That previous work on the proton–proton couplings in cyclopropanes and epoxides[7–11] has failed to reveal the correlation with substituent electronegativity and the π-electron character in the ring, we attribute primarily to the multiple substituent effects operative in the cyclopropanes previously studied and the limited range of electronegativity of substituents in the epoxides studied. Conformational changes would have to be quite large (and thus unlikely) to account for the large difference in coupling constants observed in poly-substituted cyclopropanes.

It is obvious from this work that structural assignments made simply on the basis of coupling constant magnitude, without taking into account substituent effects, could easily lead to the wrong structures; e.g., in these dichlorocyclopropanes J_{trans} in the trimethylsilyl derivative (9.4 c.p.s.) is larger than J_{cis} for the acetate derivative (7.9 c.p.s.) although simple consideration of the Karplus equation indicates that the cis coupling is larger than the trans.

We have discussed the coupling constants of these three-membered ring compounds in terms of the π-electron character of the ring and the hybridization of the carbon atoms involved. Rehybridization of the carbon atoms will necessarily change the C–C bond length and HCC' angle—two factors, in addition to substituent effects and dihedral angles, which Karplus has recently shown will also affect the coupling constant.[36]

Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates DP-60 high-resolution n.m.r. spectrometer operating at both 56.4 and 60 Mc./sec. Chemical shifts are reported in c.p.s. (at 60 Mc.) downfield from tetramethylsilane. Line positions were obtained by the side-band technique with graphical interpolation and are the average of at least six measurements. The frequency of the audio side band was measured with a Hewlett–Packard 521-C frequency counter. Chemical shifts are considered accurate to ±1 c.p.s. and coupling constants to ±0.2 c.p.s. Each sample was run as a 10% solution in carbon disulfide containing 1% tetramethylsilane as the internal standard.

2,2-Dichlorocyclopropyl acetate was prepared according to the procedure of Wagner, Kloosterziel, and van der Ven[37] in about 1% yield and separated from the contaminating 1-trichloromethylethyl acetate by preparative gas chromatography on a 2-ethylhexyl phthalate column.

Methyl trichloroacetate was prepared from A.R. trichloroacetic acid by Fischer esterification[38] using absolute methanol with concentrated sulfuric acid as the catalyst. The methyl

trichloroacetate used had b.p. 55.4–56.0° (19 mm.), reported[39] b.p. 52–54° (12 mm.).

2,2-Dichlorocyclopropyl bromide was prepared[40] following a modification of the procedure which Parham and Schweizer[41] used to prepare 2,2-dichlorobicyclo[4.1.0]heptane from cyclohexene.

Into a three-necked, 100-ml., round-bottomed flask equipped with a Hershberg stirrer, pressure equalizing dropping funnel, thermometer, and nitrogen inlet was weighed 8.65 g. (0.16 mole) of sodium methoxide (Matheson Coleman and Bell) in a drybox under nitrogen. To this was added 40 ml. of ligroin (d 0.64), which had been washed with concentrated sulfuric acid and distilled. The mixture was stirred and cooled in an ice–salt bath while 30 ml. (45 g., 0.42 mole) of vinyl bromide was added. To the bright turquoise-blue mixture was added (under nitrogen) 14.8 ml. (0.125 mole) of methyl trichloroacetate over a 3-hr. period at such a rate that the reaction temperature was held to about 5° and did not exceed 12°. The mixture was stirred for 8 additional hours under nitrogen at 0°, and then for 9 hr. at room temperature. The reaction mixture was diluted with 200 ml. of water and extracted four times with 50-ml. portions of ether. The combined organic layers were washed twice with 10-ml. portions of a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After removal of the ether and ligroin by distillation at atmospheric pressure, the product was distilled at reduced pressure to give 10.4 g. (44% yield), b.p. 102–103° (102 mm.), $n^{22.3}$D 1.5102.

Anal. Calcd. for $C_3H_3BrCl_2$: C, 18.96; H, 1.59; Cl, 37.25; Br, 42.09. Found: C, 19.12; H, 1.68; Cl, 37.00; Br, 42.20.

2,2-Dichlorocyclopropanecarboxylic Acid.—To a solution of 7 g. (0.044 mole) of potassium permanganate in 70 ml. of water was added 2.45 g. (0.018 mole) of 1,1-dichloro-2-vinylcyclopropane (Columbia Organic Chemicals Co., Inc.). The mixture was stirred at room temperature overnight; then the manganese dioxide was removed by suction filtration and washed with water. The water clear filtrate was saturated with solid potassium chloride and extracted once with ether, which was discarded. The aqueous layer was acidified with dilute hydrochloric acid and the cloudy solution extracted with four 20-ml. portions of ether. The combined ether extracts were washed twice with 10-ml. portions of a saturated solution of sodium chloride and then dried over anhydrous magnesium sulfate. The ether was removed by distillation and the slightly yellow oil was then distilled through a small vacuum-jacketed Vigreux column. The product, b.p. 63° (1 mm.), spontaneously crystallized in the condenser. The yield was 1.25 g. (45%) of white prisms, m.p. 74–75°.

Anal. Calcd. for $C_4H_4Cl_2O_2$: C, 31.00; H, 2.60. Found: C, 30.78; H, 2.55.

Vinyl acetate epoxide was prepared by perbenzoic acid epoxidation of vinyl acetate according to the procedure of Gorton and Reeder.[42] The material used for the n.m.r. spectrum had b.p. 35–37° (6 mm.).

Acknowledgment.—We wish to thank Professor Dietmar Seyferth for the sample of 1,1-dichloro-2-trimethylsilylcyclopropane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Rates of Rapid Ligand Exchange Reactions by Nuclear Magnetic Resonance Line Broadening Studies[1a]

BY RALPH G. PEARSON AND RANDOLPH D. LANIER[1b]

The rates of exchange, or limits to the rates, of several unidentate and bidentate ligands coordinated to Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) have been measured by proton n.m.r. line broadening studies. The usual order of reactivity Mn > Fe > Co > Ni ≪ Cu has been found. The exchange reactions of copper complexes are clearly second order, in agreement with an S_N2 mechanism common for planar complexes. The exchange reactions of the octahedral complexes are mixed first and second order and are explained by a solvent assisted dissociation mechanism common for octahedral complexes. It is easier to measure rates of exchange in this way for ligands containing NH protons rather than OH protons, because rates of relaxation are very large for NH protons and hence exchange rates determine the line width.

In the past few years a great deal has been learned about the mechanism of ligand substitution reactions of

metal ions in aqueous solution. This has been possible because earlier work on slowly reacting systems such as

cobalt(III) and platinum(II) has been extended by kinetic studies of very rapid substitution reactions.[2] Such reactions, with half-lives in the range of milliseconds to microseconds, require special methods of study. One of the most useful technique for fast reactions is the nuclear magnetic resonance line broadening method.[3]

A special example of this technique is the broadening that occurs as a result of exchange of a species, giving an n.m.r. signal, between a diamagnetic and a paramagnetic environment.[4] A solution containing paramagnetic metal ions, M, complexed by suitable ligands, L, and with an excess of free ligand, undergoes the exchange reaction

$$ML_n + L^* \underset{\tau_B}{\overset{\tau_A}{\rightleftarrows}} ML_n^* + L \qquad (1)$$
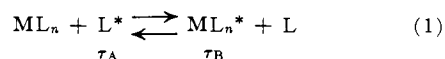
The n.m.r. spectrum of free L will show the effects of this (rapid) exchange. Of importance in determining the spectrum would be the mean lifetime in the paramagnetic environment, τ_B, and in the diamagnetic environment, τ_A, as well as the mean lifetimes of a given nuclear spin state in the two environments. T_{2B} and T_{2A}.

Solution of the Bloch equations, including chemical exchange,[5] gives the simple result,[4a] valid in most cases

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{P_B}{T_{2B} + \tau_B} \qquad (2)$$

Here $1/T_2 = \pi \Delta \nu$ is the experimental line width for L, $1/T_{2A}$ is the line width for L corrected for "outersphere" relaxation, and P_B is the fraction of the magnetically active nuclei of L bound to M at any time. In the present study it is the protons of L which give n.m.r. spectra. If L is a ligand such as ethylene glycol, separate lines are found for the methylene groups and the hydroxyl groups. Allowance must be made for the fact that a very rapid exchange of labile protons of the free ligand occurs with any hydroxyl protons in the system, such as water protons. In such a case a single average line for all labile protons will be seen and a suitable value of P_B must be calculated. Such a rapid exchange of free amine protons with water protons occurs. Coordinated amines and hydroxyl groups exchange protons only slowly, however.[4a] In the absence of paramagnetic ions, this averaged line is very narrow, less than 1 c.p.s. These proton transfers are of the acid-base type and are not to be confused with the ligand exchange of eq. 1.

The coordinated ligand L can also give an n.m.r. spectrum which will usually be very broad and displaced appreciably from the spectrum of free L. For example, ethylenediamine coordinated to nickel(II) or cobalt(II) shows an NH_2 peak about 200 p.p.m. on the high field side and a CH_2 peak about 100 p.p.m. on the low field side with respect to water.[6] At 60 Mc. these shifts are of the order of 10^3 to 10^4 c.p.s. The spectra of the coordinated L were not visible under the conditions of the work reported in this paper. However, a knowledge of the magnitudes of the shifts is important since Connick and Swift[4b] have shown that eq. 2 is in-

adequate for certain cases. Their equation is essentially

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{1}{\tau_A} \left[\frac{\dfrac{1}{T_{2B}^2} + \dfrac{1}{T_{2B}\tau_B} + \Delta\omega_B^2}{\left(\dfrac{1}{T_{2B}} + \dfrac{1}{\tau_B}\right)^2 + \Delta\omega_B^2} \right] \qquad (3)$$

where $\Delta\omega_B$ is the shift in radians/sec. of coordinated L compared to free L. Since the values of T_{2B} and τ_B are of the order of 10^{-3} to 10^{-7} sec., eq. 3 in special cases can give results quite different from 2. However, for the data reported in this paper, such a case probably does not arise. In particular, where rates of exchange dominate the line width, the rates of spin–spin relaxation are found to be very large so that T_{2B} is of the order of 10^{-5} to 10^{-7} sec. In this case, or if τ_B is as small, eq. 2 and 3 become identical. Criteria for distinguishing between line widths controlled by $\Delta\omega_B$, T_{2B}, and τ_B have been given in ref. 4a and 4b and include temperature dependence, effect of ligand concentrations and simultaneous observations of more than one n.m.r. line in L.

In the present work complexes of Mn(II), Fe(II), Co-(II), Ni(II), and Cu(II) with ammonia, ethylenediamine (en), glycine, sarcosine (N-methylglycine), and N,N-dimethylglycine in aqueous solution, and with anhydrous ethylene glycol, were studied. The line widths of protons due to the ligands were determined and rate constants for the exchange reaction 1 were calculated, or at least limits were set, by the use of eq. 2.

Experimental

The general method used was that of ref. 4a. All measurements were made with a Varian high resolution 60 Mc. spectrometer equipped with flux stabilizer. After adjusting for best resolution, sweep speeds of 1–2 milligauss per second were used to avoid errors due to drift. Under these conditions, distilled water gave a line width of less than 0.5 c.p.s. The total line width was measured directly upon the oscilloscope screen with a transparent ruler. The oscilloscope scale was calibrated by using the known splitting of the CH_2 peak in ethanol (7.5 c.p.s.), enabling one to convert mm. to c.p.s. T_2 was calculated from the relation $1/T_2 = \pi\Delta\nu$, where $\Delta\nu$ is the line width at half-peak height. The line widths were usually of the order of 10 to 30 c.p.s.

The metal salts used were reagent grade nitrates except for the reagent grade $MnCl_2$ and $FeSO_4$ used for Mn(II) and Fe(II), respectively. The salts were dried over $CaSO_4$ to remove excess water but were not anhydrous. Distilled water was used to prepare solutions as the additional line broadening was negligible. Reagent grade glycine, sarcosine, and N,N-dimethylglycine were used and ethylenediamine and NH_3 were either diluted from 12.5 and 15 M solutions in water or used as reagent grade salts. The substituted glycines were from K and K Laboratories. The glycol used was of C.P. grade.

Most measurements were made in a thermostated probe and the temperature read from a thermometer inserted directly into the probe. Temperature measurements and controls were accurate to $\pm 1°$. For work at temperatures above room temperature, a stream of compressed air was passed over a heating element controlled by a rheostat. Temperatures below room temperature were obtained by passing compressed air through a series of cold traps, usually Dry Ice–acetone. Temperatures used were 27, 55, and occasionally 5°.

The solutions of metal ion and ligand in water were prepared by dissolving weighed amounts of the metal salt and a salt of the protonated ligand in water. The pH of the solution (measured by a Beckman Model G pH meter) was then varied by addition of solid NaOH to obtain the desired free ligand concentration. The total concentration of ligand, free and protonated, was usually in the range 1.0–2.0 M to give an observable n.m.r. signal. Variations of the concentration of protonated ligand by a factor of two did not affect the results. To avoid any large salt effect, $NaNO_3$ was added to the solution to provide an initial ionic strength of 1.0 before NaOH was added. The procedure was modified for Cu(II)–glucine solutions to avoid a high base concentration and variable amounts of two solutions of pH 5.0 and 10.5, respectively, were mixed to give the desired pH. There was difficulty with air oxidation of Fe(II), Mn(II), and Co(II) in alkaline solutions. These solutions were prepared under a partial vacuum using solvents saturated with nitrogen.

The metal ion concentration was varied to check on the expected linear relationship between $\Delta\nu$ and concentration. Runs

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with different amounts of a given metal ion were normalized to a constant, convenient value. Duplicate solutions were made for most cases and two or more measurements made on each solution.

Results

The line broadening data were analyzed by plotting $\Delta\nu$ vs. [L], the free ligand concentration, at a constant value of P_B. In general, four types of plots were found as shown in Fig. 1. For case I, there is no dependence of $\Delta\nu$ on [L]. Such results were found for some nickel complexes, where the rate of exchange was so slow that only a small broadening due to "outer-sphere relaxation"[4a] was observed. Case II has ligand dependence and a nonzero intercept. This indicates that both a first-order and a second-order chemical exchange rate control the broadening (when a positive temperature dependence and near equality of OH and CH line widths confirm τ_B control). The dashed line is for the case where T_{2B} remains small compared to τ_B at all concentrations of L used. Eventually, of course, τ_B must become smaller than T_{2B} because of the relation

$$1/\tau_B = k_1 + k_2[L] \tag{4}$$

Hence at large [L], the curve must flatten out and reach a constant slope. It is possible, in principle, to obtain k_1, k_2, and T_{2B} in such cases.

The third case, III, involves [L] dependence and a zero intercept. This indicates a second-order exchange rate, when confirmed. The curvature is found when [L] becomes large enough so that T_{2B} is greater than τ_B. A plot of $(\Delta\nu)^{-1}$ vs. $([L])^{-1}$ is linear and k_2 and T_{2B} can be found.

The plot for case [IV] shows a maximum. This is due to a change in the concentration of species contributing different amounts to the line broadening. Some copper(II) systems showed case IV behavior. It was also noted that aging of copper(II) systems, when sufficiently alkaline, led to a large decrease in the amount of line broadening (other solutions were generally stable for days). It is likely that the formation of spin-paired polymers of copper(II) held together by oxygen bridges is responsible for the aging phenomenon.[7] Copper-ammonia solutions showed case IV behavior without aging. This may be due to polymerization, or, more likely, that the pentaammine of copper(II), which would form at high concentrations of NH_3,[8] is inefficient at producing line broadening. It should be pointed out that, even though Fig. 1 shows extrapolated results at a zero value of [L], all experiments actually performed had a sufficient concentration of L so that the highest complex was completely formed. The only exception would be in the case of ammonia, where the formation constants are much smaller than for the other ligands.

Tables I–VI present the kinetic data calculated from the plots of $\Delta\nu$ vs. [L] for all the systems studied. It should be appreciated that, in addition to much of the data only giving limits, the accuracy of the rate con-

TABLE I

RATE LIMITS FOR EXCHANGE OF ETHYLENE GLYCOL AT 27°

Metal ion	k_1, sec.$^{-1a}$	Temp. dependence
Mn(II)	$>1.5 \times 10^6$	Negative
Fe(II)	$>2.5 \times 10^3$	Negative
Co(II)	$>3.4 \times 10^3$	Negative
Ni(II)	4.4×10^3	$E_a > 6$ kcal.
Cu(II)	$>1.1 \times 10^5$	Negative
Cr(III)	9.7×10^4	$E_a = 6$ kcal.

^{a} From OH peak. If the greater than sign is used, the figure given is actually $1/T_{2B}$.

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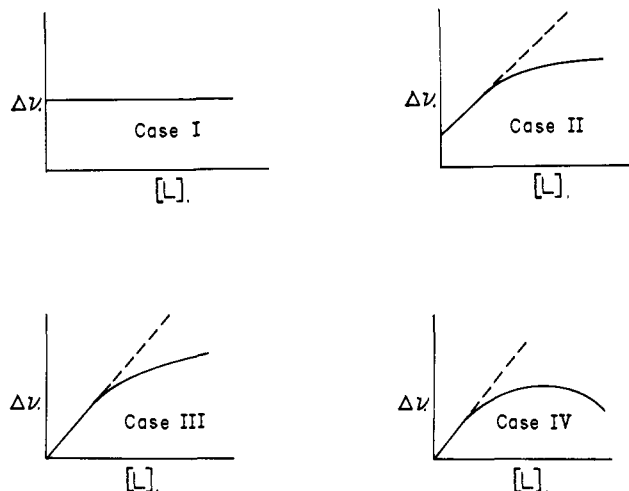

Fig. 1.—Experimental results for plots of line broadening vs. concentration of free ligand.

stants calculated is not great. This is due partly to the experimental method used but more to the complexities of the factors influencing the line widths. In particular, temperature dependencies were studied chiefly to determine if T_{2B} or τ_B was the controlling factor. This was usually easy to decide. The temperature data have also been used in a number of cases to calculate approximate activation energies. Where mixed kinetics exist, both k_1 and k_2 were estimated at all temperatures. Within the limit of experimental error, the activation energies were found to be the same for both rate constants.

TABLE II

RATE LIMITS FOR EXCHANGE OF AMMONIA AT 27°

Complex	k_1 or k_2	Temp. dependence
$Cu(NH_3)_4^{2+}$	$\geqslant 1.9 \times 10^7 \ M^{-1}$ sec.$^{-1a}$	$E_a > 4$ kcal.
$Cu(NH_3)_5^{2+}$	$>5.7 \times 10^5$ sec.$^{-1b}$	Negative
$Ni(NH_3)_5^{2+}$	$>6.3 \times 10^4$ sec.$^{-1}$	Negative
$Ni(NH_3)_6^{2+}$	$>4.5 \times 10^4$ sec.$^{-1b}$	Negative
$Co(NH_3)_5^{2+}$	$>4.7 \times 10^4$ sec.$^{-1}$	Negative

^{a} k_2 is $1.2 \times 10^7 \ M^{-1}$ sec.$^{-1}$ at 5° and temp. dep. is positive; between 27 and 55°, temp. dep. is negative. ^{b} 15 M NH_3.

TABLE III

RATE LIMITS FOR THE EXCHANGE OF ETHYLENEDIAMINE AT 27°

Complex	k_1 or k_2	Temp. dependence
$Cu(en)_2^{2+}$	$k_{OH} = 2.6 \times 10^6 \ M^{-1}$ sec.$^{-1a}$	$E_a = 7$ kcal.
	$k_{CH_2} = 1.8 \times 10^6 \ M^{-1}$ sec.$^{-1b}$	$E_a = 7$ kcal.
$Ni(en)_3^{2+}$	$k_{OH} < 1 \times 10^3$ sec.$^{-1c}$	None
	$k_{CH_2} < 2 \times 10^2$ sec.$^{-1}$	Small
$Co(en)_3^{2+}$	$k_{OH} = 4.8 \times 10^3$ sec.$^{-1} + 3.3 \times 10^3 \ M^{-1}$ sec.$^{-1d}$	$E_a = 10.5$ kcal.
	$k_{CH_2} = \underline{\hspace{1.5cm}} + 2.5 \times 10^3 \ M^{-1}$ sec.$^{-1e}$	$E_a = 10.5$ kcal.

^{a} $T_{2B} = 3 \times 10^{-7}$ sec.; range of [L] up to 12 M. ^{b} $T_{2B} = 2.4 \times 10^{-6}$ sec. ^{c} Range of [L] up to 4.0 M. ^{d} $T_{2B} = 2 \times 10^{-5}$ sec.; range of [L] up to 1.5 M. ^{e} $T_{2B} = 5 \times 10^{-5}$ sec.

Ethylene Glycol.—Table I shows data for the metal ions, including chromic ion, in pure ethylene glycol solvent. The chromium aquo ion was allowed to stand several days to allow for exchange before measuring. Only nickel ion showed the equality of OH and CH_2 broadening and the positive temperature dependence which proved that the rate of exchange ($k_1 = 1/\tau_B$) was being measured. The rate shown for Cr(III) is due to acid–base proton transfer only, as has also been shown in water and methanol.[4a] The rate limits for the other metal ions are calculated from the OH peak. It is unlikely that acid–base proton transfer is important for these divalent cations.[4a]

TABLE IV

RATE LIMITS FOR THE EXCHANGE OF GLYCINE AT 27°

Complex	k_1 or k_2	Temp. dependence
Cu(gly)$_2$	$k_{OH} = 8.2 \times 10^6 \ M^{-1}$ sec.$^{-a}$	$E_a = 6$ kcal.
	$k_{CH_2} = 2.6 \times 10^6 \ M^1$ sec.$^{-1b}$	$E_a = 6$ kcal.
Ni(gly)$_3^-$	$k_{OH} < 1 \times 10^3$ sec.$^{-1}$	Negative
	$k_{CH_2} < 3 \times 10^2$ sec.$^{-1}$	Positive
Co(gly)$_3^-$	$k_{OH} = 5.7 \times 10^3$ sec.$^{-1} + 4.8 \times 10^3 \ M^{-1}$ sec.$^{-1c}$	$E_a = 10$ kcal.
	$k_{CH_2} = 5.7 \times 10^3$ sec.$^{-1} + 3.8 \times 10^3 \ M^{-1}$ sec.$^{-1d}$	$E_a = 10$ kcal.
Mn(gly)$_2$	$k_{OH} > 1 \times 10^5$ sec.$^{-1}$	Negative
	$k_{CH_2} > 1 \times 10^4$ sec.$^{-1}$	Negative
Fe(gly)$_2$	$k_{OH} = 2.2 \times 10^4$ sec.$^{-1} + 5 \times 10^4 \ M^{-1}$ sec.$^{-1e}$	$E_a = 9.5$ kcal.
	$k_{CH_2} = 2.2 \times 10^4$ sec.$^{-1} + 3.2 \times 10^4 \ M^{-1}$ sec.$^{-1f}$	$E_a = 9.5$ kcal.

^{a} $T_{2B} = 7 \times 10^{-7}$ sec.; range of [L] up to 1.5 M. ^{b} $T_{2B} = 4 \times 10^{-6}$ sec. ^{c} $T_{2B} = 5 \times 10^{-6}$ sec.; range of [L] up to 1.7 M. ^{d} $T_{2B} = 1.2 \times 10^{-5}$ sec. ^{e} $T_{2B} = 1.2 \times 10^{-6}$ sec.; range of [L] up to 1.0 M. ^{f} $T_{2B} = 5.0 \times 10^{-6}$ sec.

TABLE V

RATE LIMITS FOR EXCHANGE OF N-METHYLGLYCINE (SARCOSINE) AT 27°

Complex	k_1 or k_2	Temp. dependence
Cu(sarc)$_2$	$k_{OH} = 6 \times 10^5 \ M^{-1}$ sec.$^{-1a}$	$E_a = 7$ kcal.
Ni(sarc)$_3^-$	$k_{CH_2} = 60$ sec.$^{-1} + 1 \times 10^2 \ M^{-1}$ sec.$^{-1}$	Positive^b
Co(sarc)$_3^-$	$k_{OH} = 6.7 \times 10^2$ sec.$^{-1} + 3.3 \times 10^3 \ M^{-1}$ sec.$^{-1c}$	$E_a = 13$ kcal.
	$k_{CH_2} = 4.2 \times 10^2$ sec.$^{-1} + 2.1 \times 10^3 \ M^{-1}$ sec.$^{-1d}$	$E_a = 13$ kcal.

^{a} $T_{2B} = 7.7 \times 10^{-5}$ sec. ^{b} Rate constant is at 54°. ^{c} $T_{2B} = 2 \times 10^{-5}$ sec. at 54°. ^{d} $T_{2B} = 5 \times 10^{-5}$ sec. at 54°. Range of [L] up to 1.5 M for all three metals.

TABLE VI

RATE LIMITS FOR EXCHANGE OF N,N-DIMETHYLGLYCINE AT 27°

Complex	k_1 or k_2	Temp. dependence
Cu(dmg)$_2$	$k_{CH_2} = 1.3 \times 10^4 \ M^{-1}$ sec.$^{-1a}$	$E_a = 9.5$ kcal.
Ni(dmg)$_3^-$	$k_{CH_2} = 70$ sec.$^{-1} + 4.7 \times 10^2 \ M^{-1}$ sec.$^{-1b}$	$E_a = 17$ kcal.
Co(dmg)$_3^-$	$k_{CH_2} = 3.2 \times 10^3$ sec.$^{-1} + 7.3 \times 10^3 \ M^{-1}$ sec.$^{-1c}$	Positive

^{a} $T_{2B} = 2.6 \times 10^{-5}$ sec.; range of [L] up to 0.7 M. ^{b} $T_{2B} = 8.9 \times 10^{-4}$ sec.; range of [L] up to 1.0 M. ^{c} $T_{2B} = 6 \times 10^{-5}$ sec.; range of [L] up to 1.0 M.

Ammonia.—Only copper(II), nickel(II), and cobalt-(II) could be studied over any range of NH$_3$ concentration because of precipitation problems. Cobalt could be studied only up to 1 M NH$_3$. In all cases, the line broadening was due to more than one species in solution and eq. 2 has to be considered in the form

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + \sum_i \frac{P_i}{T_{2i} + \tau_i} \quad (5)$$

From equilibrium data in the literature,[8] including temperature dependence, it is possible to make good estimates of the species present at any concentration of NH$_3$. Useful information could only be obtained for the higher complexes. The data in Table II represent an analysis of the plot of $\Delta\nu$ vs. [L] in terms of eq. 5 and the known equilibrium data. Copper, as mentioned, gives a type IV curve. It is assumed that the decrease in $\Delta\nu$ is not due to the formation of diamagnetic species, but to the formation of the pentaammine with relaxation control. Nickel and cobalt give type III curves. In the case of nickel, $\Delta\nu$ becomes nearly constant after about 3 M ammonia, when all the nickel is present as pentaammine or hexaammine. The initial rise of $\Delta\nu$ with [L] parallels the growth of the pentaammine at the expense of the triammine which, presumably, exchanges more slowly and contributes little to the line width.

Ethylenediamine.—Again only nickel, copper, and cobalt could be studied because of precipitation.

Both the CH$_2$ and the averaged NH–OH protons could be examined. The bisethylenediamine complex of copper(II) shows a zero intercept at zero L concentration and a slight maximum in the $\Delta\nu$–[L] plot. The maximum is ascribed to a five coordinated species at high [L]. Second-order rate constants were obtained by plotting $(\Delta\nu)^{-1}$ against $([L])^{-1}$. For both OH and CH$_2$ peaks, linear plots were found.

The line width for nickel(II), tris complex, is small and controlled by outer-sphere relaxation. Upper limits only for the rate of exchange were estimated. Cobalt(II), tris complex, shows a nonzero intercept at zero [L] for the OH peak and a zero intercept for the CH$_2$ peak, and dependence of $\Delta\nu$ on [L] for both peaks. From the OH data, first- and second-order rate constants were calculated, and from the CH$_2$ data a second-order rate constant.

Glycine.—All the divalent metal ions were soluble in the case of glycine complexes though the major species present over the range studied was the bis complex for manganese, iron, and copper and the tris complex for nickel and cobalt. The nickel complex again was nonlabile and the line width was controlled by outer-sphere relaxation (case I). Manganese(II), also case I, is very labile and the broadening is controlled by T_{2B} and not τ_B. Lower limits to the rate could be set for manganese and upper limits for nickel.

Copper(II), as usual, gave a zero $\Delta\nu$ intercept at zero [L] and type III behavior. The second-order rate constant was found from a plot of $(\Delta\nu)^{-1}$ vs. $([L])^{-1}$. Cobaltous and ferrous ions gave case II plots and k_1 and k_2 were calculated. T_{2B} was also calculated for these three ions.

Sarcosine.—Only nickel, copper, and cobalt(II) were studied with this ligand. Copper gave a case III plot and cobalt and nickel type II plots. The data for cobalt gave straight lines for $\Delta\nu$ plotted against [L] at 27° and the calculation of k_1 and k_2 was simple. All other plots were curved. For nickel it was possible to calculate values of both k_1 and k_2 from the data at 54° but not at 27°, where the rate was too slow.

Dimethylglycine.—Again only copper, nickel, and cobalt were studied. The results are similar to those for glycine and sarcosine except that nickel had a rate that was large enough to measure quite readily at 27°. Only the CH$_2$ group is available for measurement, of course, since there are no NH protons.

Discussion

The rate constants in Tables II–IV can be compared with other data in the literature in several cases. Hunt, Dodgen, and Klanberg[9] have used N^{14} resonance data to obtain a value of k_1 for Ni(NH$_3$)$_6^{2+}$ equal to 6.6 $\times$ 10^4 sec.$^{-1}$ at 25°. The activation energy was 10.1 kcal. For Cu(NH$_3$)$_4^{2+}$ the rate of exchange was found to be[9] at least ten times faster than for Ni(CH$_3$)$_6^{2+}$. These figures are in agreement with the lower rate limits given in Table II. Also Wilkins and Melson[10] have measured the rate of dissociation of the mono-ammine complex Ni(NH$_3$)$^{2+}$, where k_1 is 5.8 sec.$^{-1}$ at 25° and E_a is 14.3 kcal. Wilkins has also shown that for many nickel complexes the rates of formation are about the same, and hence rates of dissociation must be proportional to the dissociation equilibrium constants.[10,11] Using the rough rule $\Delta \log k_1 = \Delta \log K_d$, one then estimates values of 10^5 and 10^4 sec.$^{-1}$ for the dissociation rates of Ni(NH$_3$)$_5^{2+}$ and Ni(NH$_3$)$_6^{2+}$, re-

(9) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

(10) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963).

(11) R. G. Wilkins and A. K. Shamsuddin-Ahmed, *Proc. Chem. Soc.*, 399 (1959); *J. Chem. Soc.*, 3700 (1959).

spectively. These agree reasonably well with the data of Hunt and of Table II.

Wilkins' data[11] can also be used to show that the rates of dissociation of $Ni(en)_3^{2+}$ ($k_1 = 3$ sec.$^{-1}$) and $Ni(gly)_3^-$ ($k_1 = 10$ sec.$^{-1}$) are indeed too small to give line-broadening effects. It should be noted that the acid-catalyzed dissociation reported by Wilkins, and which requires that only one end of the chelate ligand be free, is some twenty to thirty times faster than the complete dissociation of both ends of the chelate, as has been shown for both ethylenediamine[12] and glycine.[13]

Hammes and Steinfeld[13] have used a relaxation method (T-jump) to study the rates of dissociation of several nickel(II) and cobalt(II) complexes. They report a value of k_1 equal to 3.8×10^3 sec.$^{-1}$ at 25° for $Co(gly)_3^-$. This may be compared with the 5.7×10^3 sec.$^{-1}$ of Table IV. Considering the difficulties of both kinds of measurement, the agreement must be regarded as quite good. Their technique would not detect the second-order exchange reaction shown in Table IV.

Morgan, using the n.m.r. method for protons, has given a value of k_2 for $Cu(en)_2^{2+}$ of 5×10^6 M^{-1} sec.$^{-1}$ and an activation energy of 5 kcal./mole.[14] His experiments were done at a pH of 11–12; the present experiments were done at a pH below 10.5. It is likely that some $Cu(en)_2(OH)^+$ is formed at the higher pH, and this may be more labile.

It will be noted that rates of exchange in Tables III–V calculated from the averaged OH–NH peaks are usually somewhat larger than those from the CH peaks. This is expected because release of the NH end of the chelate will lead to an acid–base proton exchange which will broaden the OH peak only. The extreme case is $Co(en)_3^{2+}$ where the OH peak gives a k_1 of 3.3×10^3 sec.$^{-1}$ and the CH peak shows k_1 is zero. If k_1 is entirely due to one end only being released and if Wilkins' factor[12] of 30 is valid, then the contribution of a first-order process for the complete dissociation of en would be too small to measure for the CH peak.

The difference between the OH peak and the CH peak is small for glycine and sarcosine. In these cases it is probably the carboxylate end which is usually released first. This does not lead to proton exchange and hence k_1 and k_2 for CH and OH should be the same. Copper gives the largest difference in k_2 values between the two peaks for glycine. This may be due to an additional exchange of a glycine ion coordinated through the amine group only to one of the axial positions above and below the plane of $Cu(gly)_2$.[15] Such a group would be very labile and its line-broadening contribution would be relaxation controlled (compare $Cu(NH_3)_5^{2+}$) and affect chiefly the NH_2 group.

Copper, manganese, and iron(II) have two water molecules still coordinated in most of the complexes studied. These molecules would presumably be labile and could cause OH line broadening. However, a consideration of the high rates of exchange of such water molecules and the low rates of relaxation of protons bonded to oxygen[16] suggests that the contribution of such a process to the over-all line broadening would be small. Manganese(II) would possibly be an exception and part of the difference between the OH and CH peaks for this ion in Table III could be due to

water exchange. Otherwise it should be noted that the approximate activation energies listed in Tables III–V are the same for both OH and CH peaks. This suggests that the same process is rate determining for both.

In all cases the order of reactivity found Mn(II) > Fe(II) > Co(II) > Ni(II) << Cu(II) agree with what has previously been observed for the same series.[2,4] An explanation has been given[17] in terms of crystal field theory, in which the important factor is the different loss of crystal field stabilization energy in going from the ground state to the transition state for each metal ion. To use such a theory, it is necessary to assume a mechanism and a structure for the transition state as well as for the ground state.

The data of the present work are in agreement with a number of possible mechanisms. They are best considered in combination with available information on substitution reactions of other complex ions.[2,17] It is safe to assume that the complexes of Mn(II), Fe(II), Co(II), and Ni(II) are octahedral, or slightly distorted octahedral, structures. Cu(II) has such a serious tetragonal distortion that it may be considered essentially a planar complex. It has been found[2,17] that octahedral complexes react by mechanisms which are, or strongly resemble, S_N1 or dissociation mechanisms. Planar complexes, however, have always been found to react by S_N2 or displacement mechanisms in their substitution reactions.[17]

It is significant that in Tables II–VI copper always reacts by a totally second-order process, where exchange rates are being measured. This suggests an S_N2 mechanism for copper(II) in agreement with its structure. By analogy with platinum(II) and palladium(II),[18] the first step in the reaction would be the facile replacement of an axial water by the substituting ligand. This would be followed, probably, by rearrangement to a trigonal bipyramid structure, expulsion of one end of the coordinated ligand, and return to a planar structure.
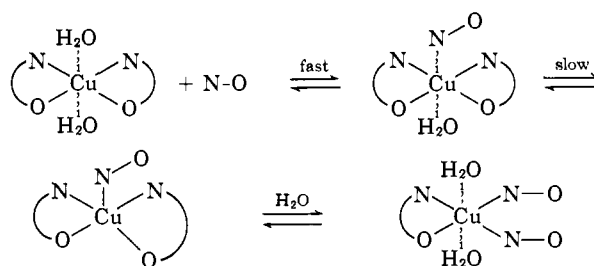
At this point exchange has been assured since the two ligands have become identical. The exchange rate would be second order. A corresponding first-order reaction in which water is the nucleophilic reagent would be too slow to be detectable because planar complexes are very sensitive to the reactivity of the nucleophile.[18]

There would be a loss of CFSE of about 2.0 Dq units of energy in going from a tetragonal ground state to a trigonal bipyramid.[17] From spectroscopic data, Dq would be 3–4 kcal. However, the remaining energy differences, due to metal–ligand attractions and ligand–ligand repulsions, would be rather small for five tightly bound groups compared to four tightly bound and two loosely bound.

(12) A. K. Shamsuddin-Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

(13) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

(14) L. O. Morgan, J. Murphy, and P. F. Cox, *ibid.*, **81**, 5043 (1959); P. F. Cox and L. O. Morgan, *ibid.*, **81**, 6409 (1959).

(15) The third en group of $Cu(en)_3^{2+}$ is attached as a unidentate ligand; J. Bjerrum, *Acta Chem. Scand.*, **2**, 297 (1948).

(16) L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959).

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958; R. G. Pearson, *J. Chem. Educ.*, **38**, 164 (1961); R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962).

(18) F. Basolo and R. G. Pearson, "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

The octahedral tris complexes would not have such easy access for an incoming ligand molecule. Instead, by a mechanism which may be described as a dissociation assisted by water (see below), one end of a bound chelate is replaced by a water molecule in a readily reversible process. After releasing one end of the chelate (a), the intermediate I could reclose the chelate (b); could react by the same dissociation mechanism to release both ends of the chelate (c); or could have the coordinated water replaced by an external ligand molecule (d). Either of the last two events would lead to exchange. The rate of exchange would be
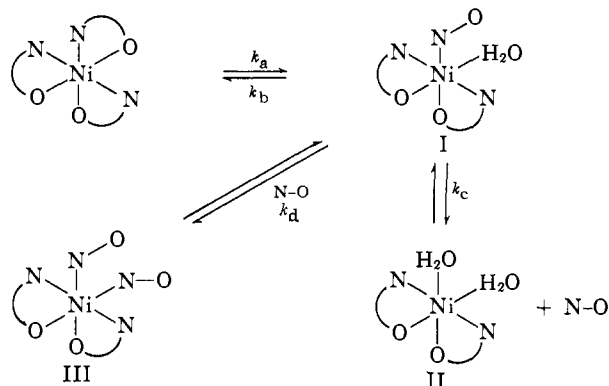
given by

$$\text{rate} = \{k_c + k_d[L]\} \quad (I)$$

Applying the steady-state treatment to I, and assuming the concentrations of II and III are very small, gives the final result for the rate of exchange

$$\text{rate} = \frac{\{k_c + k_d[L]\}k_a[\text{NiL}_3]}{k_b + k_c + k_d[L]}$$

If $k_d[L]$ is small compared to $k_b + k_c$, then the observed rate constant for exchange will be the sum of a first-order term and a second-order term, in agreement with the experimental results.

The mechanism can be tested because it should be true that k_b is 20–30 times as large as k_c, as mentioned above for $\text{Ni(en)}_3{}^{2+}$ and $\text{Ni(gly)}_3{}^-$. The first- and second-order rate constants found experimentally will be equal to $k_a k_c/k_b$ and $k_a k_d/k_b$, respectively. An examination of Tables III–V shows that in no case does $k_2[L]$ become as much as ten times k_1 for the highest [L] used. This means that $k_b + k_c$ will continue to be large compared to $k_d[L]$, and the rate will have a strong, nearly first-order dependence on [L]. Some leveling of the rate with increasing [L] may occur but would ordinarily be obscured by the normal curvature of plots of line broadening vs. [L] due to relaxation control superseding exchange control. A similar mechanism can be written for bis octahedral chelates and, in addition, a second-order path in which the reverse process, II → I, occurs can be visualized.

There is no absolute reason why a mechanism involving an SN2 attack on the metal by the incoming ligand should not account for the second-order rate constants for exchange in the octahedral systems. The chief evidence against such a process is the general failure to detect nucleophilic displacement reactions with transition metal octahedral complexes.[19] It is significant that it is the "special mechanism for chelate compounds"[17] which causes second-order kinetics without a true bimolecular reaction. When unidentate ligands such as NH_3 or CNS^- are exchanging, only first-order exchange is observed.[9]

The rate sequence glycine > sarcosine > dimethylglycine observed for copper(II) is expected for an SN2

mechanism and may be attributed to steric hindrance to the approach of the nucleophile. Similar cases are known for platinum(II).[18] For octahedral cobalt(II) and nickel(II) the opposite order is found, dimethylglycine > sarcosine > glycine. This is readily explained as steric acceleration of a dissociation mechanism and has been found for other octahedral systems.[17] Wilkins[20] has found the same order for the rate of dissociation of N-methyl-substituted ethylenediamines of nickel(II).

The water-assisted dissociations of the steps with rate constants k_a and k_c are visualized as requiring a critical extension of the metal–ligand bond, but the partial coordination of a water molecule before the bond is completely broken. This follows from the improbability on energetic grounds of a five-coordinated intermediate with a square pyramid structure.[21] Rearrangement to a trigonal bipyramid structure might occur instead in certain cases, for example, where there is no crystal field stabilization energy or where π-bonding is important. If a water molecule is required, then the transition state will be seven coordinated, with five groups in the original, octahedral positions and two groups, water and the leaving group, adjacent to each other and somewhat further away.[22]

Hush has recently calculated the theoretical crystal field levels for such a structure.[23] This enables an estimate of the crystal field contribution to the activation energy (CFAE) to be made. Table VII shows such calculations for the systems from d^5 to d^{10}. It has been assumed that a tetragonal distortion occurs for d^6, d^7, and d^9 in the ground state.

TABLE VII

CRYSTAL FIELD ACTIVATION ENERGIES

Electron configuration	d^5	d^8	d^7	d^8	d^9	d^{10}
Metal ion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ground state stabilization, Dq	0	4.57	9.14	12	9.14	0
Transition state stabilization[a]	0	6.08	8.68	10.19	8.79	0
CFAE	0	−1.51	0.46	1.80	0.35	0
Transition state stabilization[b]	0	4.57	9.14	10.00	9.14	0
CFAE	0	0	0	2.00	0	0
log K_3, gly $^{-c}$	<1	<1	3.56	3.61	<1	2.56
log K_2, gly $^-$	2.0	3.0	4.02	4.96	6.97	4.14
log K_3, en	0.88	1.99	3.10	4.26	−1.0	1.72
log K_2, en	2.06	3.25	4.83	6.40	9.30	4.66

[a] Hush's seven-coordinated structure assumed. [b] Square pyramid structure assumed. [c] K_3 and K_2 are formation constants for tris and bis complexes; data from ref. 8.

There is a serious discrepancy in the case of iron(II) for which a negative crystal field activation energy is calculated of 1.5 Dq units, or about 5 kcal. This would make ferrous complexes more labile than even manganous complexes, and with a much lower activation energy than for cobaltous complexes. This disagrees with the present work and with the related results of Swift and Connick[4b] on water exchange rates. It had earlier been shown[17] that an SN1 dissociation mechanism with a square pyramid intermediate did give results agreeing with experiments in a number of examples. The crystal field activation energies for this mechanism are also given in Table VII and can be seen to agree with the new rate data, with no abnormality for iron(II). This may mean that the transition state resembles a square pyramid (five-coordinated) more than the seven-coordinated structure of Hush. The difficulty with iron(II) may also

(19) R. G. Pearson, D. N. Edington, and F. Basolo, J. Am. Chem. Soc., 84, 3233 (1962).

(20) R. G. Wilkins, J. Chem. Soc., 4475 (1962).

(21) Reference 17, pp. 98–101 and p. 165.

(22) R. Dyke and W. C. E. Higginson, J. Chem. Soc., 2788 (1963); S. A. Johnson, F. Basolo, and R. G. Pearson, J. Am. Chem. Soc., 85, 1741 (1963).

(23) N. S. Hush, Australian J. Chem., 15, 378 (1962).

arise from the conventional assumption that crystal field effects arise from the electrostatic field of the ligands. This assumption is known to be over-simplified.[24]

The formation constants of some of the complexes undergoing exchange are also given in Table VII. The lability of copper complexes is quite at variance with the thermodynamic stability and shows that a special mechanism must be operating. For the rest, the rates correlate well with the stability data, manganese being the most labile and least stable and nickel being least labile and most stable. Compared to cobalt, however, nickel shows a slower rate of reaction than indicated by stability constants alone. This is a valid indication of crystal field, or ligand field, stabilization. Regardless of the factors which produce crystal field effects,[24] the octahedral configuration must be very well suited to a d^8 system. Any change in structure produces substantial loss of d-orbital energy. The activation energy for the first-order dissociation of $Ni(en)_3^{2+}$ is 18 kcal.,[11] which may also be considered in connection with the data of Table III.

The results for glycol exchange given in Table I call for some special comment. First of all, the rates for exchange of this chelate molecule are about the same as those previously reported for the unidentate methanol.[4a] This is understandable in terms of the mechanism of a solvent assisted dissociation. The intermediate IV guarantees exchange after only one end

IV
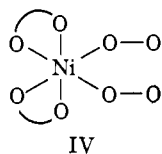
of the chelate has dissociated. A five-coordinated intermediate, V, would lead to the prediction of a greatly

reduced exchange rate for glycol compared to methanol because of rapid reclosing of the chelate ring.

V
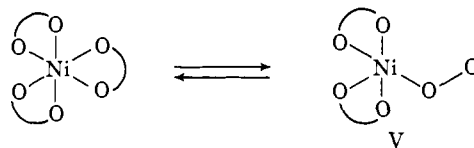
It is an interesting fact that when coordination of a paramagnetic ion occurs to oxygen compared to nitrogen, it is much more likely that rates of relaxation rather than rates of exchange are being measured by line broadening of proton n.m.r. signals. Thus $T_{2B} > \tau_B$ for oxygen coordination and $T_{2B} < \tau_B$ for nitrogen coordination. The inversion is due more to changes in T_{2B} than τ_B. Thus values of T_{2B} for oxygen coordination range from 10^{-3} to 10^{-5} sec. usually. For the same metal ions coordinated to nitrogen, T_{2B} is in the range from 10^{-5} to 10^{-7} sec. The difference may be attributed to the greater polarizability of nitrogen compared to oxygen. Thus a higher unpaired spin density due to isotropic contact interaction[25] will appear on N than on O. By polarization this spin density will be transferred to the proton bound to N and produce relaxation, shortening T_{2B}. Benson, et al., have shown that N transmits spin densities more efficiently than does O.[26]

(24) R. G. Pearson, *Record Chem. Progr.*, **23**, 53 (1962).

(25) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

(26) R. E. Benson, D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961).

Formation and Reactions of Radiation-Produced Electrons and Atomic Hydrogen in γ-Irradiated Ice

By L. Kevan, P. N. Moorthy,[1] and J. J. Weiss

Hydrogen atoms have been found in γ-irradiated ice at 77°K. containing acid salts such as potassium dihydrogen orthophosphate and sodium bisulfate. It has been shown that they are also produced, although with lower yield, in ice containing neutral salts such as sulfates, phosphates, and carbonates. The hydrogen atom yields were found to be linear with solute concentration from 0.01 M up to saturated solutions and with radiation dose up to 8 megarads but attained a stationary value at about 15 megarads. Solutes which can act as scavengers for the radiation-produced electrons (polarons), such as nitrate, nitrite, acetone, and cupric salts, decreased the hydrogen atom yields in ices containing the mononegative ions, but were ineffective in the case of polynegative oxyanion solute. Relative rates of reactions of the electron with $H_2PO_4^-$ and competing scavengers such as nitrate and nitrite ions and acetone have been determined. These reactions can be interpreted by the following mechanism: the radiation-produced electron reacts with an acid anion, *e.g.*, HSO_4^- or $H_2PO_4^-$, either by electron or by proton transfer leading eventually to the formation of a hydrogen atom; in the case of the neutral salts, the stabilized hydrogen atoms are formed only from those water molecules which are in the solvation shells of the anions.

Introduction

Hydrogen atoms have been found to be formed in the radiolysis of ice at 77°K. containing certain acids such as sulfuric, phosphoric, hydrofluoric, fluorosilicic, and fluoroboric acid.[2] In neutral ice no hydrogen atoms were observed on irradiation at 77°K. However, they have been detected at 4°K. and were found

to decay upon warming.[3] More recently, it has been reported[4a] that atomic hydrogen is produced and can be detected by electron spin resonance (e.s.r.) in γ-irradiated ice at 77°K. containing various solutes such as $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}, HSO_4^-, and SO_4^{-2} and that the hydrogen atom yields increased linearly with solute

(1) On leave from A.E.E.T., Bombay, India.

(2) R. Livingston, H. Zeldes, and E. H. Taylor, *Discussions Faraday Soc.*, **19**, 166 (1955).

(3) D. H. Piette, R. L. Rempel, M. E. Weaver, and S. Siegel, *J. Chem. Phys.*, **30**, 1623 (1959).

(4) (a) L. Kevan, P. N. Moorthy, and J. J. Weiss, *Nature*, **199**, 689 (1963); (b) J. J. Weiss, *ibid.*, **186**, 751 (1960).