Proton Magnetic Resonance Spectra in Trifluoroacetic Acid Solution. I. Alkali Metal and Quaternary Ammonium Trifluoroacetates

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Abstract: Proton magnetic resonance spectra of trifluoroacetic acid solutions of lithium, sodium, potassium, rubidium, cesium, tetramethylammonium, and trimethylphenylammonium trifluoroacetates have been obtained at a number of concentrations up to the solubility limit of each salt. In each case, the data are interpreted in terms of the formation of the hydrogen bis(trifluoroacetate) anion. This interpretation is based upon the observation of a chemical shift for the solvent hydrogen that was concentration dependent from zero to 0.5 mol fraction salt and concentration independent above 0.5 mol fraction salt for solutions of trimethylphenylammonium trifluoroacetate in trifluoroacetic acid. The chemical shift of the hydrogen of the hydrogen bis(trifluoroacetate) anion was experimentally measured to be τ −8.83 in the presence of the trimethylphenylammonium cation. Chemical shift values for the hydrogen of the hydrogen bis(trifluoroacetate) anion in the presence of the other cations studied were calculated.

Trifluoroacetic acid (HTFA) is a useful solvent for proton magnetic resonance (pmr) spectral determinations because it is a good solvent for many organic compounds and has only one pmr absorption at low field (τ −1.71 for the pure acid with tetramethylsilane (TMS) as internal reference at a probe temperature of 35.6°). While exploring the utility of HTFA as a solvent for pmr spectroscopy, it was noted that the absorption resulting from excess solvent occurred, with many compounds, at lower field than that of pure HTFA. In these cases, the position of this absorption was found to be concentration dependent and was shifted to lower field with higher solute concentration (lower HTFA concentration). These observations led us to postulate that, because of protonation of the solute molecules by HTFA, the trifluoroacetate anion was produced. If this anion would become strongly hydrogen-bonded with excess solvent, a species would be produced that would be expected to absorb at lower field than the parent acid. Since this species should be capable of undergoing rapid chemical exchange with excess HTFA, a single absorption resulting from the acidic hydrogen should result, and the downfield shift of this absorption with increasing solute concentration would be anticipated.

The composition of the products from the interaction of sodium trifluoroacetate and HTFA has been studied by Klemperer and Pimentel[2] using infrared spectroscopic and vapor pressure measurement techniques. They presented evidence for the formation of two stable acid–salt compounds of HTFA and sodium trifluoroacetate that had strong hydrogen bonds.

Recently, X-ray diffraction studies of crystalline potassium, rubidium, and cesium hydrogen bis(trifluoroacetates) have been carried out by Golič and Speakman,[3] who found that these salts consisted of two equivalent trifluoroacetate residues joined by very short hydrogen bonds ($O\cdots H\cdots O$ distances of 2.38 to 2.435 Å). To our knowledge, the only pmr data regarding the nature of the hydrogen bis(trifluoroacetate) anion is the limited study of the potassium trifluoroacetate–trifluoroacetic acid system reported by Klotz,[4] *et al.*, who set forth a postulate identical with that which prompted our investigation.

This paper presents the results of our investigation of the pmr spectra of a series of alkali metal trifluoroacetates and two quaternary ammonium trifluoroacetates in HTFA solution.

Experimental Section

Materials. Reagent grade acetic acid, HTFA, methanesulfonic acid, and *N,N*-dimethylaniline were fractionally distilled in a dry atmosphere. A middle fraction of suitable boiling range was obtained in each case. Alkali metal trifluoroacetates were prepared from the corresponding carbonates as follows. A water solution of the carbonate was diluted with HTFA until the solution was slightly acidic. Most of the water was removed *in vacuo* using a steam bath. The last traces of water were removed from the resulting salts by azeotropic distillation using a large excess of dry benzene. Finally, the benzene was removed by filtration in a dry atmosphere, and the salts were stored in a vacuum desiccator. The anhydrous nature of the alkali metal trifluoroacetates prepared was evidenced by the absence of infrared absorption in the 2.5–3.2-μ region (Nujol mulls, prepared and placed between potassium bromide plates in a dry nitrogen atmosphere).

The trimethylphenylammonium salts of HTFA and methanesulfonic acids were prepared as follows. *N,N*-Dimethylaniline was treated with excess methyl iodide and gave trimethylphenylammonium iodide, mp 239–240° (lit.[5] 228–230°) after recrystallization from 9:1 acetone–water. A water solution of the quaternary iodide was treated with an excess of silver oxide. Precipitated silver iodide and excess silver oxide were removed by filtration, and the resulting aqueous solution was titrated to pH 5.5 with the appropriate acid. Recovery of the salts was effected as described above for the alkali metal trifluoroacetates. Tetramethylammonium trifluoroacetate

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(2) W. Klemperer and G. C. Pimentel, *J. Chem. Phys.*, 22, 1399 (1954).

(3) L. Golič and J. C. Speakman, *J. Chem. Soc.*, 2530 (1965).

(4) I. M. Klotz, S. F. Russo, S. Hanlon, and M. A. Stake, *J. Amer. Chem. Soc.*, 86, 4774 (1964).

(5) N. A. Lange, "Handbook of Chemistry," 10th ed, McGraw-Hill, New York, N. Y., 1961, p 708.

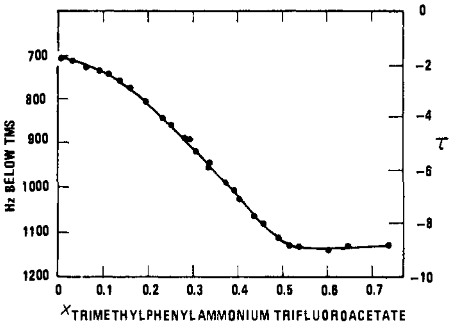

Figure 1. Pmr data for the OH absorption of solutions of trimethylphenylammonium trifluoroacetate at various mole fractions in trifluoroacetic acid.

was prepared from tetramethylammonium iodide using the method described above.

Sample Preparation. Solutions for pmr spectral determinations were prepared in 1-g glass vials with polyethylene caps. The closed vials were weighed before and after the introduction of each sample component. The samples were sometimes warmed in the vials on a small hot plate to effect solution. In these cases, the vials were weighed after heating.

Proton Magnetic Resonance Spectra. The spectral measurements were made using a Varian Associates A-60 spectrometer equipped for operation at 35.6 ± 1°. Varian Associates Pyrex nmr tubes of 5.00-mm outside diameter were closed with a tight plastic cap after being filled with about 1 ml of the solution and a few milligrams of an internal standard. Tetramethylsilane (TMS) usually served as the internal standard. Because of the low solubility of TMS in some solutions, sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) or an *N*-methyl group of a sample component (previously referred to TMS for this purpose) was occasionally used. All spectra were recorded using a sweep time of 500 sec/1000 Hz and at amplitude and rf field adjustments that provided the maximum signal to noise ratio.

Results and Their Treatment

Neat HTFA exhibits only one pmr absorption, which occurs at τ −1.71. When any of the trifluoroacetate salts examined were dissolved in HTFA, a concentration-dependent, downfield shift of the absorption resulting from HTFA was observed. The maximum extent of this downfield shift could not be observed with any of the alkali metal trifluoroacetates because of their limited solubilities.[6] Table I summarizes the pmr absorption for saturated solutions of the salts examined in HTFA.

Table I. Pmr Absorptions for Saturated Solutions of 0.10 Mol Fraction (Mf) Solutions of Some Trifluoroacetate Salts in Trifluoroacetic Acid

Cation of salt	Mf for satd soln	Pmr abs of satd soln, τ	Pmr abs of 0.10 mf soln, τ
Li^+	0.1721	−2.09	−2.00
Na^+	0.1405	−2.43	−2.12
K^+	0.2482	−3.96	−2.28
Rb^+	0.2552	−4.39	−2.37
Cs^+	0.3206	−4.94	−2.30
$(CH_3)_4N^+$	0.484	−7.88	−2.13
$C_6H_5(CH_3)_3N^+$	0.736	−8.83	−2.30

As might be anticipated, lithium and sodium trifluoroacetates were less soluble than the other alkali metal trifluoroacetates, which have larger and more electronically shielded cations. As expected, the downfield chemical shift for the saturated solutions was larger with increasing solubility of the salt. For the metal salts, the maximum observed value was τ −4.94 for cesium trifluoroacetate at 0.3206 mol fraction. The tetramethylammonium salt has a larger cation and was more soluble. The pmr absorption of a saturated solution of tetramethylammonium trifluoroacetate in HTFA (0.484 mol fraction) occurred at τ −7.88, a considerably larger downfield chemical shift than those of the alkali metal trifluoroacetates.

If the postulate advanced earlier is valid, one would expect that the hydroxyl absorption for solutions of univalent cationic trifluoroacetate salts in HTFA would shift farther downfield with increasing solute concentration and that the maximum shift would occur at 0.50 mol fraction of salt. Furthermore, it would be anticipated that with an increase in salt concentration greater than 0.50 mol fraction, the hydroxyl absorption would remain essentially at a constant position. This would be expected because the maximum concentration of the hydrogen bis(trifluoroacetate) anion [$H(TFA)_2^-$] would be formed at 0.50 mol fraction, and an added amount of salt would only serve to dilute the $H(TFA)_2^-$ anion. Of the compounds studied, this observation was possible only with trimethylphenylammonium trifluoroacetate, as is illustrated in Figure 1. The large cation resulted in increased solubility, and a saturated solution was obtained at 0.736 mol fraction. The position of absorption of the $H(TFA)_2^-$ anion is seen to be essentially constant at τ −8.83 from 0.50 to 0.736 mol fraction.

In the concentration range of 0.0–0.50 mol fraction, all of the compounds studied gave qualitatively similar results. The observed downfield chemical shifts for 0.10 mol fraction solutions of all the salts studied are given in the last column of Table I.

That the hydrogen of the $H(TFA)_2^-$ anion was undergoing rapid chemical exchange with the hydrogen of HTFA is evidenced by the fact that only one pmr absorption was present for these species. Plots of the downfield chemical shifts of these rapidly exchanging hydrogens as ordinates *vs.* the mole fraction of salt as abscissas yielded nonlinear results in the 0 to 0.50 mol fraction range for all salts examined (see Figure 1).

The position of absorption of the hydrogen of the $H(TFA)_2^-$ anion in the presence of different cations may be calculated using the relationship of Gutowsky and Saika.[7] For the rapid exchange of a proton between two sites, this relationship is given by eq 1, where

$$\tau_{\text{obsd}} = \tau_a P_a + \tau_b P_b \qquad (1)$$

τ_{obsd} is the observed chemical shift relative to TMS, and τ_a and τ_b are the chemical shifts of the hydrogen in sites a and b, respectively, relative to TMS. P_a and P_b are the fractions of hydrogens in the given sites and have the relationship to the actual mole fractions, N_a and N_b, of the species containing the hydrogens producing the observed signal as shown in eq 2. In

$$P_a = N_a/(N_a + N_b) \qquad (2)$$

our case, eq 2 may be rewritten as eq 3,[8] where the mole

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[6] Solubilities of several alkali metal trifluoroacetates in HTFA, which substantially agree with our work, have been reported by R. Hara and G. H. Cady, *J. Amer. Chem. Soc.*, **76**, 4285 (1954).

[7] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[8] For these calculations, the dimer structure for neat HTFA was assumed. Although the equations would be different, the same results would be obtained if monomeric or polymeric structures were assumed.

$$P_{(\mathrm{HTFA})_2} = 2N_{(\mathrm{HTFA})_2}/(2N_{(\mathrm{HTFA})_2} + N_{\mathrm{H(TFA)_2^-}}) \quad (3)$$

fractions are weighted for the number of exchangeable protons in their respective species.

Since TMS was chosen as the arbitrary standard, and HTFA absorbs at τ -1.71, eq 1 can be rearranged and rewritten as eq 4. If complete reaction of the

$$\tau_{\mathrm{obsd}} + 1.71P_{(\mathrm{HTFA})_2} = \tau_{\mathrm{H(TFA)_2^-}}P_{\mathrm{H(TFA)_2^-}} \quad (4)$$

anion with the acid is assumed, as shown in eq 5, the

$$2\mathrm{TFA}^- + (\mathrm{HTFA})_2 \longrightarrow 2(\mathrm{TFA}\cdots\mathrm{H}\cdots\mathrm{TFA})^- \quad (5)$$

proton fractions, $P_{(\mathrm{HTFA})_2}$ and $P_{\mathrm{H(TFA)_2^-}}$, may be calculated from the measured composition of the sample solutions. The only unknown in eq 4 is then $\tau_{\mathrm{H(TFA)_2^-}}$, the downfield chemical shift of the $\mathrm{H(TFA)_2^-}$ anion in the presence of a particular cation. When the left side of eq 4 was plotted against $P_{\mathrm{H(TFA)_2^-}}$, the value of $\tau_{\mathrm{H(TFA)_2^-}}$ was found by determining the slope of the resulting straight line. Such a plot is shown in Figure 2 for solutions of trimethylphenylammonium trifluoroacetate in HTFA in the salt concentration range 0–0.5 mol fraction.

The excellent linearity of the results shown in Figure 2 indicates that the interpretation of the exchange process and the presence of the hydrogen-bonded species is reasonable. The slope of the line shown in Figure 2 was found by the method of least squares to be τ -9.59. This slope should correspond to the chemical shift of the $\mathrm{H(TFA)_2^-}$ anion in the absence of chemical exchange with any other hydrogen, but when in the environment of the trimethylphenylammonium cation. This value is in good agreement with the values observed for solutions of trimethylphenylammonium trifluoroacetate in HTFA in the 0.50–0.736 mol fraction range, τ -8.83, as shown in Figure 1. For very high concentrations of this salt it was sometimes necessary to warm the solutions immediately prior to their measurement with the spectrometer to prevent slow crystallization of the samples. This may have produced incomplete thermal equilibration at the time some of the spectra were recorded, resulting in upfield chemical shifts from the sample's temperature elevation.

Although the data for the other salts studied were limited to a smaller concentration range, least-squares treatment provided the slope of the best line through each set of data points. In these calculations, the experimental chemical shifts were referred to HTFA at δ 0, and the resulting slopes were corrected to derive the chemical shift for $\mathrm{H(TFA)_2^-}$ in the presence of the various cations. The results are given in Table II.

The low standard deviations of the ordinate data are indicative of the excellent linearity derived for most of the plots. The differences in the slopes of the lines obtained, and therefore the chemical shift of the resulting anion, are an interesting phenomenon. These differences probably indicate the marked effect the size of the cation may have on the electron density about the hydrogen bond in the anion.

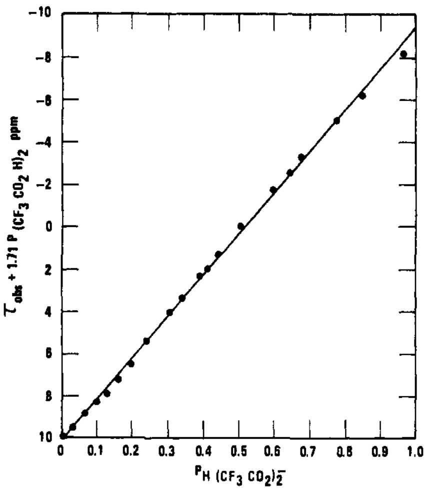

Figure 2. Linear presentation of the data from Figure 1 as treated in eq 4.

Table II. Pmr Absorption Position of the Hydrogen Bis(trifluoroacetate) Anion in the Presence of Different Cations

Salt	$\tau_{\mathrm{H(CF_3CO_2)_2^-}}$	Std dev, ppm	No. of points
CF_3CO_2Li	-5.73	0.041	10
CF_3CO_2Na	-6.94	0.035	8
CF_3CO_2K	-9.17	0.135	8
CF_3CO_2Rb	-9.44	0.080	10
CF_3CO_2Cs	-9.80	0.059	13
$CF_3CO_2N(Me)_4$	-9.66	0.219	7
$CF_3CO_2N(Me)_3C_6H_5$	-9.59	0.218	21

Discussion

Chemical Shift of Trifluoroacetic Acid. Reeves[9] has studied the concentration dependence of the chemical shift of the hydrogen of HTFA dissolved in carbon tetrachloride. We have consistently observed a chemical shift value of τ -1.71 for neat, anhydrous HTFA; this value compares favorably with that of τ -1.62 reported by Reeves.[9] The variation in the chemical shift reported for the hydrogen of HTFA was small (*ca.* 0.25 ppm) over the concentration range of 0.1–1.0 mol fraction of HTFA in carbon tetrachloride. These data were interpreted[9] that HTFA, over this concentration range in an inert solvent, consists of a mixture of dimeric and polymeric hydrogen-bonded molecules. The equilibrium concentration of these species is not much altered over the concentration range given. At lower concentration (below 0.1 mol fraction), the hydrogen of HTFA absorbed at higher field; this was interpreted as indicative of an increasing concentration of monomeric species on dilution. At 0.02 mol fraction in carbon tetrachloride, HTFA was reported to absorb at τ -0.18.[9]

The exact nature (monomeric or polymeric) of the solvent is of no great consequence in its relationship to the present study so long as the equilibrium between the various species present remains rapid and unchanged by the presence of the solute. Hence, Figure 1 was constructed assuming the presence of only monomeric acid, and the hydrogen exchange treatment presented in eq 4 and Figure 2 was carried out assuming the presence of only dimeric acid and the $\mathrm{H(TFA)_2^-}$ anion.

In the study of acetic acid–water mixtures, Gutowsky and Saika[7] found that the chemical shift of each solution could be accounted for quantitatively on the basis of the chemical shifts and concentrations of the oxygen-bonded hydrogen of each component of the system.

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[9] L. W. Reeves, *Can. J. Chem.*, **39**, 1711 (1961).

We have made a similar study of the HTFA–water system and have found the results to be very analogous.

Chemical Shift of the Hydrogen Bis(trifluoroacetate) Anion. It is generally recognized that when the base in hydrogen-bond formation is one other than an aromatic π-electron system, the pmr absorption of the hydrogen is shifted toward lower magnetic field.[10] The magnitude of such shifts has been roughly correlated with the strength of the hydrogen bond. A greater negative pmr shift has also been found to correspond to a greater change in the infrared vibrational frequency of the hydroxyl group between the gaseous and liquid states and hence corresponds to a stronger hydrogen bond.[11] The very large negative chemical shift observed for the hydrogen of HTFA in equimolar mixture with trimethylphenylammonium trifluoroacetate is suggestive of the formation of a very strong hydrogen bond.

Klemperer and Pimentel[2] have studied the interaction of sodium trifluoroacetate and gaseous HTFA using dissociation pressure techniques. They presented evidence for the formation of sodium dihydrogen tris(trifluoroacetate) (NaTFA·2HTFA) and possibly sodium hydrogen bis(trifluoroacetate) (NaTFA·HTFA). Their study was for gaseous HTFA in contact with solid salt, whereas the present study was for liquid HTFA solutions. The measurements reported herein were limited to concentrations below 0.33 mol fraction for all the alkali metal trifluoroacetates. It was therefore not possible to observe a concentration-independent chemical shift for solutions of these compounds. Whether such a concentration-independent chemical shift would obtain at 0.33 mol fraction salt, which would suggest dihydrogen tris(trifluoroacetate) formation, or at 0.50 mol fraction salt, corresponding to hydrogen bis(trifluoroacetate) $[H(TFA)_2^-]$ anion formation, or at some other mole fraction value cannot be stated. The method used does not permit a direct determination of the number of monomeric HTFA molecules associated with the anion.

No concentration-independent chemical shift was observed with the tetramethylammonium cation from 0 to 0.484 mol fraction. For this reason, and because a linear, concentration-dependent chemical shift was obtained when plotted according to eq 4, the formation of the dihydrogen tris(trifluoroacetate) anion in these solutions is unlikely. A concentration-independent chemical shift was observed for the trimethylphenylammonium cation at τ −8.83. This strongly suggests the formation of the $H(TFA)_2^-$ anion in this case. Because of the similarities in the chemical shift of this latter system with the calculated values of the shifts for the same anion from potassium, rubidium, and cesium trifluoroacetates, it seems highly probable that the $H(TFA)_2^-$ anion is formed in all of the cases studied.

Table III. Hydrogen-Bond Distances and Chemical Shifts of Some Acid Salts

	Salt	O···H···O length in crystal, Å	Chemical shift for proton in an internal H bond, τ
I.	Potassium hydrogen bis(trifluoroacetate)	2.435 ± 0.007^a	-9.17^b
II.	Cesium hydrogen bis(trifluoroacetate)	2.38 ± 0.032^a	-9.80^b
III.	Sodium hydrogen maleate	2.44	-9.95^c
IV.	Potassium hydrogen maleate	2.437 ± 0.004^c	-10.32^d
V.	Potassium hydrogen phthalate		-10.07^c
VI.	Potassium hydrogen *dl*-α,α'-diisopropylsuccinate		-9.34^d
VII.	Potassium hydrogen *meso*-α,α'-diisopropylsuccinate		5.83^d
VIII.	Potassium hydrogen *dl*-α,α'-*tert*-butylsuccinate		-9.48^d
IX.	Potassium hydrogen *meso*-α,α'-di-*tert*-butylsuccinate		5.83^d
X.	Potassium hydrogen *dl*-α,α'-dicyclohexylsuccinate		-9.34^d
XI.	Potassium hydrogen *meso*-α,α'-dicyclohexylsuccinate		5.83^d

[a] Reference 3. [b] This work. [c] S. Forsen, *J. Chem. Phys.*, **31**, 852 (1959). [d] L. Eberson and S. Forsen, *J. Phys. Chem.*, **64**, 767 (1960); these pmr absorptions were reported for DMSO solutions relative to external water. Using the pmr absorption listed for DMSO (δ 2.42) relative to water and the pmr absorption of DMSO (τ 7.50) relative to TMS, the values listed in the table have been converted to the τ scale.

Other workers have been interested in measuring the O···H···O internuclear distances and the chemical shifts of the hydrogen in compounds that form strong hydrogen bonds. Table III summarizes some of this work using acidic salts and half-neutralized dibasic acids and compares these with the results here reported. Crystallographic data have indicated the presence of very short and crystallographically symmetrical hydrogen bonds in some of the compounds listed in Table III. The large negative chemical shifts given for all of the acidic compounds listed, other than those we report, were determined in dimethyl sulfoxide solution. All these compounds readily form cyclic monoanions. It is seen from Table III that the O···H···O internuclear distance for the $H(TFA)_2^-$ anion is comparable to that of the "cyclic" hydrogen maleate anion; the chemical shifts are of the same order of magnitude.

Steric effects can readily overcome these strong hydrogen-bond forces. This is seen in the comparison of the pmr absorption of the acidic hydrogen of *dl* and meso α,α'-disubstituted succinates, compounds VI, VIII, X, and VII, IX, and XI, respectively. The α,α' substituents in the *dl* compounds do not interact sterically to a degree sufficient to disrupt a strong hydrogen bond; for the meso isomers, the opposite is observed.

Formation of strong hydrogen bonds in many of the compounds listed in Table III is to be anticipated because of the fixed close proximity of the interacting groups. Where this is not possible for steric reasons (compounds VII, IX, and XI), the formation of strong hydrogen bonds has not been observed. To our knowledge, the data we report constitute the *largest negative*

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(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 248.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 404.

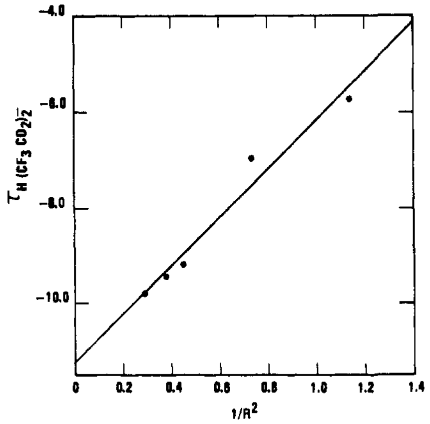

Figure 3. Correlation of the proton chemical shift of $H(CF_3CO_2)_2^-$ with a function of the radius of the associated cation.

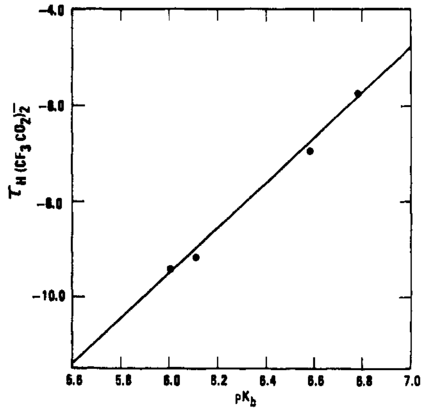

Figure 4. Correlation of the proton chemical shift of $H(CF_3CO_2)_2^-$ when associated with alkali metal cations with the pK_b of the corresponding metal acetate.

chemical shift observed for hydrogen-bond formation between a donor and acceptor species that are otherwise nonbonded.

Variation in the Value of $\tau_{H(TFA)_2^-}$. The different chemical-shift values calculated for the $H(TFA)_2^-$ anion given in Table II deserve further comment. It seems reasonable that these values must approach a maximum negative chemical shift for the "free" $H(TFA)_2^-$ anion. The presence of any cation would undoubtedly weaken the hydrogen bond of the anion and would therefore alter the magnitude of the downfield shift resulting from hydrogen-bond formation. *A priori*, it would be anticipated that the tighter the association between the cation and anion (and/or the greater the electronegativity of the cation), the smaller would be the magnitude of shift resulting from hydrogen bond formation. This seems to be manifest in the data of Table II. The cations that are more electronegative, smaller, and electronically less shielded would be expected to associate more strongly with the anion. In these cases, the chemical shift of the $H(TFA)_2^-$ anion is not so large as in other cases.

This observation has led us to attempt correlations between the chemical shifts derived in this study with an appropriate function of the radii and other parameters of the cations involved. Figure 3 shows the chemical shifts derived for the $H(TFA)_2^-$ anion in the presence of alkali metal cations plotted against the reciprocal of the respective cationic radius squared. The radii used were taken from tabulations by Gourary and Adrian.[12] This particular function of the cationic radius was chosen from a simple classical consideration of the interaction of two oppositely charged particles. The results of this correlation, while not excellent (correlation coefficient = 0.98), appear satisfactory in view of the limited number of data points and the fact that the most serious deviations are exhibited by the lithium and sodium salts. These two salts presented the most difficult experimental problems since they tenaciously hold water and were vacuum dried repeatedly before reproducible results were obtained. These two materials were also more limited in solubility than the others (Table I). This undoubtedly has led to a higher degree of uncertainty in the results derived from the data they yielded. Figure 3 was limited to the alkali metal cations since good data for their ionic radii were available from electron density maps, and since values of similar validity for the effective radii of the less spherical quaternary ammonium cations used are not available. These latter ions might be expected to have even larger radii than Cs^+. The value for the chemical shift of $H(TFA)_2^-$ in the presence of these cations was approximately 0.2 ppm to higher field than the corresponding value when the anion was associated with Cs^+. In Figure 3, the interception of the line with the ordinate axis suggests that the value of τ -11.25 would be the chemical shift of $H(TFA)_2^-$ when separated infinitely ($1/r^2 = 0$) from a cation. It may be that the actual downfield limit for this quantity is near the value indicated. It seems even more likely, however, that the practical limit has already been achieved and is less than τ -10 as reported here.

Correlation of the chemical shift data used in Figure 3 with the Pauling elemental electronegativities[13] (en) of the corresponding alkali metals gives good linearity also. The method of least squares provides the results shown in eq 6. Here the chemical shift

$$\tau_{H(TFA)_2^-} = 21.27(\mathrm{en}) - 26.98 \qquad (6)$$

of $H(TFA)_2^-$ can be calculated from the Pauling electronegativity of the element of the cation associated with this anion. The relationship as derived exhibited a standard deviation of 0.13 ppm and had a correlation coefficient of 0.997.

If the effect of these cations on the chemical shift of $H(TFA)_2^-$ is appropriately interpreted above, it would appear that the same general cationic characteristics would be instrumental in influencing the basicities of carboxylate anions in their anhydrous parent acids. For some time now, it has been recognized that potentiometric titration of metal acetates in anhydrous acetic acid could permit the simultaneous quantitative determination of two alkali metals, lithium or sodium in the presence of potassium, rubidium, or cesium.[14] The method is successful because of the greater basicity of the acetate ion when paired with the larger cations. The pK_b values for these

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(12) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, 10, 144 (1960).

(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 103.

(14) (a) C. W. Pifer and E. G. Wollish, *Anal. Chem.*, 24, 519 (1952); (b) C. W. Pifer, E. G. Wollish, and M. Schmall, *ibid.*, 26, 215 (1954); (c) A. T. Casey and K. Starke, *ibid.*, 31, 1060 (1959); (d) I. L. Shresta and M. N. Das, *ibid.*, 39, 1300 (1967).

four alkali metal acetates in anhydrous acetic acid have been reported.[14] Although these values are for acetates, and not trifluoroacetates, it would appear likely that the basicity of acetate ion toward strong acid ($HClO_4$) in acetic acid would be influenced by metal cations in a way highly similar as TFA^- is influenced as a hydrogen acceptor in hydrogen bond formation with HTFA, and consequently as it influences the chemical shift of the resulting $H(TFA)_2^-$. Figure 4 shows this to be true as it exhibits an excellent linear relationship for the chemical shifts used in Figure 3 when plotted against the pK_b values of the corresponding alkali metal acetates when in anhydrous acetic acid. The pK_b value for cesium acetate was not reported in the set of data used in Figure 4. The excellent correlation from the figure permits the estimation of this value, $pK_b = 5.94$, from the chemical shift of $CsH(TFA)_2$ reported herein.

On the basis of the above considerations it may be concluded that the presence of a cation near the $H(TFA)_2^-$ anion causes the downfield chemical shift of that anion to be smaller. The effectiveness of the cation in bringing about this effect depends largely upon the nearness of approach of the two ions. If this conclusion is valid, it would be anticipated that sodium hydrogen maleate and potassium hydrogen maleate would exhibit different chemical shifts for their intramolecular hydrogen-bonded acidic hydrogen. As is seen in Table III, this is true; the smaller cation produced an upfield shift in the pertinent absorption relative to the larger cation's effect. In this case there is a difference of only 0.37 ppm in the chemical shifts, while the analogous hydrogens of the hydrogen bonds of $NaH(TFA)_2$ and $KH(TFA)_2$ absorb 2.23 ppm differently. It must be noted, however, that the data for the maleates (III and IV) were obtained in DMSO, which is particularly effective at cationic solvation, and thereby at reducing association of cations with accompanying anions.

In order to examine the generality of the large downfield chemical shifts (decreased shielding) of hydrogen bonds formed between anions and their conjugate acids, we have extended this work in a preliminary way to the acetic and methanesulfonic acid systems. The results indicate a similar magnitude for the hydrogen-bond shift in these cases. We plan to continue the examination of the generality of this phenomenon in other liquid acids and to examine the effects of still other cations.

Acknowledgment. The authors are grateful to Professors C. L. Liotta, D. J. Royer, H. M. Neumann, and W. G. Trawick for valuable discussions during the course of this work. The expert technical assistance rendered by Miss Joyce M. Wilkins at Georgia State University in many of the experimental aspects of the work is also appreciated.

Photochemical Behavior of Ethylenediaminetetraacetate Complexes of Cobalt(III). Sensitization and Excited-State Reaction Pathways[1]

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Abstract: The direct and $Ru(bipy)_3^{2+}$ sensitized photodecompositions of $Co(HEDTA)X^-$ ($X = Cl, Br, NO_2$) have been examined. Products of redox decomposition were Co^{2+} and CO_2 in each case; ligand field excitation produced aquation of the ligand X and/or linkage isomerization ($X = NO_2$). Product yields and product ratios were strongly wavelength dependent. It is inferred that the reactive excited states have triplet spin multiplicity and that the carboxylate to cobalt charge-transfer excited state has a lower dissociation energy than the X^- to cobalt excited states.

The photochemical behavior found for most cobalt(III) complexes is reasonable photosensitivity (ϕ_{redox} is commonly about 0.2) on irradiation of their charge transfer to metal (CTTM) absorption bands but relatively little reaction following irradiation of their ligand field absorption bands ($\phi < 0.01$).[2–5] The most notable exceptions to this pattern may occur among the pentacyanocobaltate(III) complexes where irradiation of the ligand field bands appears to produce relatively large product yields.[2,6–9a] The photochemistry of cobalt(III) complexes thus presents some unique and challenging problems.

The classical problem of the photochemistry of cobalt(III) complexes has been to identify and characterize the photochemically significant intermediates.

(1) Partial support of this research by the National Science Foundation (Grant GP 24053) is gratefully acknowledged.

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