the solutions was distilled twice in a glass apparatus.

Apparatus. The measurements of the surface tension of the water solutions were performed with a torsion weight tensiometer (Cenco, Model No. 70540). All the measurements refer to 1 % solutions of fluorophosphorus compounds. The surface tension was measured at 20°C. Three independent measurements of each solution were taken. The correction factor of the instrument was 0.94.

Results and discussion. In Table 1 are collected the data from the present study. In the same table are included also the partition coefficients for the distribution of some of the fluorophosphorus compounds between water and carbon tetrachloride [2]. We recognize a rapid rise in surface activity of the fluorophosphorus compounds with the increase of their hydrocarbon content. The rise of the surface activities of the compounds is accompanied by a corresponding increase of the partition coefficients in the system CCl_4/H_2O.

From analogy with the present results we expect that fluorophosphorus compounds are capable of changing the interfacial tension between lipoids and water to a considerable degree, and in this way may play a role when the whole picture of the phosphorylating process of the enzyme is considered.

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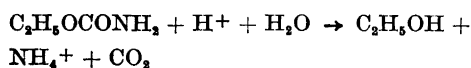2. Öksne, S. *Acta Chem. Scand.* **13** (1959) 1814.

The Rate of Decomposition of Urethane in Acid Solution

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The rate of the reaction

$$C_2H_5OCONH_2 + H^+ + H_2O \rightarrow C_2H_5OH + NH_4^+ + CO_2$$

was studied manometrically at 37.0°C in concentrated aqueous solutions of hydrochloric and sulphuric acids (c moles per liter solution). Owing to the slowness of

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

c	$k \times 10^7$	$-H_0$	a_{H_2O}
Hydrochloric acid:			
1.00	0.60	0.20	0.955
2.00	1.36	0.69	0.900
3.00	2.32	1.05	0.836
4.00	3.56	1.40	0.765
4.00 *	3.67		
5.32	5.81	1.87	0.659
6.03	7.39	2.13	0.598
Sulphuric acid:			
1.00	0.78	0.26	0.960
2.00	1.90	0.84	0.903
3.00	3.55	1.38	0.823
4.00	5.70	1.85	0.721
5.00	8.98	2.28	0.603
6.00	12.86	2.76	0.479
6.96	17.6	3.30	0.366
8.00	22.2	3.87	0.258
8.97	24.9	4.38	0.175
10.00	24.2	4.89	0.108

* The solution contained in addition 0.10 M cupric chloride.

the reaction, the final pressure was not observed but calculated from the pressure increase when, instead of urethane, calcium carbonate was dissolved. In general, only 5 to 30 % of the decomposition was observed, but in one experiment (solvent 10 M sulphuric acid) readings were taken till more than 80 % of the urethane had decomposed, and it was shown that the reaction follows the first-order law. The initial concentrations of urethane varied from 0.02 to 0.1 M. The urethane (m.p. 48.1°C) had been purified by melting and partly crystallising the commercial preparation. Velocity constants k (in sec^{-1}) are given in Table 1 together with values of the Hammett H_0 acidity function [1] and the water activities a_{H_2O} of the solutions computed from vapour-pressure data [2,3]. The velocity constant k increases more rapidly than c, but less rapidly than h_0 (where $H_0 = -\log h_0$). When the three most concentrated solutions are left out of consideration, k is roughly proportional to $h_0 a_{H_2O}^4$ as shown in Fig. 1 where $\log k$ has been plotted against $-H_0 + 4 \log a_{H_2O}$. The points fall fairly close to a straight line with the
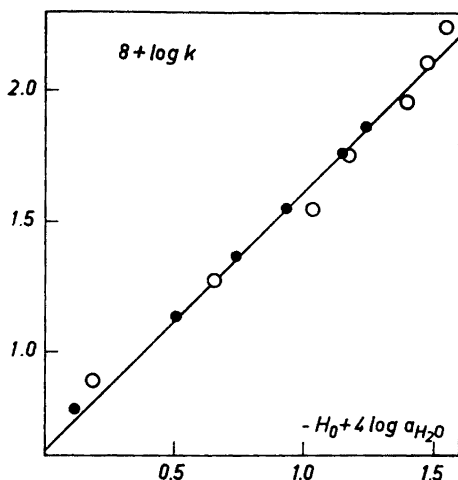
Fig. 1. Plot of log k against $-H_0 + 4$ log a_{H_2O} for the decomposition of urethane in solutions of hydrochloric acid (closed circles) and sulphuric acid (open circles). The straight line has the slope unity.

slope unity. This indicates that a bimolecular reaction between a urethane molecule (U) and the ion $H(H_2O)_4^+$ is rate-determining, since, in this case, the rate will be proportional to

$$a_U a_{H(H_2O)_4}^+ /f_{UH(H_2O)_4}^+ \qquad (1)$$
$$= [U] \, f_U a_H^+ \, a_{H_2O}^4 /f_{UH(H_2O)_4}^+$$
$$\simeq [U] \, h_0 a_{H_2O}^4$$

It has recently been derived in different ways [4-6] that the hydrogen ion in aqueous solution is hydrated with 4 molecules of water. If it is assumed that $[H(H_2O)_4^+] = c$, we obtain from expression (1) that

$$k = A c f_U f_{H(H_2O)_4}^+ /f_{UH(H_2O)_4}^+$$

where A is a constant. Since it may be expected that to a first approximation

$$\log \, (f_U f_{H(H_2O)_4}^+ /f_{UH(H_2O)_4}^+) = Bc$$

where B is a constant, we obtain the following approximate formula

$$\log \frac{k}{c} = \log A + Bc$$

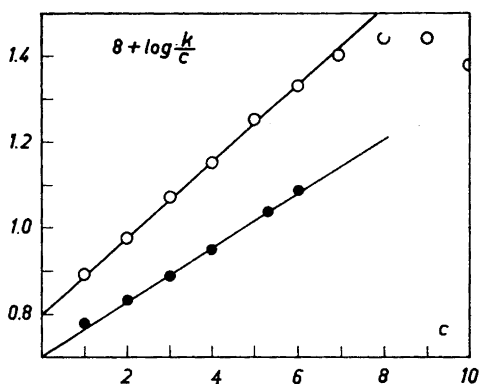In Fig. 2 it is shown that the experimental data agree well with this formula up to

Fig. 2. Plot of log $\frac{k}{c}$ against c for the decomposition of urethane in solutions of hydrochloric acid (closed circles) and sulphuric acid (open circles).

$c = 6$. From the graph is obtained for solutions of hydrochloric acid

$$\log \frac{k}{c} = 0.705 - 8 + 0.063 \, c$$

and for solutions of sulphuric acid

$$\log \frac{k}{c} = 0.801 - 8 + 0.0895 \, c$$

By extrapolation to $c = 0$ is found for hydrochloric acid $k = 5.07 \times 10^{-8} \times c$, and for sulphuric acid $k = 6.32 \times 10^{-8} \times c$. The larger value for sulphuric acid may possibly be attributed to catalysis by hydrogen sulphate ions in addition to the hydrogen ion catalysis.

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