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Progress toward an Absolute Gas-Phase Proton Affinity Scale

J. E. Szulejko and T. B. McMahon*

Contribution from the Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Abstract: The temperature dependence of the proton transfer equilibrium constants for approximately 80 pairs of bases ranging in proton affinity from N_2 to *tert*-butylamine has been examined. These data provide the basis for formulation of a revised gas-phase proton affinity scale which now appears to have a firm basis. Excellent agreement with appearance energy determinations of proton affinities as well as *ab initio* calculated values is obtained. An important finding of this work is that the value of $\Delta H_f°$ for the *tert*-butyl cation must be significantly higher than that derived from appearance energy measurements by Traeger which had formed the basis for the proton affinity assignment for isobutene, an important reference point in the proton affinity scale. The data obtained here would suggest that the proton affinity of isobutene must be revised downward by ~4 kcal mol^{-1} with important consequence for all proton affinities in the vicinity of isobutene and above. In addition significant revisions are indicated for proton affinities between those of propene and isobutene. In contrast, however, the substantial upward revision of the proton affinity scale in the basicity region above ammonia which had been proposed by Mautner and Sieck (*J. Am. Chem. Soc.* **1991**, *113*, 4448) is not supported by the present experiments.

Introduction

The study of gas-phase acidities and basicities of molecules has been a major undertaking in the field of gas-phase ion chemistry since the late 1960's. While the determination of the exothermic direction of proton transfer between two entities has sufficed to answer qualitative questions concerning *relative* acid or base strength, increasing experimental sophistication has provided, and further demanded, a reliable quantitative ion energetics data base and associated accurate acidity and basicity scales.

In principle there are three methods whereby accurate data for gaseous ion energetics may be established. The oldest, and perhaps most fundamental, method involves the determination of appearance energies associated with formation of fragment ions from stable neutral molecules by either monoenergetic electron impact[1] or photoionization techniques.[2] Other variants of this involve the measurement of ionization energies of free radicals[1b,2e,3] and threshold energy determinations of fragment ions from van der Waals clusters.[4] In each case an accurate knowledge of the energetics of the precursor neutral species is required in order that the threshold appearance energy measurement yield accurate ion energetics (eq 1).

$$M \rightarrow BH^+ + F + ne^- \qquad (1)$$

The second method for determination of ion energetics makes use of measurement of equilibrium constants for reversible proton transfer reactions, eq 2. When the equilibrium constant can be

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \qquad (2)$$

accurately determined the free energy change, $\Delta G°$, for the reaction may be readily derived, eq 3, and if the equilibrium

$$\Delta G° = -RT \ln K_{eq} \qquad (3)$$

constant is examined over a broad temperature range both $\Delta H°$ and $\Delta S°$ may be derived, eq 4. In cases where accurate data are

$$\Delta G° = \Delta H° - T\Delta S° \qquad (4)$$

available for either B_1H^+ or B_2H^+ from an appearance energy measurement then correspondingly accurate data for the other species may be obtained. This technique has been very extensively used to construct various single-temperature $\Delta G°$ scales[5] for proton transfer. With the use of multiple overlap proton transfer equilibria the energetics of each species studied were linked to one or more *proton affinity standards* determined from appearance energy measurement within the range of the scale examined.

The third method involves direct *ab initio* calculation[2m,6] of the enthalpy change for protonation, eq 5. With increasing

$$B + H^+ \rightarrow BH^+ \qquad (5)$$

sophistication of quantum mechanical treatment coupled with more powerful computational hardware, the claim[6u] has even been made that such determinations of gas-phase proton affinities are as reliable as the best experimental methods.

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In 1991 Meot-Ner and Sieck[7] published the first series of temperature dependent proton transfer equilibrium measurements which linked a number of bases which could be classified as "primary standards" based on accurate appearance energy measurements. In this way accurate experimental assignment of ΔH° and ΔS° values can be made which is much more satisfactory than the previous procedure of determination of ΔG° values at a single temperature which were then converted to ΔH° data using estimated entropy data. One of the important conclusions of that work was the finding that the proton affinity difference between the primary standard, isobutene, and ammonia was greater by more than 4.5 kcal mol^{-1} than previously assigned.[8] Subsequently, a series of experiments from this laboratory[9] involving a small subset of bases with proton affinities between those of isobutene and ammonia confirmed this greater difference. A large number of gas-phase proton affinity assignments have been made based on proton transfer equilibria relative to ammonia and ammonia had come to be regarded as a "secondary standard" in the gas-phase basicity scale. These new experiments therefore apparently demanded a higher proton affinity of ammonia and a corresponding readjustment of a large part of the upper region of the entire gas-phase proton affinity scale.

For the past several years[9,10] an ongoing endeavor in this laboratory has been to link all possible proton affinity "primary standards" by a continuous series of temperature dependent proton transfer equilibrium measurements. If all such primary standards can be successfully linked in this way the species, B, used in the linkages become accurately established secondary standards as the ΔH_f° and S° values for the corresponding protonated species, BH$^+$, are then determined. As a result a series of compounds becomes available against which all other new bases of unknown proton affinity can be examined in proton transfer equilibria. This goal has now been achieved and a revised scale of proton affinities spanning a range of over 100 kcal mol^{-1} is proposed herein.

Experimental Section

All experiments were performed on a pulsed ionization high pressure mass spectrometer constructed at the University of Waterloo configured around a VG 70-70 mass spectrometer whose geometry was reversed to provide a B-E instrument. The apparatus[9] and its capabilities have been described in detail previously.

All samples were prepared in a heated 5-L stainless steel reservoir and introduced into the high pressure ion source *via* an inlet system constructed entirely of metal, with the exception of a 15 cm, 13 mm o.d. glass tube used for high voltage isolation from the ~3 kV potential of the ion source. In most cases methane was used as the high pressure bath gas and served as both the inert third body stabilization species and proton transfer chemical ionization reagent. In a few cases, including experiments for bases of proton affinity less than that of CH_4, the bath gas composition was N_2 to which a small amount of H_2 had been added. In all cases a wide range of partial pressure ratios of the two bases under study was employed as a check of the precision and accuracy of the measured equilibrium constants. Ion source pressures ranged from 3 to 10 Torr and temperatures from 300 to 670 K. Under these conditions with pure CH_4 at a pressure of 5 Torr in the ion source m/z 17 (CH_5^+) persisted for over 3 ms after the initial (100 μs) electron gun pulse and the intensity of H_3O^+, arising from proton transfer to traces of H_2O, took ~1 ms to reach maximum. This very low H_2O background was essential to the success of experiments involving compounds of proton affinity less than that of H_2O.

For most experiments a mass resolution of ~500 was sufficient; however in several cases a resolution of ~3000 was employed, at the expense of signal intensity, to distinguish isobaric ions. For example, $C_2H_5^+$ could be readily resolved[9] from HCO$^+$. For control experiments all measurements gave equilibrium constants independent of the resolution employed, indicating that isobaric impurity ions did not affect equilibrium ion intensities at the reaction times at which equilibrium constants were calculated.

Results

Temperature dependence of the proton transfer equilibrium constant for approximately 80 pairs of bases ranging in proton affinity from N_2 to *tert*-butylamine was examined. The equilibrium constant at each temperature was determined from the ion intensity ratio of the two protonated bases at equilibrium and the partial pressure ratio of the two neutral bases, eq 6. The

$$K_{\mathrm{eq}} = \frac{I_{\mathrm{B_2H^+}}}{I_{\mathrm{B_1H^+}}}\frac{P_{\mathrm{B_1}}}{P_{\mathrm{B_2}}} \qquad (6)$$

variation of $\ln(K_{\mathrm{eq}})$ with reciprocal temperature (van't Hoff plot) for *ca.* 75 pairs of bases studied is shown in Figure 1, and the thermochemical data derived are summarized in Table I. Since the accuracy of the thermochemical data derived increases with the temperature span over which the equilibria are studied, the minimum, maximum, and mean temperatures for each equilibrium are also included in Table I. Taking the absolute value of the proton affinity of CO as 141.9 kcal mol^{-1}, based on appearance energy measurements,[2f,ℓ] the proton affinities of each of the other compounds examined can be derived. These values, together with the currently accepted values from the NIST database,[8] the values of ΔG°_{600}, and the half-reaction entropy changes, $\Delta S^\circ_{1/2}$, for the protonation are given in Table II. The NIST database had been compiled on the basis of literature data up to 1983, and while recognized as being out of date in many areas, it is nevertheless widely used as the prevailing authority on a great deal of gaseous ion thermochemistry. As discussed in detail below, for those compounds where proton affinity values are also available from appearance energy measurements, the extent to which the proton affinities obtained from proton transfer equilibria are in good agreement with these former values can be taken as a measure of the accuracy and internal consistency of the scale.

A number of the individual equilibria studied are worthy of further comment.

In the low region of the proton affinity scale where there are relatively few compounds spaced within a reasonable span of each other it was deemed extremely important to be able to use every measurement that might possibly be made. In order to obtain an additional value for the proton affinity of CO_2, for example, an experiment involving $^{13}CO_2$ and N_2O, eq 7, was

$$^{13}CO_2H^+ + N_2O \rightleftharpoons N_2OH^+ + {}^{13}CO_2 \qquad (7)$$

carried out. Due to the resolution required to baseline resolve $^{12}CO_2H^+$ and N_2OH^+ (>5000), the ^{13}C labeled analogue was

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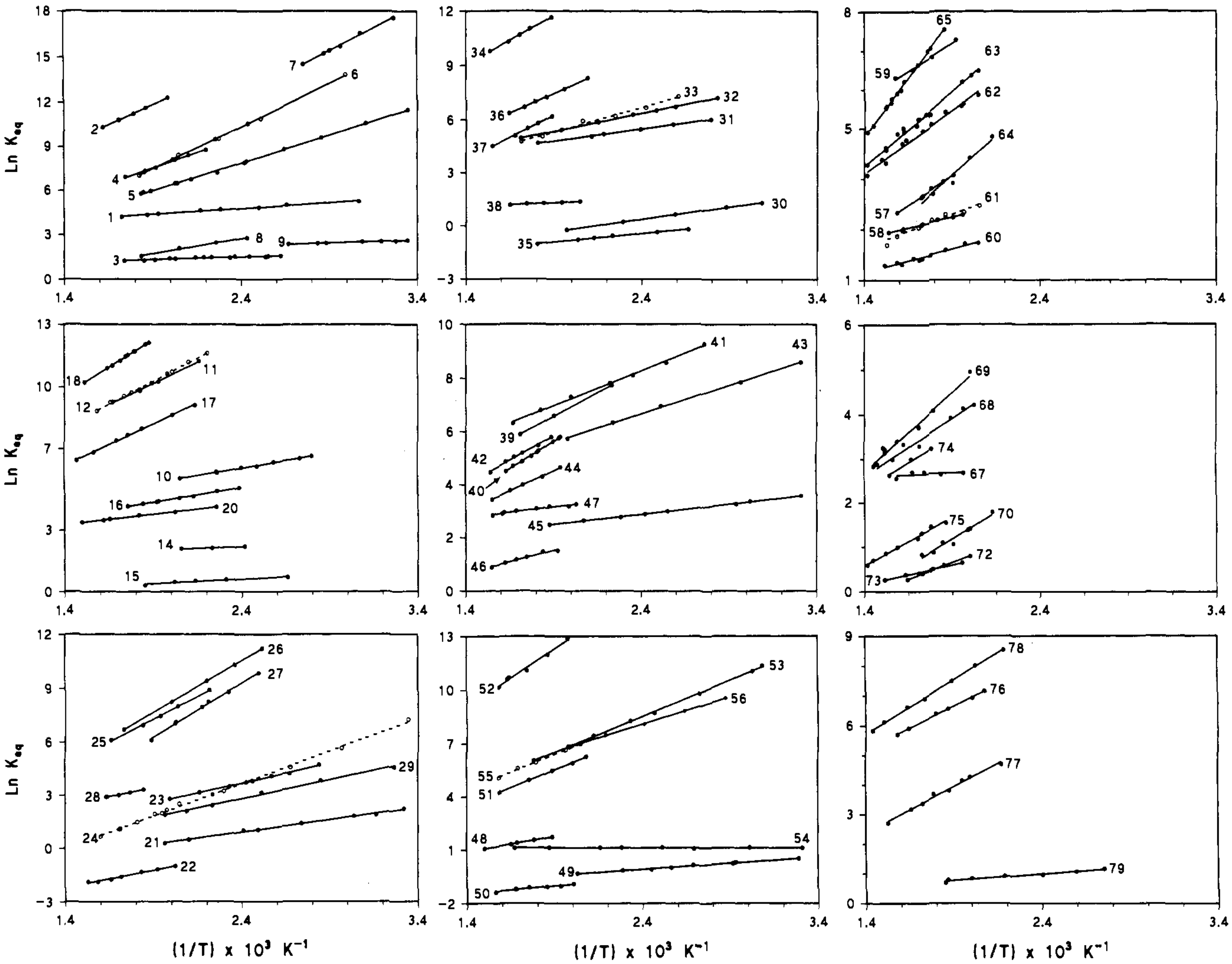

Figure 1. Van't Hoff plots of proton transfer equilibria between *ca* 75 pairs of bases. See Table I for the pair of bases referred to in Figure 1.

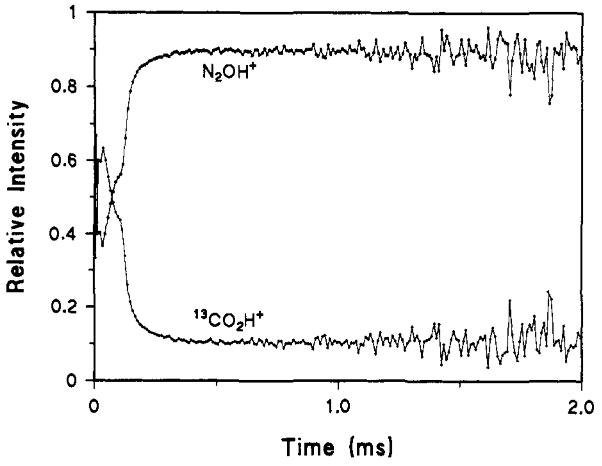

Figure 2. Time intensity profiles of protonated species N_2OH^+ and $^{13}CO_2H^+$ due to nitrous oxide and ^{13}C labeled carbon dioxide. Ion source conditions: 202 °C, nitrogen 84%, ^{13}C carbon dioxide 14%, methane 1.4%, nitrous oxide 0.03%, and total pressure 6.0 Torr.

necessary. Typical normalized ion intensity *vs* time data are shown in Figure 2.

The proton transfer reaction between N_2 and Xe was performed in a bath of N_2 to which both H_2 and Xe were added in appreciable quantities. As a result of extensive charge exchange from N_2^+ to Xe there was a significant Xe^+ abundance which potentially conflicts with XeH^+ peaks due to the multiple isotopic composition of Xe. However, since there is no ^{133}Xe isotope, in a high pressure mass spectrum such as that shown in Figure 3, the peak at m/z 133 corresponds unambiguously to $^{132}XeH^+$. Therefore, from the temporal ion intensity profiles such as those shown in Figure 4, and using the known isotopic composition of Xe in conjunction with the known Xe partial pressure, the equilibrium constant for proton transfer can be straightforwardly calculated. The value thus obtained is in fair agreement with that from a flowing afterglow study by Bohme et al.[5d]

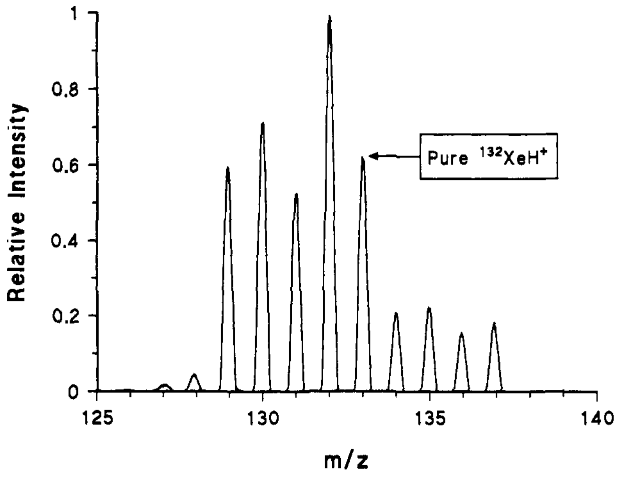

Figure 3. A partial high pressure mass spectrum of a mixture of xenon and nitrogen showing $Xe^{\cdot+}$ and XeH^+ ions. Ion source conditions: 232 °C, nitrogen 78%, hydrogen 20%, xenon 2.5%, and ion source pressure 4.3 Torr.

Table I. Summary of Thermochemical Data Derived from Proton Transfer Equilibria

rxn no.	B_1	B_2	ΔH^a	ΔS^b	$\Delta G^{\circ}{}_{300}{}^{a}$	$\Delta G^{\circ}{}_{400}{}^{a}$	$\Delta G^{\circ}{}_{600}{}^{a}$	$T_{min}{}^{c}$	$T_{max}{}^{c}$	$T_{av}{}^{c}$
1	N_2	Xe	−1.6	5.7	−3.3	−3.9	−5.0	53	307	180
2	N_2	CO_2	−10.7	3.3	−11.7	−12.0	−12.7	230	345	288
3	CO_2	CH_4	−0.8	1.2	−1.1	−1.3	−1.5	108	302	205
4[d]	CO_2	N_2O	−8.4	−1.1	−8.1	−8.0	−7.8	181	299	240
5	CH_4	N_2O	−7.6	−2.5	−6.9	−6.6	−6.1	26	272	149
6	CH_4	CO	−11.5	−6.6	−9.5	−8.9	−7.5	61	275	168
7	CH_4	C_2H_6	−11.9	−4.1	−10.7	−10.3	−9.4	33	90	61
8	N_2O	CO	−4.1	−4.4	−2.8	−2.3	−1.5	138	272	205
9	CO	C_2H_6	−0.8	2.6	−1.6	−1.8	−2.3	26	102	64
10	CO	SO_2F_2	−2.9	5.0	−4.4	−4.9	−5.9	85	215	150
11	CO	OCS	−8.1	4.8	−9.5	−10.0	−10.9	190	325	258
12	CO	SO_2	−8.8	3.8	−9.9	−10.3	−11.1	180	359	270
13[e]	C_2H_6	C_2H_4	−19.9	−1.2	−19.6	−19.5	−19.3	24	175	100
14	$(CF_3)_2CO$	SO_2	−0.7	2.7	−1.4	−1.7	−2.2	141	213	177
15	OCS	SO_2	−0.9	−0.9	−0.6	−0.5	−0.3	103	267	185
16	SO_2	C_6F_6	−2.9	3.2	−3.8	−4.2	−4.8	146	297	221
17	SO_2	CF_3CN	−8.4	0.4	−8.5	−8.6	−8.7	225	365	295
18	SO_2	CS_2	−10.5	4.5	−11.9	−12.3	−13.3	260	386	323
19[f]	C_6F_6	H_2O	(−11.3)				−6.8			327
20	CF_3CN	CS_2	−2.0	3.8	−3.2	−3.5	−4.3	170	395	283
21	CS_2	C_6HF_5	−2.8	−4.6	−1.4	−1.0	0.0	28	236	132
22	CS_2	H_2O	−3.8	−9.8	−0.9	0.1	2.0	220	380	300
23	CS_2	1,2,3,4-$C_6H_2F_4$	−4.5	−3.4	−3.5	−3.1	−2.5	79	229	154
24	CS_2	H_2S	−7.4	−10.2	−4.3	−3.3	−1.4	26	351	188
25	CS_2	1,4-$C_6H_4F_2$	−10.4	−5.4	−8.8	−8.3	−7.2	178	330	259
26	CS_2	1,2,3-$C_6H_3F_3$	−11.4	−6.5	−9.5	−8.8	−7.5	124	305	215
27	CS_2	CF_3COCH_3	−12.0	−10.3	−8.9	−7.9	−5.8	127	257	192
28	H_2O	H_2S	−3.8	−0.5	−3.7	−3.6	−3.5	269	339	304
29	C_6HF_5	H_2S	−4.2	−4.5	−2.9	−2.4	−1.5	33	236	125
30	1,2,3,4-$C_6H_2F_4$	H_2S	−2.8	−6.0	−1.0	−0.4	0.8	51	234	143
31	H_2S	1,4-$C_6H_4F_2$	−2.7	4.3	−4.0	−4.4	−5.3	85	280	183
32	H_2S	1,2,3-$C_6H_3F_3$	−4.0	3.0	−4.9	−5.2	−5.8	80	311	195
33	H_2S	1,2,4-$C_6H_3F_3$	−5.6	−0.2	−5.5	−5.5	−5.5	110	310	210
34	H_2S	C_6H_6	−10.7	3.0	−11.6	−11.9	−12.5	257	377	317
35	1,4-$C_6H_4F_2$	CF_3COCH_3	−2.0	−5.5	−0.4	0.2	1.3	102	281	192
36	1,4-$C_6H_4F_2$	C_6H_6	−8.6	−1.5	−8.1	−8.0	−7.7	205	335	270
37	1,4-$C_6H_4F_2$	CH_3OH	−10.0	−6.5	−8.0	−7.4	−6.1	257	372	315
38	CF_3COCH_3	1,2,4-$C_6H_3F_3$	−1.0	0.7	−1.2	−1.3	−1.4	215	333	274
39	1,2,3-$C_6H_3F_3$	C_6H_6	−7.0	−0.3	−6.9	−6.8	−6.8	175	312	244
40	1,2,3-$C_6H_3F_3$	CH_3OH	−8.5	−5.0	−7.0	−6.5	−5.5	243	340	292
41	1,2,4-$C_6H_3F_3$	C_6H_6	−5.2	4.1	−6.4	−6.8	−7.6	89	327	208
42	1,2,4-$C_6H_3F_3$	CH_3OH	−7.4	−2.5	−6.7	−6.4	−5.9	257	375	316
43	1,2-$C_6H_4F_2$	C_6H_6	−4.2	3.1	−5.1	−5.4	−5.9	29	232	131
44	1,2-$C_6H_4F_2$	CH_3OH	−6.1	−2.6	−5.3	−5.0	−4.5	242	372	307
45	1,3,5-$C_6H_3F_3$	C_6H_6	−1.5	2.1	−2.2	−2.4	−3.0	29	260	145
46	1,3,5-$C_6H_3F_3$	CH_3OH	−3.4	−3.5	−2.4	−2.0	−1.3	247	373	310
47	C_3H_6	C_6H_6	−1.6	3.2	−2.6	−2.9	−3.5	220	371	296
48	C_3H_6	CH_3OH	−3.4	−3.0	−2.5	−2.2	−1.6	257	393	325
49	C_6H_6	C_6H_5F	−1.3	−3.4	−0.3	0.0	0.7	31	220	126
50	C_6H_6	CH_3OH	−1.8	−5.5	−0.2	0.4	1.6	225	367	296
51	C_6H_6	HCO_2CH_3	−8.1	−4.5	−6.8	−6.3	−5.4	208	357	283
52	C_6H_6	$(CH_3)_2CO$	−13.2	−0.6	−13.0	−12.9	−12.8	233	357	295
53	C_6H_6	$C_6H_5CH_3$	−8.0	−2.1	−7.4	−7.1	−6.7	51	288	170
54	1,3-$C_6H_4F_2$	C_6H_6	0.0	2.3	−0.7	−0.9	−1.4	29	325	177
55	1,3-$C_6H_4F_2$	HCO_2CH_3	−8.2	−2.9	−7.4	−7.1	−6.5	216	358	287
56	C_6H_5F	$C_6H_5CH_3$	−6.1	1.8	−6.6	−6.8	−7.2	75	225	150
57	$C_6H_5CH_3$	*i*-C_3H_7CN	−6.2	−4.3	−4.9	−4.5	−3.6	251	357	304
58	$(CH_3)_2O$	*i*-C_4H_8	−2.1	1.2	−2.5	−2.6	−2.8	237	377	307
59	HCO_2CH_3	$(CH_3)_2CO$	−5.6	3.6	−6.7	−7.1	−7.8	247	362	310
60	*i*-C_4H_8	$(CH_3)_2CO$	−2.1	−0.5	−2.0	−1.9	−1.8	215	386	300
61	*i*-C_4H_8	$CH_3CO_2CH_3$	−3.4	−1.3	−3.0	−2.9	−2.6	213	394	303
62	*i*-C_4H_8	$CH_3CO_2C_2H_5$	−6.6	−1.7	−6.1	−5.9	−5.6	215	433	324
63	*i*-C_4H_8	$(C_2H_5)_2CO$	−7.7	−2.9	−6.8	−6.5	−6.0	215	432	324
64	*i*-C_4H_8	$CH_3OC_2H_4OH$	−8.1	−8.0	−5.7	−4.9	−3.4	197	307	257
65	*i*-C_4H_8	NH_3	−12.0	−7.3	−9.9	−9.1	−7.7	266	432	348
66[f]	*i*-C_4H_8	c-$C_3H_5COCH_3$	(−12.5)				−9.6			327
67	*i*-C_3H_7CN	$(CH_3)_2CO$	−0.4	4.6	−1.8	−2.2	−3.1	236	358	297
68	$(CH_3)_2CO$	$(C_2H_5)_2O$	−5.1	−2.0	−4.5	−4.3	−3.9	221	405	313
69	$(CH_3)_2CO$	$(C_2H_5)_2CO$	−5.4	−1.8	−4.9	−4.7	−4.3	264	433	348
70	$CH_3CO_2CH_3$	$CH_3OC_2H_4OH$	−4.8	−6.8	−2.8	−2.1	−0.7	197	307	297
71[f]	$CH_3CO_2C_2H_5$	c-$C_3H_5COCH_3$	(−6.3)				−4.2			327
72	$(C_2H_5)_2O$	$(C_2H_5)_2CO$	−1.7	−2.1	−1.1	−0.9	−0.4	286	387	337
73	$(C_2H_5)_2CO$	$C_6H_5CH_2COCH_3$	−2.9	−4.3	−1.6	−1.2	−0.4	227	335	281
74	$(C_2H_5)_2CO$	c-$C_3H_5COCH_3$	−4.9	−2.3	−4.2	−4.0	−3.6	288	374	331
75	$(C_2H_5)_2CO$	NH_3	−4.3	−4.9	−2.8	−2.3	−1.4	264	433	348
76	NH_3	C_4H_5N	−5.7	2.3	−6.4	−6.7	−7.1	208	360	284
77	C_4H_5N	CH_3NH_2	−6.2	−3.9	−5.0	−4.6	−3.8	187	382	285

Table I (Continued)

rxn no.	B_1	B_2	ΔH^a	ΔS^b	$\Delta G^\circ_{300}{}^a$	$\Delta G^\circ_{400}{}^a$	$\Delta G^\circ_{600}{}^a$	$T_{min}{}^c$	$T_{max}{}^c$	$T_{av}{}^c$
78	CH_3NH_2	$(CH_3)_2NH$	-7.1	1.4	-7.5	-7.7	-8.0	184	422	303
79	$(CH_3)_2NH$	$(CH_3)_3CNH_2$	-0.9	-0.2	-0.8	-0.8	-0.8	90	266	178
80[g]	i-C_4H_8	$(CH_3)_3CNH_2$	-31.5	-8.0	-29.1	-28.2	-26.7	266	404	335

[a] In units of kcal mol^{-1}. [b] In units of cal mol^{-1} K^{-1}. [c] In units of °C. [d] Proton transfer equilibria between $^{13}CO_2$ and N_2O. [e] Calculated from the association reaction of $C_2H_5^+$ with H_2 ($\Delta H = -12.8$ kcal mol^{-1}, $\Delta S = -27.5$ cal mol^{-1} K^{-1}). [f] ΔG°_{600} measurements and entropy estimation. [g] Calculated from the association reaction of $(CH_3)_3C^+$ with NH_3 ($\Delta H = -45.3$ kcal mol^{-1}, $\Delta S = -47.3$ cal mol^{-1} K^{-1}). Data taken from ref 9. The thermodynamical data for the neutrals are for 500 K either taken from the JANAF tables or estimated from Benson's additivity scheme.

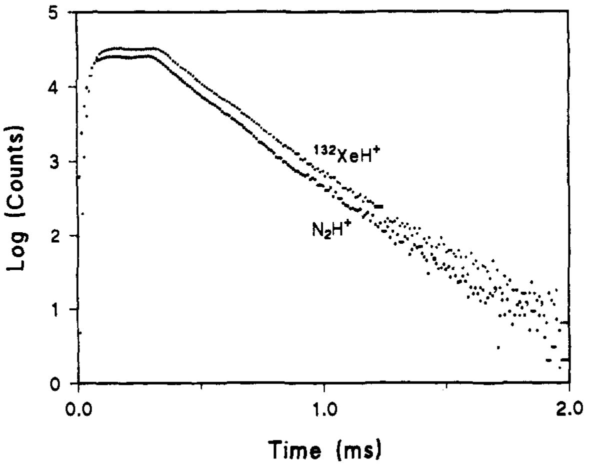

Figure 4. Time intensity profiles of protonated species $^{132}XeH^+$ and N_2H^+ due to a mixture of xenon in nitrogen containing hydrogen. Ion source conditions: 95 °C, nitrogen 78%, hydrogen 20%, xenon 2.5%, and pressure 4.4 Torr.

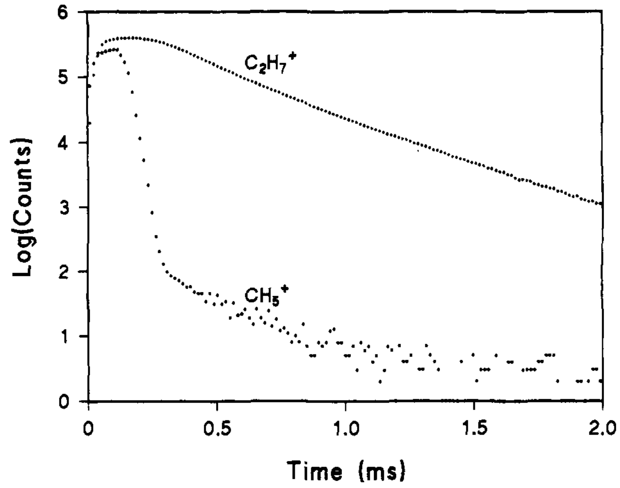

Figure 5. Time intensity profiles of protonated species CH_5^+ and $C_2H_7^+$ due to methane and ethane. Ion source conditions: 53 °C, methane ≈100%, ethane 335 ppm, and pressure 6.0 Torr.

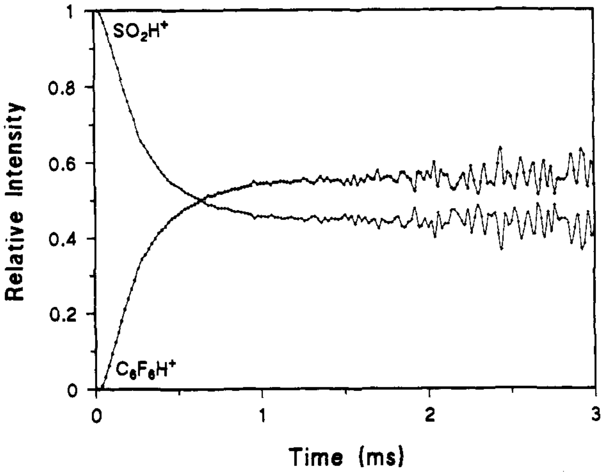

Figure 6. Time intensity profiles of protonated species SO_2H^+ and $C_6F_6H^+$ due to sulfur dioxide and hexafluorobenzene. Ion source conditions: 270 °C, sulfur dioxide 0.98%, hexafluorobenzene 0.019%, methane 99%, and pressure 8.0 Torr.

The excellent dynamic range of ion intensities and very persistent temporal profiles available on the present apparatus permits the observation of equilibrium constants of unprecedented magnitude for this type of experiment. For example, using CH_4 both as the bath gas *and* as one of the proton transfer equilibrium partners it is possible to measure equilibrium constants on the order of 5×10^7. This capability is illustrated in Figure 5 for proton transfer between CH_4 and C_2H_6, eq 8. French and

$$CH_5^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CH_4 \tag{8}$$

Kebarle[11] have carried out a similar experiment, but due to their lower dynamic range of intensities they were only able to derive a lower limit for K_{eq8} of $\geq 10^6$ at 30 °C. The ΔH° value of -12.0 kcal mol^{-1} observed for this reaction is in excellent agreement with that obtained as the sum of the ΔH° values for several smaller steps.

In a number of cases it was found that proton transfer, even in the exothermic direction, was extremely slow and care was required to ensure that the equilibrium was examined for a reaction time sufficiently long to ensure that true equilibrium ion abundances had been achieved. For example, exothermic proton transfer both to neutral fluorobenzenes and from protonated fluorobenzenes was especially slow. As shown in Figure 6 for proton transfer between SO_2 and hexafluorobenzene, eq 9,

$$SO_2H^+ + C_6F_6 \rightleftharpoons C_6F_6H^+ + SO_2 \tag{9}$$

equilibrium is not established until after approximately 2 ms. The rate constant for the forward proton transfer direction was determined to be 6.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and from the equilibrium constant of 72 at 270 °C the reverse rate constant must be 9×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. These slow rate constants significantly increase the time required to establish equilibrium and the temporal profiles must then necessarily be examined for times as long as possible.

The absolute proton affinity of C_2H_6 has been established *via* two independent means. First, the proton affinity relative to that of CO is obtained by direct proton transfer equilibrium measurements, eq 10, from which a proton affinity of 142.7 kcal

$$HCO^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CO \tag{10}$$

mol^{-1} is derived for ethane. A flowing afterglow study at 298 K by Bohme et al.[12] gave a value of ΔG°_{298} for eq 10, in good agreement with the present data. The present data are also in excellent agreement with a 400 K HPMS study by McMahon and Kebarle.[5f] Alternatively, the proton affinity of C_2H_6 may be established from the energetics of the clustering reaction for $C_2H_5^+$ onto H_2, eq 11. Experimental data, shown in Figures 7

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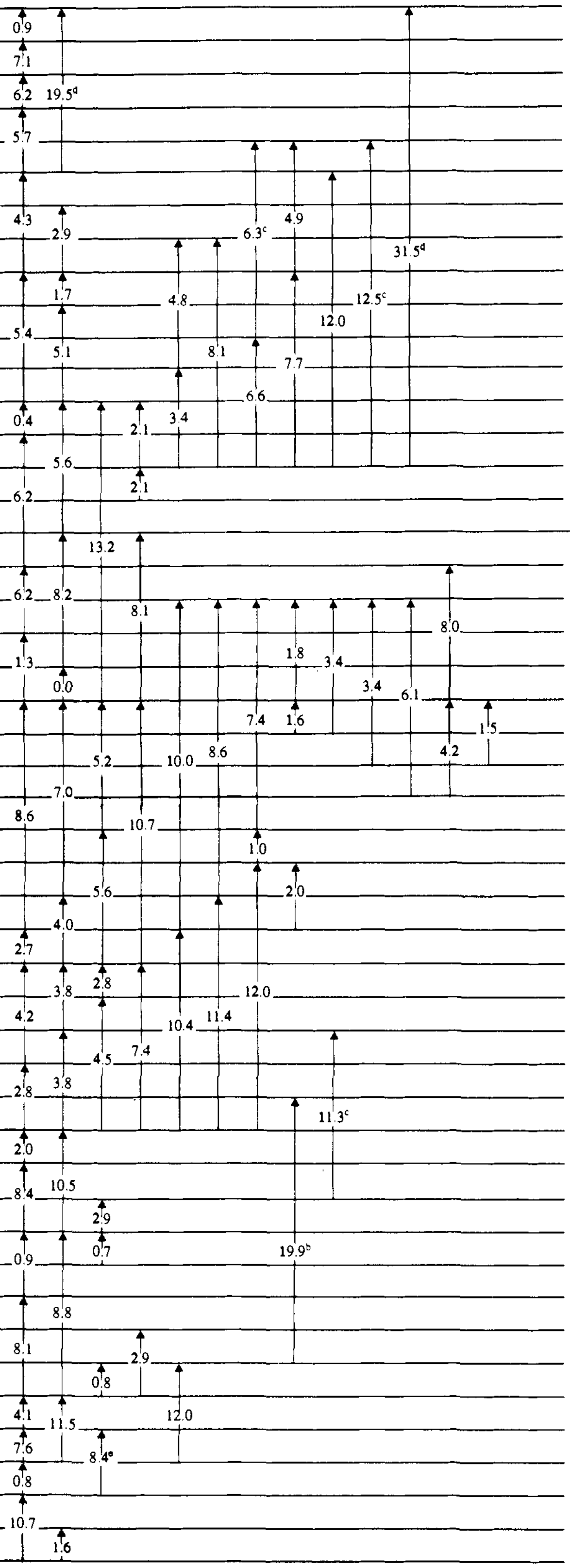
(11) French, M.; Kebarle, P. *Can. J. Chem.* **1975**, *53*, 2268.

(12) Bohme, D. K.; McKay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 2173.

Table II. Proton Affinity Ladder and Thermochemical Data Summary[e,f]



BASE	ΔPA^1	PA^2	PA^3	$\Delta G^0_{600}{}^4$	$\Delta S_{1/2}{}^5$	$\Delta S_{1/2}{}^6$
$(CH_3)_3CNH_2$	-81.5	223.4	220.8	-78.5	-2.0	-2.0
$(CH_3)_2NH$	-80.6	222.5	220.6	-77.6	-1.5	0.0
CH_3NH_2	-73.5	215.4	214.1	-69.6	-3.0	-1.0
C_4H_5N	-67.3	209.2	207.6	-65.8	1.0	.
c-$C_3H_5COCH_3$	-62.3	204.2	205.1	-60.6	2.0	.
NH_3	-61.6	203.5	204.0	-58.7	-1.5	-1.5
$C_6H_5CH_2COCH_3$	-60.2	202.1	.	-56.7	-2.5	.
$CH_3OC_2H_4OH$	-57.9	199.8	.	-54.4	-2.5	.
$(C_2H_5)_2CO$	-57.4	199.3	201.4	-57.3	2.5	.
$(C_2H_5)_2O$	-56.2	198.1	200.2	-56.5	3.5	2.5
$CH_3CO_2C_2H_5$	-56.2	198.1	200.7	-56.5	3.5	.
$CH_3CO_2CH_3$	-53.1	195.0	197.1	-53.6	4.0	.
$(CH_3)_2CO$	-51.8	193.7	196.7	-52.7	4.5	.
i-C_3H_7CN	-51.4	193.2	194.3	-49.5	0.0	.
i-C_4H_8	-49.8	191.7	195.9	-51.0	5.5	5.5
$(CH_3)_2O$	-47.1	189.6	192.1	-48.2	4.5	2.5
HCO_2CH_3	-46.2	188.1	188.9	-44.7	0.5	.
$C_6H_5CH_3$	-45.8	187.7	189.8	-45.9	3.0	.
CH_3OH	-39.8	181.7	181.9	-37.8	-0.5	1.5
C_6H_5F	-39.4	181.3	182.6	-38.5	1.5	.
1,3 $C_6H_4F_2$	-38.1	180.0	181.9	-38.0	3.0	.
C_6H_6	-38.1	180.0	181.3	-39.1	5.0	.
C_3H_6	-36.5	178.4	179.5	-35.7	2.0	.
1,3,5 $C_6H_3F_3$	-36.5	178.4	181.0	-36.2	2.5	.
1,2 $C_6H_4F_2$	-33.8	175.7	181.8	-33.2	2.0	.
1,2,4 $C_6H_3F_3$	-32.6	174.5	181.4	-31.4	1.0	.
CF_3COCH_3	-31.6	173.5	174.2	-30.0	0.5	.
1,2,3 $C_6H_3F_3$	-31.1	173.0	.	-32.3	5.0	.
1,4 $C_6H_4F_2$	-29.6	171.5	181.2	-31.2•	6.0	.
H_2S	-26.8	168.7	170.2	-26.0	1.5	2.0
1,2,3,4 $C_6H_2F_4$	-23.9	165.8	181.1	-21.7	7.0	.
H_2O	-23.1	165.0	166.5	-22.4	1.5	1.5
C_6HF_5	-22.4	164.3	179.9	-24.5	6.0	.
C_2H_4	-20.7	162.6	162.6	-21.3	4.0	.
CS_2	-19.4	161.3	164.4	-24.4	11.0	.
CF_3CN	-17.4	159.3	164.3	-19.9	7.0	.
C_6F_6	-11.9	153.8	177.7	-15.9	9.5	.
SO_2	-9.0	150.9	152.1	-11.1	6.5	.
$(CF_3)_2CO$	-8.3	150.2	150.2	-8.9	4.5	.
OCS	-8.1	150.0	150.7	-10.9	7.5	.
SO_2F_2	-2.9	144.8	146.2	-5.9	8.0	.
C_2H_6	-0.8	142.7	143.6	-2.3	5.5	.
CO	0.0	141.9	141.9	0.0	3.0	3.0
N_2O	4.1	137.8	138.8	1.5	7.0	.
CH_4	11.7	130.2	131.6	7.8	9.5	.
CO_2	12.5	129.4	129.5	9.3	8.0	7.0
Xe	21.6	120.3	118.6	17.1	10.5	10.5
N_2	23.2	118.7	118.2	22.1	5.0	4.0

[a] Proton transfer between $^{13}CO_2$ and N_2O. [b] From association reaction $C_2H_5^+ + H_2 \rightleftharpoons C_2H_7^+$. [c] $\Delta G°_{600}$ measurements and entropy estimation. [d] From the association reaction $(CH_3)_3C^+ + NH_3 \rightleftharpoons (CH_3)_3CNH_3^+$. [e] The numbers 1–6 identify the following: (1) PA difference relative to CO, (present work) i.e. ΔPA = PA(CO) − PA(base); (2) absolute proton affinity (present work) anchored to the absolute proton affinity of CO of 141.9 kcal mol^{-1}; (3) NIST database proton affinity; (4) present work $\Delta G°_{600}$ ladder relative to CO; (5) present work absolute 500 K half-reaction $\Delta S°_{1/2}$ for B → BH$^+$ referenced to the 500 K carbon monoxide $\Delta S°_{1/2}$ = 3.0 cal mol^{-1} K^{-1} taken from the JANAF tables. The van't Hoff plots' temperature range is 520 ∓ 100 K. (6) 500 K $\Delta S°_{1/2}$ estimations assuming that the protonated base has the same entropy as isoelectronic neutral analogs based on data taken from JANAF tables or estimated from Benson's additivity scheme. [f] The number enclosed by an arrow is the proton affinity difference and the arrowhead indicates the direction of exothermic proton transfer.

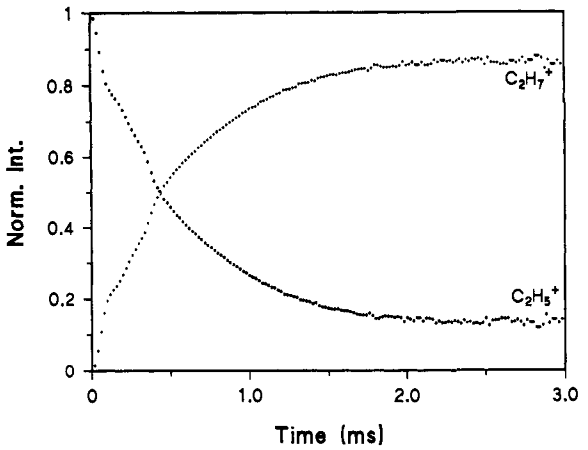


Figure 7. Time intensity profiles of the association reaction of ethyl cation ($C_2H_5^+$) with hydrogen to give protonated ethane ($C_2H_7^+$). Ion source conditions: 26 °C, methane 80%, hydrogen 20%, and pressure 7.0 Torr.

$$C_2H_5^+ + H_2 \rightleftharpoons C_2H_7^+ \qquad (11)$$

and 8, from this laboratory give $\Delta H° = -12.8$ kcal mol^{-1} and $\Delta S° = -27.5$ kcal mol^{-1} for this reaction. These differ somewhat from the Hiraoka and Kebarle[13] data of $\Delta H° = -11.8$ kcal mol^{-1} and $\Delta S° = -25.0$ cal mol^{-1} K^{-1}. The value of $\Delta H_f°(C_2H_5^+)$ is well established from PEPICO measurements by Baer[2h] as 215.6 kcal mol^{-1}, which can be taken with $\Delta H_{11}°$ to derive the $\Delta H_f°(C_2H_7^+)$ value as 202.8 kcal mol^{-1} and a proton affinity for ethane of 142.7 kcal mol^{-1}, in exact agreement with the value determined from direct proton transfer measurements. In effect, then, the proton affinity scale described in this work is anchored to two of the most accurately determined primary standards, CO and C_2H_4.

As discussed below, a key component of this work is the finding that the proton affinity of isobutene, which had been presumed to be well established,[8] should shift downward by some 4 kcal mol^{-1}. In order to ensure that this compound was well determined, independent equilibria involving eight different compounds were rigorously examined. In all cases the equilibria were well behaved and provide internally consistent confirmation of the position of isobutene in the proton affinity scale.

The proton affinity of *tert*-butylamine may be determined from the energetics of clustering[9] of t-$C_4H_9^+$ with NH_3 to be 223.2 ± 1 kcal mol^{-1} if the new $\Delta H_f°(C_4H_9^+)$ value determined here is used. Alternatively the ladder of proton transfer equilibria from isobutene to *tert*-butylamine can be used to derive a proton affinity of the amine of 223.4 ± 1 kcal mol^{-1}. Therefore it can be seen that the proton affinity difference between isobutene and *tert*-butylamine is well established by two independent measurements of a fundamentally different nature. This then lends support to the relative values of each proton affinity between these two compounds as well.

A very serious disagreement was found between the proton affinities of polyfluorobenzenes reported in the NIST database[8] and the current measurements. The proton affinity of hexafluorobenzene, for example, is some 24 kcal mol^{-1} less than the current NIST value. The pattern of substituent effects found in the present work is much more readily rationalized and a discussion of these will be the subject of a forthcoming publication from this laboratory. However, the general decrease of proton affinity with increasing fluorine substitution made this series of compounds extremely valuable in establishing the basicity scale, and hence it was important that these experimental data should also be included here.

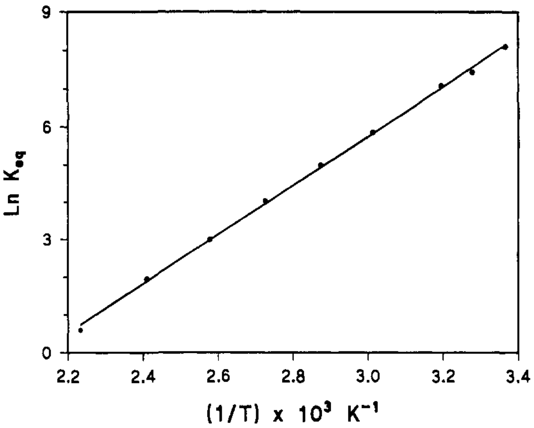


Figure 8. Association reaction van't Hoff plot of the ethyl cation with hydrogen.

Discussion

Comparison with Absolute Standard Proton Affinities. The proton affinities of each of the species studied have been assigned on the basis of the relative thermochemical data obtained here which are then referenced to an absolute proton affinity of carbon monoxide which is taken to be 141.9 kcal mol^{-1}. The resulting assignments for key compounds are compared below to values available from both appearance energy measurements and *ab initio* calculation.

1. N_2. The most recent, and most thorough, study of appearance energies of N_2H^+ was carried out by Ruscic and Berkowitz.[2e] On the basis of measurements of appearance energies of various ions derived from diimide, N_2H_2, they have assigned a proton affinity of nitrogen as ≤119.0 ± 0.9 kcal mol^{-1} at 298 K in excellent agreement with our assignment of 118.7 ± 0.4 kcal mol^{-1}. The greatest source of uncertainty in this appearance energy measurement is the value of $\Delta H°_{298}(N_2H_2)$. The most recent *ab initio* calculation of the proton affinity of N_2 by Komornicki and Dixon[6b] places it at 117.9 kcal mol^{-1}. Other, relatively recent, *ab initio* assignments[6a,c,d] range from 118.0 to 120.1 kcal mol^{-1}.

2. CO_2. Ruscic, Schwarz, and Berkowitz[2d] have recently reinvestigated the photodissociative ionization of formic acid, HCO_2H, to determine a 298 K proton affinity of CO_2 of 129.2 ± 0.5 kcal mol^{-1}, again in excellent agreement with the value determined here of 129.4 ± 0.4 kcal mol^{-1}. These data are only slightly greater than the value determined by Traeger and Kompe[2g] of 128.1 ± 0.7 kcal mol^{-1} using photoionization mass spectrometry. The *ab initio* value of 129.3 kcal mol^{-1} of Komornicki and Dixon[6b] and by Del Bene and Frisch[6k] supports the slightly higher assignment.

3. CO. Carbon monoxide has been chosen as the single absolute anchor point for our gas-phase proton affinity scale because it is the smallest species for which both photoionization appearance energy measurements and high quality *ab initio* calculations are available. Traeger[2f] has examined the dissociative photoionization of a number of formyl compounds, RCHO, to yield the formyl cation HCO^+ and arrives at a proton affinity of CO of 142.0 ± 0.7 kcal mol^{-1}. This is in excellent agreement with a value of 141.6 ± 1 kcal mol^{-1} obtained by combining $\Delta H°_{298}(HCO)$ and the ionization energy of HCO from photoelectron spectroscopy.[2ℓ] Komornicki and Dixon[6b] have analyzed the sources and possible magnitudes of error in their *ab initio* calculations for CO and HCO^+ and give a proton affinity of CO of 141.8 kcal mol^{-1} with an assigned uncertainty of ±0.5 kcal mol^{-1}. Del Bene and Frisch[6k] calculated a proton affinity of 140.8 kcal mol^{-1}. We have thus chosen to assign the basis for our scale as a proton affinity of CO of 141.9 kcal mol^{-1} both because it is midway between the Traeger[2f] experimental value and the *ab initio* calculation[6b] and because it agrees with the previous assessment for the NIST[8] proton affinity

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(13) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

tables and as such provides a common point for comparison of the two scales.

4. C_2H_4. On the basis of photoionization appearance energy measurements of $C_2H_5^+$ from ethane and ethyl halides, Traeger[2j] has derived a $\Delta H_f°_{298}$ value of 216.0 ± 0.5 kcal mol^{-1} for the ethyl cation which yields a proton affinity of ethylene of 162.2 ± 0.6 kcal mol^{-1}. Using PEPICO experiments Baer[2h] has obtained a slightly lower $\Delta H_f°_{298}$ value of 215.6 ± 1 kcal mol^{-1} from which a proton affinity of 162.6 ± 1 kcal mol^{-1} may be derived. More recently in a collaborative experimental and theoretical effort Ruscic, Berkowitz, Curtiss, and Pople[2m] have obtained a new value for the ionization energy of the ethyl radical which results in $\Delta H_f°_0(C_2H_5^+)$ value of 218.6 ± 0.8 kcal mol^{-1} and when corrected to a value at 298 K of 215.7 kcal mol^{-1} gives a proton affinity for ethylene of 162.5 ± 0.8 kcal mol^{-1}. The mean of these three values, 162.5 kcal mol^{-1}, is in excellent agreement with the proton affinity determined in this work of 162.6 ± 0.4 kcal mol^{-1}. Many *ab initio* calculations of the proton affinity of ethylene have been carried out arising from the interest in the nonclassical, bridged structure of the ethyl cation. The most recent of these, by Ruscic *et al.*,[2m] gives a proton affinity of 163.8 kcal mol^{-1}.

5. H_2O. Ng *et al.*[4a] have examined the photoionization appearance energy threshold for the production of H_3O^+ from the H_2O van der Waals dimer, $(H_2O)_2$, to obtain a proton affinity of water at 0 K of 165.8 ± 1.8 kcal mol^{-1}. When corrected to 298 K this becomes 167.2 ± 2 kcal mol^{-1}. *Ab initio* calculations[6c,f,i,k,p,u,v] of the proton affinity of water range from 164.5 to 165.3 kcal mol^{-1}. The present experimental determination of 165.0 ± 0.5 kcal mol^{-1} is in excellent agreement with the theoretical values and nearly within the lower bound of the photoionization measurement.

6. H_2S. Prest *et al.*[4b] have also determined a photoionization appearance energy for H_3S^+ from the hydrogen sulfide van der Waals dimer, $(H_2S)_2$, which gives a 0 K proton affinity of H_2S of 167.2 ± 1.4 kcal mol^{-1} and when corrected to 298 K a value of 168.7 kcal mol^{-1}. In a similar experiment Walters and Blais[4c] obtained a slightly higher appearance energy to give a proton affinity of 169.0 kcal mol^{-1}. Curtiss and Pople[6f] have calculated the proton affinity of H_2S to be 168.5 kcal mol^{-1}. A G2 *ab initio* calculation by Curtiss *et al.*[6u] gives a proton affinity of 168.9 kcal mol^{-1}. Thus both appearance energy measurements and *ab initio* calculations are in excellent agreement with the present determination of 168.7 ± 0.5 kcal mol^{-1}.

7. C_3H_6. Using PIPECO experiments Baer[2h] has determined energetics of formation of the 2-propyl cation from isopropyl iodide from which a proton affinity of propene of 179.5 ± 1.1 kcal mol^{-1} may be derived. Traeger and McLaughlin[2j] have also determined photoionization appearance energies of i-$C_3H_7^+$ from the parent chloride, bromide, and iodides and have similarly calculated a proton affinity of propene of 178.7 ± 0.5 kcal mol^{-1}. Koch, Liu, and Schleyer[6m] have recently determined an *ab initio* proton affinity of propene of 177.8 kcal mol^{-1} in which they have demonstrated that a classical 2-propyl cation structure is the most stable. The present determination of 178.4 ± 0.6 kcal mol^{-1} is in excellent agreement with all of these values.

8. i-C_4H_8. The currently accepted NIST[8] value of the proton affinity of isobutene of 196.0 kcal mol^{-1} is based, in part, upon a series of photoionization appearance energy measurements by McLoughlin and Traeger[2a] for the production of t-$C_4H_9^+$ from *tert*-butyl halides. However, in a much earlier photoionization study on neopentane, Steiner, Giese, and Ingraham[2c] obtained a $\Delta H_f°(t\text{-}C_4H_9^+)$ value of 168.5 ± 0.2 kcal mol^{-1} corresponding to a proton affinity for isobutene of 193.0 kcal mol^{-1}. An electron monochromator study of the same process by Lossing[1b] gave virtually identical results. In the same study, Lossing also investigated the ionization energy of the *tert*-butyl radical, finding it to be 6.93 ± 0.05 eV. When this value is combined with the newly revised[14] $\Delta H_f°(t\text{-}C_4H_9^\bullet)$ value of 12.3 ± 0.4 kcal mol^{-1}, a $\Delta H_f°(t\text{-}C_4H_9^+)$ value of 172.1 ± 1.2 kcal mol^{-1} is obtained, leading to a proton affinity of isobutene of 189.4 ± 1.2 kcal mol^{-1}. These several studies therefore show that there is considerable precedent for a proton affinity of isobutene markedly lower than the currently accepted value, and in agreement with the value proposed herein of 191.7 ± 0.5 kcal mol^{-1}.

9. $(CH_3)_2CO$. The current NIST evaluated proton affinity of acetone[8] of 196.7 kcal mol^{-1} is based on its position in the basicity scale relative to either ammonia or isobutene. However, appearance energy measurements for $C_3H_7O^+$ from 2-methyl-2-propanol and 1,1-dimethylpropanol by Lossing[1a] favor a lower proton affinity of 194 ± 1 kcal mol^{-1} in excellent agreement with the present data which give 193.7 ± 0.6 kcal mol^{-1}. Lee and Dyke[6n] have carried out a series of large basis set *ab initio* calculations of the proton affinity of acetone. At the highest basis set level examined, the computed proton affinity was 193.9 kcal mol^{-1} which decreased to 190.7 kcal mol^{-1} with the inclusion of basis set superposition error.

10. NH_3. Ceyer *et al.*[4d] have examined the photoionization threshold for the appearance of the ammonium ion generated from the ammonia van der Waals dimer which yields a proton affinity of ammonia of 203.6 ± 1.2 kcal mol^{-1}. The temperature dependent proton transfer equilibria experiments described in the present work give a value of 203.5 ± 0.8 kcal mol^{-1}, in excellent agreement with the molecular beam method. *Ab initio* calculations by Pople and Curtiss[6f] give a proton affinity for ammonia of 204.0 kcal mol^{-1} and DeFrees and McLean[6c] compute a value of 204.0 kcal mol^{-1}. A recent G2 *ab initio* calculation by Curtiss *et al.*[6u] also favors a proton affinity of 204.0 kcal mol^{-1} and Del Bene[6v] very recently has calculated a value of 203.7 kcal mol^{-1}. Therefore all prior data, both theoretical and experimental, do not favor an upward revision in the proton affinity of NH_3 that would be required from HPMS data[7,9] if the currently accepted value of the proton affinity of isobutene were accepted.

Comparison with ab Initio Calculations of Proton Affinities for Other Compounds. 1. Xe. A calculation by Klein and Rosmus[6e] of the potential energy curve for the dissociation of XeH^+ to H and Xe^+ leads to a value of D_0 of 3.90 eV and $\bar{\omega}_e = 2313 \pm 50$ cm^{-1} which converts to a 300 K proton affinity for Xe of ~122.0 kcal mol^{-1}. The proton affinity of 120.3 kcal mol^{-1} obtained in the present work is in reasonably good agreement with this.

2. CH_4. The proton affinity obtained from the present work (130.2 kcal mol^{-1}) is in very good to excellent agreement with the most recent *ab initio* calculations (128.4,[6f] 128.2,[6g] 129.0,[6h] 129.1,[6e] and 129.6[6b] kcal mol^{-1}).

3. N_2O. The present value of 137.8 kcal mol^{-1} is in good agreement with a recent *ab initio* calculated proton affinity[6k] of 138.7 kcal mol^{-1}. The O-protonated form is significantly more stable than any of the N-protonated structures. A recent G2 calculation by McKee and co-workers[6w] gives a value of 136.3 kcal mol^{-1}.

4. CH_3OH. Ozment and Schmiederkamp[6l] have performed *ab initio* calculations at the MP4SDTQ/6-31+G(d,p)//6-31G* level to deduce a 298 K proton affinity for methanol of 181.9 kcal mol^{-1}, in excellent agreement with the value of 181.7 kcal mol^{-1} obtained in the present work. However, Del Bene,[6j] at a lower level of calculation, has obtained a lower 298 K value of 180.4 kcal mol^{-1}.

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5. $(CH_3)_2O$. Ozment and Schmiederkamp[6i] have also performed *ab initio* calculations at the MP4SDTQ/6-31+G(d,p)//6-31G* level to deduce a 298 K proton affinity for dimethyl ether of 190.7 kcal mol^{-1}, in very good agreement with the value of 189.6 kcal mol^{-1} obtained in the present work.

6. CH_3NH_2. Ozment and Schmiederkamp[6i] have performed *ab initio* calculations at the MP2/6-31+G(d,p)//6-31G* level to deduce a 298 K proton affinity for methylamine of 216.3 kcal mol^{-1}, in very good agreement with the value of 215.4 kcal mol^{-1} obtained in the present work. The agreement at the MP4SDTQ/6-31+G(d,p)//6-31G* level is however much poorer (217.5 kcal mol^{-1}). In addition, Del Bene,[6j] again at a lower level, has calculated a 298 K value of 215.2 kcal mol^{-1} which is also in excellent agreement.

7. $(CH_3)_2NH$. Ozment and Schmiederkamp[6i] have performed *ab initio* calculations at the MP2/6-31+G(d,p)//6-31G* level to determine a 298 K proton affinity for dimethylamine of 222.8 kcal mol^{-1}, in excellent agreement with the value of 222.5 kcal mol^{-1} obtained in the present work. The agreement at the MP4SDTQ/6-31+G(d,p)//6-31G* level is somewhat poorer (224.0 kcal mol^{-1}).

8. The G2 Proton Affinity Scale of Smith and Radom. Smith and Radom[20] have very recently carried out a series of *ab initio* calculations at the G2 level of theory which is proposed to achieve thermochemical data of "chemical accuracy", i.e. to within ±2.5 kcal mol^{-1} of experimental quantities.[6u] Using this method they have obtained *ab initio* proton affinities for 15 of the compounds reported here, covering the full range of basicities from N_2 to $(CH_3)_2NH$, also found in the present experimental work. The average deviation between G2 and experimental proton affinities for these 15 compounds is 0.6 kcal mol^{-1} with the largest discrepancy of 1.7 kcal mol^{-1} occurring for the only compound containing two heavy atoms, CS_2. Significantly, these high-level calculations were also carried out for the proton affinity of isobutene and yield, almost exactly, the same value obtained in the present work of 191.7 kcal mol^{-1}. Thus substantial theoretical and experimental support exists for our new proposed scale of gas-phase proton affinities.

Entropy Changes for Proton Transfer Reactions. Also listed in Table II are the differences in $S°$ values of the protonated and unprotonated forms of each species examined which has been termed the "half reaction entropy change" for a protonation reaction. The entries for any two species in the table can be combined to give the experimental measure of the entropy change at 500 K expected for that proton transfer reaction. Also included in the table are the same "half reaction entropy changes" calculated assuming that the protonated base has the same entropy as an isoelectronic neutral species whose entropy and heat capacity[15,16] are known or can be estimated from Benson's[16] additivity schemes. For species such as N_2, Xe, CO_2, CO, H_2O, H_2S, i-C_4H_8, $(C_2H_5)_2O$, NH_3, and t-$C_4H_9NH_2$ the agreement is excellent with a difference of 1 cal mol^{-1} K^{-1} or less between the two values. The worst cases of disagreement are for CH_3NH_2 (2 eu), $(CH_3)_2O$ (2 eu), and CH_3OH (2 eu). The excellent correspondence of the experimentally determined entropy data and that estimated from known compounds again lends a high degree of confidence to the experimentally determined proton affinities.

A number of the experimental entropy changes are noteworthy. The large entropy change associated with the protonation of Xe is the simple result of the creation of the two rotational degrees of freedom of the diatomic HXe^+. The value of +9.5 cal mol^{-1} K^{-1} for protonation of CH_4 is not nearly fully accounted for by the loss of T_d symmetry in CH_4, and a considerable contribution likely therefore arises from the effect of a free internal H_2 rotor in the CH_5^+ of C_s symmetry. An *ab initio* calculation by DeFrees *et al.*[6c] has deduced a 298 K $\Delta S°_{1/2}$ value of 9.0 cal mol^{-1} K^{-1}, which compares favorably with the value from the present work.

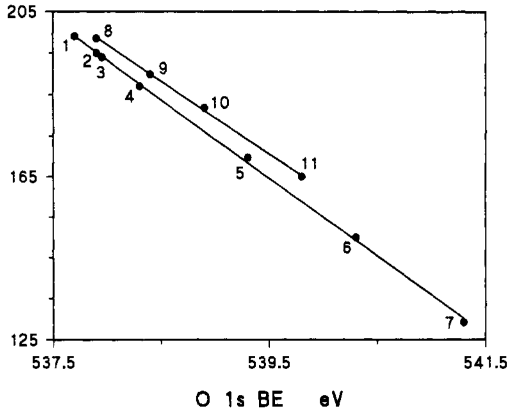

Figure 9. Oxygen 1s binding energies *versus* proton affinities for C=O type bases: (1) ethyl acetate, (2) methyl acetate, (3) acetone, (4) methyl formate, (5) carbonyl sulfide, (6) carbon dioxide and R_1OR_2 type bases, (7) diethyl ether, (8) dimethyl ether, (9) methanol, and (10) water.

A comparison of the entropy changes for protonation of CO_2, OCS, and CS_2 yields some potential structural insight for the protonated species. For CO_2 the half entropy change of 8 cal mol^{-1} K^{-1} is associated with the change from a linear triatomic to a bent oxygen protonated tetratomic which has an additional rotational degree of freedom. The corresponding entropy change for CS_2 is significantly greater at 11.5 cal mol^{-1} K^{-1} which can be understood from a consideration of the structure of $HSCS^+$ determined by *ab initio* calculations.[6q-t] These calculations show that the protonated CS_2 has a C–S bond length for the protonated sulfur atom of 1.665 Å, which is 0.115 Å longer than the C–S bond length in the neutral and corresponds to a C–S bond which may undergo either free internal rotation or at least a large amplitude vibrational motion and which then may account for the increased entropy change relative to protonated CO_2. Field and Meot-Ner[17] have also observed and commented upon the unusually high entropy of protonated carbon disulfide. In the case of OCS the entropy change is less than that for CO_2 which is due, in part, to the lower symmetry of OCS. Examination of *ab initio* calculations[6q-t] for protonated OCS shows that the O and S protonated forms are close in energy with the S-protonated form having an even longer C–S bond than that in protonated CS_2. The experimental entropy change observed is thus more consistent with an oxygen-protonated form (see Figure 9 also) as the species observed under HPMS conditions.

The pattern of half reaction entropy changes for the fluorinated benzenes allows one to predict which of these may undergo protonation on a fluorine bearing carbon. In the case of fluorobenzene the most energetically favorable site of protonation will be either *ortho* or *para* to the fluorine substituent. The fact that protonation on a non-fluorine bearing carbon leads to two hydrogen atoms being forced out of the plane of the aromatic ring leads to only a small increase in the moment of inertia of the protonated species and a small value of $\Delta S_{1/2}$ of +1.5 cal mol^{-1} K^{-1} is observed. Similarly, in the case of 1,3-difluorobenzene protonation on the carbon between the two fluorines again gives rise to a small entropy change of only 3.5 cal mol^{-1} K^{-1}. However, for 1,4-difluorobenzene the most favorable protonation appears to be on a fluorine bearing carbon, giving rise to a fluorine atom out of the plane of the benzene ring and enhancing the rotational entropy of the system. A pattern thus emerges where the highly fluorinated benzenes show larger $\Delta S_{1/2}$ values than the less extensively fluorinated benzenes. In the intermediate cases the magnitude of the entropy change therefore permits a prediction of the site of protonation to be made.

The $\Delta S_{1/2}$ value determined here for acetone of 4.5 cal mol^{-1} K^{-1} is higher than the value of near zero previously suggested by the preamble of the NIST compilation.[8] The positive value found

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[20] Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

in the present work is consistent with the creation of a restricted C–OH rotor in the ion upon protonation of acetone.

O 1s Binding Energy Correlations. It has previously been noted that for a homologous series of molecules a correlation exists between core electron binding energies and proton affinities.[5f] In the case of oxygen bases this correlation is shown in Figure 9 for the present proton affinity assignments. As can readily be seen from the data, the oxygen bases separate into two distinct groups, single bonds to oxygen and double bonds to oxygen. In situations where a proton affinity is unknown or undeterminable these correlations may be used to predict the unknown proton affinity. For example, the complexity of reactions of protonated 2-methyl-2-propanol with the parent alcohol makes proton transfer equilibrium very difficult to study. However the O 1s binding energy of the alcohol[18] allows a prediction of 194.5 kcal mol^{-1} for the proton affinity of 2-methyl-2-propanol. This is consistent with the observation of fast proton transfer[19] from t-$C_4H_9^+$ to 2-methyl-2-propanol despite the fact that the NIST tables[8] place the proton affinity of isobutene above that of 2-methyl-2-propanol.

Conclusion

The data presented here provide the first set of temperature dependent proton transfer equilibria linking bases from the very weakly basic regime of N_2 and Xe to very strong amine bases. By taking a single fixed anchor point on which to base the absolute values of proton affinities, a revised proton affinity scale has been established. The equilibria examined include 8 compounds (CO_2, CO, C_2H_4, H_2O, H_2S, C_3H_6, i-C_4H_8, and NH_3) whose gas-phase proton affinities were apparently well established, based on appearance energy measurements. As well, for 16 compounds high-quality *ab initio* calculations have been previously performed. In each case, with the exception of isobutene, excellent agreement between the equilibrium, *ab initio*, and appearance energy determined proton affinities is obtained. The exceptional case of isobutene calls into question the validity of this appearance energy determination. Examination of the literature has further revealed ample precedent for a lower value of the proton affinity of isobutene, in agreement with the conclusion arrived at here. While our revised proton affinity scale requires only minor changes in proton affinities for compounds more weakly basic than propene (with the exception of the fluorobenzenes), substantial revision of as much as 4 kcal mol^{-1} is necessary for species of basicity in the vicinity of isobutene. Fortunately, our new scale leaves the proton affinity of ammonia very close to its previously accepted value. This is of considerable importance since it had been previously concluded by Meot-Ner that the proton affinity of ammonia must be revised upward by ~4 kcal mol^{-1} and that of species in the vicinity of *tert*-butylamine by as much as 8 kcal moll^{-1}. Since very large numbers of compounds have proton affinities based on equilibria involving NH_3 as a convenient, secondary reference standard, this might have required large-scale revisions in absolute proton affinities of many compounds. The present scale leaves ammonia slightly lower (0.5 kcal mol^{-1}) than the NIST table value, and more basic amine species such as dimethylamine and *tert*-butylamine moved upward by only 2 and 2.5 kcal mol^{-1}, respectively.

Given the apparent accuracy of the scale determined in the present work, it is felt that the data obtained for these 48 compounds can be taken as a series of secondary standards against which all other proton affinity measurements might be calibrated. Since the vast majority of all proton affinities are obtained from equilibrium measurements of relative proton affinities, a simple re-evaluation of the proton affinity tables should be able to be straightforwardly carried out.

After two decades of equilibrium proton transfer measurements, it would appear that a reliable, absolute proton affinity scale is close at hand.

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