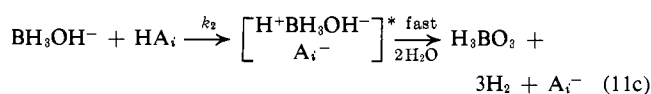
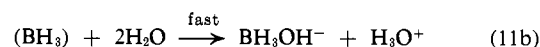
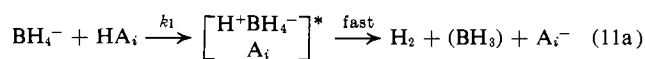


by the methods of this work, is of interest in understanding the chemistry of hydroborate ion. The most straightforward inference from the stepwise kinetics shown herein is that the intermediate is a  $-\text{BH}_3$  containing species, *i.e.*, one formed through the loss of one hydridic hydrogen from hydroborate. Postulation of a  $-\text{BH}_2$  or a  $-\text{BH}$  containing entity would require one or more fast steps in addition to the rate-limiting step in the hydrolysis of hydroborate before the proposed intermediate was reached. Moreover, we have reported<sup>14</sup> the n.m.r. spectrum of a species which occurs in solutions which also show the polarographic wave at  $E_{1/2}$  of  $-0.64$  and is undoubtedly due to the postulated intermediate. This spectrum indicates that the intermediate contains the  $-\text{BH}_3$  group. Results of electrolytic experiments, which support this conclusion, will also be reported. The purely kinetic data of Table V, however, permit a tentative conclusion about the formula of the intermediate.

The Brønsted–Christiansen–Scatchard equation<sup>15</sup> predicts that the rate constant increases or decreases with  $\mu^{1/2}$  depending on whether the product of charges on the reacting species,  $Z_A Z_B$ , is positive or negative. The relation is valid only for solutions of low ionic strength, which cannot be used when polarography is the method of analysis; for the data presented here we

shall show only that the trends in  $k_1$  and  $k_2$  as ionic strength is changed are the same. This suggests that the charge on the intermediate species is the same as that on the hydroborate ion. Reference to Table V shows that  $k_{1,\text{HCO}_3^-}$  and  $k_{2,\text{HCO}_3^-}$  change little with ionic strength, while  $k_{1,\text{NH}_4^+}$  and  $k_{2,\text{NH}_4^+}$  both decrease appreciably. While the uncertainty in  $k_{2,\text{H}_3\text{O}^+}$  is great, it seems to decrease, as does  $k_{1,\text{H}_3\text{O}^+}$ , with increasing ionic strength. On the basis of the similarity of behavior for  $k_{1,\text{HA}}$  and  $k_{2,\text{HA}}$ , we prefer for the formula of the intermediate a negatively charged  $-\text{BH}_3$  containing species, of which  $\text{BH}_3\text{OH}^-$  seems the most probable.

A mechanism for the stepwise hydrolysis reaction consistent with these results and those of other workers<sup>8–10,18</sup> can now be postulated.



## Carbonium Ion Salts. IX. Hydrogen Dihalides<sup>1,2</sup>

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Contribution from the Department of Chemistry, Harvey Mudd College,  
Claremont, California. Received August 12, 1964

*Reaction of tropenyl methyl ether with excess hydrogen halide in ether solvent yields tropenium hydrogen dichloride and hydrogen dibromide as easily preparable, stable, stoichiometric salts. Sublimation of the hydrogen dichloride affords an excellent route to tropenium chloride. Observations on the charge-transfer spectra of the hydrogen dihalides and the light sensitivity of the chloride are reported. Tetrabutylammonium hydrogen diiodide has been synthesized; this is the first characterized salt of this anion to be reported. Equilibrium dissociation vapor pressure measurements have been carried out on four hydrogen dibromides and indicate that factors other than cation size affect the stabilities of such salts.*

Exploration into the question of the possible stability of hydrogen dihalide salts was almost over before it had fairly begun. In two unfortunately often overlooked papers<sup>4</sup> Kaufler and Kunz, in 1909, reported

(1) Supported by the Petroleum Research Fund and the National Science Foundation.

(2) Reported in part in a communication: K. M. Harmon and S. Davis, *J. Am. Chem. Soc.*, **84**, 4359 (1962); and a correspondence: K. M. Harmon and P. A. Gebauer, *Inorg. Chem.*, **2**, 1319 (1963).

(3) (a) National Science Foundation Scholar; (b) American Chemical Society–Petroleum Research Fund Scholar.

the synthesis and analysis of 29 hydrogen dihalides and dihydrogen trihalides, and—in a remarkable piece of reasoning considering the information available to them—correctly deduced both the anionic nature and the order of bonding in the  $\text{XHX}^-$  moiety. Thus, several rediscoveries<sup>5,6</sup> of tetramethylammonium hydrogen dichloride and a recent communication by Tuck and Woodhouse<sup>7</sup> claiming the synthesis of the first reported hydrogen dibromide seem a bit after the fact.

Of the higher hydrogen dihalides the hydrogen dichloride is the best known. Both organic<sup>4–6,8,9</sup> and inorganic<sup>10–12</sup> salts have been prepared, and the symmetrical structure of the anion has been established by physical studies.<sup>6,9,13</sup> Reported compounds<sup>4,7</sup> of the hydrogen dibromide anion are all of the ammonium

- (4) F. Kaufler and E. Kunz, *Ber.*, **42**, 385, 2482 (1909).
- (5) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **76**, 4046 (1954).
- (6) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).
- (7) D. G. Tuck and E. J. Woodhouse, *Proc. Chem. Soc.*, 53 (1963).
- (8) A. Hantzsch, *Ber.*, **64**, 667 (1931).
- (9) D. W. A. Sharp, *J. Chem. Soc.*, 2558 (1958).
- (10) R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).
- (11) R. E. Valleé and D. H. McDaniel, *ibid.*, **84**, 3412 (1962).
- (12) A. G. Maki and R. West, *Inorg. Chem.*, **2**, 657 (1963).
- (13) S. Chang and E. S. Westrum, Jr., *J. Chem. Phys.*, **36**, 2571 (1962).

type<sup>14</sup>; these are relatively unstable and often do not give satisfactory analyses. Few physical chemical data are available on the structure of this ion.

Early attempts to prepare compounds containing the hydrogen diiodide anion resulted in black oils<sup>4</sup> or other products.<sup>8, 15</sup> In a recent paper<sup>16</sup> McDaniel and Vallée report physical studies on tetraalkylammonium iodide-hydrogen iodide adducts, but there is no indication that stoichiometric compounds were prepared.

## Results

The work herein reported was initiated by the observation that in attempts to prepare tropenium chloride by passing hydrogen chloride over an ethereal solution of tropenyl methyl ether<sup>17</sup> an excess of hydrogen chloride gave products with low tropenium ion content, which suggested the incorporation of excess hydrogen chloride in the precipitate. We then found that addition of tropenyl methyl ether to a saturated solution of hydrogen chloride in ether under a hydrogen chloride atmosphere gave high yields of tropenium hydrogen dichloride, as a white, crystalline, remarkably stable<sup>18</sup> salt. The hydrogen dichloride is moderately hygroscopic and darkens on long exposure to sunlight but can be stored in a desiccator in the dark for extended periods. The crystals do not show a discrete melting point but decompose slowly over 100°; the decomposition rate is a function of rate of heating and initial temperature.

Tropenium hydrogen dichloride has proved particularly useful as an intermediate in the preparation of the troublesome compound tropenium chloride. The chloride is implacably hygroscopic and we now find that it is extremely sensitive to light; diffuse sunlight rapidly darkens this compound through Pyrex glass, and a sunlamp destroys it in a few minutes with concurrent formation of several unidentified colored compounds. These properties make recrystallization difficult, and since the chloride is thermally unstable (it decomposes in a sublimator to yield what appears to be the same colored compounds mentioned above) sublimation does not afford a good means of purification. No route yet reported<sup>19-21</sup> has given good yields of tropenium chloride of consistent quality. We find, however, that sublimation of tropenium hydrogen dichloride gives nearly quantitative yields of tropenium chloride of excellent quality as colorless prisms; these show a much higher decomposition temperature than previously reported material.

When hydrogen bromide is used instead of hydrogen chloride, tropenium hydrogen dibromide is obtained

(14) Hantzsch<sup>8</sup> reported an acetonitrilium hydrogen dibromide which was later shown<sup>16</sup> to be an addition compound.

(15) G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, **81**, 3850 (1959).

(16) D. H. McDaniel and R. E. Vallée, *Inorg. Chem.*, **2**, 996 (1963).

(17) Method suggested by H. J. Dauben, Jr., and L. R. Honnen, private communication.

(18) This salt can be pumped for 18 hr. at less than 1 mm. with only a 1% increase in tropenium ion content. The vapor pressure of hydrogen chloride over secondary and tertiary alkylammonium halides is quite high<sup>4</sup> and cesium hydrogen dichloride is unstable over 0°. Tetramethylammonium hydrogen dichloride has a vapor pressure of 2 mm. at room temperature<sup>18</sup> which indicates that it would be rapidly decomposed under these conditions.

(19) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(20) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

(21) D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).

in good yield as yellow needles. These are excellent single crystals; they decompose with concurrent formation of tropenium bromide on warming to 100°. The hydrogen dibromide is not light sensitive and keeps indefinitely in a dry place; it is only mildly hygroscopic. The compound gives excellent analyses and appears to be the most satisfactory salt of this anion yet prepared.

We have reported<sup>22</sup> that tropenium iodide is reduced by hydrogen iodide which renders synthesis of tropenium hydrogen diiodide impossible. Hydroxytropenium iodide is not so reduced but does not appear to form an adduct with hydrogen iodide. We find, however, that treatment of tetrabutylammonium iodide with hydrogen iodide in methylene chloride followed by precipitation with cyclohexane affords tetrabutylammonium hydrogen diiodide as yellow microcrystals. This compound dissolves in oxygen-free water to give strongly acidic yellow solutions. It is sensitive to light, moisture, and oxygen but is reasonably stable in their absence. The hydrogen diiodide loses hydrogen iodide on heating or washing with acetone to form the parent iodide.

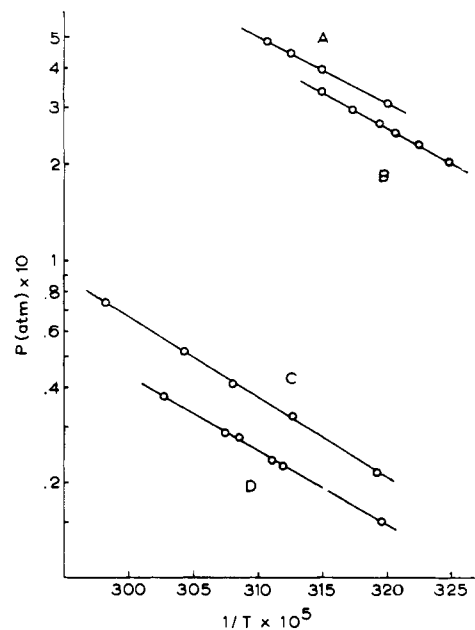


Figure 1. Variation of equilibrium vapor pressure with temperature for (A)  $(\text{CH}_3)_4\text{N}^+\text{HBr}_2^-$ , (B)  $\text{C}_5\text{H}_5\text{NH}^+\text{HBr}_2^-$ , (C)  $\text{C}_7\text{H}_7^+\text{HBr}_2^-$ , and (D)  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{HBr}_2^-$ .

Under identical conditions N-ethyl- and N-butylpyridinium iodides and tetrapropylammonium iodide failed to form hydrogen diiodides.

Equilibrium dissociation vapor pressure measurements were carried out on tropenium, pyridinium, tetramethylammonium, and tetraethylammonium hydrogen dibromides. The data in each case fitted an equation of the form  $\log P = -a/T + b$  (Figure 1); the values of the constants and of the thermodynamic quantities calculated with their use are shown in Table I.

(22) K. M. Harmon, A. B. Harmon, S. Davis, and L. L. Hesse, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 9, 1964.

**Table I.** Constants in  $\text{Log } P = -a/T + b$  and  $\Delta F^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  at 298°K. for Hydrogen Dibromides

Cation	<i>a</i>	<i>b</i>	$\Delta F^\circ$ , kcal./ mole	$\Delta H^\circ$ , kcal./ mole	$\Delta S^\circ$ , e.u.
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N <sup>+</sup>	2415	5.883	3.019	11.02	26.83
C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	2533	6.433	2.821	11.59	29.41
C <sub>3</sub> H <sub>8</sub> NH <sup>+</sup>	2156	6.321	1.240	9.860	28.91
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	2039	6.026	1.107	9.330	27.58

## Experimental

The methods for purifying, drying, and removing oxygen from methylene chloride and cyclohexane have been previously reported<sup>23,24</sup> and the oxygen-free glove box has been described.<sup>24</sup> Baker and Adamson reagent grade anhydrous ether was stored in brown bottles over sodium wire and was redistilled from calcium hydride directly into the reaction vessel before use. U. S. I. absolute alcohol was used without further treatment. Matheson anhydrous hydrogen chloride, bromide, and iodide were used without further purification. G. Frederick Smith reagent grade tetrabutylammonium iodide and Eastman Kodak Co. White Label tetraalkylammonium halides were recrystallized several times from absolute alcohol or acetone.

Melting points were taken on a Fisher-Johns block (in the glove box) and are corrected. Spectra were recorded on the Cary Model 13 spectrophotometer with silica cells; Baker and Adamson reagent grade 96% sulfuric acid was used for spectral solutions.

**Tropenium Hydrogen Dichloride.** Ether (50 ml.) was saturated with hydrogen chloride gas, and tropanyl methyl ether<sup>19</sup> (0.48 g., 3.93 mmoles) dissolved in ether (10 ml.) was injected slowly with a syringe under the surface of the solution producing an immediate white precipitate. The solution was stirred under an atmosphere of hydrogen chloride throughout this addition. When injection was complete, the solution was stirred for a few more moments, then removed to the glove box where the solvent was decanted. The crystals were washed with ether saturated with hydrogen chloride (three 10-ml. portions) and dried *in vacuo* to yield 86.4% tropanyl hydrogen dichloride (0.554 g., 3.40 mmoles) as white microcrystals; ultraviolet spectrum: (96% sulfuric acid)<sup>25</sup>  $\lambda_{\text{max}}$  268 (sh), 274 ( $\epsilon$  4350), and 280 m $\mu$ ; (water)<sup>26</sup>  $\lambda_{\text{max}}$  275 and 280 (sh) m $\mu$ .

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>Cl<sub>2</sub>: C<sub>7</sub>H<sub>7</sub>, 55.89; Cl, 43.49; neut. equiv., 81.52. Found: C<sub>7</sub>H<sub>7</sub>, 55.9; Cl, 43.28; neut. equiv., 81.90.

The tropanyl hydrogen dichloride darkened when heated and decomposed slowly over a wide range beginning about 100°. Trituration with ether gave slightly darkened tropanyl chloride as a gray powder, m.p. 101–102° (lit.<sup>19</sup> m.p. 101°).

**Tropenium Hydrogen Dibromide.** Ether (70 ml.) was saturated with hydrogen bromide gas,<sup>27</sup> and tro-

panyl methyl ether (0.961 g., 7.87 mmoles) was injected slowly under the surface of this solution with continued stirring and passage of hydrogen bromide; a snow white precipitate<sup>28</sup> formed at once. When the injection was complete the solution was stirred for a few more moments, then removed to the glove box where the solvent was decanted. The crystals were washed with ether saturated with hydrogen bromide (three 20-ml. portions) and dried *in vacuo* (until the flask warmed to room temperature) to yield 88.3% tropanyl hydrogen dibromide (1.74 g., 6.95 mmoles) as brilliant yellow microneedles; ultraviolet spectrum: (96% sulfuric acid)<sup>25</sup>  $\lambda_{\text{max}}$  268 (sh), 274 ( $\epsilon$  4310), and 280 m $\mu$ ; (water)<sup>28</sup>  $\lambda_{\text{max}}$  275 and 280 (sh) m $\mu$ .

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>: C<sub>7</sub>H<sub>7</sub>, 36.17; Br, 63.42; neut. equiv., 125.99. Found: C<sub>7</sub>H<sub>7</sub>, 35.9; Br, 63.39; neut. equiv., 125.98.

The hydrogen dibromide lost hydrogen bromide on heating to 100° to form the deeper yellow tropanyl bromide.

**Tropenium Chloride.** A sublimer was charged in the drybox with tropanyl hydrogen dichloride (0.40 g., 2.46 mmoles), evacuated, wrapped in foil, and removed to the room where sublimation was carried out for 4 hr. (70°, 0.1 mm.); this and all subsequent operations were carried out under red lights to prevent decomposition of the chloride. When sublimation was complete the sublimer was removed from the vacuum line (still under vacuum), dried, and returned to the glove box, where the hard crystal mass on the cold finger was transferred to a storage vial. The sublimation afforded a yield of 93.5% tropanyl chloride (0.29 g., 2.29 mmoles) as colorless, free-flowing prisms, m.p. darkens at 119°, decomposes at 121°; ultraviolet spectrum: (96% sulfuric acid)<sup>25</sup>  $\lambda_{\text{max}}$  268 (sh), 274 ( $\epsilon$  4340), and 280 m $\mu$ .

*Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>Cl: C<sub>7</sub>H<sub>7</sub>, 71.99. Found: C<sub>7</sub>H<sub>7</sub>, 71.9.

In the first sublimation attempted it was observed that the crystals of sublimed tropanyl chloride remained bright and clean during the night, but rapidly darkened in the morning on the side toward the window when diffuse sunlight reached them. A portion of the material was exposed to the light from a General Electric sunlamp; the crystals turned coal black within minutes. The irradiation was continued for an hour, when preliminary investigation of the material showed it to contain a pentane- or ether-soluble, yellow, apparently hygroscopic material, a plum-colored acetonitrile-soluble material, and a white, very volatile solid that turns blue on exposure to the air. Similar products have been observed on the thermal decomposition of tropanyl bromide.<sup>29</sup>

**Tetrabutylammonium Hydrogen Diiodide.** All reactants and solvents were carefully freed of oxygen, and all glassware was allowed to stand overnight in the glove box before use to remove adsorbed oxygen. All operations related to the synthesis, work-up, and

(23) K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **86**, 5511 (1964).

(24) K. M. Harmon and F. E. Cummings, *ibid.*, **87**, 539 (1965).

(25) Dauben, *et al.*,<sup>20</sup> give the spectrum of tropanyl ion in this solvent as  $\lambda_{\text{max}}$  268 (sh), 273.5 ( $\epsilon$  4350), and 280 m $\mu$ .

(26) Doering and Knox<sup>19</sup> give the spectrum of tropanyl ion in this solvent as  $\lambda_{\text{max}}$  275 ( $\epsilon$  4350) and 280 (sh) m $\mu$ .

(27) If the passage of hydrogen bromide is continued for too long a time preceding or during the reaction, a yellow, heavy liquid phase separates (presumably ethyl bromide) and the reaction, though not completed, is finished.

(28) The initial white precipitate is presumed to be the dihydrogen tri-bromide; its isolation and characterization is under investigation.

(29) H. J. Dauben, Jr., and K. M. Harmon, unpublished work in Ph.D. Thesis of K. M. H., University of Washington, 1958.

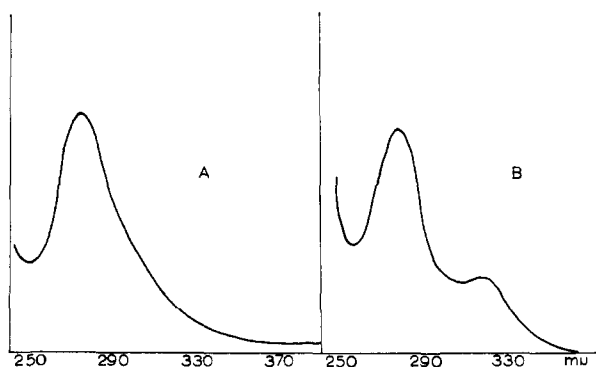


Figure 2. Ultraviolet spectra in methylene chloride of (A) tropenium chloride and (B) tropenium hydrogen dichloride;  $\epsilon$  at maximum of A is 4070.

analysis of this compound were carried out under red light.

Tetrabutylammonium iodide (2.28 g., 6.17 mmoles) was dissolved in methylene chloride (17 ml.) and a slow stream of hydrogen iodide passed over the stirred solution for 0.5 hr.; during this time the solution remained clear but took on a deep red color. Cyclohexane saturated with hydrogen iodide (70 ml.) was added; this caused a dense red oil to separate from the solution. The solvent was decanted from the dense lower layer and a second portion of cyclohexane saturated with hydrogen iodide (80 ml.) was added. The flask was rotated so as to run the oil around the walls under the solvent; nucleation occurred in a few moments, and the entire oil layer quickly crystallized to a mass of bright yellow needles. The solvent was again decanted and the crystals were dried *in vacuo* (until the flask returned to room temperature) to yield 99.5% tetrabutylammonium hydrogen diiodide (3.05 g., 6.14 mmoles) as brilliant yellow microneedles. These do not show a melting point, but rapidly lose hydrogen iodide on heating to give the parent iodide.

*Anal.* Calcd. for  $C_{16}H_{36}NI$ : HI, 0.00; I, 34.36. Calcd. for  $C_{16}H_{37}NI_2$ : HI, 25.72; I, 51.04. Found: HI, 24.99; I, 50.73.

*Attempted Preparations of Other Hydrogen Diiodides.* All reactions were carried out in a manner identical with the one just described. In each case addition of cyclohexane gave a red oil that crystallized on repeated washings.

(a) Ethylpyridinium iodide<sup>30</sup> (0.89 g., 3.71 mmoles) gave 0.80 g. of slightly yellow crystals; these were recovered starting material with a trace of hydrogen iodide absorbed.

*Anal.* Calcd. for  $C_7H_{10}NI$ : I, 53.99. Calcd. for  $C_7H_{11}NI_2$ : I, 69.92. Found: I, 54.75.

(b) Butylpyridinium iodide<sup>30</sup> (0.86 g., 3.27 mmoles) gave 0.81 g. of white crystals whose analysis showed a 20% conversion to the hydrogen diiodide.

*Anal.* Calcd. for  $C_9H_{14}NI$ : HI, 0.00. Calcd. for  $C_9H_{15}NI_2$ : HI, 32.71. Found: HI, 6.53.

(c) Tetrapropylammonium iodide (1.90 g., 6.07 mmoles) gave 1.15 g. of recovered starting material.

*Anal.* Calcd. for  $C_{12}H_{28}NI$ : I, 40.51. Calcd. for  $C_{12}H_{29}NI_2$ : I, 57.65. Found: I, 40.67.

A second portion of tetrapropylammonium iodide (0.93 g., 2.97 mmoles) was dissolved in methylene

(30) A. B. Prescott, *J. Am. Chem. Soc.*, 18, 92 (1896).

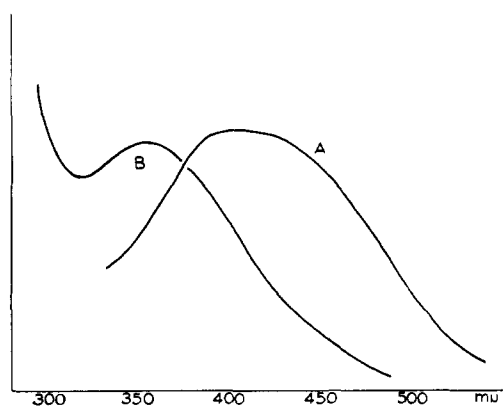


Figure 3. Visible spectra (charge-transfer band only) in methylene chloride of (A) tropenium bromide and (B) tropenium hydrogen dibromide;  $\epsilon$  at maximum of A is 1380.

chloride and treated with hydrogen iodide. The solvent was then removed *in vacuo* (no cyclohexane treatment) to give a yellow solid whose analysis showed a 40.8% conversion to the hydrogen diiodide.

*Anal.* Calcd. for  $C_{12}H_{28}NI$ : HI, 0.00. Calcd. for  $C_{12}H_{29}NI_2$ : HI, 29.00. Found: HI, 11.82.

*Charge-Transfer Spectra of Tropenium Hydrogen Dihalides.* Portions of tropenium bromide and tropenium chloride were dissolved in methylene chloride to give solutions approximately  $10^{-3} M$ . Each solution was divided into two portions; one portion was placed in a flask fitted with an inlet-outlet head, and the other was retained for comparison spectra.

When hydrogen chloride was passed over the swirled surface of the tropenium chloride solution, the bright yellow color from chloride ion to tropenium ion charge transfer<sup>31</sup> vanished at once, and the solution became colorless. An ultraviolet spectrum showed the presence of a new absorption at  $314 m\mu$  ( $\epsilon$  1700) (Figure 2) corrected for tropenium ion absorption. When hydrogen bromide was passed over the swirled surface of the tropenium bromide solution, the intense orange color from the tropenium bromide charge-transfer absorption at  $403 m\mu$  was replaced by a light yellow color; an ultraviolet spectrum showed the presence of a new peak at  $356 m\mu$  ( $\epsilon$  1300) (Figure 3).

The  $\epsilon$  values were calculated by comparison with the untreated portions of the stock solutions and the known values for the tropenium halides.<sup>31</sup>

*Dissociation Vapor Pressure Measurements of Hydrogen Dibromides.* Samples were contained in a Pyrex cell sealed to one arm of a mercury manometer.<sup>32</sup> The cell was heated by a bath controlled to  $0.01^\circ$  and pressures were read with a cathetometer accurate to 0.005 cm. At the beginning of a run the sample was evacuated and allowed to equilibrate several times until constant values were obtained. Reversibility was demonstrated by measurements at both increasing and decreasing temperatures. The time required to reach equilibrium varied from several hours to several days depending on the sample.

(31) K. M. Harmon, D. A. Davis, F. E. Cummings, and D. J. Diestler, *ibid.*, 84, 3349 (1962).

(32) Several runs were made using a Bourdon gauge to separate the mercury from the sample; values so obtained were identical with those from the direct manometric method.

Several runs were made for each compound. Representative data are plotted in Figure 1, and the thermodynamic values were calculated from them in Table I. Preparations of representative samples are given below.

(a) Tropenium hydrogen dibromide was transferred to the cell in a glove box; the cell was then evacuated and sealed to the manometric system.

*Anal.* Calcd. for  $C_7H_8Br_2$ : HBr, 32.11. Found: HBr, 32.09 (before run), 29.18 (after run).

(b) Pyridine (1 ml.) dissolved in ether (10 ml.) was injected into a saturated solution of hydrogen bromide in ether (60 ml.); a white precipitate formed at once. The solvent was decanted and the solid pyridinium bromide dried *in vacuo*.

*Anal.* Calcd. for  $C_5H_6NBr$ : HBr, 50.25. Found: HBr, 50.35.

Pyridinium bromide was transferred to the cell in a glove box; the cell was then sealed to a gas delivery system and hydrogen bromide condensed in the cell at liquid nitrogen temperature. As the cell warmed, a water-white solution formed which rapidly evolved hydrogen bromide to leave a white solid.

*Anal.* Calcd. for  $C_5H_7Br_2N$ : HBr, 67.17. Found (after run): HBr, 65.60.

(c) Hydrogen bromide was condensed onto tetramethylammonium bromide as in part b. Warming of the cell gave a water-white solution, and evaporation of the hydrogen bromide left a white solid.

*Anal.* Calcd. for  $C_4H_{13}Br_2N$ : HBr, 34.44. Found<sup>33</sup>: HBr, 39.69 (before run), 26.54 (after run).

(d) Hydrogen bromide was condensed onto tetraethylammonium bromide as in part b. Warming of the cell gave a water-white solution which lost hydrogen bromide rapidly at first and then slowly to form a clear sirup. This solidified in a few moments to a crystalline slush containing a large excess of hydrogen bromide; warming *in vacuo* was necessary to remove this excess and leave a white, crystalline solid.

*Anal.* Calcd. for  $C_8H_{21}Br_2N$ : HBr, 27.79. Found: HBr, 27.40 (before run), 24.67 (after run).

## Discussion

With the characterization of a salt of the hydrogen diiodide anion, the series of hydrogen dihalide anions is completed. Detailed structure studies have been done only on the hydrogen difluoride and hydrogen dichloride anions; however, recent spectral evidence<sup>16</sup> and the similar methods of synthesis indicate that the higher members of the series are also symmetrical hydrogen-bonded species. Detailed studies of bonding and crystal structure are needed, however, and the remarkably stable tropenium hydrogen dibromide and reasonably stable tetrabutylammonium hydrogen diiodide reported herein should be useful in such work.

Another use for such salts could be as carriers of measured amounts of acid; *i.e.*, a portion of tropenium hydrogen dihalide can be weighed accurately and then used directly as an acid in a solvent in which it is soluble or triturated with a solvent in which the tropenium halide is insoluble (*i.e.*, ether) to prepare a solution containing a known amount of hydrogen

(33) Excess hydrogen bromide was removed by pumping after the cell was attached to the manometric system until reproducible equilibrium pressure readings were obtained.

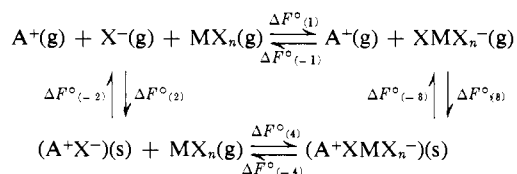
halide. Similar uses for other complex carbonium ion salts such as the tropenium haloborates can be envisioned.

The tropenium hydrogen dihalides (see Figures 2 and 3) show charge-transfer absorptions at shorter wave lengths than the corresponding halides<sup>34</sup> which would be expected for anions of higher ionization potential.<sup>35</sup> Such a higher ionization potential would be expected with the halide ion hydrogen bonded in the anion. From the known data for the relationship of the ionization potentials of halide ions to tropenium halide charge-transfer spectra,<sup>31</sup> we calculate the ionization potential of the hydrogen dichloride anion to be 87.9 kcal./mole and that of the hydrogen dibromide anion to be 84.7 kcal./mole.

Since in tetrabutylammonium hydrogen diiodide there is no mechanism for anion-cation charge transfer, the yellow color of the salt must be ascribed to the absorption of light by the anion.

During the course of previous work on the synthesis of complex tropenium halide salts,<sup>2, 2, 2-24, 36</sup> we often felt that such salts were more stable than could be accounted for by the size of the tropenium cation alone; consideration of the hydrogen dibromide dissociations reported in this paper indicate that there is actual basis for this feeling.

For the formation of a complex between a halide salt ( $A^+X^-$ ) and a nonmetal halide ( $MX_n$ ), we can formulate the following Born-Haber cycle



where  $\Delta F^\circ_{(1)} = \Delta H^\circ_{(1)} - T\Delta S^\circ_{(1)} = -\Delta F^\circ_{(-1)}$ , etc. In the equilibrium vapor pressure studies reported herein, we have been observing process ( $\neq 4$ ), and the thermodynamic values shown in Table I are, respectively,  $\Delta F^\circ_{(-4)}$ ,  $\Delta H^\circ_{(-4)}$ , and  $\Delta S^\circ_{(-4)}$  at 298°K.

For the reaction of complex formation we may write the following identities.

$$\Delta F^\circ_{(4)} = (\Delta F^\circ_{(3)} - \Delta F^\circ_{(2)}) + \Delta F^\circ_{(1)} = \Delta F^\circ_{(L)} + \Delta F^\circ_{(1)} \quad (a)$$

$$\Delta H^\circ_{(4)} = (\Delta H^\circ_{(3)} - \Delta H^\circ_{(2)}) + \Delta H^\circ_{(1)} = \Delta H^\circ_{(L)} + \Delta H^\circ_{(1)} \quad (b)$$

$$\Delta S^\circ_{(4)} = (\Delta S^\circ_{(3)} - \Delta S^\circ_{(2)}) + \Delta S^\circ_{(1)} = \Delta S^\circ_{(L)} + \Delta S^\circ_{(1)} \quad (c)$$

In the case of hydrogen dibromide formation,  $\Delta F^\circ_{(1)}$  is the free energy for forming the hydrogen bond in the gas phase and would be the same for all four of the hydrogen dibromide salts studied. The term  $(\Delta F^\circ_{(3)} - \Delta F^\circ_{(2)})$  represents the change in the free energy of the

(34) We have previously discussed<sup>2</sup> the problem of assigning a value to the charge-transfer absorption to tropenium chloride, which does not show a discrete peak. The value settled on is 320 m $\mu$  ( $\epsilon$  700), but this represents only the center of a diffuse band mass.

(35) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

(36) K. M. Harmon and A. B. Harmon, *J. Am. Chem. Soc.*, **83**, 865 (1961).

crystalline lattice on changing from the bromide to the hydrogen dibromide salt. Since our data allow us to examine differences in lattice energies rather than absolute values, it is convenient to speak of the differential lattice energy  $\Delta F^\circ_{(L)} = \Delta F^\circ_{(3)} - \Delta F^\circ_{(2)}$ . Similar terms can be written for the entropy and enthalpy expressions as shown in eq. b and c. If two salts, x and y are compared, then

$$(\Delta F^\circ_{(4)})_x - (\Delta F^\circ_{(4)})_y = \Delta(\Delta F^\circ_{(4)})_{x-y} = \Delta(\Delta H^\circ_{(L)})_{x-y} - \Delta(T\Delta S^\circ_{(L)})_{x-y} \quad (d)$$

Some comparisons of the energetics of hydrogen dibromide formation for selected pairs of cations are shown in Table II. The actual differences do not

**Table II.** Comparison of Energetics of  $A^+Br^-(s) + HBr(g) = A^+HBr_2^-(s)$  at 298°K. for Selected Pairs of Cations<sup>a</sup>

Cation x	Cation y	$\Delta(\Delta H^\circ_{(L)})_{x-y}$	$\Delta(T\Delta S^\circ_{(L)})_{x-y}$	$\Delta(\Delta F^\circ_{(4)})_{x-y}$
$C_7H_7^+$	$(CH_2)_4N^+$	-2.260	-0.536	-1.714
$C_7H_7^+$	$C_5H_5NH^+$	-1.730	-0.149	-1.581
$(C_2H_5)_4N^+$	$(CH_3)_4N^+$	-1.690	0.233	-1.912
$C_7H_7^+$	$(C_2H_5)_4N^+$	-0.570	-0.769	0.198

<sup>a</sup> All values in kcal./mole.

seem great, but they represent a considerable range in the stability of the salts. Calculated values for the vapor pressure of hydrogen bromide over the tropenium or tetraethylammonium salt at room temperature are around 5 mm., and over the pyridinium or tetramethylammonium salt around 95 mm. These differences are certainly significant to the synthetic chemist.

The relative stabilities of the hydrogen dibromide salts can be judged by a comparison of  $\Delta F^\circ_{(-4)}$ , the free energies of dissociation; indeed, the stabilities can be estimated by a glance at Figure 1, the compound with the lowest line being the most stable. To compare the effects of cation size and structure on these stabilities, however, it is better to compare values of  $\Delta F^\circ_{(4)}$ , the free energy of compound formation, and it is necessary to break this comparison into enthalpy and entropy terms. Now

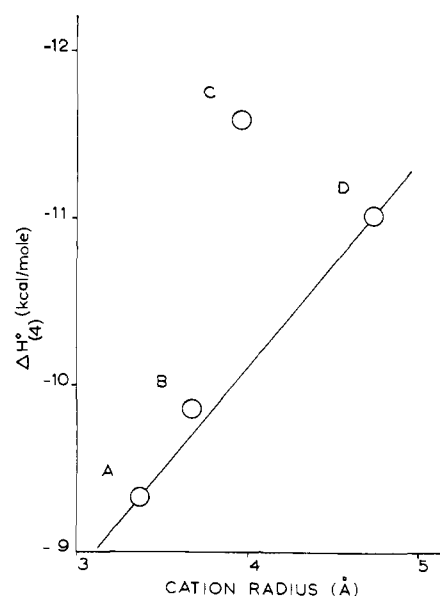
$$\Delta F^\circ_{(4)} = \Delta H^\circ_{(4)} - T\Delta S^\circ_{(4)} = [\Delta H^\circ_{(L)} - T(\Delta S^\circ_{(L)} + \Delta S^\circ_{(1)})] + \Delta H^\circ_{(1)} \quad (e)$$

Since for the type of complexes under discussion  $\Delta H^\circ_{(L)}$  is positive and the entropy term is negative (cf. discussions below), a complex halide salt can be formed only if  $\Delta H^\circ_{(1)}$ , the enthalpy of complex bond formation, is negative and large enough to outweigh the other terms in eq. e.

It is well known that large organic cations often form stable salts of singly charged complex halide anions that can be formed with difficulty, if at all, with simple inorganic cations; this is normally attributed to the effect of ion bulk on the respective crystal lattices. In an alkali metal halide, for example, small ions of roughly similar size pack closely together and coulombic forces of attraction are great. If the halide ion is replaced by a large, singly charged complex anion, these

forces are necessarily weakened as the lattice is expanded and  $\Delta H^\circ_{(L)}$  will be positive. With a large organic cation the coulombic forces within the lattice of a halide salt are weaker, and, if the cation is large enough relative to the anion and complex anion, the relative expansion on complex formation will not be great;  $\Delta H^\circ_{(L)}$  will be less positive than in the case of an alkali metal halide. Since  $\Delta H^\circ_{(1)}$  is the same for all salts of the same complex anion, we would then expect  $\Delta H^\circ_{(4)}$  (see eq. b) to increase in a negative direction as a direct function of cation size up to a certain optimum value; this has been observed for a series of hydrogen dibromide salts of tetraalkylammonium cations by McDaniel and Vallée,<sup>16</sup> who estimate the limiting value of  $\Delta H^\circ_{(1)}$  for hydrogen dibromide formation to be 12.8 kcal./mole.<sup>37</sup>

In Figure 4 we have made a plot of  $\Delta H^\circ_{(4)}$  against cation radius<sup>38</sup> for the four salts that we have studied.



**Figure 4.** Comparison of  $\Delta H^\circ_{(4)} = \Delta H^\circ_{(L)} + \Delta H^\circ_{(1)}$  with cation radius for (A)  $(CH_3)_4N^+HBr_2^-$ , (B)  $C_5H_5NH^+HBr_2^-$ , (C)  $C_7H_7^+HBr_2^-$ , and (D)  $(C_2H_5)_4N^+HBr_2^-$ .

The line connecting the two roughly spherical tetraalkylammonium ions represents the change in enthalpy of complex salt formation to be expected with an increase in cation size. The pyridinium ion falls close to this line, but there is a marked discrepancy in the

(37) Since the reported<sup>16</sup> thermodynamic values for the formation of tetraalkylammonium hydrogen dibromides were obtained by different means for different compounds, we have restudied two of them to put all of our work on the same basis. We have also made preliminary studies on tetrapropyl- and tetrabutylammonium hydrogen dibromides; both give very low vapor pressures, but the compounds do not crystallize well and are too low melting to be conveniently studied in our apparatus.

(38) Cation radii calculated from available crystallographic data (in Å.) are: tetramethylammonium,<sup>39</sup> 3.37; pyridinium,<sup>40</sup> 3.67; tropenium,<sup>41</sup> 3.96; tetraethylammonium,<sup>42</sup> 4.74. The radii calculated for pyridinium and tropenium ions are in the plane of the ring; these appear to be equal to or less than the vertical contact distances.<sup>40,41</sup>

(39) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **12**, 611 (1959).

(40) Y. Takeuchi and P. Pepinsky, *Z. Krist.*, **109**, 29 (1957).

(41) A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1**, 32 (1960).

(42) E. Wait and H. M. Powell, *J. Chem. Soc.*, 1872 (1958).

position of tropenium ion. The value of  $\Delta H^\circ_{(4)}$  for the formation of tropenium hydrogen dibromide is greater than can be accounted for by cation size alone.

The entropy of complex salt formation,  $\Delta S^\circ_{(4)} = \Delta S^\circ_{(L)} + \Delta S^\circ_{(1)}$ , is negative; the differential lattice entropy  $\Delta S^\circ_{(L)}$  might be either positive or negative (although it is probably negative for ions of as low symmetry as the hydrogen dihalides), but  $\Delta S^\circ_{(1)}$  is large and negative and probably contributes the most weight to the entropy term. Consideration of our data shows that the formation of tropenium hydrogen dibromide is hindered by entropy to a greater extent than that of the other salts studied. Examination of Table II will show that, relative to tetramethylammonium hydrogen dibromide, the tetraethylammonium salt is favored by both enthalpy and entropy factors, while the tropenium salt is favored by enthalpy and hindered by entropy. The greater stability of tetraethylammonium hydrogen dibromide over the tropenium salt comes entirely from entropy factors.

The net result of this entropy discussion is that  $\Delta S^\circ_{(L)}$  for the formation of tropenium hydrogen dibromide is more negative (or, perhaps, less positive) than for the other salts; this indicates a higher degree of ordering of the anions in the lattice of the tropenium complex salt. Crystals of tropenium hydrogen dibromide are a bright yellow (somewhat lighter in shade than the bromide), and thus charge-transfer processes are taking place in the solid. It seems possible that the existence of a weak transfer bond, such as has been postulated in crystalline tropenium iodide,<sup>41</sup> could result in more stringent requirements on anion position in the tropenium salt and account for the entropy effects noted.

The unusually low value of  $\Delta H^\circ_{(L)}$  for the formation of the tropenium salt is not easily accounted for. The ion has a different shape and polarizability than the tetraalkylammonium ions but is presumably similar in shape and polarizability to the pyridinium ion which does not show this marked effect. The most obvious different feature of the tropenium ion is its delocalized positive charge; the other three ions studied have a point unit of positive charge centered on the nitrogen nucleus, while in the tropenium ion the charge is distributed by resonance throughout the whole cation. Exactly how this delocalization of charge could produce the observed effect is certainly not clear at this time; however, in the first approximation the coulombic attraction between two diffusely charged non-spherical objects is greatest when they are of the same size, and tropenium ion salts of large anions may be stabilized by this effect. Further speculation should wait on further evidence, such as the examination of salts of other delocalized cations and investigation of the effect of the extent of delocalization of charge in the anion.

In conclusion, tropenium hydrogen dibromide is stabilized by a low positive value of  $\Delta H^\circ_{(L)}$  which outweighs adverse entropy effects and which cannot be accounted for by the ion's size. We believe that this effect may be even more marked in the tetrahaloborate salts where both absence of charge-transfer bonding and higher anion symmetry should reduce adverse entropy effects. Vapor pressure measurements on tropenium and tetraalkylammonium haloborates are in progress.

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## Reactions of Coordinated Ligands. XI. The Formation and Properties of a Tridentate Macrocyclic Ligand Derived from *o*-Aminobenzaldehyde

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*The self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) ions has been shown to produce a closed tridentate macrocyclic ligand, tribenzo[*b,f,j*]-[1.5.9]triazacyclododecine (TRI), in addition to the previously described tetradentate macrocyclic ligand. The resultant complexes exhibit pseudo-octahedral stereochemistry with the three donor nitrogen atoms of the macrocycle occupying one face of the octahedron. The other positions are occupied by a water molecule and two unidentate anions, or by water molecules alone, in the series of compounds of the composition Ni(TRI)-X<sub>2</sub>·nH<sub>2</sub>O, where n is one in all cases except for the*

*tetraphenylborate salt. The reaction to produce these cyclic ligands is assumed to include the metal ion acting as a template for the condensation. Although a tridentate macrocycle does not enclose the metal ion in the usual sense, this complex ion is remarkably stable toward ligand displacement in concentrated acids.*

### Introduction

Recently, several reactions have been reported in which metal ions serve as templates, thereby directing the steric course of the process and leading to the synthesis of species not readily obtained in the absence of the metal ion. A number of these reactions have

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