hypobromite, as the decomposition of $(\text{XO}^- \cdot \text{H}_2\text{O})$ to $\text{X}^- + \text{H}_2\text{O} + \text{O}$. In the latter case the oxygen atoms formed are responsible for the formation of bromate.

INTRODUCTION

THE photo-chemical decomposition of ions in aqueous solution was the subject of a number of investigations.¹⁻⁴ Farkas and Farkas² have suggested that the primary process of light absorption consists of the transfer of an electron from the absorbing ion to one of the water

molecules** in the hydration layer. If we assume that during this process the water molecules in the hydration layer remain oriented and retain their potential energy, the long wave-length limit of the absorption for an anion is given by the equation

$$h\nu_0 = E_- + H_- - E\text{H}_2\text{O}, \quad (1)$$

where E_- is the electron affinity of the anion in

* This paper is part of a thesis submitted to the Senate of the Hebrew University by F. S. Klein in fulfillment of the requirements for the degree of Ph.D.

¹ E. Rabinowitsch, *Rev. Mod. Phys.* **14**, 112 (1942).

² A. Farkas and L. Farkas, *Trans. Faraday Soc.* **34**, 1113 (1938).

³ J. Weiss, *Trans. Faraday Soc.* **37**, 467 (1941).

⁴ L. J. Heidt, *J. Chem. Phys.* **10**, 297 (1942).

** Professor J. Franck recently suggested that the primary light absorption process consists of the transfer of the electron to a "conduction band" of the hydration layer. According to his view, the electron is not attached to an individual molecule, but is spread over all the oriented water molecules (private communication).

the gaseous state, H_- its hydration energy, and E_{H_2O} the energy gained when the electron is attached to the oriented water molecule. E_{H_2O} is therefore related to the electron affinity of water.

In the present communication the absorption spectra and the photo-chemical decomposition of some halate and hypohalite ions were investigated with the view to extending our experimental material in this field.

EXPERIMENTAL

The *absorption spectra* of the various ions were investigated with a small Hilger spectrograph. A hydrogen discharge lamp was used as a continuous light source. Exposures were made with solutions at various concentrations in a silica cell of 10-mm thickness with plane-parallel windows, on Agfa or Ilford plates, which were sensitized with a solution of mineral oil in light petrol. The transmittance of the exposed plates at different wave-lengths was determined by a "Moll" recording microphotometer. With the aid of appropriate intensity marks, the molecular extinction coefficients $\epsilon = [\log_{10}(I_0/I)]/cd$ (c = conc. in mols per liter, d = thickness of absorbing solution in cm) were calculated in dependence of the wave-lengths according to the usual procedure.

As *light source*, a mercury lamp similar to that described by L. Farkas,⁵ was used. Figure 1 schematically illustrates the experimental arrangement. The diameter of the innermost tube (*A*) is 20 mm. The arc of 20-cm length operates on 35 v and 11.5 amp.

Distilled water, circulated through the first concentric tube (*B*) by an air-lift pump (*L*), is used for cooling. The temperature of the distilled water is controlled by the thermoregulator (*R*) and the cooler (*S*) through which ice water circulates by means of the pump (*P*). This pump is set in motion and shut off by the thermoregulator *R* and a suitable relay. Thus the temperature of the reaction vessel (*C*) can be kept constant to within $\pm 0.2^\circ\text{C}$ in the range of 15° to 38°C .

The second (*C*) and third (*D*) concentric-cylindrical vessels of volumes 113 ml and 195 ml,

respectively, are fitted with inlets and outlets of standard taper joints. The upper outlet of vessel (*C*) is connected with a gas collecting system, built on the principle of a Töpler pump. Water serves as the compressing liquid, and the amount of evolved gas can be measured with an accuracy of ± 1 percent in a graduated burette. Generally, a time lag occurs in the evolution of the gas, which is due to supersaturation of the irradiated solution with the gas formed. The outer vessel (*E*) serves to maintain a constant temperature within the reaction vessels (*C*) and (*D*).

The quantum output of the arc was measured before and after each irradiation experiment: Vessel (*C*) was filled with distilled water (or reference solution), and generally after 30

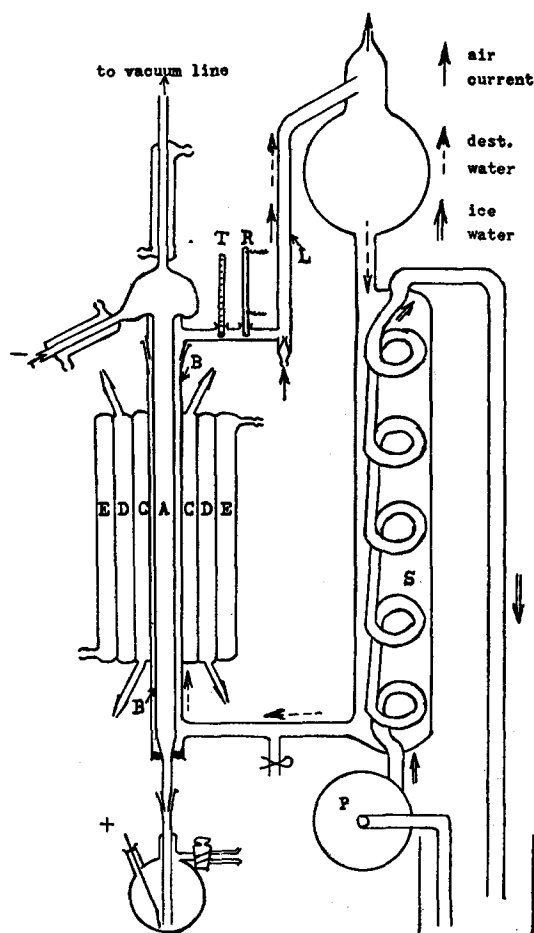


FIG. 1. View of mercury lamp and cooling system.

- | | | | |
|---|--------------------|---|------------------|
| A | arc tube | L | air lift pump |
| B | dest. water cooler | P | circulation pump |
| C | reaction vessel I | R | thermoregulator |
| D | reaction vessel II | S | ice water cooler |
| E | cooler | T | thermometer |

⁵ L. Farkas, *Zeits. f. physik. Chemie* **B83**, 23 (1933).

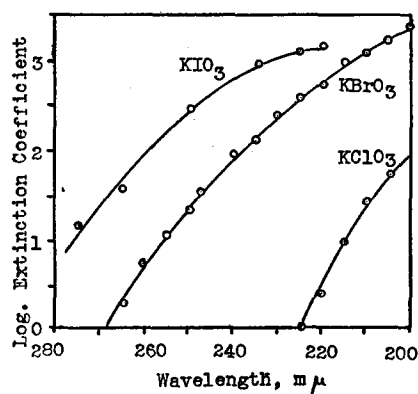


FIG. 2. Curve giving the log extinction coefficient ϵ as a function of the wave-length for chlorate, bromate, and iodate ions in aqueous solution.

minutes of irradiation the extent of decomposition of 1 *M* chloroacetic acid in vessel (*D*) was determined by titrating, according to Volhard, the chloride ions produced. For the calculation of the number of quanta absorbed, Smith and Leighton's⁶ value for the quantum yield of 0.35 at 30°C was accepted. The total light intensity of the arc in the region of 1900Å to 2600Å corresponds to about 10^{19} quanta sec.⁻¹. The light intensity of the arc first decreased rapidly (10 percent in the first three hours) and then more slowly (18 percent in the next ten hours). This was caused by the formation of a metallic silicon coating on the walls of tube (*A*). After 30 hours of use, the total decrease amounted to about 50 percent, and then the tube was taken out for cleaning. The silicon could be removed by heating the inner tube in a current of air. Because of uncontrollable changes in the light intensity, the quantum output was estimated with an error of ± 5 percent.

ANALYTICAL

The concentration of bromate, or the sum of bromate and hypobromite, was determined by

TABLE I. Hydrogen content of the evolved gas.

Expt.	Volume (ml)	Gain in weight (μg)	Percent hydrogen content
258	76.6 gas	225	0.35
259	70.0 gas	246	0.40
blank	25.0 air	9	—

⁶ R. N. Smith, W. G. Leighton, and P. A. Leighton, *J. Am. Chem. Soc.* **61**, 2299 (1939).

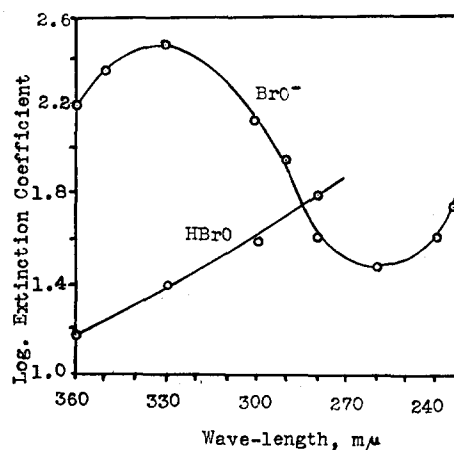


FIG. 3. Curve giving the log extinction coefficient ϵ as a function of the wave-length for hypobromite ion and hypobromous acid in aqueous solution.

adding an excess of potassium iodide to the acidified solution and titrating with 0.1 *N* sodium thiosulfate. Iodate, hypochlorite, hypobromite, and hypoiodite were estimated according to Chapin.⁷ The chlorate was determined by adding an excess of ferrous sulfate to the acidified solution, heating the mixture, and titrating the residual ferrous ion according to Zimmermann-Reinhardt.

The gas evolved from the solution was analyzed for oxygen, hydrogen, and bromine.

The light absorbed by the irradiated solution was measured according to the method described by Farkas.⁵

RESULTS

The Absorption Spectra

The light absorption by chlorate, bromate, and iodate ions is given in Fig. 2. The absorption curves of these ions are similar to those of other ions (I^- , Br^- , OH^-) which have been interpreted as electron transfer spectra. The increase of the extinction coefficient with decreasing wave-length is less steep in the present cases than that observed in the case of the halide and hydroxyl ions. The "absorption limits" corresponding to $\epsilon = 1$ are for:

ClO_3^- : 2250Å, BrO_3^- : 2700Å, and IO_3^- : 2900Å.

The absorption curve of hypobromite ion, given in Fig. 3, shows a strong resemblance to

⁷ R. Chapin, *J. Am. Chem. Soc.* **56**, 2211 (1934).

TABLE II. Dependence of the photo-decomposition of bromate on irradiation time (initial concentration of KBrO_3 : $0.0925M$; 30°C).

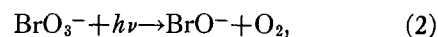
Expt.	Irrad. time (min.)	Bromate ions de-compos.	Hypo-bromite formed	Oxygen molec. formed	Quanta absorb. by sol.	Quantum yield Φ	Percent convers. of bromate	Percent hypo-bromite yield	Percent oxygen yield
		per second $\times 10^{-18}$							
122	7.5	1.51	1.10	1.75	8.42	0.18	11	73	102
121	15	1.43	1.04	1.44	8.27	0.17	20	73	(89)
123	30	1.19	0.56	1.52	8.13	0.15	33	47	100
120	60	1.11	0.22	1.50	8.28	0.13	62	20	96
119	120	0.81	0.01	1.21	7.54	0.11	91	0.6	98

that of nitrate ion.¹ The spectrum of undissoiated hypobromous acid is also given in Fig. 3.

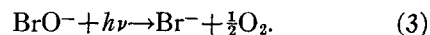
The Photo-Decomposition of the Bromate Ion

When dilute ($0.002M$ to $0.2M$) potassium bromate solutions are irradiated, they evolve gas, and the concentration of bromate decreases. Chemical analysis shows that hypobromite and bromide ions are formed. The absence of bromite in the irradiated solution was shown in a special experiment. In Fig. 4 the concentration changes of these three ions during a typical run are given. Since the hypobromite concentration passes through a maximum and the bromide concentration increases steadily, it is evident that hypobromite is an intermediate product of the decomposition. Furthermore, since the initial rate of

decomposition of bromate ($-\Delta\text{BrO}_3^-/\Delta t$) and the initial rate of the hypobromite formation ($\Delta\text{BrO}^-/\Delta t$) are equal, the main processes taking place during the irradiation can be represented by:



and



The evolved gas contains 99.2 to 99.5 percent oxygen, accompanied by a small amount of hydrogen. In two experiments the hydrogen content was quantitatively determined in an apparatus similar to that used for the micro-combustion of organic compounds. The gas, dried over magnesium perchlorate, passed first through an electrically heated capillary tube filled with palladinized asbestos. The water formed was absorbed in a tube filled with mag-

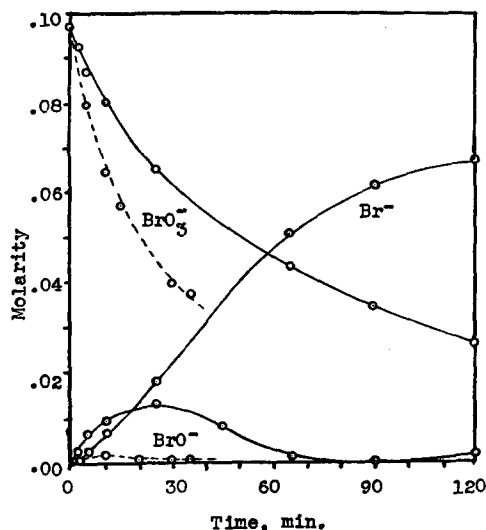


FIG. 4. Photo-decomposition of bromate. Change of concentration of bromate, hypobromite, and bromide with time.

— ammonium ions absent.
 - - - - ammonium ions present.

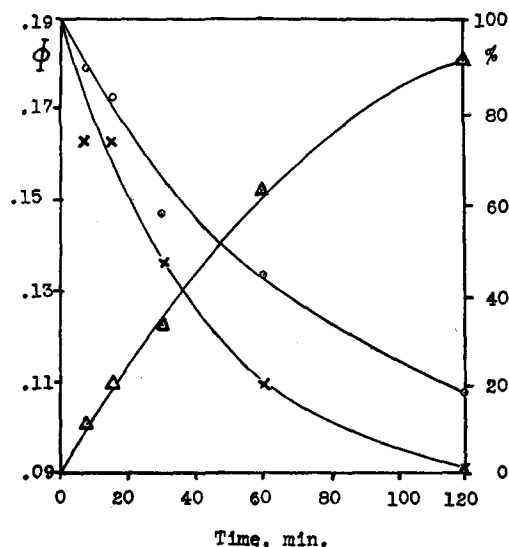


FIG. 5. Photo-decomposition of bromate. Dependence of quantum yield Φ (O), hypobromite yield (X), and bromate conversion (Δ) on time.

TABLE III. Dependence of the photo-decomposition of bromate on the initial concentration (30-min. irradiation; 30°C).

Expt.	Initial bromate conc. mole/l.	Bromate ions decompos.	per second $\times 10^{-18}$			Quantum yield Φ	Percent conv. of bromate	Percent hypobromite yield	Percent oxygen yield
			Hypobromite formed	Oxygen molec. formed	Quanta absorb. by sol.				
59	0.1847	1.45	0.73	—	9.26	0.17	20	50	—
75	0.0874	1.03	0.46	0.67	5.92	0.17	31	45	98
76	0.0106	0.24	0.02	0.24	2.43	0.10	57	7	77
77	0.0021	0.07	0.01	0.04	1.5	0.05	76	—	48

nesium perchlorate, and the tube was then weighed on a Kuhlman microbalance. The results of Table I show that in the photo-decomposition of the bromate, hydrogen is formed by a side reaction. In Tables II to VI, where the results of some experiments on the bromate decomposition are summarized, hydrogen formation is neglected.

The quantum yield of process (2) was measured at different lengths of irradiation time (cf. Table II). In Fig. 5 the true quantum yield Φ_0 was determined by extrapolating the measured quantum yield Φ to "zero" time. It is 0.19 at 30°C. The dependence of Φ on time is caused by the decrease of the absorption of the photochemically active radiation by the bromate, and the accumulation of light absorbing hypobromite (and bromide) in the course of the experiment.

The hypobromite yield (i.e., the number of hypobromite ions formed per bromate ions decomposed) also decreases during the irradiation, since hypobromite undergoes further decomposition.

If the initial concentration of the bromate solution is gradually decreased from 0.2 *M* to 0.002 *M* (cf. Table III) and the time of irradiation is kept constant, the dependence of the quantum yield and the hypobromite yield on the conversion of bromate is similar to their dependence on time (shown in Fig. 5). This is due

to the same effects as mentioned in the case of time dependence.

Change of the temperature within the range of 13.5° to 36°C does not affect the quantum yield and the value of the conversion showing the absence of rate determining secondary processes occurring in the dark.

The influence of the wave-length on the decomposition was not investigated. However, some experiments were made with various filter solutions in vessel *C* while the bromate solution was in vessel *D*. The results are given in Table IV. Since 50 percent acetic acid absorbs all light of wave-length shorter than 2300Å, it follows that at least 65 percent of the bromate decomposition is caused by the light in the spectral region of 2300Å to 2600Å. It is also seen that chloracetic acid absorbs almost all the photochemically active light.

Since every bromate ion gives on decomposition one molecule of oxygen and every hypobromite ion gives half a molecule, the number of oxygen molecules, n_{O_2} , evolved should be equal to: $\frac{1}{2}n_{BrO_3^-} - \frac{1}{2}n_{BrO^-}$. The ratio of these two quantities is given in column 10 (cf. Tables II to VI) as oxygen yield. In most experiments it is approximately 100 percent. Deviations from this value are due to errors in the measurements, if supersaturation occurs.

The influence of the following factors on the photo-decomposition of bromate was studied:

TABLE IV. Dependence of the photo-decomposition of bromate on the spectral region; experiments with various light filters (30-min. irradiation; 30°C).

Exp.	Filter sol.	Initial bromate conc. mole/l.	per second $\times 10^{-18}$			Quant. yield Φ	Percent conv. of bromate	Percent hypobromite yield	Percent oxygen yield
			Bromate ions decompos.	Hypobrom. form.	Oxygen molec. form.				
205	H ₂ O	0.0952	1.08	0.66	1.33	9.00	0.12	17.5	103
206	CH ₃ COOH, 50%	0.0936	0.70	0.32	0.91	3.80	0.18	11.5	101
209	CH ₃ ClCOOH, 2 <i>M</i>	0.940	0.02	0.01	0.04	0.20	0.11	0.4	55 (140)

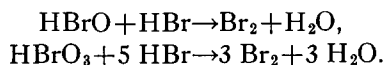
TABLE V. Dependence of the photo-decomposition of bromate on the pH (30-min. irradiation; 30°C).

Exp.	Initial brom. conc. mole/l.	Bromate in sol. of	Bromate ions decomp.	Hypo-brom. formed	Oxygen molec. formed	Quant. abs'd by sol.	Quant. yield Φ	Percent conv. of bromate	Percent hypo-brom. yield	Percent oxygen yield
			per second $\times 10^{-18}$							
192	0.0922	H ₂ SO ₄ , 4 <i>M</i>	1.72	0.30	2.20	10.74	0.16	49	17	91
109	0.0947	H ₂ SO ₄ , 0.05 <i>M</i>	1.55	0.24	1.96	11.0	0.14	43	16	(89)
124	0.0867	HBrO ₃ , 0.1 <i>M</i>	1.33	0.22	1.61	8.14	0.16	40	16	95
				(0.40)*					(46)*	
179	0.0915	NaOH, 4 <i>M</i>	1.69	0.16	2.18	9.02	0.19	49	10	89

* Corrected for losses of bromine in the oxygen evolved.

(a) The addition of either hypobromite or bromide, or both, had no influence on the primary photo-reaction; the over-all quantum yield decreases, however, since part of the photo-active radiation is absorbed by the added ions.

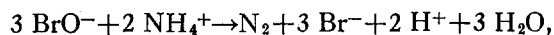
(b) The addition of 0.02 M to 4.0 M potassium hydroxide has no influence on either the value of the quantum yield or on the nature of the reaction products. In the acid range, when 0.1 M bromic acid or mixtures of sulfuric acid and potassium bromate are irradiated, the decomposition is accompanied by secondary reactions forming elementary bromine in accordance with the equations:



Part of the elementary bromine is carried off with the oxygen evolved. The second reaction gives an apparent increase in bromate conversion. The results of some experiments are summarized in Table V. The quantum yield is not much effected by the change of the pH.

It should be mentioned that in case the bromate solution is acidified with hydrochloric acid, a thermal reaction takes place in which chlorine and hypobromous acid are formed;⁸ due to these, the light absorption changes considerably as time goes on. Consequently, both the quantum yield and the conversion are much lower than under the conditions of the experiments in Table V.

(c) Certain cations in the bromate solution may effect the secondary reactions. Thus, if potassium bromate is irradiated in the presence of ammonium ion, the hypobromite formed reacts according to the equation:



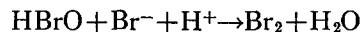
⁸ Unpublished results of this laboratory.

and its concentration is, therefore, low during the photo-decomposition. The active radiation in the spectral range of 2300Å to 2600Å is absorbed by bromate alone and consequently the rate of decomposition in this case is 60 percent to 100 percent greater than in the absence of ammonium ion (cf. Fig. 4).

The photo-decomposition of silver bromate has some special features, too. Aside from the fact that all the bromide is precipitated as silver bromide, elementary silver is also formed, and it is not possible to detect any hypobromite in the solution. This reaction was not investigated in sufficient detail in order to decide as to whether elementary silver is a primary product of the photo-decomposition of silver bromate or whether it is formed from secondary products.

The Photo-Decomposition of Hypobromite Ion

The decomposition of potassium hypobromite was studied only in alkaline solutions, since in acid solution it decomposes thermally according to:



and in neutral solution, the dark reaction,



is very fast.

Upon irradiation of an alkaline hypobromite solution, oxygen, bromate, and bromide ions are formed. In Fig. 6, the concentration changes of these ions during an experiment are given. While the bromate curve passes through a flat maximum, the hypobromite curve falls steeply toward zero. The comparison of the initial decomposition rate of hypobromite ($-\Delta\text{BrO}^-/\Delta t$) with the initial rate of formation of bromate ($\Delta\text{BrO}_3^-/\Delta t$) shows a ratio of $-\Delta\text{BrO}^-/\Delta\text{BrO}_3^- \geq 4$.

TABLE VI. Photo-decomposition of various halate ions (30-min. irradiation; 30°C).

Exp.	Halate ion	Init. halate conc. mole/l.	Halate ions decomp.	Hypo-halite formed	Oxygen molec. formed	Quant. abs'd by sol.	Quant. yield Φ	Percent conv. of halate	Percent hypo-halite yield	Percent oxygen yield
			per second $\times 10^{-18}$							
168	ClO_3^-	0.1006	0.217	0.00	0.254	0.85	0.26	6.0	0.0	78
116	BrO_3^-	0.0930	1.64	0.58	2.18	9.06	0.18	46	35	100
197	IO_3^-	0.0997	0.196	0.02	0.234	(8.22)	(0.02)	5.0	11	83

The quantum efficiency Φ of the hypobromite decomposition was determined only for that spectral region which is absorbed by chloroacetic acid was found to be about 0.4.

The Photo-Decomposition of Chlorate and Iodate Ion

The primary photo-decomposition of these two ions is similar to that of the bromate (cf. Table VI).

Since the absorption limit of the chlorate is at a shorter wave-length, the total number of quanta is about twelve times smaller than that in the case of the bromate, and the conversion is correspondingly low. The quantum yield of the chlorate decomposition is about the same as that of the bromate. Careful determinations could not detect any hypochlorite. Evidently the hypochlorite formed by the photo-decomposition of the chlorate ions decomposes immediately under the influence of the strong radiation in

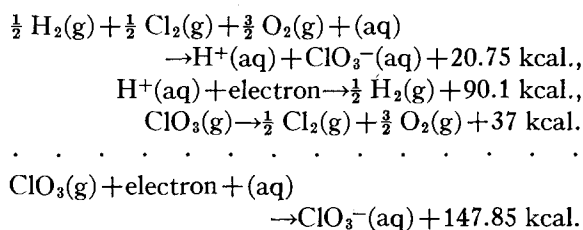
the spectral range 2500A to 2600A, which in this case is absorbed by the hypochlorite alone. The yield of chloride ions is, therefore, 100 percent. Perchlorate is not formed.

Though the absorption by the iodate ion begins at a longer wave-length, the photo-decomposition is comparatively slow because of the fact that the hypoiodite produced is unstable and iodine is set free. Iodine absorbs the active radiation strongly and thereby retards the iodate decomposition.

DISCUSSION

If we assume that the absorption spectra of the halate ions given in Fig. 2 are electron transfer spectra, the energy corresponding to the absorption frequency should be given by Eq. (1). Only in the case of chlorate ion are experimental data available which allow to check the validity of this relation.

The value for $E_{\text{ClO}_3^-} + H_{\text{ClO}_3^-}$ is obtained from the following equations:



The sum of $E_- + H_-$ thus calculated for a number of monovalent anions from the latest thermodynamic data, is listed in Table VII, together with the above value for the chlorate ion. From the absorption limit of these anions with relation (1), $E_{\text{H}_2\text{O}}$ can be calculated. The deviation from the mean value of 22.5 kcal. is not very great,*** and in view of the inaccuracy to which the deter-

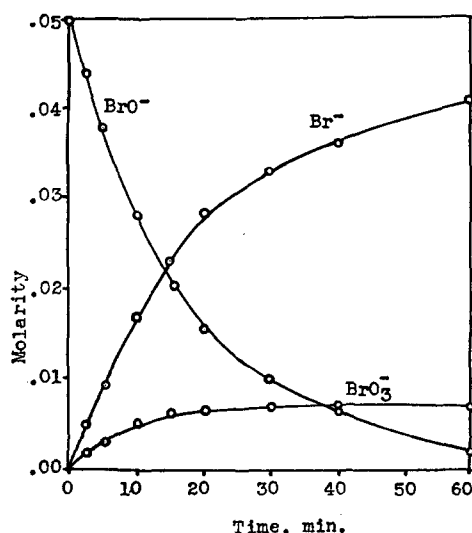


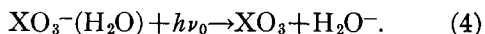
FIG. 6. Photo-decomposition of hypobromite. Change of concentration of hypobromite, bromate, and bromide with time.

*** Farkas and Farkas (see reference 2) calculated 18 kcal. for $E_{\text{H}_2\text{O}}$ since they used a somewhat lower figure for the heat of reaction of $\text{H}^+(\text{aq}) + \text{electron}$.

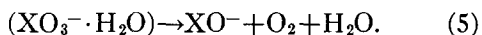
mination of the absorption limit is amenable, it seems that E_{H_2O} is essentially independent of the nature of the anion.

In the case of bromate and iodate ions, by assuming $E_{H_2O}=22$ kcal., and using known values for the heats of formation of $BrO_3^-(aq)$ and $IO_3^-(aq)$ from the elements (102 kcal. and 145 kcal., respectively), the heats of formation of the hypothetical compounds BrO_3 and IO_3 may be calculated. With $h\nu_{BrO_3^-}=106$ kcal. and with $h\nu_{IO_3^-}=99$ kcal., $\Delta H_f^\circ BrO_3^-$ is +23 kcal. and $\Delta H_f^\circ IO_3^-$ is -28 kcal. Because of the lack of any thermochemical data concerning the oxides of bromine, the former figure is only of theoretical interest; the latter may be related to the heat of formation of $I_2O_5(c)$, $\Delta H_f^\circ I_2O_5 = -42.0$ kcal.

The primary process of the absorption of the three halate ions is given by:



In the case of the halide ions, when, after the light absorption, the electron returns to its initial state, the energy liberated is dissipated as heat. On the other hand, in the case of the halate ions, the energy gained by the reverse process of (4) may induce a decomposition according to



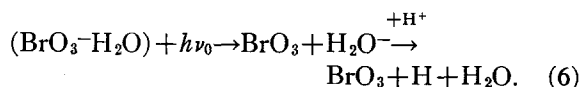
The thermal decomposition of chlorate and bromate into oxygen and hypohalite ion is exothermic, the heat of reaction being 5 kcal. and 10 kcal., respectively. The corresponding reaction with iodate possibly occurs as well, since the heat liberated in process (5) considerably exceeds the heat of reaction of -34.5 kcal. The "self"-decomposition of the complex $(XO_3^- \cdot H_2O)$ is most probably the reason for the far higher quantum yield in the present cases as compared with that of the halide ions.

A further possibility for a photo-chemical change is the process in which the electron jumps from its intermediate state in the hydration layer to a positive ion. In the case of the halide ions, hydrogen ions mainly serve as electron acceptors and if their concentration is increased, the quantum yield of the hydrogen evolution also increases. The presence of hydrogen in the gas obtained in the photo-decomposition of bromate in the pH range 6 to 8 indicates that an analogous

TABLE VII. Comparison of ionic energies (Eq. 1) to experimental values.

Ion	A	$h\nu_0$ kcal.	$H^- + E^-$ kcal.	E_{H_2O} kcal.
Cl^-	2060	137.5	159	21.5
Br^-	2310	122.8	145.7	22.9
I^-	2720	104.2	128.9	24.7
OH^-	2200	129	155	26.0
SH^-	2750	103	121	18.0
ClO_3^-	2250	126	148	22.0

process occurs according to



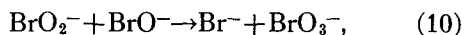
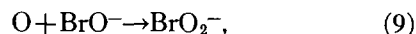
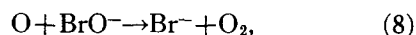
The corresponding quantum yield is less than 0.001, but not much lower than the quantum yield of the hydrogen evolution in neutral or slightly alkaline solutions of iodides.

The ultimate products of the secondary reactions accompanying (6) are in the case of BrO_3 , necessarily Br^- , O_2 , and hypobromite, and it is not difficult to give various reaction schemes which will lead to these products.

A process similar to (5) in the case of hypobromite may lead to its decomposition according to



though the dissociation of BrO^- into Br^- and O requires about 52 kcal. If we postulate the following secondary reactions



the formation of bromate during the photo-decomposition of hypobromite is readily explained. The relative probabilities of (8) and (9) will determine the ratio $-\Delta BrO^- / \Delta BrO_3^-$ which in the experiments was about 4.

It may be mentioned that the photo-decomposition of hypochlorite apparently involves similar reactions, since in this case, too, besides chloride and molecular oxygen, chlorate is formed in an appreciable quantity.⁹

⁹ A. J. Allmand and W. W. Webb, Zeits. f. physik. Chemie A131, 189 (1928).