STUDIES IN BLUE PERCHROMIC ACID

Part I—Kinetics of the Decomposition of the Blue Perchromic Acid in Various Organic Media

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BARRESWIL[1] observed in 1847, that a deep blue solution is produced when a concentrated solution of chromic acid is mixed with hydrogen peroxide. If ether be shaken up with the blue solution, the aqueous layer is decolourised, and the ethereal layer retains the blue product. It was further observed by Grosvenor[2] that the blue compound is also soluble in ethyl acetate, amyl chloride, and various amyl esters. It is insoluble in carbon disulphide, benzene, toluene, carbon disulphide and various oils. The ethereal solution gives dirty violet precipitates with various alkaloids and amines, and when the precipitates are dried and treated with acids and ether, the blue solution is again obtained. Berthelot,[3] moreover, showed that with strong acids and a solution of dichromate, hydrogen peroxide gives the blue colour of the hypothetical blue perchromic acid. With the weaker acids, the colour is violet and not blue. The blue perchromic acid as extracted with ether or ethyl acetate is stable only for a few hours ; it decomposes with the evolution of oxygen. Various attempts have been made by Barreswil, Aschoff,[4] Brodie,[5] Martinon,[6] Berthelot, Riesenfeld,[7] Spitalsky[8] and others to elucidate the nature of this blue perchromic acid. In spite of the extensive work of Riesenfeld and Spitalsky, on the catalytic decomposition, not much work has been done on the kinetics of the decomposition of the blue perchromic acid itself. In the present series of papers, we propose to undertake the study of this blue perchromic acid from various standpoints with an idea to work out the conditions under which the acid is produced, its stability and decompositions, and also the various organic reactions in which the acid may be used.

Preparation of the Blue Acid

In all the experiments recorded in this paper, the blue perchromic acid was prepared from potassium dichromate (5% solution), dilute sulphuric

acid (2 N) and hydrogen peroxide (1·8 N). These solutions, as well as ether, were cooled in ice. 80 c.c. of the dichromate solution were taken in Jena conical flasks, also cooled to the ice temperature, and to this solution were added 20 c.c. of the dilute sulphuric acid. 40 to 50 c.c. of the hydrogen peroxide solution were added to the mixture, and immediately, the reaction mixture was shaken with about 120 c.c. of the ice-cooled ether. The ethereal layer which extracted out the blue perchromic acid was separated out from the aqueous layer by separating funnel. The proper separation was very necessary in the study of the reactions and therefore, all care was taken to ensure it.

The concentration of the blue acid thus extracted depended on the mode of preparation and the quantity of hydrogen peroxide used. The concentrations of the acid were determined in terms of the iodine liberated from potassium iodide in presence of dilute sulphuric acid, the iodine being titrated with hypo (N/20). A known volume of the blue acid was also evaporated to dryness over water-bath, and the residue left was weighed. The residue was further ignited in the platinum crucible and also weighed.

For each set of experiments, the same blue perchromic acid was used for proper comparison. This is necessary, because each preparation of the blue perchromic acid gives the acid of different strengths and characteristics.

The decomposition of the blue acid follows the monomolecular formula, and therefore the velocity constants were determined by the use of the equation :

$$K = \frac{1}{t} \log \frac{a}{a-x} = \frac{2 \cdot 303}{t} \log_{10} \frac{a}{a-x},$$

where a is the initial concentration, and $a - x$ the concentration at the time t.

Influence of Temperature on Decomposition

The 10 c.c. of the blue perchromic acid, prepared by the method given, left a residue of 0·0294 g. when evaporated over water-bath. This residue when ignited in the platinum crucible weighed 0·0198 g. of Cr_2O_3.

Different portions of the same acid were allowed to stand in Jena conical flasks in thermostats maintained at 10°, 20° and 30° ± 0·2. 2 c.c. of the blue acid were pipetted out from time to time, and immediately transferred to potassium iodide solution acidified with dilute sulphuric acid. The iodine liberated was titrated with hypo (N/20).

TABLE I

At 10°			At 20°			At 30°		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	4·2		19	4·1		0	4·15	
		0·000443			0·00148			0·00293
60	3·95		39	3·7		15	3·75	
		0·000659			0·00235			0·00560
120	3·5		79	3·1		30	2·8	
		0·000693			0·00210			0·00734
180	3·15		109	2·65		45	2·15	
		0·000670			0·00225			0·00736
240	2·9		139	2·2		60	1·5	
		0·000776			0·00225			0·00718
300	2·45		169	1·85		75	1·2	
		0·000807			0·00234			0·00737
360	2·15		199	1·6		90	0·9	
		0·000847			0·00222			0·00791
420	1·85		229	1·3		105	0·6	
		0·000960			0·00237			
480	1·45		259	1·05				
		0·00100			0·00251			
540	1·2		289	0·85				
		0·00100						
600	1·0							
Average K/2·303		0·000923			0·00229			0·00743
Induction period		300 mins.			70 mins.			40 mins.

The decomposition of blue perchromic acid is very slow at 0° C. ; it takes more than 20 hours to undergo decomposition. At lower temperatures there is a pronounced induction period, and therefore, the monomolecular values of K show also a slight continuous increase with time. At temperatures above 30°, the decomposition is very rapid. The values of log K plotted against inverse temperatures $\left(\frac{1}{T}\right)$ give a straight line, showing that Arrhenius equation is applicable to the decomposition of the blue perchromic acid.

From the results recorded above, it is also seen that there is a marked induction period at low temperatures within which the values of K show a continuous increase.

Decomposition of the Blue Acid in Presence of Benzene

It is known that the blue perchromic acid is not extracted out by benzene, but benzene being miscible with ether, it was found interesting to study the decomposition of the acid in ethereal solution in presence of

benzene. The blue acid was prepared by mixing 80 c.c. of 5% potassium dichromate, 20 c.c. of 2 N sulphuric acid, 50 c.c. of 1·8 N hydrogen peroxide and 120 c.c. of ether. From the ethereal extract of the perchromic acid, the following four combinations were made, keeping the total volume 30 c.c. and maintaining the same concentration of the blue acid. The decompositions of these four combinations at 30° were studied as in the previous experiments.

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + benzene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + benzene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + benzene 10 c.c.

TABLE II

No benzene			2 c.c. benzene			6 c.c. benzene			10 c.c. benzene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	7·7		3	7·65		6	6·95		9	5·4	
		·01026			·01060			·01321			·0124
15	5·4		18	5·3		21	4·2		17·5	4·25	
		·00912			·00999			·0134			·0138
30	4·1		34	3·75		36	2·75		24	3·35	
		·00976			·01009			·0133			·0141
45	2·8		48	2·75		51	1·7		32	2·5	
		·00940			·00999			·0161			·0162
60	2·1		63	1·95		66	0·75		54	1·0	
		·00987			·01004			·0155			·0188
75	1·4		78	1·4		81	0·45		69	0·5	
		·00985			·01090			·0162			·0177
90	1·1		93	0·9		96	0·3		84	0·25	
		·00977			·01050						
105	0·75		108	0·6							
		·00985			·01040						
120	0·5		123	0·4							
Average K/2·303		·00973			·01031		I	·0133		I	·0134
							II	·0159		II	·0175

It will be seen from the results recorded in Table II, that the decomposition of the blue acid is faster in presence of benzene than in ether alone. When the concentration of benzene is increased, it appears as if the decomposition is taking place in two stages : the monomolecular constants of the second stage are larger than those of the first stage. It is very likely that benzene reacts chemically with perchromic acid, and this secondary reaction influences the primary decomposition of the blue acid. The study of the

products formed by the reaction of benzene and perchromic acid is reserved for a subsequent paper.

Decomposition of the Blue Acid in Presence of Toluene

The decomposition kinetics of the blue perchromic acid was studied in presence of toluene also in the same way as in the previous case. The blue acid was prepared and extracted with ether, 10 c.c. of the acid on evaporation on water-bath left a residue of 0·0682 g., and this residue on ignition weighed 0·0448 g. of Cr_2O_3. The decomposition of the following combinations was investigated at 30° C.:

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + toluene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + toluene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + toluene 10 c.c.

TABLE III

No toluene			2 c.c. toluene			6 c.c. toluene			10 c.c. toluene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	6·05		3	5·25		6	4·6		9	3·15	
		·00899			·0086			·0165			·0254
15	4·35		18	3·9		21	2·6		14	2·35	
		·01040			·0119			·0188			·0224
30	2·95		33	2·3		36	1·25		24	1·45	
		·00974			·0115			·0188			·0260
45	2·2		48	1·6		51	0·65		29	0·95	
		·00962			·0123			·0168			·0252
60	1·6		63	0·9		66	0·45		39	0·55	
		·00961			·0120						·0241
75	1·15		78	0·65					44	0·45	
		·01000			·0113						·0271
90	0·75		93	0·5					54	0·3	
Average K/2·303		·0097			·0118			·0177			·0250

From these results, it will be seen that monomolecular constants are obtained when the decomposition of perchromic acid takes place in the presence of toluene. With the increased concentrations of toluene, we get an increased value of K.

Decomposition of the Blue Acid in Presence of Xylene

The results on the decomposition kinetics of the blue perchromic acid in presence of xylene are given in Table IV. The blue acid was prepared

in the way already described. 10 c.c. of this acid when dried on water-bath left 0·058 g. of residue which on ignition gave 0·0387 g. of Cr_2O_3. The decomposition of the following combinations was studied at 30°.

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + xylene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + xylene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + xylene 10 c.c.

TABLE IV

No xylene			2 c.c. xylene			6 c.c. xylene			10 c.c. xylene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	4·9		3	4·4		6	4·2		9	2·9	
		·0077			·0079			·0097			·0281
15	3·75		18	3·35		21	3·0		14	2·1	
		·0077			·00877			·0107			·0308
30	2·85		33	2·4		36	2·0		24	1·0	
		·0087			·00862			·00931			·0308
45	2·15		48	1·8		51	1·6		29	0·7	
		·00906			·00882			·01003			·0286
60	1·4		63	1·3		66	1·05		39	0·4	
		·00931			·00910			·0096			·0281
75	1·1		78	0·9		81	0·8		44	0·3	
		·0087						·00938			
90	0·8					96	0·6				
Average K/2·303		·00892			·00875			·00976			·02928

In the presence of xylene, perchromic acid decomposition rate is increased. With 2 c.c. of xylene, the change observed is not marked, whereas with 10 c.c. of it, the rate of decomposition increases about three times.

It is very significant to see that the decomposition influence is most prominent in the case of xylene and the least in the presence of benzene. Toluene shows an intermediate behaviour as is shown in the following table:

TABLE V

Hydrocarbon	K_1 in absence of hydrocarbon	K_2 with 10 c.c. hydrocarbon	K_2/K_1
Benzene	·02241	·04030	1·79
Toluene	·02235	·05757	2·57
Xylene	·02054	·06747	3·28

We have observed that along with the decomposition of perchromic acid, traces of aldehydes are formed from toluene and xylene, which give indication with Schiff's reagent. We are also studying the decomposition products of the blue acid.

Summary

The decomposition kinetics of the blue perchromic acid was studied under various conditions. The decomposition reaction is monomolecular. The value of K at 10° is 0·002125, at 20° 0·005273 and at 30° 0·01711 to 0·02241. The values differ slightly with different preparations. The values of log K plotted against 1/T give straight line, showing that Arrhenius equation is valid. From the study of kinetics, we find that there is a marked induction period also.

The rate of decomposition of the blue acid is markedly increased in the presence of benzene, toluene and xylene. When these hydrocarbons are present to the extent of 33 per cent. of the ethereal solution, the values of K increase 1·79 times with benzene, 2·57 times with toluene and 3·28 times with xylene, when the temperature maintained is 30°.

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