[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES AND DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Analysis of the Effect of Chemical Exchange on a High-resolution N.m.r. Spin–Spin Doublet: Application to N-Methylacetamide[1,2]

BY MASATAMI TAKEDA[3] AND E. O. STEJSKAL[4]

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A theoretical treatment of the problem of calculating, from nuclear magnetic resonance measurements, the mean lifetime τ of a proton involved in an exchange reaction is given. τ is related to the frequency separation $\delta\omega_e$ of the two peaks in a spin–spin doublet produced by the exchanging proton when exchange is relatively slow, to the width of the observed signal at half maximum $\delta\omega_{1/2}$, under conditions of fairly rapid exchange where a broad singlet is observed, and, under conditions in which exchange is very rapid, to the ratio I/I_0, where I is the maximum amplitude of the observed singlet, and I_0 the expected maximum amplitude for $\tau = 0$. This theoretical analysis has been applied to studies of aqueous solutions of N-methylacetamide and N-methylformamide, at various pH values, to determine the velocity of proton exchange between these amides and their conjugate acids according to the reaction: $\mathrm{RCONHCH_3 + (H_3O)^+ \underset{k_{2A}}{\overset{k_{1A}}{\rightleftharpoons}} (RCONH_2CH_3)^+ + H_2O}$. The value of k_{1A} was determined from a study of the N-methyl peak in the spectrum of these compounds. This peak is a narrow singlet below pH 0; it broadens, and then becomes a doublet, at pH values between 1 and 4. From the data, k_{1A} is calculated to be 200 ± 70 sec.$^{-1}$ M^{-1} at 25° for N-methylacetamide and, from more limited data, to be 10 ± 3 sec.$^{-1}$ M^{-1} for N-methylformamide. The former value is in reasonably good agreement with the recent determination of the same constant by Berger, Loewenstein and Meiboom.

In solutions of acids or bases which exchange protons with a solvent such as water, nuclear magnetic resonance spectra may vary in structure as the pH changes, owing to variation in the rate of proton exchange. Sharply defined multiplets under conditions in which exchange is very slow often show broadening and overlap of the lines under conditions of moderately rapid exchange and fuse into a single line when the exchange rate is high enough. The quantitative theory of such phenomena was first developed by Gutowsky, McCall and Slichter,[5] and has been extended by several authors, notably by Gutowsky, *et al.*,[6,7] and by Meiboom, *et al.*[8,9] In the present communication, a method is presented for the calculation of the mean lifetime τ of a proton involved in such an exchange reaction, when it gives rise to a spin–spin doublet in the n.m.r. spectra under conditions of very slow proton exchange. The value of τ can be inferred in three ways: (1) when exchange is very slow, τ may be estimated from the frequency separation $\delta\omega_e$ of the two peaks in the doublet; (2) when exchange is moderately rapid, and a broad singlet is observed, τ is estimated from the width $\delta\omega_{1/2}$ of the observed signal at half maximum; (3) when exchange is very rapid, τ is determined by the ratio I/I_0, where I is the maximum amplitude of the observed singlet, and I_0 is the expected amplitude for $\tau = 0$. Several of the relations given here are closely related to others already in use, as is indicated below. We have stated this complete series of connected relations in an attempt to facilitate their comparison and use.

Previous studies on amino acids in this Laboratory[10] have shown the effects of varying pH on the multiplet structure of the $\mathrm{CH_2}$ protons of glycine, and analogous effects with other amino acids. The theoretical treatment presented here arose from n.m.r. studies by one of us (M. T.) on solutions of N-methylacetamide and N-methylformamide, both of which show a clearly defined doublet due to the N-methyl group at pH values near 5. The components of the doublet gradually coalesce and finally fuse into a singlet at lower pH values; the observed effects can be interpreted in terms of changes in the velocity of proton exchange on the adjoining –CONH– group, as discussed later in this paper. During the course of these studies we learned of the independent research of Berger, Loewenstein and Meiboom.[11] Since their studies were so complete, our own experimental measurements were not carried further and are considerably more limited in scope than those of Berger, *et al.* A brief report of our own measurements is given, however, to illustrate the method of theoretical analysis developed here, and to provide confirmatory evidence for the results obtained by Berger, *et al.*

A Systematic Procedure for Analysing the Effect of Chemical Exchange on a Spin–Spin Doublet.—Gutowsky, McCall and Slichter[5] have derived the expression presented in equation (1) governing the effect, on a spin–spin doublet, of chemically exchanging the nucleus responsible for the doublet, where ω_1 is the angular frequency of precession of the nuclei under observation about H_1, the magnitude of the applied alternating magnetic field; M_0 is the equilibrium value of the magnetization due to these nuclei; T_2 is their spin–spin relaxation time; $\Delta\omega$ is the angular frequency of the applied alternating magnetic field measured about the frequency at which the transition would be ex-

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(2) Reprints of this paper may be obtained from Professor John T. Edsall, Biological Laboratories, Harvard University, Cambridge 38, Mass.

(3) Research scholar under the Smith–Mundt and Fulbright Acts (1955–1956); on leave of absence from Tokyo College of Science and now returned there.

(4) National Science Foundation Postdoctoral Fellow. Department of Chemistry, University of Wisconsin, Madison 6, Wisconsin.

(5) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

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(7) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(8) E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 630 (1957).

(9) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).

(10) M. Takeda and O. Jardetzky, *ibid.*, **26**, 1346 (1957).

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$$\left\langle \tilde{G} \right\rangle = \frac{-\omega_1 M_0 \tau \left\{ 2 + \left[\frac{1}{T_2} - i\Delta\omega \right] \tau \right\}}{\left(1 + \tau \left[\frac{1}{T_2} - i \left\{ \Delta\omega + \frac{\delta\omega}{2} \right\} \right] \right) \left(1 + \tau \left[\frac{1}{T_2} - i \left\{ \Delta\omega - \frac{\delta\omega}{2} \right\} \right] \right) - 1} \qquad (1)$$

pected to occur in the absence of the spin–spin interaction; $\delta\omega$ is the magnitude of the spin–spin interaction measured in angular frequency units; and τ is the average lifetime of the nucleus producing the doublet. For convenience, define

$$\begin{aligned} Q &= T_2\delta\omega \\ t &= \tau\delta\omega \qquad (2) \\ Z &= \Delta\omega/\delta\omega \end{aligned}$$

The observed signal is proportional to the real part of (1). In terms of (2) this may be written

$$\mathrm{Re} \left\langle \tilde{G} \right\rangle = \left(- \frac{\omega_1 M_0}{\delta\omega} \right) \frac{Q \left\{ Z^2 + \left(\frac{2}{t} + \frac{1}{Q} \right) \left[\left(\frac{2}{t} + \frac{1}{Q} \right) + \frac{Q}{4} \right] \right\}}{Q^2 Z^4 + Q^2 Z^2 \left[\left(\frac{2}{t} + \frac{1}{Q} \right)^2 + \frac{1}{Q^2} - \frac{1}{2} \right] + \left[\left(\frac{2}{t} + \frac{1}{Q} \right) + \frac{Q}{4} \right]^2} \qquad (3)$$

When both τ and T_2 are allowed to increase without bound, this expression predicts two lines of equal intensity separated by a frequency interval $\delta\omega$. If T_2 is large but finite while τ is infinite, (3) predicts two sharply peaked frequency distributions separated by an interval somewhat less than $\delta\omega$; this is due to the overlap of the two distributions. As T_2 and τ are both permitted to be finite, the behavior of (3) is such that for some values two peaks are produced and for others only a single peak is to be expected. In particular, if T_2 is large enough, it can be expected that as τ is decreased from infinity to zero, the spectrum will change continuously from a doublet to a singlet. It is found that a doublet can be expected as long as

$$\left(\frac{2}{t} + \frac{1}{Q} \right) + \frac{1}{2Q} - 2 \left(\frac{2}{t} + \frac{1}{Q} \right)^3 > 0 \qquad (4)$$

and that the separation between the peaks, $\delta\omega_e$, is given by

$$\frac{\delta\omega_e}{\delta\omega} = \left\{ \left[4Q \left(\frac{2}{t} + \frac{1}{Q} \right)^3 + (Q^2 + 8) \left(\frac{2}{t} + \frac{1}{Q} \right)^2 + (Q^2 + 2) \left(\frac{2}{t} + \frac{1}{Q} \right) \frac{2}{Q} + 1 \right]^{1/2} - 4 \left(\frac{2}{t} + \frac{1}{Q} \right)^2 - \left(\frac{2}{t} + \frac{1}{Q} \right) Q \right\}^{1/2} \qquad (5)$$

$\delta\omega_e$ is the separation between the two maxima in the observed signal obtained by differentiating (3) with respect to Z and setting the resultant expression equal to zero. The inequality (4) is simply the condition that $\delta\omega_e$ will be real and non-zero. Equation 5 becomes indeterminate as Q increases without bound; however, it may be shown easily that as $Q \rightarrow \infty$, $\delta\omega_e/\delta\omega \rightarrow [1 - (8/t^2)]^{1/2}$. Gutowsky and Holm[7] similarly base their analysis on the observation of the separation between two peaks in the spectrum. Since they treat the effect of exchange between two chemically non-equivalent positions, their final result differs somewhat from ours.

For those conditions for which $\delta\omega_e$ vanishes, two alternative observations are possible. The width of the observed signal at half maximum, $\delta\omega_{1/2}$, is useful in the region of moderately rapid exchange. $\delta\omega_{1/2}$ is given by

$$\frac{\delta\omega_{1/2}}{\delta\omega} = \left\{ \left[\left(\frac{1}{t} + \frac{1}{Q} \right)^2 \left(\frac{2}{\frac{2}{t} + \frac{1}{Q}} - \frac{8}{t} \right)^2 + \left(\frac{4}{Q} \left[\frac{2}{t} + \frac{1}{Q} \right] + 1 \right)^2 \right]^{1/2} + \left(\frac{1}{t} + \frac{1}{Q} \right) \left(\frac{2}{\frac{2}{t} + \frac{1}{Q}} - \frac{8}{t} \right) \right\}^{1/2} \qquad (6)$$

This expression is indeterminate when $t = 0$, but for this case it is shown easily that $\delta\omega_{1/2}/\delta\omega = 2/Q$. Since this expression is designed to yield the width of the spectrum at the point where it possesses an amplitude one half of that at $\Delta\omega = 0$, its use is not theoretically restricted to the singlet case; and it may prove useful in the region of a very poorly resolved doublet. This measurement of the width at half-maximum differs only very slightly from one of the methods used by Meiboom, *et al.*[8,9]

In the region of very rapid exchange, the ratio of I, the maximum amplitude of the observed singlet, to I_0, the maximum amplitude of the singlet expected for $\tau = 0$, is most useful. This is given by

$$\frac{I}{I_0} = \frac{\left(\frac{2}{t} + \frac{1}{Q} \right)}{\left(\frac{2}{t} + \frac{1}{Q} \right) + \frac{Q}{4}} \qquad (7)$$

This expression also has no restriction except practicality in its application.[12] The ratio indicated is between I_0 and the amplitude at $\Delta\omega = 0$.

Equations 5, 6 and 7, from which τ must be obtained, are such that graphical methods are most convenient in the treatment of the experimental data. This appears to be true even for (7) which might be solved easily for τ. Because of the choice made in (2), it is possible to plot a family of curves for each of these equations which are not only universally applicable to experiments of this kind, but also convenient to apply to the experimental data. In Fig. 1 $\delta\omega_e/\delta\omega$ as a function of $1/\tau\delta\omega$ for various values of $T_2\delta\omega$ is represented. (Compare Fig. 1, ref. 7.) Figure 2 gives a similar plot of $\delta\omega_{1/2}/\delta\omega$ as a function of $\tau\delta\omega$ for various values of $T_2\delta\omega$. (Compare Fig. 4, ref. 9.) Lastly, in Fig. 3, I/I_0 *vs.* $\tau\delta\omega$ is shown for various values of $T_2\delta\omega$.

To obtain τ it is clearly necessary to know T_2 (obtainable either from the spectrum in question when $\tau = 0$ or from some other unaffected portion of the spectrum) and $\delta\omega$ (obtained from the spectrum when $\tau = \infty$ by means of successive approxi-

(12) NOTE ADDED IN PROOF.—Dr. Christine D. Jardetzky has pointed out to us that Eq. 7 implies that the peak heights I and I_0 are not influenced by saturation. This is realized theoretically when the conditions $\gamma^2 H_1^2 T_1 T_2 << 1$ and $\gamma^2 H_1^2 T_1 T_2(0) << 1$ are satisfied, where γ is the gyromagnetic ratio for protons, H_1 the intensity of the radio-frequency field, T_1 the longitudinal relaxation time, and T_2 and $T_2(0)$ refer to the effective transverse relaxation times defined by the lines with peak heights I and I_0, respectively. Experimentally it is sufficient to show that the sweep rate and H_1 settings used for obtaining the spectra lie within a range of sweep rate and H_1 settings for which the ratio I/I_0 remains constant.

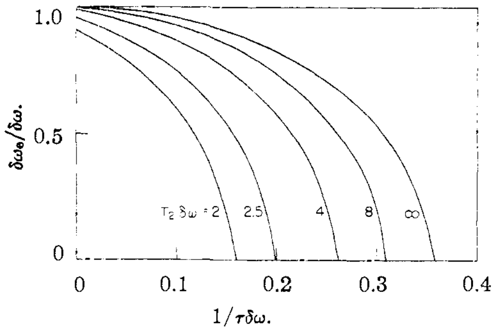

Fig. 1.—$\delta\omega_e/\delta\omega$ as a function of $1/\tau\delta\omega$ for various values of $T_2\delta\omega$.

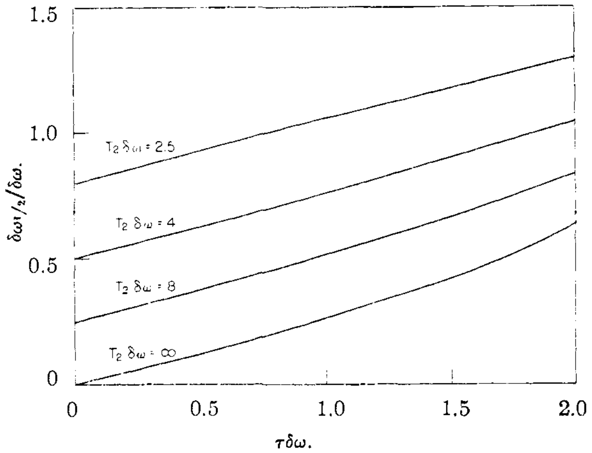

Fig. 2.—$\delta\omega_{1/2}/\delta\omega$ as a function of $\tau\delta\omega$ for various values of $T_2\delta\omega$.

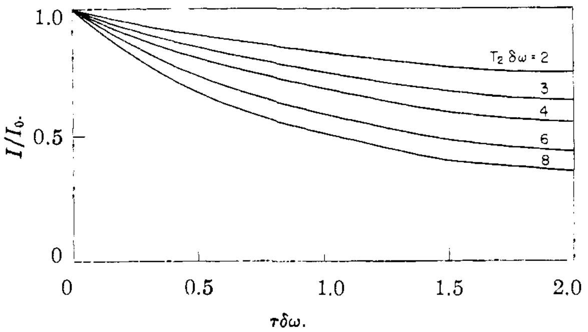

Fig. 3.—I/I_0 as a function of $\tau\delta\omega$ for various values of $T_2\delta\omega$.

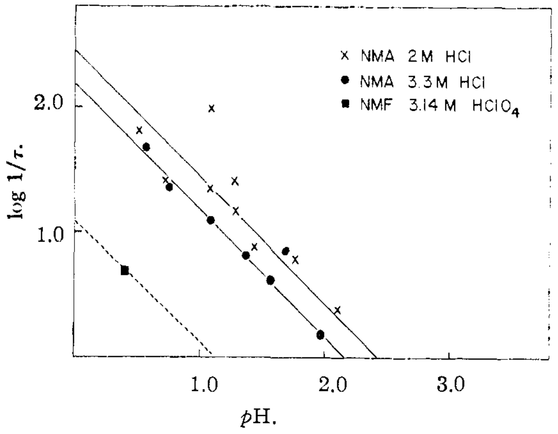

Fig. 4.—log $1/\tau$ as a function of pH in solutions of N-methylacetamide and N-methylformamide. The points marked ● were obtained in 3.3 M $HClO_4$, not in HCl (see Table I).

mation to Fig. 1); $\delta\omega_e$, $\delta\omega_{1/2}$ and I are observed from the spectrum itself under the conditions for which τ is desired. I_0 can be obtained either from the spectrum when $\tau = 0$ or from some other portion of the spectrum unaffected by the exchange and having an intensity known to be simply related to I_0. The value of τ is obtained by fitting the experimental data to the curves given.

For the sake of completeness, it should be mentioned that Meiboom, *et al.*,[8,9] have developed another method of analysis, which differs from the three presented above and is useful in the region of slow exchange, involving the ratio of maximum to central minimum intensity for the resolved doublet.

Experimental Studies on N-Methylacetamide and N-Methylformamide.—The proton magnetic resonance spectra were observed in aqueous solutions of different pH values, using a Varian Spectrometer with super stabilizer, at 40.01 mc. constant frequency. The temperature of measurement was 25 ± 1°.

Solutions were prepared from C.P. grade N-methylacetamide and N-methylformamide (Eastman Organic Chemicals). The samples were used as received, without further purification. The presence of a small amount of impurity was indicated by the results of the pH titrations. Solutions were prepared at 6 to 10 molar concentration and diluted with known volumes of water or of acid or basic solutions. For the composition and pH values of these solutions, see Tables I and II. The pH of the solutions was measured on a Beckman pH meter.

Experimental Results and Calculation of Velocity Constants.—At pH values below 0 and above 10, the exchange rate is high and the N-methyl resonance is a narrow singlet in both compounds. The rate of exchange was determined in the intermediate pH range from quantitative measurements of the broadening, and subsequent collapse into a single line, of the N-methyl doublet, by the procedures described above.

Typical records of the spectra obtained have been reported already by Berger, Loewenstein and Meiboom[9] (see their Fig. 2), and our spectra are essentially identical. From these observations the average lifetime of the amide proton may be calculated. In the region of relatively slow exchange, the frequency interval between the two components of the doublet peak, $\delta\omega_e$, was measured. In the rapid exchange region, the peak intensity I of the N-methyl line was measured relative to the peak intensity I_0 of the acetyl–methyl line, assuming that the peak intensity of the N-methyl line approaches that of the acetyl–methyl line as $\tau \rightarrow 0$. This limiting value of τ is observed in extremely acid or basic solutions. The value of T_2 was obtained from the width of the acetyl–methyl line. Following the procedure already given we determined $\delta\omega = 5.19$ c.p.s. $= 32.6$ rad. sec.$^{-1}$ and $T_2\delta\omega = 4.10$, and then calculated the average lifetime of the amide proton from the data given in the tables.

The experimental data at two concentrations of N-methylacetamide are shown in Table I. At each concentration, different concentrations of acid (HCl or $HClO_4$) were added and the pH was

TABLE I

N-METHYLACETAMIDE

pH	K_b	$\delta\omega_e$, sec.$^{-1}$	$\frac{\delta\omega_e}{\delta\omega}$	$\delta\omega_{1/2}$, sec.$^{-1}$	$\frac{\delta\omega_{1/2}}{\delta\omega}$	I/I_0	$1/\tau$, sec.$^{-1}$	log $1/\tau$
2 M Solutions with added HCl								
3.81	. .							
2.10	1.08	4.70	0.91				2.45	0.39
1.76	0.85	3.38	.65				6.03	.78
1.58	.81							
1.43	.82	1.97	.38				7.74	.89
1.28	.92			4.33	0.83		25.5	1.41
						0.54	14.8	1.1_7
1.08	.78			3.0	.58		98.8	1.9_9
						.59	21.7	1.3_4
0.72	.87					.62	25.0	1.4_0
.50	.93					.81	65.2	1.8_1
3.3 M Solutions with added $HClO_4$								
3.82								
1.97	1.14	4.93	0.95				1.55	0.19
1.68	1.18	2.60	.50				7.09	.85
1.55	1.36					0.33	4.08	.61
1.37	1.59					.39	6.52	.81
1.07	1.58					.50	12.2	1.09
0.75	0.98					.60	22.5	1.35
.56	1.01					.75	46.6	1.67

TABLE II

DATA IN 3.117 M N-METHYLFORMAMIDE SOLUTIONS WITH ADDED $HClO_4$

pH	K_b	$\delta\omega_e$, sec.$^{-1}$	$1/\tau$, sec.$^{-1}$
1.50	0.26	5.0	<2.0
1.11	.29	5.0	<2.0
0.75	.36	. .	. .
0.40	.34	3.4	5.1

determined. The calculated apparent basicity constant K_b of the amide, defined by the equation

$$K_b = (MH^+)/(M)(H^+)$$

where (M) denotes the concentration of N-methylacetamide, and (MH^+) denotes that of its conjugate acid, was calculated from the measured pH, and from the concentrations of the N-methylacetamide and the acid added. We note that K_b is the reciprocal of the acidity constant K_a, and log K_b = pK_a. The value of (H^+) was taken as the anti-logarithm of the measured pH, without attempting corrections for activity coefficients. In spite of the uncertainty introduced by this assumption, the values of K_b recorded in Table I are surprisingly constant, and lie close to 1.

The values of τ, the mean lifetime of the protons in the exchange reaction, are calculated in the two right-hand columns of Table I and the right-hand column of Table II. It will be seen that at the higher pH values (2.1 to 1.5 in Table I) the calculations are made from $\delta\omega_e$, making use of equation 5. At intermediate pH values, 1.4 to 1, calculations are made from $\delta\omega_{1/2}$ making use of equation 6. In the most acid solutions from pH 1 to 0.5 or less, calculations are made from the value of I/I_0 using equation 7. The number of measurements on N-methylformamide was very limited, and the few values of τ which are recorded were determined from equation 5. The resulting values of τ are plotted in Fig. 4. In this figure it is shown that for N-methylacetamide there is a linear relation (with unit slope) between average lifetime τ and pH between 0 to 2. Hence we assume this reaction mechanism, following Berger, *et al.*[9]

$$RCONHCH_3 + (H_3O)^+ \underset{k_{2A}}{\overset{k_{1A}}{\rightleftarrows}} (RCONH_2CH_3)^+ + H_2O$$

for proton exchange

$$1/\tau = k_{1A}\,(H_3O^+)$$

$$\log (1/\tau) = \log k_{1A} - pH$$

The data of Fig. 4 show some scatter; the values obtained for 3.3 M N-methylacetamide solutions lie generally somewhat below those obtained in 2 M solutions. Two lines have accordingly been drawn in the figure, in an attempt to fit the data, the upper line for the data at 2 M, with an ordinate intercept at log $(1/\tau)$ = 2.43, and the lower line for the 3.3 M solutions with an ordinate intercept at log $(1/\tau)$ = 2.16. These values correspond to velocity constants k_{1A} of 270 and 140 sec.$^{-1}$ M^{-1}, respectively. As a mean value we take

$$k_{1A} = 200 \pm 70 \text{ sec.}^{-1}\ M^{-1}, \text{ at } 25°$$

Berger, *et al.*,[9] obtained a value of k_{1A} = 380 ± 40 sec.$^{-1}$ M^{-1} at 23°, which agrees moderately well with our value.

For N-methylformamide (see Table II) only one measurement was made, and from this value we find

$$k_{1A} = 10 \pm 3 \text{ sec.}^{-1}\ M^{-1}$$

assuming the same type of pH dependence of τ. The value of K_b was found to be close to 0.30. Thus the conjugate acid of N-methylformamide is a stronger acid than the conjugate acid of N-methylacetamide, as might be expected on structural grounds.

We note that there is at least a qualitative correlation between the values of the equilibrium constants K_b and the velocity constants for proton binding k_{1A} when the two N-methyl amides are compared. The value of k_{1A} is about 20 times as great for N-methylacetamide as for N-methylformamide, whereas K_b is about 3 times as great. Goldfarb, Mele and Gutstein[13] have determined log K_b = pK_A for N-methylacetamide as −0.46 from ultraviolet absorption measurements in dilute solution. Our value of pK_A = 0 at concentrations of 2–3.3 M is of the same order of magnitude, and exact comparison is not warranted in view of the great difference in conditions of measurement.

In the alkaline transition region, Berger, Loewenstein and Meiboom[9] obtained the rate constant k_{1B}, based on the assumed mechanism shown

$$CH_3CONHCH_3 + OH^- \underset{k_{2B}}{\overset{k_{1B}}{\rightleftarrows}} CH_3CON^-CH_3 + H_2O$$

$$k_{1B} = (5.2 \pm 1.0) \times 10^6 \text{ sec.}^{-1}\ M^{-1}$$

In our experiments an accurate analysis of the data in this region was not completed. However, the transition of line shape from the doublet to the

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(13) A. R. Goldfarb, A. Mele and N. Gutstein, THIS JOURNAL, **77**, 6194 (1955).

singlet was found in the pH region 8 $\sim$ 9, for both N-methylformamide and N-methylacetamide. Our finding is thus in qualitative agreement with their results.

We are indebted to Professor John T. Edsall for his active interest in this work and for advice in the preparation of the manuscript.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Infrared Spectra of Charge-transfer Complexes. III. Complexes with Bromine, Chlorine and Iodine Monochloride. Solvent Effects Involving X–H Stretching Frequencies

BY WILLIS B. PERSON, RONALD E. ERICKSON[1] AND ROBERT E. BUCKLES

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Infrared spectra of a number of charge-transfer complexes involving bromine as the acceptor have been studied in the region of the Br–Br stretching vibration. The infrared absorption due to the Cl–Cl stretch in the benzene–Cl_2 complex has been reinvestigated and the intensity estimated. In addition several more complexes of iodine monochloride have been studied. These studies are correlated in terms of the plot of ϵ_a, the added effective charge due to complex formation, against $\Delta k/k$, the relative change in force constant due to complex formation; in fact the same relation is found to fit all the complexes studied thus far (with ICl,[2] ICN,[3] Br_2, Cl_2 and hydrogen-bond complexes[3]). This is interpreted as providing further support for the model of the bonding in the complex in terms of the two resonance structures: $D{-}{-}{-}X{-}Y \leftrightarrow (D{-}X)^{+}{-}{-}{-}Y^{-}$. This resonance model can also be related successfully to the very large body of experimental data on X–H stretching frequencies correlated by Bellamy, *et al.*[21]

Introduction

As part of the program begun recently in this Laboratory on the investigation of the effect of charge-transfer complex formation on the spectra of the molecules involved[2,3] and in continuation of a study of molecular complexes with halogens[4] we have extended the experimental observations on the infrared spectra of bromine complexes reported earlier.[5] Although the infrared spectra of halogen complexes had been studied before,[6,7] it was not until the work of Collin, D'Or, and Alewaeters on the infrared spectra of Br_2 and Cl_2 in benzene[8] that it became apparent that the most dramatic changes in the vibrational spectra of molecules participating in charge-transfer complexes would occur in the halogen vibration.[9] This was confirmed in the study of iodine monochloride where it was observed that the spectrum of the halogen shows regular changes in half intensity width, frequency and intensity as the strength of the charge-transfer complex increases.[2] These changes were interpreted[2] in terms of the charge-transfer theory,[10] and the resonance structures

$$\underset{a}{D\ldots X{-}Y} \qquad \underset{b}{(D{-}X)^{+}\ldots Y^{-}}$$

Here D is the donor molecule and X–Y is the acceptor bond. The solid lines represent covalent bonds and the dotted lines represent Coulomb and/or van der Waals attractions. As the formation constant of the complex becomes larger, the importance of structure b in the ground state increases; this explains the changes in infrared spectra of ICl satisfactorily.[2]

The qualitative similarity of these changes to the changes in the O–H bond in hydrogen-bond formation is notable. In order to compare these similarities on a more quantitative basis, the correlations of Huggins and Pimentel[11] between frequency shift and intensity increase for hydrogen-bonded systems were modified.[3] When ϵ_a, the increased effective charge as defined in reference 2, was plotted against $\Delta k/k$, the relative change in the force constant of the X–Y diatomic molecules, it was found that not only could the data for the hydrogen-bonded system be fitted to a straight line, but also the data for ICl complexes and for ICN complexes (for the I–C stretch) could be fitted to the same straight line.[12] In addition, the point for Br_2–benzene[5] seemed to fit on the curve.

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(1) Monsanto Predoctoral Fellow, 1957–1958.

(2) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958), paper I of this series.

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(9) However, more recent studies by Ferguson (see for example E. E. Ferguson, *Spectrochim. Acta*, **10**, 123 (1957), and references cited there) indicate that the changes in the spectrum of the donor are indeed just as great as in the spectrum of the acceptor. These changes are not readily observable because of interference from the uncomplexed donor which is usually present in large excess.

(10) (a) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); (b) *Rec. trav. chim.*, **75**, 845 (1956).

(11) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

(12) The simplest interpretation of ϵ_a given in references 2 and 3 is that it is the additional charge on the Y atom in the complex due to the contribution from the resonance structure b. Its definition in terms of the experimental data is given in the equation

$$\epsilon = \frac{d\mu}{dQ} = \epsilon_0 + \epsilon_a = 1.537 \times 10^{-2}\sqrt{B/\mu}$$

Here B is the apparent integrated molar absorption coefficient in darks (see footnote 15); μ is the reduced mass in atomic mass units; and ϵ_0 is the effective charge of the uncomplexed molecule (in carbon tetrachloride solution). The relative change in force constant, $\Delta k/k$, is defined by

$$\Delta k/k = (k_0 - k_{complex})/k_0$$

Here k_0 is the force constant for the uncomplexed X–Y molecule and $k_{complex}$ is the force constant for this bond in the complex. The X–Y bond is treated throughout as a diatomic molecule, an approximation which should be reasonably correct for the cases considered here.