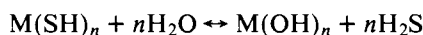


electronic structure of the bonds with sulfur does not, however, seem to be particularly present in our data.

Essential to the chemistry of metals as electrophiles in competing for ligand sites is their strength relative to  $H^+$ . For the alkali and alkaline earth metals this situation is displayed in Figure 2 or Table III, and all the alkali metals are seen to be poorer electrophiles than  $H^+$ , as expected. When considering the energy per bond formation (as opposed to the total binding energy) of the alkali metal hydrosulfides,  $H^+$  is found to divide these metals into two distinct groups.  $Be^{2+}$  is clearly a stronger electrophile than  $H^+$ ,  $Ca^{2+}$  (and most likely  $Sr^{2+}$  and  $Ba^{2+}$ ) are considerably weaker electrophiles, whereas  $Mg^{2+}$  is on the borderline having slightly less binding energy toward  $SH^-$  than has  $H^+$ . The monovalent and heavier bivalent metals thus require low  $[H^+]$  to form hydrosulfides while  $Be-S$  bonds may be formed in acidic media. It is important to bear in mind that solvent effects drastically can change this picture, however.

The reactions previously studied in the present work apply primarily to the gas phase. In aqueous solution several additional complications are introduced in the calculation of reaction energies, such as the hydration of especially the ions and competing reactions to those already considered with  $H_2O$  and  $OH^-$ . It is far beyond the scope of the present investigation to study the full set of reactions that will take place when all these ligands are present. Instead we have considered the relative affinities toward O and S ligands as revealed in the gas-phase reaction



which at the same time provides an indication of the reliability of some of the previous results in this investigation as it is known that the alkaline hydrosulfides readily are dissolved in aqueous solution. By optimizing the structure and calculating the total energies of  $LiOH$  and  $Be(OH)_2$  (see Table II) we find

the energy of the above reaction to be 7.6 kcal/mol for  $M = Li$  and  $-17.8$  kcal/mol for  $M = Be$ . In other words,  $Be$  is predicted to be more stable as  $Be(OH)_2$  than as  $Be(SH)_2$  when  $H_2O$  is present.

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## Ionization Energies of Organic Compounds by Equilibrium Measurements

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**Abstract:** The determination of the equilibrium constants for a number of charge transfer equilibria has generated a scale of relative values of  $\Delta G^\circ$  for the charge transfer reactions. The factors contributing to  $\Delta S^\circ$  for these reactions were elucidated by carrying out experimental determinations of the entropy changes for some of the equilibria. The values of  $\Delta H^\circ$  were used to generate a scale of relative ionization energies of 41 organic compounds and NO. Standardization of the scale using the spectroscopically determined values of the ionization potentials of NO, benzene, and furan was accomplished by calculating the relationship between adiabatic ionization potentials and the "enthalpies of ionization" measured in these experiments. The spectroscopically determined IPs of six of the compounds were reproduced in this way, thus verifying the technique.

### Introduction

In recent years, experimental techniques have been developed which permit the determination of equilibrium constants for ion-molecule equilibria in the gas phase.<sup>1</sup> Using this approach a variety of information about the thermochemical properties of ions has been generated. For instance, scales of relative basicities of numerous organic compounds have been derived from overlapping series of proton transfer equilibrium constants. Quantitative information about the differences in

the heats of formation of alkyl carbonium ions has been obtained from equilibrium constants of hydride transfer and halide transfer reactions.

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

It has been suggested,<sup>2a-c</sup> and preliminary results from this laboratory have indicated,<sup>2d,e</sup> that values for the enthalpies of charge transfer reactions derived from the equilibrium constants of charge transfer equilibria:

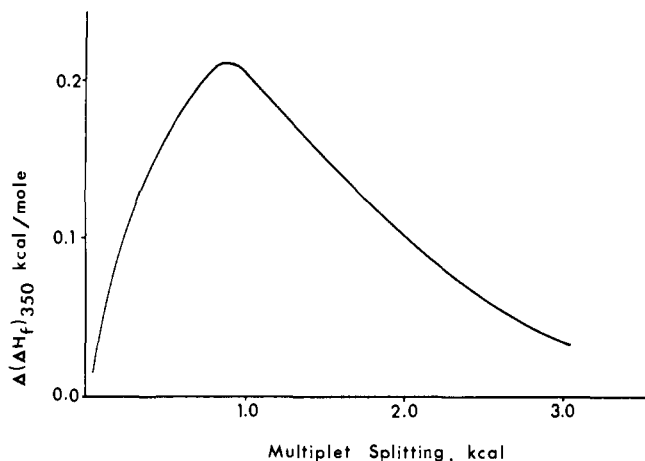


Figure 1. The contribution to the heat of formation of an electronically degenerate species at 350 K from multiplet splitting (eq VII).



can be related to the differences in adiabatic ionization potentials:

$$\Delta H^\circ (\text{charge transfer}) = [\Delta H_f(A) - \Delta H_f(A^+)] + [\Delta H_f(B^+) - \Delta H_f(B)] \approx \text{IP}(B) - \text{IP}(A) \quad (\text{II})$$

If II is correct, charge transfer equilibrium constant determinations may be used to generate scales of relative ionization potentials, which can be related to an absolute energy scale by including as one reactant a molecule for which the ionization potential is well established.

It should be mentioned that the application of eq I and II to results generated from equilibrium measurements in the gas phase would be meaningless if the charge transfer process occurred through some mechanism which did not involve an intimate collision; i.e., such a process would not meet the criteria of thermodynamic equilibrium. However, it is well known that collisions of thermal olefinic and aromatic ions with their neutral counterparts result in the formation of long-lived complexes. For instance, stable  $(C_4H_8)_2^+$  and (aromatic) $_2^+$  cluster ions are observed at pressures as low as  $10^{-3}$  Torr.<sup>3</sup> It can therefore be assumed that there is equilibration among the vibrational modes of the two reactants in the collision complex in charge transfer reactions.

In this paper, we examine the relationship of the "enthalpy of ionization"

$$\Delta H_{\text{ionization}} = \Delta H_f(A^+) - \Delta H_f(A) \quad (\text{III})$$

to the adiabatic ionization potential. Enthalpies of ionization for a number of organic molecules are derived from charge transfer equilibrium constants, and are related wherever possible to adiabatic ionization potentials. The entropy changes associated with the charge transfer equilibria have been experimentally determined for several cases, and the factors influencing the entropy changes have been investigated.

### Experimental Section

The charge transfer equilibrium constants were determined using the NBS pulsed ion cyclotron resonance spectrometer, which has been described previously.<sup>2d,4</sup> The analyzer cell was externally heated, and the temperature within the cell was measured with thermocouples attached to the body of the cell. The energy of the ionizing electrons was 25 eV, and the duration of the ionizing pulse was 3 ms. Except for the cases in which the equilibrium constant was determined as a function of temperature, the operating temperature was 350 K. Most of the determinations were carried out by introducing into the instrument a mixture of the two relevant compounds which had been made up on a vacuum line so that the ratio of the two components was

accurately known. In a few cases in which one of the compounds had a particularly low vapor pressure, an alternate procedure was followed in which the two compounds were flowed into the instrument through separate inlets, and the relative amounts of the two were estimated from pressure readings of the ionization gauge, which had to be separately calibrated for the two components. The relative accuracies of results from the two types of experiments will be discussed in the Results section. Other factors affecting the accuracy of equilibrium constant determinations in this instrument have been discussed in detail.<sup>2d</sup>

Whenever other processes (fragmentation, ion-molecule reactions) occurring in a system resulted in the formation of an ion having a mass 1 amu lower than that of the molecular ion, the abundance of that  $(M-1)$  ion was monitored and the abundance of its  $^{13}\text{C}$ -labeled analogue was calculated and subtracted from the measured abundance of ions of mass  $M$ .

### Results and Discussion

**Relationships between  $\Delta H_{\text{ionization}}$  and the Adiabatic Ionization Potential.** The adiabatic ionization potential, the quantity measured by most physical techniques for determining ionization energies, corresponds to the energy difference between the ground vibrational and rotational level of the lowest electronic state of the ion and the ground vibrational and rotational level of the lowest electronic state of the molecule. This is rigorously equal to the difference in the heats of formation of the ion and the molecule at 0 K.

$$\text{IP}(\text{adiabatic}) = \Delta H_{f0}(A^+) - \Delta H_{f0}(A) \quad (\text{IV})$$

The quantity resulting from the determination of charge transfer equilibrium constants, the "enthalpy of ionization" (eq III); is the difference between the heats of formation of the ion and the corresponding molecule at some temperature above 0 K (300–400 K in this study). It is clear that  $\Delta H_{\text{ionization}}$  is equal to the adiabatic ionization potential only in the event that the integrated heat capacities of the ion and the molecule are identical. It is useful to examine the factors which influence the values of the heat capacities of ions and molecules to attempt to predict the magnitudes of any differences.

The translational and rotational contributions to  $C_p$  for a given three-dimensional species are given by<sup>5</sup>

$$C_p(\text{tr} + \text{rot}) = \frac{7}{2}R + 0.0914(B/T)^2 \approx \frac{7}{2}R \quad (\text{V})$$

where  $B = (2.799 \times 10^{-39})/I$ , and  $I$  is the moment of inertia in  $\text{g cm}^2$ . The second term can never contribute significantly for values of  $I$  in the usual range of orders of magnitude, so

$$\Delta C_p(\text{tr} + \text{rot})_{M^+ - M} \approx 0 \quad (\text{VI})$$

For most of the ions considered here, the ground electronic state is a doublet. If there is any splitting of the energies of the degenerate states, there will be a contribution to the heat capacity of the ion, given by<sup>5b</sup>

$$C_p(\text{elec}) = R \left( \frac{\Delta\epsilon}{kT} \right)^2 \frac{e^{\Delta\epsilon/kT}}{(1 + e^{\Delta\epsilon/kT})^2} \quad (\text{VII})$$

(where  $\Delta\epsilon$  is the magnitude of the multiplet splitting) which will not be matched by a corresponding term for the neutral molecule, which usually has a singlet ground electronic state. It can be seen that when  $\Delta\epsilon/kT \gg 1$  the upper state can be ignored and when  $\Delta\epsilon/kT \ll 1$  the distinction between the two states can be ignored. In the temperature range from 0 to 400 K, only multiplet splittings of 0.05–3 kcal can contribute significantly to the heat of the formation of an entity. Figure 1 gives an estimate of the contribution to the heat of formation of a species at 350 K as a function of  $\Delta\epsilon$  (obtained by a numerical integration of eq VII from 0 to 350 K). It can be seen that in the temperature range of interest here the maximum contribution to the heat of formation of a degenerate species due to multiplet splitting is  $\sim 0.2$  kcal/mol. Table I lists values of  $\Delta C_p(\text{elec})$  for benzene and NO, for which the multiplet

**Table I.** Differences between Adiabatic Ionization Potentials ( $\Delta H_{f0}(\text{ion}) - \Delta H_{f0}(\text{molecule})$ ) and Ionization Enthalpies at 350 K ( $\Delta H_{f350K}(\text{ion}) - \Delta H_{f350K}(\text{molecule})$ ) Calculated from Differences in Vibrational Frequencies and Electronic Multiplet Splittings<sup>j</sup>

	$\int_0^{350} C_{p(\text{vib})} dT + g \int_0^{350} C_{p(\text{elec})} dT = \Delta \int_0^{350} C_p dT$	IP <sup>h</sup>	$(\Delta H_{\text{ionization}})_{350}^i$		
NO <sup>+</sup> -NO	-0.0035 <sup>a</sup>	-0.126	-0.13	213.63 ± 0.01	213.50 ± 0.1
C <sub>6</sub> H <sub>6</sub> <sup>+</sup> -C <sub>6</sub> H <sub>6</sub>	-0.022 <sup>b</sup>	+0.210	+0.19	213.24 ± 0.05	213.43 ± 0.1
c-C <sub>4</sub> H <sub>4</sub> O <sup>+</sup> -c-C <sub>4</sub> H <sub>4</sub> O	+0.002 <sup>c</sup>	<0.04	~+0.04	204.84 ± 0.02	204.84 ± 0.06
C <sub>6</sub> H <sub>5</sub> F <sup>+</sup> -C <sub>6</sub> H <sub>5</sub> F	~-0.001 <sup>d</sup>	<0.04		212.15 ± 0.11	212.15 ± 0.11
CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> <sup>+</sup> -CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	~-0.015 <sup>d</sup>	<0.04		203.4 ± 0.2	203.4 ± 0.2
C <sub>2</sub> H <sub>4</sub> <sup>+</sup> -C <sub>2</sub> H <sub>4</sub>	+0.22 <sup>e</sup>	<0.04		0.16 <sub>300}</sub>	
				0.22 <sub>350}</sub>	
				0.28 <sub>400}</sub>	

<sup>a</sup> Vibrational frequencies of ion and molecule from ref 6b. <sup>b</sup> Vibrational frequencies of ion and molecule from ref 7c. <sup>c</sup> Vibrational frequencies of ion and molecule from ref 7b. <sup>d</sup> Vibrational frequencies of ion and molecule from ref 7c. <sup>e</sup> Vibrational frequencies of ion and molecule from ref 6c. <sup>f</sup> Calculated from eq IX by numerical integration. <sup>g</sup> Calculated from eq VII by numerical integration. <sup>h</sup> Reference 11. <sup>i</sup> IP +  $\Delta \int_0^{350} C_p dT = (\Delta H_{\text{ionization}})_{350}$ . <sup>j</sup> Values are given in kcal/mol.

splittings are respectively 0.84<sup>6a</sup> and 0.34 kcal.<sup>5b,6b</sup> For most other molecules of interest here, data on the degree of multiplet splitting is unavailable; the assumption is made that  $\Delta\epsilon$  is usually small (<0.1 kcal).<sup>6a,c</sup>

For a given mode of vibration of a molecule at temperature  $T$ , there is a contribution<sup>5</sup> to  $C_p$  of

$$C_p(\text{vib}) = R \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \quad (\text{VIII})$$

where  $x = h\nu_i/c/kT$ .

This means that for every vibrational frequency which changes when the molecule is ionized there will be a difference between the heat of formation of the ion and molecule at elevated temperatures which differs from that at 0 K, i.e.,  $C_p(\text{vib})_{\text{ion}} \neq C_p(\text{vib})_{\text{molecule}}$ . This difference can be estimated by summing over all the vibrational frequencies which are different in the ion and the molecule:

$$\Delta(\Delta H_{\text{ionization}})_{0-350K} = \left[ R \int_0^{350} \sum_i \frac{x_i e^{x_i} dT}{(e^{x_i} - 1)^2} \right]_{M^+} - \left[ R \int_0^{350} \sum_i \frac{x_i e^{x_i} dT}{(e^{x_i} - 1)^2} \right]_M \quad (\text{IX})$$

Rough generalizations<sup>6a,7</sup> about the effect of ionization upon molecular vibrations are (1) that the bond or bonds whose vibrations are most affected are those from which the electron was removed, and (2) removal of a bonding electron reduces the vibrational frequency of the bond, removal of an antibonding electron increases the vibrational frequency, and removal of a nonbonding electron has little effect.

Most of the compounds for which  $\Delta H_{\text{ionization}}$  values were measured in this study are substituted benzenes, for which the first ionization potential corresponds to the removal of a delocalized  $\pi$  electron from the ring.<sup>6,7</sup> In such compounds it has been shown that ionization to the lowest electronic state of the ion has little effect on the modes and frequencies of vibration.<sup>6a,7</sup> Estimates from eq IX of the differences in the integrated vibrational heat capacities of the ion and the molecule for benzene, fluorobenzene, toluene, and furan are given in Table I; in every case, the difference is small (<0.05 kcal/mol).

Values of  $\Delta H_{\text{ionization}}$  for *cis*- and *trans*-2-butene have also been included in the results presented here. Data concerning the vibrational frequencies of the 2-butene ions are not available. However, it is known that the lowest ionization potential in olefins results from removal of an electron from the C=C  $\pi$  bond,<sup>6a,c,8</sup> and that this leads to a lowering of the frequency of the symmetric C=C stretch (from 1623 to 1230 cm<sup>-1</sup> in ethylene) and a substantial reduction in the frequency of the twisting around the C=C bond (from 1027 to 430 cm<sup>-1</sup> in ethylene). An approximation of the difference in the integrated vibrational heat capacities of olefin ions and molecules esti-

mated from the changes in vibrational frequencies in ethylene and ethylene ion is also given in Table I.

The calculations summarized in Table I lead to the conclusion that for most substituted benzenes, the heat capacities of the molecule and the corresponding ion are effectively the same, so that the adiabatic ionization potential is expected to be the same as the 300-400 K enthalpy of ionization within experimental error. For species such as NO, benzene or olefins, for which the heat capacities of the ion and molecule differ, a comparison requires an estimate for  $\Delta \int C_p dT$ :

$$\text{IP}(\text{adiabatic}) = \Delta H_{\text{ionization}} - \Delta \int_0^T C_p dT \quad (\text{X})$$

**Entropy Changes for Ion-Molecule Equilibria.** Figure 2 shows the network of values of  $\Delta G^\circ$  determined from charge transfer equilibrium constant measurements at 350 K for 41 organic compounds and NO. The figure also shows the corresponding network of values of  $\Delta H^\circ$  derived from the measured free-energy changes. In order to obtain these values of  $\Delta H^\circ$  for charge transfer equilibria, it was necessary to determine or calculate values for the entropy change associated with each equilibrium where the calculations can be made from the usual statistical mechanical considerations.

$$\Delta S^\circ = \Delta S_{\text{rot}} + \Delta S_{\text{vib}} + \Delta S_{\text{elec}} + \Delta S_{\text{intermolecular}} \quad (\text{XI})$$

Except for species such as the benzene ion, which undergoes a Jahn-Teller distortion, it is not expected that there should be any difference in symmetry between an aromatic molecule and the corresponding molecular ion; in such cases there will be no contribution to the entropy change from  $\Delta S_{\text{rot}}$ , i.e., from changes in the moment of inertia or symmetry number. For most of the reactant pairs studied here, it is also expected that there should be no contribution to the entropy change from changes in the degeneracy of the electronic states or vibrational frequencies between products and reactants. Therefore, in most cases, it was assumed that the only contribution to the entropy change would be that resulting from the modification of the rotational energy of the reactant molecules due to the approach of the ions. As has been pointed out recently,<sup>1b,2e,9</sup> this contribution can be estimated from the expression

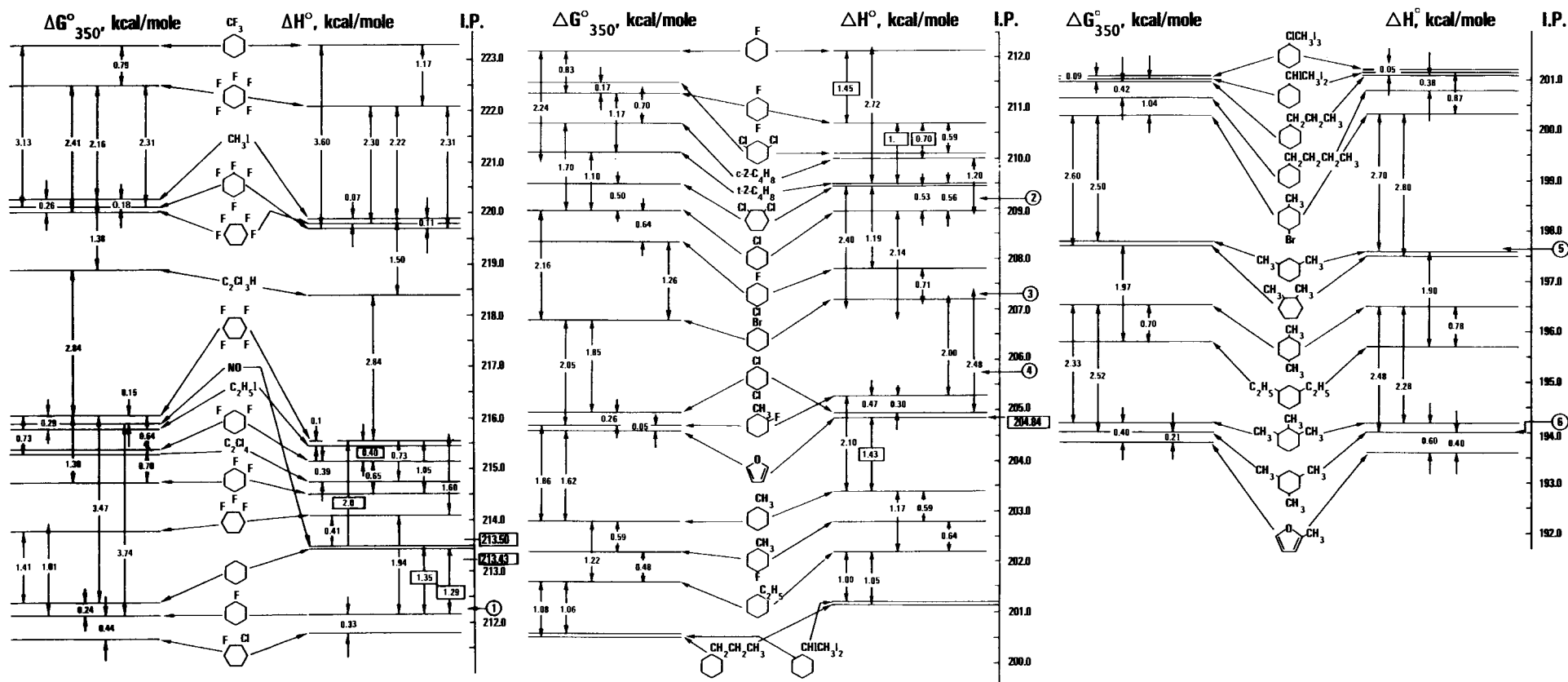
$$\Delta S_{\text{intermolecular}} = R \ln Z_f/Z_r \quad (\text{XII})$$

where  $Z_f$  and  $Z_r$  are respectively the ion-molecule collision rates in the forward and reverse directions (which are estimated from the usual formulations based on ion-molecule potentials of interaction).<sup>10</sup>

Verification that

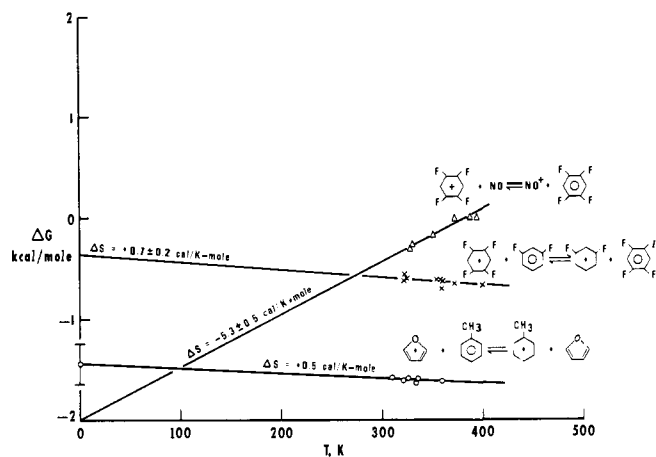
$$\Delta S = \Delta S_{\text{intermolecular}} \quad (\text{XIII})$$

for aromatic species having low symmetry is given by an ex-



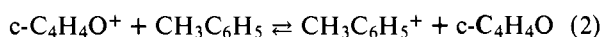
**Figure 2.** Values of  $\Delta G^{\circ}_{350}$  determined from charge transfer equilibrium constants, and the corresponding values of  $\Delta H^{\circ}$ , derived or measured from the  $\Delta G^{\circ}$  values as described in the Discussion. Boxed values of  $\Delta H^{\circ}$  were derived from experimental determinations of  $\Delta S^{\circ}$ . Also included is an energy scale (in kcal/mol) normalized to the values of  $\Delta H_{\text{ionization}}$  derived in Table I and based on spectroscopically determined ionization potentials of NO, benzene, and furan (indicated on the figure). For comparison, results from the

study of Meot-Ner and Field (ref 12) are indicated by numbered arrows on the energy scale. (The  $\Delta G^{\circ}_{450}$  values reported have been converted to  $\Delta H^{\circ}$  values making the same assumptions about  $\Delta S^{\circ}$  as are made in this study.) Key: (1)  $\text{C}_6\text{H}_5\text{F}$ ; (2)  $\text{C}_6\text{H}_5\text{Cl}$ ; (3)  $\text{C}_6\text{H}_5\text{Br}$ ; (4) *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ ; (5) *o*-( $\text{CH}_3$ ) $_2\text{C}_6\text{H}_4$ ; (6) 1,3,5-( $\text{CH}_3$ ) $_3\text{C}_6\text{H}_3$ .

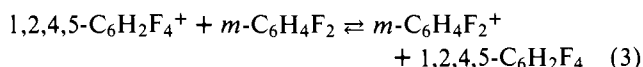


**Figure 3.** Experimentally determined values of  $\Delta G^\circ$  as a function of the absolute temperature for the equilibria: ( $c\text{-C}_4\text{H}_4\text{O}^+ + \text{CH}_3\text{C}_6\text{H}_5 \rightleftharpoons \text{CH}_3\text{C}_6\text{H}_5^+ + c\text{-C}_4\text{H}_4\text{O}$ ) (O); ( $1,2,4,5\text{-C}_6\text{H}_2\text{F}_4^+ + m\text{-C}_6\text{H}_4\text{F}_2 \rightleftharpoons m\text{-C}_6\text{H}_4\text{F}_2^+ + 1,2,4,5\text{-C}_6\text{H}_2\text{F}_4$ ) (X); ( $1,2,4,5\text{-C}_6\text{H}_2\text{F}_4^+ + \text{NO} \rightleftharpoons \text{NO}^+ + 1,2,4,5\text{-C}_6\text{H}_2\text{F}_4$ ) ( $\Delta$ ). For the furan-toluene equilibrium (O), the intercept is the difference in the values of  $\Delta H_{\text{ionization}}$  given in Table I.

perimental determination of the entropy change for the equilibria



and



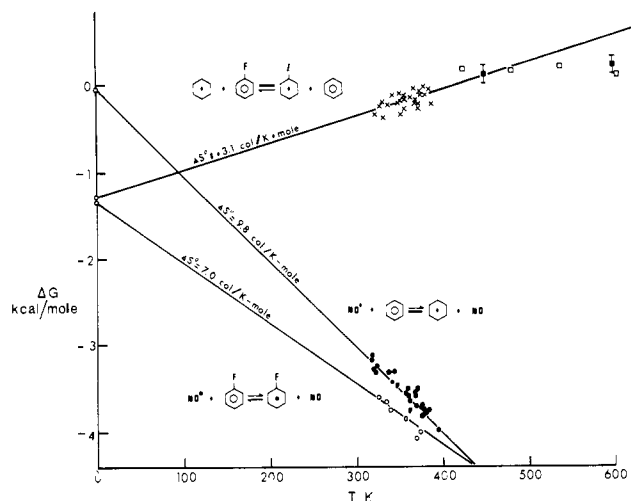
The values of  $\Delta G^\circ$  determined as a function of temperature for equilibria 2 and 3 are shown in Figure 2. Such a plot, in which the intercept is the enthalpy change at 300–400 K for the reaction and the slope is the negative of the entropy change, is a graphical representation of the usual calculation of thermodynamic quantities from eq I assuming linearity over a limited temperature range. The negative of the slope of the line given by the experimental points for eq 2 corresponds to an entropy change of  $+0.5 \pm 0.1$  cal/K·mol in good agreement with the value of  $+0.5$  cal/K·mol predicted from eq XII. In order to obtain increased accuracy in the determination of the entropy change, the intercept has been taken as the difference between the values of  $\Delta H_{\text{ionization}}$  calculated from the spectroscopically determined ionization energies of furan and toluene<sup>11</sup> in Table I.

The results shown in the figure for equilibrium 3 correspond to an entropy change of  $+0.7 \pm 0.2$  cal/K·mol, in good agreement with the value of  $+0.5$  cal/K·mol predicted from eq XII.

For equilibria involving NO, there will be a contribution to the entropy change resulting from a net change in electronic degeneracy between products and reactants. As discussed above, for most of the species investigated, the degeneracy of the ground state of the molecule is 1, and that of the ion is 2; these changes are usually the same for both reactants, and therefore cancel. In the case of NO, the ground state of the molecule ( $^2\Pi$ ) has a degeneracy of 4, while that of the ion ( $^1\Sigma^+$ ) has a degeneracy of 1. Thus, the charge transfer equilibrium



will have associated with it a value of  $\Delta S_{\text{electronic}}$  of  $\pm 4.2$  cal/K·mol (depending on which is taken as the forward direction) in the usual case that the degeneracies of M and  $\text{M}^+$  are respectively 1 and 2. That is, if M does not undergo any changes of structure, the total entropy change for equilibrium 4 will be



**Figure 4.** Experimentally determined values of  $\Delta G^\circ$  as a function of the absolute temperature for the equilibria: ( $\text{NO}^+ + \text{C}_6\text{H}_5\text{F} \rightleftharpoons \text{C}_6\text{H}_5\text{F}^+ + \text{NO}$ ) (O); ( $\text{NO}^+ + \text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_6^+ + \text{NO}$ ) ( $\bullet$ ); and ( $\text{C}_6\text{H}_6^+ + \text{C}_6\text{H}_5\text{F} \rightleftharpoons \text{C}_6\text{H}_5\text{F}^+ + \text{C}_6\text{H}_6$ ) (X). For the benzene-fluorobenzene equilibrium, values from ref 3c, Table I ( $\blacksquare$ ) and ref 3e, Figure 1 ( $\square$ ) are included. Intercepts are the differences in the values of  $\Delta H_{\text{ionization}}$  of the compounds (Table I).

( $\Delta S_{\text{intermolecular}} + \Delta S_{\text{electronic}}$ ). This expectation was verified by experimental determinations of the entropy change for the equilibria



and



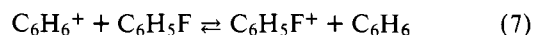
The results are given in Figures 3 and 4. The total predicted and measured entropy changes can be summarized as follows:

$$\begin{aligned} \text{equilibrium 5: } & (+4.2 + 2.3) \\ & = +6.5 \text{ cal/K·mol, predicted} \\ & = +7.0 \pm 0.4 \text{ cal/K·mol, measured} \end{aligned}$$

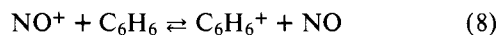
$$\begin{aligned} \text{equilibrium 6: } & (-4.2 - 1.8) \\ & = -6.0 \text{ cal/K·mol, predicted} \\ & = -5.3 \pm 0.5 \text{ cal/K·mol, measured} \end{aligned}$$

(where the latter number in parentheses is the value of  $\Delta S_{\text{intermolecular}}$  predicted from eq XII).

In the case of highly symmetrical species, there is the possibility that the ion undergoes a Jahn-Teller distortion, so that there will be a net contribution to the entropy change because of changes in the symmetry number and moment of inertia of the relevant species. For example, in benzene, loss of the outermost  $\pi$  electron produces an ion in a  $^2E_{1g}$  state which is distorted by Jahn-Teller forces to produce  $^1B_{1g}$  and  $^2B_{2g}$  ions of  $D_{2h}$  symmetry. That is, there is a change from the  $D_{6h}$  symmetry of the neutral molecule to  $D_{2h}$  symmetry in the ion, which corresponds to an entropy change of  $\pm 2.4$  cal/K·mol for  $\Delta S_{\text{rot}}$  in charge transfer equilibria involving benzene species. Since  $\Delta \epsilon$  for the splitting between the states is small (0.84 kcal), the total degeneracy of  $\text{C}_6\text{H}_6^+$  should be taken to be 4 in calculating  $\Delta S_{\text{electronic}}$ . An experimental determination of the entropy changes for the equilibria



and



was made; the results are shown in Figure 3. For both these

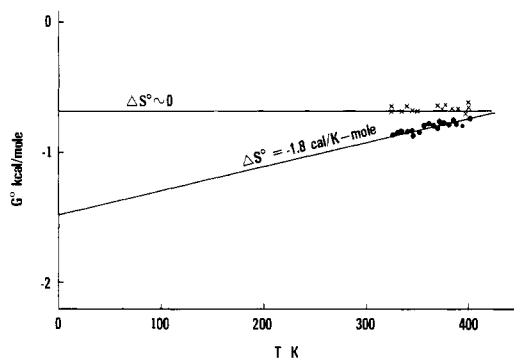


Figure 5. Experimentally determined values of  $\Delta G^\circ$  as a function of temperature for the equilibria:  $(\text{C}_6\text{H}_5\text{F}^+ + p\text{-C}_6\text{H}_4\text{F}_2 \rightleftharpoons p\text{-C}_6\text{H}_4\text{F}_2^+ + \text{C}_6\text{H}_5\text{F})$  (●);  $(p\text{-C}_6\text{H}_4\text{F}_2^+ + \text{cis-2-C}_4\text{H}_8 \rightleftharpoons \text{C}_4\text{H}_8^+ + p\text{-C}_6\text{H}_4\text{F}_2)$  (×).

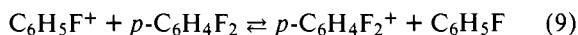
equilibria, accurate spectroscopically determined values of the ionization potentials are available<sup>11</sup> for all the relevant species and sufficient information is available to estimate  $\Delta H_{\text{ionization}}$ , as discussed above (Table I). These values are used to derive the intercepts in the figure in order to increase the accuracy of the entropy change determinations. In a preliminary account of these entropy change determinations,<sup>2c</sup> no distinction was made between  $\Delta H_{\text{ionization}}$  and the adiabatic ionization potential. Therefore, the intercepts, assumed to be equal to  $(\text{IP}_A - \text{IP}_B)$ , were slightly in error for equilibria involving NO or benzene, where  $\Delta H_{\text{ionization}} \neq \text{IP}$ , as discussed above. This accounts for the slight differences in the values of  $\Delta S$  reported in that communication and those derived from the same experimental results here. For equilibrium 7, the predicted entropy change is  $(\Delta S_{\text{rot}} + \Delta S_{\text{elec}} + \Delta S_{\text{intermolecular}})$  or  $(-2.4 - 1.4 + 0.5 = -3.3 \text{ cal/K-mol})$ ; the experimentally measured entropy change is  $-3.1 \pm 0.5 \text{ cal/K-mol}$ .

In the case of equilibrium 8, the predicted entropy change is  $(\Delta S_{\text{rot}} + \Delta S_{\text{elec}} + \Delta S_{\text{intermolecular}})$  or  $(+2.4 + 5.5 + 1.8 = +9.7 \text{ cal/K-mol})$ , which may be compared with the experimentally determined value of  $+9.8 \pm 0.4 \text{ cal/K-mol}$ . For this reaction, sufficient data are available<sup>6</sup> about the fundamental vibrational frequencies of the ions and molecules to permit a calculation of  $\Delta S_{\text{vibrational}}$ . The predicted value is  $-0.05 \text{ cal/K-mol}$ .

As discussed above, for most substituted benzene species, there is little difference in the modes and frequencies of vibration of the ion and the neutral molecule, so  $\Delta S_{\text{vib}}$  should be even smaller than in equilibria involving benzene for other cases studied here.

Thus, in calculating the experimental values for  $\Delta H^\circ$  from  $\Delta G^\circ_{350}$  (Figure 2), the assumption was generally made initially that the entropy change could be predicted from eq XIII, except for equilibria involving NO or benzene (where the considerations just described apply) or olefins. When this assumption was inadequate, the fallacy was easily detected because of the discrepancies which appeared in the interlocking scale of  $\Delta H^\circ$  values. This occurred only for equilibria involving para-disubstituted halobenzenes. Therefore, the entropy changes associated with equilibria involving  $p\text{-C}_6\text{H}_4\text{F}_2$  were also experimentally determined.

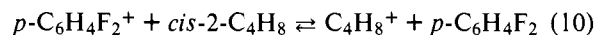
The entropy change for the equilibrium



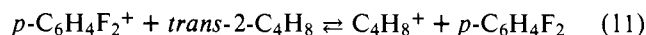
is  $-1.8 \pm 0.6 \text{ cal/K-mol}$  (Figure 5). The value predicted for  $\Delta S_{\text{intermolecular}}$  is  $-0.2 \text{ cal/K-mol}$ . If the observed entropy change were due to some distortion in the  $p\text{-C}_6\text{H}_4\text{F}_2^+$  ion, one would expect the ion to have a lower symmetry than the corresponding molecule, and the resulting entropy change would be positive rather than negative. It is possible that the measured entropy change reflects a splitting of the electronic degeneracy

in the para-disubstituted ion,<sup>6c</sup> if the degeneracy of the ion were taken to be 1, the predicted entropy change would be  $-1.4 \text{ cal/K-mol}$ , in fairly good agreement with the experimental measurement. The entropy changes apparently associated with the transition between  $p\text{-C}_6\text{H}_4\text{F}_2$  and  $p\text{-C}_6\text{H}_4\text{F}_2^+$  were assumed to apply to all other para-disubstituted halobenzenes.

The entropy changes for the equilibria



and

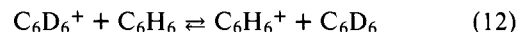


appear to be close to zero ( $\Delta S^\circ = 0.0 \pm 0.7$ ). Accepting that the transition ( $p\text{-C}_6\text{H}_4\text{F}_2^+ \rightarrow p\text{-C}_6\text{H}_4\text{F}_2$ ) is not associated with an entropy change (i.e., no net change in structure or electronic degeneracy), this would imply that the transition ( $2\text{-C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_8^+$ ) must also be associated with an entropy change of zero. However, a calculation from eq IX of the temperature dependence of  $\Delta H_{\text{ionization}}$  of ethylene (Table I) reveals that for olefinic species, the assumption that  $\Delta H_{\text{ion}}$  remains constant over the temperature range of the experiment is no longer correct. It can be calculated that for ethylene,  $\Delta H_{\text{ionization}}$  increases by approximately  $0.12 \text{ kcal/mol}$  between 300 and 400 K. A similar increase would be expected for  $\Delta H_{\text{ionization}}$  of the butenes; a temperature effect of this magnitude on  $\Delta H^\circ$  would mask the observation of the expected positive entropy change.

**Ionization Energies of Organic Compounds.** Table II shows the ionization enthalpies of the organic compounds derived from the results given in Figure 1, taking as reference standards the ionization enthalpies calculated in Table I from the spectroscopic ionization potentials of NO, benzene, and furan.<sup>11</sup> As discussed above, for most of the substituted benzenes included (exceptions are para-disubstituted benzenes) it can be assumed that  $\Delta H_{\text{ionization}}$  is equal, within the cited error limits, to  $\text{IP}(\text{adiabatic})$ .

As can be seen from an examination of Figure 2, the internal consistency of the scale and the agreement between the measured changes in  $\Delta H_{\text{ionization}}$  involving the standard compounds indicate an internal error limit of better than  $\pm 0.05 \text{ kcal/mol}$  for most of the measurements. Therefore, the overall error limit cited for most of the results in Table II is taken as the largest error limit cited for an ionization potential of a standard compound in that part of the scale (usually  $\pm 0.1$  or  $0.2 \text{ kcal/mol}$ ). For several compounds, larger error limits ( $\pm 0.3$  or  $\pm 0.4 \text{ kcal/mol}$ ) have been cited. An examination of the figure will reveal that these correspond to cases for which there is somewhat more scatter in the experimental data, or to compounds which are tied into the scale with but a single determination. Most of the larger error limits are associated with compounds of low vapor pressure, for which the equilibrium constants were determined by flowing the two compounds into the instrument through two separate inlets. Such a determination involves two separate calibrations of the ionization pressure gauge, and the assumption that the flow rates of the two compounds remain reasonably constant during the equilibrium constant determination, and therefore, it is not surprising that the error limits are noticeably larger than those for determinations made with premixed mixtures (where no pressure gauge calibration is necessary, and the ratio of the concentrations of the two compounds is well known and remains constant).

One result omitted from Figure 2 for reasons of crowding is the measured value of  $\Delta G^\circ$  for the equilibrium



for which a value of  $-0.03 \text{ kcal/mol}$  was obtained. It is expected<sup>11</sup> that a difference in this direction and of this magnitude should be observed.

Table II. Ionization Energies of Organic Compounds Determined through Equilibrium Constant Measurements<sup>e</sup>

compd	$\Delta H_{\text{ionization}} (350 \text{ K})$		$IP_{\text{lit}}^c$		method <sup>b</sup>
	kcal/mol	eV	kcal/mol	eV	
Aromatic Hydrocarbons					
benzene	213.43 ± 0.1	9.255 ± 0.005 <sup>a</sup>	213.24 ± 0.05	9.247 ± 0.002	S
benzene- <i>d</i> <sub>6</sub>	213.47 ± 0.1	9.257 ± 0.005	213.32 ± 0.05	9.251 ± 0.002	S
toluene	203.4 ± 0.2	8.82 ± 0.01	203.4 ± 0.2	8.82 ± 0.01	S
<i>o</i> -xylene	197.5 ± 0.3	8.56 ± 0.01	{ 197.8 ± 0.2 197.4 ± 0.2	{ 8.58 ± 0.01 8.56 ± 0.01	{ S PI
<i>m</i> -xylene	197.6 ± 0.3	8.57 ± 0.01	197.4 ± 0.2	8.56 ± 0.01	PI
<i>p</i> -xylene	196.5 ± 0.3	8.52 ± 0.01	{ 195.5 194.7 ± 0.3	{ 8.48 8.445 ± 0.015	{ S PI
ethylbenzene	202.2 ± 0.2	8.768 ± 0.008	{ 202.2 ± 0.2 202.0 ± 0.2	{ 8.77 ± 0.01 8.76 ± 0.01	{ S PI
1,2,3-trimethylbenzene	194.2 ± 0.4	8.42 ± 0.02	195.5 ± 0.2	8.48 ± 0.01	PI
mesitylene	194.0 ± 0.3	8.41 ± 0.01	193.5 ± 0.2	8.39 ± 0.01	PI
<i>n</i> -propylbenzene	201.15 ± 0.2	8.723 ± 0.008	201.1 ± 0.2	8.72 ± 0.01	PI
cumene	201.2 ± 0.2	8.725 ± 0.008	200.4 ± 0.2	8.69 ± 0.01	PI
<i>n</i> -butylbenzene	200.8 ± 0.3	8.71 ± 0.01	200.4 ± 0.2	8.69 ± 0.01	PI
<i>tert</i> -butylbenzene	201.2 ± 0.2	8.725 ± 0.008	200.2 ± 0.2	8.68 ± 0.01	PI
1,3-diethylbenzene	195.7 ± 0.3	8.49 ± 0.01			
Halogenated Aromatic Compounds					
bromobenzene	207.2 ± 0.4	8.98 ± 0.02	{ 206.4 207.1 ± 0.5 208.2 ± 0.2	{ 8.950 8.98 ± 0.02 9.03 ± 0.01	{ PI PI PI
chlorobenzene	208.9 ± 0.2	9.059 ± 0.008	{ 208.7 209.2 ± 0.5 209.4 ± 0.2	{ 9.05 9.07 ± 0.02 9.08 ± 0.01	{ S PI PI
<i>o</i> -dichlorobenzene	209.5 ± 0.3	9.08 ± 0.01	{ 208.9 209.2 ± 0.2	{ 9.06 9.07 ± 0.01	{ PI PI
<i>m</i> -dichlorobenzene	210.1 ± 0.3	9.11 ± 0.01	210.3 ± 0.2	9.12 ± 0.01	PI
<i>p</i> -dichlorobenzene	205.1 ± 0.3	8.89 ± 0.01	206.15 ± 0.2	8.94 ± 0.01	PI
<i>o</i> -fluorochlorobenzene	211.8 ± 9.3	9.18 ± 0.01	211.1 ± 0.2	9.155 ± 0.01	PI
<i>p</i> -fluorochlorobenzene	207.8 ± 0.2	9.011 ± 0.008	213.5	9.26	PE
fluorobenzene	212.15 ± 0.11	9.200 ± 0.005 <sup>a</sup>	212.15 ± 0.11	9.200 ± 0.005	S
<i>o</i> -difluorobenzene	214.1 ± 0.2	9.284 ± 0.008	214.7	9.31	PI
<i>m</i> -difluorobenzene	215.2 ± 0.1	9.332 ± 0.004	225.5 ± 0.5	9.78 ± 0.02	EI
<i>p</i> -difluorobenzene	210.7 ± 0.1	9.137 ± 0.004	211.0 ± 1.4	9.15 ± 0.06	PI, PE
1,2,4-trifluorobenzene	214.55 ± 0.2	9.304 ± 0.008	214.4 ± 1.1	9.30 ± 0.05	PE
1,2,3,4-tetrafluorobenzene	219.83 ± 0.1	9.532 ± 0.004	221.6	9.61	PI
1,2,3,5-tetrafluorobenzene	219.79 ± 0.1	9.531 ± 0.004	220.2	9.55	PI
1,2,4,5-tetrafluorobenzene	215.6 ± 0.1	9.349 ± 0.004	216.5	9.39	PI
pentafluorobenzene	222.1 ± 0.1	9.631 ± 0.004	226.9	9.84	PI
<i>p</i> -bromotoluene	200.3 ± 0.3	8.68 ± 0.01	199.9 ± 0.4	8.67 ± 0.02	PI
<i>o</i> -fluorotoluene	205.4 ± 0.2	8.907 ± 0.008	205.6 ± 0.2	8.915 ± 0.01	PI
<i>p</i> -fluorotoluene	202.8 ± 0.2	8.794 ± 0.008	202.6 ± 0.2	8.785 ± 0.01	PI
$\alpha,\alpha,\alpha$ -trifluorotoluene	223.3 ± 0.1	9.685 ± 0.004	223.3 ± 0.1	9.685 ± 0.005	S
Olefins					
<i>cis</i> -2-butene	210.0 ± 0.2	9.108 ± 0.008	210.41 ± 0.05	9.124 ± 0.002 <sup>d</sup>	PE
<i>cis</i> -2-butene- <i>d</i> <sub>8</sub>	210.2 ± 0.2	9.116 ± 0.008	210.59 ± 0.05	9.132 ± 0.002 <sup>d</sup>	d
<i>trans</i> -2-butene	209.9 ± 0.2	9.100 ± 0.008	210.22 ± 0.05	9.116 ± 0.002 <sup>d</sup>	d
<i>trans</i> -2-butene- <i>d</i> <sub>8</sub>	210.11 ± 0.2	9.111 ± 0.008	210.45 ± 0.05	9.126 ± 0.002 <sup>d</sup>	d
Oxygenated Compounds					
furan	204.84 ± 0.06	8.883 ± 0.003 <sup>a</sup>	204.84 ± 0.02	8.883 ± 0.001	S
2-methylfuran	193.6 ± 0.3	8.39 ± 0.01	193.5 ± 0.2	8.39 ± 0.01	PI
Alkyl Iodides					
methyl iodide	219.9 ± 0.07	9.538	219.9 ± 0.07	9.538 ± 0.003	S
ethyl iodide	215.5 ± 0.1	9.346 ± 0.005	215.5 ± 0.1	9.346 ± 0.005	S

<sup>a</sup> Reference standard. Value of  $\Delta H_{\text{ionization}}$  calculated (Table I) from IP value from the literature. <sup>b</sup> S = optical spectroscopy; PI = photoionization threshold; PE = photoelectron spectroscopy; EI = electron-impact threshold measurement. <sup>c</sup> Reference II. <sup>d</sup> Value for IP(*cis*-2-C<sub>4</sub>H<sub>8</sub>) from references listed under 11 and in ref 13 was independently verified through threshold photoelectron spectroscopy. This value is taken as a comparison standard for estimates of the ionization potentials of the other butenes, assuming that  $\Delta S^\circ$  for charge transfer (C<sub>4</sub>D<sub>8</sub><sup>+</sup> + C<sub>4</sub>H<sub>8</sub>) is zero, and that  $\Delta \int C_p dT$  for two olefinic reactant species will be the same. <sup>e</sup> Additional comparison standard: NO,  $\Delta H_{\text{ionization}} = 9.258 \pm 0.004$  eV (213.50 ± 0.1 kcal/mol) at 350 K; see Table I.

Figure 2 also indicates the results determined for some of these molecules by Meot-Ner and Field<sup>12</sup> in a high-pressure mass spectrometer at 450 K. Their measured free-energy changes have been corrected for the same entropy changes measured or assumed here, so that the results from the two

studies can be compared directly. It can be seen that except for *p*-dichlorobenzene, the results of the high-pressure mass spectrometric study are in agreement with the results reported here within ±0.2 kcal/mol. Because the overall scale of ionization enthalpies based on these results reproduces the spec-

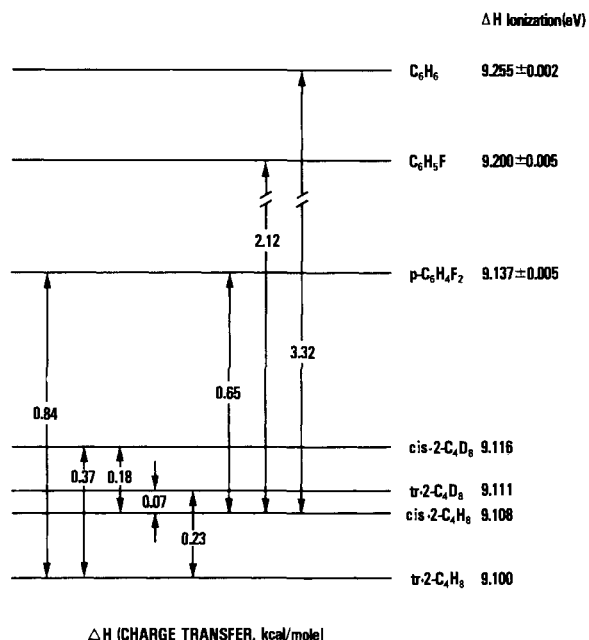


Figure 6. Values of  $\Delta H^\circ$  (charge transfer) measured at 350 K for equilibria involving *cis*- and *trans*-2-C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>D<sub>8</sub> (see Discussion), related to the values of  $\Delta H_{\text{ionization}}$  as derived in Table I.

trioscopically determined ionization potentials<sup>11</sup> of toluene, ethylbenzene, fluorobenzene,  $\alpha,\alpha,\alpha$ -trifluorotoluene, methyl iodide, and ethyl iodide, also shown in Table II, the validity of the values reported here and the approximation  $\Delta H_{\text{ionization}} \approx \text{IP}(\text{adiabatic})$  is confirmed.

These results permit a choice between conflicting values in the literature<sup>11</sup> for the ionization potentials of bromobenzene, chlorobenzene, and *o*-dichlorobenzene, and update values previously reported for *p*-xylene, 1,2,3-trimethylbenzene, mesitylene, cumene, *tert*-butylbenzene, *o*-fluorochlorobenzene, *o*-difluorobenzene, *m*-difluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, and pentafluorobenzene. For 14 other compounds, ionization potentials reported in the literature are confirmed, within the cited error limits. Additional information is necessary in order to interpret values of  $\Delta H_{\text{ionization}}$  of para-dihalogenated benzenes in terms of ionization potentials.

It should also be noted that these results indicate that the ordering of the ionization potentials of *cis*- and *trans*-2-butene from spectroscopic measurements<sup>11</sup> is opposite that reported earlier.<sup>3</sup> In order to verify this result the equilibria for charge transfer between the various C<sub>4</sub>D<sub>8</sub>-C<sub>4</sub>H<sub>8</sub> pairs (*cis*-*cis*, *trans*-*trans*, *cis*-*trans*) were also determined. The thermodynamic network derived from the results determined at 350 K (Figure 6) is internally consistent to  $\pm 0.01$  eV. Although, as shown in Table I, it is expected that for olefins the enthalpy of ionization does not correspond to the adiabatic ionization potential because of the large differences between the vibrational frequencies of the ion and the molecule (eq XI), such differences in the integrated heat capacities of the molecule and corresponding ion should, at least approximately, cancel in an equilibrium between two olefins. Furthermore, there should be no net entropy change. Therefore, the results given in Figure

6 should indicate the correct ordering of the ionization potentials of the 2-butenes and the correct magnitude of the difference between them. The absolute values of  $\Delta H_{\text{ionization}}$  cannot be quantitatively interpreted in terms of adiabatic ionization energies without information about the vibrational frequencies of the butene ions, and the entropy changes associated with charge transfer involving these species. It should be noted, however, that if it is assumed that the difference in heat capacities between the ethylene ion and neutral molecule (Table I) is the same for the butenes, then the results given in Figure 5 are consistent with an entropy change of  $\pm 1.2$  cal/K-mol associated with the (C<sub>4</sub>H<sub>8</sub>-C<sub>4</sub>H<sub>8</sub><sup>+</sup>) transition, and lead to estimated ionization potentials of 9.117 and 9.108 eV for *cis*- and *trans*-2-butene, respectively. These values agree within 0.01 eV with values determined spectroscopically or in photoionization or photoelectron spectroscopy experiments. The values given in Table II for the ionization potentials of *cis*- and *trans*-2-C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>D<sub>8</sub> are based upon the fairly well established value from the literature<sup>13</sup> for IP(*cis*-2-C<sub>4</sub>H<sub>8</sub>) and the measured enthalpies of charge transfer shown in Figure 6, assuming that the differences in ion-molecule integrated heat capacities cancel in equilibria between two olefins.

**Acknowledgment.** The authors would like to acknowledge with special gratitude invaluable discussions with Dr. Henry Rosenstock concerning the relationship between the enthalpy of ionization and the adiabatic ionization potential. Thanks also are due to Dr. Roger Stockbauer who performed threshold photoelectron experiments to verify the ionization potentials of the 2-butenes.

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