

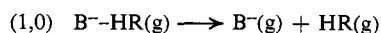
Hydrogen-Bonding Energies to Negative Ions from Gas-Phase Measurements of Ionic Equilibria

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Abstract: The enthalpy and entropy changes for the reactions $(\text{BHR})^- = \text{B}^- + \text{HR}$ were determined by measurements of the temperature dependence of the gas-phase equilibria. For the series $\text{Cl}^- \text{--HR}$ the $\Delta H = D(\text{Cl}^- \text{--HR})$ was found to increase in the order $\text{RH} = \text{HOH}, \text{CH}_3\text{OH}, (\text{CH}_3)_3\text{COH}, \text{Cl}_3\text{CH}, \text{C}_6\text{H}_5\text{OH}, \text{CH}_3\text{COOH}$, and HCOOH . It is suggested that this is the order of increasing gas-phase acidity of RH and that the hydrogen-bond energy increases with the gas-phase acidity of RH . Comparison of the present results with earlier work in which RH was kept constant (HOH) and the nature of B^- was varied suggests that in general the bond energy $\text{B}^- \text{--HR}$ increases with increase of $D(\text{B}^- \text{--H}^+)$, *i.e.*, with the basicity of B^- and with decrease of $D(\text{R}^- \text{--H}^+)$, *i.e.*, the acidity of RH . Such general considerations suggest also the order of energies $D(\text{F}^- \text{--HF}) < D(\text{Cl}^- \text{--HCl}) < D(\text{Br}^- \text{--HBr})$. A discussion on the probable values of $D(\text{F}^- \text{--HF})$, $D(\text{Cl}^- \text{--HCl})$, and $D(\text{Br}^- \text{--HBr})$ is given.

The hydrogen-bond dissociation energy $D(\text{B}^- \text{--HR})$ which is equal to the enthalpy change $\Delta H_{1,0}$ for the reaction



can be determined by measuring the equilibrium constants $K_{1,0}$ and their temperature dependence. van't Hoff plots of $K_{1,0}$ provide the ΔH and ΔS of the reactions. Studies of gas-phase ionic equilibria were started in our laboratory nearly 10 years ago and were mainly directed toward determining successive enthalpy $\Delta H_{n,n-1}$ and entropy $\Delta S_{n,n-1}$ changes for the association of polar molecules to positive or negative ions in the gas phase as represented by the reaction



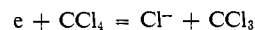
Previous studies include the positive ions H^+ , with $\text{C} = \text{H}_2\text{O}$,¹ NH_3 ,² and CH_3OH ³ and the alkali ions, with $\text{C} = \text{H}_2\text{O}$;⁴ the negative halide ions with H_2O ;⁵ OH^- and O_2^- with H_2O ;⁶ and CN^- , NO_2^- , and NO_3^- with H_2O .⁷ The determination of hydrogen-bonding energies as represented by reaction (1,0) obviously is an integral part of the above studies, since these reactions represent the first step in the stepwise solvation of a negative ion observable in the gas phase.

In the present work measurements were made of the (1,0) equilibria using a single ion, Cl^- , and a number of hydrogen-bonding species RH (CH_3OH , $(\text{CH}_3)_3\text{COH}$, CCl_3H , $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH , and HCOOH). The ion Cl^- was selected because it is conveniently produced and because it is a typical noble gas negative ion, neither small like F^- nor large like I^- . The work was undertaken in order to explore further relationships between the basicity of B^- , the acidity of HR , and the strength of the hydrogen bond in $\text{B}^- \text{--HR}$. The existence of such relationships was suggested by previous

work^{6,7} dealing with the hydration equilibria involving various negative ions.

Experimental Apparatus and Method of Measurement

The apparatus and method of measurements have been described in some detail elsewhere.^{5,7} Only a brief outline will be given here. The equilibrium constants $K_{n,n-1}$ were measured by mass spectrometric detection of the ions escaping from a reaction chamber-ion source. For a typical experiment, the reaction chamber contained the hydrogen-bonding gas RH at a known pressure between 0.5 and 5 Torr. The reactant Cl^- ions were produced by adding traces (0.1 Torr) of CCl_4 to the gas in the reaction chamber. The gas was bombarded by 2-keV electrons. The reactant ions were probably produced by dissociative electron capture of near thermal electrons, *i.e.*



The negative ions then react with RH , forming $\text{Cl}^-(\text{RH})_n$ complexes. Suitable choice of temperature and pressure allows one to observe a given equilibrium $(n,n-1)$. The equilibrium ion composition in the reaction chamber is observed by sampling the ions bleeding out from a narrow slit leading to a vacuum chamber containing a mass spectrometer. Pulsing of the ionizing electron beam allows one to study the kinetics of the approach to equilibrium and to observe the formation of stationary concentration ratios of the ions as equilibrium is achieved.⁷ The equilibrium constants were determined by using the equation

$$K_{n,n-1} = I_{n-1} P_{\text{RH}} / I_n$$

where I_n and I_{n-1} are the mass spectrometrically detected ion intensities of $\text{Cl}^-(\text{RH})_n$ and P_{RH} is the pressure of RH in the reaction chamber.

Results and Discussion

(a) **Results.** The equilibrium constants for the reaction $\text{Cl}^- + \text{CH}_3\text{COOH}$ obtained at various constant temperatures and variable CH_3COOH pressure are shown in Figure 1. The equilibrium constants are seen to be independent of pressure in the experimental range 0.8–2 Torr. Similar results were obtained for the other systems. Shown in Figure 2 are van't Hoff plots for the newly measured reactions of Cl^- . Examination of the figure immediately establishes the increasing stability of the complexes of Cl^- with RH in the order $\text{HOH}, \text{CH}_3\text{OH}, (\text{CH}_3)_3\text{COH}, \text{Cl}_3\text{CH}, \text{C}_6\text{H}_5\text{OH}, \text{CH}_3\text{COOH}, \text{HCOOH}$. The $\Delta H_{1,0} = D(\text{Cl}^- \text{--HR})$, $\Delta G_{1,0}^\circ$, and $\Delta S_{1,0}^\circ$ obtained from the plots in Figure 2 are given in Table I. The data in Table I are arranged in order of increasing $\Delta H_{1,0}$, *i.e.*, increasing hydrogen-bonding energies of $\text{Cl}^- \text{--HR}$.

(1) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

(2) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, **72**, 742 (1968).

(3) P. Kebarle, R. N. Haynes, and G. Collins, *J. Amer. Chem. Soc.*, **89**, 5753 (1967).

(4) I. Dzidic and P. Kebarle, *J. Phys. Chem.*, **74**, 1966 (1970).

(5) M. Arshadi, R. Yamdagni, and P. Kebarle, *ibid.*, **74**, 1475 (1970); P. Kebarle, M. Arshadi, and J. Scarborough, *J. Chem. Phys.*, **49**, 817 (1968).

(6) M. Arshadi and P. Kebarle, *J. Phys. Chem.*, **74**, 1483 (1970).

(7) J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

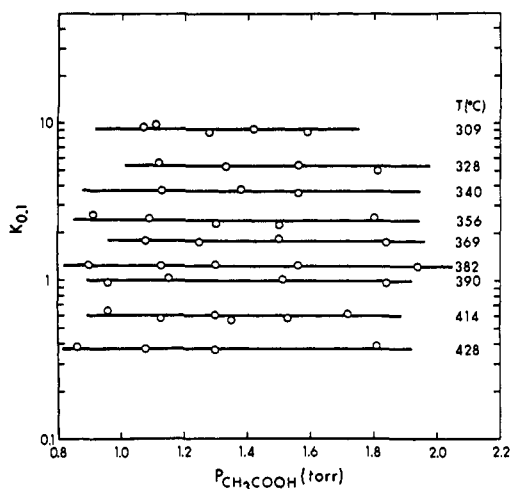


Figure 1. Equilibrium constants $K_{0,1}$ for the reaction $\text{Cl}^- + \text{CH}_3\text{COOH} = (\text{ClHOOCH}_3)^-$ as a function of acetic acid pressure and reaction temperature; standard state 1 Torr.

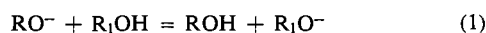
(b) Relationship between Acidity of HR and Hydrogen Bonding in B^--HR . It was pointed out in earlier publications^{6,7} that the strength of the hydrogen bond in a given negative ion B^--HR increases with the

Table I. Thermodynamic Data Obtained for Reaction (1,0): $\text{Cl}^--\text{HR} = \text{Cl}^- + \text{HR}$

| RH | $\Delta H_{1,0}^a$ kcal/mol | $\Delta S_{1,0}^{\circ,a}$ eu | $\Delta G_{1,0}^{\circ,b}$ kcal/mol |
|---------------------------------|--------------------------------|----------------------------------|--|
| H_2O | 13.1 | 16.5 | 8.2 |
| CH_3OH | 14.1 | 14.8 | 9.7 |
| $(\text{CH}_3)_3\text{COH}$ | 14.2 | 10.3 | 11.1 |
| CH_3Cl | 15.2 | 14.8 | 10.8 |
| $\text{C}_6\text{H}_5\text{OH}$ | 19.4 | 15.5 | 14.8 |
| CH_3COOH | 21.6 | 19.3 | 15.8 |
| HCOOH | 37.2 | 39.6 | 25.4 |

^a Standard state 1 atm. ^b 298°K, standard state 1 atm.

basicity of B^- and the acidity of HR. To examine relationship, one might first consider a given base (a proton acceptor) B^- interacting with a series of different HR's. The $\Delta H_{1,0}$ results in Table I represent exactly such a series. The order HOH , CH_3OH , $(\text{CH}_3)_3\text{COH}$, Cl_3CH , $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH , HCOOH thus should give RH compounds of increasing gas-phase acidity. On the whole, the order follows acid strength notions that one may carry over from wet chemistry, where acid strength increases in the order HOH , phenol, acetic acid, formic acid. However, the order HOH , CH_3OH , $(\text{CH}_3)_3\text{COH}$, Cl_3CH is not the same as that occurring in liquid solutions. In the gas phase, one deals with reactions of isolated molecules so that the effect of the solvent molecules is absent. Thus it is to be expected that the gas-phase acidities, which represent an intrinsic molecular property, will not necessarily follow the same order as that found in solutions. The need for a concept of gas-phase acidity became evident in this laboratory through the work on gas-phase solvation of negative ions.^{5,6} Independently, Brauman and Blair,⁸ examining gas-phase ion-molecule reactions of the type



(8) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

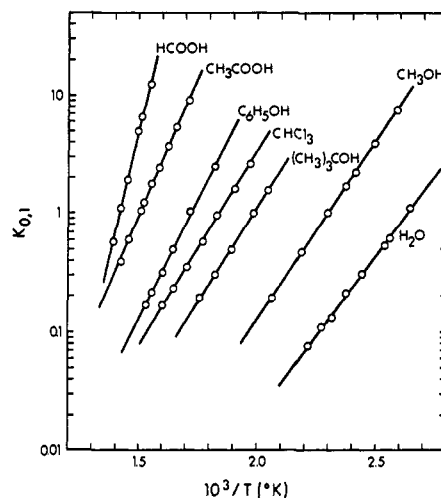


Figure 2. van't Hoff plots of equilibrium constants $K_{0,1}$ for the reactions $\text{Cl}^- + \text{HR} = (\text{ClHR})^-$. The plots show that the stability of Cl^--HR increases in the order $\text{HR} = \text{H}_2\text{O}$, CH_3OH , $(\text{CH}_3)_3\text{COH}$, $\text{C}_6\text{H}_5\text{OH}$, Cl_3CH , $\text{C}_6\text{H}_5\text{OH}$, CH_3COOH , and HCOOH .

drew attention to the energetics of gas-phase acid-base reactions. In Brauman's experiments, the above reaction could be observed to proceed from left to right only if it did not have an appreciable activation energy. This meant that the reaction must be exothermic or near thermoneutral and that R_1OH is a stronger acid than ROH . In this manner Brauman^{8,9} established the acidity order HOH , CH_3OH , $(\text{CH}_3)_3\text{COH}$, $\text{C}_6\text{H}_5\text{OH}$, which is the same as that suggested by the present work. Low-pressure ion-molecule reaction studies of reactions like (1) have been also reported by Tiernan¹⁰ and Beauchamp.¹¹

Table II. Heterolytic Bond Dissociation Energies $D(\text{H}^+-\text{R}^-)$ Obtained from Literature^a

| HR | $\Delta H_f(\text{HR})$ | $\text{EA}(\text{R})$ | $\Delta H_f(\text{R})$ | $D(\text{H}^+-\text{R}^-)$ |
|--------------------------|-------------------------|-----------------------|------------------------|----------------------------|
| HOH | -57.8 ^b | 42.2 ^c | 9.3 ^b | 390.3 |
| HF | -64.8 ^b | 79.5 ^e | 18.9 ^b | 369.3 |
| HCCl_3 | -24.65 ^b | ~48 ^f | 14 ^e | ~356.7 |
| HOC_6H_5 | -23.05 ^c | ~43 ^f | 9 ⁱ | ~353 |
| HNO_2 | -19 ^b | 53 ^g | 7.9 ^b | 339.6 |
| HCl | -22.1 ^b | 83.3 ^e | 29.1 ^b | 333.3 |
| HBr | -8.7 ^b | 77.5 ^e | 26.7 ^b | 323.6 |
| HNO_3 | -32.3 ^b | ~71 ^h | ~(-5.4) ^d | ~322.6 |
| HI | 6.33 ^b | 70.6 ^e | 25.5 ^b | 314.2 |

^a Gas-phase acidity increases from top to bottom, i.e., with decrease of $D(\text{H}^+-\text{R}^-)$. All data in kilocalories per mole. ^b "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note No. 270-3, U. S. Government Printing Office, Washington, D. C., 1968. ^c E. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, NBS Circular No. 500, U. S. Government Printing Office, Washington, D. C., 1952. ^d Estimated on the basis of $D(\text{H}-\text{ONO}_2) \approx D(\text{H}-\text{ONO}) = 79.5$. ^e R. S. Berry, *Chem. Rev.*, **69**, 533 (1969). ^f Estimated on the basis of $\text{EA}(\text{OH}) \leq \text{EA}(\text{OC}_6\text{H}_5)$. ^g W. A. Chupka and J. Berkowitz, presented at the 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Ga., 1971. ^h Estimated on the basis of a private communication from W. A. Chupka and J. Berkowitz. ⁱ P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2943 (1965). ^j R. K. Curran, *J. Chem. Phys.*, **34**, 2007 (1961).

(9) J. I. Brauman and L. L. Blair, *ibid.*, **92**, 5986 (1970).

(10) E. G. Jones and T. O. Tiernan, presented at the 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Ga., 1971.

(11) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970), and references therein.

Table III. Correlation of Bond Energies $D(B^-HR)$ and $D(BH-R^-)$ with Heterolytic Energies of Table II^a

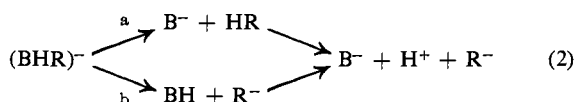
| BH | B ⁻ | OH ⁻ | F ⁻ | CCl ₃ ⁻ | OPh ⁻ | NO ₂ ⁻ | Cl ⁻ | Br ⁻ | NO ₃ ⁻ | I ⁻ | RH |
|-------------------|----------------|-----------------|-------------------|-------------------------------|------------------|------------------------------|-------------------|-------------------|------------------------------|----------------|-------------------|
| HOH | | 24 | 23 | | | 14.3 | 13.1 | 12.6 | 12.4 | 10.2 | HOH |
| HF | | 44 | | | | | (14) ^b | | | | HF |
| HCCl ₃ | | | | | | | 15.2 | | | | HCCl ₃ |
| HOPh | | | | | | | 19.4 | | | | HOPh |
| HNO ₂ | | 65 | | | | | | | | | HNO ₂ |
| HCl | | 70.1 | (50) ^b | 38.6 | 39.1 | | (24) ^c | (16) ^c | | | HCl |
| HBr | | 79.3 | | | | | | (18) ^c | | | HBr |
| HNO ₃ | | 80.1 | | | | | | | | | HNO ₃ |
| HI | | 86.3 | | | | | | | | | HI |
| | R ⁻ | OH ⁻ | F ⁻ | CCl ₃ ⁻ | OPh ⁻ | NO ₂ ⁻ | Cl ⁻ | Br ⁻ | NO ₃ ⁻ | I ⁻ | |

^a All values are in kilocalories per mole; gas-phase acidity of RH increases from top to bottom (of BH from left to right). ^b Interpolated value. ^c Extrapolations from R. Yamdagni and P. Kebarle, *Can. J. Chem.*, in press. At the higher temperatures required to observe the (1,0) equilibrium, the observed lifetime of the Cl⁻ ion in the reaction chamber was found to be much shorter than the lifetime of the clustered Cl⁻(HCl)_n species at lower temperature. This precluded the measurement of the $\Delta H_{1,0}$ energy.

As a quantitative measure of the gas-phase acidity of RH, one may choose⁶⁻⁸ the heterolytic bond dissociation energy $D(R^-H^+) = D(R-H) + I_p(H) - EA(R)$, where D , I_p , and EA stand for bond dissociation energy, ionization potential, and electron affinity. Evidently the smaller $D(R^-H^+)$, the bigger the gas-phase acidity. (The above definition neglects entropy changes. This is done for convenience, since the thermochemical data necessary to evaluate the entropy changes in the heterolytic dissociation reactions are almost nonexistent.)

The heterolytic dissociation energies for a number of compounds RH are shown in Table II together with the thermochemical data used for the evaluation of $D(R^-H^+)$. Comparing these $D(R^-H^+)$ with the data of Table I, one finds that the hydrogen bonds $D(Cl^-HR)$ increase as the heterolytic energies $D(R^-H^+)$ decrease, which is in agreement with the suggested acidity dependence.

(c) **Dependence of the H Bond $D(B^-HR)$ on the Basicity of B and Comparison of the Bonds $D(B^-HR)$ and $D(BH-R^-)$.** Gas-phase solvation equilibria dealing with hydrogen bonding in a series where the acid RH = HOH is kept constant and the base B⁻ = OH⁻, F⁻, NO₂⁻, Cl⁻, Br⁻, NO₃⁻, and I⁻, is varied were presented in an earlier publication.⁷ The negative ions OH⁻... I⁻ listed above are arranged in order of decreasing base strength, *i.e.*, decreasing $D(B^-H^+)$ (see Table II). The measured $\Delta H_{1,0} = D(B^-HOH)$ were found⁷ to decrease in the same order, showing that the hydrogen bonds follow the basicity of the ion B⁻. These data together with the results obtained in the present experiments (Table I) are summarized in Table III, which presents the bond energies in ions (RHB)⁻ in a square arrangement. The square is divided into an upper right and a lower left half by the diagonal representing the symmetric compounds for which R = B. The upper right half gives hydrogen bonding energies, *i.e.*, $D(B^-HR)$, while the lower left half gives the energies $D(BH-R^-)$. These energies were calculated on basis of eq 2, which expresses the possible steps leading to the



total heterolytic dissociation of the ion (BHR)⁻ to B⁻ + H⁺ + R⁻. Path a is partial dissociation leading to B⁻ + HR and corresponds to $D(B^-HR)$. Path b,

corresponding to $D(R^-HB)$, is assumed to require higher energy than path a. The cycle shown in eq 2 leads to the relationship

$$D(BH-R^-) - D(B^-HR) = D(R^-H^+) - D(B^-H^+) \quad (3)$$

The $D(BH-R^-)$ values given in Table III were obtained by substituting the experimental hydrogen-bond energies $D(B^-HR)$ (upper right half, Table III) and the heterolytic dissociation energies of Table II into eq 3.

By selecting the lower energy path a of eq 2 as that describing the hydrogen-bond energy, we have followed usual convention where the weaker bond is considered to be due to H bonding, while the stronger bond is considered to involve bonding other than H bonding, *i.e.*, covalent, etc. The convention of considering the bonding to be different may be meaningful when the two bonds are of very different strength but it becomes meaningless when the bonds become of similar energy. Therefore, somewhat similar trends in the dependence of basicity and acidity may be expected in both types of bonds. This becomes evident as one examines the data in Table III. The decrease of B⁻HR with decreasing basicity of B⁻ (from left to right) was already discussed. Significantly, the (BH-R⁻) energies (row containing HCl) also follow the same trend, decreasing in the order $D(HO^-HCl) > D(F^-HCl) > D(Cl_3C^-HCl) \approx D(PhO^-HCl)$. Similarly, the already discussed increase in B⁻HR with increasing acidity of HR (from top to bottom in Table III) is paralleled by the energies $D(BH-R^-)$, *i.e.*, $D(HO^-HOH) < D(HO^-HF) < D(HO^-HNO_2) < D(HO^-HCl) < D(HO^-HBr) < D(HO^-HI)$. From these general trends, we would also expect the order $D(F^-HF) < D(F^-HCl) < D(F^-HBr) < D(F^-HI)$. It should be noted that in this series only $D(F^-HF)$ would be conventionally considered a hydrogen-bond energy. The other three bond dissociation energies belong to path b. Nevertheless, the series, even though it does not only involve hydrogen bonds, is still very instructive, since it reveals the effect of the increasing acidity of HR and goes perhaps against the chemical intuition of the reader who is accustomed to thinking of the F⁻-HF as the strongest bond on the dihalogen negative ions.

(d) **The Bond Energies in the Symmetric Compound (RHR)⁻.** Of the symmetric compounds belonging to the diagonal in Table III, only $D(HO^-HOH) = 24$ kcal/mol has been determined directly by equilibrium measurements.^{9,7} The value for $D(Cl^-HCl) \approx 24$

kcal was extrapolated from equilibria measurements¹² of the reaction $\text{Cl}^-(\text{HCl})_n = \text{Cl}^-(\text{HCl})_{n-1} + \text{HCl}$. In these experiments, only $\Delta H_{2,1}$ and $\Delta H_{3,2}$ could be measured.¹³ The $D(\text{Br}^--\text{HBr})$ value was extrapolated¹² from a similar but even less complete set of data. Thus both values are quite uncertain. Nevertheless, they appear much more in line with the other data in Table III than the low values $D(\text{Cl}^--\text{HCl}) \approx 14.2$ and $D(\text{Br}^--\text{HBr}) = 12.8$ obtained by McDaniel and Valleé.¹⁴

The values of the three symmetric dissociation energies in the diagonal and the general trend of the data in the square array of Table III suggest some interesting extrapolations. One may expect that the energies would decrease when one moves along the diagonal from the upper left corner, $D(\text{HO}^--\text{HOH})$, to the lower right corner, $D(\text{I}^--\text{HI})$. Such a decrease is indicated by the data. The decrease is slow, which is not unexpected since two opposing trends come into play. As the acidity of the proton donor increases, which is favorable to bonding, the basicity of the identical proton acceptor decreases, which is unfavorable to bonding.

From the position of $(\text{FHF})^-$ in Table III, one would expect $D(\text{F}^--\text{HF}) < D(\text{HO}^--\text{HOH}) = 24$ kcal. This is a somewhat disturbing finding, since there is considerable evidence that the bond in FHF^- is higher than 24 kcal. The early estimates of this energy have been summarized by Waddington.¹⁵ Waddington's own estimate, based on lattice energy calculations and the heat of the reaction $\text{CsF}(\text{s}) + \text{HF}(\text{g}) = \text{CsHF}_2(\text{s})$, leads to $D(\text{F}^--\text{HF}) = 58$ kcal, while various early theoretical estimates¹⁵ based on classical ion dipole interactions lead to equally high values. More recent theoretical calculations based on MO evaluations of the energies of HF_2^- , F^- , and HF have given the energies $D(\text{F}^--\text{HF}) \geq 28$,¹⁶ 40,¹⁷ and 52¹⁸ kcal/mol. An experimental determination by Harrell and McDaniel¹⁹ based on equating the ΔH for the reaction $\text{N}(\text{CH}_3)_4\text{HF}_2(\text{s}) \rightarrow \text{N}(\text{CH}_3)_4\text{F}(\text{s}) + \text{HF}(\text{g})$ to $D(\text{F}^--\text{HF})$ gives a value of 37 kcal/mol. While the above values represent a rather bewildering choice, all of them except that in ref 16 fall considerably higher than 30 kcal. In view of this fact, one may consider the following explanations. If one assumes that the FHF^- value may be expected to fit into a correlation like that of Table III, then the experimental value for $D(\text{HO}^--\text{HOH})$ could be too low. A value of $D(\text{HO}^--\text{HOH}) = 36$ kcal has indeed been obtained by Friedman²⁰ from measurements based on a different technique. On the other hand, the value in Table III is based on two separate equilibrium mea-

surements^{6,7} and is essentially identical with the result of 24.3 kcal obtained in a recent theoretical calculation.²¹ The second possibility is that the FHF^- is special and does not fit in the Table III correlation. While this could be the case, we doubt that the value could be as large as twice $D(\text{HO}^--\text{HOH})$. Thus we feel that the present data are consistent only with a fairly low difluoride dissociation energy around 30 ± 5 kcal/mol.

(e) **A Simple Empirical Equation Relating H-Bond Energy with Acidity.** In section b it was shown that the hydrogen-bond energy $D(\text{B}^--\text{HR})$ decreases with the heterolytic bond energy $D(\text{H}^--\text{R}^-)$. If one assumes a simple linear relationship, one obtains eq 4, where

$$D(\text{B}^--\text{HR}) = C_1 - bD(\text{H}^--\text{R}^-) \quad (4)$$

C_1 and b are constants for a given B^- compound. In section c it was shown that $D(\text{B}^--\text{HR})$ increases with the basicity of B^- , i.e., with increasing $D(\text{B}^--\text{H}^+)$. Again considering a simple linear relationship, one would obtain eq 5, where C_2 and a are constants for a

$$D(\text{B}^--\text{HR}) = aD(\text{B}^--\text{H}^+) - C_2 \quad (5)$$

given RH compound. That eq 5 holds approximately for the series $\text{RH} = \text{HOH}$ and $\text{B}^- = \text{HO}^-$, F^- , NO_2^- , Cl^- , Br^- , NO_3^- , and I^- was shown in a previous publication (Figure 5 of ref 7). The $D(\text{B}^--\text{HOH})$ values are given in the upper row of Table III. These data give a best fit for $a = 0.2$ and $C_2 = 52.5$ kcal/mol. Combining eq 4 and 5, one obtains the general eq 6.

$$D(\text{B}^--\text{HR}) = aD(\text{B}^--\text{H}^+) - bD(\text{R}^--\text{H}^+) = 0.2 D(\text{B}^--\text{H}^+) - 0.134D(\text{R}^--\text{H}^+) \quad (6)$$

The value $b = 0.134$ was obtained by considering that eq 4 with $\text{RH} = \text{HOH}$ is a special case of eq 5, where $C_2 = bD(\text{HO}^--\text{H}^+) = 52.5$ kcal/mol.

According to (6), the hydrogen-bond strength in (B^--HR) is due to a partial heterolytic bond formation between B^--H^+ and a corresponding partial dissociation of the R^--H^+ bond. However, the partial bond dissociation (factor 0.134) is smaller than the partial bond formation (factor 0.2). Equation 6 predicts all numerical values given in Table III quite well, as is easily verified with use of the heterolytic energies of Table II. The higher bond energies $D(\text{BH}^--\text{R}^-)$ (corresponding to path b of eq 2) can be obtained by eq 7, which follows from (6)

$$D(\text{BH}^--\text{R}^-) = (1 - b)D(\text{B}^--\text{H}^+) - (1 - a)D(\text{H}^--\text{R}^-) \quad (7)$$

and (4). Obviously, eq 6 and 7 and the numerical values of the constants a and b represent only a fit of the present experimental data. Whether equations as simple as (6) and (7) will be able to predict a wide range of data remains to be seen. Thus for $\text{B} = \text{R}$, eq 6 and 7 become identical and lead to $D(\text{R}^--\text{HR}) = 0.066D(\text{R}^--\text{H}^+)$, which gives $D(\text{F}^--\text{HF}) = 24.4$, $D(\text{Cl}^--\text{HCl}) = 22$, $D(\text{Br}^--\text{HBr}) = 21$ kcal/mol. Evidently, the predicted $D(\text{Cl}^--\text{HCl})$ value is close to that given in Table III. However, the F^--HF value appears too low (see discussion in section d) and the spread between $D(\text{F}^--\text{HF})$ and $D(\text{Br}^--\text{HBr})$ appears also too low.

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(12) R. Yamdagni and P. Kebarle, unpublished work.

(13) At the higher temperatures required to observe the (1,0) equilibrium, the observed lifetime of the Cl^- ion in the reaction chamber was found to be much shorter than the lifetime of the clustered $\text{Cl}^-(\text{HCl})_n$ species observed at lower temperatures. This precluded the measurement of the $\Delta H_{1,0}$ energy.

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Since starting to write this paper, we have discovered that a relationship very similar to eq 6, but involving free energy changes (logarithms of acidity constants), was proposed much earlier by Gordon²² in a paper

(22) J. E. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

dealing with stabilities of B⁻-HR compounds in liquid solutions.

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Quenching of the Uranyl Fluorescence by Aromatic Molecules

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Abstract: Quenching constants, K_q 's, for the uranyl fluorescence quenching by aromatic molecules having widely different substituents were measured in aqueous acetone solutions at room temperature. The Stern-Volmer relationship was obtained between relative fluorescence intensity and the concentration of most of the aromatic quenchers. The rates decreased with the viscosity of the medium. A linear relationship was found between $\log K_q$ and $\sigma + 0.25(\sigma^+ - \sigma)$ of the substituents, with ρ values of -1.10 in aqueous 80% acetone and -0.83 in aqueous 10% acetone. A correlation was found between the rates of fluorescence quenching and the respective rates of nitration. The results suggest that the rate-determining step of the quenching process involves a π -complex formation between the excited uranyl ions and the quenchers.

One of the most important processes for fluorescence quenching reactions is the mechanism in which a complex (exciplex) formation between the fluorescer, F*, and the quencher, Q, by encounter collision is involved:¹ $F^* + Q \rightleftharpoons \text{complex} \rightarrow \text{quenching}$.

On the other hand, the formation of σ^2 and π^3 complexes between the aromatic system and inorganic cations has been proposed as the reaction intermediates. It was expected that the uranyl fluorescence quenching by the aromatic molecule might relate to the above interesting problems, since it is possible that donor-acceptor interaction arises in the excited state even though there is no affinity in the ground state between the uranyl ion and aromatic molecule.

The present work was undertaken to investigate the mechanism of the uranyl fluorescence quenching by the aromatic system in solution on the basis of kinetic data, especially the substituent effects on the rates, in comparison with the similar and well-established mechanisms.

Experimental Section

Guaranteed reagents and doubly distilled water were used for all preparations. The uranyl concentration (as nitrate) was usually 0.02 M. The temperature was kept constant within the error $\pm 1^\circ$

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by means of a simple attachment of water circulation through a thermostat. The measurements of fluorescence intensities were carried out by means of a Hitachi 204 fluorescence spectrophotometer.

Results and Discussion

Evidence for Encounter Collision Mechanism. Figure 1 illustrates the Stern-Volmer plots for the quenching of the uranyl fluorescence by aromatic molecules, where I_i^0 and I_i are the relative intensities of fluorescence in the absence and in the presence of quencher (Q), and the slope, or the quenching constant, K_q , is a measure of the relative quenching rate. The linear relationship is evidence for the mechanism of bimolecular (collisional) deactivation by the quencher, assuming that the efficiency of unimolecular quenching *via* initial complex formation is not equal to that of bimolecular (collisional) quenching. The long lifetime of the excited state of the uranyl ion, 10^{-4} - 10^{-3} sec,⁴ is favorable for the collisional mechanism.

Another way to determine whether the quenching reaction is unimolecular (initial complex formation between the quencher and the ground state uranyl ions) or bimolecular collision between the quencher and the excited uranyl ions is to see the effect of viscosity of the medium on the rate.⁵ The effect of viscosity using liquid paraffin (Table I) supports the excited state collision mechanism. This is also supported by other facts: (1) very low solubility of the uranyl ions in benzene and (2) no change in the absorption spectra of the mixture solution of benzene and the uranyl ions, sug-

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