Carbon-13 Chemical Shifts of the Carbonyl Group. IV. Dilution Curves for Acetic Acid in Representative Solvents[1–3]

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Abstract: C^{13} chemical shifts of the carbonyl group of acetic acid were determined in the solvents water, acetone, chloroform, and cyclohexane over the range of volume fractions of acetic acid from 1.0 to about 10^{-3}. Relatively large dilution effects on the C^{13} shifts were observed with acetone as solvent, a smaller effect with chloroform, and only small effects in water or cyclohexane as solvents. A curious hump was found in the water dilution curve. These results are understandable in terms of the influences of making and/or breaking of hydrogen bonds between the carboxyl group and various species.

The structural identity of the species present when carboxylic acids are present in solutions or in their pure gaseous, liquid, or crystalline states has been a subject of interest for many years.[4,5] Various physical methods[4–28] including infrared,[6–12,19,28] Raman,[4,5,19] and proton magnetic resonance[14–18,23–25] spectroscopy have been applied to the problem of distinguishing between the monomeric, dimeric, and other species. In the light of the considerable contribution made by previous proton n.m.r. investigations to the understanding of these systems, we have applied C^{13} magnetic resonance techniques, which seemed ideally suited to such a study on the basis of the reported effects of hydrogen bonding on carbonyl C^{13} shifts[2,29–32] and on the C^{13} shifts of the substituted carbon atom of phenol.[33] Since the carboxyl group of acetic acid has the combined acid–base properties of the basicity of a carbonyl group and the acidity of a hydroxyl group attached to sp^2-hybridized carbon, a comparison of solvent effects on the carboxyl-C^{13} shifts with the previous results[2,28–33] seemed promising. This is a particularly attractive approach in view of the uncertainty cast upon much of the proton magnetic resonance results due to spurious shifts introduced in the hydroxyl resonances by the presence of small quantities of water in the acetic acid or solvents employed.[14]

Experimental Section

Materials. The glacial acetic acid employed in natural abundance experiments was reagent grade (99.8%) from Mallinckrodt. In the experiments performed with enriched material, acetic acid-1-C^{13} (57 atom % C^{13}) from Volk Radiochemical Co. was employed. The solvents were Matheson Coleman and Bell Spectrograde materials with very low water contents as determined by Karl Fischer titrations[34]: acetone, <0.5% water; cyclohexane, <0.001%; chloroform (from which stabilizing ethanol was removed by passage through an alumina column), 0.024%. Distilled water was deionized by passage through an ion-exchange column before use. In the preparation, dilution, and transferring of solutions of C^{13}-labeled acetic acid in the anhydrous solvents, calibrated syringes and automatic pipets were employed in a glove box filled with a dry nitrogen atmosphere.

C^{13} Magnetic Resonance Measurements. The C^{13} n.m.r. spectra were obtained at 35° at a frequency of 15.085 Mc./sec., using dispersion mode, rapid passage conditions as previously described by Lauterbur.[35] The sample container was similar to that described by Spiesecke and Schneider,[36] except no provision was made for spinning the sample; it consisted of two concentric thin-walled spherical bulbs of invariant mutual orientation, the inner bulb containing the reference material which was C^{13}-labeled carbon disulfide.[37] Small corrections for bulk susceptibility differences between samples, made necessary because of imperfections in the

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(2) Part III: G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2752 (1965).

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Table I. C^{13} Chemical Shifts of $CH_3C^{13}O_2H$ in Various Solutions[a]

	Volume fraction of acetic acid										
Solvent	0.500	0.333	0.250	0.125	0.0625	0.0313	0.0156	0.00781	0.00390	0.00195	0.000975
Acetone	17.6		19.1	20.0	20.9	21.3	21.5	21.8	21.9	21.8	22.1
Chloroform	15.3		15.1	15.3	15.6	15.6	15.9	16.4	17.0	17.9	18.6
Water	16.6	16.8	16.6	16.5	16.2	16.3	16.3	16.2	16.3	16.2	16.3
Cyclohexane	15.5		15.7	15.8	15.9	16.0	16.0	16.1	16.0	16.4	16.4
Acetic acid	←					15.4					→

[a] In p.p.m. with respect to $C^{13}S_2$; slight corrections for bulk suceptibility differences have been applied to the raw data.

geometry of the cell, were applied to the raw data, but in no case amounted to more than 0.2 p.p.m. The calibration of the reference was carried out by the usual procedure,[38] yielding −64.9 p.p.m. with respect to benzene. Chart calibration was accomplished by frequent repetition of the spectrum of dimethyl carbonate, for which the internal chemical shift is known to be 102.7 p.p.m.[2] During the period within which the data reported here were obtained, only small statistically random variations in chart calibration (p.p.m./cm.) were noted, and the shifts reported in this paper may be considered internally self-consistent within the limits of about ±0.15 p.p.m.

Results

Carbon-13 chemical shifts of the carbonyl group of acetic acid were determined in solutions of various concentration in the solvents water, acetone, chloroform, and cyclohexane. Measurements using C^{13} in its natural abundance were performed with solutions of acetic acid volume fractions from one to one-sixteenth, while enriched acetic acid-1-C^{13} (57 atom % C^{13}) was employed in the more dilute solutions. In all cases the shifts of the carboxyl group in the highest dilutions studied were upfield from that in pure acetic acid. However, the manner in which the shifts changed with concentration was found to be different in each solvent. These results are presented in Table I and in Figure 1.

Discussion

The results displayed in Table I and Figure 1 show solvent effects on the acetoxyl resonance spanning a range of about 7 p.p.m. Irrespective of the explanation of these results, their magnitude indicates a need for caution in attributing small chemical shift differences obtained between samples of different carboxylic acids in different solvents and/or at different concentrations to structural influences between the solutes themselves.

Viewing the simultaneous acidic and basic properties of the carboxyl group in terms of ketone carbonyl groups and phenolic hydroxyl groups as models, the trends shown in Figure 1 can be accounted for qualitatively by referring to the solvent effects on the C^{13} shifts determined previously for those systems.[2,29–33] The experiments with ketones[2,29–32] indicate that we should expect a decrease in shielding to accompany an increase in hydrogen bonding to the carbonyl oxygen of the carboxyl group. A downfield shift with increasing hydrogen bonding of the hydroxyl hydrogen of the carboxyl group to a basic center is also predicted on the basis of the downfield trend in the shifts of the substituted carbon atom of phenol with increasing solvent basicity.[33] Thus an increase in hydrogen bonding to the carbonyl oxygen and by the hydroxyl hydrogen should both lead to a decrease in shielding at that carbon atom, with the former effect being considerably more influential in determining the resulting shift.[2,29–33]

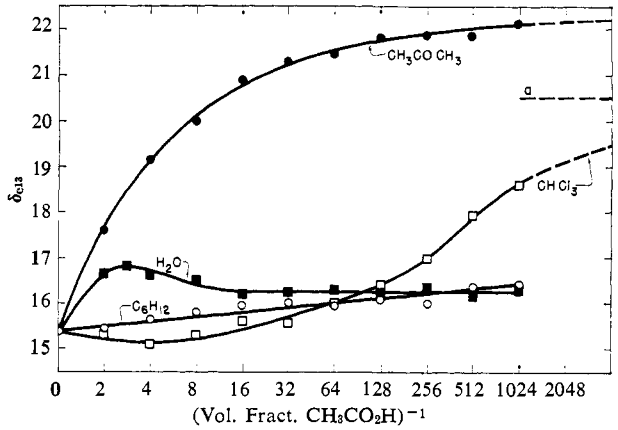

Figure 1. C^{13} chemical shifts of $CH_3C^{13}O_2H$ *vs.* (volume fraction of acetic acid)$^{-1}$ in the solvents acetone ●, water ■, cyclohexane ○, and chloroform □.

These relationships can be considered most directly in terms of the making and breaking of hydrogen bonds in the following equilibria between polymeric, dimeric, and monomeric acetic acid (HOAc) and the hydrogen-bonded complex of acetic acid with solvent (S).

$$2\text{HOAc} \rightleftharpoons (\text{HOAc})_2 \quad (1)$$

$$n\text{HOAc} + m(\text{HOAc})_2 \rightleftharpoons (\text{HOAc})_{n+2m} \quad n = 1, 2, \ldots; \quad m = 1, 2, \ldots \quad (2)$$

$$(\text{HOAc})_n + n\text{S} \rightleftharpoons n[\text{S}\cdot\text{HOAc}] \quad n = 1, 2, \ldots \quad (3)$$

Cyclohexane. The dilution curve for the carboxyl C^{13} shift in this solvent shows only a gradual increase in shielding with decreasing acetic acid concentration, the entire range of the plot spanning only 1 p.p.m. If one accepts the premise based on the above-mentioned model and the previously reported C^{13} solvent effects[2,29–33] that hydrogen bonding is the most important influence in these shifts, then the relative insensitivity in cyclohexane appears to indicate that hydrogen bonding is roughly equally important at all stages of the dilution. This is consistent with the explanation that acetic acid exists largely as dimers in both its pure liquid state and in solution in nonpolar solvents. This view has been widely used in explanations of infrared and proton magnetic resonance results.[4–6,8–16,23,24,27,28] However, the importance of trimers and higher polymers in pure acetic acid and in concentrated solutions also has been discussed,[6,15,20–24,27] and while the cyclic structure I has been commonly accepted for the dimer, the open

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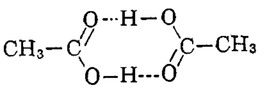
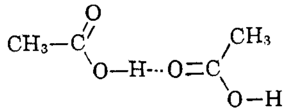


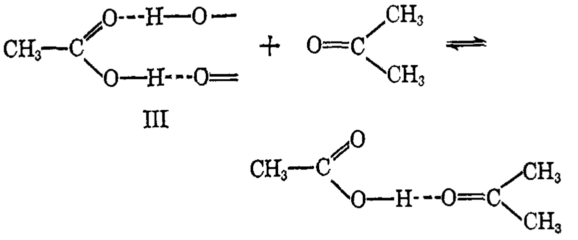
I



II

dimer structure II has also been given consideration.[6,20–22,27] The small increase in shielding which accompanies dilution in cyclohexane may be due to other factors; however, it is tempting to rationalize it in terms of shifting equilibria 1 and/or 2 to the left. Proton magnetic resonance data have been interpreted as indicating that the hydrogen bonds in higher polymers are not as strong as in the dimer.[23,24,27] However, Davis and Pitzer,[15] in referring to the proton experiments, have pointed out that "such an argument does not seem reasonable since the polymers presumably have lower entropy per monomer unit but are formed preferentially at higher concentrations in competition with the dimer" and that "H-bonds in the polymer in crystals are shorter than the bonds in cyclic dimers." The latter view, that hydrogen bonds are stronger on the average in the polymer, is consistent with the trend observed in the present study. Rough extrapolation of the C^{13} shift to infinite dilution in cyclohexane yields a crude estimate of the chemical shift in cyclic dimer (about 16.5 p.p.m.).[27]

Acetone. This solvent represents the case of molecules with basic centers, but with no protons acidic enough for hydrogen bonding. The acetone–acetic acid system has been studied previously by proton magnetic resonance,[14,16,24] and the results have been interpreted primarily in terms of equilibrium 3. The present results are consistent with this interpretation. Thus, while (1) and/or (2) may also be involved in the region of the dilution curve corresponding to high concentration of acetic acid, the trend to higher shielding with increasing dilution is consistent with the destruction of hydrogen bonds to the carbonyl group of acetic acid which is implied in equilibrium 3. We can represent the implied transformation in more detail as



III

IV

(4)

where structure III represents cyclic or open-chain dimer or higher polymers. Since in both III and IV the hydroxyl group is hydrogen bonded to a carbonyl group, the main change experienced by the carboxyl group in transformation 4 is the destruction of a hydrogen bond to the carbonyl oxygen center. On the basis of previous results[2,29–32] this change could readily account for an effect on the shift of the magnitude observed here. It appears that at the lowest concentrations employed in this study (volume fraction, $^1/_{1024}$) the dilution curve has nearly reached the asymptotic limit which might be expected when the transformation III → IV is essentially complete. Thus, a rough estimate (22.2 p.p.m.) can be made for the chemical shift of the complex IV. If the contribution which the hydroxyl hydrogen bond makes to this shift were known, then the shift of monomeric acetic acid could be determined. We estimate this contribution to be on the order of -3 p.p.m.,[33] so that a value of about 25 p.p.m. can be estimated for the shift of nonhydrogen-bonded, monomeric acetic acid in an environment of carbonyl compounds.[39] Perhaps a more reliable estimate can be made when dilution curves for phenol shifts become available.

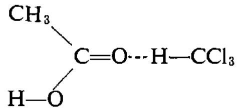
On the basis of the smooth dilution curve for acetic acid in acetone which appears to level off at an asymptotic value of about 22.2 p.p.m. (δ_{IV}) characteristic of the complex IV, one can estimate an equilibrium constant for the formation of the complex according to equilibrium 3 with $n = 2$. If one makes the additional assumption that at an apparent acetic acid volume fraction of 0.125 the only acetic acid species present in appreciable concentrations are the dimer and the complex IV and that the chemical shift of the former in this medium (δ_d) can be approximated by that of pure acetic acid, then one can calculate the fraction of acetic acid present as dimer and as complex, denoted by x_d and x_{IV}, respectively, by the usual type of equation.[17]

$$\delta_{obsd} = \delta_d x_d + \delta_{IV} x_{IV} \tag{5}$$

By this method one obtains[40]

$$K = \frac{[IV]}{[(HOAc)_2]^{1/2}[acetone]} = 0.23\ (mole/l.)^{-1/2}$$

Chloroform. This solvent is of interest because its ability to function as a hydrogen-bonding acid has been well demonstrated,[4,5] whereas, unlike most acids, it contains no appreciably basic center. The gross upfield trend of the C^{13} resonance with decreasing concentration can be explained in terms of equilibrium 3 where the nature of the complex (S·HOAc) can now be represented by structure V. Thus, the shift in equilibrium 3 to the right, which would be promoted by dilution in chloroform, involves breaking of the hydrogen bond in which the hydroxyl group participates in structure III and replacement of a strong hydrogen bond to the carbonyl oxygen (from a carboxyl hydrogen) by a weaker hydrogen bond (from a chloroform hydrogen). At infinite dilution, the former effect might be expected to contribute an increase in shift of about 3 p.p.m., and the latter an increase of about 2 p.p.m.,[41] causing the shift to approach a value near that indicated by the dotted line a in Figure 1. Thus an upfield trend of the observed magnitude is consistent with our



V

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(39) Factors other than hydrogen bonding would be influential in determining the exact value of the shift.

(40) Taking $\delta_d = 16.5$, the value obtained from the extrapolation in cyclohexane, gives the alternative value 0.21. These values can be compared with 0.11 $(mole/l.)^{-1/2}$ obtained for the acetonitrile–acetic acid system: C. P. Nash, private communication.

(41) This estimate was made by multiplying the difference between the infinite dilution shifts of acetone in acetic acid and in chloroform (4.0 p.p.m.: G. E. Maciel and J. J. Natterstad, unpublished results) by the apparent sensitivity of the carbonyl shift of ethyl acetate relative to acetone (0.50, ref. 2).

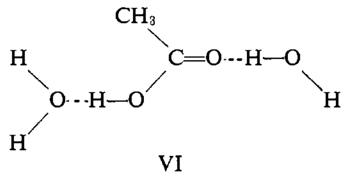
interpretations based on hydrogen bonding. Clearly the dilution curve has not yet leveled off even at the lowest concentration studied, so that appreciable concentrations of both I and V are present, and it is not possible to obtain the chemical shift of the complex V directly from these data. These interpretations are consistent with the measurements of Barrow and Yerger[42] who have determined the equilibrium constants for the formation of both acetic acid dimers and the complex V from monomer acetic acid in chloroform solution. From their values of about 120 and 0.2 mole^{-1} l., respectively, one calculates a value 0.02 (mole/l.)$^{-1/2}$ for the equilibrium constant of reaction 6.

$$^{1}/_{2}(HOAc)_2 + CHCl_3 \rightleftharpoons V \qquad (6)$$

From these equilibrium constants, one estimates that in a 0.017 *M* solution (volume fraction 9.75×10^{-4}) in chloroform the acetic acid should exist roughly one-third in the form of dimer and two-thirds in the form of V. Then, from an expression analogous to eq. 5, one would predict a value of about 20 p.p.m. for the chemical shift of V, in agreement with our discussion above, and the speculated form of the dotted curves in Figure 1.

The slight decrease in chemical shift in concentrated solutions of acetic acid in chloroform (with respect to the shift in pure acetic acid) would be difficult to explain in terms of our model based on hydrogen bonding. However, it reaches a maximum magnitude of only 0.3 p.p.m. (only about twice the experimental error) and could be due to factors other than those which are considered in this paper.

Water. The data obtained in aqueous solutions are of interest because water, unlike the other solvents employed, has the important chemical property in common with acetic acid of functioning both as a base and as an acid in the formation of hydrogen bonds. Thus, it can readily be imagined that whichever hydrogen bonds are destroyed, as acetic acid polymers or dimers dissociate, are replaced by hydrogen bonds between acetic acid and water. The fact that the chemical shifts obtained in very dilute solution in the solvents water and cyclohexane are nearly the same seems reasonable if the predominant species in the latter case is the cyclic dimers, whereas in the former solvent it can be represented by structure VI; in both cases the acidic and basic sites of the carboxyl group are utilized in hydrogen bonding. In the most dilute solution studied, about 3% of the acetic acid exists in the dissociated form. However, with the chemical shift differences of acetic acid and acetate ion amounting to only 4.3 p.p.m.,[31,43] such small amounts of acetate ion could influence the observed shift only by about the amount of expected experimental error.



VI

The maximum observed in the dilution curve at an acetic acid volume fraction of about $^{1}/_{3}$ is of interest because of its relationship to other work[7,14,17,18,20–22,25,26] and its implication that in the initial stages of dilution, the number or strength of hydrogen bonds decreases in the "average acetic acid units," this reduction being reversed in later stages of the dilution. Previous investigators[18,25,26] have reported a hump at about 50% by volume in the dilution curve of the proton magnetic resonance shift of the hydroxyl group in solutions of acetic acid in water. Their explanations were partly based on the fact that a rapid equilibrium exists between the hydroxyl protons of water and acetic acid, and that under the conditions of the experiment only the weighted-average proton shift was obtained.[18,25] This type of explanation is clearly not applicable to the present data, obtained from a nucleus which does not undergo chemical exchange with solvent.

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