Hydrolysis of t-Butyl Chloride in Water containing Hydrogen Peroxide or Poly(vinylpyrrolidone)

By **Michael J. Blandamer** * and **Jill R. Membrey**, Department of Chemistry, The University, Leicester LE1 7RH

Kinetics of hydrolysis have been measured for t-butyl chloride in water containing various amounts of either hydrogen peroxide or poly(vinylpyrrolidone) (PVP). When hydrogen peroxide was added, the rate constant increased, but when PVP was added, the rate constant decreased. In the latter case, the activation parameters follow a trend which indicates that no significant changes occur in water–water interactions when PVP is added to water.

KINETICS of hydrolysis of t-butyl chloride have been studied in a wide range of binary liquid mixtures.[1-3] Moreover, the activation process is thought to require extensive reorganisation of water surrounding the substrate. Consequently, any gross modification of water–water interaction brought about by another solute or co-solvent should be reflected by a change in the kinetic parameters.

The measurements reported here for the H_2O_2–H_2O system were made because we were interested to know the effect of adding a co-solvent in a case where the mixing was supposedly dominated by intercomponent association, as indicated by the negative value[4-6] for

---

[1] R. E. Robertson and S. E. Sugamori, *Canad. J. Chem.*, 1972, **50**, 1353.

[2] R. E. Robertson and S. E. Sugamori, *J. Amer. Chem. Soc.*, 1967, **91**, 7254.

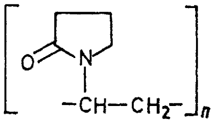
[3] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[4] A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, 1953, **15**, 161.

[5] P. A. Giguere, O. Knop, and M. Falk, *Canad. J. Chem.*, 1958, **36**, 883.

[6] G. Scatchard, G. M. Kavanagh, and L. B. Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715.

the excess molar Gibbs function of mixing, G^E. These measurements provide a possible reference point from which the effect on the kinetics of other solvents and the water soluble polymer PVP (I) can be considered.



(I)

EXPERIMENTAL

Materials.—Hydrogen peroxide (AnalaR) was diluted with freshly distilled water. t-Butyl chloride was re-distilled. The PVP (B.D.H.) had an average molecular weight of 700,000. The PVP solutions were prepared by adding weighed amounts of PVP to freshly distilled water.

Kinetics.—The reaction was followed by monitoring, automatically, the change of conductivity with time of very dilute solutions of t-butyl chloride. The conductivity cells were connected to a flask wherein the solutions were stirred before being blown over into the conductivity cells. In this way, problems associated with the low solubility of t-butyl chloride were overcome. Indeed, we attribute the reported induction period[7] to this low solubility rather than to some novel feature of the reaction mechanism.

The rate constants were calculated by the procedure suggested by Moore,[8] and the activation parameters by the method developed by Clarke and Glew,[9] modified for the analysis of kinetic data using transition state theory.

RESULTS

At five temperatures over the range $273 \leqslant T \leqslant 293$ K, the rate constant for the hydrolysis of t-butyl chloride increased when hydrogen peroxide was added. Rate data were obtained for three mixtures where the mole fractions of hydrogen peroxide were 0·03, 0·1, and 0·17. Unfortunately, measurements could not be made at higher temperatures or with more concentrated peroxide solutions because occlusion of oxygen bubbles on the electrodes produced wild fluctuations in the conductivity of the solutions. This was still a problem for the system reported here but rate data could be measured satisfactorily. The compositions of several mixtures were checked before and after kinetic runs by titrating the iodine liberated from potassium iodide against sodium thiosulphate. The change in mole fraction arising from peroxide decomposition was negligibly small. The thermodynamic activation parameters were calculated by using two regression coefficients[9] (Table 1). The difficulties encountered with the peroxide decomposition meant that the rate constants were insufficiently precise (±5%) to warrant using a more sophisticated analysis.

The rapid increase in viscosity which results from addition of PVP to water[10] also resulted in experimental difficulties. The system becomes difficult to stir and so the preparation of a homogeneous solution within the time limit set by the chemical reaction becomes difficult. Nevertheless, reasonable kinetic data were obtained for solutions containing up to 7·5% by weight of PVP (w_2). The reaction followed first-order kinetics over at least three half-lives. Rate data were obtained at 5 K intervals over the range 278—308 K for solutions with w_2 = 0·5, 1, 3, 5, and 7·5. At low temperatures and in solutions containing small amounts of PVP the rate constants were reproducible within ±1%. However, as either temperature or w_2 was increased, the accuracy fell rapidly, as shown by the standard deviation in the activation enthalpy, $\Delta H^\ddagger$ (Table 2).

TABLE 1

Kinetic data for the hydrolysis of t-butyl chloride in water–hydrogen peroxide

Mole fraction of H_2O_2	10^3k (283·2 K)/ s^{-1}	10^2k[a] (298 K)/ s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$T\Delta S^\ddagger$/ kJ mol^{-1}
0·03	4·57 ± 0·01	3·77	97·1 ± 0·2	16 ± 0·2
0·1	7·51 ± 0·05	5·24	90·3 ± 1·3	9·9 ± 1·3
0·17	9·52 ± 0·16	5·6	78·6 ± 3·9	−1·5 ± 3·9

[a] Extrapolated values at 298 K.

TABLE 2

Kinetic data for hydrolysis of t-butyl chloride in water containing PVP

PVP w_2 (%)	10^3k (278 K)/ s^{-1}	$\Delta G^\ddagger$ (298 K)/ kJ mol^{-1}	$\Delta H^\ddagger$ (298 K)/ kJ mol^{-1}	$T\Delta S^\ddagger$ (298 K)/ kJ mol^{-1}
0[a]	1·68	81·65	94·37	12·72
0·5	1·58	82·54	88·5 ± 0·9	5·9 ± 0·9
1	1·49	83·21	86·1 ± 1·5	3·1 ± 1·5
3	1·42	83·12	86 ± 3	3·2 ± 3
5	1·33	83·64	84 ± 5	0·2 ± 5
7·5	1·09	84·69	82 ± 12	−2·7 ± 12

[a] Kinetic data calculated from data in ref. 13.

DISCUSSION

At fixed temperature, the Gibbs free energy of activation, $\Delta G^\ddagger$, increased when PVP was added but decreased when hydrogen peroxide was added. However, in both cases, $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ decreased. The increase in rate constant when hydrogen peroxide is added is therefore a consequence of a less marked change in $T\Delta S^\ddagger$. Indeed, if the solvent variation of $\Delta H^\ddagger$ solely determined the change in rate constant, then the latter would increase when t-butyl alcohol, ethanol, propanol, tetrahydrofuran, or acetonitrile was added to water.[1,2] The uniqueness of hydrogen peroxide in increasing the rate constant arises[11] because the change in $\Delta H^\ddagger$ is just sufficient to dominate the decrease in $T\Delta S^\ddagger$. This is not the case for these organic co-solvents and for PVP and so $\Delta G^\ddagger$ increases and k decreases.

In recent analyses of the effect of co-solvents on the kinetics of hydrolysis of t-butyl chloride and other substrates in water-rich mixtures, the importance of solvent effects on the initial state has been stressed.[1-3,12] In these terms, therefore, an increase in the rate constant when H_2O_2 is added may stem from a destabilisation of the initial state. This may be linked, at least qualitatively, with the negative G^E value for this binary mixture, bearing in mind that when the co-solvent is a monohydric alcohol, tetrahydrofuran, or acetonitrile, the rate constant decreases and here G^E is positive. The subtle change from systems where the change in

---

[7] P. A. Adams, J. G. Sheppard, and E. R. Swart, *J.C.S. Chem. Comm.*, 1973, 663.

[8] P. J. Moore, *J.C.S. Faraday I*, 1972, **68**, 1890.

[9] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

[10] J. A. Glasel, *J. Amer. Chem. Soc.*, 1970, **92**, 375.

[11] M. J. Blandamer and J. R. Membrey, *J.C.S. Chem. Comm.*, 1973, 614.

[12] E. Grunwald and A. Effio, *J. Amer. Chem. Soc.*, 1974, **96**, 423.

$T\Delta S^\ddagger$ determines the change in rate constant to a system where the change in $\Delta H^\ddagger$ is important cannot be accounted for precisely.

The cryoprotective properties of PVP have attracted considerable interest. However, the actual state of water in the PVP–H_2O system is the subject of considerable controversy. The consensus of opinion seems to be that the polymer immobilises water, and some authors claim that this water has an ice-like structure.[13] For example, the near-i.r. spectrum of HOD in D_2O changes when PVP is added,[14] and the changes indicate a marked water-structure-forming action by PVP.[15] As indicated above, if the water were involved in this tightly organised structure, marked changes in rate constant and activation parameters would be expected when PVP is added to t-butyl chloride in water. However, the kinetic data show a pattern of behaviour which resembles the modest changes when an organic co-solvent is added to water. The near compensation between $T\Delta S^\ddagger$ and $\Delta H^\ddagger$ (Table 1) is also similar to that observed in other systems. The kinetic data support the conclusions reached by Glasel [10] concerning the state of water in the PVP system. Glasel bases his conclusions on deuteron magnetic resonance data, which show that the relaxation rate for D_2O in PVP is essentially the same as that in bulk water. It appears that, from the kinetic viewpoint, the majority of the water in the PVP system is held in a mesh of PVP polymer and that its structure is not grossly modified.

We thank the S.R.C. for support.

[4/466 *Received, 11th March,* 1974]

---

[13] H. H. G. Jellinek in 'Water and Aqueous Solutions,' ed. R. A. Horne, Wiley, London, 1972, ch. 3.

[14] J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, 1966, **45**, 2868.

[15] M. J. Blandamer and M. F. Fox, in 'Water—A Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1973, vol. 2, ch. 8.