The Rate of Decomposition of Urethane in Acid Solution II

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In an earlier paper [1] the rate of decomposition of urethane was studied at 37.0°C in concentrated solutions of hydrochloric and sulphuric acids (c M). The first-order rate constant k (in sec^{-1}) could, up to $c = 6$, be expressed for solutions of hydrochloric acid by

$$\log(k/c) = 0.705 - 8 + 0.063\,c$$

and for solutions of sulphuric acid by

$$\log(k/c) = 0.801 - 8 + 0.0895\,c$$

It was suggested that the rate-determining step is a bimolecular reaction between a urethane molecule and a hydrated hydrogen ion (probably $H(H_2O)_4^+$, but here for simplicity written as H^+) on which reaction the strong acids exert a kinetic salt effect. In the earlier paper it was for both acids assumed that $[H^+] = c$. For sulphuric acid this is only a very rough approximation. The values of $[H^+]$ given in Table 1 are presumably more accurate. They were computed from estimates of the two dissociation constants of sulphuric acid made by Young and Blatz [2] mainly on the basis of measurements of intensities of Raman-lines carried out by Rao [3]. In Fig. 1 is shown that, when $\log(k/[H^+])$ is plotted against c, the points fall (up to $c = 7$) very close to a straight line with the equation

$$\log(k/[H^+]) = 0.768 - 8 + 0.094\,c$$

By extrapolation to $c = 0$ is obtained $k/[H^+] = 5.86 \times 10^{-8}$, a value that is higher than that found for hydrochloric acid (5.07×10^{-8}), possibly due to catalysis by hydrogen sulphate ions.

Measurements were also carried out on solutions of perchloric acid (prepared by dilution of Merck's Perchloric Acid, 60 %, pro analysi). The results are given in Table 1, and in Fig. 1 is shown a plot of $\log(k/[H^+])$ against c (where $[H^+] = c$). Instead of a straight line is obtained a curve with a minimum for a value of c between 2 and 3. By extrapolation to $c = 0$ is, however, found nearly the same value of $k/[H^+]$ as for hydrochloric acid.

Table 1. Rate of decomposition of urethane at 37.0°C.

Sulphuric acid			Perchloric acid	
c	$[H^+]$	$k \times 10^7$	c	$k \times 10^7$
1.00	1.07	0.78	1.00	0.497
2.00	2.11	1.90	2.00	0.968
3.00	3.13	3.55	3.00	1.44
4.00	4.14	5.70	4.00	2.05
5.00	5.11	8.98	5.00	2.94
6.00	6.01	12.86	6.00	4.23
6.96	6.68	17.6	7.00	6.03
8.00	7.15	22.2	8.00	7.69
8.97	7.48	24.9		
10.00	7.11	24.2		

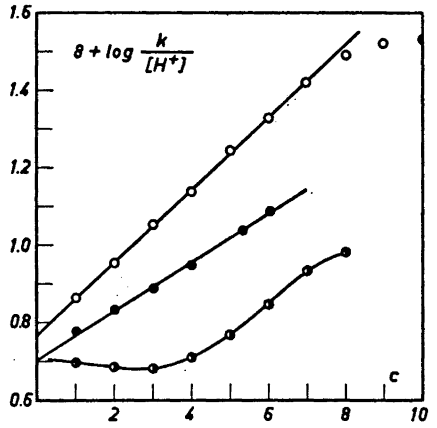

Fig. 1. Plot of $\log(k/[H^+])$ against c for the decomposition of urethane in solutions of sulphuric acid (open circles), hydrochloric acid (closed circles), and perchloric acid (semi-closed circles).

1. Pedersen, K. J. *Acta Chem. Scand.* **14** (1960) 1448.
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3. Rao, N. R. *Indian J. Phys.* **14** (1940) 143.

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