PHOTOIODINATION OF SODIUM TARTRATE IN AQUEOUS SOLUTION

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Sodium tartrate was iodinated with aqueous iodine in presence of light of different wave-lengths, at different temperatures and different concentrations of acceptor and active molecules

Most of the photoiodinations, that have been investigated, were done in presence of KI. Iodine is not much soluble in water and hence a concentrated solution of I_2 cannot be obtained. In aqueous solution in presence of KI, however an additional complexity is brought into the reaction, for in presence of KI an additional reaction $KI + I_2 = KI_3$ occurs.

In reaction in aqueous solution, this complexity can be avoided and it may be expected that in aqueous solution iodination may be also similar to other photohalogenation processes such as brominations.

Dhar (*Proc. K. Akad. Wetensch, Amsterdam*, 1916, **18**, 1097) first showed that sodium tartrate can be iodinated in presence of light. Dhar and Bhattacharyya studied the reaction in presence of KI and found that the reaction is unimolecular (*J. Indian Chem. Soc.*, 1929, **6**, 147). They studied the reaction under different wave-lengths of light and at temperature 20°, 30° and 40°. Photoiodination of sodium tartrate in aqueous solution has not been studied till now although photoiodination of some other salts such as potassium oxalate (Dhar, Bhattacharyya and Mukherjee, *J. Indian Chem. Soc.*, 1935, **12**, 151), sodium formate (Bhagwat, *ibid.*, 1940, **17** 304) in aqueous solution has been investigated. With the end in view mentioned above we investigated the reaction and found certain peculiarities as noted below.

EXPERIMENTAL

Resublimed I_2 was mixed with one-fourth its weight of KI and sublimed again. This I_2 was dissolved in conductivity water by shaking in a shaker. Sodium tartrate (E. P. Merck) was recrystallised from conductivity water and dissolved in conductivity water. The solutions of I_2 and sodium tartrate were kept in a thermostat and mixed in the dark. Immediately 3 c.c. of the mixture were withdrawn and titrated with approximately 0·001N $Na_2S_2O_3$ by using a microburette. The source of light was a point-o-lite lamp of 100 C. P. By keeping the centre of the lamp at a distance of 27·5 cm. from the reaction cell, the intensity of light was kept the same throughout the experiment. The mixture in the reaction cell was then exposed to light kept parallel by means of a lens. Heat rays were cut off by allowing the light to pass through a filter of $N/20$ $CuSO_4$ solution. At various intervals of time, measured by means of a stop-watch, 3 c.c. of the reaction mixture were withdrawn and titrated mith approximately 0·001N-$Na_2S_2O_3$ using a microbruette. By means of Wratten filters, lights of different wave-lengths were separated.

Since for every withdrawal of 3 c.c. of the reaction mixture, a vacuous space occurred into which I_2 could vaporise and since I_2 might also diffuse through the reaction cell, it was hence first investigated whether any error occurred due to these two factors. The escape of I_2 due to these factors was found quite negligible.

Table I gives the reaction rate in dark at 20°. The dark reaction is unimolecular. k is the unimolecular constant catculated from $k = \frac{1}{t} \log \frac{a}{a-x}$.

TABLE I

Sodium tartrate (0·42N) + I_2 (aq.) (0·1614 N/100). Temp = 20°

Time.	$Na_2S_2O_3$.	k.	Time.	$Na_2S_2O_3$.	k.
0 min.	5·15 c c.	—	120	4·91	0·0001725
60	5·03	0·00017	180	4·79	0·000175
			—	Mean k	0·0001725

Concentrations in brackets always represent the final concentrations after mixing the reactants.

Table II gives the reaction rate when exposed to lights of different wave-lengths. In presence of light, it has been noticed that the unimolecular constant k progressively decreases. There is, due to some cause as yet unknown, a rapid consumption of I_2 at the beginning. This large consumption of I_2 at the beginning is responsible for the diminution of unimolecular constant, for it is superimposed upon the reaction which is afterwards strictly unimolecular. Hence the unimolecular constant should be calculated not from zero time but by eliminating the first reaction. When this is done it is found that k again becomes constant. k' is the unimolecular constant calculated by eliminating the first reading. It may be pointed out here that in photobromination of tartaric acid by Ghosh and Basu (*J. Indian Chem. Soc.*, 1925, **2** 163 ; 1928, **5**, 342) there was observed also a progressive diminution of unimolecular constant k. To explain this they evaluated an equation (*ibid.*, 1928, **5**, 361) and obtained a constant by its application. In the present case a uniform value of the constant has always been obtained when k was calculated from the second reading of titration.

TABLE II

Time = 20°, Na-tartrate (0·42N) + I_2, aq. (0·1614 × $10^{-2}N$).

White light.				Blue light (408·5-490·5 $\mu\mu$)		
Time.	$Na_2S_2O_3$.	k.	k'.	$Na_2S_2O_3$.	k.	k'.
0 min.	5·17 c.c.			5·21 c.c.		
10	4·74	0 00377		4·82	0·00338	
30	4·56	0·00182	0·00084	4·67	0·00158	0·000685
60	4·30	0·00133	0·000846	4·45	0·00114	0·00069
120	3·83	0·00108	0·00084	4·05	0·00091	0·000686
180	3·44	0·000982	0·00082	3·65	0·00086	0·00071
		Mean k'	0·000836		Mean k'	0·000692

Greenish blue light (442—489·5 $\mu\mu$)				Red light (645 to 595 $\mu\mu$)		
Time.	$Na_2S_2O_3$.	k.	k'.	$Na_2S_2O_3$.	k.	k'.
0 min.	5·56 c.c.			5·59 c.c.		
10	5·30	0·00208		5·44	0·00118	
30	5·18	0·00103	0·00050	5·17	0·00113	
60	5·0	0·00077	0·000506	5·02	0·00078	0·00042
120	4·66	0·00064	0·000508	4·75	0·00059	0·000408
180	4·37	0·00058	0·000492	4·46	0·00054	0·000428
		Mean k'	0·000501		Mean k'	0·000418

It appears from Table II that the reaction rate is greatest in presence of white light and decreases as the wave-length is increased. The dark reaction is negligibly small in comparison with light reactions.

Table III summarises the reaction rate at different concentrations of sodium tartrate at a constant concentration of I_2 and Table IV, the same at different concentrations of I_2 but at a constant concentration of sodium tartrate. All the reactions are studied in presence of white light and at temperature 20°. Since in all these cases, also, there is a progressive diminution of k the unimolecular constant calculated from zero time, as noticed in the data supplied for different wavelengths, the values of k' only, which for each of these experiments had always a good constant value, have been given and compared.

TABLE III

Constant conc. of $I_2 = 0{\cdot}1614 \times 10^{-2}$ N.

Conc. of Na-tartrate	k'.
0·21 N	0·000561
0·42	0·000836
0·84	0·00115
1·26	0·00152

TABLE IV

Constant conc. of Na-tartrate = 0.042 N.

Conc. of Na-tartrate.	k'.
0·1614 N/100	0·000836
0·1614 N/200	0·00115
0·1614 N/400	0·00179

TABLE V

Wave-length.	k'_{20}.	k'_{60}.	Temp. coeff.
White	0·00836	0·00157	1·87
Blue (490·5-408.5 $\mu\mu$)	0·000692	0·00130	1·88
Greenish blue (442-489·5$\mu\mu$)	0·000501	0·00103	2·05
Red (645-595 $\mu\mu$)	0·000418	0·000875	2·08

Thus the greater the initial concentration of sodium tartrate, the greater is the reaction rate whereas the greater the initial concentration of I_2, the less is the rate. It is also evident that k' is proportional directly to the square root of concentration of sodium tartrate and inversely to the square root of concentration of I_2. That with increase in the concentration of acceptor molecules, the reaction rate increases and with increase in the concentration of I_2 molecules the reaction rate decreases had also been observed in photobromination of tartaric acid by Ghosh and Basu (*loc. cit.*). Table V gives the temperature coefficients of the reaction rates under different wave-lengths of light.

CONCLUSIONS

The peculiarity of this reaction is in the large consumption of I_2 at the beginning. Whether this anomaly is due to certain photosensitive impurity which is hitherto undetected, or due to formation of certain intermediate complex, remains a subject for further investigation.

(*i*) Photoiodination of sodium tartrate is a unimolecular reaction with respect to iodine concentration. (*ii*) The monomolecular constant increases with increase of the initial concentration of sodium tartrate. (*iii*) The monomolecular constant increases with decrease of the inital concentration of iodine—an interesting peculiarity which was observed in the case of photobromination of tartaric acid by Ghosh and Basu. (*iv*) The temperature coefficient varies from 1·87 to 2·08 for different wave-lengths. (*v*) There is a progressive diminution of unimolecular constant when calculated from the first reading ; but when calculated from the second, a very good unimolecular constant is obtained in all cases. This leads us to infer that large amount of I_2 is consumed at the very beginning after the reactants are mixed up by some reaction not yet known and unconnected with the main photoiodination process.

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