On Photochemical Reaction between Bromine and Tartaric acid in Aqueous Solution. Part II.

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The photochemical reaction between bromine and tartaric acid in aqueous solutions has previously been investigated in this laboratory (This *Journal*, 1925, 2, 165). In view of some very interesting and peculiar results obtained therein we have thoroughly revised and enlarged the previous work. This and the next paper of the series will embody the results of our fresh investigations.

EXPERIMENTAL.

The experimental arrangement was exactly the same as before, only the Wratten filter was replaced by solutions of different substances in order to isolate different regions of wavelength. Our investigations show that the Wratten filter, previously used, transmitted a large amount of photochemically inactive rays so that the intensity of the photo-chemically effective rays was very small. This accounts for the very large periods of induction and small velocity constants obtained in the previous work.

Since withdrawal of 2 c.c. of the reaction mixture each time leaves a vacant space in the reaction cell (4×4×1 cm.) into which the bromine would evaporate, experiments were first made to find out if this would affect our readings. Experiments with a N/30 solution of bromine at 33° showed that the effect was negligible.

Experiments on the rate of hydrolysis of a N/30 bromine solution at 33° showed that the rate was negligible, the unimolecular constant falling off from 0·00028 to 0·000136 in four hours. Light did not accelerate the rate of hydrolysis.

2 C.c. of the reaction mixture were withdrawn at different intervals throughout the present investigation and titrated with N/200 thiosulphate.

The constants of the reaction, throughout this paper, are calculated on the basis of a unimolecular reaction with respect to bromine $(K=\frac{1}{t}\log_{10}\frac{a}{a-x})$, the time being reckoned in minutes.

The Dark Reaction.

The velocity of the dark reaction between bromine and tartaric acid solutions was found to be negligible in comparison with the light reaction and is characterised by very large induction periods. Table I gives the dark reaction.

TABLE I.

Tartaric acid—M/7·5.   Bromine—N/30.   Temp.—33·3°.

Time in mins.	N/200 Br.	Unimolecular constant.	Period of induction.
0	12·45 c.c.	—	
341	10·45	—	5½ hours.
375	10·1	·00044	
427	9·7	·00038	
500	9·05	·00039	

By raising the temperature to 48° the velocity constant increased to 0·0044 thus giving the very high value 4·6 as the temperature coefficient of the dark reaction.

The reaction was then carried out under the stimulus of light from a 1000 c.p. point-o-little lamp, rendered parallel by means of a lens. For the initial measurements only N KNO_2 (1 cm.) and $N/20CuSO_4$ (1 cm.) filters were employed to cut off the ultraviolet and the heat rays. Tables II-V indicate the typical data obtained at different intensities of the incident light and Tables VI and VII summarise all the data at different concentrations of the acid and bromine.

TABLE II.

Tartaric acid—M/7·5.   Bromine—N/30.   Temperature—33°.

Intensity of incident light—2¾ Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	12·55 c.c.	—	
15	12·3	—	15 minutes.
39	10·3	·00321	
67	9·1	·00252	
106	7·55	·00230	
147	6·15	·00228	

On repeating the above experiment in presence of a trace of iodine the induction period rose to 30 mins. and the velocity constant fell slightly.

TABLE III.

Tartaric acid M/7·5. Bromine—N/40. Temp.—33·2°.

Intensity of incident light—10 Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	9·15 c.c.	—	
10·5	7·9	·00608	
30	6·0	·00610	Nil.
70	3·9	·00529	

TABLE IV.

Tartaric acid—M/3. Bromine—N/50. Temperature—33·2°.

Intensity of incident light—31 Hefners-at-100 cm.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	7·95 c.c.	—	
5	7·65	—	
13	5·0	·0231	4 Minutes.
23	3·15	·0214	
40	1·3	·0220	

TABLE V.

Intensity of incident light—72 Hefners-at-100 cm.

Tartaric acid—M/24. Bromine N/50. Temperature—33·8°.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	7·65	—	
5·5	6·15	·0172	
10	5·3	·0159	
19	4·3	·0132	Nil.
28	3·5	·0121	
43	2·55	·0111	

It will be seen that in all the above experiments (*vide* Tables II & V), except at relatively very high concentration of tartaric acid (*vide* Table IV) where it remains fairly constant, the unimolecular constant gradually tends to diminish. This phenomenon we have found throughout our experiments and we intend to deal with this point in a subsequent paper.

<center>TABLE VI.</center>

Intensity of incident light—31 Hefners-at-100 cm.—(same as in Table IV.) Temp.—33·3°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of unimolecular constant.	Mean constant.
M/24	N/100	1½ mins.	·0200 — ·0173	·0183
M/15	,,	2½ mins.	·0262 — ·0235	·0252
M/3	,,	4 mins.	·0558 — ·0540	·0549
M	,,	3 mins.	·154 — ·151	·153
M/24	N/50	1½ mins.	·0073 — ·0061	·0069
M/15	,,	2½ mins.	·0101 — ·0080	·0088
M/3	,,	4 mins.	·023 — ·021	·022
M	,,	17 mins.	·052 — ·046	·048
M/15	N/30	2½ mins.	·00618 — ·00443	·0056
M/3	,,	4 mins.	·0143 — ·0110	·0126
M	,,	14 mins.	·0243 — ·0239	·0241
M/3	N/20	Nil	·0069 — ·0060	·0062
M	,,	12 mins.	·0143 — ·0128	·0134
M/3	N/10	Nil	·0084 — ·0025	·0030
M	,,	13 mins.	·0052 — ·0046	·0050

TABLE VII.

Intensity of incident light—72 Hefners-at-100 cm. (same as in Table V). Temp.—33·6°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of unimolecular constant.	Mean constant.
M/24	N/50	Nil	·0172 — ·0111	·014
M/15	,,	Nil	·0246 — ·0183	·018
M/3	,,	Nil	·0425 — ·0403	·0420
*M	,,	6 mins.	·146 — ·141	·144
M/15	N/30	Nil	·0108 — ·0064	·0084
M/3	,,	Nil	·0232 — ·0202	·0218
*M	,,	6 mins.	·0386 — ·0346	·0368
M/3	N/20	Nil	·0187 — ·0121	·0160
*M	,,	4 mins.	·0247 — ·0211	·0230
M/3	N/10	Nil	·0108 — ·00501	·0087
*M	,,	2 mins.	·00944 — ·0088	·0090

Period of Induction.

It will be seen from above that the period of induction varies from 20 mins. to nil. For the same concentration of bromine an increase in the concentration of tartaric acid increases the period of induction. An increase in the concentration of bromine at the same concentration of tartaric acid slightly diminishes the induction period—as will be clear from data marked with asterisks (*) in Tables VI and VII. An increase in the intensity of light also diminishes the period of induction.

Another fact, which appears rather puzzling and which will be discussed later, is the influence of the initial concentration of bromine on the unimolecular constant. It will be at once clear from the data given in Tables VI and VII that concentration of tartaric acid remaining the same, unimolecular velocity constants diminished considerably as the initial bromine concentration increased.

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Experiments at various Wavelengths.

We next carried out the reaction at various wavelengths using different solutions as filters. A bromine filter was tried first and then the different filters recommended by Plotnikow were used. Table VIII summarises the results.

TABLE VIII.

Tartaric acid—M/7·5. Bromine—N/30. Temp.—33·6°.

Filters.	Wavelength limit.	Schwerpunkt.	Intensity : Hefners-at-100 cm.	Period of induc-tion.	Limits of unimolecu-lar const.	Mean const.
·3N Bromine (1 cm.) & N/20 CuSO₄ (1 cm.)			19	45 mins.	·00202 — ·0016	·0018
The same			52	20 ,,	·0035 — ·0023	·0030
Methyl vio-let & potas-sium chromate.	718-639 μμ	665·9 μμ	75	80 ,,	·00136 — ·00130	·00133
KMnO₄,K₂CrO₄ & NiSO₄	614-576 μμ	591·9 μμ	8·5	90 ,,	·0015 — ·0013	·0014
CuCl₂ & K₂CrO₄	540-505 μμ	533 μμ	3·5	80 ,,	·00198 — ·00150	·0018
CuSO₄ & Methyl green	526-494-458 μμ	488·5 μμ	11·5	Nil	·0110 — ·0059	·0089
Methyl violet & CuSO₄	478-410 μμ	488 μμ	3·8	Nil	·0054 — ·0031	·0048

The last two filters, therefore, corresponding to the blue and deep blue regions are the most and almost equally efficient photo-chemi-cally. Absorption measurements with a Johansen thermopile behind the reaction cell filled with water and N/30 bromine solution showed that the reaction mixture (1 cm. thick) absorbed about 18% of the radiation 488·5 μμ and 448 μμ and 2 % of 533μμ while it showed very little absorption at other regions.

It will be seen that for blue and violet light of wavelengths shorter than 500 μμ even for weak intensities of light the period of inductions is approximately zero and the velocity of reaction is very,

large compared with the corresponding value for lights of very much higher intensity at larger wavelengths.

It will be seen from the previous observations that the reaction in blue light is characterised by greater simplicity and we shall now describe the results of our experiments in blue light (488·5 $\mu\mu$) and the effect of various addition agents on the reaction.

Tables IX, X, XI give the typical results while Table XII summaries the results of the reaction in blue light.

TABLE IX.

Intensity of incident light (488·5 $\mu\mu$)—6 Hefners-at-100 cm.

Tartaric acid—M/3. Bromine—N/30. Temp.—33·5°.

Time in mins.	N/200 Bromine.	Unimolecular const.	Period of induction.
0	12·55 c.c.	—	
8	11·2	—	4 minutes.
16	9·15	·0110	
46	5·5	·0061	
76	3·2	·0080	

TABLE X.

Intensity of incident light (488·5 $\mu\mu$)—6 Hefners-at-100 cm.

Tartaric acid—M. Bromine—N/30. Temp.—33·6°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	13·0 c.c.	—	
	12·7	—	5 minute
10	10·55	·0161	
16	8·9	·0140	
41	3·7	0147	

TABLE XI.

Intensity of incident radiation (488·5 $\mu\mu$) — 2 Hefners-at-100 cm.

Tartaric acid — M/7·5.   Bromine — N/30.   Temp. — 33·6°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	13·1 c.c.	—	
30	12·9	—	35 minutes
60	11·4	—	
90	9·7	·00234	
141	7·6	·00218	
201	5·6	·00219	

As in the case of experiments in white light the unimolecular constant, except in the case of relatively higher concentration of tartaric acid, has a tendency to diminish. This tendency is more marked at higher intensities of incident light. The induction period rapidly increases as the intensity of incident radiation diminishes.

TABLE XII.

Temperature — 33·5°.

Conc. of tartaric acid.	Conc. of bromine.	Intensity of blue light (Hefners-at-100 cm.).	Period of induction.	Limits of unimolecular constant.	Mean constant.
M/7·5	N/30	11·5	Nil	·0110 — ·0059	·0089
M/15	,,	6	Nil	·0047 — ·0032	·0042
M/3	,,	6	4 mins.	·0110 — ·0080	·0095
M	,,	6	5 mins.	·0161 — ·0136	·0150
M/3	N/20 (·96)	6	Nil	·00610 — ·0051	·0054
M/3	N/50	6	4 mins.	·0202 — ·0183	·0190
M/3	N/75	6	5 mins.	·049 — ·051	·050
M/7·5	N/30	2	35 mins.	·00234 — ·0021	·0028
M/15	N/30	2	20 mins.	·00174 — ·00171	·00173

As before the induction period increases with increase in concentration of tartaric acid and diminishes with the increase in concentration of bromine and intensity of incident light. The constant of unimolecular reaction increases with increase in concentration of tartaric acid but diminishes considerably as the initial concentration of bromine is increased.

Determination of the Temperature Coefficient in Blue Light.

Table XIII shows that the temperature coefficient of the reaction in blue light is 2.

TABLE XIII.

Intensity of incident light (488·5 $\mu\mu$)—5·8 Hefners-at-100 cm.

Temp.	Conc. of Br.	Conc. of tartaric acid.	Limits of unimolecular constants.	Mean const.	Period of induction.
24°	N/30 (1·1)	M/3	·00404 — ·00336	·00380	10 mins.
34°	N/30 (1·1)	M/3	·00881 — ·00663	·00760	5 mins.

The temperature co-efficient of the dark reaction is, as has already been mentioned, 4·6.

Application of Einstein's Law.

The quantum efficiency of the reaction can throw some light on its mechanism. We shall, therefore, find out the relation between the number of quanta absorbed and the number of molecules reacting.

Absorption measurements, as has already been mentioned, with a Johansen thermopile showed that a N/30 aqueous solution of bromine, 1 cm. thick, absorbed only 18% of the incident blue light (488·5 $\mu\mu$) transmitted by filters recommended by Plotnikow. Measurements of extinction coefficient of bromine solutions with a spectro-photometer, however, showed that a 1 cm. layer of N/30 bromine solution should absorb 80% of incident blue light. From this it is evident that Plotnikow's filters are imperfect.

We shall take the results in Table IX. Taking Gerlach's value of 900 ergs. per sq. cm. per second at a distance of 1 metre for the energy emitted by a Hefner-lamp and remembering that only 18%

of the incident light was absorbed we have the number of quanta absorbed

$$= 900 \times 6 \times \frac{18}{100} \times \frac{1}{6\cdot5 \times 10^{-17}} \times \frac{488\cdot5 \times 10^{-7}}{3 \times 10^{10}}$$

$$= 243\cdot5 \times 10^{11} \text{ quanta per sq. cm. per second.}$$

Since in 8 mins. the change in 2 c.c. of reaction mixture is $(11\cdot2-9\cdot15)$ $2\cdot05$ c.c. of $N/200$ bromine after the induction period is over, the number of molecules transformed per sq. cm. per second

$$= \frac{2\cdot05}{2 \times 2 \times 2 \times 100} \times \cdot001 \times \frac{1}{8 \times 60} \times 6\cdot1 \times 10^{28}$$

$$= 325\cdot600 \times 10^{13} \text{ molecules per sq. cm. per second.}$$

Thus for one quantum of light ($488\cdot5$ $\mu\mu$) absorbed, about 13 molecules disappear.

Table XIV summarises the quantum efficiency under different concentrations of tartaric acid, the intensity of the incident blue light being in all cases 6 Hefners-at-100 cm.

<div align="center">TABLE XIV.</div>

Conc. of tartaric acid.	Conc. of bromine.	No. of Br. molecules transformed per quantum.	Remarks.
M/3	N/75	58	After the period of induction.
M	N /30	23	After the period of induction.
M/3	N/30	13	After the period of induction.
M/7·5	N/30	17	No period of induction.
M/15	N/30	6	No period of induction.

The quantum efficiency is thus large.

Experiments in Presence of Sodium Hydrogen Tartrate.—The photo-chemical reaction between bromine and tartaric acid was carried out in presence of Na·H-tartrate at a constant concentration. The object was to find out how an increase in the concentration of hydrogen tartrate ion which we shall always indicate by HT' and a

change in the initial p_H would affect the velocity of reaction and the induction period.

It was first found out that the dark reaction between bromine, tartaric acid and sodium hydrogen tartrate was negligible at 32°— with a sodium hydrogen tartrate concentration of M/15, tartaric acid concentration of M/15 and bromine concentration of N/30, the velocity constant fell gradually from ·00059 to ·00024.

p_H values for the mixtures of NaH-tartrate and tartaric acid were determined by the potentiometric method.

Tables XV, XVI, XVII, XVIII indicate the typical reaction in blue light and Tables XIX and XX summarise the data.

TABLE XV.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

NaH-tartrate—M/30 }
Tartaric acid—M/30 } M/15 ; p_H = 2·71.

Bromine. — N/30.   Temp.—33·5°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Period of induction.
0	12·9 c.c.	—	Nil
5	10·15	·0208	
20	6·0	·0166	
30	4·25	·0161	
42	2·8	·0158	

TABLE XVI.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

NaH-tartrate—M/30 }
Tartaric acid—29/30 M } M ; p_H = 1·4

Bromine. —N/30.   Temp.—33·5°.

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·1 c.c.	—	Nil
6	8·25	·0335	
11	6·2	·0295	
18	4·25	·0306	

TABLE XVII.

Intensity of incident light (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

$$\left.\begin{array}{l}\text{NaH-tartrate—M/30} \\ \text{Tartaric acid—M/10}\end{array}\right\} \text{M/7·5}; \quad p_H \; -2·4$$

Bromine—N/30.   Temp.—33·5° .

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·25 c.c.	—	3 minutes.
10	10·9	—	
20	7·3	·0174	
30	6·6	·0109	
40	5·2	·0107	
55	3·8	·0101	

TABLE XVIII.

Intensity of incident light (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

$$\left.\begin{array}{l}\text{NaH-tartrate—M/30} \\ \text{Tartaric acid—3M/10}\end{array}\right\} \; \text{M/3} ; \quad p_H \; -1·9.$$

Bromine—N/30.   Temp.—33·5°.

Time in mins.	N/200 Bromine.	Constants.	Period of induction.
0	12·7 c.c.	—	7 minutes.
7	11·45	—	
12	9·9	·0126	
19	7·8	·0139	
27	6·35	·0128	
37	4·6	·0132	

TABLE XIX.

Intensity of incident light (488·5 $\mu\mu$)—3·84 Hefners-at-100 cm.

Conc. of NaH-tartrate—M/30.   Temp.—33·5°.

Conc. of tartaric acid.	Sum of conc. of NaH — tartrate and tartaric acid.	Conc. of Br.	p_H	Induction period.	Limits of constants.	Mean constant.
M/30	M/15	N/30	2·71	Nil	·0208 — ·0158	·0184
M/10	M/7·5	,,	2·4	Nil	·0263 — ·0161	·0217
3M/10	M/3	,,	1·9	Nil	·0286 — ·0217	·0267
29M/30	M	,,	1·4	Nil	·0335 — ·0295	·031
M/10	M/7·5	N/50	2·4	Nil	·0411 — ·0353	·0385
M/10	M/7·5	N/20	2·4	Nil	·0194 — ·0122	·0163

TABLE XX.

Intensity of incident radiation (488·5 $\mu\mu$)—1·3 Hefners-at-100 cm.

Conc. of NaH-tartrate M/30.   Temp.—33·5°.

Conc. of tartaric acid.	Sum of conc. of Na-H— tartrate and tartaric acid.	Conc. of Br.	p_H	Induction period.	Limits of constant.	Mean const.
M/10	M/7·5	N/30	2·4	4 mins	·0174 — ·0101	·0140
M/10	M/7·5	N/50	2·4	4 ,,	·0285 — ·0192	·0245
3M/10	M/3	N/30	1·9	7 ,,	·0139 — ·0126	·0134
29M/30	M	N/30	1·4	17 ,,	·0168 — ·0164	·0165

It will be seen by comparing the above data with those in absence of NaH-tartrate given in Table XII that the presence of NaH-tartrate greatly accelerates the reaction and diminishes the period of induction. Again from Table XX it will appear that keeping the initial bromine concentration constant at N/30, if the pH value of the solution is diminished, i.e., the concentration of hydrogen ion is increased, the induction period for weak light (1·3 Hefners) increases. It should be noticed also that the unimolecular constant simultaneously increases.

It will also appear from Table XXI, where the ratios of the velocity constants are compared with intensity ratios, that the ratios of the

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corresponding velocity constants is equal to the ratio of the square root of the intensities of incident radiation.

TABLE XXI.

Conc. of NaH-tartrate— M/30 throughout.

Conc. of tartaric acid.	Sum of conc. of NaH-tartrate and tartaric acid.	Conc. of bromine.	Ratio of square root of intensities.	Ratio of velocity constants.
M/10	M/7·5	N/30	$\sqrt{\dfrac{3\cdot84}{1\cdot3}}=1\cdot7$	$\dfrac{\cdot0217}{\cdot0140}=1\cdot6$
3M/10	M/3	,,	1·7	$\dfrac{\cdot0267}{\cdot0134}=2\cdot0$
29M/30	M	,,	1·7	$\dfrac{\cdot0310}{\cdot0165}=1\cdot9$
M/10	M/7·5	N/50	1·7	$\dfrac{\cdot0385}{\cdot0245}=1\cdot6$
				Mean — 1·85

Effect of Hydrobromic Acid.

Since HBr is one of the products of reaction it was thought advisable to note its effect on the reaction. It was also felt that since p_H has a large influence on the period of induction as just noted, addition of HBr to the reaction mixture previous to exposure to light might furnish a clue as to the mechanism of induction period.

Tables XXII, XXIII, XXIV give the typical data while Table XXV summarises all the observations.

TABLE XXII.

Intensity of light $(488\cdot5\mu\mu)$—11·5 Hefners-at-100 cm.

Tartaric acid—M/3. Bromine—N/30. Initial conc. of HBr—Zero.

Temp.—33·3°.

Time in mins.	N/200 Bromine.	Unimolecular constant.	Induction period.
0	12·9 c.c.	—	Nil
5	10·7	·0162	
15	7·9	·0142	
26	6·2	·0122	
39	4·55	·0116	
56	3·15	·0109	

TABLE XXIII.

HBr—N/200 ; other conditions same as in Table XXII.

Time in mins.	N/200 Bromine.	Constant.	Period of induction.
0	13·1 c.c.	—	2 minutes
5	12·15	—	
16	9·7	·00889	
26	8·1	·00838	
46	5·6	·00820	
64	4·2	·00782	

TABLE XXIV.

HBr— N/100 ; other conditions same as in Table XXII.

Time in mins.	N/200 Bromine.	Const.	Period of induction.
0	13·05 c.c.	—	17 minutes.
5	12·5	—	
15	11·15	—	
30	8·8	·00685	
45	6·7	·00737	
60	5·2	·00737	

TABLE XXV.

Intensity of light $(488·5\mu\mu)$—11·5 Hefners-at-100 cm.

Tartaric acid— M/3. Bromine—N/30.   Temp.—33·3°.

Initial conç. of HBr.	Period of induction.	Limits of unimolecular constant.	Mean constant.
Nil	Nil	·016 — ·0109	·0140
N/200	2 mins.	·00889 — ·00782	·0083
N/150	3 mins.	·00845 — ·00779	·0080
N/100	17 mins.	·00737 — ·00685	·0072
N̄/75	22 mins.	·00687 — ·00635	·0066
N/50	35 mins.	·00598 — ·00552	·00575

It will thus transpire from the foregoing results that addition of HBr diminishes the velocity of the reaction but increases considerably the period of induction. It also introduces an induction period where there was none. The effect increases with inceasing concentration of the HBr added initially. It will also be seen from above data that if no HBr be added initially, although there is no induction period, the velocity constants diminish very rapidly (*vide* Table XXII). If, however, we add some HBr to start with, the period of induction, the duration of which is proportional to the amount of HBr added, makes its appearance but the velocity constants do not diminish so rapidly. Such results are indeed to be expected. In the absence of any HBr, as the reaction proceeds, HBr is generated and gives rise to H^+ ions the concentration of which thus changes considerably relatively to the initial concentration. As we have already seen H^+ ions act retardingly on the reaction and thus greatly diminish the velocity of reaction. If, however, HBr be added initially, the relative increase in the concentration of H^+ ion is not considerable and therefore the retarding influence on the velocity of the reaction does not increase to very great extent. In presence of HBr, the duration of the induction period should, therefore, be proportional to the concentration of HBr added and the velocity constants should not diminish as rapidly as in its absence.

The experiments in presence of HBr thus throw a good deal of light on the mechanism of the reaction and we intend to discuss it more thoroughly in a subsequent paper.

Photochemical After-effect.—We have investigated more fully the after-effect exhibited by this reaction. The reaction mixture was first exposed for short periods to intense parallel radiation from 1000 c.p. point-o-lite lamp using $CuSO_4$ and KNO_3 filters and then quickly transferred to darkness. The after-effect persisted for about half-an-hour. Table XXVI indicates the typical result and Table XXVII summarises the observations. The constants have been calculated in the same way as in Part I. The intensity of the radiation was 72 Hefners-at-100 cm., concentration of tartaric acid $M/3$ and that of bromine $N/30$. Temperature was maintained at 32°.

TABLE XXVI.

Time in mins.	N/200 Bromine.	Unimolecular constants for after-effect.
0	13·5 c.c.	

After illumination for 5 mins. kept in the dark and then

0	9·7	
5½	9·0	·0425
15	8·5	·0354
25	8·2	·0372

Final 8·0

Time of exposure in mins.	Limits of const. for after-effect.	Mean const. for after-effect.	Unimolecular const. for the light reaction under same conditions,
5	·0425 — ·0354	·0385	
8	·0396 — ·0331	·0365	·0218
16	·0526 — ·0417	·0422	
25	·0451 — ·0359	·0400	

It will be seen that the velocity coefficient for the after-effect is of the same order as obtained in Part I and does not depend on the period for which the system is illuminated before it is removed to darkness.

Reactions in Red Light.—We tried to find out if the addition of a blue substance like $CuSO_4$ to the reaction mixture would make the reaction proceed quickly in red light which is practically not absorbed at all by bromine solutions. For this purpose the reaction without any $CuSO_4$ was first carried out in red light obtained by using methyl violet and potassium chromate filters. The reaction in red light shows a very large period of induction and then proceeds very slowly. Table XXVIII gives only a few of our observations.

TABLE XXVIII.

Intensity of incident radiation (665·9$\mu\mu$)—68 Hefners-at-100 cm.

Temp.—33.7°.

Conc. of tartaric acid.	Conc. of bromine.	Induction period.	Limits of uni-molecular constant.	Mean constant.
M/15	N/30	50 mins.	·0012 — ·00099	·0010
M/3	,,	100 ,,	·00201 — ·00185	·00192
M/3	N/75	210 .,	·0070 — ·0066	·0068

The addition of $CuSO_4$ in all cases increased the induction period and diminished the velocity constants.