in Table I. The new thermodynamic information provided by this work is the dT/dP values for the pretransition and subtransition (Table I). The three phase boundaries in the P, T diagram shown in Figure 3 have similar slopes. In the case of the GI \rightarrow GII transition, the 1-atm intercept is in full agreement with T_t observed by DSC.¹⁴ The GII \rightarrow GIII transition extrapolates to $T_t = -12$ °C at 1 atm, which is considerably higher than the value inferred from Raman scattering.¹⁷

The Clausius-Clapeyron equation $dT/dP = T_t \Delta V / \Delta H$ is used to calculate the volume changes ΔV accompanying first-order phase transitions from measured dT/dP, T_t , and ΔH values. Table I shows that both enthalpy and volume changes are much smaller between gel phases compared to the main $LC \rightarrow GI$ transition. Independent densitometry measurements yield ΔV values for the main and pretransition which agree well with the present work (Table I).^{fi}

Conclusion

The fluorescence intensity ratio method has been used to study the thermotropic behavior of dilute DMPC dispersions. Intramolecular excimer formation appears more sensitive than fluorescence depolarization to gel-gel phase transitions.¹¹⁻¹³ The observed high-pressure phase boundaries are in agreement, where comparison can be made at 30 °C, with the results from Raman scattering.^{5,10} As in Raman,^{5,10,19} the I_M/I_E discontinuities show

that the GII \rightarrow GIII transition is more clearly defined than the $GI \rightarrow GII$ transition, consistent with the assignment of a major structural transition to the GII \rightarrow GIII subtransition and a minor step increase in trans conformers to the GI \rightarrow GII pretransition.¹⁵ We conclude that the perturbation induced by the probe molecule is negligible with respect to the location of structural bilayer transformations. The structural identity of the different phases must come from other methods, but the determination of their boundaries and potentially, the transition kinetics, will be a convenient application of intramolecular excimer probes.

The salient results is that dT/dP for gel transitions are similar in value to the main $(LC \rightarrow GI)$ transition in DMPC. Therefore, low enthalpy transitions are accompanied by low volume changes. This generalization should serve as a useful guide for the mapping of phospholipid phase diagrams, especially at low temperatures and high pressures.

The molecular mechanism responsible for $I_{\rm M}$ and $I_{\rm E}$ changes at gel-gel transitions is unknown. The fluidity perspective is not applicable for gel polymorphism, despite contrary discussion.^{1,20} It is equally evident that the dynamic behavior of intramolecular excimers contains additional information about conformational trapping and quenching. However, important clues about structural rearrangements cannot be obtained from the excitedstate kinetics until tested in homogeneous fluid, liquid crystalline, and crystalline phases.

The Proton Affinity of CS

D. Smith* and N. G. Adams

Department of Space Research, University of Birmingham, Birmingham B15 2TT, England (Received: June 26, 1985)

We have studied the reactivity of HCS⁺ ions with several molecules at 300 K using a SIFT apparatus. The measured rate coefficients for the proton-transfer reactions of HCS⁺ with C₂H₃OH and CH₃SH are appreciable fractions of their respective collisional rate coefficients and from this we deduce that the proton affinity of CS is 188.2 ± 1 kcal mol⁻¹. This value differs from the literature value by some 13 kcal mol⁻¹ but is in close agreement with a very recent theoretical value.

Introduction

The selected ion flow tube (SIFT) has become a most valuable experimental tool for the study of ion-neutral reactions under thermal conditions. Since its inception we, and others, have exploited it to determine the rate coefficients and product ion distributions for a large number of reactions,¹ including many considered to be important in the synthesis of interstellar molecules.² SIFT experiments are also being performed to provide thermochemical data relating to gas-phase ions (see below). Much of the available data is being used in detailed ion-chemical schemes which can now correctly model the relative densities of many interstellar molecular species.^{3,4} However, a long-standing problem has been the inability of the schemes to correctly model the observed HCS⁺/CS abundance ratio. In considering this problem (which we now believe to be resolved⁵), we carried out TABLE I: Experimental Rate Coefficients, k, Measured at 300 K for the Proton-Transfer Reactions of HCS⁺ with a Series of Molecules, M, and Colisional Rate Coefficients, k_c, Calculated for 300 K Using the ADO Theory^a

М	PA (M), ^b kcal mol ⁻¹	$k, cm^3 s^{-1}$	$k_c,$ cm ³ s ⁻¹
NH ₃	204.0	2.0×10^{-9}	1.82×10^{-9}
CH ₁ COCH ₁	196.7	2.4×10^{-9}	2.40 × 10 ⁻⁹
С, Н, ОН	188.3	8.2×10^{-10}	1.75×10^{-9}
CH ₃ SH	187.4	4.5×10^{-10}	$\simeq 1.6 \times 10^{-9}$
HCN	171.4	$<1 \times 10^{-12}$	2.62×10^{-9}
H ₂ S	170.2	$<1 \times 10^{-12}$	1.35×10^{-9}

"Reference 18. Also HCS⁺ does not react with H₂CO, H₂O, CH₄, CO₂, CO, O₂, N₂, and H₂. ^bLiterature values.⁷

a SIFT study of the reactions of HCS⁺ with several known interstellar molecules. This study showed that HCS⁺ is a relatively unreactive ion, a result which is consistent with its relatively large abundance in interstellar clouds. Moreover, the observation that

⁽¹⁶⁾ Heremans, K. Rev. Phys. Chem. Jpn. 1980, 50, 259.
(17) Wong, P. T. T.; Mantsch, H. H. Can. J. Chem. 1982, 60, 2137.
(18) Nagle, J. F.; Wilkinson, D. A. Biophys. J. 1978, 23, 159.

⁽¹⁹⁾ Wong, P. T. T.; Mantsch, H. H. J. Phys. Chem. 1985, 89, 883. (20) Viriot, M. L.; Guillard, R.; Kauffman, I.; Andre, J. C.; Siest, G. Biochim. Biophys. Acta 1983, 733, 34.

⁽¹⁾ N. G. Adams and D. Smith in "Reactions of Small Transient Species",

A. Fontijn and M. A. A. Clyne, Ed.; Academic Press, London, 1983, p 311.
 (2) D. Smith and N. G. Adams, Int. Rev. Phys. Chem., 1, 271 (1981). (3) T. J. Millar and A. Freeman, Mon. Not. R. Astron. Soc., 207 405 (1984).

⁽⁴⁾ C. M. Leung, E. Herbst, and W. F. Huebner, Astrophys. J., Suppl. Ser., 56, 231 (1984).

⁽⁵⁾ T. J. Millar, N. G. Adams, D. Smith, and D. C. Clary, Mon. Not. R. Astron. Soc., in press.

Letters

HCS⁺ does not undergo proton-transfer reactions with certain molecules indicates that the proton affinity (PA) of CS is significantly greater than the literature value.^{6,7}

Experimental Section

The SIFT technique has been described in detail elsewhere.^{8,9} It is sufficient to say here that the HCS⁺ ions were generated in an electron impact ion source (containing a mixture of CS_2 and H₂) and then injected into a helium carrier gas which transports the ions along a flow tube toward a downstream mass spectrometer detection system. The ions rapidly translationally and rotationally thermalize in the helium. To check for any residual vibrational excitation in the HCS⁺ ions, the CS₂ and H₂ source gas pressures were varied over as wide a range as possible and the reactivity of the ions was investigated with those species for which proton transfer is endothermic (see Table I). No variation in reactivity was observed for any CS_2/H_2 source pressure indicating that no significant vibrational excitation of the HCS⁺ existed in those ions that reached the downstream reaction zone of the SIFT. This procedure has been used to detect residual vibration excitation in, for example, H_3^+ ions¹⁰ and N_2^+ ions.¹¹ Reactant gases were added to the helium carrier gas/HCS+ swarm and rate coefficients determined and product ions identified in the usual way.^{9,12} All the measurements were made at 300 K.

Results and Discussion

The results of this study are summarized in Table I. The only observed reaction process was proton transfer, e.g.

$$HCS^{+} + M \rightarrow MH^{+} + CS \tag{1}$$

Proton transfer can occur if the gas-phase basicity (GB) of the reactant molecule (M) exceeds that of CS, i.e., if, in reaction 1, GB(M) > GB(CS). If the entropy change in the reaction, ΔS , is zero, then the reaction can proceed if the proton affinity (PA) of the reactant molecule exceeds that of CS, i.e., if PA(M) >PA(CS). ΔS can generally be estimated for proton-transfer reactions from a consideration of rotational symmetry numbers⁷ and it is indeed often zero or quite small for such reactions. The reactions of HCS⁺ with NH₃ and CH₃COCH₃ were fast, i.e., the measured rate coefficients, k, were essentially equal to the respective collisional rate coefficients, k_c , as is usual for appreciably exothermic proton-transfer reactions.¹³ Conversely, no reaction

- (12) N. G. Adams and D. Smith, J. Phys. B, 9, 1439 (1976).

(13) D. K. Bohme in "Interactions between Ions and Molecules", P. Ausloos, Ed., Plenum, New York, 1975, p 489.

occurred between HCS⁺ and HCN (or H₂S). This brackets PA(CS) between $PA(CH_3COCH_3)$ and PA(HCN) which are given in the most recent data compilation⁷ as 196.7 and 171.4 kcal mol^{-1} respectively, consistent with the literature value for PA(CS) of 175 kcal mol^{-1,6,7} However, HCS⁺ reacts with both C_2H_5OH and CH_3SH , the measured k being appreciable fractions of the respective k_c . This indicates that PA(CS) is close to PA(C₂H₅OH) and PA(CH₃SH), being only slightly greater than the latter (since the ΔS of these reactions is close to zero). We can estimate the ΔH° for these reactions using the relationship $k \sim k_{\rm c}/2$. $\exp(-\Delta H^{\circ}/RT)$, in which we assume that reaction would proceed at half the collision rate if it were thermoneutral. Thus for the C_2H_5OH reaction, $\Delta H^{\circ} \sim 0.04$ kcal mol⁻¹, and for the CH₃SH reaction, $\Delta H^{\circ} \sim 0.35$ kcal mol⁻¹. Therefore PA(CS) is indicated to be within the range 188.4 to 188.0 kcal mol⁻¹, having a mean value of 188.2 kcal mol⁻¹ with a maximum estimated uncertainty of ± 1 kcal mol⁻¹. We are gratified to find that a recent calculation indicates the *absolute* value of PA(CS) to be 189.5 kcal mol⁻¹ with a maximum uncertainty of ± 1.2 kcal mol⁻¹,¹⁴ which is clearly in excellent agreement with our derived value. This gives great credence to the calculated value of PA(CS), the value of PA-(C₂H₅OH) previously established by experiment, and our current procedure.

Measurements of both forward and reverse rate coefficients for nearly thermoneutral ion-neutral reactions are generally straightforward using a SIFT apparatus and especially valuable if the SIFT is temperature variable. Thus the technique is very useful for determining equilibrium constants for bimolecular reactions. Its value therefore in ordering proton affinities and determining enthalpy and entropy changes in ion-neutral reactions is obvious. We have exploited our variable-temperature SIFT to great effect in this regard.¹ Quite recently, we have determined, using this approach, $PA(H_2) - PA(O_2)$ to be 0.33 kcal mol^{-1,15} and PA(CO) - PA(HCl) to be 2.7 kcal mol^{-1.16} This latter value is much smaller than the literature difference of 7.1 kcal mol^{-1} . Also, by studying the nearly thermoneutral reaction $N^+ + H_2 \rightarrow$ NH⁺ + H in our selected ion flow drift tube (SIFDT), we have determined the *absolute* PA of N atoms to be 81.4 kcal mol^{-1.17} This absolute PA(N) and the absolute PA(CS) provided by theory and supported by experiment are valuable reference points in the determination of an absolute proton affinity scale for atoms and molecules.

Acknowledgment. We are grateful to Dr. T. J. Millar for valuable discussions. We are also grateful to the United States Air Force and to the Science and Engineering Research Council for financial support.

- (16) D. Smith and N. G. Adams, Astrophys. J., in press.
 (17) N. G. Adams and D. Smith, Chem. Phys. Lett., 117, 67 (1985).
- (18) T. Su and M. T. Bowers in "Gas Phase Ion Chemistry", Vol. 1, M. T. Bowers, Ed., Academic Press, New York, 1979, p 84.

⁽⁶⁾ T. McAllister, Astrophys. J., 225, 857 (1978)

⁽⁷⁾ S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data, 13, 695 (1984).

⁽⁸⁾ N. G. Adams and D. Smith, Int. J. Mass Spectrom. Ion Phys., 21, 349 (1976).

⁽⁹⁾ D. Smith and N. G. Adams in "Gas Phase Ion Chemistry", Vol. 1, M. T. Bowers, Ed., Academic Press, New York, 1979, p 1.
(10) N. G. Adams and D. Smith, Astrophys. J., 248, 373 (1981).
(11) D. Smith and N. G. Adams. Phys. Rev. A, 23, 2327 (1981).

⁽¹⁴⁾ P. Botschwina and P. Sebald, J. Mol. Spectrosc., 110, 1 (1985). (15) N. G. Adams and D. Smith, Chem. Phys. Lett., 105, 604 (1984).