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A DETERMINATION OF PROTON-TRANSFER EQUILIBRIUM CONSTANTS IN BENZENE/HALOBENZENE MIXTURES AT VARIOUS TEMPERATURES USING A HIGH-PRESSURE ION SOURCE

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ABSTRACT

A pulsed ion source has been designed and constructed for use with a Kratos MS 50 mass spectrometer in studies of ion—molecule reactions at total pressures from 1 to 5 torr at temperatures between 300 and 600 K. The source is demonstrated to be suited for the measurement of equilibrium constants as a function of temperature for proton-transfer reactions involving benzene and halogenated benzenes. The gas-phase basicity order $C_6H_5F > C_6H_5Br$, $C_6H_6 > C_6H_5Cl$ is established at 334 K and shown to be quite sensitive to temperature. Extrapolation of experimental data leads to $C_6H_6 > C_6H_5Cl > C_6H_5F$ above 850 K and to $C_6H_5F > C_6H_5Cl > C_6H_6$ below 270 K. The standard enthalpy changes derived from van't Hoff plots indicate a proton affinity order $C_6H_5F > C_6H_5Cl > C_6H_6$ which appears to be independent of temperature in the temperature range of the measurements. The standard entropy changes obtained from these plots provide insight into the site(s) of protonation of C_6H_5F and C_6H_5Cl.

INTRODUCTION

The development of the pulsed high-pressure ion source has provided a valuable instrument for studies of the kinetic behaviour of ion—molecule reactions. It has proved particularly well suited for the measurement of equilibrium constants as a function of temperature and thus for the determination of the thermodynamics of ion—molecule reactions [1,2]. For example, van't Hoff plots for the equilibrium constants of proton-transfer reactions have provided values for the standard entropy and enthalpy changes associ-

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ated with the transfer of a proton from one molecule to another. The latter changes provide a measure of differences in the proton affinities of molecules which are of considerable practical value in chemical ionization mass spectrometry (CIMS). In this study a pulsed ion source has been designed and built for use with an MS 50 (Kratos Ltd.) mass spectrometer for investigations of ion—molecule reactions at temperatures between 300 and 600 K and total pressures in the range 1—5 torr. The source has been applied in measurements of equilibrium constants at 334 K for proton-transfer reactions involving benzene and a variety of halobenzenes, viz. reactions of the type

$$C_6H_5XH^+ + C_6H_5Y \rightleftharpoons C_6H_5X + C_6H_5YH^+ \qquad (1)$$

with X and Y = H, F, Cl, or Br. The standard free-energy changes derived from the equilibrium constants provide a measure of the differences in the gas-phase basicities of these compounds. For several of these reactions the equilibrium-constant measurements were extended over a temperature range from 288 to 568 K to provide values for the associated standard entropy and enthalpy changes. The entropy changes are compared with theoretical expectations to provide insight into the site(s) of protonation of the halogenated benzenes. Furthermore, comparisons are made with the pulsed ion source studies of Lau and Kebarle [3], which provide an independent assessment of the performance of the source developed in this study, and with the recent determinations reported by Hartmann and Lias [4] using the ion cyclotron resonance (ICR) technique.

EXPERIMENTAL

Design and construction of ion source

The pulsed ion source was designed and constructed for use with an MS 50 (Kratos Ltd.) mass spectrometer. It was modelled after the version developed by Kebarle [1,2]. A drawing of the ion source is shown in Fig. 1. The source block is constructed from copper (chosen for its high thermal conductivity) suitably drilled to provide a reactor (B) of 1 cm^3 volume which is then nickel flashed and gold plated to provide an inert surface. All other metal parts are of stainless steel. The electron trap and repeller plates are mounted in ceramic bonded to small flanges. The razor-blade slits (1 × 0.0025 cm) for electrons and ions are also mounted on flanges. Gold "O" rings ensure gastight seals when these items are fitted.

The electron beam assembly A, attached to the block, has focusing grids 1 and 2 inserted between the filament and the electron slit. A wide-mesh grid (40 wires cm^{-1}, 81% transmission) is mounted, separated by 1 cm on either side, between the source block and the ion-beam centering plates. The mesh reduces field penetration into the reactor and facilitates the pumping away of gas streaming from the ion exit slit, thereby reducing the degree of colli-

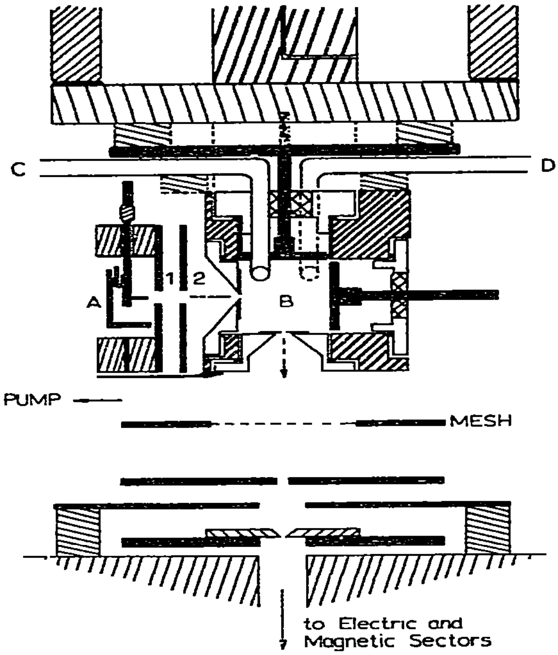

Fig. 1. Drawing of the pulsed high-pressure ion source.

sionally-induced ion decomposition in the emergent ion beam.

A heater coil set into the back of the source block provides heating which is controlled by a platinum resistance sensor embedded at one end of the block. The temperature is measured using a copper/constantan thermocouple embedded at the opposite end. Cooling can be achieved to a limited extent via a thick but flexible copper ribbon in good thermal contact with the source block, via an electrically insulating disc.

Premixed reactant gas is introduced directly into the source via C, its pressure in the reactor being measured through D which is connected to the pressure head of an MKS "Baratron" pressure meter (Type 77). C and D are sealed to hollow electrical feedthroughs in the source flange using "Viton" "O" rings. The reactants are mixed and stored in a heated 5-dm^3 glass bulb from which they pass through an automatic pressure control valve (Granville Phillips, Series 216).

Pumping in the source housing is provided by a 15-cm diffusion pump (Edwards Speedivac E06, containing Santovac 5 oil) connected by a 10-cm diameter pipe (length 15 cm). Operating pressures of up to 8 torr could be achieved in the reactor.

Method of operation

Mixtures of volatile liquids were accurately made up by weight using chemicals of "Analar" purity. In general a 0.05 or 0.1 cm^3 aliquot of the mixture was injected through a septum into the 5-dm^3 heated-oven reservoir bulb containing methane (Matheson Gas Products, 99.9% minimum purity) at 1 atmosphere. 10 cm^3 of SF_6 (Air Products Ltd., 99.9% purity) was introduced by gas syringe.

A schematic diagram of the pulsed source experiment is shown in Fig. 2. The pulse generator A (Advance Instruments, PG52) transmits simultaneously a triggering pulse to an analogue multichannel analyzer E (BIOMAC-1000, Data Labs Ltd.) and, via an optical isolator B, to the pulse generator C (which is floated at the source voltage of up to 8 kV).

Grid 1 of the source is normally held at ~ -12.5 V with respect to the filament and is therefore gated "off". Grid 2 is held at +27.5 V with respect to the filament which is at -400 V with respect to the source block. A positive-going (+25 V) square-wave pulse from C to grid 1 gates the beam on for a period variable from <1 μs upwards. Periods from 20 to 40 μs were used in the experiments reported here. Ion—molecule reactions ensue after ionization of the reactant mixture by the 400-eV electron pulse. The repeller and trap are normally shorted to the block and the mesh ion-focusing grid is maintained at a potential of < -100 V with respect to the source to keep the reactor as close to field-free conditions as possible. The ions which drift out of the exit slit either by diffusion or mass flow are detected by mass analysis in the usual manner. In a pulsed experiment the mass spectrometer is tuned

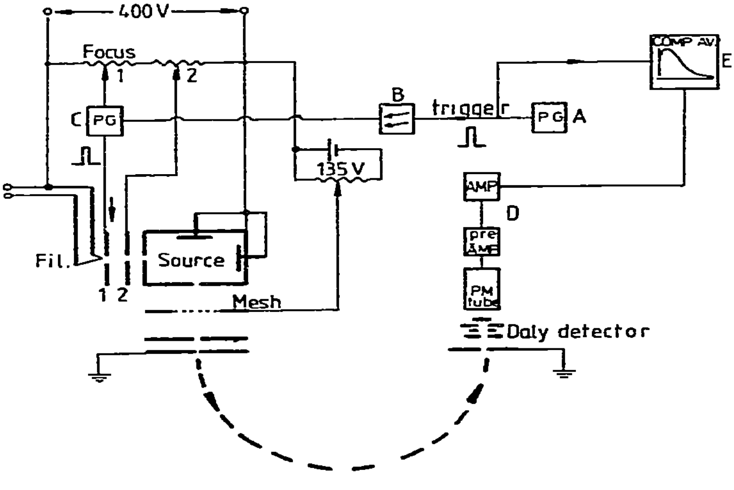

Fig. 2. Schematic diagram of the pulsed-source experiment.

to one particular ion whose intensity is followed as a function of time for 5 ms after the electron pulse (or until all ions in the reactor have decayed). The ion signal at D is collected in E. Generally, between 5 and 10×10^3 cycles were found necessary to reach acceptable signal-to-noise ratios.

Apart from these modifications the source operates from the MS 50 source supply unit. Normal CI mass spectra can be recorded by gating the source "on" continuously.

Sources of error

(a) Mass discrimination at the detector

The gain of the detector (a Daly detector [13] modified by Kratos Ltd.) was measured in the *m/z* range 15—217. The relative response to all ions over this range was found to be within 1.00 ± 0.06 and hence this is not a significant source of error.

(b) Temperature measurement

The thermocouple leads were connected to a digital voltmeter (DVM) outside the source-housing via solid tungsten feedthroughs in the source flange. Over most of the operating temperature range the DVM reading provided a temperature within ±2° of the source-block temperature. However, at the highest temperatures of the source block, some differential heating of the source flange occurred which introduced a temperature gradient down the electrical feedthroughs. Measurements of the change in the DVM reading introduced by such an effect indicated that an uncertainty of up to 5°C ($<1\%$) could be introduced at the highest temperatures. The assumption that the gas in the reactor is at the same temperature as the source block is reasonable at the pressures used, with temperature gradients in the block reduced to a minimum by the use of copper.

(c) Ion sampling

The degree to which the "raw" ion-signal ratio measured with the mass spectrometer corresponds to the equilibrium ion ratio established at the high pressures in the ion source is, of course, crucial to the success of these measurements. The gas is lost from the source only through the slits. The gas flow is estimated to be in the molecular/intermediate range. Also, the ions rapidly diffuse to the exit slit by ambipolar diffusion, particularly at elevated temperatures. The systematic error which may be introduced due to different diffusion losses of unequal-mass ions was minimized by the addition of small amounts of SF_6. The addition of SF_6 changes, as a result of its large cross-section for the capture of thermal electrons, the ambipolar diffusion from positive-ion—electron to positive-ion—negative-ion for which the diffusion coefficients are less sensitive to mass. The exact magnitude of the discrimination introduced by the gas flow and the ion diffusion is very difficult to assess. Since the two effects are likely to be small and tend to cancel, a correction to the raw ion ratio is probably not warranted, particularly given the uncertainty introduced by the observed scatter of the data.

RESULTS AND DISCUSSION

Methane chemical ionization spectra

As a first step, an attempt was made to characterize the benzene and halobenzene chemistry initiated by ionization in CH_4 and thus to identify the ion chemistry concomitant with the protonation of these molecules. Chemical ionization spectra were recorded for benzene and the individual halobenzenes under conditions representative of those ultimately adopted in the equilibrium-constant measurements. The spectra were obtained with the source operating in the continuous-ionization mode and are shown in Fig. 3. They are quite similar to those reported by Harrison and co-workers for a somewhat higher temperature of 423 K and lower pressures (between 0.3 and 0.5 torr) [5,6].

An inspection of the spectra in Fig. 3 clearly indicates that protonated benzene and halobenzenes are established as predominant ions by the acids CH_5^+ and H_3O^+ (which arises from H_2O impurities). The peak corresponding to a $(M - X + CH_4)^+$ species is by far the most predominant in the CI spectrum of C_6H_5F. The origin of this ion has received considerable attention [7,8]. It has been ascribed both to a direct dehalogenation reaction via com-

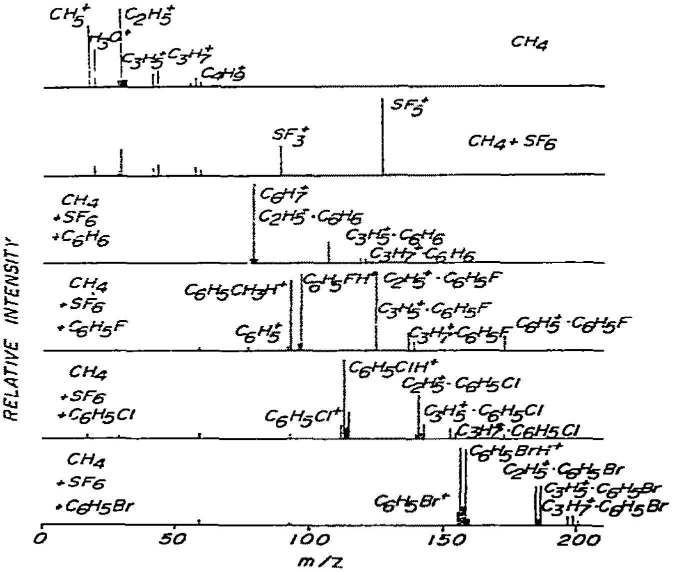

Fig. 3. Methane chemical ionization spectra recorded at total pressures between 1.3 and 1.8 torr, temperature between 335 and 345 K, and a mixing ratio for $CH_4/SF_6/C_6H_5X$ of ~400/1/1.

plex formation:

$$CH_5^+ + C_6H_5F \rightarrow C_6H_5CH_3H^+ + HF \tag{2}$$

and to a two-step sequence of the type

$$CH_5^+ + C_6H_5F \rightarrow C_6H_5^+ + HF + CH_4 \tag{3}$$

$$C_6H_5^+ + CH_4 \rightarrow C_6H_5CH_3H^+ \tag{4}$$

Both of these schemes appear to have found support from ICR measurements carried out at much lower pressures [7,9]. Further clarification has come from a recent selected ion flow tube (SIFT) study which favours the latter scheme [10]. Room-temperature measurements in He and H_2 buffer gas at ~0.5 torr showed that CH_5^+ reacts rapidly ($k > 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) with C_6H_5F and C_6H_5Cl to produce exclusively $C_6H_5XH^+$ and $C_6H_5^+$ according to what is viewed as a dissociative proton-transfer mechanism:

$$CH_5^+ + C_6H_5XH \rightarrow (C_6H_5XH^+)^* + CH_4 \tag{5a}$$

$$\hookrightarrow C_6H_5^+ + XH \tag{5b}$$

There was no evidence for the direct formation of a toluenium ion (<1%). Separate measurements indicated the formation of such an ion by a rapid association between the phenylium ion and CH_4 in He buffer. The $C_6H_5XH^+$ ion activated by the proton-transfer reaction (5a) was observed to dissociate under the SIFT conditions by ~50% and ~10% for X = F and Cl respectively. Also the H_3O^+ ion was observed to react rapidly ($k > 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) with C_6H_5F and C_6H_5Cl but exclusively by proton transfer. These results are in both qualitative and nearly quantitative agreement with the CI spectra for C_6H_5F and C_6H_5Cl in Fig. 3 given the large excess of CH_4 which ensures almost complete conversion of $C_6H_5^+$ into $C_6H_5CH_3H^+$ under CI conditions. Some minor amounts of the $C_6H_5^+$ intermediate were observed in the C_6H_5F spectrum together with an ion at $m/z = 173$ which is likely to correspond to the adduct $C_6H_5^+ \cdot C_6H_5F$. The adducts of the type $C_2H_5^+ \cdot C_6H_5X$ and $C_3H_5^+ \cdot C_6H_5X$ which were observed in this study for X = H, F, Cl and Br have been reported previously by Harrison et al. [5,6]. In addition we have observed trace amounts of ions corresponding to adducts of the type $C_3H_7^+ \cdot C_6H_5X$ and higher adducts of the type $R^+ \cdot (C_6H_5X)_2$, as well as adducts of the type $C_6H_5XH^+ \cdot C_6H_5X$. Only the formation of the latter adducts represents a reaction-sink which may compete with the proton-transfer equilibria under investigation. However, at the operating temperatures and pressures adopted in these studies, the rate of formation of these adducts appeared to be sufficiently depressed to be negligible.

Trace amounts of SF_6 were added to the pure CH_4 to attach electrons and so establish a positive/negative-ion plasma which reduces the rate of positive-ion diffusion. The CI spectrum for SF_6 indicates a rapid reaction with CH_5^+. This was confirmed by the SIFT measurements [10] which showed a rapid proton transfer leading to complete dissociation according to

$$CH_5^+ + SF_6 \rightarrow (SF_6H^+)^* + CH_4 \quad (6a)$$

$$\hookrightarrow SF_5^+ + HF \quad (6b)$$

The origin of the SF_3^+ remains uncertain, although it may arise, at least in part, by direct dissociative ionization of SF_6. Both SF_3^+ and SF_5^+ appeared to react with the added C_6H_5X, presumably by charge-, halide- or hydride-transfer. Preliminary SIFT measurements [10] have indicated a fast reaction between SF_5^+ and C_6H_5Cl which is dominated by charge transfer with a minor contribution by halide transfer.

Equilibrium-constant measurements

Operation of the source in the pulsed mode allowed the ion chemistry to be followed as a function of time. In particular, with two halobenzenes added in an appropriate ratio, it became feasible to monitor the approach to and attainment of equilibrium between the two corresponding protonated halobenzenes coupled by the proton-transfer reaction (1) as has been shown previously by other workers using this method. Figure 4 shows the variation of ion intensities with reaction time for a mixture containing C_6H_5F and

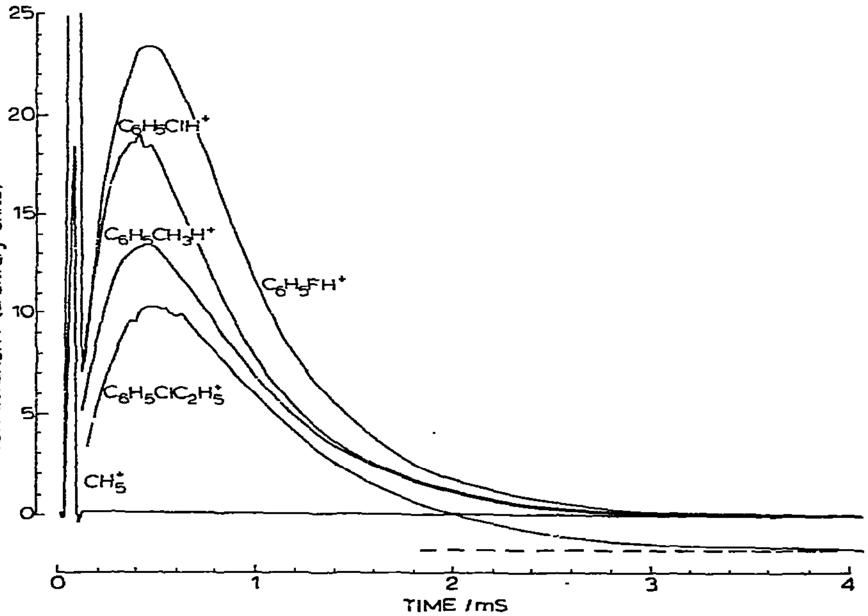

Fig. 4. Profiles of ion intensity versus reaction time recorded in the pulsed mode for a mixture of C_6H_5Cl and C_6H_5F in CH_4 (and SF_6) at 382 K and a total pressure of 1.2 torr. $[C_6H_5Cl]/[C_6H_5F] = 1/0.5185$, pulse width = 40 μs.

C_6H_5Cl in the molar ratio of 0.519 to 1, at 382 K. The intensity of the protonated halobenzenes rises quickly at the expense of CH_5^+ and then decays as a result of ambipolar (ion—ion) diffusion and ion—ion recombination. During their formation and throughout their decay the halobenzenes remain coupled through the proton-transfer reaction

$$C_6H_5ClH^+ + C_6H_5F \rightleftharpoons C_6H_5FH^+ + C_6H_5Cl \qquad (7)$$

The $C_6H_5CH_3H^+$ which arises from reactions (3) and (4) does not enter into this couple due to its lower activity, viz. proton transfer to C_6H_5F or C_6H_5Cl is endoergic at this temperature. The cluster ion $C_2H_5^+ \cdot C_6H_5Cl$ arises from $C_2H_5^+$ as described previously. The concomitant depletion of C_6H_5Cl is negligible because of its much higher concentration.

Chemical equilibrium was assumed to be achieved for reaction (7) when the "raw" ratio of ion signal intensities $I_{C_6H_5FH^+}/I_{C_6H_5ClH^+}$ became independent of time. The equilibrium constant was then determined from the expression

$$K = I_{C_6H_5FH^+}[C_6H_5Cl]/I_{C_6H_5ClH^+}[C_6H_5F] \qquad (8)$$

No corrections were applied to eliminate sampling errors which may be associated with the escape of ions through the exit slit of the ion source. The measurements were repeated at 334 K over a range of total pressures from 1.15 to 2.96 torr for concentration ratios $[C_6H_5Cl]/[C_6H_5F]$ of 1.23 and 4.41. Seven measurements provided a mean value of 1.73 within the maximum limits of ±0.10. This is reasonably representative of the results obtained for the following additional proton-transfer reactions investigated at 334 ± 2 K:

$$C_6H_7^+ + C_6H_5F \rightleftharpoons C_6H_5FH^+ + C_6H_6 \qquad (9)$$

$$C_6H_7^+ + C_6H_5Cl \rightleftharpoons C_6H_5ClH^+ + C_6H_6 \qquad (10)$$

$$C_6H_5ClH^+ + C_6H_5Br \rightleftharpoons C_6H_5BrH^+ + C_6H_5Cl \qquad (11)$$

$$C_6H_5BrH^+ + C_6H_5F \rightleftharpoons C_6H_5FH^+ + C_6H_5Br \qquad (12)$$

In these studies the total pressure was varied from 1.1 to 3.0 torr and the ratio of neutral concentrations was varied for each system by at least a factor of 2 and up to a factor of 9.

Reactions (7), (9) and (10) were also investigated as a function of temperature over as wide a range and at as many temperatures as possible. The results are shown in the form of van't Hoff plots in Fig. 5. The van't Hoff plots are of reasonably good quality. A least-squares analysis of the equilibrium constants (or average values) determined at the various temperatures indicated a probable error [11] of less than 6% in the slopes and intercepts. Reaction (7) was investigated at 15 temperatures between 310 and 541 K at total pressures in the range 0.87—3.34 torr with $[C_6H_5Cl]/[C_6H_5F]$ having values between 0.795 and 4.41. For reaction (9) equilibrium constants were

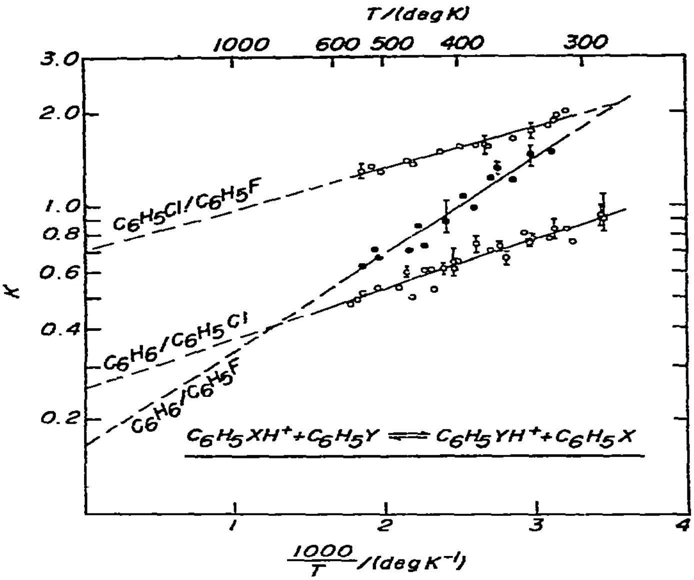

Fig. 5. Measured variation of the equilibrium constants with temperature. The vertical bars represent the range in values at a specific temperature. The straight lines through the points were arrived at by the method of least squares.

measured at 14 temperatures between 321 and 539 K at total pressures from 1.06 to 3.39 torr with $[C_6H_6]/[C_6H_5F]$ = 0.793 and 1.26. Finally, reaction (10) was measured at 27 temperatures between 288 and 568 K at total pressures from 1.00 to 3.25 torr with $[C_6H_6]/[C_6H_5Cl]$ having values between 0.335 and 1.57.

The equilibrium constants derived for reactions (7) and (9)—(12) at 334 K are included in Fig. 6. They are estimated to be accurate to within ±30%, this being the maximum deviation from the average encountered. The degree of internal consistency may be appreciated from a comparison of single-step

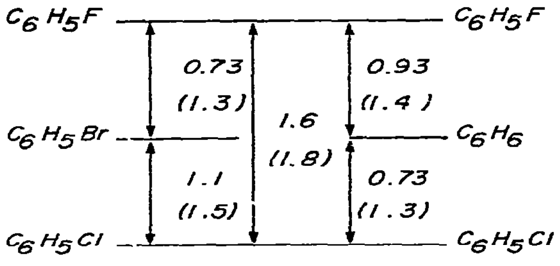

Fig. 6. Relative acidities of benzene and halogenated benzenes at 334 K. The preferred direction of proton transfer is towards the top. The standard free-energy change (in kJ mol^{-1}) is given, along with the equilibrium constant (in parentheses).

TABLE 1

A comparison of thermochemical quantities [a] determined for proton-transfer equilibria of the type $XH^+ + Y \rightleftharpoons YH^+ + X$

X, Y	HPMS [b]	ICR [c]	This study
$X = C_6H_6$, $Y = C_6H_5F$			
$-\Delta H^0$	5.4	3.4	5.9 ± 1.5
$-\Delta S^0$	15 ± 1	11 ± 1	15 ± 2
$X = C_6H_6$, $Y = C_6H_5Cl$			
$-\Delta H^0$	4.6	2.1	3.0 ± 0.8
$-\Delta S^0$	14 ± 1	9.2 ± 2.9	11 ± 2
$X = C_6H_5Cl$, $Y = C_6H_5F$			
$-\Delta H^0$			2.5 ± 0.6
$-\Delta S^0$			2.8 ± 1.0

[a] ΔH^0 in units of kJ mol^{-1} and ΔS^0 in units of J mol^{-1} deg^{-1}.
[b] High-pressure mass spectrometry, ref. 3.
[c] Ion cyclotron resonance spectrometry, ref. 4.

with double-step measurements. Good agreement is obtained between the values $K_9K_{-10} = 1.4 \times 1.3 = 1.8$, $K_{11}K_{12} = 1.5 \times 1.3 = 1.9_5$, and $K_7 = 1.8$, as is to be expected if the measured values correspond to true equilibrium constants.

Changes in thermodynamic-state properties

Figure 6 gives the standard free-energy changes at 334 ± 2 K derived from the measured equilibrium constants using the relationship *

$$\Delta G^0 = -RT \ln K \qquad (13)$$

These establish the gas-phase basicity order $C_6H_5F > C_6H_5Br, C_6H_6 > C_6H_5Cl$ at 334 K which spans a range of only ~1.7 kJ mol^{-1}. The van't Hoff plots in Fig. 5 show this order to be quite sensitive to temperature, changing to $C_6H_6 > C_6H_5Cl > C_6H_5F$ above ~850 K and to $C_6H_5F > C_6H_5Cl > C_6H_6$ below 270 K. The maxim that halosubstituents decrease the basicity of benzene is upheld only above a temperature of 400 K at which there is a reversal in the relative basicity of benzene and fluorobenzene. The basicity of benzene exceeds that of chlorobenzene already at 270 K. Below this temperature fluorination and chlorination will *increase* the basicity of benzene.

The standard enthalpy and entropy changes derived from the van't Hoff plots are given in Table 1 together with estimates of the associated uncertainties which were arrived at from a consideration of the extreme values of the slopes and intercepts which can be reasonably accommodated by the data.

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* The standard state is here defined as 1 atmosphere pressure at the specified temperature *T*.

The standard enthalpy changes indicate a proton affinity order $C_6H_5F > C_6H_5Cl > C_6H_6$, which appears to be independent of temperature in the temperature range of the measurements (the van't Hoff plots appear to be linear). It is interesting to note that this proton affinity order corresponds to the basicity order only at temperatures below 270 K, at which $T\Delta S^0$ becomes sufficiently small for both ΔH^0 and ΔG^0 to exhibit the same sign. Clearly, when dealing with compounds that have very similar basicities, as is the case here, caution should be exercised in the interpretation of basicities (and their order) as of proton affinities (and their order) when these are based on equilibrium-constant measurements carried out at only a single temperature, and it is imperative that the temperature be clearly defined and specified in any report of an order or a scale of basicities.

Table 1 contains a comparison with results obtained by Lau and Kebarle [3] in a manner similar to this study and by Hartmann and Lias [4] using an ICR spectrometer at much lower total pressures ($\sim 10^{-6}$ torr) and a somewhat narrower temperature range (320—400 K). The agreement with Kebarle's results is quite good in the case of reaction (9) for which the corresponding van't Hoff plots are nearly parallel, with similar values of equilibrium constants. For reaction (10) Kebarle's van't Hoff plot intersects the plot determined in this study but again absolute values agree within experimental error over the entire temperature range. The agreement with the ICR results is less satisfactory but still probably within the experimental error of the two techniques. For both reactions (9) and (10) (reaction (10) was investigated at only two temperatures in the ICR study), the ICR values for the equilibrium constants are consistently lower and suggest a more gradual dependence on temperature.

Reaction (7) was investigated only in the present study for which it provides an additional check for internal consistency, albeit that unknown systematic errors possibly introduced in the measurement of ion concentration ratios and thus in the determination of ΔS^0 are not precluded. Nevertheless, the agreement between the following quantities is satisfying:

$$\Delta H_9^0 - \Delta H_{10}^0 = 5.9 - 3.0 = 2.9, \quad \text{and} \quad \Delta H_7^0 = 2.5 \text{ kJ mol}^{-1} \tag{14}$$

$$\Delta S_9^0 - \Delta S_{10}^0 = 15 - 11 = 4, \quad \text{and} \quad \Delta S_7^0 = 2.8 \text{ J deg mol}^{-1} \tag{15}$$

Entropy and site(s) of protonation

Protonation of the halogenated benzenes can be envisaged to occur at either the halogen substituent or the *meta*, *ortho* or *para* positions on the ring. While the experimental enthalpy-changes do not provide direct information regarding the preferred site of protonation, some insight into the site(s) of protonation may be gained from a consideration of the changes in entropy associated with the proton-transfer reactions investigated. For example, Lau and Kebarle [3] have shown that the value for $\Delta S^0 = -15 \pm 1$ J mol^{-1} deg^{-1} determined by them for the protonation of both fluoro- and chloro-benzene by $C_6H_7^+$, was that expected from essentially exclusive protonation at the *para* position. The expected ΔS^0 was taken to be that associated with the changes in rotational symmetry numbers associated with these two reactions, according to

$$\Delta S^0 \simeq \Delta S^0_{\mathrm{rot}} \simeq R \ln[(\sigma_{\mathrm{AH^+}}\sigma_{\mathrm{B}})/(\sigma_{\mathrm{BH^+}}\sigma_{\mathrm{A}})] \qquad (16)$$

where σ represents the external symmetry number, A represents benzene, and B represents the halogenated benzene. Translational entropies and moments of inertia were assumed to cancel. Protonation at the *para* position leads to the highest symmetry in BH^+ ($\sigma_{BH^+} = 2$) and therefore to the most negative change in entropy, viz. —9.1 J mol^{-1} deg^{-1} for $\sigma_A = 12$, $\sigma_B = 2$, and $\sigma_{AH^+} = 2$. Protonation at any other position on the ring (*ortho* or *meta*) or on the halogen results in a lower symmetry in BH^+ and a less negative change in entropy, viz. —9.1 mol^{-1} deg^{-1} for $\sigma_{BH^+} = 1$. The results obtained in the present study require only a slight modification to this picture. In the case of fluorobenzene our measurements indicate the same change in entropy as that determined by Lau and Kebarle [3] and so lead to the same conclusion regarding its site of protonation by $C_6H_7^+$. But for chlorobenzene our measurements indicate a change in entropy of —11 ± 2 J mol^{-1} deg^{-1} which implies that the protonation now also occurs to some degree at one or more of the three other positions (*ortho*, *meta*, or Cl). A similar conclusion can be reached from the entropy of —2.8 ± 1.0 J mol^{-1} deg^{-1} determined for the proton transfer from protonated chlorobenzene to fluorobenzene (which is very similar to the difference of —4.0 J mol^{-1} deg^{-1} between the entropy changes associated with the protonation of the two halogenated benzenes by $C_6H_7^+$). A value of 0 would result from protonation of chlorobenzene exclusively at the *para* position while a value of —5.8 would pertain to complete protonation at non-*para* positions.

Hartmann and Lias [4] have recently proposed that a contribution to the entropy change in these ion—molecule reactions arises from the modification of the rotational energy of the molecule owing to the approach of the ion. The contribution is calculated from the ratio of the forward and reverse collision rate constants. For the protonation by $C_6H_7^+$ of C_6H_5F and C_6H_5Cl it amounts to +2.1 J mol^{-1} deg^{-1}, respectively. The overall entropy changes predicted for these two reactions are then —12.6 and —11.7 J mol^{-1} deg^{-1}, respectively, when protonation is assumed to proceed exclusively at the *para* position. Since protonation at the *para* position results in the most negative values for ΔS^0, the Hartmann and Lias model cannot account for the lower experimental value of —15 J mol^{-1} deg^{-1} obtained by Lau and Kebarle [3] for both reactions and in this study for the protonation of fluorobenzene. On the other hand, Hartmann and Lias [4] find their experimental values (see Table 2) to be in agreement with their predictions. But it should be pointed out that the measurements of Hartmann and Lias were carried out only at a very limited number of temperatures over a narrow temperature range. The experience gained in the present study suggests that both the number of temperatures and the temperature range accessible in these ICR measurements were not sufficiently adequate for a definitive determination of ΔS^0. Also the theoretical approach to the calculation of entropy changes adopted by Hartmann and Lias has recently been questioned [12].

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