naphthyl-, and di-*n*-amyl-silane as well as *p*-methoxyphenylsilane were recorded using a Perkin-Elmer Model 21 infrared spectrometer. Where possible, the compounds were examined in the gas phase (using a 10 cm. cell equipped with potassium bromide windows); otherwise the spectra were obtained from a capillary film of the pure liquid.

Discussion of the Spectra

The infrared spectra of the monosubstituted silanes exhibit a band of striking intensity in the 938 to 917 cm.$^{-1}$ region. This exceptional intensity is attributed to the fact that two deformation vibrations of the SiH_3– group occur at very nearly the same frequency.

Absorption in this region also has been reported by West and Rochow[11] for disubstituted silanes; however, no frequency assignments for this region were made in that paper. The spectrum of diamylsilane, a previously unreported compound, is included for comparison.[14] On the basis of our work we can now say that the strong band occurring in the 938 to 917 cm.$^{-1}$ region which is common to disubstituted silanes arises from the deformation mode of the $SiH_2=$ group. The agreement in frequency and intensity of this band with the $SiH_2=$ bending frequency occurring at 953 cm.$^{-1}$ in dichlorosilane[15] and at 940 cm.$^{-1}$ dibromosilane[16] leaves little doubt that the absorption in the 925 cm.$^{-1}$ region for the disubstituted silanes results from the $SiH_2=$ deformation mode. Also it should be noted that absorption in this region remains essentially constant throughout the spectra of 38 compounds[17] containing two or three hydrogen atoms attached to the silicon.

The spectral analogy to halosilanes is further supported by the observation that the SiH_2R_2 compounds exhibit one or two strong bands from 862 to 826 cm.$^{-1}$.[11] This absorption is due in part to silicon–carbon stretching but undoubtedly also arises from a rocking mode of the $SiH_2=$ group. Further, as might be expected from the monohalosilanes, the silyl compounds absorb weakly or not at all in this region.

Regarding other parts of the spectra we also have observed the symmetrical deformation frequency of the methylene groups alpha to a silicon atom as reported by Kaye and Tannenbaum[7e] in the 1200 to 1182 cm.$^{-1}$ region. Also on the basis of our method of preparation we feel that any absorption in the 1130 cm.$^{-1}$ region is not due to ether.

Acknowledgment.—We are grateful for the coöperation of Miss J. Dickey who did the analyses and to Mr. Dana Mayo for his help in interpreting the spectra. We wish particularly to acknowledge the support by the Office of Naval Research under Contract Nonr-908(02)-Task NR 356321.

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[15] J. A. Hawkins and M. K. Wilson, *J. Chem. Phys.*, **21**, 360 (1953).

[16] J. A. Hawkins, S. R. Polo and M. K. Wilson, *ibid.*, **21**, 1122 (1953).

[17] Though not reported in this paper, most of these spectra were recorded in connection with this work. Spectra in the literature include references 8e, 10a and 12.

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

A Raman Spectroscopic Study of Complexes Involving Dimethyl Ether and HCl, DCl HBr[1,2]

BY GUIDO L. VIDALE AND ROBERT C. TAYLOR

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A detailed investigation of the dimethyl ether–HCl system has been carried out by Raman spectroscopy between –100 and 0° and over the concentration range from 0 to approximately 87 mole per cent. HCl. The results give excellent evidence for the existence of three intermolecular complexes, each having an optimum temperature and concentration range of stability in the liquid. The results of similar investigations of the dimethyl ether–DCl and dimethyl ether–HBr systems are interpreted in support of the designation of the simple 1:1 complex as a hydrogen bonded structure and of the other higher complexes as oxonium compounds. The stoichiometry and possible configuration of the higher complexes are discussed briefly.

Introduction

Considerable interest, theoretical as well as experimental, has been shown recently in the study of complex formation between electron donor molecules and electron acceptors. One such system is that of dimethyl ether and HCl which is often cited as an example of a mixture in which a strong Lewis acid–base interaction occurs between the components. This system is representative of a very large number of quite similar systems involving higher ethers, alcohols and other oxygen containing compounds interacting with strong mineral acids. However, despite the relative simplicity of the molecules involved and the absence of complications introduced by association in the pure components, previous spectroscopic investigations have been limited both in number and in scope and detailed knowledge of the species present in the liquid is quite incomplete. Since information on the nature of complexes present in such mixtures not only is vital to a better understanding of many important organic reaction mechanisms but also is important in the study of complex formation *per se*, suitable experimental methods have been developed and a detailed Raman spectroscopic study has been carried out to supply this information.

No previous infrared examination of the dimethyl ether–HCl system appears to have been made. However, Gordy and Martin[3,4] and Szobel[5] have in-

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[1] Based on a dissertation submitted by Guido L. Vidale in partial fulfillment of the requirements of the Ph.D. degree to the Horace H. Rackham School of Graduate Studies, University of Michigan, September, 1954.

[2] Presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1954.

[3] W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

[4] W. Gordy and P. C. Martin, *ibid.*, **9**, 215 (1941).

[5] L. Szobel, *Compt. rend.*, **218**, 347, 834 (1944).

vestigated the infrared spectra of solutions of HCl in excess diethyl ether in the hydrogen stretching region. Their results show that the two molecules interact strongly through the hydrogen of the HCl but give little other information. The Raman spectrum of the HCl–dimethyl ether system has been examined by Briegleb and Lauppe[6] and by Wolkenstein and co-workers.[7] The former observed a number of bands in the region of skeletal frequencies that could not be attributed to either of the pure components and which they interpreted in terms of a single complex species having both the hydrogen and chlorine atoms attached to the oxygen as well as the two methyl groups. The data were obtained at only one concentration and one temperature. The later work by Wolkenstein extended the study to three different concentrations, the results being discussed in terms of two discrete complexes involving, respectively, one and two molecules of HCl per molecule of ether. Both sets of investigators used unfiltered exciting light and mention being troubled by continuous background scattering. The complexity of some of the spectra obtained in the present study makes it virtually certain that these previous Raman papers are based on incomplete data because of the confusion introduced into the spectra by overlapping bands arising from multiple excitation, and the obscuring of important weak bands by the continuous background. In the Russian work, the failure to obtain spectra over a wider range of concentration resulted in several incorrect assignments, notably the assignment of a skeletal band to a hydrogen motion, and the erroneous conclusion that the effect of concentration caused some of the maxima of skeletal bands to shift position appreciably.

Experimental

Materials.—Dimethyl ether, hydrogen chloride and hydrogen bromide were obtained as compressed gases in steel cylinders from The Matheson Co. They appeared to be of high purity but were given a bulb to bulb distillation on the vacuum line before use. Deuterium chloride was prepared from benzoyl chloride and heavy water (99.6% deuterium from the Norsk Hydro-Elektrisk Kvaelstofaktieselskab) by the method described by Brown[8]; its spectrum showed no evidence of any hydrogen. Considerable care was exercised in the preparation of the samples to exclude traces of dust which would increase background scattering. Measured amounts of the purified components were allowed to evaporate slowly through an ultrafine sintered glass filter and condense in the carefully cleaned Raman cell. Traces of mercury vapor, which were found to react in the sample to give fine suspensions of mercury halides, were eliminated by rigorously excluding any of the metal and using a null reading Bourdon gage for pressure measurements. After preparation, the samples usually were sealed off in the Raman cells and stored at Dry Ice temperatures until examination. No decomposition was observed spectroscopically or otherwise in the case of the HCl solutions but HBr cleaved the ether so rapidly in solutions containing less than one mole of HBr per mole of ether that it proved difficult to obtain usable spectra in this concentration range. In more concentrated solutions, the cleavage rate was much slower and spectra could be obtained from freshly prepared samples before significant decomposition had occurred.

Equipment and Procedures.—The Raman tube was contained in a small unsilvered Dewar with plane windows in the bottom and centered with cork supports. Air or nitrogen precooled to the desired temperature was admitted to the Dewar at the bottom, the temperature of the sample being monitored by a fine thermocouple connected to a Leeds and Northrup recording potentiometer. The temperature of the air stream was likewise monitored and controlled at any desired value by a small heater operated by the recorder. The temperature gradient along the sample when the arc was operating was found to be from 5 to 7° under normal operating conditions. A Toronto type mercury arc drawing about 20 amperes from the 220 volt d.c. mains through a ballast resistor was used in the light source, the exciting light being heavily filtered with saturated $NaNO_2$ and Rhodamine 5GDN Extra dye solutions to reduce the already low background and cut out unwanted mercury lines. The spectra were recorded photographically with a Gaertner Raman spectrograph with a f/3.5 camera having a dispersion in the blue of about 180 cm.$^{-1}$ per mm.

The frequencies of the band maxima were determined by direct measurement on the plate with a Mann comparator, by measurement on a 25:1 enlarged microphotometer tracing made with a Leeds and Northrup Knorr-Albers microphotometer, or both, depending on the sharpness and intensity of the band. Over 200 separate spectra were obtained in the course of the investigation and roughly half of these were measured. The numerical values listed for the band maxima thus represent the average of numerous measurements. A difference of 5 cm.$^{-1}$ in band maxima appearing in the spectra of two different solutions is considered significant and more than the likely experimental error.

Experimental Results

In preliminary work, the Raman spectrum of dimethyl ether (hereafter referred to as DME) was obtained in both the liquid and gaseous states, the assignment of bands agreeing with that given in Herzberg[9] except for minor details.[10] The three frequencies which are of primary interest in this study are the skeletal motions of the C–O–C chain vibrating as a bent symmetrical triatomic molecule. For simplicity, the notation listed by Herzberg for DME will not be used and the customary notation for a triatomic molecule will be employed instead, *viz.*, the frequency associated with the symmetrical stretching motion of the methyl groups, considered as mass points, will be designated ν_1, the symmetrical bending motion will be ν_2, and the unsymmetrical stretching motion will be ν_3.

It was found that when the spectra of solutions having progressively higher mole ratios of HCl to DME were examined at a temperature of −90°, systematic changes occurred which are described as follows for the spectral region in the immediate neighborhood of ν_1. The initial addition of HCl to liquid DME caused a sharp, well-defined band to appear on the low frequency side of ν_1 while the intensity of ν_1 itself was reduced. With further addition of HCl, the intensity of this new band, which will be designated as ν_1^A, increased until it reached a maximum at a mole ratio of HCl to DME of 1:1 while the intensity of ν_1 decreased until it was nearly zero at the same concentration. As the HCl concentration was increased beyond a 1:1 ratio, the intensity of ν_1^A decreased until in a 3:1 solution it also had virtually disappeared. Simultaneously with the decrease in intensity of ν_1^A, two new bands appeared, one located at a higher frequency than ν_1^A and one at a lower. The intensity of the band at the higher frequency, designated as ν_1^B, increased fairly rapidly with HCl concentration,

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(7) A. Gantmacher, M. Wolkenstein and J. Syrkin, *Acta Physicochim. U.S.S.R.*, **12**, 786 (1940); **14**, 157 (1941).

(8) H. C. Brown and C. G. Root, THIS JOURNAL, **64**, 2223 (1942).

(9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, pp. 353–354.

(10) G. L. Vidale and R. C. Taylor, to be published elsewhere.

reached a maximum in a solution having a HCl: DME ratio somewhere between 3:1 and 4:1 and then dropped off. The intensity of the third band, ν_1^C, first became noticeable at about a 3:1 ratio, increased steadily with concentration, and was the dominant band in a 6:1 solution, the most HCl rich mixture examined.

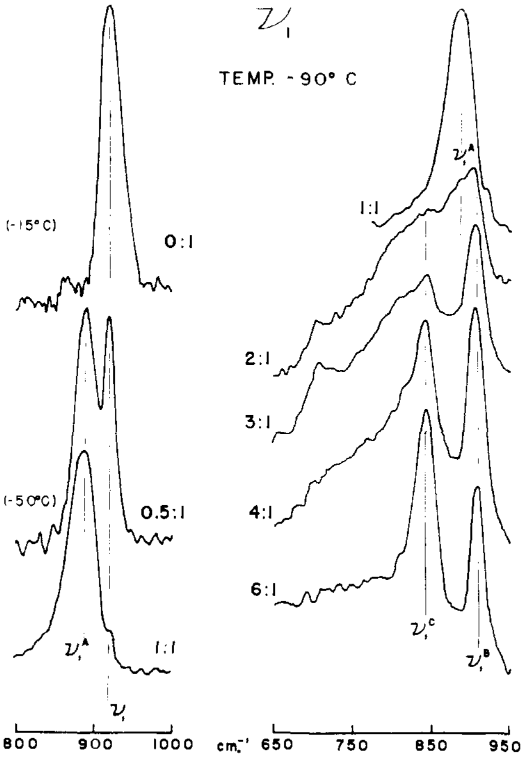

Fig. 1.—ν_1 region for various HCl-$(CH_3)_2O$ ratios.

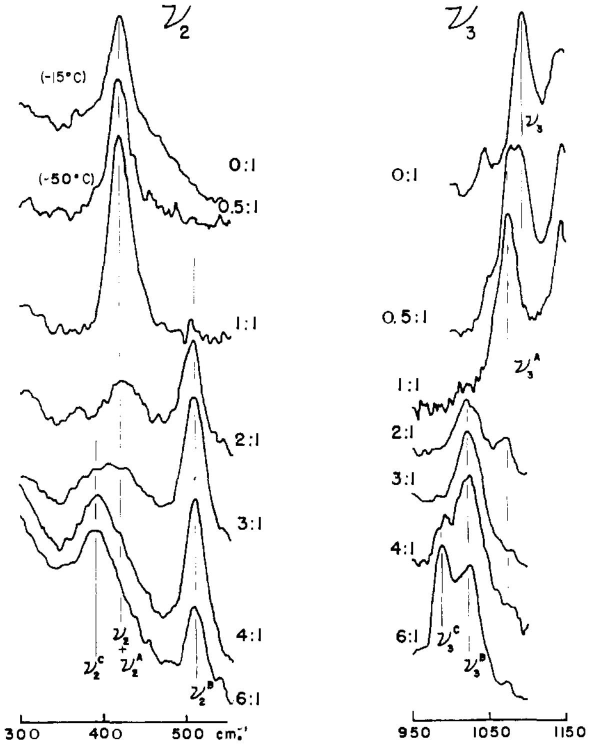

Fig. 2.—ν_2 and ν_3 regions for various HCl-$(CH_3)_2O$ ratios. temp. −90°.

These changes in the spectral region around ν_1 were accompanied by an almost exactly similar series of changes in the spectral regions around ν_2 and ν_3, and by somewhat less well-defined changes in the region of the methyl group frequencies. Figures 1 and 2 show these changes by reproductions of microphotometer tracings of the three spectral regions for a series of concentrations. The frequencies of the band maxima were found not to be concentration dependent and the average measured values are listed in Table I.

TABLE I

SKELETAL MOTION FREQUENCIES OF DIMETHYL ETHER AND DIMETHYL ETHER COMPLEXES WITH HCl, DCl AND HBr IN THE LIQUID STATE AT −90°

(liq. at −15°)		ν_1 cm.$^{-1}$	σ^a cm.$^{-1}$	ν_2 cm.$^{-1}$	σ cm.$^{-1}$	ν_3 cm.$^{-1}$	σ cm.$^{-1}$
Dimethyl ether		920	0.5	420	0.3	1095	0.4
HCl complexes	A	886	0.4	420	0.3	1077	0.4
	B	906	.3	511	.2	1022	1.0
	C	842	.4	391	.8	990	1.0
DCl complexes	A	894	0.4	422	0.3	1078	0.3
	B	905	.7	503	.8	(1032)	?
	C	854	.4	382	.5	1023	0.9
HBr complexes	A	. .		. .		. .	
	B	902	0.3	509	0.9	1021	0.6
	C	830	.3	389	.4	976	.5

[a] Standard deviation of the mean.

DCl Solutions.—The concentration dependence of the spectra obtained from DCl–DME mixtures was found to parallel strikingly the changes found in the HCl solutions, both as to the number of new bands appearing and the concentration range in which they were observed. A detailed comparison of the spectra revealed that the C–O–C skeletal frequencies of the 1:1 complex remained virtually unchanged in the substitution of D for H. The data in Table I show that the differences on isotopic substitution in the frequency values of ν_2^A and ν_3^A are about the same as the experimental error. The shift of 8 cm.$^{-1}$ in the position of ν_1^A is considered to be an apparent shift caused by interference from a deuterium bending motion which overlaps it. The close similarity of the spectra of the 1:1 complexes in the skeletal region is shown much more clearly in Fig. 3. In contrast to the 1:1 case, isotopic substitution was found to cause a noticeable shift in the frequencies of the complexes present in the HCl rich solutions. These shifts are clearly beyond experimental error, the largest being 33 cm.$^{-1}$. In addition, the spectra are markedly different in appearance (Fig. 4).

HBr Solutions.—In the acid-rich solutions two sets of bands were observed which greatly resembled those attributed to complexes B and C in the HCl solutions. These bands reached intensities comparable to those in the HCl system at smaller HBr:DME ratios (Fig. 4) and the skeletal frequencies had very nearly the same numerical value (Table I). Despite the experimental difficulties in examining solutions containing less than one mole of HBr per mole of ether, sufficient information was obtained to indicate that no compound analogous to compound A in the HCl system was present in the HBr system.

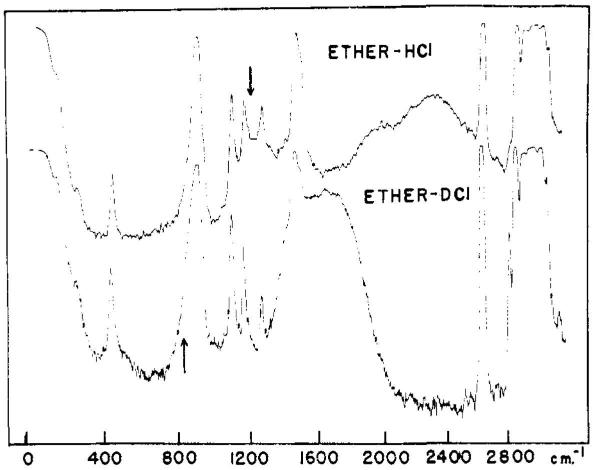

Fig. 3.—Raman spectra of the 1:1 complexes of HCl and DCl with dimethyl ether at −85°.

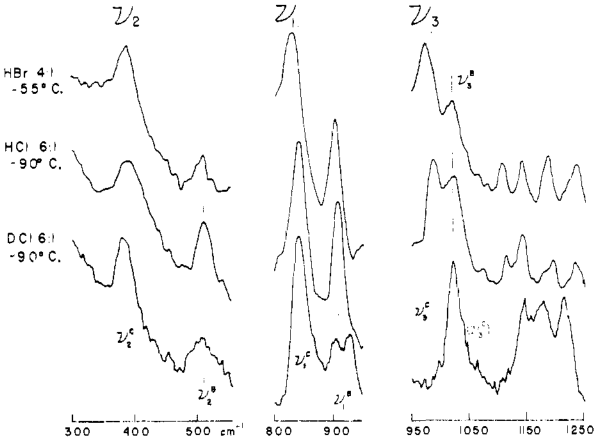

Fig. 4.—Spectra of $(CH_3)_2O$ complexes with HBr, HCl and DCl.

Effect of Temperature on the Skeletal Frequencies.—In the 1:1 HCl solution, temperature was found to have little effect on the spectrum except for a slight broadening of the A bands and a shift of their maxima a few wave number units in the direction of the free DME bands as the temperature increased. The spectra of the HCl-rich solutions, in contrast, were found to be markedly temperature sensitive. Higher temperatures caused a progressive decrease in the intensity of the B and C bands and favored the appearance and progressive increase in intensity of the A bands. The free HCl band simultaneously increased in intensity. In the HBr solutions where frequencies analogous to the A bands of the HCl system were not found, temperature had little effect on the spectra over the liquid range (−55 to 0°).

Hydrogen Frequencies.—Previous work reported in the literature has shown that hydrogen association bands in hydrogen bonded systems usually have a low intensity in the Raman effect. Their clear observation in the present work was made possible by the low background of the Toronto arc and the careful filtering of the exciting light. In ether-rich solutions, the hydrogen stretching band was observed to be at least 800 cm.$^{-1}$ wide with a maximum near 2250 cm.$^{-1}$ and a secondary maximum or shoulder around 1900 cm.$^{-1}$. The intensity of this shoulder was markedly temperature sensitive as shown in Fig. 5. In addition to the stretching band a deformation hydrogen band was located centered around 1200 cm.$^{-1}$. In acid-rich solutions, the hydrogen stretching band was somewhat less broad, more intense and more strongly polarized than the band in the 1:1 solution, and exhibited but a single maximum near 2600 cm.$^{-1}$. The bending motion was observed as a band about 800 cm.$^{-1}$. Although these deformation motions were quite weak and partially obscured by overlying skeletal frequencies, they were fairly certainly identified by means of their isotope shift which was very nearly the square root of two. The deformation bands in the 1:1 solutions are indicated by arrows in Fig. 3.

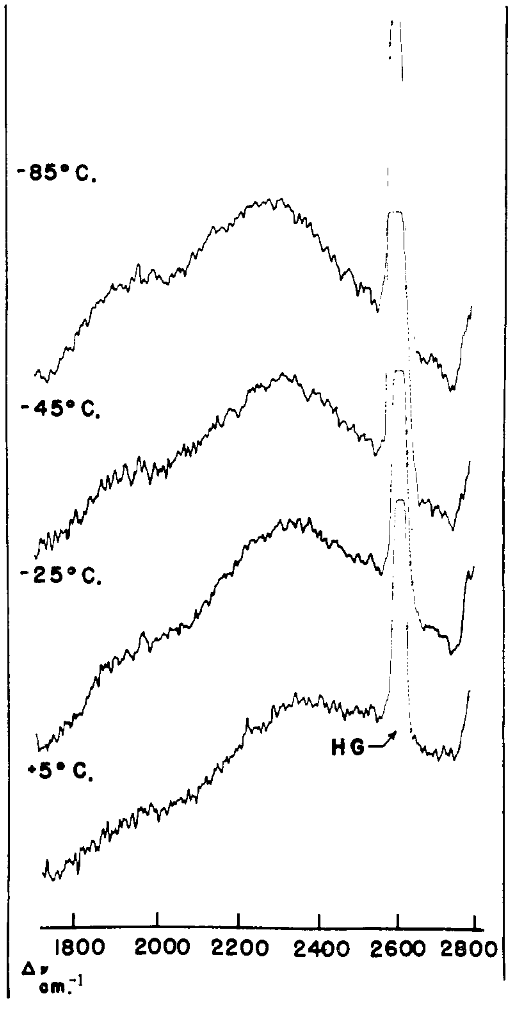

Fig. 5.—The effect of temperature on the hydrogen association band of the 1:1 dimethyl ether–HCl complex.

The free HCl band near 2800 cm.$^{-1}$ was absent in solutions containing less than a 3:1 mole ratio of HCl:DME at −90°; it was clearly distinguishable and steadily increased in intensity as the HCl concentration increased beyond this value. The free

HBr band first appeared in the spectra of solutions having around a 2:1 ratio of HBr to DME.

Discussion

Despite the complexity of the spectra of the HCl–DME system, their interpretation seems fairly straightforward. The appearance of three new sets of bands as distinct and intense as those observed is primary evidence of the formation of three discrete intermolecular compounds, each, in this case, being well-defined and stable within a given concentration range in the solution. A comparison of the spectra of the complexes with that of DME indicates that the interaction does not involve the breaking of any of the classical bonds of the ether but does lead to a rather severe perturbation of the molecule, especially in the case of the B and C complexes. The marked similarity between the spectra of the 1:1 solutions of HCl and DCl in the skeletal region indicates that the A complex may be classified as a normal hydrogen bonded structure whose formation depends primarily on the electrostatic interaction between the proton and the oxygen. On the other hand, the isotope shift in the skeletal frequencies of the B and C compounds strongly suggests that here the proton is participating in the corresponding normal vibrations of the DME skeleton and that the complexes, therefore, may be designated as oxonium compounds. The latter conclusion is supported by the data from the HBr–DME solutions. From the fact that HBr is a better proton donor than HCl, it would be predicted that oxonium complexes in the HBr–DME system would be more likely to occur, and would form and be stable in solutions containing a lower concentration of HBr. Moreover, since the anion would have but a secondary effect on the internal vibrations of the cation, the spectra of oxonium complexes in the two systems should be quite similar. The data in Table I and Fig. 4 show good agreement with these predictions. The failure to observe bands corresponding to the hydrogen bonded complex A in the HCl system is entirely consistent with the negligible tendency of bromine to form hydrogen bonds.

The rather unusual conductivity curve found by Maass and McIntosh[11] for the HCl–DME system is explained very nicely by these conclusions from the spectral data. They found a very low conductivity in solutions containing less than one mole of HCl per mole of DME where only the hydrogen bonded complex is present. At the 1:1 composition, complex A begins to react with the additional HCl to give the oxonium species B and the conductivity shows an almost discontinuous tenfold increase. With further addition of HCl, the conductivity increases at a somewhat slower rate until around a 4:1 composition where the slope again increases as the B complex is converted to the C. The solutions exhibited a maximum specific conductivity in the neighborhood of a 6:1 ratio at which concentration the conductivity was comparable to that of 0.5 M KCl in water.

Structure and Composition of Complexes.—From the spectral results plus chemical arguments, there seems little doubt that complex A has the formula $(CH_3)_2O \cdot HCl$. Use of the photographic method in the present work made it impractical to attempt to establish the composition of species B and C by the concentration dependence of their band intensities. However, the presence of a congruent melting point at 0.8 mole fraction in the phase diagram of the system[11,12] makes it likely that complex C is $(CH_3)_2O \cdot 4HCl$, while the observations that the bands of complex A had largely disappeared at a 3:1 concentration while those of complex C were just appearing seem to favor the composition $(CH_3)_2O \cdot 3HCl$ for complex B. This composition is the least certain of the three, however. Since neither free DME bands nor the free HCl band appeared at −90° in the concentration range between 1:1 and 3:1, it can be concluded that the equilibrium constants for the reactions DME + HCl → complex A and complex A + 2HCl → complex B are fairly large, whereas that for the reaction complex B + HCl → complex C is much smaller, perhaps being of the order of unity.

With regard to the structure of the oxonium compounds, it seems probable that only one HCl is directly involved with the oxygen of the ether since ions of the type H_4O^{++} are known to be energetically unlikely. The other HCl molecules then must be associated with the chlorine of the primary HCl. More detailed arguments leading to these same conclusions have been given by Wolkenstein.[7] The mechanism by which the secondary HCl molecules are held together is probably weak hydrogen bonding since the attraction of a chlorine in HCl for the proton of a neighboring molecule, although not strong, appears sufficient for the formation of a weak hydrogen bond which is stable at low temperatures.[13,14] If this structure is accepted, the attachment of a second HCl to the chlorine atom in the 1:1 complex must be instrumental in changing the character of the complex from the hydrogen bonded type to the oxonium. This change perhaps is best discussed in terms of the potential energy function describing the potential energy of the proton as a function of the internuclear distance between the oxygen and the chlorine. In the 1:1 complex the potential energy curve can be assumed to have two unequal minima, one near the oxygen and the deeper one containing the proton near the chlorine. The effect of another HCl molecule approaching the rear of the first may be either to alter the relative depths of the two minima or shift the position of the deeper minimum toward the oxygen atom so that the two partially coalesce. In either case, a transfer of positive charge to the oxygen results and the process serves as a good example of an "assisted interaction" as described by Mulliken.[15] The difference between complexes B and C is much less than between A and B, and indeed may consist only of the dissociation of an ion pair into free ions assisted by further solvation of the anion. The high conductivity of the solutions in the 6:1 concentration range suggests this explanation.

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[13] B. Vodar, R. Freymann and Yeou Ta, *J. Phys. Rad.*, **9**, 41, 282 (1938).

[14] D. F. Hornig and W. E. Osberg, *J. Chem. Phys.*, **23**, 662 (1955).

[15] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

The Hydrogen Frequencies.—The bands associated with motions of the proton responsible for the complex formation yielded less specific information than did the skeletal bands since they were characteristically broad and diffuse and of rather low intensity. The hydrogen stretching band of the 1:1 hydrogen bonded complex is of particular interest. From the evidence afforded by the skeletal frequencies, it does not seem reasonable that the great breadth of this band can be attributed to such causes as the presence of multiple coördinated species or chain-like polymeric fragments, nor to the possibility that the lifetime of the complex may be short compared to the time for the radiative transition. The secondary maximum around 1900 cm.$^{-1}$ similarly is not easily explainable on the basis of a non-uniform distribution of polymeric species, while the possibility that it may be due to a difference band involving the motion of the HCl vibrating as a unit against the ether does not agree with the temperature effect. These explanations have all been offered in the literature to account for the breadth and frequent structure in hydrogen bond association bands. Their inapplicability in the present case suggests that they may be of less significance than supposed in the cases where they do appear to be possible explanations.

In addition to the stretching motion, the proton in the hydrogen bond should have a transverse motion at right angles to the bond.[16] Bands associated with such motions have received but little attention in the past and have been observed much less frequently than the stretching motions. In practically all cases reported, the transverse motion actually has been the bending motion of the R-X-H angle in the system R-X-H . . . Y, where R is some group or atom attached to the electronegative atom which is bonded to the hydrogen. In the 1:1 complex of HCl and dimethyl ether, no other group is attached to the chlorine atom and consequently the sole restoring force to a transverse motion of the proton must arise from the potential function of the (hydrogen) bond alone. The magnitude of the frequency is perhaps higher than might be expected under such circumstances and must be associated with a restoring force constant of appreciable size. If the assignment is correct, this observation not only is difficult to reconcile with the suggestions that hydrogen bonds may be non-linear in some systems but also points up the fact that such transverse motions may be quite important in testing any theoretical description of the hydrogen bond.

The DCl System.—The conclusions reached for the HCl system appear to hold quite well in the DCl system although there are certain minor inconsistencies which probably may be attributed to the differences in zero point energies and the consequent effect on the equilibrium constants. One of the more puzzling of these was the observation that substitution of deuterium for hydrogen in the oxonium complexes resulted in an increase in the frequencies of some of the skeletal motions. This behavior is contrary to the order rule of isotopic substitution and may indicate that the complexes in the two systems are not exactly identical. Any other explanation is not immediately obvious although it may be pointed out that the potential function previously referred to very likely is highly asymmetric and the proton vibrations, therefore, strongly unharmonic. In such a case, it is not inconceivable that the difference in the zero point amplitudes of vibration between hydrogen and deuterium may somehow affect the skeletal motions in the manner observed.

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