An absolute proton affinity scale in the 130–140 kcalmol− 1 range

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An absolute proton affinity scale in the ~130–140 kcal mol⁻¹ range

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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, P.A.(CO_2), $= 128.5 \pm 1.0$ kcal mol⁻¹, utilizing the literature value of P.A.$(Br) = 131.8$ 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 CO(141.4), HBr(138.8), N_2O(137.3), HCl(133.0), Br(131.8), CH_4 (130.0), and CO_2(128.5). Proton affinities have also been determined for Br_2(140.0), NO(127.0), and CF_4(126.5), the last two values being obtained from selected ion flow drift tube measurements. An upper limit to P.A.(SF_6) of 127 kcal mol⁻¹ has been inferred from the instability of SF_6 H^+ 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 range[2] is in error and indeed that the value of the proton affinity of CH_4, P.A.$(CH_4) = 132$ 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 P.A.(CH_4) and P.A.(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[6] and the adiabatic ionization potential of HCO[7] as P.A.$(CO) = 141.6$ kcal mol⁻¹. The value for P.A.(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.[8]

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-

troduced 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 SIFDT 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 SIFDT experiments.[11] 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.,

$$HBr^+ + CH_4 \overset{k_f}{\underset{k_r}{\rightleftarrows}} CH_5^+ + Br \qquad (1)$$
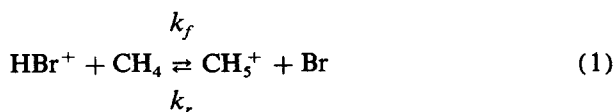
due to difficulties in producing Br atoms. In an unsuccessful attempt to do this, Br$_2$ was discharged in an excess of He using a microwave discharge. No evidence for dissociation was observed in spite of the numerous allowed transitions to repulsive Br$_2$ states.[13] A large fractional dissociation 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.(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 knowing precisely the temperature dependence of K. Our

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

$$HBr^+ + CO_2 \overset{k_f}{\underset{k_r}{\rightleftarrows}} HCO_2^+ + Br \qquad (2)$$
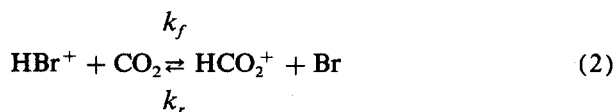
to determine the major contribution to the temperature dependence of K and then to estimate the maximum possible range of temperature dependences for the exothermic k_r and accept the uncertainty in this as the uncertainty in ΔH and hence the uncertainty in the proton affinity of CO$_2$ (or CH$_4$) relative 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 $A_f = 2.7 \times 10^{-10}$ cm^3 s^{-1} and $\Delta E_f = 2.96 \pm 0.2$ 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 $\Delta H(2) = \Delta E_f = 2.96$ 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 $\Delta E_r = -0.55$ 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.(CO$_2$) = P.A. (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 $S(HCO_2^+) + S(Br) - S(HBr^+) - S(CO_2) = (55.6 \pm 0.8) + 41.8 - 49.0 - 51.1 = -2.7 \pm 0.8$ e.u., where the S are standard entro-
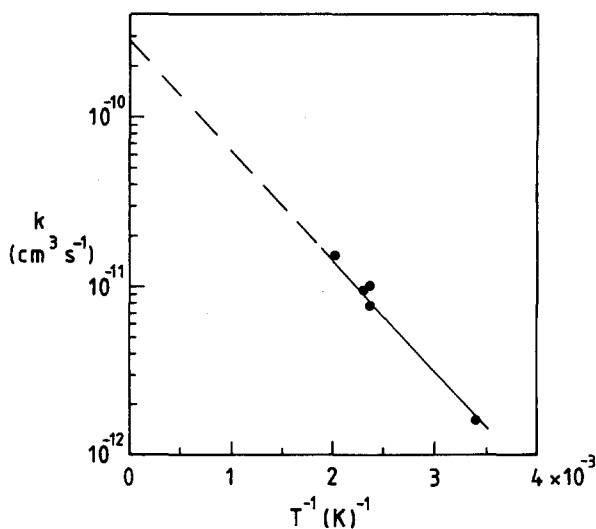

FIG. 1. An Arrhenius plot of the rate coefficient k vs reciprocal temperature T^{-1}, for the proton transfer from HBr$^+$ to CO$_2$ [reaction (2)] obtained from truly thermal SIFT data. The extrapolation to the ordinate gives an intercept which is consistent with that expected by modifying the Langevin collisional rate coefficient by a factor dependent on an entropy change in the reaction (as obtained from standard entropies, see the text).

pies and the dominant uncertainty is in $S(HCO_2^+)$.[14] This gives, from above, a pre-exponential factor for k_r, i.e., $A_r = A_f \exp(-\Delta S/R) = 1.1 \times 10^{-9}$ cm^3 s^{-1} with limits between 7.5×10^{-10} and 1.7×10^{-9} cm^3 s^{-1} by virtue of the uncertainty in $\Delta S(2)$ and thus k_r can be obtained from $A_r \exp(-\Delta E_r/RT)$. The Langevin collisional rate coefficient, k_L, which is 7×10^{-10} cm^3 s^{-1}, is actually a rather likely value for $k_r(2)$. This would correspond to $\Delta S = -2.0$ e.u., or $S(HCO_2^+) = 56.4$ 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.$(CO_2) = (128.5 \pm 1.0)$ kcal mol^{-1}, where we believe the ± 1 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

$$HBr^+ \rightarrow H^+ + Br, \tag{3}$$

so that P.A.$(Br) = \Delta H_f(H^+) + \Delta H_f(Br) - \Delta H_f(HBr^+)$. Values are available for $\Delta H_f(H^+) = 365.7$ kcal mol^{-1} [8] and $\Delta H_f(Br) = 26.741$ kcal mol^{-1} [14] and also $\Delta H_f(HBr^+) = \Delta H(HBr) + $ I.P.(HBr) with $\Delta H_f(HBr) = -8.70$ 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.(HBr) (the ionization potential of HBr).[15]

A value of I.P.(HBr) $= 11.677$ eV $\pm 0.004 = 269.27$ kcal mol^{-1} derived from a predissociation limit is available[15] and Huber and Herzberg[5] 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 reported[16] and this differs in energy by 0.73 kcal

mol^{-1}, which is quite significant within the 1.0 kcal mol^{-1} uncertainty we claim for relative proton affinities in our ladder. Any change in P.A.(Br), either due to a change in I.P.(HBr) or otherwise, would of course shift the proton affinity scale correspondingly. The value of 11.677 ± 0.004 eV seems reasonably secure, but this point should be kept in mind in case revisions of P.A.(Br) arise. Accepting this value and the other values quoted above, leads to P.A.(Br) $= 131.84$ kcal mol^{-1}. We use P.A.(Br) $= 131.8$ kcal mol^{-1} as the reference of our proton affinity ladder. An NBS compilation[3] gives P.A.(Br) $= 132$ kcal mol^{-1}, presumably deduced in the same manner, although a more recent compilation[4] gives 132.4 kcal mol^{-1}. Use of the literature value of $D_0(HBr^+) = 3.894$ eV[5] to deduce P.A.(Br) from $HBr^+ \rightarrow Br + H^+$, gives P.A.(Br) $= 130.9$ 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.(Br) in such detail.

With P.A.$(CO_2) = 128.5 \pm 1.0$ 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

$$CH_5^+ + CO_2 \rightleftharpoons HCO_2^+ + CH_4 \tag{4}$$

has been measured as a function of temperature. The van't Hoff plot gives $\Delta H = 1.54 \pm 0.4$ kcal mol^{-1}, which leads to P.A.$(CH_4) = 130.0$ kcal mol^{-1} consistent with the observed endothermicity of the forward reaction (1) (k_f as written). This endothermicity of 1.5 kcal mol^{-1} agrees well

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

Molecule	Present ± 1 kcal mol^{-1}	NBS[a]	NBS[b]	Bohme et al.[c]	Other
CO	141.4	141.9	142	141.4 ± 0.4	141.6 ± 1[c,d]
					141.4[k]
					142.6[l]
Br$_2$	140.0				
HBr	138.8	136.0	139		139.9[h]
					140.4[j]
N$_2$O	137.3	136.5	138.8	137.0 ± 1.4	
HCl	133.0	134.8	136.6		134.6[h]
					134.5[i]
Br	131.8	132	132.4		
CH$_4$	130.0	132	131.6	130.5 ± 2.0	129.0[g]
CO$_2$	128.5	130.9	130.7	128.6 ± 2.1	130.6[f]
NO	~ 127.0	~ 127	131		135 ± 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.
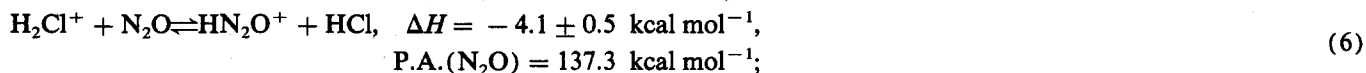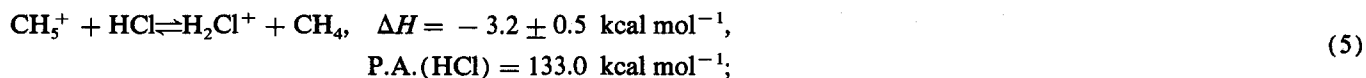[j] Reference 23.
[k] Reference 24.
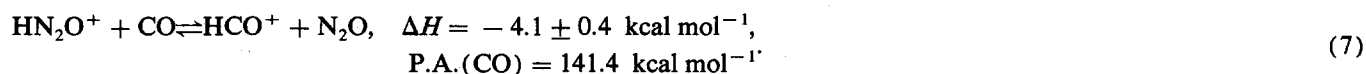[l] Reference 25.
[m] Reference 26.

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 1.0×10^{-9} cm^3 s^{-1}. This gives $\Delta H(1) = RT \ln k_L/k_f(1)$ $= 0.6 \ln (1 \times 10^{-9}/5.8 \times 10^{-11})$ kcal mol$^{-1} = 1.7$ 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:

$$CH_5^+ + HCl \rightleftharpoons H_2Cl^+ + CH_4, \quad \Delta H = -3.2 \pm 0.5 \text{ kcal mol}^{-1},$$
$$P.A.(HCl) = 133.0 \text{ kcal mol}^{-1}; \tag{5}$$

$$H_2Cl^+ + N_2O \rightleftharpoons HN_2O^+ + HCl, \quad \Delta H = -4.1 \pm 0.5 \text{ kcal mol}^{-1},$$
$$P.A.(N_2O) = 137.3 \text{ kcal mol}^{-1}; \tag{6}$$

and

$$HN_2O^+ + CO \rightleftharpoons HCO^+ + N_2O, \quad \Delta H = -4.1 \pm 0.4 \text{ kcal mol}^{-1},$$
$$P.A.(CO) = 141.4 \text{ kcal mol}^{-1} \tag{7}$$

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 $-(4.4 \pm 0.4)$ kcal mol^{-1}.[17]
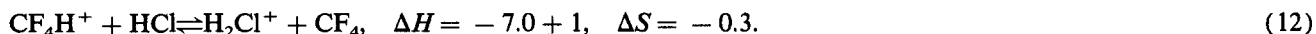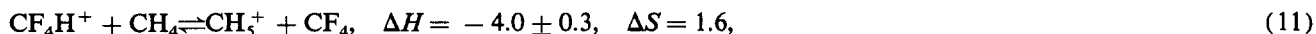
Similarly, a van't Hoff plot for the reaction

$$H_2Br^+ + CO \rightleftharpoons HCO^+ + HBr \tag{8}$$

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

The proton affinity of Br$_2$ 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.(Br$_2$) $= 140.0 \pm 1$ kcal mol^{-1}.

Proton affinities of CF$_4$ 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 CF$_4$ 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.):

$$CF_4H^+ + CO_2 \rightleftharpoons HCO_2^+ + CF_4, \quad \Delta H = -1.7 \pm 0.4, \quad \Delta S = 0.4, \tag{9}$$

$$CF_4H^+ + NO \rightleftharpoons HNO^+ + CF_4, \quad \Delta H = -0.5 \pm 0.08, \quad \Delta S = -3.7, \tag{10}$$

$$CF_4H^+ + CH_4 \rightleftharpoons CH_5^+ + CF_4, \quad \Delta H = -4.0 \pm 0.3, \quad \Delta S = 1.6, \tag{11}$$

$$CF_4H^+ + HCl \rightleftharpoons H_2Cl^+ + CF_4, \quad \Delta H = -7.0 \pm 1, \quad \Delta S = -0.3. \tag{12}$$

Taking the values of P.A. from Table I, we deduce the following values of P.A.(CF$_4$) 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.(CF$_4$) $= 126.5$ 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} cm^3 s^{-1} at 300 K, therefore, the reaction is obviously nearly thermoneutral and P.A.(CF$_4$) $\approx$ P.A.(NO).

Also, from the intercepts of the ln K vs (KE)$^{-1}$ plots

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 $S(CF_4H^+)$ 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 equilibria of the neutrals in these reactions is not very important. Since exothermic proton transfer generally occurs on every collision for the reactions between a wide variety of ions and neutrals, perhaps it should not be
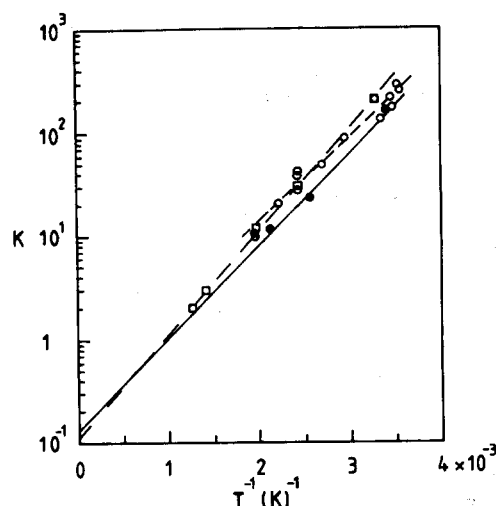
FIG. 2. A van't Hoff plot (filled circles) of the equilibrium constant K ($= k_f/k_r$) vs reciprocal temperature T^{-1} for the proton transfer reaction $N_2OH^+ + CO \rightleftharpoons HCO^+ + N_2O$ [reaction (7)] obtained from truly thermal SIFT data. Also included are the previous flowing afterglow 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 linear[17] 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.(CF_4) were determined in this manner].

SF_6 does not form a stable protonated ion and this gives the upper limit to P.A.(SF_6) listed in Table I (see below).

IV. DISCUSSION

A. P.A.(CO_2)

The critical proton affinity in the present study is that of CO_2 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.*,[14] but with a significantly smaller uncertainty. P.A.(CO_2) has been calculated to be 130.6 kcal mol^{-1}[19] 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.(CH_4)

The value of P.A.(CH_4) = 130.0 kcal mol^{-1} agrees with the equivalent value given by Bohme *et al.*,[14] 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.(CH_4) yielding a value of 129.0 kcal mol^{-1}.[20] This is in satisfactory agreement (within the ± 1 kcal mol^{-1} uncertainty) with the present study.

C. P.A.(HCl), P.A.(HBr), and P.A.(N_2O)

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 134.6[21] and 134.5 kcal mol^{-1},[22] although smaller than the more recent NBS value[4] 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}[4] and with the two theoretical values of 139.9[21] and 140.4 kcal mol^{-1}.[23] The value of P.A.(N_2O) = 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 $HCO \rightarrow HCO^+ \rightarrow H^+ + CO$ if ΔH_f(HCO) and I.P.(HCO) are known. Recently, improved values of both of these quantities have become available. Chuang *et al.*[6] have determined ΔH_f(HCO) at 298 K to be 9.99 ± 0.19 kcal mol^{-1} and Dyke[7] 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 calculation[24] 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.(CF_4), P.A.(NO), and P.A.(SF_6)

The present value of P.A.(CF_4) = 126.5 ± 1 kcal mol^{-1} is in good agreement with the NBS compilations which give P.A.(CF_4) ~ 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.(CF_4) ~ 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^{-1}[26] clearly seems to be too large. Protonation at the N gives the most stable form HNO^+.

CF_4H^+ ions are observed to be readily dissociated, viz.

$$CF_4H^+ \rightarrow CF_3^+ + HF. \tag{13}$$

The energy required for this decomposition is
$\Delta H =$ A.E.(CF_3^+/CF_4) $+ \Delta H_f$(HF) $- \Delta H_f$(F) $- \Delta H_f$(H^+) $+$ P.A.(CF_4) $=$ P.A.(CF_4) $- 122$ kcal mol^{-1} [where A.E.(CF_3^+/CF_4) is the appearance energy of CF_3^+ from CF_4]. Since CF_4H^+ does have observable stability, then P.A.(CF_4) must exceed 122 kcal mol^{-1}, probably by at least several kcal mol^{-1}. A value of A.E.(CF_3^+/CF_4) = 327.5 ± 2.3 kcal mol^{-1} has recently been determined[27] and is far smaller than previous literature values which would be quite inconsistent with the observed facile CF_4H^+ collisional breakup given as reaction (13). The reaction

$$HBr^+ + SF_6 \rightarrow SF_5^+ + HF + Br \tag{14}$$

occurs on about every collision since $k(14) = 8 \times 10^{-10}$ cm^3 s^{-1} at 300 K. This is analogous to the similar reaction of HCl$^+$ with SF$_6$ which gives only SF$_5^+$ (and HF + Cl).[27] From both of these results, it can be presumed that SF$_6$H$^+$ is unstable toward decomposition to SF$_5^+$ + HF which implies that the ΔH is negative for the SF$_6$H$^+ \rightarrow$ SF$_5^+$ + HF decomposition. For this ΔH = P.A.(SF$_6$) + A.E. (SF$_5^+$/SF$_6$) + ΔH_f(HF) $- \Delta H_f$(F) $- \Delta H_f$(H$^+$) = P.A.(SF$_6$) $-$ 127 kcal mol^{-1}, when the recently revised value of A.E.(SF$_5^+$/SF$_6$) = 322.4 $\pm$ 0.7 kcal mol^{-1}[27] is utilized. Therefore, P.A.(SF$_6$) < 127 kcal mol^{-1}. No value (or limit) for P.A.(SF$_6$) appears to have been given previously in the literature.

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