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Ultrasonic Investigation of the Rate of Hydrolysis of Potassium Cyanide

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The kinetics of the hydrolysis of the cyanide ion have been studied by ultrasonic absorption measurements over the frequency range 30 kc to 25 Mc. A single relaxation frequency has been observed which depends on concentration in the manner expected theoretically for the hydrolysis reaction The relaxation frequency at 25°C is 450 kc for a 0.01M solution and 950 kc for 0.05M. The corresponding forward and reverse rate constants calculated for the reaction $CN^+H_2O=HCN+OH^-$ are $k_1=5.2\times10^4$ sec⁻¹ and $k_{-1}=3.7\times10^{-1}$ $10^9 M^{-1}$ sec⁻¹ at 25°C. From the magnitude of the maximum excess acoustic absorption per wavelength $(90 \times 10^{-6} \text{ at } 25^{\circ}\text{C} \text{ for the } 0.05M \text{ solution})$, the partial molal volume change ΔV° for the process is calculated to be $-12.4 \text{ cm}^3/\text{mole}$. The temperature dependence of the relaxation frequency indicates an energy of activation for the process $HCN+OH^-\rightarrow CN^-+H_2O$ of 6 ± 2 kcal/mole.

INTRODUCTION

THE measurement of ultrasonic absorption provides L a means for determining the rate constants for reactions which occur far too rapidly to be studied kinetically by more conventional methods. Relaxation times obtained from absorption data can be used to calculate the kinetic parameters for systems ordinarily at equilibrium when the forward and/or reverse reactions have actual or effective first-order half-lives of 10⁻⁵ to 10⁻⁹ sec. Such reactions can be studied acoustically provided the volume change or entropy change for the process is of a sufficient magnitude to couple the reaction to the acoustic waves and hence show up as excess sound absorption. For example, in a 10^{-2} M solution with a degree of dissociation $\delta = 10^{-2}$ and a relaxation time of 10^{-7} sec, the volume change must be at least several cm³/mole of reaction in order that the relaxation process may be observed by acoustic absorption techniques. The entropy change required for the reaction to be coupled to the acoustical waves through the periodic temperature variations associated with the waves is usually prohibitively large for aqueous solutions because the variation of temperature with pressure under adiabatic conditions is small.

Only a limited number of protolytic reactions have been studied by the ultrasonic relaxation method. These include the relaxation processes in aqueous solutions of ammonia and sulfur dioxide. The excess acoustic absorption¹ observed in ammonia solutions can be attributed^{2,3} to the perturbation of the equilibrium $NH_3+H_2O \cong NH_4^++OH^-$. More recently Eigen and his co-workers⁴ have studied the rate of hydrolysis of SO₂ by an ultrasonic absorption method.

The purpose of the present investigation has been to

Vermont, Burlington, Vermont ¹K. Tamm, G. Kurtze, and R. Kaiser, Acustica 4, 380 (1954).
 ²M. Eigen, Z. physik, Chem. 1, 176 (1954).
 ³M. Eigen and J. Schoen, Z. Elektrochem. 59, 483 (1955).
 ⁴M. Eigen, K. Kustin, and G. Maas, Z. physik. Chem. 30, 130 (1957).

(1961).

determine the kinetic parameters for the hydrolysis of the cyanide ion by means of ultrasonic absorption measurements. One reason for investigating this reaction is to compare the rate constants for it with those for other proton-transfer reactions such as the ionization of water and ammonia. A particular advantage of the cyanide system is that the excess relaxation absorption can be uniquely interpreted in terms of a one-step reaction. Such has not been the case with many of the other systems previously studied by ultrasonic relaxation techniques, for example, the various polyvalent electrolytes.

THEORY

For kinetic purposes a hydrolysis reaction may be represented by an equation of the following form since the concentration of water is essentially constant:

$$A \underset{k=1}{\overset{k_1}{\underset{k=1}{\longrightarrow}}} B + C.$$
 (a)

The rate constants and concentrations are related to the relaxation time by

$$dC_{\rm B}/dt = k_{\rm I}C_{\rm A} - k_{-\rm I}C_{\rm B}C_{\rm C} = -(C_{\rm B} - \bar{C}_{\rm B})/\tau, \quad (1)$$

where τ is the relaxation time associated with the return of the concentration $C_{\rm B}$ to its equilibrium value $\bar{C}_{\mathbf{B}}$ after being perturbed by the pressure variations associated with the acoustic waves. From Eq. (1) it follows that

$$\tau = \frac{1}{2\pi f_r} = \frac{1}{k_1 + (\bar{C}_{\rm B} + \bar{C}_{\rm C})k_{-1}} = \frac{1}{k_1 + 2\delta C_0 k_{-1}},\qquad(2)$$

where f_r is the relaxation frequency and δ is defined by $\delta = \overline{C}_{\mathbf{B}}/C_0$ in which C_0 is the molar concentration of the electrolyte if it were entirely in the form of A.

The relaxational or excess acoustic absorption per wavelength associated with a dissociation or hydrolysis equilibrium is given by

$$(\alpha\lambda)_{r} = \frac{\pi (\Delta V^{0})^{2}}{\beta_{0}RT} \cdot \frac{\delta C_{0}(1-\delta)}{1000(2-\delta)} \cdot \frac{\omega\tau}{1+\omega^{2}\tau^{2}}, \qquad (3)$$

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FIG. 1. Block diagram of the apparatus for the measurement of ultrasonic absorption by the spherical resonator method.

where ΔV^0 is the partial molal volume change for the reaction, β_0 is the isothermal compressibility of the solution, ω is the angular frequency, α is the amplitude absorption coefficient, λ is the wavelength, and T is the absolute temperature. The isothermal compressibility β_0 is for all practical purposes the same as the adiabatic compressibility β_s which is given by $\beta_s = 1/(\rho c^2)$ where ρ is the density and c is the acoustic velocity. Equation (3) has a maximum value at $\omega_r = 1/\tau$, where ω_r is the angular relaxation frequency.

Often acoustic absorption data are expressed in terms of the ratio α/f^2 where f is frequency. This ratio is related to $(\alpha\lambda)_r$ by

$$\frac{\alpha}{f^2} = \frac{(\alpha\lambda)_r}{cf} + \left(\frac{\alpha}{f^2}\right)_{\infty},\tag{4}$$

where $(\alpha/f^2)_{\infty}$ is the value for this ratio at a frequency high compared to the relaxation frequency. Equation (4) exhibits two regions in which the value of α/f^2 is independent of frequency: $\omega \ll \tau$ and $\omega \gg \tau$. The inflection point in the curve occurs where $\omega_r = 1/\tau$. Thus the relaxation frequency and hence the relaxation time can be determined from the position of either the maximum in the $(\alpha\lambda)_r$ curve or the inflection point in the α/f^2 curve. The individual rate constants can be calculated from the relaxation time by Eq. (2) if the equilibrium constant for the reaction is known. In many instances, $2\delta C_0 k_{-1} \gg k_1$, and the determination of the relaxation time τ gives k_{-1} directly. The magnitude of the relaxational absorption per wavelength allows the calculation of the partial molal volume change ΔV^0 associated with the reaction from Eq. (3). For dilute solutions, the term $(\alpha/f^2)_{\infty}$ in Eq. (4) is, to a very close approximation, the value of (α/f^2) for the solvent at any frequency involved in the measurements. Such is the case in the present study since the most concentrated solution used in this work was 0.05M.

EXPERIMENTAL

For the frequency range 30 to 300 kc, measurements were made by the spherical-resonator method with 12and 50-liter Pyrex-glass resonators. The experimental technique was similar to that described by Leonard and Wilson,^{5,6} Kurtze and Tamm,⁷ and Karpovich.⁸ Figure 1 shows a block diagram of the apparatus. The necks of the 12- and 50-liter flasks were reduced to approximately 1.2 cm o.d. in an attempt to reduce mode conversion and subsequent boundary losses with a large neck. During the measurements, the spherical vessels were supported on piano wire in a vacuum chamber. The liquid-filled resonators were excited acoustically by means of a small stack of ammonium dihydrogen phosphate (ADP) crystals coupled to the walls of the vessels. The acoustical frequency was adjusted to correspond to a radial mode in each case. Such modes are characterized by a minimum of wall losses. The vessels were driven acoustically for a length of time sufficient to reach steady state and then the excitation stopped. The subsequent decay of sound within the vessel was followed by a second stack of ADP crystals, the signal from which was amplified and recorded on a Bruel and Kjaer high-speed logarithmic recorder. A series of measurements was made with the 12- and 50liter vessels filled with degassed distilled water and then degassed cyanide solutions at particular radial modes. The net difference in decay rate was then related to the excess amplitude absorption coefficient by the equation

 $\alpha = (0.115/c) [(\mathrm{dB}/t)_{\mathrm{solution}} - (\mathrm{dB}/t)_{\mathrm{water}}], \quad (5)$

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⁵O. Wilson and R. Leonard, Tech. Rept. 4, Department of Physics, University of California, U. S. Office of Naval Research Contract No. N6 onr 27507, Project No. NR 014302 (June 1951). ⁶O. Wilson and R. Leonard, J. Acoust. Soc. Am. **26**, 223 (1954).

⁷G. Kurtze and K. Tamm, Acustica 3, 33 (1953).

⁸ J. Karpovich, J. Acoust. Soc. Am. 26, 819 (1954).

where the quantity (dB/t) is the observed decay rate expressed in decibels per sec.

Equation (5) involves the assumption that the wall losses were the same for the cyanide solutions and for pure water. This assumption is reasonable when the wall losses are small compared to the observed absorption for the solutions. Such was the case in the present work for all measurements made at frequencies above 80 kc. Even at frequencies well below this value, Eq. (5) is still expected to be a rather good approximation. The wall losses depend on the acoustical impedance and viscosity of the liquid in the vessel. Since both of these quantities are essentially the same for pure water and the dilute cyanide solutions, no significant difference in wall losses would be expected. The validity of this assumption at low frequencies can be gauged from an examination of the low-frequency points in the graphs which will be subsequently presented. The 50-liter flask offered some advantage over the 12-liter flask at low frequencies because the wall losses were somewhat smaller.

Great care must be taken to insure that the liquids contain no gas bubbles during the ultrasonic absorption measurements. For this reason, the liquids were carefully degassed prior to the absorption measurement. Degassing was accomplished by subjecting the liquid in the spherical vessel to sound waves (10 or 20 kc) of sufficient amplitude to cause cavitation within the vessel. The pressure above the liquid was reduced to increase the rate of degassing.

Due to the weight of the 50-liter liquid-filled resonator and the subsequent danger of implosion, the degassing equipment was built as an integral part of the absorption apparatus. Figure 2 shows the experimental arrangement. The liquid-filled vessel was placed on the piano-wire support within the vacuum chamber. Sound at 10 kc from the magnetostrictive transducer was coupled to the vessel by means of a light-grade oil within a reservoir above the transducer. During the degassing operation the pressure within both the vessel and the vacuum chamber was reduced. Afrer removal of dissolved gases the coupling oil was drained from the reservoir and any oil remaining on the bottom of the 50-liter resonator was carefully removed.

Precautions must be taken to prevent the development of any temperature gradient within the liquidfilled vessels. Such a gradient would seriously disturb the symmetry of the sound field and would be expected to give rise to additional wall losses. For this reason, for the majority of the measurements the liquid was introduced into the resonator at a temperature corresponding to that at which the ultrasonic absorption measurement was to be made and the vacuum chamber was carefully thermostated at this temperature.

Despite the above precaution, it was found that the lowest rates of decay corresponding to radial modes were not observed immediately after the degassing operation and that reproducible values could not be obtained before two or three days after the degassing operation.



FIG. 2. Magnetostrictive transducer assembly for the sonic degassing of the 50-liter system.

This situation is not unique to water or aqueous solutions but has been observed in the laboratories of Western Reserve University and elsewhere⁵ in general with the spherical resonator method. The reason for this lack of reproducible low decay rates in the first day or so following the degassing operation is open to question. It may be associated with the presence of a few residual microbubbles trapped within the crevices on the vessel walls or a small thermal gradient between the top and bottom of the vessel.

At frequencies above 300 kc the spherical resonator method becomes very difficult to use because of the very narrow bandwitdhs associated with single radial modes. For this reason, in the range 300 to 1000 kc measurements were made by a statistical reverberation technique in which a number of modes were excited simultaneously. The experimental method was similar to that described by Kurtze and Tamm⁷ and also Lawley and Reed.⁹ A block diagram of the apparatus used in the present work is shown in Fig. 3. A 3-liter spherical Pyrex vessel with its neck reduced to 0.9 cm o.d. was excited statistically with an 8-kc bandwidth of random noise. Two barium titanate disks were coupled to the walls of the vessel with one used for exciting the vessel and the other for measuring the decay of the sound level after the excitation had been stopped. The exponential decay rates were photographed from the cathode ray screen of a Tektronix oscilloscope (model 543) with a Polaroid Land camera and the decay rates were determined analytically. The measurements were interpreted by means of Eq. (5)in much the same manner as with the spherical resonator technique.

The pulse-echo technique was also used to measure the ultrasonic absorption at the single frequency of 25 Mc. This technique has been described by Pinkerton¹⁰ and also by Andreae et al.¹¹ The ratio of the excess absorption to the overall absorption of the solutions decreases very rapidly with increasing frequency above the relaxation frequency. Thus even at the lowest

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⁹ L. Lawley and R. Reed, Acustica 5, 316 (1955). ¹⁰ J. Pinkerton, Proc. Phys. Soc. (London) B62, 286 (1949). ¹¹ J. Andreae, R. Bass, E. Heasell, and J. Lamb, Acustica 8,

^{121 (1958).}



FIG. 3. Block diagram of the apparatus for the measurement of ultrasonic absorption by the statistical reverberation method.

frequency for which the pulse-echo technique appears valid, i.e., 5 Mc, the absorption of the solutions was sufficiently close to the value for pure water that no significant difference in the experimental values would be expected provided there was not a second relaxation frequency above that studied by the reverberation techniques. The absorption coefficients measured for the potassium cyanide solutions at 25 Mc were the same as those for distilled water $(\alpha/f^2 = 22 \times 10^{-17}$ sec² cm⁻¹) within experimental error. Thus it does not appear that any higher-frequency relaxation effects associated with the ionic components are involved in the potassium cyanide system.

EXPERIMENTAL RESULTS

In Fig. 4 are plotted the values for α/f^2 for the 0.01 and 0.05*M* potassium cyanide at 25°C. In Fig. 5 are



FIG. 4. Ultrasonic absorption (α/f^2) in 0.01 and 0.05*M* KCN solutions at 25°C. Dashed line represents the literature value $(\alpha/f^2=22\times10^{-17})$ for distilled water; \oplus 0.01*M*; \bigcirc 0.05*M*.

plotted values for $(\alpha\lambda)_r$ for the same two solutions. The graphs in these figures provide evidence for a single relaxation frequency. Both the relaxation frequency and the magnitude of the absorption at this frequency are concentration dependent as would be expected on the basis of Eqs. (2) and (3).

It should be noted that the shapes of the curves drawn through the experimental points in Figs. 4 and 5 are not contingent upon having data on both sides of the relaxation frequency. All that is necessary is that approximately half the curve be characterized by experimental data. The exact shape of the curves in both cases is determined by the factors $[\omega \tau/(1+\omega^2 \tau^2)]$ and $[1/(1+\omega^2 \tau^2)]$ in Eqs. (3) and (4), respectively.

For the hydrolysis equilibrium,

$$CN^-+H_2O \xrightarrow{k_1}_{k_{-1}} HCN+OH^-,$$
 (b)

the equilibrium constant is given by the equation

$$K_{h} = \frac{C_{\text{HCN}}C_{\text{OH}}}{X_{\text{H}_{2}\text{O}}C_{\text{CN}}} = \frac{K_{w}}{K_{\text{HCN}}} = \frac{k_{1}}{k_{-1}} = \frac{\delta^{2}C_{0}}{1-\delta}, \qquad (6)$$

where K_w and $K_{\rm HCN}$ are the dissociation equilibrium constants for water and HCN, respectively, and $X_{\rm H_2O}$ is the mole fraction of water and will be replaced by 1 for the remainder of this paper. The appropriate calculation using $K_w = 1.008 \times 10^{-14}$ and $K_{\rm HCN} = 7.2 \times 10^{-10}$ gives $K_h = 1.40 \times 10^{-5}$ at 25°C. This value corresponds to a degree of hydrolysis (δ) of 0.0167 for the 0.05*M* KCN solution and 0.0367 for the 0.01*M* solution.

In Table I are given values for the forward and reverse rate constants for the two solutions at 25°C calculated from Eq. (2). The average values are $k_{-1}=3.7\times10^9M^{-1}$ sec⁻¹ and $k_1=5.2\times10^4$ sec⁻¹.

From Eq. (2) the ratio of the relaxation frequencies f_r for the 0.01 and 0.05*M* solutions can be calculated. The predicted value for this ratio is 2.26 or approximately $(5)^{i}$; the experimental value is 2.1. The ratio of the excess absorption as given by the quantity $(\alpha\lambda)_r$ for the 0.01 and 0.05*M* solutions can also be calculated at the relaxation frequency from Eq. (3). The theoretical value is 2.28; the experimental value is 2.0.

For relatively dilute solutions, the relaxation time may be approximated by the equation

$$\tau \cong 1/2(\mathrm{KC}_0)^{\frac{1}{2}}k_{-1},\tag{7}$$

since $\delta \ll 1$ and $(k_1/2\delta C_0 k_{-1}) \gg 1$. For frequencies well below the relaxation frequency, (i.e., $\omega^2 \tau^2 \ll 1$), Eq. (3) then becomes

$$(\alpha\lambda)_{r} \cong [\pi(\Delta V^{0})^{2}/1000\beta_{0}RT](\omega/4k_{-1}), \qquad (8)$$

and the absorption is independent of concentration. The curves in Figs. 4 and 5 support this prediction.



FIG. 5. Absorption per wavelength in 0.01 and 0.05M KCN at 25°C.

The close agreement between the predicted and experimental values for the various parameters describing the relaxation curves in Figs. 4 and 5 represents convincing evidence that the mechanism responsible for the relaxational absorption is indeed the hydrolysis reaction.

The volume change for reaction b, defined as

$$\Delta V^{0} = \bar{V}_{\rm HCN} + \bar{V}_{\rm OH} - \bar{V}_{\rm CN} - \bar{V}_{\rm H_{2}O}, \qquad (9)$$

can be calculated from either Eq. (3) or (8) with $R=8.314\times10^7$ ergs mole⁻¹ °K⁻¹, $\beta_0=44.7\times10^{12}$ cm²/ dyne, $c=1.498\times10^5$ cm sec⁻¹, $C_0=5\times10^{-2}$ mole/liter, $\delta=0.0167$, and $(\alpha\lambda)_{\tau}=90\times10^{-6}$ at the relaxation frequency. The result is $\Delta V^0=\pm12.4$ cm³/mole. Since the partial molal volume of KOH is much less than that of KCN, ΔV^0 for the reaction is negative.

Figure 6 shows the effect of reducing the temperature of the 0.01M KCN on the relaxation process. The magnitude of the absorption at frequencies below the relaxation frequency increased and the relaxation

TABLE I. Relaxation frequencies and rate constants for the hydrolysis of potassium cyanide at 25°C.

solution molarity	<i>f</i> , kc	δ	$k_{-1} \frac{M^{-1} \sec^{-1}}{\times 10^{-9}}$	$k_1 \sec^{-1}$ ×10 ⁻⁴	
0.01	450	0.0367	3.8	5.3	
0.05	950	0.0167	3.6	5.0	
		av	3.7	5.2	

frequency decreased from 450 kc at 25°C to 320 kc at 16°C. An examination of Eq. (8) for the wavelength absorption when $\omega^2 \tau^2 \ll 1$ shows that the rate constant k_{-1} at 16°C can be calculated from

$$(k_{-1})_{289} = \frac{(\alpha\lambda)_{298}}{(\alpha\lambda)_{289}} \frac{\beta_{298}}{\beta_{289}} \frac{298}{289} (k_{-1})_{298}.$$
 (10)

The volume change ΔV^0 has been assumed to remain constant over this temperature range. The calculation is very approximate since the values of the wavelength absorption at any frequency are dependent on how accurately the curve-fitting procedure has been carried out. The appropriate calculation with $\beta_{239}=46.5\times10^{-12}$ and $\beta_{298}=44.7\times10^{-12}$ cm²/dyn results in $(k_{-1})_{299}=$ $2.5\times10^9M^{-1}$ sec⁻¹. This rate constant can also be calculated from the relaxation frequency if the hydrolysis equilibrium constant at 16°C is known. From data given by Rossini *et al.*,¹² the enthalpy change for reaction *a* is +2.5 kcal/mole. This corresponds to $K_n=$ 1.2×10^{-5} at 16°C. The rate constants are then $k_{-1}=$ $2.9\times10^9 M^{-1}$ sec⁻¹ and $k_1=3.5\times10^4$ sec⁻¹. The enthalpy of activation can be estimated from the equation

$$\frac{d\ln(k/T)}{d(1/T)} = -\frac{\Delta H^*}{R}.$$
(11)

The result is $\Delta H^* = 6 \pm 2$ kcal/mole for the process HCN+OH⁻ \rightarrow H₂O+CN⁻.



FIG. 6. Absorption per wavelength in 0.01M KCN at 16° and 25°C.

¹² F. Rossini, D. Wagman, W. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Series I, Table 23-13, March 1948.

Reaction	$k_1 \sec^{-1}$	$k_{-1} M^{-1} \sec^{-1}$	References
HSO₄ [−] ⇒H ⁺ +SO₄ [−]	~109	1×10 ¹¹	a
CH₃COOH≓H+CH₃COO-	8×105	4.5×1010	b
H₂S≓H++SH-	4.3×10 ³	7.5×10 ¹⁰	C
HF≓H++F~	6.7×10 ⁷	1×10 ¹¹	C
$H_2O \rightleftharpoons H^+ + OH^-$	2.5×10 ⁻⁵	1.4×1011	<i>a</i> , <i>d</i>
$NH_3+H_2O = NH_4^++OH^-$	5×10 ⁵	3×1010	a, b, e
$(CH_3)_{\delta}N+H_2O \rightleftharpoons (CH_3)_{\delta}NH^++OH^-$	6×10 ⁵	1×1010	f
CN [−] +H ₂ O ⊂ HCN+OH [−]	5.2×104	3.7×10 ⁹	present work

TABLE II. Rate constants for proton-transfer reactions.

^a Reference 2. ^b Reference 3.

^d M. Eigen and L. De Maeyer, Z. Elektrochem. 59, 986 (1955).

e Reference 1.

^f M. Eigen, Z. Elektrochem. 64, 115 (1960).

DISCUSSION OF RESULTS

In the preceeding analysis of the hydrolysis reaction, the assumption has been made that the activity coefficients of all the reacting species are unity. This assumption may be open to some question since the activity coefficients for the charged species would be expected to be appreciably less than unity due to the moderately high ionic strength of the solutions. If activity coefficients are taken into account, the equation for the rate of hydrolysis becomes

$$\frac{dC_{\rm HCN}}{dt} = k_1 \frac{\gamma_{\rm CN} - C_{\rm CN}}{\gamma^*} - k_{-1} \frac{\gamma_{\rm HCN} \gamma_{\rm OH} - C_{\rm HCN} C_{\rm OH}}{\gamma^*}, \quad (12)$$

where γ_i represents the activity coefficient of the species indicated by the subscript, and γ^* is the activity coefficient of the activated complex. The activity of water is assumed to be constant and is included in the formal rate constant k_1 . The activity coefficient $\gamma_{\rm HCN}$ should be very close to unity in the present work since it represents an uncharged species. No information is available as to the value of γ^* . The activated complex, however, is probably a species with a net charge of minus one: i.e., HO---H+--CN-. In solutions of only moderate ionic strength (less than 10^{-1}), the activity coefficients of unit-charged ions are all expected to be approximately equal to the mean activity coefficient. If such is true for the activated complex, the activity coefficients should cancel out in Eq. (12)to a reasonable approximation. Equation (2) for τ then should remain unchanged over the range of concentrations involved in the present work even if activity coefficients are taken into account. Likewise the values for k_1 and k_{-1} in Table I remain unchanged provided the activity coefficient of the activated complex is equal to the mean activity coefficient.

Table II compares the forward and reverse rate constants for the hydrolysis of the cyanide ion with the rate constants for other very fast protolytic reactions. The rate constant k_{-1} for the reverse of the hydrolysis reaction is much smaller than the corresponding secondorder rate constants for reactions between oppositely charged ions. This is not surprising when one considers the details of the processes involved in the protontransfer. With oppositely charged ions, the proton leaves behind an uncharged species as it bonds chemically with the anion. For example, consider the following case:



For the reverse of the hydrolysis reaction, however, the proton leaves behind a negatively charged ion as it is transferred to the hydroxyl ion to form water; i.e.,

$$NCH+OH\rightarrow NC\cdots H \cdots OH\rightarrow NC+HOH.$$
 (d)

On the basis of electrostatic considerations, the potential energy barrier would be expected to be higher

^c M. Eigen and K. Kustin, J Am. Chem. Soc. 82, 5952 (1960).

for reaction (d) than for reaction (c). The experimental results support this conclusion. Reactions (c) and (d) are an oversimplification of the situation and do not provide an adequate basis for estimating the potential energy barriers. The relative bond strengths as well as the role of solvent molecules must be taken into consideration.

The authors plan to study hydrolysis reactions in other systems by similar techniques.

ACKNOWLEDGMENTS

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Electron Spin Resonance in an Irradiated Single Crystal of Tetramethyl Ammonium Chloride*

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An analysis of the electron spin resonance spectrum of γ -irradiated crystals of N(CH₃)₄Cl shows that the paramagnetic species stable at room temperature is (CH₃)₃N⁺. The isotropic coupling constants are found to be 18.0 G for the nitrogen and 26.7 G for the methyl protons. All methyl protons are found to be equivalent. The radical is probably planar and is found to execute restricted rotation at room temperature.

THE irradiation of organic and inorganic solids with ionizing radiation is known to produce paramagnetic centers, some of which are found to be stable at room temperature. The electron spin resonance (ESR) spectrum of such a species gives a maximum of information when oriented radicals are studied. Several workers have investigated oriented radicals using single crystals.¹⁻³ In general these radicals are held in place within the unit cell by intermolecular hydrogen bonds, although a reorientation of the radical may occur shortly after its formation.⁴ Substituent groups such as methyl are generally found to be rotating at room temperature.5,6

Recently the radical H_3N^+ has been observed at room temperature in irradiated ammonium perchlorate.7 This radical is found to be undergoing a restricted rotation at room temperature and thus the radical is not held in a fixed position in the crystal lattice. It seemed probable

4, 169 (1961)

that the next radical in this series, $(CH_s)_3N^+$, would have a similar thermal stability. Various tetramethyl methyl ammonium salts were irradiated and a paramagnetic species corresponding to (CH₃)₃N⁺ was found in the chloride at room temperature.

EXPERIMENTAL

Reagent-grade tetramethyl ammonium chloride was purified by successive recrystallization from anhydrous ethyl alcohol, and single crystals were grown from the same solvent. Since the chloride is hygroscopic, the crystals were handled in a dry box. The crystals were γ irradiated using a Co source at doses of about 5×10^{20} eV/g in sealed tubes at 0° and at -196°C. After the irradiation the crystals appeared yellow in color. They were coated with a thin film of collodion to protect against moisture during the observations.

Tetramethyl ammonium chloride is tetragonal⁸ containing two molecules per unit cell, space group P_4/nmm ; the cell dimensions are a=7.78 A and c=5.53 A.

The crystal axes were identified by a polarizing microscope and were aligned for ESR observations on an optical goniometer. The crystals were rotated on a Lucite pillar and the angle of rotation was read on a scale graduated in degrees. The spectra were taken

^{*} Research performed under the auspices of the U.S. Atomic Energy Commission.

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⁸ R. W. G. Wyckoff, Z Krist. 67, 91 (1928).