International Journal of Mass Spectrometry and Ion Processes, 117 (1992) 387-394
Elsevier Science Publishers B.V., Amsterdam

On the protonation and proton affinity of SF_6*

G.I. Mackay,[1] H.I. Schiff and D.K. Bohme
Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ont. M3J 1P3 (Canada)

(First received 21 January 1992; in final form 30 March 1992)

ABSTRACT

The kinetics of the protonation of SF_6 were examined in a combined flowing afterglow/selected-ion flow tube study of the reactions of H_3^+, CH_5^+, N_2OH^+, HCO^+, $C_2H_7^+$, $C_2H_5^+$, and H_3O^+ with SF_6 in hydrogen carrier gas at pressures in the range 0.20–0.46 Torr and at a temperature of 298 ± 2 K. Production of SF_6H^+ was observed, but only as a minor (1%) channel in the reaction of HCO^+ with SF_6. Otherwise SF_5^+ was observed as the dominant product ion. The proton affinity (PA) of SF_6 was derived from the observed reactivities and non-reactivities with SF_6 to be 138 ± 3 kcal mol^{-1}. The low rate coefficient for the reaction of HCO^+ with SF_6, $k = 5.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, was used to derive a value for PA(SF_6) of 137 ± 1 kcal mol^{-1} which is the value recommended for adoption.

Keywords: SF_6; proton affinity; kinetics; flowing afterglow; SIFT.

INTRODUCTION

Reactions of protonated molecules with SF_6 have attracted attention only recently and largely in connection with the formation of the ion SF_5^+. About 5 years ago, in a study of the appearance energy of SF_5^+, Tichy et al. [1] reported the occurrence of reaction 1

$$HCl^+ + SF_6 \rightarrow SF_5^+ + HF + Cl \qquad (1)$$

in which SF_5^+ is the only observed product ion. Reaction 1 was found to be rapid, $k_1 = (1.25 \pm 0.25) \times 10^{-9}$ cm^3 molecule^{-1}s^{-1}, and, because of the failure to observe SF_6H^+ as a product, F^- abstraction was assumed to be an alternative mechanism to proton transfer. The failure to observe the formation of SF_6H^+ in a subsequent study of the analogous reaction of HBr^+

Correspondence to: D.K. Bohme, Department of Chemistry, York University, North York, Ont. M3J 1P3, Canada.

* Dedicated to Professor Charles H. DePuy on the occasion of his 65th birthday.

[1] Present address: Unisearch Associates Inc., 222 Snidercroft Rd., Concord, Ont. L4K 1B5, Canada.

with SF_6, which was observed to proceed according to reaction 2

$$HBr^+ + SF_6 \rightarrow SF_5^+ + HF + Br \tag{2}$$

with a rate coefficient of $8 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, prompted Adams et al. [2] to propose that SF_6H^+ is not thermodynamically stable against decomposition to SF_5^+ and HF. With the assumption that the dissociation of SF_6H^+ into SF_5^+ and HF is exothermic, these authors deduced a value for the proton affinity (PA) of SF_6 of $\leqslant 127\,kcal\,mol^{-1}$ using eqn. 3

$$\begin{aligned}\Delta H &= PA(SF_6) + AE(SF_5^+/SF_6) + \Delta H_f(HF) - \Delta H_f(F) - \Delta H_f(H^+) \\ &= PA(SF_6) - 127\,kcal\,mol^{-1} \\ &\leqslant 0\end{aligned} \tag{3}$$

where $AE(SF_5^+/SF_6)$ is taken to be $322.4 \pm 0.7\,kcal\,mol^{-1}$ [1] and the standard enthalpies of formation of HF, F, and H^+ are taken from Lias et al. [3].

In a high pressure mass spectrometer study of the formation and reactivity of SF_5^+, Stone and Wytenberg [4] found that reaction 4

$$CH_5^+ + SF_6 \rightarrow SF_5^+ + HF + CH_4 \tag{4}$$

also generates SF_5^+ with the exclusion of SF_6H^+. These authors reported a rate coefficient of $1.5 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$ at two temperatures, 299 K and 380 K, in CH_4 buffer gas at 4.5 Torr, and concluded from this observation that the basicity of SF_6 is equal to or greater than the basicity of CH_4. Since basicity is defined as the standard free energy change for the removal of a proton from a protonated molecule, this conclusion is based on the assumptions that reaction 4 proceeds by dissociative proton transfer and that the standard free energy change ΔG° is $\leqslant 0$ for the proton transfer which precedes dissociation. Stone and Wytenberg also refer to a communication from T.B. McMahon that reaction 4 was observed to occur at every collision in a Fourier transform ion cyclotron resonance (FT-ICR) cell at 10^{-9} Torr. From this latter observation they concluded that the proton transfer from CH_5^+ to SF_6 is also exothermic or thermoneutral and that consequently $PA(SF_6) \geqslant PA(CH_4)$. Since $PA(CH_4) = 130.0 \pm 1\,kcal\,mol^{-1}$ [2], this lower limit is slightly higher than the upper limit of $127\,kcal\,mol^{-1}$ reported by Adams et al. [2].

Still further reactions of protonated molecules with SF_6 have been observed by Petrie et al. [5] who report rate coefficients of $k_5 = 1.3 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$ and $k_6 = 1.2 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$ for reactions 5 and 6.

$$HCN^+ + SF_6 \rightarrow SF_5^+ + HF + CN \tag{5}$$

$$CNH^+ + SF_6 \rightarrow HNCF^+ + SF_5 \tag{6}$$

Again, SF_6H^+ was not observed as a product ion. Reaction 6 involves the low energy isomer of protonated CN, $PA(CN)_N \approx 142\,kcal\,mol^{-1}$ [5], and is interesting in that it does not produce either SF_5^+ or SF_6H^+. Possible mechanisms for reaction 6 include F-atom transfer or F^- transfer followed by charge transfer. It is also interesting to note that the failure to observe proton transfer in reaction 6 provides an upper limit of $\approx 142\,kcal\,mol^{-1}$ on the proton affinity of SF_6 if the entropy change is taken to be negligible.

So it appears that protonated SF_6 has not yet been observed experimentally, in spite of the many previous studies of reactions of SF_6 with protonated molecules under a variety of different experimental conditions. The protonated molecules which have been used so far have a range of proton affinities from PA(Cl) = 122 [3] to $PA(CN)_N \approx 142\,kcal\,mol^{-1}$ [5]. The studies of their reactivities suggest that the proton affinity of SF_6 lies somewhere between $PA(CH_4) = 130.0 \pm 1$ [2] and $PA(CN)_N \approx 142\,kcal\,mol^{-1}$ [5]. Here we report results of a systematic proton transfer bracketing study of $PA(SF_6)$ with a single instrument in which the chosen protonated reactant molecules have proton affinities lying in a wider range from 101 to $167\,kcal\,mol^{-1}$. The results of this study significantly reduce the uncertainty in the measured value for $PA(SF_6)$ and also provide the first direct evidence for the existence of SF_6H^+.

EXPERIMENTAL

The experiments were performed with a selected-ion flow tube (SIFT) apparatus which has been described in detail elsewhere [6]. The measurements were taken with the apparatus operating either in the SIFT mode [6] or in the more traditional flowing afterglow (FA) mode [7]. Hydrogen was used as the buffer gas at pressures in the range 0.20–0.46 Torr and the average gas velocity had values in the range $(7.2–7.7) \times 10^3\,cm\,s^{-1}$. The effective reaction length was 46 cm and the gas temperature was $298 \pm 2\,K$.

Reactions of SF_6 were investigated with seven protonated molecules: H_3^+, CH_5^+, N_2OH^+, HCO^+, $C_2H_7^+$, $C_2H_5^+$, and H_3O^+. All seven reactions were investigated with the apparatus operating in the SIFT mode. In this mode, the protonated molecules were generated by ion/molecule reactions either in the electron impact source with mixtures of H_2 and the gas to be protonated, or in the flow tube by selecting H_2^+ and adding the gas to be protonated upstream of the reaction region. The reactions of CH_5^+, HCO^+, and H_3O^+ with SF_6 were also studied in the FA mode. CH_5^+ and HCO^+ were produced simply by adding methane or carbon monoxide downstream of the ionizer and upstream of the reaction region. H_3O^+ was generated from the reaction of H_3^+ with water impurities in the hydrogen buffer gas. All reagent gases were of normal

TABLE 1

Rate coefficients (in units of $10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$) measured for proton transfer reactions of protonated molecules, XH^+, with SF_6 in hydrogen buffer gas at pressures in the range 0.20–0.46 Torr and at a temperature of 298 ± 2 K using the SIFT [6] and FA [7] techniques

Reaction of XH^+ with SF_6[a]	P.D.[b]	k_{exptl}[c]	k_c[d]	PA(X)[e]
$H_3^+ + SF_6 \rightarrow SF_5^+ + HF + H_2$	1.00	3.1	2.89	101.3 [10]
$CH_5^+ + SF_6 \rightarrow SF_5^+ + HF + CH_4$	1.00	1.1	1.27	130.0 [2]
$N_2OH^+ + SF_6 \rightarrow SF_5^+ + HF + N_2O$	1.00	0.34	0.845	137.3 [2]
$HCO^+ + SF_6 \rightarrow SF_5^+ + HF + CO$	0.99	0.0055	1.01	141.4 [11]
$\rightarrow SF_6H^+ + CO$	0.01			
$C_2H_7^+ + SF_6 \rightarrow$ products		$\leqslant 0.0005$	0.97	142.1 [12]
$C_2H_5^+ + SF_6 \rightarrow$ products		$\leqslant 0.0005$	1.01	162.6 [10]
$H_3O^+ + SF_6 \rightarrow$ products		$\leqslant 0.0005$	1.24	166.5 [10]

[a] Reactions are listed in order of increasing proton affinity of X.

[b] Product distribution for the reaction of HCO^+ was determined from the FA measurements.

[c] The accuracy of the experimental rate coefficients is estimated to be ± 30%. The precision of the measurements was better than ± 20%.

[d] The collision rate coefficients are calculated using the Langevin theory [8]. The polarizability of SF_6, 4.48 Å^3, was taken from ref. 9.

research grade. The data analysis and sources of uncertainty associated with the determination of rate constants have been described elsewhere [6,7].

RESULTS

The results of the measurements for the seven proton transfer reactions which were investigated are summarized in Table 1.The protonated reactant molecules cover a range of PAs from $PA(H_2) = 101.3$ to $PA(H_2O) = 166.5\,kcal\,mol^{-1}$ [10]. There is an obvious correlation between the magnitude of the reaction rate coefficient and the PA of the protonated reactant molecule—the rate coefficient decreases as the PA of the protonated reactant molecule increases. Figure 1 shows measurements made in the FA mode for the reaction of HCO^+ with SF_6 which was the only reaction for which SF_6H^+ was observed as a (minor) product ion. We should emphasize that the FA mode provided a much higher dynamic range for the decay of the reactant ion and the rise in the product ions than the SIFT mode because of the much higher initial reactant ion signal (higher by a factor of between 10^2 and 10^3). The SF_6H^+ ion was observed only in the FA mode; the dynamic range was too small to observe the production of SF_6H^+ from this reaction in the SIFT mode.

Our rate coefficient for reaction 4 is in agreement, within experimental

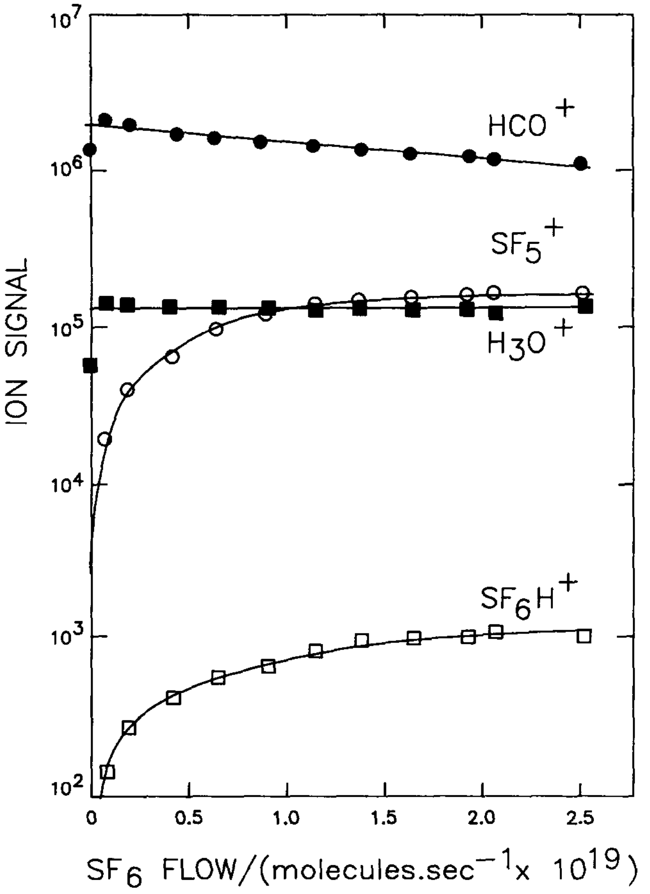

Fig. 1. Raw data accumulated for the reactions of HCO^+ and H_3O^+ with SF_6 using the FA technique. The buffer gas is hydrogen and the flow of CO is 1.22×10^{18} molecules s^{-1}. $P = 0.36$ Torr, $\bar{v} = 7.7 \times 10^3 \text{cm s}^{-1}$, $L = 46$ cm, and $T = 298$ K. The initial rise in the HCO^+ and H_3O^+ signals can be attributed to the change in diffusion from electron/ion to ion/ion as a consequence of the attachment of free electrons to the added SF_6.

error, with the value determined by Stone and Wytenberg [4] in the high pressure mass spectrometer study with CH_4 as a buffer gas.

DISCUSSION

Previous workers have assumed that the production of SF_5^+ in reactions of protonated molecules with SF_6 proceeds by dissociative proton transfer, reactions 7 and 8

$$XH^+ + SF_6 \rightarrow SF_6H^+ + X \quad (7)$$

$$SF_6H^+ \rightarrow SF_5^+ + HF \quad (8)$$

rather than by F^- transfer, viz. that proton transfer precedes dissociation of the SF_6H^+. This assumption can be justified on the basis of previous experience with other reactions which shows that proton transfer is facile when thermodynamically allowed [11], including the protonation of the related CF_4 molecule [2]. Our observation of SF_6H^+ as a product of the reaction of HCO^+ with SF_6 adds credence to this assumption. The mechanism is analogous to the protonation of ethane for which we have observed dissociation of $C_2H_7^+$ into $C_2H_5^+ + H_2$ [12].

The standard enthalpy change, ΔH°_{298}, for the proton transfer reaction 7 is related to the standard free energy change, ΔG°_{298}, and standard entropy change, ΔS°_{298}, according to relation 9 and to PAs according to relation 10

$$\Delta H^\circ_{298} = \Delta G^\circ_{298} + T\Delta S^\circ_{298} \tag{9}$$

$$\Delta H^\circ_{298} = \mathrm{PA(X)} - \mathrm{PA(SF_6)} \tag{10}$$

Accordingly, when $\Delta G^\circ_{298} \leqslant 0$ is used as the criterion for spontaneity, the observation of rapid proton transfer can be used to place a lower limit on the value of $\mathrm{PA(SF_6)}$ according to relation 11

$$\mathrm{PA(SF_6)} \geqslant \mathrm{PA(X)} - T\Delta S^\circ_{298} \tag{11}$$

Also, the failure to observe rapid proton transfer can be used to place an upper limit on $\mathrm{PA(SF_6)}$ according to relation 12 [11]:

$$\mathrm{PA(SF_6)} \leqslant \mathrm{PA(X)} - T\Delta S^\circ_{298} \tag{12}$$

Table 2 shows the limiting values derived for $\mathrm{PA(SF_6)}$ when the observed fast reactions of CH_5^+ and N_2OH^+ with SF_6 are taken to be exoergic for proton transfer and the observed slow reactions (or non-reactions) of HCO^+ and $C_2H_7^+$ are taken to be endoergic for proton transfer. Taken together, these results establish that $\mathrm{PA(SF_6)} = 138 \pm 3$ kcal mol^{-1}. We have adopted values of 130.0 ± 1 [2], 137.3 ± 1 [2], 141.4 ± 0.4 [11], and 142.1 ± 1.2 kcal mol^{-1} [12] for the proton affinities of CH_4, N_2O, CO, and C_2H_6 respectively. In the calculation of the change in standard entropy for reactions of type 7, the standard entropies of CH_5^+, N_2OH^+, HCO^+, and $C_2H_7^+$ were taken to be 50.4 ± 0.5, 57.3 ± 1.3, 48.04 ± 0.2, and 58 ± 3 cal mol^{-1} deg^{-1} [11]. The entropy of protonation of SF_6 was taken to be 6 ± 1 cal mol^{-1} deg^{-1} which is expected from the values for the entropy of protonation of other similar molecules [13].

The observed rate constant for the reaction of HCO^+ with SF_6 provides a second, independent method for deriving a value for $\mathrm{PA(SF_6)}$ given that $\Delta G^\circ_{298} = -RT\ln K$ where $K = k_f/k_r$. Expression 13

$$\mathrm{PA(SF_6)} - \mathrm{PA(CO)} - T\Delta S^\circ = -RT\ln(7.05 \times 10^{-10}/5.5 \times 10^{-12}) \tag{13}$$

becomes valid with the reasonable assumptions that the observed reaction of

TABLE 2

Thermochemical results for proton transfer and dissociative proton transfer reactions between protonated molecules XH^+ and SF_6[a]

XH^+	PA(X)[b]	$\Delta S°$	$T\Delta S°$	$\Delta G°$	$\Delta H°$	$PA(SF_6)$
CH_5^+	130.0 ± 1	0 ± 2	0 ± 1	$\leqslant 0$	$\leqslant 0 \pm 1$	$\geqslant 130 \pm 2$
		37 ± 1	11.1 ± 0.3	$\leqslant 0$	$\leqslant 11.1 \pm 0.3$	
N_2OH^+	137.3 ± 1	1 ± 2	0.3 ± 0.6	$\leqslant 0$	$\leqslant 0 \pm 0.6$	$\geqslant 137 \pm 2$
		39 ± 2	11.6 ± 0.6	$\leqslant 0$	$\leqslant 11.6 \pm 0.6$	
HCO^+	141.4 ± 0.4	5 ± 1	1.5 ± 0.3	$\geqslant 0$	$\geqslant 1.5 \pm 0.3$	$\leqslant 140 \pm 1$
		43 ± 1	12.8 ± 0.3	$\geqslant 0$	$\geqslant 12.8 \pm 0.3$	
$C_2H_7^+$	142.1 ± 1.2	3 ± 4	1 ± 1	$\geqslant 0$	$\geqslant 1 \pm 1$	$\leqslant 141 \pm 2$
		40 ± 4	12.1 ± 1.2	$\geqslant 0$	$\geqslant 12.1 \pm 1.3$	

[a] All thermochemical parameters are in kcal mol^{-1} except for $\Delta S°$ which is in cal mol^{-1} deg^{-1}. For each reaction the top line refers to the proton transfer reaction $XH^+ + SF_6 \rightarrow SF_6H^+ + X$, while the line below refers to the dissociative proton transfer reaction $XH^+ + SF_6 \rightarrow SF_5^+ + HF + X$.

[b] See text for references.

HCO^+ with SF_6 proceeds predominantly by dissociative proton transfer and that the thermodynamically preferred proton transfer between SF_6H^+ and CO proceeds at the collision rate, $k_c = 7.05 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. When $\pm 30\%$ is taken as the uncertainty in the measured rate constant and the values for $T\Delta S°$ and PA(CO) given in Table 2 are adopted, a value of 137 ± 1 kcal mol^{-1} results for $PA(SF_6)$. This value is, within experimental error, in agreement with, but more accurate than, the value obtained with the bracketing technique and so is the value which we recommend for adoption.

$PA(SF_6) = 137 \pm 1$ kcal mol^{-1} is intermediate between the lower limit of 130.0 ± 1 kcal mol^{-1} set by the observation of a fast proton transfer between CH_5^+ and SF_6 in the FT-ICR experiment of McMahon (referred to in ref. 4) and the upper limit of ≈ 142 kcal mol^{-1} set by the failure to observe proton transfer between CNH^+ and SF_6 in the SIFT experiments of Petrie et al. [5]. It exceeds the upper limit set by the proposal of Adams et al. [2] that the dissociation of SF_6H^+ into SF_5^+ and HF is exothermic. Our new value for $PA(SF_6)$ predicts that the dissociation of SF_6H^+ is endothermic by 10 ± 2 kcal mol^{-1} according to eqn. 3 but is exoergic by 1 ± 3 kcal mol^{-1}.

ACKNOWLEDGMENTS

D.K.B. is grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to the Canada Council for a Killam Research Fellowship. Valuable discussions with T.B. McMahon and J.A. Stone are also appreciated.

REFERENCES

1 M. Tichy, G. Javahery, N.D. Twiddy and E.E. Ferguson, Int. J. Mass Spectrom. Ion Processes, 79 (1987) 231.

2 N.G. Adams, D. Smith, M. Tichy, G. Javahery, N.D. Twiddy and E.E. Ferguson, J. Chem. Phys., 91 (1989) 4037.

3 S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, J. Phys. Chem., Ref. Data, 17 (1988) 1.

4 J.A. Stone and W.J. Wytenberg, Int. J. Mass Spectrom. Ion Processes, 94 (1989) 269.

5 S. Petrie, C.G. Freeman, M. Moet-Ner, M.J. McEwan and E.E. Ferguson, J. Am. Chem. Soc., 112 (1990) 7121.

6 (a) G.I. Mackay, G.D. Vlachos, D.K. Bohme and H.I. Schiff, Int. J. Mass Spectrom. Ion Phys., 36 (1980) 259.
(b) A.B. Raksit and D.K. Bohme, Int. J. Mass Spectrom. Ion Processes, 55 (1983) 69.

7 D.K. Bohme, R.S. Hemsworth, H.W. Rundle and H.I. Schiff, J. Chem. Phys., 58 (1973) 3054.

8 G. Gioumousis and D.P. Stevenson, J. Chem. Phys., 58 (1958) 294.

9 E.W. Rothe and R.B. Bernstein, J. Chem. Phys., 31 (1959) 1619.

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

11 D.K. Bohme, G.I. Mackay and H.I. Schiff, J. Chem. Phys., 73 (1980) 4976.

12 G.I. Mackay, H.I. Schiff and D.K. Bohme, Can. J. Chem., 59 (1981) 1771.

13 G. Javahery, J. Glosik, N.D. Twiddy and E.E. Ferguson, Int. J. Mass Spectrom. Ion Processes, 98 (1990) 225.