

# PHOTOCHEMICAL AFTER-EFFECT IN THE BROMINE-OXALATE REACTION

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## INTRODUCTION

DHAR<sup>1</sup> (1925) discovered that a mixture of oxalic acid and bromine exposed to light for a short time and then brought back into the dark shows a greater rate of bromine reduction than a mixture that has not been illuminated. The photochemical after-effect was found to be of a short duration. The unimolecular velocity constants after irradiation approached the dark reaction rate in about half an hour from the time of darkening. No bromide was used in the reaction mixture.

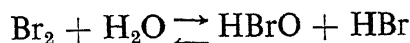
The reaction between potassium oxalate and bromine has formed the subject of extensive studies by Bhattacharya and Dhar<sup>2</sup> (1929), and Bhattacharya, Prakash and Dhar<sup>3</sup> (1932). These authors studied the reaction between bromine and neutral potassium oxalate, and measured the quantum efficiency of the photochemical reaction in the mercury arc light, as well as the reaction velocity and light absorption under varying conditions. Griffith, Mckeown and Winn<sup>4</sup> (1933) have discussed at length the photochemical reactions between bromine and neutral oxalate and free oxalic acid. None of these workers, however, made any observation about the photochemical after-effect in these reactions. With the exception of Dhar's<sup>1</sup> preliminary experiment referred to above, there is no record in the literature of work on the photochemical after-effect in the oxalic acid-bromine reaction. It was, therefore, thought desirable to study this reaction in detail in order to throw some light on the mechanism of the after-reaction. The present paper contains some observations on the photochemical after-effect in the reaction between free oxalic acid and bromine. It is significant to note that the reaction between bromine and neutral potassium oxalate has also been found by the author to exhibit a marked photochemical after-effect of several hours' duration.

## EXPERIMENTAL

Kahlbaum's analytical reagents were employed in this investigation. The experiments were conducted in pyrex glass bulbs, duly cleaned and steamed before use. The experiments on the oxalic acid-bromine reaction were conducted at 35° C. This reaction has been found by Dhar<sup>1</sup> to be approximately unimolecular with respect to bromine. The dark reaction

produces hydrobromic acid which exerts a retarding effect on the rate of bromine reduction. In order to minimise the fall in the unimolecular velocity constants with the progress of the reaction, an excess of potassium bromide was employed in the reaction mixture. The change in bromine concentration was determined from time to time by adding an excess of potassium iodide to 5 c.c. of the reaction mixture in the dark and titrating the liberated iodine with standard thiosulphate solution. The reaction between oxalic acid and iodine is negligible under the conditions of these experiments. Due care was taken to prevent the action of light on the reaction mixture during titration.

The oxidation reaction between oxalic acid and hypobromous acid has not been considered, because under the conditions of the experiments described here, the formation of hypobromous acid by hydrolysis



is negligible. Due to the presence of hydrogen and bromide ions, the hydrolytic equilibrium is suppressed with the disappearance of hypobromous acid. All the experiments described here have been carried out in the presence of a large excess of bromide ions. The hydrolysis constant of the above equilibrium is of the order<sup>5</sup> of  $10^{-8}$  and even in the absence of such an initial excess of bromide ion as used in these experiments the formation of hypobromous acid is practically negligible.

Fig. 1 shows the results obtained by using N/10 oxalic acid, N/120 bromine and N/5 potassium bromide. Curve 1 shows the course of the

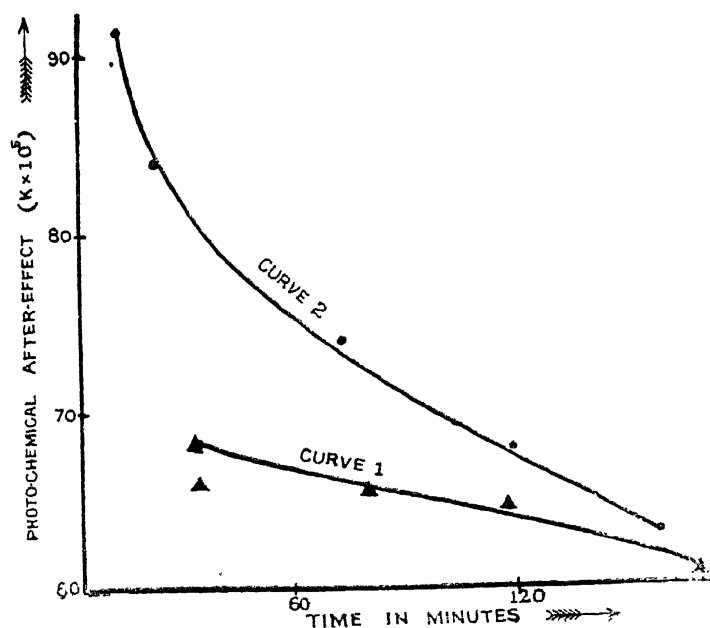


FIG. 1

dark reaction, and Curve 2 shows the course of bromine reduction after illumination of the reaction mixture for 30 minutes by the light (filtered through water) of a 500-watt gas-filled filament lamp operated at 220 volts. The distance between the reaction vessel and the lamp was 50 cm. These results are recorded in Tables I-II. The velocity constant has been calculated according to the unimolecular formula,  $K = 1/t \log a/a-x$ , where 't' is the time in minutes and 'a' the initial concentration of bromine in terms of c.c. of thiosulphate, and 'x' the change in time 't'.

TABLE I

*In the dark throughout*

<i>t</i>	<i>a-x</i>	<i>K.10<sup>6</sup></i>
0	8.30	..
52	7.65	681
54	7.30	664
132	6.80	656
196	6.20	646
287	5.50	609

TABLE II

*Exposed to light for 30 mts. and then measured bromine reduction in the dark*

<i>t</i>	<i>a-x</i>	<i>K.10<sup>6</sup></i>
0	6.50	..
15	6.30	907
37	6.05	841
81	5.60	799
120	5.30	738
200	4.75	681
270	4.40	627

As the object of these experiments was to study the photochemical after-effect, no attempt was made to study the light absorption and quantum efficiency. These aspects of the reaction have been extensively studied by Dhar and co-workers<sup>1,2,3</sup> and Griffith, *et al.*<sup>4</sup>

It may be emphasized that the photochemical after-effect is essentially a dark reaction initially stimulated by irradiation for a short time. From these experiments it is seen that the photochemical after-effect persists for over four hours. The activity in the pre-illuminated reaction mixture diminishes first rapidly and later on gradually until the velocity constants approach the dark reaction rate. The course of the after-reaction cannot be represented by any kinetic equation. It appears that in the primary light reaction some activated intermediate product is formed which causes the measured after-effect and at the same time disappears in other ways. The total change in bromine concentration cannot be represented by any simple formula. Similar 'decay curves' have been obtained in the photochemical after-effect in the reaction between iodine and oxalate<sup>5</sup> (1939).

Irradiation of  $\text{H}_2\text{C}_2\text{O}_4\text{-Br}_2\text{-KBr}$  mixture by quartz mercury vapour lamp gave the results that have been shown in Fig. 2 and recorded in Tables

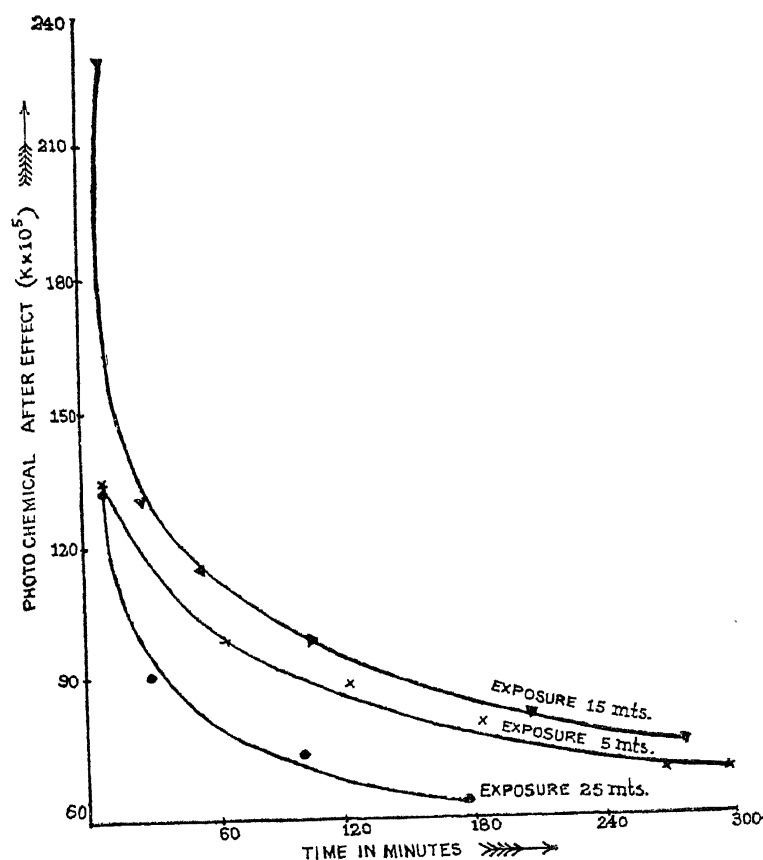


FIG. 2

III-V. The 'decay curves' show that there is a rapid fall in activity just after cutting off the illumination, so that it has been largely reduced by the time the first reading for the photochemical after-effect is taken. The results also show that the photochemical after-effect increases with increasing periods of pre-illumination up to a certain stage. When the

TABLE III

*Exposure 3 mts.*

<i>t</i>	<i>a-x</i>	<i>K.10<sup>5</sup></i>
0	6.50	∞
10	6.30	136
63	5.65	96
120	5.05	91
180	4.65	81
300	4.05	69

TABLE IV

*Exposure 15 mts.*

<i>t</i>	<i>a-x</i>	<i>K.10<sup>5</sup></i>
0	4.80	∞
10	4.55	232
25	4.45	131
50	4.20	116
101	3.80	100
200	3.40	84
275	3.10	76

TABLE V

*Exposure 25 mts.*

<i>t</i>	<i>a-x</i>	<i>K.10<sup>5</sup></i>
0	3.30	∞
10	3.20	134
30	3.10	90
97	2.80	74
174	2.55	64

irradiation is prolonged for some time, the after-effect shows a diminution. The observed diminution in the photochemical after-effect may be due to the retarding effect of hydrobromic acid which is produced in considerable concentration in the course of the reaction. This point is being investigated.

When the concentration of potassium bromide is diminished, the dark reaction becomes more rapid, and no after-effect of illumination can be observed when the concentration of potassium bromide is sufficiently reduced. It appears that the photochemical after-effect is very largely masked by the rapid rate of the dark reaction, and the former can be detected only when the dark rate has been considerably reduced by employing larger concentrations of potassium bromide.

It was noticed that when the original concentration of bromine in  $\text{H}_2\text{C}_2\text{O}_4\text{-Br}_2\text{-KBr}$  mixture was restored in the dark immediately after the complete photo-reduction of bromine, the rate of reaction now obtained with added bromine was slightly lower than the dark rate and no 'secondary after-effect'<sup>6</sup> could be observed.

#### *Potassium oxalate and bromine*

A marked photochemical after-effect was noticed for the first time in the reaction between neutral potassium oxalate and bromine. They react rapidly at room temperature in the dark, and no photochemical after-effect could be detected at such temperatures. When, however, the dark reaction was damped by employing a large excess of potassium bromide and by carrying out the experiments at a lower temperature, a marked after-effect of illumination was observed.

*Dark reaction.*—The dark reaction between bromine and neutral potassium oxalate has been studied by a large number of workers. The dark reaction has been found to be unimolecular with respect to bromine. It has been established by the author that the reaction between potassium oxalate and bromine in the presence of a large excess of potassium bromide and oxalate is unimolecular with respect to bromine. In the absence of added bromide and considerable excess of oxalate the dark reaction is complex, but in the present study this complexity has been largely avoided by using large concentrations of both oxalate and bromide and isolating the reaction. The dark reaction has been studied under different conditions of temperature and concentration. Some typical experiments have been recorded in Tables VI–VIII. The concentrations were  $\text{N}/10 \text{ K}_2\text{C}_2\text{O}_4$ ,  $\text{N}/5 \text{ KBr}$  and  $\text{N}/120 \text{ Br}_2$ .

TABLE VI  
Temp. 0.3°–0.8° C.

<i>t</i>	<i>a</i> – <i>x</i>	K.10 <sup>6</sup>
0	7.70	..
60	7.45	238
120	7.25	218
206	6.95	216
252	6.65	253

TABLE VII  
Temp. 10° C.

<i>t</i>	<i>a</i> – <i>x</i>	K.10 <sup>5</sup>
0	6.80	..
15	6.35	198
37	5.85	177
64	5.20	182
105	4.45	175
179	3.10	191

TABLE VIII  
Temp. 25° C.

<i>t</i>	<i>a</i> – <i>x</i>	K.10 <sup>4</sup>
0	7.20	..
13	3.60	232
19	2.40	251
24	1.80	245

The above experiments show that the unimolecular velocity constants ( $K = 1/t \log a/a - x$ ) are fairly constant and the dark reaction is unimolecular with respect to bromine.

*Photochemical after-effect.*—The photochemical after-effect was studied by irradiating the reaction mixture at 0.3°–0.8° C. in a glass thermostat placed at a distance of 50 cm. from the lamp (500-watt gas-filled filament lamp operated at 220 volts). The results are recorded in Tables IX–X.

TABLE IX  
*N*/10  $K_2C_2O_4$ , *N*/4 *KBr*,  
*N*/120  $Br_2$

<i>t</i>	<i>a</i> – <i>x</i>	K.10 <sup>6</sup>	
0	7.30	..	
60	7.15	150	} 138
120	7.05	126	

TABLE X  
*N*/8 *KBr*, other conditions  
same as in Table IX

<i>t</i>	<i>a</i> – <i>x</i>	K.10 <sup>6</sup>	
0	7.40	..	
60	7.15	248	} 251
120	6.95	253	

Illumination 10 mts.			After-effect
152	4.40	..	..
182	4.30	333	195
312	4.05	225	87
420	3.95	175	37

Illumination 10 mts.			After-effect
172	3.20	..	..
213	3.10	334	83
330	2.85	318	67
421	2.70	294	43
540	2.50	280	29

In Tables IX-X, the after-effect has been evaluated by subtracting the rate of the dark reaction from the rate after irradiation. The first three readings above the line give dark reaction rates which were found to be in agreement with those obtained in dark reactions studied independently. The readings after switching off the light have been taken so long as the after-effect rates are distinctly higher than the dark rate. It is found that a marked after-effect of illumination is obtained after a short illumination (10 mts.) by the light of 500-watt filament lamp, and the after-effect persists for several hours as in the case of the oxalic acid-bromine reaction. It is clear from Table X that when the bromide concentration is reduced, the dark reaction becomes more rapid and the photochemical after-effect is considerably diminished. It was found that with N/2 potassium oxalate, and N/8 potassium bromide, the reduction of bromine in the dark was very rapid ( $K \cdot 10^5 = 121$ ), and no after-effect could be detected under these conditions.

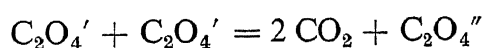
#### DISCUSSION

It is not possible at this stage to explain the mechanism of the photochemical after-effect in the oxalic acid-bromine and the oxalate-bromine reactions. From the experimental results obtained, it appears that some reactive intermediate product is formed by the primary photochemical reaction between bromine and oxalate ion which continues its active influence after darkening, thus causing the photochemical after-effect. The velocity constant at any time in the after-reaction would, therefore, represent the mass of this active product at that time. This reacts with bromine more rapidly than the oxalate ion  $C_2O_4^{2-}$  and causes the photochemical after-effect, while decaying spontaneously in other ways. Abel and Schmidt<sup>7</sup> (1935) reported the existence of the univalent oxalato ion  $C_2O_4^{\cdot -}$  of long life in the iodine-oxalate reaction, and suggested that the photochemical after-effect in this reaction is an evidence of the existence of this ion. This intermediary product which was suspected on kinetic grounds by Abel,<sup>8</sup> Schmidt and Retter (1932) had been originally postulated by Berthoud (1924)<sup>9</sup> in the photochemical reaction between potassium oxalate and iodine. Abel, *et al.*<sup>8</sup> further concluded from kinetic measurements on the iodine-oxalate reaction that the photo-formation and accumulation of univalent oxalato ion  $C_2O_4^{\cdot -}$  of long life following irradiation of the reaction mixture is responsible for enhanced activity after subsequent darkening, the half-ion continuing its active influence on iodine and at the same time decaying spontaneously in other ways. More recently a detailed investigation of the marked photochemical after-effect of long duration in the iodine-oxalate reaction has been carried out<sup>6</sup> (1940), and a mechanism has been suggested

dispensing with the assumptions about the existence of activated molecules of long life as postulated by Mukerji and Dhar<sup>10</sup> (1928) and depending solely upon a simple extension of the Berthoud chain mechanism (involving the univalent oxalato ion  $C_2O_4'$ ) for the oxalate-iodine photo-reaction.

Experimental observations described in the present paper indicate that a close similarity exists between the photochemical after-effect in the iodine-oxalate reaction<sup>6</sup> and the photochemical after-effect between bromine and oxalic acid or potassium oxalate under discussion. As already stated the formation of the univalent oxalato ion  $C_2O_4'$  has been postulated by Berthoud<sup>9</sup> (1924) as a part of the mechanism involved in the bromine-oxalate photo-reaction. If it is assumed that the univalent oxalato ion so produced in the light reaction reacts with bromine more slowly than the rate at which it is formed in light, so that an excess of this active ion accumulates, the photochemical after-effect can be accounted for by the high reactivity towards bromine of this ion which carries on the chain when the illumination is withdrawn. The variation in the magnitude of the photochemical after-effect with the period of pre-illumination shows that the formation of  $C_2O_4'$  in light is faster than the rate at which they are used up, so that an excess of this ion accumulates depending on the period of pre-illumination. A similar mechanism has been postulated in the reaction between oxalic acid and potassium permanganate involving the half-ion  $C_2O_4'$  (1943)<sup>11</sup>.

The failure to detect the 'secondary after-effect' (MacMahon and Lal, 1940)<sup>6</sup> in this reaction suggests that when all the bromine is used up in the light reaction, the univalent oxalato ions left behind after cutting off the illumination rapidly disappear by self-combination:



This self-combination of the oxalato ion has been assumed to be responsible for the decay of the photochemical after-effect in the iodine-oxalate reaction.<sup>6</sup> The decay of the photochemical after-effect in reactions involving bromine may also be ascribed to the gradual disappearance of the chain carrier  $C_2O_4'$  in the above manner.

A complete elucidation of the mechanism of the photochemical after-effect in this reaction must await the results of further research. Experiments are already in progress in this direction. The above tentative mechanism has been suggested in the absence of further experimental evidence.

#### SUMMARY

A marked photochemical after-effect has been observed in the oxalic acid-bromine reaction in the presence of excess of potassium bromide.



The after-effect persists for several hours after cutting off the illumination, and increases with increasing periods of pre-illumination up to a certain stage. If the illumination is continued for longer periods the after-effect shows a diminution. The study of the retarding action of hydrobromic acid which is a product of the reaction may explain this diminution. When the bromine that has been photochemically removed in the light reaction is restored in the end solution in the dark immediately after the completion of the photo-reaction, no 'secondary after-effect' is observed.

Under suitable conditions the photochemical reaction between potassium oxalate and bromine is followed by a marked photochemical after-effect which persists for several hours. No 'secondary after-effect' could be detected in this reaction.

The 'decay' of the photochemical after-effect is very rapid just after the illumination is withdrawn and is relatively slower afterwards. It appears that the active intermediate product formed in the light reaction reacts with bromine giving the photochemical after-effect and is at the same time destroyed in other ways.

A tentative mechanism of these after-effects has been suggested involving the formation of the univalent oxalato ion  $C_2O_4'$ .

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