

308. The Catalytic Reduction of Organic Halogen Compounds: 5-Chloro-5-alkylbarbituric Acids.

By G. K. HUGHES and A. KILLEN MACBETH.

5-Chloro-5-alkylbarbituric acids are rapidly reduced in aqueous-alcoholic solution in the presence of colloidal platinum, and the rate of the unimolecular reaction can be determined conductometrically. In general, the velocity constant varies but little with the alkyl group, the *isopropyl* acid being exceptional. The reduction of the chloro-acids proceeds more quickly than that of the corresponding bromo-derivatives, the ratio in the cases examined being about 4. The halogen atom in the chloro-acids is also removed by the action of hydrazine hydrate.

It was shown (J., 1926, 1248) that 5:5-dichloro- and 5:5-dibromo-barbituric acids are reduced by hydrazine hydrate with the removal of one of the halogen atoms, and also (J., 1931, 1870) that the bromine atom is similarly removed from 5-bromo-5-alkylbarbituric acids. The labile nature of the halogen atom in the latter compounds was further demonstrated (J., 1934, 769) by the fact that they undergo reduction in aqueous-alcoholic solution in the presence of catalysts, notably colloidal platinum, the alcohol acting as the hydrogen donor and being oxidised to acetaldehyde. As the conductivities of the barbituric acids present in the system are negligible compared with that of the halogen acid formed during reduction, the reaction was followed conductometrically, and the results were found to be reproducible when the catalyst was dispersed throughout the system as colloidal platinum. When the concentration of alcohol was sufficiently high to be assumed constant throughout, the reductions were found to be unimolecular; moreover, the velocity constants were nearly equal for all the alkyl acids examined except the *isopropyl* acid, which was markedly higher.

The previous observations have now been supplemented by examination of a corresponding series of *chloroalkylbarbituric acids*, the technique previously described (*ibid.*) being followed. The unimolecular relationship is expressed in terms of observed resistances at known times, *viz.*,

$$k = [1/(t_2 - t_1)] \log_e (R_{t_1} - R_\infty)R_{t_2}/(R_{t_2} - R_\infty)R_{t_1}$$

and the constancy of k is tested by the slope of the curves obtained when $\log R_t/(R_t - R_\infty)$ is plotted against time. The graphs show more divergence from the straight line than in the case of the bromo-acids, but the velocity constants determined from the slope of the straight portions do not show much variation for the various acids except the *isopropyl* compound, which again has a higher value of k . In this connexion it is of interest that, when the bromomalonic esters of *isopropyl* and other secondary alcohols were treated with hydrazine hydrate (Gallus and Macbeth, J., 1937, 1810), there was a deficiency in the nitrogen liberated.

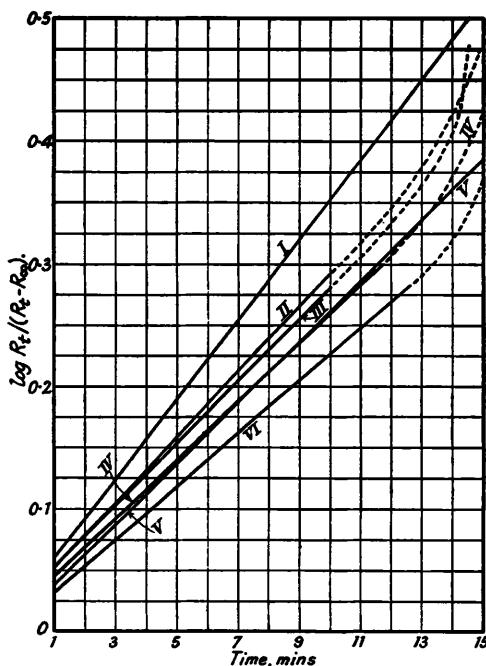
As previously observed, the velocity constant varies with the sample of colloidal platinum used, and the complete series of observations was therefore carried out with the same preparation of the catalyst (*viz.*, Pt VII). A control on this was maintained by repeating the measurements with the initial substance after the examination of the full series was completed, and in general it was found that the agreement between the constants thus obtained was within the margin of experimental error when the age of the colloidal preparation did not exceed 8 days.

Typical results are recorded in the experimental part and are shown graphically. The following values of k (\log_{10} ; min.^{-1}) are derived from the slopes of the graphs over the region from 2 to 10 mins.

Substituted barbituric acid.	100 <i>k</i> .	Substituted barbituric acid.	100 <i>k</i> .
5-Chloro-5-methyl	2.47	5-Chloro-5-butyl	2.60
5-Chloro-5-ethyl	2.12	5-Chloro-5-isoamyl	2.59
5-Chloro-5-propyl	2.39	*5-Bromo-5-isoamyl	0.613
5-Chloro-5- <i>isopropyl</i>	3.34	*5-Bromo-5- <i>isopropyl</i>	0.962

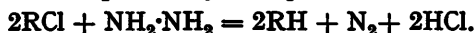
* The differences between the present values and those previously recorded (J., 1934, 772) are solely due to the different platinum sols used.

It is seen that the velocity constant for the chloro- is 3.48 times that for the bromo-isopropyl acid, the ratio in the corresponding isoamyl acids being 4.23. The reactivity here is in the opposite sense to that generally observed in the alkaline reduction of halogen compounds by hydrazine hydrate (Macbeth *et al.*, J., 1922, 121, 904, 1117, 2169; 1925, 127, 892) in which the bromine atom was more labile in the cases examined.



- I, 5-Chloro-5-isopropylbarbituric acid.
 II, 5-Chloro-5-butylbarbituric acid.
 III, 5-Chloro-5-isoamylbarbituric acid.
 IV, 5-Chloro-5-propylbarbituric acid.
 V, 5-Chloro-5-methylbarbituric acid.
 VI, 5-Chloro-5-ethylbarbituric acid.

5-Chloro-5-alkylbarbituric acids are reduced by hydrazine hydrate, the reaction proceeding more slowly in the case of the higher derivatives. Approximately 1 g.-atom of nitrogen is liberated per g.-mol. of the chloro-acid, except with the isopropyl derivative. The reduction may therefore be expressed by the equation



EXPERIMENTAL.

In the hydrazine estimations, alcoholic solutions of the chloro-acids were prepared containing 0.001 g.-mol. per 10 c.c. This volume was washed into a van Slyke nitrometer with 5 c.c. of absolute alcohol, and 2 c.c. of hydrazine hydrate (50%) were subsequently added. The volumes recorded after the analytical data are those of nitrogen corrected to *N.T.P.*

5-Chloro-5-methylbarbituric acid was prepared by passing a brisk stream of chlorine into a finely powdered suspension of 5-methylbarbituric acid in warm water; it crystallised from the hot solution on cooling, and after two recrystallisations from water had m. p. 201—202° (Found : Cl, 20.1. $\text{C}_5\text{H}_7\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 20.1%) (0.1765 G. gave 11.8 c.c., *i.e.*, 14.6 g./g.-mol.).

5-Chloro-5-ethylbarbituric acid was prepared by direct chlorination as above; after recrystallisation from water, it had m. p. 191—192° (Found : Cl, 18.3. $\text{C}_6\text{H}_7\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 18.6%) (0.1905 G. gave 11.6 c.c., *i.e.*, 14.5 g./g.-mol.).

5-Chloro-5-n-propylbarbituric acid was prepared by adding an excess of sulphuryl chloride to a solution of 5-propylbarbituric acid in chloroform; the chloro-acid dissolved when the mixture was warmed, and crystallised on cooling. Recrystallised from water or chloroform,

it had m. p. 190—191° (Found: Cl, 17.1. $C_7H_9O_3N_2Cl$ requires Cl, 17.4%) (0.2045 G. gave 11.3 c.c., *i.e.*, 14.1 g./g.-mol.).

5-Chloro-5-isopropylbarbituric acid, prepared as for the isomer and recrystallised from chloroform, had m. p. 188—189° (Found: Cl, 17.3%). Its reaction with hydrazine hydrate was very slow and a satisfactory end-point was not obtained.

5-Chloro-5-n-butylbarbituric acid, similarly prepared, was obtained as silky needles on recrystallisation from chloroform, m. p. 138—139° (Found: C, 16.2. $C_8H_{11}O_3N_2Cl$ requires Cl, 16.3%) (0.2185 G. gave 11.6 c.c., *i.e.*, 14.5 g./g.-mol.).

5-Chloro-5-isoamylbarbituric acid, prepared by the same method, separated on cooling as long silky needles; recrystallised from water, it had m. p. 164—165° (Found: Cl, 15.1. $C_9H_{13}O_3N_2Cl$ requires Cl, 15.3%) (0.2325 G. gave 11.7 c.c., *i.e.*, 14.6 g./g.-mol.).

Conductometric Measurements.—In the following table the numbers in parentheses after the name of the chloro-acid indicate the cell used in that experiment, the constant of cell I being 0.149 and that of cell II 0.298. The experimental solutions were prepared by running equal volumes of the colloidal platinum sol (J., 1927, 2600) and an $M/200$ -solution of the chloro-acid in 20% aqueous alcohol into the conductivity cell, all the solutions and vessels having previously been brought to constant temperature in a thermostat at 30°. The electrodes were unplatinised, and resistances were measured on a Pye dial-type bridge, an oscillator combination being used in the determination of the null point. The results obtained with a particular sample (Pt VII) of colloidal platinum are recorded below and in the figure.

t , mins.	R_t	$\log \frac{R_t}{(R_t - R_\infty)}$	t , mins.	R_t	$\log \frac{R_t}{(R_t - R_\infty)}$	t , mins.	R_t	$\log \frac{R_t}{(R_t - R_\infty)}$
Chloromethylbarbituric acid (I).			Chloroethylbarbituric acid (I).			Chloro- <i>n</i> -propylbarbituric acid (I).		
2	1100	0.0623	2	1250	0.0575	2	1040	0.0699
3	800	0.0882	3	920	0.0801	3	785	0.0942
4	650	0.1113	4	742	0.1018	4	645	0.1176
5	550	0.1351	5	634	0.1218	5	552	0.1409
6	480	0.1588	6	554	0.1425	6	486	0.1642
7	428	0.1827	7	446	0.1620	8	398	0.2107
8	388	0.2065	8	407	0.1854	9	367	0.2343
9	357	0.2305	9	373	0.2082	10	339	0.2607
10	330	0.2560	11	316	0.2332	12	297	0.3144
12	287	0.3118	13	269	0.2929	15	247	0.4196
14	254	0.3754	15	232	0.3729	∞	153	
∞	147		∞	155				
Chloroisopropylbarbituric acid (I).			Chlorobutylbarbituric acid (II).			Chloroisoamylbarbituric acid (II).		
2	1100	0.0697	2	1910	0.0784	2	1900	0.0763
3	710	0.1133	3	1470	0.1036	3	1490	0.0998
4	545	0.1543	4	1200	0.1308	4	1220	0.1255
5	458	0.1911	5	1030	0.1567	5	1050	0.1496
6	406	0.2229	6	910	0.1823	6	920	0.1756
8	336	0.2883	7	820	0.2079	7	828	0.2003
9	312	0.3210	8	747	0.2348	8	750	0.2277
10	293	0.3530	9	685	0.2640	9	692	0.2535
12	263	0.4200	10	637	0.2822	10	640	0.2825
15	234	0.5179	12	550	0.3638	12	546	0.3570
∞	163		15	449	0.5155	16	430	0.5401
			∞	312		∞	306	

THE JOHNSON CHEMICAL LABORATORIES,
UNIVERSITY OF ADELAIDE.

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