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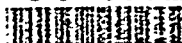
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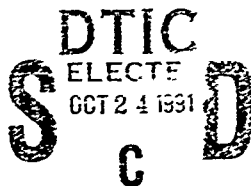
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30 September 1991

Ms. B. Green,
Department of the Air Force,
Air Force Office of Scientific Research (AFSC),
European Office of Aerospace Research and Development,
223/231 Old Marylebone Road,
LONDON NW1 5TH.



Dear Ms. Green,

Grant No. AFOSR 88-0122

I apologise for the delay in providing this information relating to grant AFOSR 88-0122 held by the late Professor Twiddy. I have, at last, received a short report for the period November 1988 - November 1990 from his final research student now based in Canada. I enclose this together with copies of reprints or manuscripts of 2, 3, 5, 7 and 8. I note that the title of 8 has been slightly modified in the publication. I regret that there are no reprints or manuscripts available for the others, but I am attempting to acquire them for you.

I also enclose the Report of Inventions and Subcontracts form, duly signed.

I regret that this final report on this grant is not altogether satisfactory. However, you will understand that the period in which it would normally have been prepared coincided with Professor Twiddy's final confinement in hospital, and there was no other member of staff involved to take charge of its preparation at that time.

Yours sincerely,

Lance Thomas

Lance Thomas.

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 91	3. REPORT TYPE AND DATES COVERED Final Scientific		
4. TITLE AND SUBTITLE Vibrationally Excited Ions: Quenching Reaction Enhancement, Lifetimes		5. FUNDING NUMBERS AFOSR-88 - 0122		
6. AUTHOR(S) Dr Lance Thomas				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University College of Wales, Aberystwyth Department of Physics Penglais Aberystwyth, Dyfed SY23 3BZ UK		8. PERFORMING ORGANIZATION REPORT NUMBER EOARD TR-91-10		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) European Office of Aerospace Research and Development, Box 14, FPO New York 09510-0200		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; Distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) 1. The evaluation and application of a SIFDT to the measurement of proton affinity differences. 2. The isomers of N_2CH^+ , energy separation and proton affinity 3. Radiative lifetimes of $HCl^+(v=1)$ and $DCl^+(v=1)$ 4. HBr^+ ion chemistry				
14. SUBJECT TERMS			15. NUMBER OF PAGES 2	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

Final summary report on USEOARD Grant AFOSR 88-D122
held by Professor N. D. Twiddy from November 1988 to November 1990.

This grant was used in part to finance a number of research projects carried out in the ion laboratory of the Physics Department, University College of Wales, Aberystwyth.

This research utilised the selected ion flow drift tube (SIFDT) and a modified selected ion flow tube (SIFT) and is summarised below:

1. The vibrational quenching rate of HCl^+ ($v = 1$) and DCI^+ ($v = 1$) ions in collision with Ar and Kr atoms at 300K was measured in order to investigate the effect of changing the vibrational and rotational energy levels while keeping the inter-molecular interaction potential unchanged. Measured vibrational quenching rate constants disproved the Landau-Teller type vibrational mechanism modelled for the molecular ion, modified by the existence of the attractive potential. [Ref. 1].
2. Determination of proton affinity differences in the range $\sim 130 - 140 \text{ Kcal mol}^{-1}$ established that the non-thermal selected ion flow tube (SIFDT) was a powerful tool for such measurements.

In conjunction with this work, similar, comparable studies were carried out by Professors David Smith and Nigel Adams at Birmingham University using VT SIFT and the results were further proof that the SIFDT could be used for the determination of proton affinity differences. [Refs. 2,3,4].
3. Vibrational radiative lifetimes (Einstein A coefficient) of positive ions were measured for the first time by modifying a selected ion flow tube (SIFT). This new method was demonstrated by the measurement of the lifetimes of HCl^+ ($v = 1$) and DCI^+ ($v = 1$). [Refs. 1,5,5].
4. The reactions of HBr^+ ions with various neutral ions was studied. The variation of rate constants with the centre of mass energy was investigated. This study clearly showed that the proton transfer reactions of HBr^+ with both CH_4 and CO_2 were endothermic, implying that the proton affinities of CH_4 and CO_2 are less than that of Br. The reaction with SF_6 was found to be fast, contrary to the available data on heats of formation which suggests that the reaction should be endothermic. [Refs. 7,10].
5. The measured rate constants for the reaction of N_2OH^+ with CH_4 and NO , as functions of central mass kinetic energy, established two isomeric forms of N_2OH^+ , HNNO and NNOH^+ . Reaction with CH_4 allowed a determination of the N-protonated N_2O as $131.5 \pm 1 \text{ kcal mol}^{-1}$, lying energetically above the O-protonated N_2O by $6.2 \pm 0.5 \text{ kcal mol}^{-1}$. This latter value should be compared to the recently obtained theoretical value of $7.1 \text{ kcal mol}^{-1}$. [Ref. 8,9].
6. The proton transfer equilibrium constant between He and Ne has been measured, using SIFT. This gives a very precise difference between their proton affinities (or dissociation energies). [Ref. 11].

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10. A review of Proton Affinity Scale in the Range 126-142 kcalmol⁻¹ using a non-thermal selected ion flow drift tube (SIFDT). M. Tichy, G. Javahery, N.D. Twiddy and E.E. Ferguson. Proc. Symp. on Atomic and Surface Physics (SASP), Obertraun, Austria, 1990.
11. Measurement of the Equilibrium constant for the Reaction $\text{HeH}^+ + \text{Ne} = \text{NeH}^+ + \text{He}$ in a selected flow tube. J. Glosik, N. D. Twiddy, G. Javahery and E.E. Ferguson. Int. J. Mass Spec. and Ion Proc. (in press).



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An absolute proton affinity scale in the ~ 130 – 140 kcal mol $^{-1}$ range

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(Received 20 December 1988; accepted 1 June 1989)

The dependences on temperature of the rate coefficients for the endothermic proton transfer reactions of HBr^+ with CO_2 and CH_4 have been obtained in a variable-temperature selected ion flow tube. The measurements have been used to determine the 300 K proton affinity of CO_2 , $\text{P.A.}(\text{CO}_2) = 128.5 \pm 1.0$ kcal mol $^{-1}$, utilizing the literature value of $\text{P.A.}(\text{Br}) = 131.8$ kcal mol $^{-1}$, obtained from the dissociation energy of HBr^+ , as a primary standard. The proton affinity difference between CO_2 and CH_4 has been substantiated by equilibrium constant measurements as a function of temperature for proton transfer between CO_2 and CH_4 . Similar equilibrium constant measurements have been used to determine the proton affinities of HCl , N_2O , HBr , and CO , giving a proton affinity ladder ordered (in kcal mol $^{-1}$) as $\text{CO}(141.4)$, $\text{HBr}(138.8)$, $\text{N}_2\text{O}(137.3)$, $\text{HCl}(133.0)$, $\text{Br}(131.8)$, $\text{CH}_4(130.0)$, and $\text{CO}_2(128.5)$. Proton affinities have also been determined for $\text{Br}_2(140.0)$, $\text{NO}(127.0)$, and $\text{CF}_4(126.5)$, the last two values being obtained from selected ion flow drift tube measurements. An upper limit to $\text{P.A.}(\text{SF}_6)$ of 127 kcal mol $^{-1}$ has been inferred from the instability of SF_6^+ towards dissociation into SF_5^+ and HF .

I. INTRODUCTION

During the course of studies at Aberystwyth of vibrational relaxation of hydrogen halide ions, it was observed that the proton transfer reactions of HBr^+ with both CH_4 and CO_2 are endothermic.¹ This shows that a recently proposed upward revision of the proton affinity scale in the 120–145 kcal mol $^{-1}$ range² is in error and indeed that the value of the proton affinity of CH_4 , $\text{P.A.}(\text{CH}_4) = 132$ kcal mol $^{-1}$ in the National Bureau of Standards (NBS) tables^{3,4} (which are currently the most widely used references on proton affinities and thermochemical data) is somewhat too large. In order to quantify the proton affinity differences among Br , CH_4 , and CO_2 , the dependences on temperature of the rate coefficients for endothermic proton transfer from HBr^+ to CH_4 and CO_2 have been measured using the variable-temperature selected ion flow tube in Birmingham. The problem in determining values of proton affinity is in setting the absolute scale since most laboratory measurements yield only relative proton affinities, these usually being obtained from equilibrium constant measurements. The proton affinity of Br provides a particularly useful reference point since it is related simply to the spectroscopically known dissociation energy of HBr^+ .⁵

With the availability of these new (smaller) values of $\text{P.A.}(\text{CH}_4)$ and $\text{P.A.}(\text{CO}_2)$, it was considered worthwhile to determine the equilibrium constants for a number of additional proton transfer reactions as a function of temperature, and this has led to revised values for the proton affinities of HCl , N_2O , HBr , and CO . This new P.A. ladder is believed (conservatively) to yield absolute proton affinities reliable

to ± 1 kcal mol $^{-1}$. One of the largest P.A. differences between the species included in this study is that between Br and CO . However, the P.A. of CO can also be considered as a primary standard since it can be determined from recently improved measurements of the heat of formation of HCO^+ and the adiabatic ionization potential of HCO^+ as $\text{P.A.}(\text{CO}) = 141.6$ kcal mol $^{-1}$. The value for $\text{P.A.}(\text{CO})$ derived from this study agrees with this within 0.2 kcal mol $^{-1}$, although both values have stated uncertainties of ± 1 kcal mol $^{-1}$.

An excellent review of the absolute proton affinity scale with comparisons between experiment and theory, discussion of the precision of various theoretical approaches, and discussion of certain conventions and nomenclature has recently been given by Dixon and Lias.⁶

II. EXPERIMENTAL

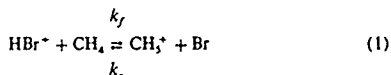
The thermal energy measurements were carried out using the Birmingham variable-temperature selected ion flow tube (SIFT) and some nonthermal measurements were made using the Aberystwyth selected ion flow drift tube (SIFDT). These techniques have been adequately described in the literature.^{9,10} The protonated reactant ions HX^+ were formed in high pressure electron impact ion sources containing mixtures of H_2 with the molecular gases X . It is known that resonant proton transfer reactions efficiently relax vibrationally excited ions to their ground vibrational states and the pressure in the ion source was sufficient to allow several collisions of the ions with their parent gas to occur before extraction. For the HBr^+ studies, only HBr was in-

roduced into the ion source. The ions were then injected into pure He carrier gas in which they kinetically and rotationally thermalized and the appropriate reactant gas was added downstream. In the case of the SIFT studies, the ion internal and kinetic energies were equilibrated at a mean energy determined by the ratio E/N , where E is the electric field applied to the reaction zone and N is the He carrier gas number density. This aspect of the operation of drift tubes has been discussed in many texts.¹¹ Rate coefficients were determined in the usual manner for both the SIFT and SIFT experiments. Rate coefficients for forward (k_f) and reverse (k_r) reactions were made under essentially identical conditions of carrier gas flow rate, pressure, and temperature with only the source gas X and the reactant gas being interchanged. Thus the equilibrium constants (i.e., the ratio of k_f and k_r) are subject to smaller errors than the absolute rate coefficients and are considered to be accurate to within $\pm 10\%$. Proton transfer was the only reaction process observed in all cases. Measurements were made at 300 K and at other temperatures up to 500 K.

III. RESULTS

In order to determine relative proton affinities, the dependence of the equilibrium constant K on temperature T needs to be determined. Then both the enthalpy ΔH and entropy ΔS changes can be derived from the slope and intercept, respectively, of a van't Hoff plot (according to the relation $\ln K = -\Delta G/RT = -\Delta H/RT + \Delta S/R$, where K can be either the experimental equilibrium constant or, equivalently, the ratio k_f/k_r).¹² The former is measured in relatively high pressure experiments and the latter in the lower pressure flow tube experiments. For a great deal of the available data in the literature, temperature dependences were not obtained. Only the values of K at room temperature were determined and values of ΔS were inferred from theoretical arguments in order to enable ΔH and thus the proton affinity differences to be determined.

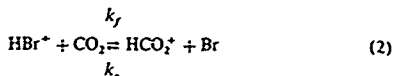
In the present study, for the two reactions of HBr^+ with CH_4 and CO_2 , it was not possible to measure the reverse rate coefficient for the reaction with Br, e.g.,



due to difficulties in producing Br atoms. In an unsuccessful attempt to do this, Br_2 was discharged in an excess of He using a microwave discharge. No evidence for dissociation was observed in spite of the numerous allowed transitions to repulsive Br_2 states.¹³ A large fractional dissociation would have been required to yield a quantitative value for $k_r(1)$. However, experiments using Br_2 (in the absence of the discharge) did yield the first value obtained for $P.A.(\text{Br}_2)$.

The dominant contribution to the temperature dependence of $K(1) [= k_f(1)/k_r(1)]$ is in $k_f(1)$, the rate coefficient for the endothermic reaction, which we have measured. Thus the problem is in not knowing the weak temperature dependence of $k_r(1)$ and therefore in not

approach to this problem is to use Arrhenius plots of k_f for reactions (1) and (2)



to determine the major contribution to the temperature dependence of K and then to estimate the maximum possible range of temperature dependences for the exothermic k_r and accept the uncertainty in this as the uncertainty in ΔH and hence the uncertainty in the proton affinity of CO_2 (or CH_4) relative to Br. This is an acceptable uncertainty and thus provides the basis for the present proton affinity scale.

From the Arrhenius plot of $\ln k_f(2)$ vs T^{-1} , shown in Fig. 1, we find that $k_f(2) = A_f \exp(-\Delta E_f/RT)$, where $A_f = 2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $\Delta E_f = 2.96 \pm 0.2 \text{ kcal mol}^{-1}$. Therefore $\Delta H(2) = \Delta E_f - \Delta E_r = 2.96 - \Delta E_r$, where ΔE_r describes the (unknown) temperature dependence of the exothermic reaction. The rate coefficients for exothermic proton transfer reactions are generally close to the collisional rate coefficients and exhibit little or no temperature dependence in the thermal energy regime. If k_r is temperature independent, then $\Delta H(2) = \Delta E_f = 2.96 \text{ kcal mol}^{-1}$. Alternatively, by inspection of the published data for a range of reactions, we estimate that the variation of k_r with temperature is a maximum of T^{-1} . This is equivalent to an effective $\Delta E_r = -0.55 \text{ kcal mol}^{-1}$ at 300 K, assuming again an Arrhenius-type expression for $k_r(2) = A_r \exp(-\Delta E_r/RT)$. Therefore we conclude that $\Delta H(2)$ lies between 3.0 and 3.5 kcal mol^{-1} and thus that $P.A.(\text{CO}_2) = P.A.(\text{Br}) - \Delta H(2)$ lies between 128.3 and 128.8 kcal mol^{-1} .

The rate coefficient $k_r(2)$ can be deduced from $A_f(2)$ and the entropy change for the reaction $\Delta S(2)$, as shown below. $\Delta S(2)$ can be equated to $S(\text{HCO}_2^+) + S(\text{Br}) - S(\text{HBr}^+) - S(\text{CO}_2) = (55.6 \pm 0.8) + 41.8 - 49.0 - 51.1 = -2.7 \pm 0.8 \text{ eu}$, where the S are standard entropy

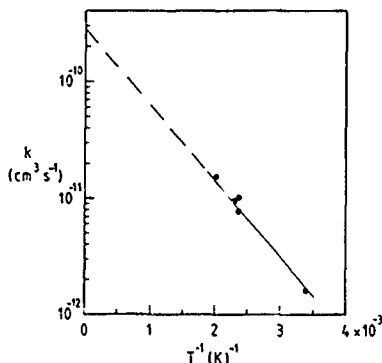


FIG. 1. An Arrhenius plot of the rate coefficient k vs reciprocal temperature T^{-1} , for the proton transfer from HBr^+ to CO_2 [reaction (2)] obtained from truly thermal SIFT data. The extrapolation to the ordinate gives an intercept which is consistent with that expected by modifying the Langevin collisional rate coefficient by a factor dependent on an entropy

pies and the dominant uncertainty is in $S(\text{HCO}_2^+)$.¹⁴ This gives, from above, a pre-exponential factor for k_2 , i.e., $A_2 = A_1 \exp(-\Delta S/R) = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ with limits between 7.5×10^{-10} and $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ by virtue of the uncertainty in $\Delta S(2)$ and thus k_2 can be obtained from $A_2 \exp(-\Delta E/RT)$. The Langevin collisional rate coefficient, k_L , which is $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, is actually a rather likely value for $k_2(2)$. This would correspond to $\Delta S = -2.0 \text{ e.u.}$, or $S(\text{HCO}_2^+) = 56.4 \text{ e.u.}$, the upper limit of the stated uncertainty in the literature value. The present analysis is therefore a consistent one and we accept $P.A.(\text{CO}_2) = (128.5 \pm 1.0) \text{ kcal mol}^{-1}$, where we believe the $\pm 1 \text{ kcal mol}^{-1}$ uncertainty is rather conservative, i.e., probably too large.

To obtain the absolute proton affinity of CO_2 , we have used the absolute proton affinity of Br. Since this is the anchor to our proton affinity ladder, we discuss it in some detail. The proton affinity of Br is defined as the endothermicity of the dissociation



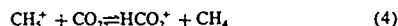
so that $P.A.(\text{Br}) = \Delta H_f(\text{H}^+) + \Delta H_f(\text{Br}) - \Delta H_f(\text{HBr}^+)$. Values are available for $\Delta H_f(\text{H}^+) = 365.7 \text{ kcal mol}^{-1}$ ⁸ and $\Delta H_f(\text{Br}) = 26.741 \text{ kcal mol}^{-1}$ ¹⁶ and also $\Delta H_f(\text{HBr}^-) = \Delta H(\text{HBr}) + I.P.(\text{HBr})$ with $\Delta H_f(\text{HBr}) = -8.70 \text{ kcal mol}^{-1}$.⁴ (All values of P.A. and ΔH_f referred to in this paper are for 298 K.) However, there is some uncertainty in the value of $I.P.(\text{HBr})$ (the ionization potential of HBr)¹⁵

A value of $I.P.(\text{HBr}) = 11.677 \text{ eV} \pm 0.004 = 269.27 \text{ kcal mol}^{-1}$ derived from a predissociation limit is available¹⁵ and Huber and Herzberg⁵ have adopted 11.67 eV as an average of an earlier photoionization and two photoelectron spectra measurements, but a smaller value of 11.645 eV has also been reported¹⁶ and this differs in energy by 0.73 kcal

mol^{-1} , which is quite significant within the $1.0 \text{ kcal mol}^{-1}$ uncertainty we claim for relative proton affinities in our ladder. Any change in $P.A.(\text{Br})$, either due to a change in $I.P.(\text{HBr})$ or otherwise, would of course shift the proton affinity scale correspondingly. The value of $11.677 \pm 0.004 \text{ eV}$ seems reasonably secure, but this point should be kept in mind in case revisions of $P.A.(\text{Br})$ arise. Accepting this value and the other values quoted above, leads to $P.A.(\text{Br}) = 131.84 \text{ kcal mol}^{-1}$. We use $P.A.(\text{Br}) = 131.8 \text{ kcal mol}^{-1}$ as the reference of our proton affinity ladder. An NBS compilation³ gives $P.A.(\text{Br}) = 132 \text{ kcal mol}^{-1}$, presumably deduced in the same manner, although a more recent compilation⁶ gives $132.4 \text{ kcal mol}^{-1}$. Use of the literature value of $D_0(\text{HBr}^+) = 3.894 \text{ eV}$ ⁵ to deduce $P.A.(\text{Br})$ from $\text{HBr}^+ \rightarrow \text{Br} + \text{H}^+$, gives $P.A.(\text{Br}) = 130.9 \text{ kcal mol}^{-1}$, a value appropriate to 0 K . It is because of such possible confusion that we have elaborated on the deduction of $P.A.(\text{Br})$ in such detail.

With $P.A.(\text{CO}_2) = 128.5 \pm 1.0 \text{ kcal mol}^{-1}$ thus established, other proton affinities can be obtained from van't Hoff plots, i.e., the dependences of equilibrium constants on temperature. This approach is free of the uncertainty involved in the HBr^+ reactions in which the equilibrium constants cannot be measured. The values of P.A. deduced in this manner are listed in Table I, together with values of P.A. for several other molecules.

The K for the reactions



has been measured as a function of temperature. The van't Hoff plot gives $\Delta H = 1.54 \pm 0.4 \text{ kcal mol}^{-1}$, which leads to $P.A.(\text{CH}_4) = 130.0 \text{ kcal mol}^{-1}$ consistent with the observed endothermicity of the forward reaction (1) (k_f as written). This endothermicity of $1.5 \text{ kcal mol}^{-1}$ agrees well

TABLE I Proton affinities (kcal mol^{-1}) at 300 K

Molecule	Present $\pm 1 \text{ kcal mol}^{-1}$	NBS ^a	NBS ^b	Bohme <i>et al.</i> ^c	Other
CO	141.4	141.9	142	141.4 $\pm$ 0.4	141.6 $\pm$ 1.4 ^d 141.4 ^e 142.6 ^f
Br ₂	140.0				
HBr	138.8	136.0	139		139.9 ^g 140.4 ^h
N ₂ O	137.3	136.5	138.8	137.0 $\pm$ 1.4	
HCl	133.0	134.8	136.6		134.6 ⁱ 134.5 ^j
Br	131.8	132	132.4		
CH ₄	130.0	132	131.6	130.5 $\pm$ 2.0	129.0 ^k
CO ₂	128.5	130.9	130.7	128.6 $\pm$ 2.1	130.6 ^l
NO	~127.0	~127	131		135 $\pm$ 3 ^m
CF ₄	~126.5	~126	~126		
SF ₆	< 127				

^a Reference 3

^b Reference 4

^c Reference 6

^d Reference 7

^e Reference 14

^f Reference 19

^g Reference 20

^h Reference 21

ⁱ Reference 22

^j Reference 23

^k Reference 24

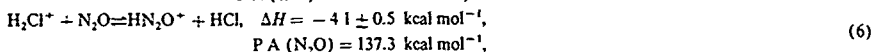
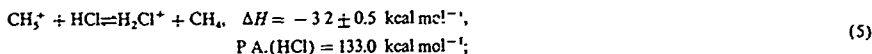
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^m Reference 26

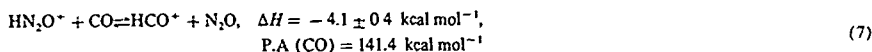
with the value that is obtained from $k_f(1) = k_L(1) \exp -\Delta H(1)/RT$, where k_L , the Langevin collision rate coefficient for the forward reaction, is $1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This gives $\Delta H(1) = RT \ln k_L/k_f(1) = 0.6 \ln (1 \times 10^{-9}/5.8 \times 10^{-11}) \text{ kcal mol}^{-1} = 1.7 \text{ kcal mol}^{-1}$. This qualitatively supports the premise that proton

transfer often occurs on essentially every exothermic collision and for endothermic reactions the Boltzmann factor determined by ΔH yields the fraction of reactions that are exothermic.

Van't Hoff plots have also been used to obtain values of ΔH , and hence P.A., for the following reactions:



and



A van't Hoff plot of the data for reaction (7) is given in Fig. 2 together with previous data.^{17,18} The $\Delta H(7)$ obtained in the present study is in good agreement with the earlier value of $-(4.4 \pm 0.4) \text{ kcal mol}^{-1}$.¹⁷

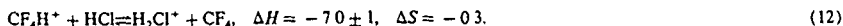
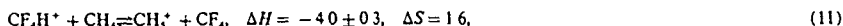
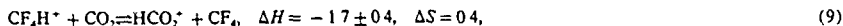
Similarly, a van't Hoff plot for the reaction



gives $\Delta H(8) = -2.6 \pm 0.5 \text{ kcal mol}^{-1}$ and P.A. (HBr) = 138.8 kcal mol⁻¹.

The proton affinity of Br₂ is bracketed between those of HBr and CO on the basis of observed reaction exothermicities, although van't Hoff plots were not obtained, so that we take P.A. (Br₂) = 140.0 ± 1 kcal mol⁻¹.

Proton affinities of CF₄ and NO have been determined from van't Hoff plots of $\ln K$ vs the reciprocal of the relative ion-neutral kinetic energy (KE) obtained using the Aberystwyth SIFDT, in which KE is varied by the application of an electric field. It is not obvious that such data can be used for van't Hoff plots since the applied electric field increases the translational and presumably the rotational energy of the ions, and possibly the vibrational energy of the ions to an uncertain degree, but does not effect the rotational and vibrational energy of the neutrals, so that thermodynamic equilibrium does not exist among the reactants. It is known that such $\ln K$ vs (KE)⁻¹ plots may not be linear. Indeed, in the case of the equilibrium for reaction (7), such KE plots were not linear.¹⁷ In the present studies, we did obtain a number of linear $\ln K$ vs (KE)⁻¹ plots and the consistency of the values of ΔH and ΔS obtained from several plots convinces us that they yield good values. It may be that when there are problems associated with lack of rotational and/or vibrational equilibrium, this is manifest as nonlinearity in such plots, but when there are not significant departures from equilibrium for particular reactions, linear plots are obtained whose slopes and intercepts relate to the usual thermodynamic quantities ΔH and ΔS . Regardless of the generality or validity of this statement, the present data are so redundantly consistent that there can be little doubt as to their validity. The following reactions involving proton transfer from CF₄ were found to give linear $\ln K$ vs (KE)⁻¹ plots, yielding the following parameters from the slopes and intercepts (ΔH is in kcal mol⁻¹, ΔS is in e.u.):



Taking the values of P.A. from Table I, we deduce the following values of P.A. (CF₄) from the reactions indicated in parentheses: 126.8(9), 126.0(11), and 126.2 kcal mol⁻¹ (12). This is too consistent to be random and a value of P.A. (CF₄) = 126.5 kcal mol⁻¹ has been chosen which should be reliable to the ± 1 kcal mol⁻¹ precision of Table I. From reaction (10), we deduce P.A. (NO) = 127.0 kcal mol⁻¹. Both the forward and reverse rate coefficients for this reaction are larger than 10⁻¹⁰ cm³ s⁻¹ at 300 K, therefore, the reaction is obviously nearly thermoneutral and P.A. (CF₄) ≈ P.A. (NO).

for reactions (9)–(12), we have tested the consistency of the data from entropy considerations. Using known entropies for the reactant neutrals and other ions,¹⁴ we have calculated $S(\text{CF}_3\text{H}^+)$ with the following results: 66.6, 66.6, 66.8, and 66.7 e.u. from the ΔS data for reactions (9)–(12). This consistency indicates that the $\ln K$ vs (KE)⁻¹ van't Hoff plots do have validity in these cases, in spite of the lack of a solid theoretical basis for such plots. Presumably, the lack of rotational and vibrational equilibrium of the neutrals in these reactions is not very important. Since exothermic proton transfer generally occurs on every collision for the reactions between

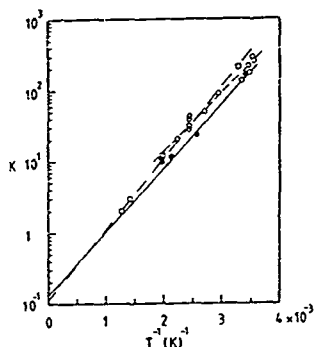


FIG. 2. A van't Hoff plot (filled circles) of the equilibrium constant K ($=A_p/A_s$) vs reciprocal temperature T^{-1} for the proton transfer reaction $\text{N}_2\text{O} + \text{CO} \rightleftharpoons \text{HCO}^+ + \text{N}_2\text{O}$ (reaction (7)) obtained from truly thermal SIFT data. Also included are the previous flowing afterglow data of Hemsworth *et al.* (Ref. 18) (open circles) and Lindinger *et al.* (Ref. 17) (squares).

too surprising that a change in vibrational and/or rotational energy states is not very important. We do know of, however, the counterexample of reaction (7) referred to above for which the $\ln K$ vs $(KE)^{-1}$ van't Hoff plot is not linear¹⁷ and thus we do not generalize on this point. This recent capability for determining proton affinities in drift tubes will be elaborated elsewhere and is not critical to the revised proton affinity scale proposed here [only P.A.(NO) and P.A.(CF₃) were determined in this manner].

SF₆ does not form a stable protonated ion and this gives the upper limit to P.A.(SF₆) listed in Table I (see below).

IV. DISCUSSION

A. P.A.(CO₂)

The critical proton affinity in the present study is that of CO₂ which we link to that of Br as the anchor of our P.A. ladder. The value of 128.5 kcal mol⁻¹ seems to be secure within our ± 1 kcal mol⁻¹ error limit for the reasons given above. This value is definitely smaller than the NBS values,^{3,4} although by only ~ 2 kcal mol⁻¹. It is in excellent agreement with the value 128.6 ± 2.1 kcal mol⁻¹ deduced by Bohme *et al.*,¹⁶ but with a significantly smaller uncertainty. P.A.(CO₂) has been calculated to be 130.6 kcal mol⁻¹¹⁹ with a basis set that tends to give P.A. values 2–3 kcal mol⁻¹ too large according to Dixon and Lias,⁸ and thus this is also consistent with the present value.

B. P.A.(CH₄)

The value of P.A.(CH₄) = 130.0 kcal mol⁻¹ agrees with the equivalent value given by Bohme *et al.*,¹⁶ again with an improved uncertainty, as shown in Table I. The value is 2 kcal mol⁻¹ smaller than the NBS values^{3,4} A very high level calculation has been made for P.A.(CH₄) yielding a value of 129.0 kcal mol⁻¹.²⁰ This is in satisfactory agreement with-

C. P.A.(HCl), P.A.(HBr), and P.A.(N₂O)

The value of P.A.(HCl) = 133.0 kcal mol⁻¹ is in fair agreement with the earlier NBS value of 134.8 kcal mol⁻¹,³ and two theoretical values of 134.6²¹ and 134.5 kcal mol⁻¹,²² although smaller than the more recent NBS value⁶ of 136.6 kcal mol⁻¹. The value of P.A.(HBr) = 138.8 kcal mol⁻¹ is substantially greater than the earlier NBS value of 136.0 kcal mol⁻¹,³ but is in good agreement with the more recent NBS value of 139 kcal mol⁻¹,⁶ and with the two theoretical values of 139.9²¹ and 140.4 kcal mol⁻¹.²³ The value of P.A.(N₂O) = 137.3 kcal mol⁻¹ agrees reasonably well with the previous values.^{3,4,14}

D. P.A.(CO)

As previously stated, P.A.(CO) can be considered as a basic standard in the P.A. scale because it can be deduced from $\text{HCO} \rightarrow \text{HCO}^+ \rightarrow \text{H}^+ + \text{CO}$ if $\Delta H_f(\text{HCO})$ and $I.P.(\text{HCO})$ are known. Recently, improved values of both of these quantities have become available. Chuang *et al.*⁶ have determined $\Delta H_f(\text{HCO})$ at 298 K to be 9.99 ± 0.19 kcal mol⁻¹ and Dyke⁷ has remeasured the adiabatic I.P.(HCO) to be 8.14 ± 0.04 eV. This yields P.A.(CO) = 141.6 ± 1 kcal mol⁻¹ in remarkable agreement with our thermochemical ladder based on P.A.(Br). A high level calculation²⁴ gives P.A.(CO) = 141.4 kcal mol⁻¹, for protonation on the C which is more stable than protonation on the O by ~ 40 kcal mol⁻¹. A value of P.A.(CO) = 142.6 kcal mol⁻¹ has also been deduced from earlier absolute measurements of the appearance potential of HCO^+ from H_2CO .²⁵

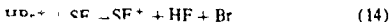
E. P.A.(CF₃), P.A.(NO), and P.A.(SF₆)

The present value of P.A.(CF₃) = 126.5 ± 1 kcal mol⁻¹ is in good agreement with the NBS compilations which give P.A.(CF₃) ~ 126 kcal mol⁻¹.^{3,4} Somewhat more usefully, we find from a kinetic energy van't Hoff plot that P.A.(NO) - P.A.(CF₃) ~ 0.5 kcal mol⁻¹, giving P.A.(NO) = 127.0 kcal mol⁻¹. This agrees with the earlier NBS value for P.A.(NO) of ~ 127 kcal mol⁻¹.³ The theoretical value for P.A.(NO) of 135 ± 3 kcal mol⁻¹²⁶ clearly seems to be too large. Protonation at the N gives the most stable form HNO^+ .

CF₃H⁺ ions are observed to be readily dissociated, viz



The energy required for this decomposition is $\Delta H = A.E.(\text{CF}_3^+/\text{CF}_3) + \Delta H_f(\text{HF}) - \Delta H_f(\text{F}) - \Delta H_f(\text{H}^+) + \text{P.A.}(\text{CF}_3) = \text{P.A.}(\text{CF}_3) - 122$ kcal mol⁻¹ [where $A.E.(\text{CF}_3^+/\text{CF}_3)$ is the appearance energy of CF_3^+ from CF_3]. Since CF_3H^+ does have observable stability, then P.A.(CF₃) must exceed 122 kcal mol⁻¹, probably by at least several kcal mol⁻¹. A value of $A.E.(\text{CF}_3^+/\text{CF}_3) = 327.5 \pm 2.3$ kcal mol⁻¹ has recently been determined²⁷ and is far smaller than previous literature values which would be quite inconsistent with the observed facile CF_3H^+ collisional breakup given as reaction (13). The reaction



occurs on about every collision since $k(14) = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. This is analogous to the similar reaction of HCl^+ with SF_6 which gives only SF_5^+ (and $\text{HF} + \text{Cl}$).²⁷ From both of these results, it can be presumed that SF_6H^+ is unstable toward decomposition to $\text{SF}_5^+ + \text{HF}$ which implies that the ΔH is negative for the $\text{SF}_6\text{H}^+ \rightarrow \text{SF}_5^+ + \text{HF}$ decomposition. For this $\Delta H = \text{P.A.}(\text{SF}_6) + \text{A.E.}(\text{SF}_5^+/\text{SF}_6) + \Delta H_f(\text{HF}) - \Delta H_f(\text{F}) - \Delta H_f(\text{H}^+) = \text{P.A.}(\text{SF}_6) - 127 \text{ kcal mol}^{-1}$, when the recently revised value of $\text{A.E.}(\text{SF}_5^+/\text{SF}_6) = 322 \pm 0.7 \text{ kcal mol}^{-1}$ ²⁷ is utilized. Therefore, $\text{P.A.}(\text{SF}_6) < 127 \text{ kcal mol}^{-1}$. No value (or limit) for $\text{P.A.}(\text{SF}_6)$ appears to have been given previously in the literature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge extensive advice and assistance from Dr. Sharon G. Lias in the subject treated here. We also have profited greatly from discussions with Dr. Peter Botschwina. The financial support of the S.E.R.C. for the work at both Aberystwyth and Birmingham is gratefully acknowledged.

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RADIATIVE LIFETIMES OF VIBRATIONALLY EXCITED HCl^+ ($v = 1$) AND DCI^+ ($v = 1$) IONS

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(Received 16 October 1989)

ABSTRACT

Vibrational radiative lifetimes of positive ions have been measured for the first time in a selected ion flow tube. Values determined are HCl^+ ($v = 1$), $\tau = 4.5 \pm 1$ ms and DCI^+ ($v = 1$), $\tau = 17 \pm 4$ ms. A reaction with N_2 to produce N_2H^+ , which is endothermic and slow for $v = 0$ and exothermic and fast for $v > 0$ is used to monitor the population of vibrationally excited ions as a function of distance in a helium buffered tube. There is agreement within experimental error of lifetimes measured in low pressure experiments at Orsay and with the calculated lifetimes. Vibrational quenching rate constants for both ions by helium are found to be less than $10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 300 K.

INTRODUCTION

A recent study of the vibrational relaxation of HCl^+ ($v = 1$) and DCI^+ ($v = 1$) by Ar and Kr [1] was carried out in this laboratory in order to test the dependence of quenching efficiency on vibrational and rotational energy level spacing whilst keeping the intermolecular potential between ion and quencher essentially unchanged. The vibrationally excited ions were measured by their reaction with N_2 to produce N_2H^+ , a reaction which is endothermic and slow for $v = 0$ and exothermic and fast for $v > 0$ [2]. The so called monitor ion technique has been used to measure a number of vibrationally excited ion collisional quenching rate constants [3-7]. The monitor ion technique has also been used for radiative lifetime measurements of vibrationally excited ions in a low pressure triple cyclotron experiment [8,9]. The present study is the first

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application of the monitor ion technique to the measurement of vibrational radiative lifetimes in the collision dominated conditions of a flow tube.

EXPERIMENTAL

The modified selected ion flow tube (SIFT) apparatus used is shown in Fig 1. Helium is introduced into the tube at the injector plate IP to establish a gas flow along the tube at a gas pressure of 0.3–0.75 Torr and a flow velocity of $30\text{--}70\text{ m s}^{-1}$, the gas being extracted by the mechanical pump R. Ions generated in an electron impact ion source S enter the quadrupole mass filter Q1 so that only the ions selected for study are injected into the helium carrier gas flow through the central aperture in the injector plate IP. The ions HCl^+ and DCI^+ are generated from HCl or DCI in the ion source and a small percentage, 1–2%, of these are vibrationally excited to the $v = 1$ level. The near vertical Franck-Condon ionization precludes a significant fraction of $v > 1$ ions being present. The ions are carried down the tube by the helium gas flow. The concentration of the vibrationally excited species varies down the tube due to several factors. In addition to the radiative decay ($v = 1 \rightarrow v = 0$), which is the parameter this experiment is designed to measure, the ions are lost by diffusion to the walls, but since the tube length is constant this does not enter the analysis, provided it can be assumed that both ions diffuse at the same rate in the gas mixtures employed. There could be quenching of the ($v = 1$) level in collision with helium atoms, but we have already established that this process is very slow [1]. If it were significant the measured lifetimes would decrease with increasing helium pressure but no such variation was observed over a pressure range from 0.3 to 0.75 Torr.

A monitor ion method was employed to determine the variation of the concentration of the HCl^+ ($v = 1$) along the tube. HCl^+ and DCI^+ ions in their ground state ($v = 0$) react very slowly with N_2 but the same ions when

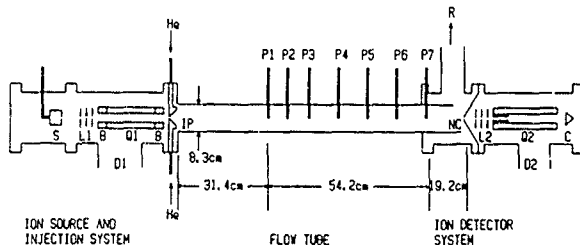


Fig 1 SIFT apparatus showing modifications for vibrational lifetime measurement

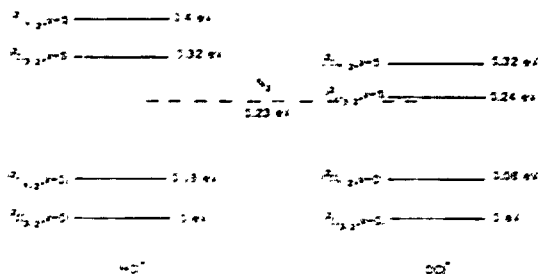


Fig. 2. Relative energy levels for HCl^+ and DCI^+ in reaction with N_2 as a monitor gas.

vibrationally excited ($v > 0$) proton transfer rapidly to give N_2H^+ [2]. Therefore N_2 is introduced into the flow tube at one of the seven identical gas entry ports P1 to P7 with a sufficient rate of N_2 flow that all the vibrationally excited ions are converted to N_2H^+ within a centimetre or so of the entry port position. The resulting N_2H^+ signal in the detection mass spectrometer Q2 is then a measure of the vibrational ion population in the region of this particular entry port. Repetition at the other six ports gives the variation of HCl^+ ($v > 0$) along the tube.

There is a further complication in that there is an additional source of production of N_2H^+ (N_2D^+) other than from HCl^+ ($v > 0$) or DCI^+ ($v > 0$). The energy levels given in Fig. 2 show that the separation between HCl^+ ($v=2$, $v=0$) and N_2 is 0.13 eV, so there is a possibility of N_2H^+ production from the high energy tail of this ion energy distribution. This process will give rise to a N_2H^+ (N_2D^+) signal which will be proportional to the length of the column of N_2 in the tube, i.e. 3.5 cm for P1 to 19 cm for P7, so this N_2H^+ signal will not be constant but will vary with the position of the entry port. The magnitude of this contribution can be estimated from a study of the N_2H^+ (N_2D^+) signal variation with N_2 monitor gas injection rate and the appropriate correction determined. In practice this correction was between 5 and 20% for the N_2 flows employed.

With this correction applied, if the ion source produced only vibrationally excited ions in the $v=1$ state the observed variation along the flow tube would be a single exponential decay so that a logarithmic plot of ion count against position along the tube should be linear. In fact for both ions the corrected log plots were not linear but curves of monotonically decreasing slope. If, contrary to expectation from the Franck-Condon factors, high vibrational levels were present the curvature would not have this form but have a monotonically increasing slope. The observed shape is characteristic of

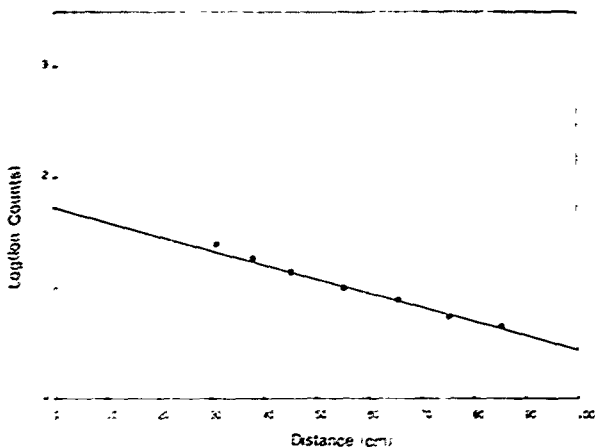


Fig. 3. Variation of the observed N_2H^+ signal with position of the monitor gas (N_2) entry port.

two independent ionic species decaying at different rates. This is not the only possible interpretation of such a curve but in the absence of precise information on the species actually present it represents the simplest interpretation and the data are analyzed using this assumption. The curve has to be analyzed as a double exponential but there are only seven experimental points and the portion of the double exponential which can be experimentally investigated is determined by three factors, the length of the flow tube, the gas flow velocity and the values of the lifetimes of the species being studied. The last factor means that the cases of HC_2^+ and DCI^+ are markedly different.

For HCl^+ the log plot is almost linear (Fig. 3) with only the first and second points off the straight line. This means the slow rate can be determined quite accurately, 4.5 ± 1 ms, while the initial fast decay can only be roughly estimated to be ~ 1 ms.

For DCI^+ , since both the lifetimes are longer, the experimental points do not give as good an estimate of the slow rate but the fast decay can be measured quite accurately. Ideally the tube length should be four times longer for the DCI^+ study to give comparable data to HCl^+ . Thus a curve fitting procedure for two exponentials was used which yields an initial decay of 3 ± 0.5 ms and a slow decay of 17 ± 4 ms.

RESULTS AND DISCUSSION

Whatever the distribution of energy levels in the tube, vibrational or electronic, the longest lifetimes are associated with the ($v = 1$) radiative lifetimes so that the measured radiative lifetimes are, for HCl^+ ($v = 1$), 4.5 ± 1 ms and for DCI^+ ($v = 1$), 17 ± 4 ms. The results are given in Table I together with theoretical values and the Orsay tricyclotron data. The shorter lifetimes of ~ 1 ms and 5 ± 0.5 ms for HCl^+ and DCI^+ respectively are tentatively attributed to higher vibrational states of these ions populated indirectly by electronically excited $^2\Sigma^+$ ions cascading to the ground electronic state, followed by vibrational radiation. The long lifetime components, i.e., the $\tau = 1$ populations, are compatible with $\text{HCl} \rightarrow \text{HCl}^+$ Franck-Condon factors.

The large isotope effect for both components almost surely implies a vibrational origin of these transitions. There are no long lived or metastable states of HCl^+ . The quartet states are purely repulsive. The only stable electronic state $^2\Sigma^+$ radiates by an allowed transition in microseconds. What seems likely is a large population of $^2\Sigma^+$ ions, for which the ionization Franck-Condon factors are very non-diagonal, as seen in the photoelectric spectrum [10] followed by radiation down to the ground state, again with non-diagonal Franck-Condon factors. The distribution might be very broad, yielding a distribution of vibrational lifetimes, all shorter than that for $\tau = 1$ (going approximately as $\tau = \tau^2$ as described below). Due to the problem of cascading, e.g., $\tau = 4 \rightarrow \tau = 3$, $\tau = 3 \rightarrow \tau = 2$, $\tau = 2 \rightarrow \tau = 1$, $\tau = 1 \rightarrow \tau = 0$, etc., only the longest lifetimes, i.e., $\tau = 1 \rightarrow \tau = 0$ can be deconvoluted from the experimental data. All vibrational states with $\tau > 1$ have the same fast reaction with the monitor. Sometimes the so-called double harmonic approximation is valid for small amplitude vibrations, leading to $\tau^{-1} \propto \nu^2 v$, where ν is the vibrational frequency and τ the radiating state vibrational quantum number. The double harmonic approximation means, (a) mechanical harmonicity, i.e., applicability of a harmonic oscillator to describe the vibrational frequency, and (b) electrical harmonicity, i.e., a linear dependence

TABLE I
Radiative lifetimes (ms) for HCl^+ ($\tau = 1$) and DCI^+ ($\tau = 1$)

	This work	Other experiments	Theory
HCl^+ ($\tau = 1$) 2468.6 cm ⁻¹	4.5 ± 1	3.4 ± 1.2 [15]	4.6 [13]
DCI^+ ($\tau = 1$) 1864.0 cm ⁻¹	17 ± 4	13.2 ± 3 [15]	19 [14]

of the dipole moment on bond length. The mechanical criteria are valid for such strong bonds as HCl , HCl^+ , etc., for low values of v . The dipole moment function however may be very non-linear. For example in the case of CH^+ and CD^+ , the slope of dipole moment versus bond length changes sign [11]. When these two conditions are met, then isotopic substitution yields lifetime ratios equal to the vibrational frequency ratio to the fourth power.

The derivation of the double harmonic approximation, whilst straight forward, has a bit of subtlety involved and we find a considerable confusion on this point. The familiar expression of the Einstein A coefficient for the spontaneous radiation rate, $A \propto \langle v|\mu|v' \rangle^2$, would seem to imply a v^3 relationship, not v^4 . The peculiarity that the dipole moment matrix element, an integral over space, has a frequency dependence is deceptive. This relationship has been derived, as a text book example, in the excellent book of Atkins [12]. It can also be deduced from the frequency dependence of the normalization factors of the harmonic oscillator wavefunctions (Hermite polynomials).

Applications are numerous, e.g., the ratio of radiative lifetimes of DF/HF , 3.47 is equal to the vibrational frequency ratio to the 4.017 power; that of DCI/HCl , 3.63 equals the vibrational frequency ratio to the 4.00 power, much better than the lifetimes are known.

In the present case the predicted ratio $\tau(\text{DCI}^+ (v=1))/\tau(\text{HCl}^+ (v=1)) = 3.6$ fits all the experimental data as well as the theory easily within the error limits. Rosmus [13] did find a linear dipole moment function theoretically. There is a slight correction required in the case of ions, since the dipole moment depends on the choice of origin, which must be taken as the centre of mass and therefore changes upon isotopic substitution. However because of the very large $\text{Cl}/\text{H,D}$ mass ratio this correction ($x = M_{\text{H}}/M_{\text{Cl}}$) is negligible.

Another consequence of the double harmonic approximation is that $\tau \propto 1/\nu$. Since the validity of the DHA is established by the ratio of $\text{DCI}^+/\text{HCl}^+$ lifetimes, one can use this to predict the lifetime dependence on v , for low values of v . At higher values of v the parabolic harmonic oscillator potential clearly cannot be valid, and the linearity of the dipole moment function must also vanish, since the dissociation limit of $\text{HCl}^+ \rightarrow \text{Cl}^+ + \text{H}$ would have a different sign of dipole moment than the bound proton on Cl^+ . One can fairly confidently predict however for $\text{HCl}^+ (v)$, $\tau(v) = 2.3$ ms and 1.5 ms for $v = 2, 3$ while for $\text{DCI}^+ (v)$, $\tau(v) = 9.7$ ms and 6.4 ms for $v = 2, 3$, assuming the theory is probably better than the experiment.

The other, somewhat trivial (and very well known) result of the harmonic oscillator approximation alone is that only $\Delta v = 1$ transitions will occur, i.e., the transition probabilities for $\text{HCl}^+ (v=2) \rightarrow \text{HCl}^+ (v=0) + h\nu$, etc., will be extremely small.

This study has been successful despite the adverse conditions for these two

ions, namely, the very low yield of vibrationally excited ions ($< 3\%$) while approximately half the HCl^+ (DCI^+) ground state ions are in the upper $^2\pi_{1/2}$ state and can contribute to the N_2H^+ (N_2D^+) production. Clearly under more favourable conditions the method would perform even better and would be suitable for measurement of lifetime in the range 1–40 ms. The method would benefit from a facility to readily change the length of the flow tube and from the use of a monitor gas entry port whose position could be continuously varied along the tube.

CONCLUSIONS

A new method for the measurement of vibrational radiative lifetimes, using flow tubes, has been demonstrated by the measurement of the lifetimes of HCl^+ ($v = 1$) and DCI^+ ($v = 1$). The ions HCl^+ ($v = 1$) and DCI^+ ($v = 1$) were measured only by the chance that collisional quenching measurements were being carried out on these ions and the radiative lifetimes were an unanticipated by-product. There are certainly more favourable cases which can be studied, namely those for which larger fractional vibrationally excited state populations can be obtained. However the technique is not of universal application. It requires the existence of a suitable ion state sensitive monitor, i.e., a neutral that can be used to detect vibrationally excited ions by virtue of fast reactions which are slow for non-vibrationally excited ions. This will normally be a result of an energetic threshold lying between two ion vibrational levels.

Another restriction is that the ions cannot be relaxed collisionally in the helium buffer gas during the radiative lifetimes. This will probably restrict lifetime measurements to relatively high frequency vibrations, but this remains to be determined. Finally the range of radiative lifetimes available is limited to perhaps a range from 1–40 ms, which includes however a large number of ions.

ACKNOWLEDGEMENTS

Valuable discussion with Dr P. Rosmus and Dr G. Mauclaire are gratefully acknowledged and also the technical assistance of Mr David Wareing. The work was supported by an SERC research grant.

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REACTIONS OF HNNO^+ AND NNOH^+ IONS WITH CH_4 AND NO AS A FUNCTION OF RELATIVE KINETIC ENERGY

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(Received 18 December 1989)

ABSTRACT

Rate constants for the reaction of the two isomers of protonated N_2O , HNNO^+ and NNOH^+ , with CH_4 and NO have been measured as a function of relative kinetic energy. The CH_4 measurements allow a determination of the proton affinity of N_2O on N of $131.5 \pm 1 \text{ kcal mol}^{-1}$ and an isomeric energy difference of $6.2 \pm 0.5 \text{ kcal mol}^{-1}$. This latter value should be compared with the recently obtained theoretical value of $7.1 \text{ kcal mol}^{-1}$.

INTRODUCTION

Two species of protonated nitrous oxide are produced from the reaction $\text{N}_2\text{O}^+ (\text{X}^2\Pi) + \text{H}_2 \rightarrow \text{N}_2\text{OH}^+ + \text{H}$ $\Delta H = -17.5 \text{ kcal mol}^{-1}$ [1] as deduced from the differing reactivities of the two ions with CH_4 and NO [1]. Recently [2] these observations have been interpreted as corresponding to the two forms of protonated nitrous oxide, NNOH^+ and HNNO^+ , the oxygen-protonated isomer being the most stable [2]. This is in accord with ab initio quantal calculations [3]. The difference in proton affinity of N_2O , protonated on N, and CH_4 was deduced to be $-1.3 \pm 1.3 \text{ kcal mol}^{-1}$ and the absolute proton affinity of N_2O , protonated on N, $131.3 \pm 1.3 \text{ kcal mol}^{-1}$ [2]. This was deduced from the evident endothermicity of the proton transfer from HNNO^+ to CH_4 and is simply the average between the maximum endothermicity permitted by the observed rate constant and zero endothermicity. The maximum endothermicity was taken to be $kT \ln (k_t/k)$, where k_t is the Langevin rate constant [1]. Any larger value for ΔE would give a Boltzmann factor too small to be consistent with observation. Very large endothermicities of course lead to unobservably slow reactions at thermal energy.

With the recent, rather surprising, finding that some proton transfer reactions measured as a function of relative kinetic energy in a drift tube lead to valid Arrhenius plots, it has become possible to use drift tubes to measure proton affinity differences in this way [4]. It is by no means obvious that valid Arrhenius plots should be obtained from relative kinetic energy dependences of rate constants. The situation is far from a thermodynamically equilibrated one. The ion velocity distributions are not Maxwellian and the ions, while probably rotationally equilibrated to the average centre of mass kinetic energy, in general will not be vibrationally equilibrated, and the neutral reactant will have a 300 K Boltzmann distribution rather than being equilibrated at the appropriate relative centre of mass average energy. However, a large number of proton-transfer reactions have been measured in both the exothermic and endothermic directions [4] and linear Arrhenius plots obtained in all cases except two reactions involving N_2OH^+ ions. It is now clear that the mixture of the two isomeric N_2OH^+ species contributed to that problem. The Arrhenius plots for the endothermic and exothermic directions of reaction were combined to yield linear van't Hoff plots from which values for ΔH and ΔS for the reactions were obtained.

The values of ΔH obtained from the seven reactions studied [4] gave proton affinity differences that deviate from the most precise proton affinity scale currently existing [5] in the relevant proton affinity range (~ 120 – 142 kcal mol^{-1}) by an average value of 0.36 kcal mol^{-1} . The uncertainty in the PA scale is ± 1 kcal mol^{-1} . The van't Hoff intercepts gave average differences for the entropy changes for reaction with known or calculated entropy differences of 1 cal $\text{mol}^{-1} \text{K}^{-1}$, which corresponds to a deviation in values of $T\Delta S$ of only 0.3 kcal mol^{-1} at 300 K, differences well within the uncertainties of the entropies of the ions involved.

The conclusion of this investigation was that linear Arrhenius plots derived from relative kinetic energy dependences of reaction rate constants for proton transfer reactions yield reliable thermodynamic data. It is not yet clear to what extent this finding can be justified theoretically but the evidence certainly justifies the use of this technique. Presumably when, and if, problems arise because of the non-thermodynamic translational, rotational and vibrational distributions involved, this will lead to non-linear Arrhenius plots. It seems to be very improbable that one will obtain linear plots yielding incorrect thermodynamic data.

EXPERIMENTAL

The experimental apparatus and procedure are the same as described in [4]. The N_2OH^+ and CH_5^+ ions were both generated in a high pressure ion source

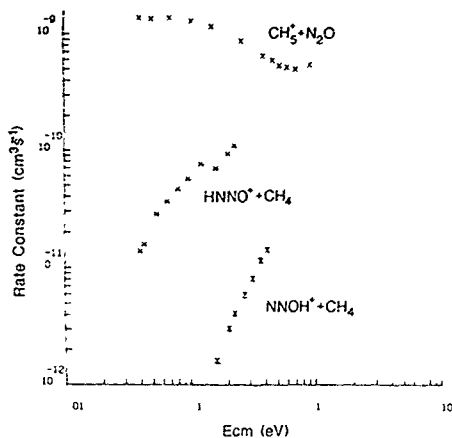
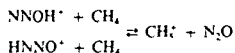


Fig. 1 Variation of rate constant with kinetic energy in both forward and reverse directions for the reaction



A 50:50 mixture of H_2 and N_2O was used for N_2OH^+ , since this gave maximum yield of N-protonated N_2O . CH_5^+ was obtained from CH_4 .

RESULTS AND DISCUSSION

The measured kinetic energy dependences of the rate constants are shown in Fig. 1. The resulting Arrhenius plots are given in Fig. 2.

Energy of the HNNO^+ ion

The linear Arrhenius plot for the endothermic HNNO^+ proton transfer with CH_4 leads to an activation energy of $1.5 \text{ kcal mol}^{-1}$ for this reaction. The appropriate way to obtain the value for ΔH of this reaction is of course to consider also the temperature dependence of the reverse reaction. There is a slight problem in the present case since only the overall rate constant between CH_5^+ and N_2O has been measured (Fig. 1) and the distribution between the two possible products, HNNO^+ and NNOH^+ has not been determined. In the low energy range ($\text{KE} < 0.2 \text{ eV}$) of the $\text{HNNO}^+ + \text{CH}_4$ measurement this is

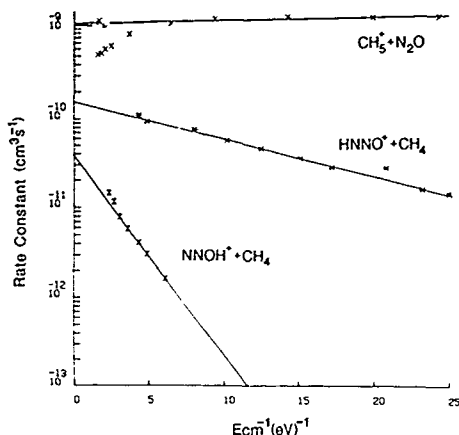


Fig 2 Arrhenius plots for the reaction
 $\text{NNOH}^+ + \text{CH}_4 \rightleftharpoons \text{CH}_3^+ + \text{N}_2\text{O}$
 $\text{HNNO}^+ + \text{CH}_4$

not a serious problem. The $\text{CH}_3^+ + \text{N}_2\text{O}$ rate constant is independent of KE and it is more likely that the two channels are both constant than that there is a compensating energy dependence. The total rate constant equals the Langevin collision rate constant, $k_L = 2\pi e(\alpha/\mu)^{1/2} = 1.1(-9)\text{cm}^3\text{s}^{-1}$ within the experimental uncertainty and this remains true for KE values small compared with the interaction well depth ($\sim 0.3\text{eV}$). The bond energies for $\text{NO}^+ \cdot \text{N}_2\text{O}$ and $\text{O}_2^+ \cdot \text{N}_2\text{O}$ are 0.33eV and 0.47eV [6]. The Arrhenius plot for the $\text{CH}_3^+ + \text{N}_2\text{O}$ reaction is linear in the low KE region (Fig. 2) and the van't Hoff plot for



gives a value 1.4kcal mol^{-1} , not significantly different from the value obtained from the Arrhenius plot alone. While not very sensitive, this does suggest that there is not a drastic change in HNNO^+ production by the $\text{CH}_3^+ + \text{N}_2\text{O}$ reaction in this limited energy range. These values are in good accord with the previously deduced value $1.3 \pm 1.3\text{kcal mol}^{-1}$ [2] and of course are much more precise.

The PA of N_2O , protonated on N, then becomes $131.5 \pm 1\text{kcal mol}^{-1}$,

using $PA(CH_4) = 130.0 \pm 1 \text{ kcal mol}^{-1}$ [5]. This latter value is determined by the temperature dependence of the proton transfer with CO_2 (a van't Hoff plot) which in turn is tied to the $PA(Br)$ as an absolute standard by an Arrhenius plot. It was not possible to measure the reverse reaction $HCO_2^+ + Br \rightarrow HBr^+ + CO_2$, since it was not possible to react Br atoms in the earlier experiment. It is the uncertainty in this temperature dependence which leads to the $\pm 1 \text{ kcal mol}^{-1}$ estimated uncertainty in $PA(CO_2) = 128.5 \pm 1 \text{ kcal mol}^{-1}$ and hence in $PA(CH_4)$. Recently a precise value for $PA(CO_2)$ has been obtained from the appearance potential for HCO_2^+ production from H_2CO_2 [7] which does not suffer from this problem: $PA(CO_2) = 129.2 \pm 0.5 \text{ kcal mol}^{-1}$. If one accepts this higher value of $PA(CO_2)$ and hence a higher value of $PA(CH_4)$ by the same amount, $0.7 \text{ kcal mol}^{-1}$ one would deduce $PA(N_2O)(\text{on N}) = 132.2 \pm 0.5 \text{ kcal mol}^{-1}$. In either case it is quite clear that the $PA(N_2O)(\text{on N})$ is as well known as the other proton affinities in this energy range.

It is interesting to note the reasonable agreement between the present value ($132 \text{ kcal mol}^{-1}$) and the estimated value $127 \pm 7 \text{ kcal mol}^{-1}$ determined by Beach et al. [8] from the inner shell ionization of C in $HNCO$, $HNCO + h\nu$ (295.89 eV) $\rightarrow HNC^+ + O + e$, utilizing the "equivalent cores approximation". This supports the utility of this remarkable method for obtaining useful estimates of otherwise unknown proton affinities.

Energy of the $NNOH^+$ ion

It is not possible to produce a van't Hoff plot for the reaction $NNOH^+ + CH_4$ because the accessible linear portions of the two Arrhenius plots do not overlap significantly on the E_{cm} scale.

The Arrhenius plot for the $NNOH^+ + CH_4$ reaction (Fig. 2) has a definite curvature at $KE_{cm} > 0.3 \text{ eV}$ and measurements below about $KE_{cm} = 0.15 \text{ eV}$ are not possible since the rate constant is then $< 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The activation energy obtained from the linear portion of the Arrhenius plot for the forward reaction is $7.9 \text{ kcal mol}^{-1}$, while for the reverse reaction the corresponding Arrhenius plot yields $0.2 \text{ kcal mol}^{-1}$. Thus the enthalpy change of the reaction is $7.9 - 0.2 = 7.7 \text{ kcal mol}^{-1}$. This leads to $PA(NNOH^+) = 137.7 \pm 1 \text{ kcal mol}^{-1}$ quite close to the temperature-variable SIFT measurement of $137.4 \pm 1 \text{ kcal mol}^{-1}$ [5].

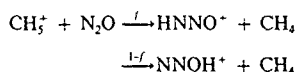
Isomeric energy difference

The energy difference between the two isomers will be the difference between the enthalpy changes for the two reactions namely $7.7 - 1.5 = 6.2 \pm 0.5 \text{ kcal mol}^{-1}$.

This should be compared with the theoretical calculation [3] giving $7.1 \text{ kcal mol}^{-1}$. We favour a value lower than $7.1 \text{ kcal mol}^{-1}$ because the reaction of the N-protonated N_2O with CH_4 is clearly endoergic (Fig. 1). If the $\text{PA}(\text{N}_2\text{O})$ on O is $137.3 \text{ kcal mol}^{-1}$ then the $\text{PA}(\text{N}_2\text{O})$ on N would be $137.3 - 7.1 = 130.2 \text{ kcal mol}^{-1}$ which is almost equal to the $\text{PA}(\text{CH}_4)$ so that the reaction of the N-protonated N_2O would be thermoneutral, contrary to the evidence of Fig. 1.

Entropy of N_2OH^+ and the reverse reaction branching ratio

If the entropy of N_2OH^+ can be estimated, the branching ratio f for the reverse reaction



can be determined from the experimental data

Since the rotational constants, and hence entropies, of all isoelectronic molecules are practically the same, a good estimate of $S(\text{N}_2\text{OH}^+)$ would be $57 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ since $S(\text{NH}_3) = 57.1 \text{ cal K}^{-1} \text{ mol}^{-1}$, $S(\text{HNCO}) = 56.9 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $S(\text{HOCN}) = 57.0 \text{ cal K}^{-1} \text{ mol}^{-1}$. Furthermore $S(\text{N}_2\text{OH}^+) = 57 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ gives an entropy of protonation of N_2O of $4.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ in good agreement with the usual range of values found, e.g. CH_4 (5.9), HCl (4.6), CO_2 (4.5), NC (3.4), HBr (4.9) and CF_4 (5.9) $\text{cal K}^{-1} \text{ mol}^{-1}$. On this isoelectronic argument the entropies of the two isomeric forms of N_2OH^+ will be identical and this is confirmed by the rotational constant data calculated by Yamashita and Morokuma [3]

$$\begin{array}{ccccccc} & \text{N}_2\text{OH}^+ & & \text{CH}_4 \rightarrow & & \text{CH}_3^+ & + \text{N}_2\text{O} \\ S(\text{cal K}^{-1} \text{ mol}^{-1}) = & 57 \pm 1 & & 44.5 & & 50.4 & 52.5 \end{array}$$

gives

$$\Delta S = 1.4 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Then from the van't Hoff plot of Fig. 3 the intercept gives $K = 8.4$ so that

$$S = R \ln(8.4f)$$

where f is the branching ratio for the reverse reaction

Thus $f = 25\%$, but assuming error limits of $\pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ gives $f = 15\text{--}40\%$

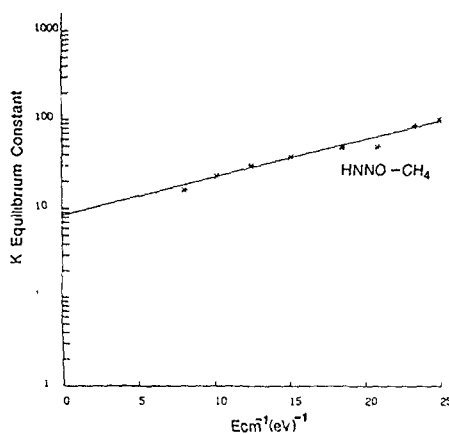
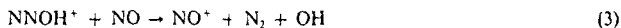


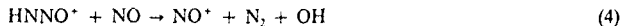
Fig. 3 A van't Hoff plot for the reaction $\text{HNNO}^+ + \text{CH}_4 \rightleftharpoons \text{CH}_3^+ + \text{N}_2\text{O}$

Reactions with NO

The rate constants for the reactions



and



are shown in Fig. 4. While neutral products are not measured, $\text{N}_2 + \text{OH}$ is the only exothermic possibility in each case [2]. Reaction 3 is a simple dissociative charge-transfer. The ions Ar_2^+ , Ne_2^+ and He_2^+ were earlier found to dissociatively charge-transfer with NO [9]. The initial decrease of k with increased KE followed by a subsequent increase is characteristic for slow ($k \ll k_1$) positive ion-neutral charge-transfer reactions [10]. This is qualitatively considered to be evidence for complex formation at low energies and a direct process at high energies. The problem has not been treated quantitatively for any system. One expects the division between high and low energies, i.e. the location of the minimum to be comparable with the interaction well depth, approximately 0.2–0.3 eV, qualitatively consistent with the present broad minimum, which lies in the 0.1–0.2 eV range. Reaction 4 on the other hand is considerably more complex. In order to get the O and H atoms in the

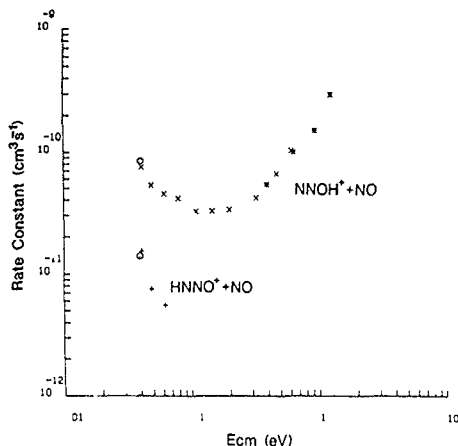


Fig. 4 Variation of rate constant with kinetic energy for the reaction
 $\text{NNOH}^+ + \text{NO} = \text{NO}^+ + \text{N}_2 + \text{OH}$
 $\text{HNNO}^+ + \text{NO}$

necessary proximity to form the required OH bond a slightly endothermic ($\sim 4 \text{ kcal mol}^{-1}$) proton transfer to NO was proposed [2], driven by the $\sim 6 \text{ kcal mol}^{-1}$ electrostatic attraction, followed by an exothermic proton transfer to the more stable O position [2]. At this point the reactants are in the same configuration as they would be in the collision of reaction 3 and dissociative charge transfer occurs.

It is clear that reaction 4 must be less efficient than reaction 3, as a consequence of this necessary rearrangement prior to charge transfer and this is evident in Fig. 4. It is also clear that complex formation is required and therefore that the rate constant must decrease sharply with KE, a prediction made earlier [2] which is clearly borne out. It was proposed earlier [2] that at elevated KE the proposed intermediate ($\text{ONN} \cdots \text{HNO}^+$) might dissociate as $\text{HNO}^+ + \text{N}_2\text{O}$ but this is not observed up to the maximum energy (0.06 eV) at which reaction 4 is measured, but of course it could not be since the reaction to produce $\text{HNO}^+ + \text{N}_2\text{O}$ is 0.17 eV (4 kcal mol^{-1}) endothermic.

SELECTED ION FLOW DRIFT TUBE STUDIES OF THE REACTION OF HBr^+ WITH VARIOUS NEUTRAL MOLECULES

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(First received 20 October 1989, in final form 6 November 1989)

ABSTRACT

The reactions of HBr^+ with CF_4 , NO , CO_2 , CH_4 , N_2O , SO_2 , COS , H_2S and SF_6 have been studied in a SIFT apparatus. For some reactions the variation of rate constant with centre of mass collision energy E_{cm} has been investigated. The rate constant for the CH_4 reaction exhibits an unusual variation with E_{cm} which is shown to be due to the different energy variations of the proton transfer, hydrogen abstraction and electron transfer channels.

The reduced mobilities of HBr^+ and H_2Br^+ in helium have been determined up to $E/N \sim 120 \text{ Td}$.

INTRODUCTION

A SIFT study in this laboratory [1] of the reactions of HCl^+ with neutrals demonstrated that the proton transfer reaction $\text{HCl}^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{Cl}$ could be used to distinguish between ground state and vibrationally excited HCl^+ . This has recently been exploited for a study of the vibrational quenching of both HCl^+ ($v = 1$) and DCI^+ ($v = 1$) [2] by neutrals and for the measurement of the radiative lifetimes of these two vibrational species [3].

The present study had similar objectives and it seemed possible that neutrals such as N_2 , Xe and CF_4 might provide suitable monitor gases for vibrationally excited HBr^+ . For HBr^+ there is the additional complication that the spin orbit ground state splitting ($^2\pi_{1/2}$, $^2\pi_{3/2}$) is large (0.32 eV) and is thus comparable to the vibrational level spacing of 0.29 eV, illustrated in Fig. 1. This precluded studies of HBr^+ (v) vibrational relaxation but did yield the new results on HBr^+ chemistry reported here.

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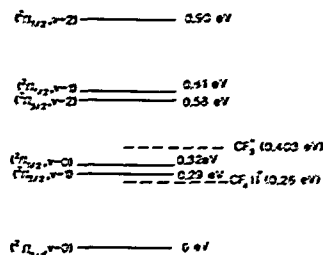


Fig. 1. Relative energy levels for HB^+ in reaction with CF_4 as a monitor gas. The endothermicities for CF_4H^+ and CF_3^+ production are 0.26 and 0.403 eV respectively.

EXPERIMENTAL

The HB^- was generated from HBr in either a low pressure or high pressure electron impact ion source, selected by a quadrupole mass filter and injected into the helium carrier gas stream in the flow tube. Some 20 cm downstream the reactant neutral was added to the flowing gas and the ionic species measured as a function of neutral reactant flow rate, by means of a second quadrupole mass spectrometer located at the end of the flow tube [4]. The reaction rate constant k was determined from the exponential decay of the HB^- count versus reactant flow rate. The variation of k with centre of mass collision energy E_{cm} can be studied by enhancing the ion energy by applying a longitudinal electric field along the flow tube.

MOBILITIES OF HBr^+ AND $\text{H}\cdot\text{Br}^+$

The determination of the rate constant with an electric field in the drift tube requires a knowledge of the transit time of the ions down the flow tube. The velocity of the ions in these circumstances is much greater than the bulk gas velocity. This time is determined from pulsed operation of wire meshes inserted in the flow tube before the reaction region and just in front of the detection mass spectrometer. From such measurements the reduced mobility can be readily calculated and since this data has not previously been published the values for HBr^+ and H_2Br^+ in helium are given in Table 1.

TABLE 1

The reduced mobilities of HBr^+ and H_2Br^+ ions in He at 300 K*

E/N (Td)	K_0 ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	
	HBr^+	H_2Br^+
5	20.6	20.0
10	20.1	19.4
15	19.7	18.75
20	19.15	18.25
25	18.7	17.75
30	18.25	17.25
40	17.4	16.4
50	16.7	15.7
60	16.0	15.0
70	15.4	14.5
80	14.8	14.0
90	14.25	13.5
100	13.75	13.0
110	13.25	12.5
120	12.8	12.2

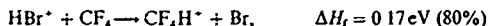
*Accuracy: the total error in the experimental data is believed not to exceed $\pm 7\%$.

EXPERIMENTAL RESULTS

The room temperature measurements are summarized in Table 2, which gives the measured rate constants at room temperature (k_{300}) together with the ion products. Also tabulated are the Langevin or ADO collision rate constants (k_c) as appropriate and the endothermicities, ΔH_f . In some cases the variation of rate constant with centre of mass energy E_{cm} has been studied and the results are shown in Fig. 2.

 CF_4

This reaction has two channels



and $k_{300} = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, or approximately $0.01 \times$ collision rate constant k_c , as a consequence of the endothermicity CF_4 therefore has particular interest as a possible monitor gas for vibrational studies. The energy levels are shown in Fig. 1 from which it is clear that with an ion source producing only HBr^+ ($^2\pi_{1/2}$) one has a double monitor in CF_4 because CF_3^+ would arise only from HBr^+ ($^2\pi_{3/2}$, $v \geq 2$) while CF_4H^+ would be produced by all vibrationally

TABLE 2

HBr⁺ ion chemistry

Reactant	Products	ΔH_f (eV)	$10^{10} k_c^a$ (cm ³ s ⁻¹)	$10^{10} k_{300}^b$ (cm ³ s ⁻¹)	Product distribution (300 K)
CF ₄	CF ₄ H ⁺ + Br	+0.17	6.05	0.07	80
	CF ₃ ⁺ + HF + Br	+0.40			20
NO	NO ⁺ + HBr	-2.48	6.78	3.0	100
CO ₂	CO ₂ H ⁺ + Br	-0.13	7.05	0.03	100
CH ₄	CH ₃ ⁺ + Br	+0.026	10.2	0.83	100
N ₂ O	N ₂ OH ⁺ + Br	-0.25	7.61	9.6	100
SO ₂	HSO ₂ ⁺	-1.37	13.0	16	100
COS	COS ⁺ + HBr	-0.55	11.3	12	75
	HCOS ⁺ + HBr	-0.92			25
H ₂ S	H ₂ S ⁺ + HBr	-1.25	13.0	15.6	65 ± 5
	H ₃ S ⁺ + Br	-1.75			35 ± 5
SF ₆	SF ₅ ⁺ + HF + Br		6.87	8.1	100

^a Calculated Langevin or ADO collision rate constant.^b Measured rate constant at 300 K.

excited HBr⁺ ($^2\pi_{3/2}$, $v \geq 1$). However, with the present ion source the situation is complicated by substantial yields of HBr⁺ ($^2\pi_{1/2}$), the ground vibrational state of which can produce CF₄H⁺, while the production of CF₃⁺ would arise for HBr⁺ ($^2\pi_{3/2}$, $v \geq 2$) and HBr⁺ ($^2\pi_{1/2}$, $v \geq 1$). Because ground state splitting is the same order as the vibrational level spacing, interpretation is difficult. Vibrational relaxation studies of HBr⁺ (v) ions could be carried out using CF₄ as a monitor if a suitable HBr⁺ ($^2\pi_{3/2}$) ion source could be found, e.g. a plasma source in which electrons deexcite HBr⁺ ($^2\pi_{1/2}$) in superelastic collisions

CH₄

This is a particularly interesting case because of the unusual variation of rate constant with E_{cm} , Fig. 3. At 300 K the rate constant is $\sim 0.1 k_c$, the dominant process being proton transfer with a small component of H abstraction while electron transfer is endoergic by 1 eV. As the E_{cm} is increased up to 0.15 eV the rate constant exhibits a curious S shape. The explanation becomes clear from the variation of the three reaction channels illustrated in Fig. 3.

For E_{cm} up to 0.35 eV, proton transfer is the only channel of significance and it rises to a maximum at $E_{cm} = 0.2$ eV followed by a decrease so that this channel defines the total rate constant energy variation over this region. At $E_{cm} > 0.5$ eV the rapid rise of the H abstraction channel H₂Br⁺ by over an order of magnitude, makes its contribution, together with the onset of the

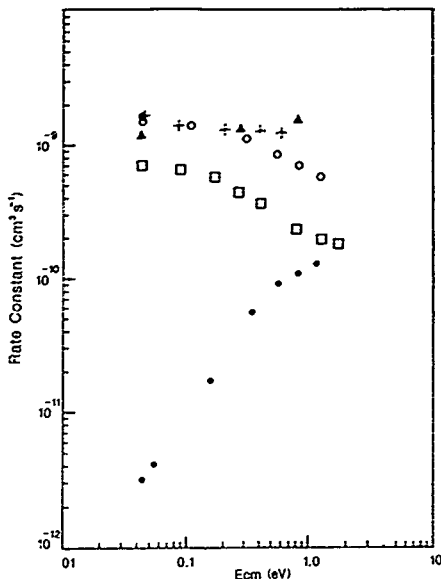


Fig 2 Measured rate constants for the reactions of HBr^+ with, $\bullet$, CO_2 , $\square$, SF_6 , $\circ$, SO_2 , $+$, H_2S , and $\blacktriangle$, N_2O as a function of kinetic energy E_{cm}

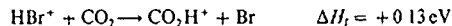
electron transfer channel CH_4^+ at $E_{\text{cm}} > 1 \text{ eV}$. The overall result is that the total rate constant now increases for $E_{\text{cm}} > 0.8 \text{ eV}$.

NO



Charge transfer is strongly exothermic and proceeds with a rate constant $k = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which is $0.4 k_c$.

CO_2



Only proton transfer was observed, there being a marked variation of k with E_{cm} by over an order of magnitude (Fig 2)

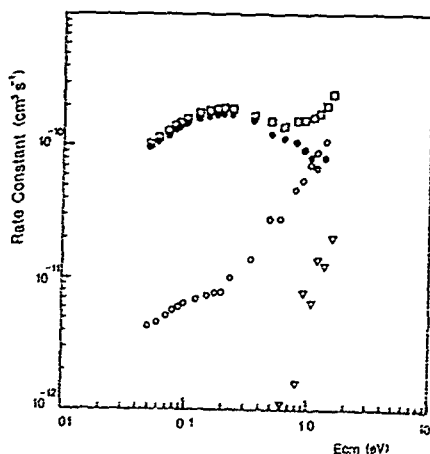
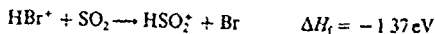
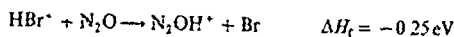


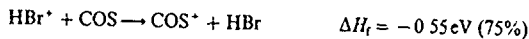
Fig 3 Measured rate constants for the reaction of HBr^+ with CH_4 as a function of kinetic energy E_{cm} . $\square$, total rate constant. Contributions from the three reaction channels are as follows: $\bullet$, proton transfer, $\circ$, H atom abstraction, and ∇ , charge transfer.

N_2O and SO_2



Both reactions involve only proton transfer with $k \approx k_c$. No E_{cm} study was made of the N_2O reaction but the SO_2 reaction showed a marked decrease of k as E_{cm} increased (Fig 2).

COS and H_2S

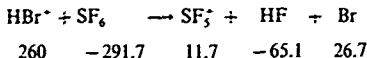


The reactions are similar in that in each case $k \approx k_c$ and there are two

channels, electron and proton transfer, the former being the major channel in both reactions. A study with centre of mass energy showed no significant variation of rate constant.

SF₆

At 300 K the reaction with SF₆ was fast, being of the order of the Langevin rate k_L . This implies that the reaction occurs at every collision for all ions, i.e. not just the HBr⁺ (²π_{1/2}) reacting. This is surprising since the available data on heats of formation suggest that the reaction should be endoergic. The heats of formation for the reaction expressed in kcal mol⁻¹ are



which indicates the reaction should be 5 kcal mol⁻¹ endothermic whereas it is obviously exothermic. The energies are from Lias et al. [5] except for the value of $\Delta H_f(\text{SF}_5^+)$ which is obtained from the appearance energy (AE) of SF₅⁺ from SF₆ deduced in ref. 6. Since $\Delta H_f(\text{HBr}^+)$ is unlikely to be in error by as much as 5 kcal mol⁻¹ it appears that the value of $\Delta H_f(\text{SF}_5)$, or equivalently $\text{AE}(\text{SF}_5^+/\text{SF}_6)$, must be too high by ~5 kcal mol⁻¹. The value of $\text{AE}(\text{SF}_5^+/\text{SF}_6) = 13.98 \pm 0.03 \text{ eV} = 322.4 \text{ kcal mol}^{-1}$ given in ref. 6 was over 1 eV below current literature values and the lower limit was defined by the relation $\text{AE}(\text{SF}_5^+/\text{SF}_6) = D(\text{SF}_5-\text{F}) + \text{IE}(\text{SF}_5)$ where $\text{IE}(\text{SF}_5) > \text{IE}(\text{NH}_3) = 10.14 \text{ eV}$ based on the measurement of Babcock and Streit [7] who found the reaction of SF₅⁺ with NH₃ to be fast. Since the IE is not likely to be significantly in error this indicates that the value of $D(\text{SF}_5-\text{F}) = 3.9 \text{ eV}$ must be too high [8].*

The rate constant decreases with increasing E_{cm} (Fig. 2)

DISCUSSION

The kinetic energy dependences of the proton transfer reactions of HBr⁺ with CH₄ and CO₂ clearly show that both reactions are endothermic and therefore that the proton affinities of CH₄ and CO₂ are less than that of Br (131.8 kcal mol⁻¹) which is obtained with precision from the spectroscopic dissociation energy of HBr⁺ [11]. Since this unambiguous result is at odds

* After this work was submitted, a paper by Stone and Wytenberg [9] appeared which supports the lower value for $\text{AE}(\text{SF}_5^+/\text{SF}_6)$ reported here. They report $\text{AE}(\text{SF}_5^+/\text{SF}_6) < 13.78 \text{ eV}$ deduced from the exothermicity of the reaction $\text{CH}_5^+ + \text{SF}_6 \rightarrow \text{SF}_5^+ + \text{CH}_4 + \text{HF}$. A better value would be $< 13.87 \pm 0.04 \text{ eV}$, since a better value for the proton affinity of CH₄ ($130 \pm 1 \text{ kcal mol}^{-1}$) is now available [10] than the value $132 \text{ kcal mol}^{-1}$ used by Stone and Wytenberg [9]. Both studies make clear that the present values $\Delta H_f(\text{SF}_5)$ and $D(\text{SF}_5-\text{F})$ in the literature are too high.

with certain recently established proton affinity scales [12] we have pursued this investigation in collaboration with Smith and Adams at Birmingham, where a variable temperature SIFT exists, in order to refine the present PA scale, by referencing it to the PA of Br [10].

The fast exothermic reactions are expected both for proton transfer and electron transfer. When both channels are exothermic, they both occur with significant fractions of the product distribution.

ACKNOWLEDGEMENTS

We are grateful to Mr. David Wareing for his technical assistance. This work was supported by an SERC grant.

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The application of a selected ion flow drift tube to the
determination of proton affinity differences.

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Abstract

The forward and reverse rate constants for nine proton transfer reactions have been measured as a function of relative kinetic energy using a selected ion flow drift tube (SIFDT). In all but two cases van't Hoff plots of the equilibrium constant against reciprocal centre of mass collision energy were linear and values of the enthalpy and entropy changes were obtained from slope and intercept respectively. Since H is a measure of the difference between the proton affinities of the two neutral species, the data can be used to provide a proton affinity difference ladder. This ladder agrees extremely well with the established proton affinity scale. The experimental values of entropy change agree well with values calculated from the entropies of the individual ions and neutrals. The agreements of the H 's and S 's so determined establishes the validity, and utility, of a SIFDT apparatus for proton affinity studies, when linear pseudo van't Hoff plots are obtained. In the present study two N_2OH^+ measurements gave non-linear Arrhenius and van't Hoff plots, and had to be rejected, in agreement with the

earlier work. Some speculations of why drift tube measurements lead to reliable thermodynamic data, in spite of the lack of thermodynamic equilibrium between internal and translational modes, are presented.

Introduction

Experimental determinations of the forward and backward rate constants for proton transfer reactions of the general type



have been widely used,^{1,2,3} to obtain data on proton affinities. If the equilibrium constant $K = k_f/k_r$ is measured as a function of temperature then from a van't Hoff plot of $\log K$ versus $1/T$ the enthalpy and entropy changes, H and S , can be determined from the slope and the intercept on the ordinate respectively. The value of H is equal to the difference of the proton affinities of X and Y and S is related to the ion structures. Often, K is measured only at 300K and S is determined from known or theoretical entropies.

Recently in connection with unrelated studies, we made the chance observation that the proton transfer reactions of HBr^+ with both CO_2 and CH_4 are endoergic⁴: It was immediately evident that the proton affinities of CO_2 and CH_4 are less than the proton affinity of Br . This indicated that the NBS tabulated values⁵ for $\text{PA}(\text{CH}_4)$ was slightly too high (in agreement with a recent high level theoretical calculation⁶) and particularly that a recently proposed increase⁷ in proton affinities for CH_4 and CO_2 is clearly incorrect.

The problem in establishing an absolute proton affinity scale lies in determining one or more fixed points to anchor the relative scales that have been deduced by van't Hoff plots as described above. Since the proton affinity of Br is known with spectroscopic precision⁸ from the dissociation energy of HBr^+ , this suggested the possibility of obtaining an improved PA scale anchored to $\text{PA}(\text{Br})$.

In order to establish PA's relative to Br, and to each other, proton transfer reaction rate constants were measured in a temperature variable SIFT at Birmingham⁹. Values for PA's of CO , Br_2 , HBr , N_2O , HCl , CH_4 and CO_2 were determined relative to Br, with what is believed to be an improved accuracy, conservatively estimated to be better than $\pm 1 \text{ kcal mol}^{-1}$. For six common species the new scale has average deviations from the NBS scale of $1.7 \text{ kcal mol}^{-1}$, with a maximum deviation of $2.8 \text{ kcal mol}^{-1}$ (for HBr). In most cases the new values of PA are slightly smaller than the NBS values, but not in every case.

In the course of these studies we have learned, to our surprise, that reliable PA differences can be obtained from "van't Hoff" plots of rate constant vs reciprocal average centre of mass kinetic energies i.e. from SIFDT measurements. This has important practical implications because the wide KE range (1 eV) far exceeds the maximum temperature variation possible ($< 900^\circ\text{K}$ 0.1 eV), allowing much larger P.A. differences to be spanned for a single reaction. Also elevated temperature flow tubes are notoriously difficult to operate and maintain.

The applicability of SIFDT'S to thermochemical problems is quite surprising since the internal degrees of freedom are not equilibrated with the translation kinetic energy. The neutral reactants maintain 300K rotational and vibrational temperatures, the ions attain rotational equilibrium with the relative KE in a few collisions¹⁰, but the ion vibrations do not¹¹, at least for low KE's and the relatively small number of collisions of the ions with the buffer in typical SIFDT experiments.

We were reinforced in this expectation, or perhaps more properly, led to this expectation by experience with the forward and reverse proton transfers between N_2O and CO , for which linear van't Hoff plots vs T^{-1} are obtained², yielding reliable proton affinity differences and entropy changes in reaction, whereas KE^{-1} van't Hoff plots were markedly non linear. The Arrhenius plots for both forward and reverse reactions i.e.

$k = A \exp(-E/RT)$ were also linear in this case, whereas the "Arrhenius" plot for N_2OH^+ reaction with CO as a function of KE^{-1} was non-linear. We still find non-linear Arrhenius plots for N_2OH^+ reacting with CO and also with HBr but we find linear plots for 14 other reactions and it appears that the non-linearity is, at least to some extent, a problem peculiar to N_2OH^+ , perhaps related to the existence of two isomeric forms lying very close in energy.

The present paper shows that reliable PA differences and entropy changes are obtained from KE^{-1} plots by comparison of these measurements with available data on well understood reactions. In the case of N_2OH^+ , and presumably for other ions as yet

unmeasured, for which the non-thermodynamic equilibrium is important, linear plots are not obtained and one would not attempt to deduce H and S . For this reason it appears that one would not be led to errors using the SIFDT technique.

The Lindinger et al² paper was a detailed study of flow-drift tubes using various carrier gases (He , N_2 , Ar) and showed that the proton transfer reactions of N_2OH^+ were very dependent upon the vibrational excitation of the ions and that a helium buffer was less effective in producing vibrational excitation than a heavier buffer. This is now well understood from the vibrational quenching study of vibrationally excited ions that have been subsequently obtained¹¹.

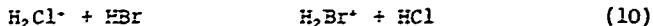
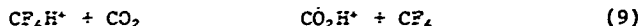
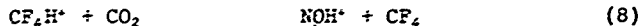
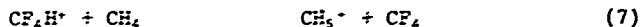
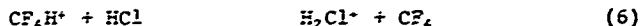
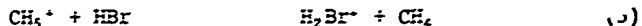
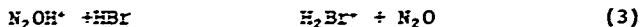
Experimental

The measurements were made in the Aberystwyth selected-ion flow-drift tube apparatus which has been described previously¹². The ions studied N_2OH^+ , H_2Br^+ , HCO^+ , H_2Cl^+ , CF_3H^+ , NOH^+ , CO_2H^+ and CH_5^+ were generated in a high pressure ion source using HCl , HBr , CO_2 , CH_4 , or CO mixed with H_2 .

The neutral reactant was added further downstream and the centre of mass collision energy E_{cm} was varied by varying the axial drift tube electric field. In such an apparatus the forward reaction rate constant can be determined as a function of E_{cm} . The corresponding data for the reverse reaction is obtained straightforwardly in a second experiment injecting the appropriate ion and neutral species.

Results and Discussion

The nine reactions studied were:-



The van't Hoff plots for these nine reactions are shown in figures 1 and 2 together with the data of Lindinger et al² for reaction(2). It is evident that there is excellent agreement between Lindinger et al and the present measurements so that the non-linearity of the van't Hoff plot for (2) is not in question. For reaction(3) the non-linearity is even more pronounced and it would again be quite impossible to determine either H or S. Both the above reactions involve the ion N_2OH^+ .

For the remaining seven reactions (4) to (10), in which N_2OH^+ is not involved, the pattern is entirely different. These give linear van't Hoff plots yielding values of H and S listed in Table 1. Such plots can be represented by the expression

$$\ln K = S/R - H/RT = S/R - 3 H/2E_{cm} \text{ where } E_{cm} = RT$$

This will only yield linear plots if H and S do not change significantly over the energy range of the investigation.

Presumably a significant variation of H and S with E_{ca} would result in a non-linear van't Hoff plot. If significant vibrational excitation of the ions by the strong applied field occurred this would change the value of H as the E_{ca} is varied, producing non-linearity. Therefore it can be concluded that in the case of the 7 good van't Hoff plots these effects are insignificant. This implies that the value of S obtained from the intercept should be in good agreement with that calculated from the entropies of the ions and molecules involved in these reactions and this should be a sensitive test of the above conclusions. The data so obtained is given in Table 1.

The good agreement between the H 's obtained and the established values and the good agreement between calculated S 's and the values obtained from the intercepts establishes the validity of the SIFDT apparatus for such measurements.

The average deviation in H between the present measurements and the proton affinities of ref.9 is $0.36 \text{ kcal mol}^{-1}$, well within the uncertainty of any present proton affinity scale including that of ref.9. The average deviation in S determined from the intercepts of Fig.1 and calculated values is $1.0 \text{ cal K}^{-1} \text{ mol}^{-1}$. This would correspond to $T \Delta S = 0.3 \text{ kcal mol}^{-1}$ at 300K and is generally within uncertainties of the entropies of the ions involved. The maximum deviation is only $1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$.

The only ions of Table I whose entropies are known are HCO_2^+ (55.6±0.8), CH_3^+ (50.4±0.5) and HCO^+ (48.0±0.2) from Bohme et al³. The entropy of H_2Cl^+ is assumed equal to that of the isoelectronic H_2S , 49.2eu, that of H_2Br^+ equal to that of H_2Se = 54.2eu and $S(\text{HNO}^+)$ is taken equal to $S(\text{HCO})$ = 53.7eu. The one undetermined entropy $S(\text{CF}_3\text{H}^+)$ is determined as the best fit to equations 6,7,8 and 9 so that only 6 of the 7 entropy fits are independent. The values of $S(\text{CF}_3\text{H}^+)$ deduced is 55.4 cal $\text{K}^{-1} \text{mol}^{-1}$. This gives an entropy of protonation of CF_3 of 5.9 cal $\text{K}^{-1} \text{mol}^{-1}$ consistent with the usual range of values found e.g. CH_4 (5.9), HCl (4.6), CO_2 (4.5), NO (3.4) and HBr (4.9). The quality of these or probably any other such available ion entropies are not sufficiently good to justify serious structural consideration.

It should be noted that the value for $S(\text{HCO}^+)$ used in Table 1 is not the value 48 from Bohme et al³ but rather the value 52.1 which is the entropy of the isoelectronic HCN . It is felt that the value 48 is too low and cannot be correct for the following reasons. This would give an increase in entropy due to protonation of CO of less than 1 cal $\text{K}^{-1} \text{mol}^{-1}$, which as seen above is far below the usual increases observed. The entropies of isoelectronic species are generally in very close agreement. Additionally the entropy of HCO^+ should be very close to the entropy of HCO when corrected for the difference in spin degeneracy of the singlet HCO^+ and doublet HCO , i.e. $S(\text{HCO}^+) - S(\text{HCO}) = R \ln 2 = 52.3 \text{ cal K mol}^{-1}$ which is very close to $S(\text{HCN})$, as it should be for such similar species. The entropy is determined by mass, rotational constants and to a lesser extent vibrational

... the same in these

three species, HCO^+ , HCN and HCO so far as entropy calculations are concerned. The observed S for reaction (4) is of course in itself a strong argument for the large $S(\text{HCO}^+)$ value.

One qualification must be made concerning our comparisons of (PA) values with those of ref.9, namely, temperature variable measurements involving CF_4 and NO proton transfer reactions were not carried out in Birmingham and the values of $\text{PA}(\text{CF}_4)$ and $\text{PA}(\text{NO})$ in ref.9 are those deduced from the present SIFDT studies. One could simply reduce the 7 cases of agreement by two, leaving 5 cases of agreement to support the present justification for the use of the SIFDT. The situation is somewhat better than this however, for two reasons.

It is obvious from the occurrence of very fast proton transfer between CF_4 and NO in both directions ($>10^{-10} \text{ cm}^3 \text{ s}^{-1}$) that their PA's are closely the same, i.e. the uncertainty in their PA difference is clearly less than $0.5 \text{ kcal mol}^{-1}$ independent of any knowledge of T or KE dependence. Secondly the PA's of both CF_4 and NO agree within better than 1 kcal mol^{-1} with values previously determined⁵, although the new values⁹ are certainly more precise.

There is strong evidence that the non-linearity of the van't Hoff plots for reactions (2) and (3) is related to the N_2OH^+ ion. A linear van't Hoff plot implies that there must be linear Arrhenius plots associated with both k_r and k_f for each reaction. For the nine reverse reactions studied we have 18 Arrhenius plots, 16 of which are linear and 2 are markedly non-linear. The last two are for the reactions $\text{N}_2\text{OH}^+ + \text{CO}$ $\text{HCO}^+ + \text{N}_2\text{O}$ and N_2OH^+

+ HBr $\text{H}_2\text{Br}^+ + \text{N}_2\text{O}$ and are illustrated in Figure 3. It is these two Arrhenius plots which when combined with the two linear Arrhenius plots for the appropriate reverse reactions produce the two non-linear van't Hoff plots of Figure 2 that are associated with reactions (2) and (3).

To supplement the above data there are two other reactions which have been studied previously, but which were measured in one direction only. These are



so that only Arrhenius plots for the reverse direction are available, but these can be used to establish an approximate link to Br although this link is less accurate since the slope of the forward reaction Arrhenius plots are not known. The uncertainty in the estimates of the small temperature dependences of the fast exothermic reaction is the origin of the uncertainty in the present PA scale⁹. The Arrhenius plots give $H = 0.6$ and 3.0 kcal mol⁻¹ respectively. The value 3.0 kcal mol⁻¹ for (12) agrees well with the value deduced from the T dependence of (12), to which the PA scale is tied⁹. The Arrhenius plot for $\text{HBr}^+ + \text{CH}_4$ is shown in Fig.3.

Let us consider briefly, and speculatively, why SIFDT studies of proton transfer reactions may yield linear Arrhenius rate constants, and therefore linear van't Hoff equilibrium constant plots, yielding correct values of H and S , as we have established for the present several cases.

What is clear is that rotations and vibrations of the neutral reactants are not excited in the SIFDT, i.e. they remain in a thermal (300K) distribution. It is also likely that the ions are rotationally equilibrated with the relative KE, consistent with theoretical prediction¹³ and experiment¹⁰ in the case of atomic buffer gases, as for He in the present case. The major uncertainty concerns ion vibrational excitation. It is uncertain to what extent the ions are vibrationally excited in the He buffer gas. The presumptive evidence, from the validity of the KE "van't Hoff" plots is that rotations and vibrations play no role. As a general observation, it has been commonly observed that exoergic proton transfer occurs on nearly every collision for small molecules such as considered here. This suggests that the sole criterion is energy and not the rotational and vibrational states involved except as they contribute to making an endoergic reaction exoergic.

With regard to rotation, one does not expect a significant rotational effect in such reactions, in part because the rotational quanta are so small and one expects small J change propensities, a sort of angular momentum conservation.

With regard to vibration, He is an extremely poor vibrational exciter, especially for the high frequency H stretching modes and most of the experiments are carried out at energies below the H stretching energy threshold. The linearity of the plots of Fig.1. clearly indicate that there is not an onset of vibrational excitation with a consequent sharp change of reactivity. The extent of vibrational excitation of the lower frequency bending

modes is unknown, and quite possibly significant but apparently does not yield an effect.

The proton transfer reaction



known to be proton transfer and not H atom transfer as a result presumably of the much weaker H_2^+ bond, has been studied as a function of v and KE^{14} . The results are quite consistent with the present deduction of a weak vibrational effect. The cross section decreases very slightly with v at low $E_{\text{cm}} = 0.11\text{eV}$ and very much less at $E_{\text{cm}} = 0.46\text{eV}$ and not at all at $E_{\text{cm}} = 0.93\text{eV}$. At low centre of mass KE 's, where there is a slight change in rate constant with v , there would be no vibrational excitation in a drift tube (it would be energetically impossible) and at high KE where there might be vibrational excitation there is no vibrational effect on rate constant. One does not know how generalized this situation is but it accords well with present findings.

It is known that vibrational energy can effectively drive an otherwise endoergic reaction, e.g. the slow endoergic $\text{HCl}^+ (v=0) + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{Cl}$ becomes very fast for $v = 1^{15}$.

With regard to the very non linear behaviour of the N_2OH^+ reactions, shown in Fig.2, we might suppose that this is a consequence of the occurrence of two isomeric forms, N_2OH^+ and N_2OH^+ , separated by only $6 \pm 1.3 \text{ kcal mol}^{-1}$ ^{16,17}. There are also two isomeric forms of HCO^+ and HNO^+ but the energy separations are much larger, larger than the KE 's involved in the

drift tube. The two forms are known to be produced in the SIFDT source and to have different reactivities¹⁸. Since the van't Hoff temperature plots were well behaved^{2,9}, one may ask why the KE plots were different. One possibility is that the different ion sources produced different distributions of isomers. Possibly in the higher pressure variable temperature flow tube ion source the ions were relaxed to the lowest energy form. Alternatively, perhaps the higher energy collisions in the SIFDT, where the non-linearity becomes severe, induce transitions between the two isomers.

Conclusions

The use of SIFDT's, in which rate constants are measured as a function of relative ion-neutral kinetic energy has been found to yield linear Arrhenius plots for a number of forward and reverse proton transfer reactions and hence linear van't Hoff plots from their ratio. The values of H and S are found to be in excellent agreement with the established values for these reactions. The only deviations from linearity observed involved protonated nitrous oxide. This may be related to the existence of two closely lying N_2OH^+ isomers, only 6 kcal mol⁻¹ apart in energy. It thus appears that KE van't Hoff plots are often linear and when they are they yield valid thermochemical data. When such plots are not linear, for whatever reason, for example as a consequence of the inherent non-thermodynamic equilibrium between vibrations and translations in a drift tube, this will not lead to error since the non-linearity will preclude such use. This expanded role for flow drift tubes is potentially very useful

because of the extremely limited capability for making temperature variable ion-molecule reaction rate constant measurements.

ACKNOWLEDGEMENT.

We are grateful to Mr. David Wareing for technical assistance. The work has been funded by the Science and Engineering Research Council and the United States Air Force.

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Table 1

Values of H and S from $\ln K_{eq} = S/R - 3 H/2E_{cm}$

H is in kcal mol⁻¹ and S is in cal K⁻¹ mol⁻¹

Reaction No.	Reaction	- H	- H(ref.9)	S	S(calc)
4.	$H_2Br^+ + CO = HCO^+ + HBr$	2.0	2.6	+1.4	0
5.	$CH_5^+ + HBr = H_2Br^+ + CH_4$	9.1	8.8	-1.7	-1.0
10.	$H_2Cl^+ + HBr = H_2Br^+ + HCl$	6.0	5.8	+0.6	+0.3
6.	$CF_4H^+ + HCl = H_2Cl^+ + CF_4$	7.0	6.5	-0.2	-1.3
7.	$CF_4H^+ + CH_4 = CH_5^+ + CF_4$	4.0	3.5	-1.7	0
8.	$CF_4H^+ + NO = HNO^+ + CF_4$	0.6	0.5	-3.7	-2.5
9.	$CF_4H^+ + CO_2 = HCO_2^+ + CF_4$	1.7	2.0	+0.4	-1.3

Entropies of neutrals from Benson (Ref. 19)

Entropies of CO_2H^+ and CH_5^+ from Bohme et al (ref.3)

$S(HCO^+)$ assumed = $S(HCN)^- = 52.1$

$S(H_2Cl^+)$ " = $S(H_2S)^- = 49.2$

$S(HNO^+)$ " = $S(HCO) = 53.7$

$S(H_2Br^+)$ " = $S(H_2Se) = 52.4$

$S(CF_4H^+)$ best fit to equations 6,7,8 and 9 = 68.4

Figure Captions

Fig.1 Showing van't Hoff plots for reactions (4) to 10)

Fig.2 Showing non-linear van't Hoff plots obtained for reactions (2) and (3). Reaction (2): present, + reference 2, Reactions (3): present,

Fig.3 Showing Arrhenius plots for reactions (2) and (3).
 Reaction (2) : forward , reverse .
 Reaction (3) : forward , reverse .
 The Arrhenius plot for reaction (11) is also shown plotted as .

Values of H and S from $\ln K_{eq} = S/R - 3 H/2E_{cm}$

H is in kcal mol⁻¹ and S is in cal K⁻¹ mol⁻¹

Reaction	-H	-H*	S	S(calc)#
$H_2Br^+ + CO = HCO^+ + HBr$	2.0	2.6	+ 1.4	0
$CH_5^+ + H^+ = H_2Br^+ + CH_4$	9.1	8.8	-1.7	-1.0
$H_2Cl^+ + HBr = H_2Br^+ + HCl$	6.0	5.8	+0.6	+0.3
$CF_4H^+ + HCl = H_2Cl^+ + CF_4$	7.0	6.5	-0.2	-1.3
$CF_4H^+ + CH_4 = CH_5^+ + CF_4$	4.0	3.5	-1.7	0
$CF_4H^+ + NO = HNO^+ + CF_4$	0.6	0.5	-3.7	-2.5
$CF_4H^+ + CO_2 = HCO_2^+ + CF_4$	1.7	2.0	+0.4	-1.3

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CONCLUSIONS

The reaction $\text{N}_2\text{OH}^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{N}_2\text{O}$ is found to be endothermic by 1.5 and 7.7 kcal mol⁻¹ for N-protonated and O-protonated N_2O respectively. This corresponds to an isomeric energy difference of 6.2 ± 0.5 kcal mol⁻¹. The proton affinity of N-protonated N_2O is 131.5 ± 1 kcal mol⁻¹ and for that of O-protonated N_2O is 137.7 ± 1 kcal mol⁻¹, taking the value of $\text{PA}(\text{CH}_4)$ to equal 130.0 kcal mol⁻¹. The rate constants for both HNNO^+ and NNOH^+ with NO to produce $\text{NO}^+ + \text{OH} + \text{N}_2$ have been measured as a function of the relative kinetic energy. The rate constant for the reaction of NNOH^+ with NO is a minimum at low energy as typically observed for charge-transfer reactions, while the HNNO^+ reaction falls sharply with increased KE, consistent with the intermediate complex mechanism mooted earlier to explain the complicated reaction [2].

ACKNOWLEDGEMENTS

Acknowledgements are due to Mr. David Wareing for technical assistance. The work was supported by a grant from the Science and Engineering Research Council.

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