

atoms in the parent molecule, these results may indicate some preference for abstraction of deuterium atoms or the presence of non-scavengable "hot" radicals. The former suggestion would seem to be somewhat contrary to expectations based either on zero point energy or bond strengths. Ethane formation is reduced essentially to zero in the presence of nitric oxide.

Oxygen does not reduce the ammonia yield. There must be a  $\text{CNH}_4$  radical formed in the primary process, but since oxygen greatly reduces hydrogen formation a second  $\text{CNH}_4$  radical is not formed to a large extent by abstraction of hydrogen atoms by hydrogen atoms. However other radicals formed by secondary reactions with oxygen may abstract hydrogen atoms. Abstraction by  $\text{HO}_2$  is improbable, but further speculation

about secondary reactions involving oxygen seems to be fruitless.

Reaction 8 is probably the ammonia-forming reaction. If this reaction occurs when oxygen is present,  $\text{CNH}_4$  radicals must not react with oxygen at all rapidly. An alternative would have  $\text{CNH}_4$  react either with oxygen or with some other radical than  $\text{CNH}_4$  to give ammonia. Reaction with oxygen would almost certainly be followed by secondary reactions to give more  $\text{CNH}_4$  radicals.

Thus either 8 must occur even when oxygen is present or some radical, e.g.,  $\text{OH}$  or  $\text{CH}_3\text{O}$ , reacts with  $\text{CNH}_4$  to give ammonia and a complete molecule, viz.,  $\text{CH}_2\text{O}$  or  $\text{CH}_3\text{CHO}$ . More work on this point would be desirable.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## Halide Anions as Proton Acceptors in Hydrogen Bonding<sup>1</sup>

BY ADAM ALLERHAND<sup>2</sup> AND PAUL VON RAGUÉ SCHLEYER<sup>3</sup>

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The effect of quaternary ammonium halides on the X-H stretching frequencies of methanol, propargyl bromide and several deuterated haloforms in inert solvents has been studied. Very large spectral shifts, attributed to X-H... anion hydrogen bonding, were observed. The magnitudes of these shifts depended to a marked extent on the halide anion, in the order  $\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$ . Variations in the cation had little effect with  $\text{I}^-$  and  $\text{Br}^-$ , but influenced the X-H... $\text{Cl}^-$  shifts to a pronounced degree. Covalently bound halogen atoms were very much weaker proton acceptors and gave an inverse spectral shift order. A novel technique for investigating hydrogen bonding of  $\text{CDX}_3$  to inorganic salts was studied, using acetone as solvent. Ionic salts such as  $\text{NaI}$  produced large spectral shifts in this system, but covalent salts such as  $\text{HgCl}_2$  did not.

Intermolecular hydrogen bonding has been studied extensively by infrared spectroscopic methods.<sup>4</sup> In most cases the proton acceptor is a covalent compound containing an oxygen or nitrogen atom and the solvent is  $\text{CCl}_4$  or another "inert" liquid. Despite the expectation that anions should give the strongest hydrogen bonds, only a few experimental results have been published in which an anion is the proton acceptor.<sup>5-7</sup> Most ionic compounds are not soluble in the usual infrared spectroscopic solvents, but some quaternary ammonium salts overcome this limitation. Lund<sup>6</sup> observed large spectral shifts ( $\Delta\nu$ ) between the "free" OH and NH stretching vibrational bands of several proton donors and the bands due to XH... anion association; with a common proton donor the magnitude of  $\Delta\nu$  was found to vary with the nature of the anion in the ammonium salt. Bufalini and Stern<sup>6</sup> studied the behavior of the X-H stretching of methanol and other proton donors in the absence and presence of quaternary ammonium salts. In benzene solution at the concentrations of methanol employed in the absence of electrolyte, both methanol monomer and "dimer" bands were present. The addition of the ionic compound caused the disappearance of the "dimer" band and the appearance of a new absorption at a lower frequency, attributed to the methanol... anion complex;  $\Delta\nu$  again was found to vary with the anion. A similar investigation has been reported recently by Hyne and Levy.<sup>7</sup> A solution of *t*-butyl alcohol in  $\text{CCl}_4$  showed three bands, at 2.74, 2.86 and 2.96  $\mu$ ,

assigned to monomer, "dimer"<sup>8</sup> and polymer, respectively. The polymer band was very weak, but the addition of tetrabutylammonium bromide caused a very marked growth in intensity of the 2.96  $\mu$  band. Although the possibility that this intense band was due to alcohol... anion hydrogen bonding was admitted, Hyne and Levy noted that the position of the new band corresponded to that of *t*-butyl alcohol polymer, and concluded that the most probable role of the ammonium salt was to stabilize the polymeric form of the alcohol by serving as nucleation centers for the aggregation of alcohol molecules. However, the reported dependence of the XH... anion stretching frequency on the nature of the anion<sup>6,7</sup> cannot easily be rationalized on the basis of enhanced proton donor association in the presence of ionic species, but can be readily explained if hydrogen bonding to the anion is occurring.

All previous investigations on the effects of ionic compounds on XH bands have employed spectrometers equipped with low resolution NaCl prisms and the frequencies observed were accurate only to  $\pm 20 \text{ cm}^{-1}$  or worse. In view of the ambiguity of interpretation summarized above and our interest in hydrogen bonding to covalently bonded halogen atoms,<sup>9,10</sup> we have studied the nature of XH... halide ion interaction using high resolution spectrophotometers.

Alcohols self-associate readily because they are both good proton donors and good proton acceptors. The shifts in  $\nu_{\text{OH}}$  from monomeric to polymeric bands are very large. If by coincidence  $\nu_{\text{OH}}$  for the polymer were approximately the same as  $\nu_{\text{OH}}$  for the alcohol... anion hydrogen bonded species, it would be difficult to distinguish between the two, although the possibility of polymer formation could be reduced greatly by using very dilute solutions of alcohol.

(1) Paper VIII of a series on hydrogen bonding; paper VII, *J. Am. Chem. Soc.*, **85**, 371 (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962.

(2) Merck Foundation Fellow, 1960-1961; Esso Foundation Fellow, 1961-1962.

(3) Alfred P. Sloan Research Fellow.

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

(5) H. Lund, *Acta Chem. Scand.*, **12**, 298 (1958).

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(7) J. B. Hyne and R. M. Levy, *Can. J. Chem.*, **40**, 692 (1962); *cf.*, J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963).

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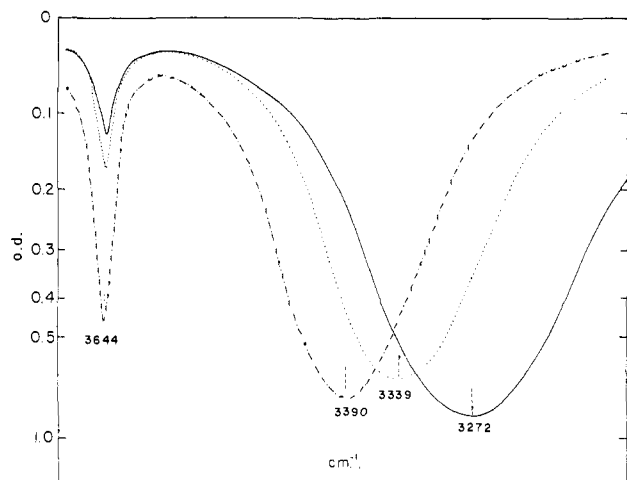


Fig. 1.—The effect of quaternary ammonium halides on the OH stretching frequency of methanol in  $\text{CCl}_4$  solution; 10-mm. cells: —, 0.006  $M$  methanol in 0.033  $M$  tetrabutylammonium chloride in  $\text{CCl}_4$ ; . . . . ., 0.006  $M$  methanol in 0.034  $M$  tetrabutylammonium bromide in  $\text{CCl}_4$ ; - - - -, 0.012  $M$  methanol in 0.033  $M$  tetraheptylammonium iodide in  $\text{CCl}_4$ .

An X-H compound that is a relatively good proton donor, but a poor proton acceptor will not self-associate readily; moreover, the frequency shift on self-association will be very small. If anions *do* act as proton acceptors, they must be very strong proton acceptors on the basis of the observed spectra,<sup>5-7</sup> and will produce large X-H shifts. Consequently, if X-H is chosen properly, it will be possible to decide whether ionic compounds only enhance X-H self-association<sup>7</sup> (in which case the observed frequencies would not be appreciably lower than those observed in pure liquid X-H) or whether the ions are actually engaged in hydrogen bonding to X-H<sup>5,6</sup> (in which case large frequency shifts would occur).

A good choice of X-H for this purpose would be a compound,  $\text{R}-\text{C}\equiv\text{C}-\text{H}$ , such as propargyl bromide. Self-association in terminal acetylenes is incomplete even in the pure liquids<sup>11,12</sup>; the spectral shifts due to self-association are very small ( $10-20 \text{ cm}^{-1}$ ).<sup>11</sup> Terminal acetylenes are, however, fairly good proton donors.<sup>11-13</sup> Another good proton donor would be chloroform;  $\nu_{\text{CH}}$  is practically the same in pure liquid  $\text{CHCl}_3$  and in dilute  $\text{CCl}_4$  solution,<sup>14</sup> but strong proton acceptors produce shifts up to  $100 \text{ cm}^{-1}$  and more on the C-H band of chloroform.<sup>15,16</sup> However, since the quaternary ammonium salts absorb strongly in the C-H region, chloroform-*d* is more convenient to use. The C-D stretching frequency of  $\text{CDCl}_3$  is essentially the same in liquid  $\text{CDCl}_3$  and in dilute  $\text{CCl}_4$  solution, but decreases by  $84 \text{ cm}^{-1}$  in triethylamine.<sup>17</sup>

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We report here the results of investigations of the effects of ionic salts on O-H, C-H and C-D vibrational frequencies.

### Experimental

Most infrared spectroscopic measurements were carried out on a Perkin-Elmer model 421 grating spectrophotometer and a few on a Perkin-Elmer model 21 spectrophotometer equipped with a lithium fluoride prism and a Reeder thermocouple detector. Gaseous carbon monoxide and hydrogen chloride and atmospheric water vapor were used for calibrations. The following types of matched cells were used: 1- and 10-mm. cells of a quartz transparent in the near infrared and 1-mm. sodium chloride cells. We believe our results to be accurate to within  $\pm 2 \text{ cm}^{-1}$  for the unassociated X-H frequencies, to within  $\pm 3 \text{ cm}^{-1}$  for the broader absorption bands of the hydrogen bonded C-H and C-D groups, and to within  $\pm 4 \text{ cm}^{-1}$  for the hydrogen bonded OH groups. All measurements were carried out at an average room temperature of  $23^\circ$ . The small variations at room temperature had no observable effect on the positions of the absorption frequencies.<sup>18</sup> All measurements were made at least twice and some were repeated later with freshly prepared samples. Excellent reproducibility was observed. Changes in concentrations of proton donors and acceptors produced no significant changes in the positions of peaks.

Spectral grade carbon tetrachloride and dichloromethane were used as solvents, without further purification. Commercially available chemicals were used, except for the following:

Bromoform-*d* and bromodichloromethane-*d* were kindly supplied by Dr. R. E. Kagarise.

Tetrabutylammonium chloride was prepared by refluxing an alcoholic solution of tetrabutylammonium iodide in the presence of excess silver chloride.<sup>19</sup> The resulting crude compound was very difficult to crystallize. After two recrystallizations from a 2:1 (v./v.) mixture of benzene and petroleum ether (b.p.  $60-70^\circ$ ), the compound had m.p.  $92.5-94.2^\circ$  (lit.<sup>6</sup> m.p.  $92 \pm 1^\circ$ ).

**Preparation of Tetrabutylammonium Fluoride.**—A total of 15.7 g. of tetrabutylammonium iodide was added to a stirred aqueous solution of 5.4 g. of silver fluoride. After heating on a water-bath for 10 minutes the silver iodide precipitate was filtered off and discarded. The aqueous solution was evaporated on a vacuum rotating evaporator, since the compound began to decompose at  $100^\circ$ . The viscous substance that remained after prolonged evaporation showed no water absorption in the infrared. All attempts at crystallization failed. Infrared and n.m.r. spectra were in accord with the tetrabutylammonium fluoride structure. Fluoride ion was determined colorimetrically. *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{36}\text{NF}$ : F, 7.3. Found: F,  $8.1 \pm 0.5\%$ . This compound has been prepared previously by a different method,<sup>20</sup> but no physical data were reported.

### Results

**Effect of Salts on  $\nu_{\text{OH}}$  of Methanol.**—In the absence of added salts, very dilute (*ca.* 0.005  $M$ ) solutions of methanol in  $\text{CCl}_4$  gave only a narrow monomeric OH stretching band at  $3643 \text{ cm}^{-1}$ . In the presence of even small concentrations (*ca.* 0.03  $M$ ) of tetraalkylammonium salts, the spectra were dramatically different; very broad and intense bands appeared at lower frequencies (Fig. 1). The position of these bands did not vary with changes in concentration of salt and methanol but did vary appreciably with the nature of the anion (Fig. 1 and Table I); a comparison of these varied positions was of interest because of previous results with covalently bonded halogen atoms.<sup>9,10</sup> Unfortunately, it was not possible to use a common cation—tetrabutylammonium—for all four halide anions because of the negligible solubility of the iodide in  $\text{CCl}_4$ . Tetraheptylammonium iodide was used instead; such slight changes in cation had little effect on the magnitude of spectral shifts in the iodide series (Table II and below). The frequencies of the broad bands decreased and consequently  $\Delta\nu$  increased in the order iodide < bromide < fluoride < chloride; the frequency change was smaller between the chloride and fluoride than between the other members of the series (Table I).

All four tetrabutylammonium halides are quite soluble in dichloromethane; the above results were con-

(18) Small variations of temperature may have an appreciable effect on hydrogen bonding equilibria, but the effect on infrared frequencies is very small. See, e.g., E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

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TABLE I

THE EFFECT OF HALIDES ON THE OH STRETCHING FREQUENCIES OF METHANOL AND PHENOL IN CARBON TETRACHLORIDE SOLUTIONS<sup>a</sup>

Proton donor, <i>M</i>	Proton acceptor, <i>M</i>	$\nu_{\text{OH}}$ bonded <sup>b</sup>	$\Delta\nu^c$	Path length, mm.
0.074 methanol	0.96 tetrabutylammonium fluoride	3293	349	1
.006 methanol	0.033 tetrabutylammonium chloride <sup>d</sup>	3272	371	10
.007 methanol	N-Hexadecylpyridinium chloride (satd.)	3288	356	10
.074 methanol	0.1 triphenylantimony dichloride	None	None	1
.022 phenol	.17 tetrabutylammonium bromide	~3135 <sup>e</sup>	~476	1
.006 methanol	.034 tetrabutylammonium bromide <sup>d</sup>	3339	304	10
.007 methanol	.033 trioctylpropylammonium bromide	3334	307	10
.012 methanol	.033 tetraheptylammonium iodide <sup>d</sup>	3390	255	10
.2 methanol	None	3349 <sup>f</sup>	294	1

<sup>a</sup> All frequencies are in  $\text{cm}^{-1}$ . <sup>b</sup> A much weaker monomeric hydroxyl band appears at  $3643 \pm 2 \text{ cm}^{-1}$  with methanol, but is practically absent in the phenol example. In pure  $\text{CCl}_4$  solution the monomeric OH bands of methanol and phenol appear at 3643 and 3611  $\text{cm}^{-1}$ , respectively. <sup>c</sup>  $\Delta\nu = \nu_{\text{OH}}$  free -  $\nu_{\text{OH}}$  bonded. <sup>d</sup> Wide changes in concentrations of proton donor and proton acceptor did not produce variations in the positions of the bands. For example, the bonded peak positions with 0.06 *M* tetrabutylammonium bromide were 3338  $\text{cm}^{-1}$  for 0.001 *M* methanol (1-cm. cells), 3334  $\text{cm}^{-1}$  for 0.013 *M* methanol (1-mm. cells), 3338  $\text{cm}^{-1}$  for 0.08 *M* methanol (1-mm. cells), and 3338  $\text{cm}^{-1}$  for 0.11 *M* methanol (1-mm. cells); also with 0.3 *M* salt, 3335  $\text{cm}^{-1}$  for 0.024 *M* methanol (1-mm. cells). The bonded peak positions with 0.10 *M* tetraheptylammonium iodide were 3388  $\text{cm}^{-1}$  for 0.001 *M* and for 0.010 *M* methanol (1-cm. cells), 3391  $\text{cm}^{-1}$  for 0.10 *M* methanol (1-mm. cells). With 0.010 *M* iodide the positions were 3387  $\text{cm}^{-1}$  for 0.001 *M* and for 0.010 *M* methanol (1-cm. cells), 3392 for 0.10 *M* methanol (1-mm. cells) and (3400  $\text{cm}^{-1}$ ) for 0.30 *M* methanol (1-mm. cells), a position shifted by interference from the adjacent dimer band at 3529  $\text{cm}^{-1}$ . With 0.001 *M* iodide, a band at 3389  $\text{cm}^{-1}$  was noted with 0.010 *M* methanol (1-cm. cells). <sup>e</sup> The position of this band is somewhat uncertain due to the large solvent absorption produced by the tetrabutylammonium bromide in this region; reported at  $3205 \pm 20 \text{ cm}^{-1}$ .<sup>5</sup> <sup>f</sup> Polymer band; reported at 3341  $\text{cm}^{-1}$  by L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

TABLE II

THE EFFECT OF IONIC HALIDES ON THE OH STRETCHING FREQUENCY OF METHANOL IN DICHLOROMETHANE SOLUTION<sup>a</sup>

Proton acceptor <sup>b</sup>	$\nu_{\text{Free}}$	$\nu_{\text{Bonded}}$	$\Delta\nu$
Fluoride			
Tetrabutylammonium <sup>c</sup>	3621	3283	338
Chlorides			
Tetraethylammonium	3623	3289	334
Tetrabutylammonium	3623	3268 <sup>d</sup>	355
N-Hexadecylpyridinium <sup>e</sup>	3624	3300	324
Tetraphenylarsonium <sup>f</sup>	3625	3320	305
Bromides			
Tetraethylammonium	3625	3341	284
Tetrapropylammonium	3622	3337	285
Tetrabutylammonium	3625	3334 <sup>g</sup>	291
Trioctylpropylammonium	3625	3337	288
N-Hexadecylpyridinium	3624	3335	289
Iodides			
Tetrapropylammonium	3623	3386	237
Tetrabutylammonium	3623	3385	238
Tetrapentylammonium	3624	3389	235
Tetraheptylammonium	3622	3384	238
N-Methylquinolinium <sup>h</sup>	3623	3396	227
N-Hexadecylpyridinium	3625	3397	228
Triphenylmethylarsonium	3623	3386	237

<sup>a</sup> All frequencies in  $\text{cm}^{-1}$ . All measurements carried out in 1-mm. matched cells; methanol concentration 0.074 *M*. <sup>b</sup> Concentration 0.2 *M* unless noted. <sup>c</sup> 0.27 *M*. <sup>d</sup> Reported  $3289 \pm 20 \text{ cm}^{-1}$  in benzene solution.<sup>6</sup> <sup>e</sup> Supersaturated. <sup>f</sup> 0.1 *M*. <sup>g</sup> Reported  $3361 \pm 20 \text{ cm}^{-1}$  in benzene solution.<sup>6</sup> <sup>h</sup> Saturated solution.

firmed by carrying out measurements in that solvent (Table II). In the presence of the salts the spectra of methanol behaved just as in  $\text{CCl}_4$  solution again showing broad bands at lower frequencies, very close in position to those observed for a given halide in  $\text{CCl}_4$  solution (Tables I and II). From the hydrogen bonding point of view, dichloromethane is not an "inert" solvent, but is one capable of acting as a weak proton acceptor, giving rise to small spectral shifts. Methanol monomer absorbs at 3625  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , a shift of 18  $\text{cm}^{-1}$  from the value in  $\text{CCl}_4$ . This shift in position of the monomeric peak coupled with the very small shift of the broad (association) band in going from  $\text{CCl}_4$  to  $\text{CH}_2\text{Cl}_2$  solution resulted in slightly smaller  $\Delta\nu$ 's in the latter solvent (Tables I and II), contrary to usual behavior.<sup>21</sup>

The greater solubility of salts in  $\text{CH}_2\text{Cl}_2$  permitted a study of the effect of changing the cation on the spectral shift to a common anion (Tables I and II). The effects were much smaller than those observed with changes in the anion, and seemed to depend on both the sizes of the cations and anions.<sup>5,6</sup> There were only minor alterations in position of the bonded peaks with change in cation with iodide and bromide anions, but a pronounced effect was observed with chloride anion, which has the smallest ionic radius of the three. The cations with the smallest effective size gave the smallest spectral shifts; this size effect was most pronounced for the smallest anion studied, chloride ion.

**Effect of Salts on  $\nu_{\text{C-H}}$  of Propargyl Bromide.**—Since the position of absorption of the acetylenic C-H band is rather close to the region of strong C-H absorptions of the tetraalkylammonium halides, the concentrations of ionic compound and cell thicknesses were chosen to minimize this problem; well matched cells were used. The results (Table III) are illustrated in Fig. 2.

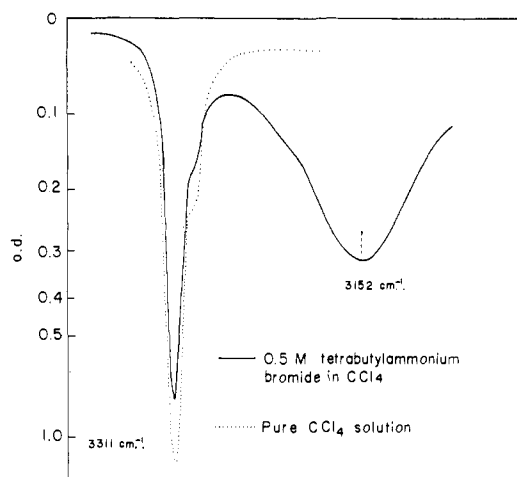


Fig. 2.—The effect of 0.5 *M* tetrabutylammonium bromide on the acetylenic C-H stretching frequency of propargyl bromide; concn. 5  $\mu\text{l./ml.}$  in  $\text{CCl}_4$  solution; 1-mm. cells.

At low concentrations in  $\text{CCl}_4$  solution, propargyl bromide gave a narrow band at 3311  $\text{cm}^{-1}$  with a small

(21) A study of the effects of change of solvent on the frequency shifts of hydrogen bonded groups<sup>1</sup> indicated that the positions of association ("bonded") peaks of strong hydrogen bonds are relatively insensitive to modifications of the environment.

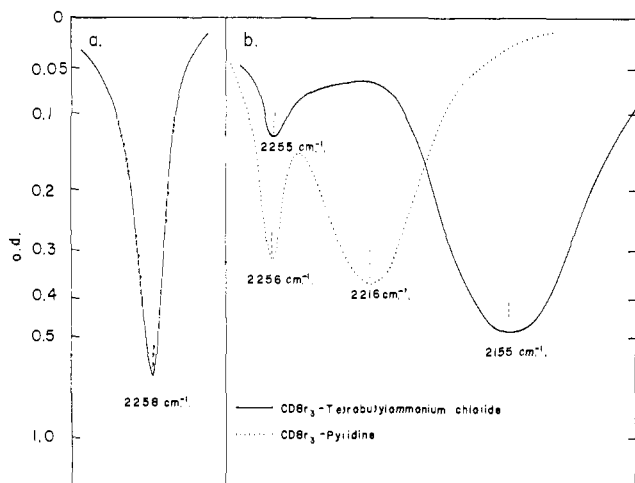


Fig. 3.—(a)  $\nu_{C-D}$  of  $CDBr_3$  in  $CCl_4$  solution; concn., 30  $\mu$ l./ml.; 1-mm. cells. (b) The effect of proton acceptors on the C-D stretching frequency of bromoform in  $CCl_4$  solution; concentrations: —,  $CDBr_3$ , 10  $\mu$ l./ml., 0.5  $M$  tetrabutylammonium chloride; . . . .,  $CDBr_3$ , 20  $\mu$ l./ml., 1  $M$  pyridine; 1-mm. cells.

shoulder at about  $3294\text{ cm.}^{-1}$ .<sup>11,12</sup> On addition of quaternary ammonium salt a broad band appeared at lower frequency displaced by more than  $120\text{ cm.}^{-1}$  from the narrow band (Fig. 2). This behavior is analogous to that observed with well established proton acceptors such as pyridine or dimethyl sulfoxide, except that  $\Delta\nu$ 's are larger for the quaternary ammonium salts (Table III).

TABLE III

THE EFFECT OF PROTON ACCEPTORS ON THE ACETYLENIC C-H STRETCHING FREQUENCY OF PROPARGYL BROMIDE IN CARBON TETRACHLORIDE SOLUTION<sup>a</sup>

Proton acceptor, $M$	$\nu_{C-H}$ bonded <sup>b</sup>	$\Delta\nu^c$
0.5 tetrabutylammonium bromide	3152	159
0.5 tetraheptylammonium iodide <sup>d</sup>	3185	126
1 pyridine	3198	113
1 dimethyl sulfoxide	3209	102

<sup>a</sup> All frequencies are in  $\text{cm.}^{-1}$ ; path length 1-mm.; propargyl bromide concentration 5  $\mu$ l./ml. <sup>b</sup> A narrow strong band at  $3311\text{ cm.}^{-1}$  and a small shoulder at about  $3294\text{ cm.}^{-1}$  are present in all these spectra. In dilute  $CCl_4$  solution propargyl bromide shows a band at  $3311\text{ cm.}^{-1}$  with a shoulder at  $3294\text{ cm.}^{-1}$ . Pure liquid propargyl bromide shows only a band at  $3294\text{ cm.}^{-1}$ . The spectrum of this compound has been studied previously.<sup>12</sup> <sup>c</sup>  $\nu_{CH}$  "free" taken at  $3311\text{ cm.}^{-1}$ . <sup>d</sup> This supersaturated solution is stable for several hours.

**Effect of the Salts on  $\nu_{C-D}$  of Deuterated Haloforms.**—In dilute  $CCl_4$  solution, the deuterated haloforms  $CDCl_3$ ,  $CDBrCl_2$  and  $CDBr_3$  show only a narrow C-D stretching band near  $2250\text{ cm.}^{-1}$ . In the presence of a small concentration of tetraalkylammonium halide, a broad band appeared at lower frequency (Table IV and Fig. 3). The displacement of this band ( $\Delta\nu$ ) depended both on the nature of the haloform and the ionic halide.  $\Delta\nu$ 's increased in the order  $CDCl_3 < CDBrCl_2 < CDBr_3$  and also  $I^- < Br^- < Cl^-$ . The latter was the same order observed for  $\nu_{OH}$  of methanol (Table I).

The C-D spectra of deuterated haloforms in the presence of quaternary ammonium salts were analogous to those in the presence of well established proton acceptors such as pyridine and dimethyl sulfoxide, but again  $\Delta\nu$ 's are larger in the case of the ammonium salts (Table IV). These results correspond closely to those observed for acetylenic C-H bands (Table III), but the  $\Delta\nu$ 's of Table III are not proportional to the  $\Delta\nu$ 's of a given haloform in Table IV.

Despite the fact that haloforms are known to form hydrogen bonds of moderate strength with acetone,<sup>22,23</sup>

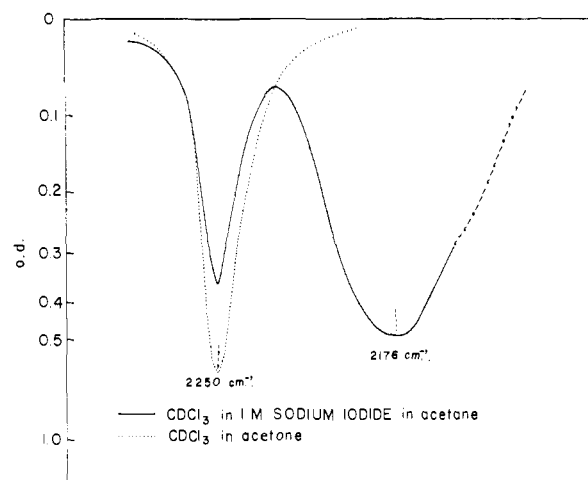


Fig. 4.—The effect of sodium iodide on the C-D stretching frequency of chloroform-*d* in acetone solution; concn. of  $CDCl_3$ , 10  $\mu$ l./ml.; 1-mm. cells.

the spectral shifts haloform-acetone are near zero (Tables IV and V),<sup>17,23</sup> although the band widths are appreciably broadened. We have taken advantage of this behavior to use acetone as a solvent for haloform-anion spectral shift measurements, since the anions are much the stronger proton acceptors (Fig 4 and Table V). Solubility in acetone permitted the use of inorganic salts as proton acceptors; the contrast in behavior between ionic salts ( $LiCl$ ,  $LiBr$  and  $NaBr$ ) and covalent  $HgCl_2$ <sup>24</sup> was noteworthy. The few measurements made preclude definite conclusions, but it may be possible to extend this novel technique to other solvents and to many other salts.

## Discussion

The behavior of the deuterated haloforms and propargyl bromide C-D and C-H bands in the presence of added salts makes untenable the "aggregation hypothesis" of Hyne and Levy<sup>7</sup> (see Introduction) and supports the suggestions that hydrogen bonding to anions is involved.<sup>5,6</sup> Pure liquid chloroform-*d* shows only a narrow band in the C-D stretching region at a position unchanged from that in dilute  $CCl_4$  solution. Consequently, addition of a quaternary ammonium halide to a  $CCl_4$  solution of  $CDCl_3$  should have little effect on the position but only should increase the intensity of this band, were aggregation involved. The appearance of a new broad band at a considerably lowered frequency (Fig. 3 and Table IV) can only be explained satisfactorily by  $Cl_3C-D \cdots X^-$  hydrogen bonding. The behavior of propargyl bromide (Fig. 2 and Table III) is quite similar, and the same conclusion is reached.

The strong dependence of  $\Delta\nu_{OH}$  on the nature of the anion, observed previously<sup>5,6</sup> and confirmed here (Tables I and II), is further evidence against "aggregation" and in favor of specific interactions,  $O-H \cdots X^-$  hydrogen bonding. For methanol as proton donor,  $\Delta\nu$  decreases by more than  $100\text{ cm.}^{-1}$  (ca. 30%) when tetrabutylammonium chloride is replaced by the respective iodide (Table II). Furthermore, formation of "clusters" of methanol to give a strong polymeric band is not likely in 0.006  $M$  solutions even in the presence of tetraalkylammonium salts (Table I). The complete lack of dependence of  $\Delta\nu$  on concentration eliminates the possibility of "aggregation" at moderately higher concentrations of alcohol.

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TABLE IV

THE EFFECT OF PROTON ACCEPTORS ON THE C-D STRETCHING FREQUENCIES OF SOME DEUTERATED HALOFORMS IN CCl<sub>4</sub> SOLUTIONS<sup>a</sup>

	CDCl <sub>3</sub>			CDBrCl <sub>2</sub>			CDBr <sub>3</sub>		
	<sup>ν</sup> CD "Free"	Bonded	Δν	<sup>ν</sup> CD "Free"	Bonded	Δν	<sup>ν</sup> CD "Free"	Bonded	Δν
Pure liq. haloform- <i>d</i>	2253			2254 <sup>c</sup>			2250		
None <sup>b</sup>	2252			2254			2258		
0.5 <i>M</i> tetrabutylammonium chloride	<sup>d</sup>	2167	85 <sup>e</sup>	2252	2163	89	2255	2155	100
0.5 <i>M</i> tetrabutylammonium bromide	2250	2175	75	2253	2175	78	2257	2167	90
0.5 <i>M</i> tetraheptylammonium iodide <sup>f</sup>	2252	2185	67	2253	2185	68	2256	2178	78
1 <i>M</i> pyridine	2251	2223	28	2253	2221	32	2256	2216	40
1 <i>M</i> dimethyl sulfoxide	<sup>d</sup>	2233	19 <sup>e</sup>	<sup>d</sup>	2231	23 <sup>g</sup>	2257	2229	28
2 <i>M</i> acetone							2254		

<sup>a</sup> All frequencies are in cm.<sup>-1</sup>. All measurements were carried out in 1-mm. matched cells; concentration of haloform-*d*, 10-30 μl./ml. <sup>b</sup> Haloform-*d* in CCl<sub>4</sub> solution. <sup>c</sup> S. R. Polo, A. Palm, F. L. Voelz, F. F. Cleveland, A. G. Meister, R. B. Bernstein and R. H. Sherman, *J. Chem. Phys.*, **23**, 833 (1955). <sup>d</sup> Shoulder. <sup>e</sup> <sup>ν</sup>CD "free" taken at 2252 cm.<sup>-1</sup>. <sup>f</sup> This supersaturated solution is stable for several hours. <sup>g</sup> <sup>ν</sup>CD "free" taken at 2254 cm.<sup>-1</sup>.

The order of frequency shifts  $\Delta\nu_{\text{XH}\dots\text{Cl}^-} > \Delta\nu_{\text{XH}\dots\text{F}^-} > \Delta\nu_{\text{XH}\dots\text{Br}^-} > \Delta\nu_{\text{XH}\dots\text{I}^-}$  observed (Tables I-IV) is, with the exception of the anomalous fluoride ion position, the inverse of the order of Δν's reported when covalent halides were used as proton acceptors<sup>9,10</sup>; in the latter case the order was F < Cl < Br < I. The covalent halides gave much smaller Δν's than the ionic halides, e.g., Δν of methanol in CCl<sub>4</sub> solution was 41 cm.<sup>-1</sup> with butyl bromide<sup>9</sup> and 304 cm.<sup>-1</sup> with tetrabutylammonium bromide (Table I). As expected,<sup>4</sup> hydrogen bonding to anions is much stronger than to the corresponding covalently bonded atoms.<sup>6,10</sup> Covalent metal halides behave similarly, e.g., triphenylantimony dichloride (Table I) and mercuric chloride (Table V).

TABLE V

THE EFFECT OF SALTS ON THE C-D STRETCHING FREQUENCIES OF DEUTERATED HALOFORMS IN ACETONE SOLUTION<sup>a</sup>

Proton acceptor	CDCl <sub>3</sub>			CDBr <sub>3</sub>		
	<sup>ν</sup> CD "Free"	Bonded	Δν	<sup>ν</sup> CD "Free"	Bonded	Δν
None <sup>b</sup>	2250	None	..	2254	None	..
1 <i>M</i> mercuric chloride	2250	<sup>c</sup>	..	2256	<sup>c</sup>	..
Satd. lithium chloride <sup>d</sup>	2251	2191	60	..	..	..
1 <i>M</i> lithium bromide	2250	2190	60	..	..	..
0.5 <i>M</i> tetrabutylammonium bromide	2251	2158	93	..	..	..
1 <i>M</i> sodium iodide	2251	2176	75	2256	2177	79
Satd. tetraheptylammonium iodide	2251	2173	78	..	..	..

<sup>a</sup> All frequencies in cm.<sup>-1</sup>. All measurements carried out in 1-mm. matched cells with haloform-*d* concentration 10-20 μl./ml. Under these conditions acetone absorbs strongly between 2100 and 2160 cm.<sup>-1</sup>, necessitating the use of wide slits. <sup>b</sup> Haloform-*d* in acetone solution. <sup>c</sup> Asymmetry on low frequency side of "free" peak only. <sup>d</sup> Approximately 0.2 *M*.

The relative position of tetrabutylammonium fluoride, between chloride and bromide, in magnitude of Δν is curious (Tables I and II). For ionic halides Δν's are expected to increase with increasing electronegativity and decreasing ionic radius.<sup>25</sup> The OH stretching frequency of water is shifted appreciably by negative ions; these shifts decrease in the series F<sup>-</sup> > Cl<sup>-</sup> > I<sup>-</sup>.<sup>26</sup> It is well established that quaternary ammonium salts in inert solvents such as CCl<sub>4</sub> exist mainly as ion pairs and larger aggregates.<sup>27</sup> It is possible that cation-anion interactions and aggregations are in part re-

sponsible for the anomalous spectral shift behavior (Tables I and II).

The dependence of the magnitude of the spectral shift on cation size and anion size has already been commented on. With chloride ion, the smallest anion studied, the variation of Δν to methanol was marked, ranging from 305 cm.<sup>-1</sup> (tetraphenylarsonium cation) to 357 cm.<sup>-1</sup> (tetrabutylammonium cation) (Table II). It is possible that this cation effect would be even more pronounced for fluoride ion, which is even smaller than chloride ion, and that a particularly large cation is needed for fluoride ion to show "optimum" hydrogen bonding spectral shifts. Unfortunately, quaternary ammonium fluorides are not available commercially, their preparation in the pure state is laborious, and few have been characterized in the literature.

Quaternary ammonium halides give the largest hydrogen bonding frequency shifts which have been observed in inert solvents, equilibria are particularly favorable for association, and the halide salts are chemically inert. Consequently, such quaternary compounds are particularly suitable for studies involving weak proton donors such as C-H bonds, more suitable than dimethyl sulfoxide or pyridine which we have used for this purpose.<sup>16</sup>

Kagarise<sup>23</sup> has observed that the enthalpy of interaction of haloforms with acetone in hexane solution decreases in the order CDCl<sub>3</sub> > CDBrCl<sub>2</sub> > CDBr<sub>3</sub>. Correlation of Δ*H* with Δν cannot be made since haloform-acetone spectral shifts are close to zero<sup>17</sup>; a much stronger proton acceptor than acetone is needed. The results of Table IV show that Δν's of deuterated haloforms follow the inverse of the order observed by Kagarise. This result illustrates again the breakdown of the Badger-Bauer rule<sup>23</sup> relating spectral shifts with enthalpies of hydrogen bonding.<sup>29</sup>

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