

# Surface Tension of Water Solutions of Fluorophosphorus Compounds

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In connection with a study of the action of fluorophosphorus compounds as potent inhibitors of cholinesterases it was desirable to investigate whether these com-

pounds possessed surface active properties. Such properties may be expected to exert influence upon biochemical reactions due to the fact that enzymatic processes depend to a great extent upon the presence of lipid-water interfaces. The observation of the very strong polar character of the phosphoryl group<sup>1</sup> suggests that fluorophosphorus compounds with sufficient large hydrocarbon groups may possess considerable surface activity.

*Materials.* The preparation of the fluorophosphorus compounds was performed as previously described<sup>1</sup>. The water used for making

Table 1. Surface tension of water solutions of fluorophosphorus compounds (1 %). Temperature: 20°C.

Compound	Observed values	Corrected values, dyn/cm	Distribution coefficients CCl <sub>4</sub> /H <sub>2</sub> O
Pure water	77.4, 77.2, 77.0	72.6	—
$\begin{array}{c} \text{CH}_3\text{O} \quad \text{O} \\ \diagdown \quad // \\ \text{P} \\ \diagup \quad \backslash \\ \text{CH}_3\text{O} \quad \text{F} \end{array}$	70.0, 70.1, 69.8	65.8	0.9
$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \quad \text{O} \\ \diagdown \quad // \\ \text{P} \\ \diagup \quad \backslash \\ \text{C}_2\text{H}_5\text{O} \quad \text{F} \end{array}$	56.7, 56.8, 56.9	53.3	3.46
$\begin{array}{c} (\text{CH}_3)_2\text{CHO} \quad \text{O} \\ \diagdown \quad // \\ \text{P} \\ \diagup \quad \backslash \\ (\text{CH}_3)_2\text{CHO} \quad \text{F} \end{array}$	37.2, 38.2, 38.0	35.5	38.3
$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \diagdown \quad // \\ \text{P} \\ \diagup \quad \backslash \\ (\text{CH}_3)_2\text{CHO} \quad \text{F} \end{array}$	65.7, 66.4, 66.2	62.0	—
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{O} \\ \diagdown \quad // \\ \text{P} \\ \diagup \quad \backslash \\ (\text{CH}_3)\text{CHO} \quad \text{F} \end{array}$	52.3, 52.4, 52.6	49.3	—

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\*. 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  $\text{CCl}_4/\text{H}_2\text{O}$ .

From analogy with the present results we expect that fluorophosphorus compounds are capable of changing the interfacial tension between lipids 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.

1. Aksnes, G. and Gramstad, T. *Acta Chem. Scand.* **14** (1960). *In press.*
2. Oksne, S. *Acta Chem. Scand.* **13** (1959) 1814.

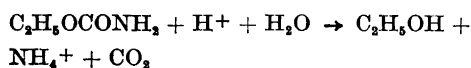
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## The Rate of Decomposition of Urethane in Acid Solution

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The rate of the reaction



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.

$c$	$k \times 10^7$	$-H_0$	$a_{\text{H}_2\text{O}}$
<i>Hydrochloric acid:</i>			
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
<i>Sulphuric acid:</i>			
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  $\text{sec}^{-1}$ ) are given in Table 1 together with values of the Hammett  $H_0$  acidity function<sup>1</sup> and the water activities  $a_{\text{H}_2\text{O}}$  of the solutions computed from vapour-pressure data<sup>2,3</sup>. 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  $h_0 a_{\text{H}_2\text{O}}^4$  as shown in Fig. 1 where  $\log k$  has been plotted against  $-H_0 + 4 \log a_{\text{H}_2\text{O}}$ . The points fall fairly close to a straight line with the