

state of the metal ion as well as the nature of the ligands present are important in metathesis. Finally, these results suggest a bracketing for $D^\circ(\text{Fe}^+-\text{CH}_2)$ between 77 and 87 kcal/mol which is somewhat lower than the previously reported value of 96 ± 5 kcal/mol obtained by using ion beam techniques.²¹

We are currently studying the reactions of FeCH_2^+ and CoCH_2^+ with a variety of alkanes, cyclic alkanes, cyclic polyenes, and several other simple molecules such as N_2 , O_2 , CO , CO_2 , etc.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the U.S. Department

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Registry No. FeCH_2^+ , 90143-30-9; CoCH_2^+ , 76792-07-9; FeCD_2^+ , 93604-57-0; CoCD_2^+ , 93604-58-1; ethene, 74-85-1; propene, 115-07-1; 2-methylpropene, 115-11-7; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8; 1-hexene, 592-41-6; 3-methyl-1-butene, 563-45-1; 2-methyl-1-butene, 563-46-2; *trans*-2-methyl-2-butene, 513-35-9; 1,3-butadiene, 106-99-0; 1-butene-1,1-*d*₂, 26119-76-6; ethyne, 74-86-2; propyne, 74-99-7.

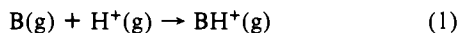
Bridging the Gap. A Continuous Scale of Gas-Phase Basicities from Methane to Water from Pulsed Electron Beam High Pressure Mass Spectrometric Equilibria Measurements

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received September 7, 1984

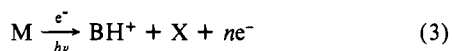
Abstract: Pulsed electron beam high pressure mass spectroscopic techniques have been used to study proton transfer equilibria involving a large number of compounds less basic than H_2O . The data obtained allow construction of a continuous scale of gas-phase proton affinities from CH_4 ($\text{PA} = 134.7 \text{ kcal mol}^{-1}$) upward. A number of new thermochemical inferences may be drawn, including a new value for the proton affinity of CO ($145.6 \text{ kcal mol}^{-1}$). Previous flowing afterflow data by Bohme et al. for compounds less basic than CH_4 may also be used to extend the continuous gas-phase basicity scale down to oxygen atom. Comparisons of data derived in the present work and proton affinities from appearance potential measurements for CO_2 , N_2 , and O have been made. An excellent correlation between gas-phase proton affinity of oxygen bases and the corresponding O_{1s} binding energies obtained from ESCA experiments is obtained. The value of using ESCA data to predict unknown proton affinities is presented.

The investigation of gas-phase basicities of molecules has been a major preoccupation of the field of gas-phase ion chemistry for over 2 decades.² The proton affinity of a molecule, B, defined as the negative of the enthalpy change for eq 1 in the gas phase, is a quantitative measure of gas-phase basicity. The earliest



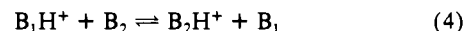
$$\text{PA}(\text{B}) = -\Delta H^\circ_1 = \Delta H_f^\circ(\text{B}) + \Delta H_f^\circ(\text{H}^+) - \Delta H_f^\circ(\text{BH}^+) \quad (2)$$

studies of proton affinities were based on a determination of ΔH°_1 with $\Delta H_f^\circ(\text{BH}^+)$ arrived at from electron impact or photoionization appearance potential measurements of BH^+ fragments from more complex molecules, eq 3.³⁻⁵ Such determinations suffered



from the difficulty of identifying exactly the threshold for appearance of BH^+ and also relied on thermochemical data for the

neutral species B, M, and X. In the late 1960's, with the advent of the techniques of flowing afterglow,⁶ high-pressure mass spectrometry,⁷ and ion cyclotron resonance⁸ for the study of ion molecule reactions at thermal energies a more direct method for the determination of relative proton affinities became available. Since only exothermic or near thermoneutral ion-molecule reactions proceed with significant rates, these techniques allowed ready observation of the exothermic direction of proton transfer, eq 4, between bases B_1 and B_2 which allowed qualitative relative



proton affinities to be established. Further advances in the above study of near-thermoneutral proton transfer reactions in both forward and reverse directions have allowed equilibrium constants, K_4 , to be determined, either from a known ratio of neutral pressures of B_1 and B_2 and observed steady-state ionic abundances of B_1H^+ and B_2H^+ or from direct determination of forward and reverse rate constants, eq 5. From the observation of many proton

$$K_4 = \frac{[\text{B}_2\text{H}^+]}{[\text{B}_1\text{H}^+]} \frac{P_{\text{B}_1}}{P_{\text{B}_2}} = \frac{k_4}{k_{-4}} \quad (5)$$

transfer equilibria involving small steps up the basicity scale, relative proton affinity⁹⁻¹² scales spanning 60-70 kcal mol⁻¹ were

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established. These three techniques, operating under very different conditions of pressure and time domain, gave relative basicity results in gratifyingly good agreement.

The relative proton affinity scales resulting from equilibrium measurements have been centered on the basicity region above water⁹⁻¹¹ and the basicity region below carbon monoxide.¹² In both cases, in order to extract useful thermochemical data for ionic species it was necessary to convert the relative scales to absolute ones based on one or more accurately known absolute proton affinities. Until recently, the only basicity standard for the proton affinity region above water was isobutene.¹³ The *tert*-butyl cation (protonated isobutene), however, has had a range of values of ΔH_f° assigned recently based on various appearance potential measurements.¹⁴ Very recently Baer¹⁵ has carried out highly accurate photoelectron-photoionization coincidence studies, and Traeger^{14,16} and Rosenstock et al.¹⁷ have carried out photoionization studies of $C_2H_5^+$ derived from a variety of ethyl halides which allowed an accurate determination of the proton affinity of ethylene as 162.6 ± 0.5 kcal mol⁻¹. Subsequently, ion cyclotron resonance equilibria measurements¹⁸ linked the proton affinity of H₂O to that for C₂H₄ establishing a new, lower value of 166.7 kcal mol⁻¹ for the basicity of water, which provided a good anchor point for the gas-phase basicities of compounds more basic than H₂O.

The gas-phase basicity region below CO has similarly suffered from uncertainty in absolute proton affinity standards.^{12,19} Bohme has linked the basicities of H₂, O₂, Kr, O, N₂, Xe, CO₂, CH₄, N₂O, and CO by proton transfer equilibrium measurements, and taking the oxygen atom as the absolute anchor point (PA(O) = 116.1 kcal mol⁻¹) based on appearance potential measurements of OH⁺ from H₂O, H₂O₂, and OH he has obtained acceptable agreement with the proton affinity of CO based on appearance energy measurements for HCO⁺ (PA(CO) = 141.0 kcal mol⁻¹). However, none of the appearance energy measurements involved above were of comparable rigor or accuracy to those carried out for C₂H₅⁺.

With the exception of a number of qualitative studies, the basicity region between CO and H₂O has remained largely unexplored. This gap of some 25 kcal mol⁻¹ has left a large "hole" in the otherwise continuous ladder of basicities from the weakest atomic and molecular bases to the strongest organic bases (tertiary amines and tetra(*N*-alkyl)-1,8-diaminonaphthalenes). In the present work we wish to report pulsed electron beam high pressure mass spectrometric measurements of proton transfer equilibria involving molecules with proton affinities between those of CH₄ and H₂O, including C₂H₄. These multiple overlap equilibria measurements thus provide a continuous scale of gas-phase basicities through the entire proton affinity scale and, significantly, anchor the region of weak basicities to the accurately known proton affinity of ethylene. This anchoring has led to several new thermochemical inferences.

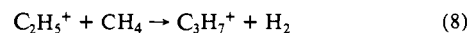
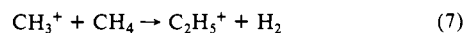
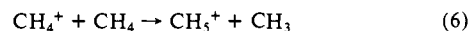
The highly accurate proton affinity data that became available for small molecules as a result of the construction of this scale also provide a fertile ground for quantum chemists to test the rigor and accuracy of methods for obtaining accurate thermochemical data from ab initio calculations.

Experimental Section

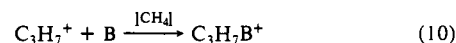
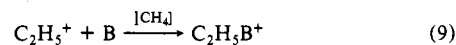
All proton transfer equilibria measurements were carried out at 400 K with a pulsed electron beam high pressure mass spectrometer (HPMS)

described in detail previously.²⁰ The apparatus was recently updated incorporating a LeCroy Model 3921 multichannel analyzer to allow dwell times per channel as short as 1 μ s. Typically 4 μ s/channel was employed with 512 channels giving an effective observation time of over 2 ms after initial ionization.

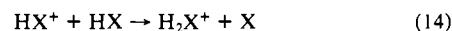
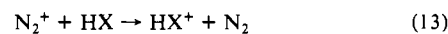
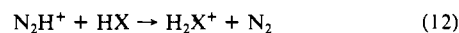
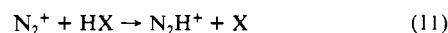
A typical gas-phase-basicity measurement involved preparation of a mixture of ultra-high-purity methane (Matheson) and the two bases under study to a total pressure of approximately 600 torr in a 5-L glass bulb at 400 K. Typical partial pressures of individual bases were from 0.2 to 10 mtorr. This gas mixture was then flowed through the high-pressure ion source at a constantly maintained pressure in the range 2.5 to 5.0 torr. Gas-phase ion-molecule reactions in methane, eq 6-8, pro-



duced chemical ionization reagents for the bases B₁ and B₂. For the majority of the bases studied here only CH₅⁺ was sufficiently acidic to act as a protonating agent. In many cases, termolecular clustering of the alkyl cations with the weak bases was also observed, eq 9 and 10.



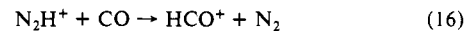
For bases with proton affinities near methane, CH₄ was inappropriate as the major gas. In such cases high-purity nitrogen was substituted as the bath gas. For hydrogen-containing bases, HX (X = CH₃, Cl, Br), formation of protonated HX was accomplished by one or both of the sequences of equations 11 and 12 or 13 and 14. If neither of the bases



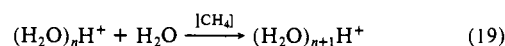
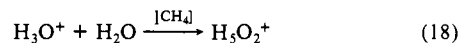
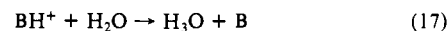
involved in the equilibrium contained hydrogen, a small amount of either CH₄ or H₂ was added. In addition, all equilibria involving CO were duplicated with N₂ as the major gas to avoid complications due to the C₂H₅⁺ - HCO⁺ mass ambiguity. In the presence of CO, C₂H₅⁺ is known to cluster rapidly and exothermically via eq 15 under the experimental conditions used. This reaction effectively eliminated any C₂H₅⁺ at long



reaction times in CH₄-CO mixtures and thus any *m/e* 29 observed at long time should be HCO⁺. Excellent agreement with CH₄ and N₂ as bath gases was obtained. The N₂H⁺-HCO⁺ mass ambiguity in N₂-CO mixtures is not a problem due to rapid, exothermic proton transfer to CO, eq 16.



An additional procedure had to be incorporated into the usual HPMS technique owing to the very weakly basic nature of the compounds under study. Due to the presence of water as a persistent impurity, even at the part per million level, in the gases used and the glass vacuum system, exothermic proton transfer to H₂O followed by termolecular clustering of H₃O⁺ with H₂O, eq 17-19, effectively caused the BH⁺ signal to disappear before adequate equilibrium observations could be made. In



order to circumvent this problem the inlet flow to the ion source was passed through a U-trap which could be appropriately cooled. It was found necessary to use cold bath temperatures below -75 °C to adequately eliminate interferences due to ion-molecule reactions with H₂O. This restriction effectively limited the range of compounds usable for basicity studies to those with vapor pressures greater than 0.01 torr at -75 °C and freezing points below -75 °C. Typical cold baths used were: dry ice-acetone (-75 °C), acetone slush (-95 °C), *n*-pentane slush (-129 °C), and isopentane slush (-155 °C).

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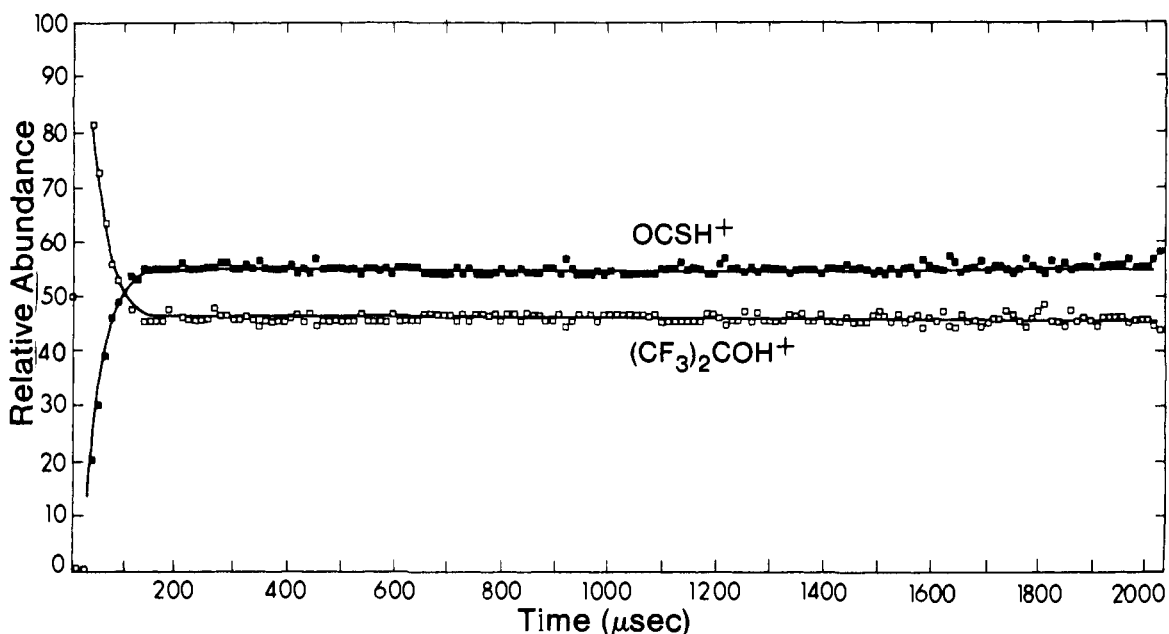


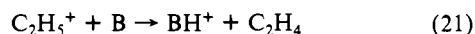
Figure 1. Relative ionic abundances of protonated species as a function of time after initial ionization in a 5:1 mixture of $(CF_3)_2CO:OCS$ — $P_{CH_4} = 3.4$ torr; $P_{(CF_3)_2CO} = 5.5$ mtorr; $P_{OCS} = 1.1$ mtorr.

Results

Equilibrium constants, K_4 , were calculated for each proton transfer equilibrium form eq 5 with the observed steady-state ionic abundances and the experimentally prepared partial pressures of B_1 and B_2 . Each equilibrium was examined several times with mixture ratios of B_1 and B_2 which typically varied by a factor of 10. Equilibrium constants usually varied by less than 20%. A typical plot of variation of ionic abundances with time after the electron beam pulse is shown in Figure 1 for 5:1 mixture of $(CF_3)_2CO:OCS$ with methane as the bath gas. Free energy changes, ΔG°_4 , for each of the equilibria examined were calculated from eq 20. Each of the free energy changes obtained is summarized in the ladder of Table I.

$$\Delta G^\circ_4 = -RT \ln K_4 \quad (20)$$

The proton affinity of C_2H_4 is chosen as the absolute anchor point for the gas-phase-basicity scale. As a result free energy changes, ΔG°_{21} , for proton transfer from $C_2H_5^+$ are also summarized in Table I. The multiple overlap experiments carried



out yielding ΔG°_4 values lead to a variation in individual ΔG°_{21} values of less than ± 0.2 kcal mol $^{-1}$. In each case, the mean ΔG°_{21} value is reported. Following the practice recommended by Taft et al.¹⁰ and Lias et al.,⁵ the uncertainty in ΔG°_{21} values is taken as the range of values derived from all possible different combinations of directly determined ΔG°_4 values. In this fashion random errors are largely eliminated and the uncertainty in ΔG°_{21} values is comparable to the uncertainty of ΔG°_4 measurements.

Entropy changes, ΔS°_{21} , are also included in Table I. In order to carry out such calculations, entropies of each of the ionic species and, in some cases, neutral species had to be estimated. The value of $S^\circ(C_2H_5^+)$ was calculated to be 54.8 cal K $^{-2}$ mol $^{-1}$ from a complete statistical thermodynamic analysis based on a non-classical bridged structure calculated by Pople et al.²¹ to be the most stable form of $C_2H_5^+$ and vibrational frequencies determined from ab initio calculations of force constants. Entropies of the remaining protonated bases were calculated primarily from known entropies of isoelectronic neutral molecules with appropriate translational entropy corrections. For examples, $S^\circ(HCO^+)$ was estimated to be 48.6 cal mol $^{-1}$ K $^{-1}$ based on a value for $S^\circ(HCN)$ of 48.2 cal K $^{-1}$ mol $^{-1}$, $S^\circ(H_2Cl^+)$ was estimated as 49.7 cal K $^{-1}$

Table I. Thermochemical Data Relevant to Proton Transfer Equilibria Observed at 400 K

B	ΔG°_4	ΔG°_{21}	ΔS°_{21}	ΔH°_{21}	PA(B)
H ₂ S		-6.5	-1.4	-7.1	169.7
CF ₃ CH ₂ OH	1.8	-5.6	-0.4	-5.8	168.4
CS ₂	0.9, 2.1, 3.2, 5.3	-4.5	2.6	-3.5	166.1
H ₂ O	1.2, 3.4	-3.3	-1.2	-3.8	166.4
CF ₃ CN		-1.2	-1.3	-1.7	164.3
C ₂ H ₄	1.3, 2.7	(0.0)	(0.0)	(0.0)	(162.6)
CF ₃ COCl	1.6	1.6	-0.4	1.4	161.2
SO ₂	5.5, 10.3	7.1	0.6	7.3	155.3
OCS	0.4, 1.8, 7.4	7.5	1.6	8.1	154.5
(CF ₃) ₂ CO	1.5	9.0	-0.4	8.8	153.8
HI	1.3, 1.8, 5.2, 5.5	10.3	3.6	11.7	150.9
CF ₃ I	3.8	10.8	3.6	12.2	150.4
SO ₂ F ₂	2.0	12.8	-0.4	12.6	150.0
C ₂ H ₆	2.9, 4.6	15.7	0.1	15.7	146.9
CO	5.9, 7.1	17.4	-1.0	17.0	145.6
HBr	1.2, 2.3, 4.2	18.7	2.4	19.7	142.9
N ₂ O	0.7	19.8	2.0	20.6	142.0
CF ₃ Br	4.2	19.9	3.6	21.3	141.3
CF ₃ Cl	3.0, 4.6, 4.2	22.2	3.4	23.6	139.0
NF ₃	6.5, 6.7	22.9	-2.6	21.9	140.7
HCl	4.3	24.0	2.6	25.0	137.6
CH ₄	2.6	26.5	3.6	27.9	134.7

^akcal mol $^{-1}$ (± 0.2 kcal mol $^{-1}$). ^bcal mol $^{-1}$ K $^{-1}$ (± 1 cal mol $^{-1}$ K $^{-1}$).
^ckcal mol $^{-1}$ (± 0.5 kcal mol $^{-1}$). ^dkcal mol $^{-1}$ (± 1 kcal mol $^{-1}$).

mol $^{-1}$ based on a value of $S^\circ(H_2S)$ of 49.2 cal K mol $^{-1}$, and $S^\circ(HN_2O^+)$ was estimated as 57.0 cal K $^{-1}$ mol $^{-1}$ based on the values of $S^\circ(HN_3)$, $S^\circ(HNCO)$, and $S^\circ(HOCN)$ of 57.1, 56.9,

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Table II. Proton Affinities for Species Less Basic than CH₄

species (M)	PA(M), kcal mol ⁻¹	other data
CH ₄	134.7	
CO ₂	133.2	131.0 ^a
Xe	122.6	
N ₂	122.0	114, ^b 125 ^c , 129 ^d , 120 ^e
O	120.7	116.3, ^f 118.4 ^g
HF	120.4	

^aReference 34. ^bReference 36. ^cReference 37. ^dReference 35. ^eReference 38. ^fReferences 40 and 41. ^gReference 42.

and 57.0 cal K⁻¹ mol⁻¹ respectively. In cases where entropies of isoelectronic neutrals were unknown, they were estimated from either group equivalent methods or bond additivity schemes.²² For example, S°(CF₃CNH⁺) was estimated to be 72.4 cal K⁻¹ mol⁻¹ based on a calculation of S°(CF₃C≡CH) from group equivalent methods; S°(CF₃CH₂OH₂⁺) was similarly estimated from S°(CF₃CH₂NH₂) to be 78.8 cal K⁻¹ mol⁻¹. Values of ΔS°₂₁ thus determined should be accurate to within 1 cal mol⁻¹ K⁻¹.

Enthalpy changes for proton transfer relative to C₂H₄, ΔH°₂₁, were calculated from eq 22 with the experimentally determined ΔG°₂₁ values at 400 K and the estimated ΔS°₂₁ described above. These values are also summarized in Table I.

$$\Delta H^{\circ}_{21} = \Delta G^{\circ}_{21} + T\Delta S^{\circ}_{21} \quad (22)$$

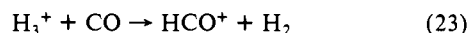
In the final column of Table I the absolute proton affinities of each of the species examined are summarized, calculated from ΔH°₂₁ and a proton affinity of C₂H₄ of 162.6 ± 0.5 kcal mol⁻¹. The uncertainty in recommended proton affinity values is taken as ±1 kcal mol⁻¹ based on the combined uncertainties in the proton affinity of ethylene and ΔH°₂₁ values.

Proton affinity measurements for species less basic than methane were not attempted in the present study due to difficulties associated with operating only with H₂ as a proton source in the HPMS apparatus. However, the relative proton affinity data of Bohme¹² for gas-phase basicities below CO can be combined with the absolute value of PA(CO) determined here to calculate new proton affinities for CO₂, Xe, N₂, and O. In addition, data by Beauchamp²³ relating the proton affinity of HF to that of N₂ can be used to calculate a new value of PA(HF). Proton affinities below CH₄ thus derived are summarized in Table II.

Discussion

The proton transfer equilibrium data presented above provide the basis for construction of an accurate gas-phase-basicity scale for species less basic than H₂O. Included in this scale are ethylene and carbon monoxide. Initially it had been hoped that the proton affinities of both C₂H₄ and CO, based on appearance potential measurements, could be used as fixed anchor points for the proton affinity scale. Appearance potential data for C₂H₅⁺¹⁵⁻¹⁷ and HCO⁺³ predicted a proton affinity difference between C₂H₄ and CO of ~20 kcal mol⁻¹. Unfortunately, this proton affinity difference was not reproduced by the proton transfer equilibrium measurements which yielded a value for PA(C₂H₄) - PA(CO) of only 17.3 kcal mol⁻¹. Since the proton affinity of C₂H₄ appears to be very accurately established by a number of PEPICO¹⁵ and photoionization appearance potential measurements^{16,17} on C₂H₅⁺, it is concluded that the appearance potential measurements to date for HCO⁺ have not yielded the adiabatic threshold. This conclusion is consistent with the findings of Haney and Franklin²⁴ from a study of translational energy of decomposition of HCO⁺ ions at threshold derived from CH₃CHO, HCO₂H, and C₂H₃CHO. Analysis of their data reveals that the translational energy of HCO⁺ fragment ions is relatively constant as a function of electron energy near threshold. Rosenstock et al.³ have interpreted these data in terms of an activation barrier associated with

unimolecular decomposition of the parent molecular ions. These authors have used the translational energy measurements to correct the photoionization appearance potential measurements for HCO⁺ from CH₃CHO and HCO₂H²⁵ to arrive at a value of ΔH_f^o(HCO⁺) of 194.3 ± 0.5 kcal mol⁻¹. This value for ΔH_f^o of the formyl cation yields a proton affinity of CO of 145.0 kcal mol⁻¹ in excellent agreement with the present determination. The previously accepted value for the proton affinity has been taken to be 142.5 kcal mol⁻¹, based on photoionization appearance potential measurements of HCO⁺ from CH₂O by Guyon, Chupka, and Berkowitz.²⁶ A similar value based on data for the same system by Mathews and Warneck of 141.8 kcal mol⁻¹²⁵ has also been derived. Unfortunately, the experiment of Haney and Franklin does not allow for accurate determination of the translational energy of decomposition in production of HCO⁺ from CH₂O since the very light neutral product (H) carries off the majority of the translational energy of decomposition.²⁷ However, in view of the very considerable geometry changes taking place in dissociation of CH₂O⁺ to HCO⁺ and H and the similarity of such a dissociation to those of CH₃CHO⁺ and HCO₂H⁺ it seems highly probable that a similar activation barrier to decomposition of the CH₂O⁺ molecular ion may be present thus entailing the adiabatic appearance potential for HCO⁺ to not be reached. This conclusion is supported by recent ab initio calculations by Radom²⁸ which analyzed the lowest energy dissociation pathway for CH₂O⁺ into HCO⁺ and H and which reveal a small activation barrier to decomposition. Nobes and Radom²⁹ have also carried out highly accurate ab initio calculations which take account of electron correlation and zero-point energy changes for the proton transfer reaction, eq 23, and obtain a value for ΔH°₂₃ of 44.0 kcal mol⁻¹.



Combining this with the accurately known proton affinity of H₂ of 101.3 kcal mol⁻¹³⁰ gives a value for proton affinity of CO of 145.3 kcal mol⁻¹ in excellent agreement with the present determination. In addition, very large basis set ab initio calculations by DeFrees³⁴ which also include electron correlation and zero-point energy contributions yield a value for the proton affinity of CO of 145 kcal mol⁻¹. Thus taken together all of the above evidence strongly supports the assignment of a new, higher value for the proton affinity of CO of 145.6 kcal mol⁻¹.

The proton affinities of HCl, HBr, and HI have been determined by Polley and Munson³² to be 135 ± 2, 140 ± 1, and 147 ± 2 kcal mol⁻¹, respectively, based on occurrence, or nonoccurrence of proton transfer from species of known proton affinity to the halogen acids. Lee et al.³² have also determined proton affinities of HCl and HBr of 135 ± 1 and 141 ± 1 kcal mol⁻¹, respectively, from photoionization appearance potential measurements of protonated hydrogen halides from the van der Waals dimers. The values for proton affinity of HCl, HBr, and HI of 137.6, 142.9, and 150.9 kcal mol⁻¹, respectively, determined in the present study are in very good agreement with these previous determinations.

As noted above, for compounds less basic than methane new values for proton affinity may be arrived at by linking the previous flowing afterglow relative basicity data to the new scale presented here. It is also then possible to compare these proton affinity data to those derived from appearance potential measurements. The proton affinity of CO₂ arrived at by proton transfer equilibrium

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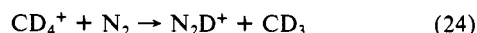
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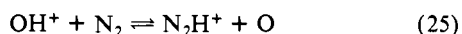
measurements is 133.2 kcal mol⁻¹. Photoionization appearance potential experiments³⁴ for CO₂H⁺ derived from HCO₂H yield a value of 130.9 kcal mol⁻¹ for PA(CO₂). Again given the fact that a significant geometry change occurs during the dissociation of HCO₂H⁺ to CO₂H⁺ + H, a small activation barrier to dissociation may exist, causing the adiabatic appearance potential to be slightly overestimated. The agreement between the present determination of 133.2 kcal mol⁻¹ and the appearance potential value of 130.9 kcal mol⁻¹ may thus be regarded as being very good.

For species less basic than CO₂, the agreement between proton transfer equilibria and appearance potential data is less satisfactory. The proton affinity of N₂ derived from the present work and Bohme's data is 122.0 kcal mol⁻¹. The only appearance potential data for N₂H⁺ are from experiments involving dissociative ionization of N₂H₂ produced in a microwave discharge in anhydrous hydrazine.³⁵⁻³⁷ These experiments all suffer from the possibility of producing excited N₂H₂ and the very large uncertainty in Δ*H*_f^o(N₂H₂). These shortcomings are manifested by the range of proton affinities for N₂ derived from the data of 114-129 kcal mol⁻¹. Shannon and Harrison³⁸ have observed reaction 24 in CD₄-N₂ mixtures. On the basis of the assumption

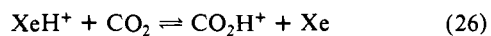


that only ground-state CD₄⁺ is involved and making corrections for deuterium vs. hydrogen energetics, a lower limit for the proton affinity of N₂ of 120 kcal mol⁻¹ may be derived. Ab initio calculations employing a 4-31G basis set by Yamabe and Hira³⁹ yield a value for proton affinity of N₂ of 123.0 kcal mol⁻¹. The value derived in the present study of 122 kcal mol⁻¹ is thus consistent with all of the above experimental and theoretical data.

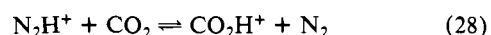
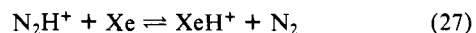
The most serious disagreement between proton transfer equilibrium data and proton affinities derived from mass spectrometric appearance potential measurements occurs in the case of the oxygen atom. Bohme et al.¹² have investigated equilibrium 25 to find a value of Δ*H*_f^o of -1.3 kcal mol⁻¹. This combined with



a proton affinity of N₂ of 122.0 kcal mol⁻¹ yields a value for proton affinity of O of 120.7 kcal mol⁻¹. Thermochemical data for OH⁺ have been obtained both by photoionization appearance potential measurements for OH⁺ from H₂O⁴⁰ and by photoelectron spectroscopic determination of the ionization potential of OH.⁴¹ Both of these experiments yield a proton affinity of O of 116.3 kcal mol⁻¹ and appear highly accurate. There are three possible reasons for the disagreement between the values above of 120.7 and 116.3 kcal mol⁻¹. The first possibility is that the scale of proton affinities derived in this work is incorrect by 4 kcal mol⁻¹. Given the very good agreement between our scale and other absolute measurements and the self-consistency of multiple overlap equilibria, this possibility seems unlikely. The second possibility is an error in the flowing afterflow experiments relating the proton affinities of CH₄ and O. One possible source of error is the experiment involving Xe and CO₂, eq 26, which could not be examined at 298 K because of the excessively large equilibrium constant at low temperature. In order to circumvent this problem, this reaction



was examined at 800 K.^{12,19} However, the proton affinity difference between Xe and CO₂ was also obtained by examination of equilibria 27 and 28 and good agreement with the directly measured eq 25 obtained. The final possible source of disagreement



is that the true adiabatic appearance potential of OH⁺ from either

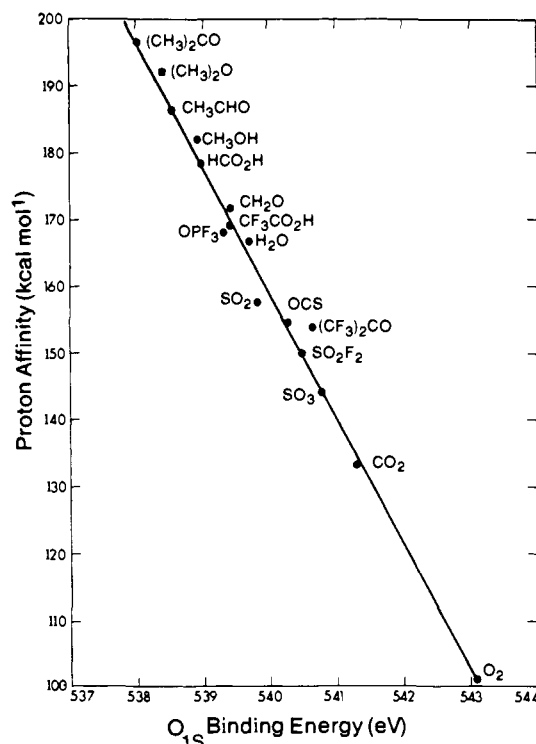
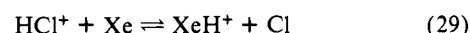


Figure 2. Variation of proton affinities of oxygen bases as a function of O_{1s} binding energy.

H₂O or OH has not been observed. The appearance potential measurement of OH⁺ from H₂O may have involved translational energy release while the ionization potential of OH was obtained by base line subtraction of spectra of H₂O, and these factors could conceivably lead to a 4 kcal mol⁻¹ error in determination of the adiabatic threshold. This conjecture is supported by an indirect measurement of the ionization potential of OH by Chupka and Berkowitz,¹² involving appearance energies for ions, including OH⁺, derived from HOF. These experiments yield a value of 12.9 eV for the ionization potential of OH at 0 °K. These data may then be used to derive a proton affinity for the oxygen atom of 118.4 kcal mol⁻¹, giving an indication that Δ*H*_f^o(OH⁺) from mass spectrometric appearance potential measurements is not yet definitive. Proof that either the photoionization data for OH⁺ or the flowing afterglow data relating the oxygen atom to stronger bases is in error can be found in the recent SIFT experiments of Twiddy et al.⁴⁷ These authors have observed the thermal ion-molecule reaction, eq 29, to be moderately fast, indicating that the proton affinity of Xe is greater than or comparable to that of Cl. This experiment thus requires that PA(Xe) be 123 kcal



mol⁻¹ in disagreement with the previous assignment, 118.0 kcal mol⁻¹, but in accord with the present assignment of 122.6 kcal mol⁻¹. This experiment thus lends strong support to the proton affinity assignments presented here.

Correlations with Core Binding Energies. Several studies have been carried out recently correlating gas-phase proton affinities of molecules with core binding energies associated with a particular

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basic site.⁴³⁻⁴⁵ Studies for oxygen 1s core binding energies were initially thought to show slightly different correlations for singly and doubly bonded oxygen.⁴³ However, later studies, based on improved core binding energy measurements, showed that all hydroxyl, ether, aldehyde, and ketone organic bases fit a single correlation.⁴⁴

This good correlation was confined to molecules more basic than H₂O due to the unavailability of reliable data for more weakly basic species. The data reported in the present work provide the basis for testing such a correlation over a much larger basicity range for a greater variety of functional groups. A plot of gas-phase proton affinity as a function of oxygen 1s binding energy is shown in Figure 2 for all of the oxygen bases examined in the present study and several others more basic than H₂O. It may be readily seen that an excellent correlation between the two quantities exists over a range of basicities of a least 100 kcal mol⁻¹. In addition, a variety of inorganic oxygen bases such as O₂, CO₂, SO₃, SO₂F₂, OCS, and SO₂ is included. These results thus show that the gas-phase proton affinity of a molecule is intimately related to the core binding energy of the most basic atomic site in the molecule. The relationship between proton affinity in kcal mol⁻¹ and oxygen 1s core binding energy in eV given by eq 30 may thus be used to predict proton affinities for molecules for which the core binding energy is known. For example, ozone,

$$PA(B) = (438.90 - 0.8(O_{1s}B.E.))23.06 \quad (30)$$

O₃, has measured oxygen 1s binding energies of 541.5 eV for the terminal oxygens and 546.2 eV for the central oxygen.⁴⁶ From these data it is possible to predict that O₃ will protonate on a terminal oxygen with a proton affinity of 131 kcal mol⁻¹. Such interpolations should prove extremely valuable in situations such as this where the difficulty in handling of the species makes an equilibrium proton affinity determination impractical.

Conclusion

Multiple overlap proton transfer equilibria measurements have been used to define a new absolute proton affinity scale for the basicity region less basic than H₂O. The data predict a proton affinity of CO of 145.6 kcal mol⁻¹, roughly 3 kcal mol⁻¹ greater than previously accepted based on appearance potential data. More recent ab initio calculations and considerations of translational energy release upon fragmentation support the new higher value. Good agreement for proton affinities of the hydrogen halides with those determined by molecular beam photoionization studies of the van der Waals dimer is obtained. For molecules less basic than CH₄, the present scale plus previous flowing afterglow data allow prediction of new proton affinities for CO₂, N₂, Xe, and HF. Some discrepancy appears to exist between equilibrium and appearance energy determinations of the proton affinity of the oxygen atom.

Correlations between oxygen 1s binding energy and proton affinity reveal a strong interdependence of these two quantities. The core binding energies may be used to predict proton affinities for molecules where experimental determination would be difficult.

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Registry No. H₂S, 7783-06-4; CF₃CH₂OH, 75-89-8; CS₂, 75-15-0; H₂O, 7732-18-5; CF₃CN, 353-85-5; C₂H₄, 74-85-1; CF₃COCl, 354-32-5; SO₂, 7446-09-5; OCS, 463-58-1; (CF₃)₂CO, 1479-49-8; HI, 10034-85-2; CF₃I, 2314-97-8; SO₂F₂, 2699-79-8; C₂H₆, 74-85-1; CO, 630-08-0; HBr, 10035-10-6; N₂O, 10024-97-2; CF₃Br, 75-63-8; CF₃Cl, 75-72-9; NF₃, 7783-54-2; HCl, 7647-01-0; CH₄, 74-82-8; CO₂, 124-38-9; SO₃, 7446-11-9; CF₃CO₂H, 76-05-1; CH₂O, 50-00-0; HCO₂H, 64-18-6; CH₃OH, 67-56-1; CH₃CHO, 75-07-0; (CH₃)₂O, 115-10-6; (CH₃)₂CO, 67-64-1; F₃PO, 13478-20-1.

Laser Flash Photolysis Study of the Photochemistry of Ring-Substituted β -Phenylpropiophenones¹

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Abstract: The triplet states of an extensive series of ring-substituted β -phenylpropiophenones have been characterized by phosphorescence emission spectroscopy and in laser flash photolysis studies. Substitution in the β -phenyl ring has only a small effect on the triplet lifetime, determined at -70 °C for the series, and on the Stern-Volmer slopes for triplet quenching by 1-methylnaphthalene determined in benzene and *tert*-butyl alcohol solutions at room temperature. Substitution in the 1-phenyl ring, on the other hand, has a more pronounced effect on the triplet lifetime. This is attributed to a dependence of the efficiency of β -phenyl deactivation on the degree of n,π^* character of the lowest triplet state. Arrhenius parameters for triplet decay were determined in toluene and methanol solutions for β -phenyl-*p*-methoxypropiophenone. The rather low pre-exponential factor obtained in these experiments is provided as evidence for a rather specific geometry for deactivation in the excited state. Stern-Volmer quenching of β -phenylpropiophenone triplets by 1-methylnaphthalene was investigated in a series of nine solvents of widely differing polarity and viscosity. The effects are quite small, indicating a compensation of changes in k_q by the triplet lifetime. The triplet-state behavior of β -phenylpropiophenone moieties in polymeric systems was investigated with a series of copolymers of methyl methacrylate and the methacrylate esters of hydroxy-substituted phenylalkyl ketones. Stern-Volmer quenching of the polymeric ketones with 1-methylnaphthalene indicates that there is essentially no difference between the behavior of polymer-incorporated β -phenylpropiophenone moieties and that of the analogous monomeric derivatives.

The ability of aromatic rings to deactivate n,π^* carbonyl triplets has been recognized for a number of years.⁴⁻⁶ For example, this

is the reason why the triplet lifetimes for ketones such as benzophenone never exceed a few microseconds in benzene at ambient

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