Gas-Phase Proton Affinity and Protonation Entropy Scale between Acetaldehyde and Methyl Acetate. An Experimental Evaluation and Comparative Analysis

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The thermochemistry associated with the gas-phase proton affinity scale between acetaldehyde and methyl acetate has been reinvestigated by variable-temperature equilibrium measurements using pulsed electron beam high-pressure mass spectrometry. This experimentally difficult and sometimes kinetically inaccessible subset is particularly important since it provides the only bridge between the expansive lower and upper scales. Data were taken from 497 to 665 K, with an average temperature for all base pair combinations of 584 K. Special care was taken to ensure that the measurements accurately reflected both the $\Delta H°$ and $\Delta S°$ values within this temperature range. The present data indicate that earlier values from this laboratory within the same subset were expanded by ∼13% in both $\Delta G°$ and $\Delta H°$, although no evidence was found for a similar expansion in our original ladder for bases with proton affinities above isobutene, which was used as the reference base in that study. A detailed analysis and comparison between experimental and computational scales is presented, emphasizing both the $\Delta H°$ and $\Delta S°$ values associated with protonation. Significant differences in the thermochemistry are found to exist between the present data and the most recent experimental ladder within this important bridging region.

Introduction

In 1990 this laboratory reported an investigation of the cationic chemistry occurring in i-C_4H_8−NH_3 mixtures using the technique of pulsed high-pressure mass spectrometry.[1] One of the unexpected results, derived from proton-transfer equilibrium measurements, was the observation that the measured proton affinity (PA) difference between i-C_4H_8 and NH_3 was apparently some 18.4 kJ/mol greater than that recommended in an earlier compilation/evaluation by Lias et al.[2] (henceforth referred to as LLL). This prompted us to initiate a much broader study utilizing variable-temperature equilibria measurements to generate an interlocking ladder of PAs extending from C_3H_6 to $(Me)_3N$ (Me = CH_3, Et = C_2H_5, etc.). Prior to that project almost all kinetic scales had been based on ΔG measurements taken at single temperatures (relative basicities only). The resulting Mautner−Sieck (NIST) scale[3] was anchored to the reference standard i-C_4H_8, with an assumed PA(600 K) of 820 kJ/mol taken principally from earlier photoionization and appearance energy measurements.[2,4] This same reference value for i-C_4H_8 (820 kJ/mol) was assumed by Szulejko and McMahon in a subsequent experimental article;[5] they confirmed the new experimental PA difference between i-C_4H_8 and NH_3 and suggested, as did NIST, that the PA of t-$C_4H_9NH_2$ should be increased by more than 30 kJ/mol over the LLL value. Szulejko and McMahon (SM) then reported[6] an extremely wide experimental scale spanning a range of more than 430 kJ/mol. The reference base for this ladder was CO, with an assumed PA of 594 kJ/mol. An important result of their effort was the suggestion that the previously assumed PA of i-C_4H_8 (820 kJ/mol) was incorrect and that a downward revision of approximately 17.6 kJ/mol was required in the recommended value (although no accumulated error limits were stated). A similar reduction in the PA of i-C_4H_8 had been previously proposed in the computational analyses of Smith and Radom[7] as well as PEPICO studies by Keister et al.[8] which revised the heat of formation of t-$C_4H_9^+$ reported in the so-called "GIANT" tables.[4] Examination of the SM ladder reveals essentially two separate scales, one extending from N_2 to MeOH and the other from i-C_4H_8 to t-$C_4H_9NH_2$, with no bridge to i-C_4H_8 from below. The connection between these two segments was from C_6H_6 to $(Me)_2CO$, covering a reported range of 57.3 kJ/mol (13.7 kcal/mol). Their scale also indicated a difference in ΔS_{prot} of 13.8 J/(mol·K) between the two simple esters HCO_2Me, which was one of the bridging compounds, and $MeCO_2Me$, which was tied to $\Delta S°_{prot}(Me)_2CO$, another bridging molecule. This result was reported without comment, although there is no apparent reason a proton-transfer reaction between two structurally similar bases should involve a large entropy change. Within the bridging region, errors in $\Delta S°_{prot}$ could affect assignment of protonation entropies for the entire upper PA region since accumulated $\Delta S°$ values are carried over from molecule to molecule as one moves farther from the reference base CO. Our earlier subset in this region[3] extending from C_3H_6 to i-C_4H_8 also seemed to be expanded in both $\Delta H°$ and $\Delta G°$ compared with the computational and SM thermochemistry. Considering all of this, it seemed appropriate to carry out a detailed reinvestigation of this particular segment. The focus was on the subset of the PA scale between MeCHO and $MeCO_2Me$, which essentially brackets the "critical" region in question. We note that there is a general paucity of suitable candidates for proton-transfer partners within this range. For example, protonated aldehydes (other than MeCHO) and alcohols readily undergo thermally activated unimolecular dehydration,[9] which eliminates two classes of potential reactants since the equilibrium measurements must be carried out at elevated temperatures to minimize clustering with polar components. By default, our experimental skeletal framework was constructed using simple nitriles. Although the protonated forms cluster efficiently with their parent molecules,[10] which somewhat restricts the available temperature range, they do not pyrolyze, isomerize, or react with their parent neutrals or other molecules chosen for study other than via proton donation.

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The goal was 3-fold: (i) to define, as accurately and precisely as possible, an interlocking ladder of PAs between MeCHO and $MeCO_2Me$ in order to clarify/resolve existing inconsistencies in the literature; (ii) to generate a concurrent $\Delta S°$ ($\Delta G°$) scale over this range for the same reactants in order to probe and verify entropy changes associated with protonation of various base functions; (iii) to compare and discuss the interrelationship between the present results and existing computational and experimental scales as they relate to the PA range above and including MeCHO.

Experimental Section

Measurements were carried out using the NIST pulsed high-pressure mass spectrometer, which has been described in detail previously.[3] Since one of the primary goals in this study was the definition of reliable $\Delta S°$ values for the proton-transfer reactions, the mass-dependent discrimination/detector response characteristics of the quadrupole system were carefully reevaluated periodically using calibration techniques outlined in earlier articles.[3,11] The application of instrumental corrections to the observed equilibrium ion ratios modify ln K_{equil} ($\Delta G°$) and the corresponding $\Delta S°$ for the reaction pair, which is derived from the intercept of the van't Hoff plot. The $\Delta H°$ value, which reflects only the slope of the van't Hoff plot, is unaffected by this procedure. The largest correction applied was in the MeCN/toluene system, which required a 34% decrease in the recorded intensity of m/z 93 ($C_7H_9^+$) relative to m/z 42 ($MeCNH^+$) under the conditions of those particular measurements.

With the exception of i-C_4H_8, all of the proton-transfer partners chosen were liquids at room temperature. Consequently, mixtures of known relative concentrations could be accurately prepared for study from carefully dried starting materials in large volumes (milliliter levels) without sacrificing reproducibility. Microliter-sized samples of these premixed solutions could then be injected into the sample introduction reservoir (3.0 L, 420 K) of the gas-handling system on a day-to-day basis without introducing random makeup errors due to scatter in reactant ratios. Solutions comixed with MeCHO were prepared, handled, and injected at 250 K to minimize evaporative loss, while i-C_4H_8 was introduced using standard expansion techniques incorporating calibrated volumes. All reactant mixtures were diluted with CH_4 containing trace CCl_4 as an electron capture agent. Total ion source pressures ranged from 3 to 6 mbars. Concentrations of proton-transfer partners were usually adjusted to provide a BH^+/AH^+ ion intensity ratio of approximately unity at equilibrium in order to facilitate detection of any subtle changes in this critical parameter at long reaction times due to side reactions, cluster dissociation, etc. Specifics for individual systems are given either in the text, figure captions, or tables.

Ionization was induced by a 1 keV electron pulse of 0.2−0.6 ms duration. Temporal ion profiles were monitored for 4−10 ms after termination of the pulse, and equilibrium ion ratios were typically taken from accumulated data averaged over a 2−3 ms range after equilibrium had been achieved. A total of 299 separate measurements were carried out, all of which were used in constructing the van't Hoff plots or $\Delta G°$ scale unless it was apparent that competing reactions precluded their inclusion. The data were taken intermittently over a period of approximately two years.

Results

van't Hoff plots for the proton-transfer equilibria are given in Figures 1 and 2. The minimum number of data points used to construct an individual plot (17) was for the C_7H_8/EtCN system. Twenty-six measurements, representing the maximum, were used for both the EtCN/i-C_4H_8 and i-PrCN/$(Me)_2CO$ pairs. The variously labeled points in Figures 1 and 2 indicate mixtures with different reactant mole fractions as identified in the captions. Thermochemical values derived from the plots for the various equilibria are summarized in Table 1along with a discussion of error limits associated with the data.

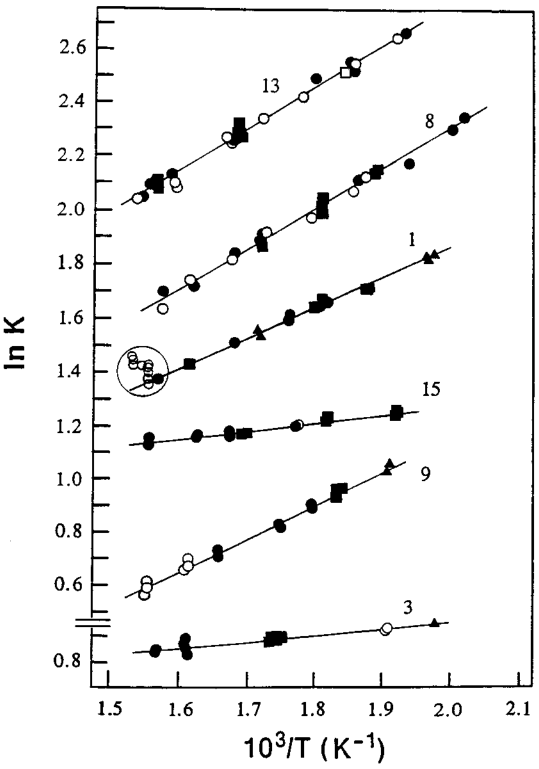

Figure 1. van't Hoff plots for the proton-transfer equilibrium $AH^+ + B \rightleftarrows BH^+ + A$. Numbering corresponds to base pair combinations as given in Table 1. Variously configured data points indicate different reactant mole fractions in CH_4. Entries as follows: reaction number, base A:base B; data point symbol, mole fraction A:mole fraction B, entry in ( ) is exponent, base 10. (1) MeCHO:MeCN; ●, 3.9(−4):6.0(−5); ■, 2.1(−4):3.1(−5); ▲, 1.4(−4):2.1(−5). See text for meaning of circled points. (3) $MeCN:HCO_2Me$; ●, 3.7(−4):1.4(−4); ■, 2.4(−4):8.8(−5); ○, 7.8(−5):2.9(−5); ▲, 2.9(−5):1.1(−5). (8) HCO_2Me:EtCN; ○, 3.3(−4):5.7(−5); ●, 1.3(−4):1.0(−5); ■, 2.2(−4):1.9(−5). (9) Toluene:EtCN; ○, 2.0(−4):9.7(−5); ■, 7.4(−5):3.7(−5); ●, 9.7(−5):4.9(−5); ▲, 2.9(−5):1.4(−5). (13) i−PrCN:$(Me)_2CO$; ■, 2.0(−4):2.5(−5); □, 5.9(−5):7.3(−6); ●, 7.7(−5):9.5(−6); ○, 6.8(−5):8.2(−6). (15) $(Me)_2CO:MeCO_2Me$; ●, 1.7(−4):5.3(−5); ■, 8.6(−5):2.6(−5).

Separate bridging routes between the same two bases gave essentially identical results for ΔPA (numbers in parentheses below refer to the individual reaction pair numbers given in Table 1). The direct measurement between MeCN and EtCN (5) gave a $\Delta H°$ of 14.6 kJ/mol, while the indirect paths through HCO_2Me (3,8) or C_7H_8 (4,9) yielded 14.4 and 14.2 kJ/mol, respectively. Similarly, the directly measured ΔPA between EtCN and $(Me)_2CO$ was 23.3 kJ/mol, compared with 23.3 and 23.1 kJ/mol for the ladders through i-PrCN (10,13) or i-C_4H_8 (11,14). Cumulative $\Delta G°$ values spanning subsets were also very consistent irrespective of the routes taken between the lower and upper limits. For the $\Delta G°$ between MeCHO and EtCN, the various routes and the associated overall $\Delta G°_{600}$ values were as follows (kJ/mol): (1,5) 21.5; (1,3,7,9) 21.6; (1,4,9) 22.1; (1,3,8) 20.8; (2,8) 21.5, and (2,7,9) 22.3. Within the upper segment, the directly measured $\Delta G°_{600}$ between EtCN and $(Me)_2CO$ (12) was 22.1 kJ/mol, while the bridges through i-C_4H_8 (11,14) and i-PrCN (10,13) gave 22.1 and 22.3 kJ/mol, respectively. The final ΔPA and $\Delta G°_{600}$ values obtained from

TABLE 1: Summary of Thermochemical Data Derived from Proton-Transfer Equilibria[a]

rxn. no.	A	B	ΔH^b	ΔS^c	$\Delta G°_{600}{}^b$	$T_{\min}{}^d$	$T_{\max}{}^d$	$T_{\mathrm{av}}{}^d$
1	MeCHO	MeCN	−9.3 (0.4)	−3.0 (0.8)	−7.5 (0.9)	234	378	306
2	MeCHO	HCO_2Me			−12.5 (0.8)			
3	MeCN	HCO_2Me	−1.8 (0.6)	+4.2 (1.0)	−4.3 (1.1)	233	365	299
4	MeCN	C_6H_5Me	−3.8 (0.6)	+11.9 (0.9)	−11.0 (1.1)	260	377	319
5	MeCN	EtCN	−14.6 (0.8)	−1.0 (1.3)	−14.0 (1.5)	262	372	317
6	MeCN	iPrCN			−26.1 (0.5)			
7	HCO_2Me	C_6H_5Me			−6.2 (0.4)			
8	HCO_2Me	EtCN	−12.6 (0.6)	−6.0 (1.1)	−9.0 (1.3)	224	362	293
9	C_6H_5Me	EtCN	−10.4 (0.7)	−11.3 (1.1)	−3.6 (1.3)	251	372	312
10	EtCN	iPrCN	−9.8 (0.6)	+2.0 (1.1)	−11.0 (1.2)	241	385	313
11	EtCN	iC_4H_8	−13.5 (0.7)	+1.5 (1.1)	−14.4 (1.3)	270	373	322
12	EtCN	Me_2CO	−23.3 (0.7)	−2.0 (1.2)	−22.1 (1.4)	269	382	326
13	iPrCN	Me_2CO	−13.5 (0.6)	−3.7 (1.0)	−11.3 (1.2)	246	377	312
14	iC_4H_8	Me_2CO	−9.6 (0.4)	−3.1 (0.7)	−7.7 (0.8)	230	392	311
15	Me_2CO	$MeCO_2Me$	−2.7 (0.4)	+5.2 (0.8)	−5.8 (0.9)	247	369	308

[a] Thermochemical values for the reaction $AH^+ + B \rightleftarrows BH^+ + A$. The standard uncertainty for each entry arising from random effects is given in parentheses and is derived from the standard deviations of the slopes (for $\Delta H°$) and intercepts (for $\Delta S°$) in the least-squares fit of the experimental data to a linear regression analysis. The indicated uncertainties are these values multiplied by a coverage factor obtained for the *t*-distribution for a confidence interval of 0.95, with *n*-2 degress of freedom, where *n* is the number of data points in each individual plot. [b] In units of kJ/mol. [c] In units of J(mol•K). [d] In units of °C.

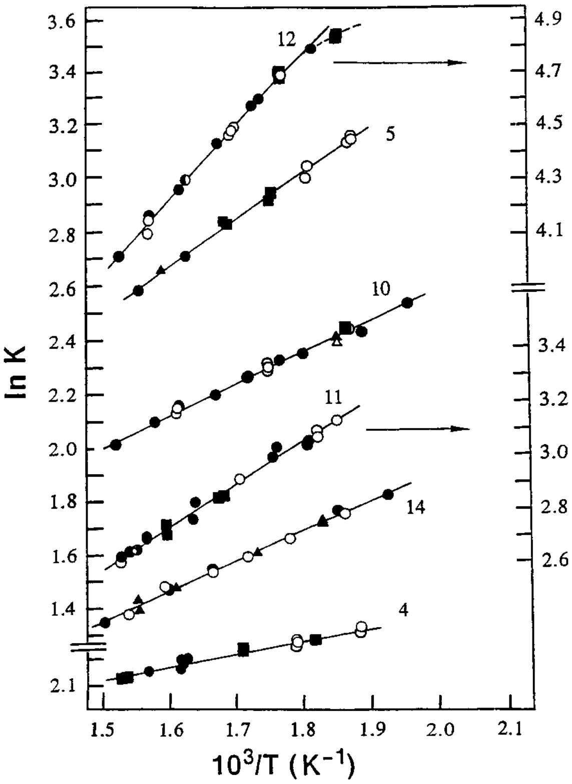

Figure 2. van't Hoff plots for the proton-transfer equilibrium $AH^+ + B \rightleftarrows BH^+ + A$. Numbering corresponds to base pair combinations as given in Table 1. Variously configured data points indicate different reactant mole fractions in CH_4. Entries as follows: reaction number, base A:base B; data point symbol, mole fraction A:mole fraction B, entry in ( ) is exponent, base 10. (4) MeCN:Toluene; ●, 4.2(−4):5.2(−5); ○, 8.6(−5):1.0(−5); ■, 2.1(−4):2.6(−5). (5) MeCN:EtCN; ○, 3.7(−4):1.3(−5); ■, 1.9(−4):6.5(−6); ▲, 5.0(−4):1.7(−5); ○, 1.1(−4):3.7(−6). (10) EtCN:*i*-PrCN; ○, 3.7(−4):3.7(−5); △, 8.7(−5):8.7(−6); ▲, 3.7(−5):3.7(−6); ■, 1.3(−4):1.3(−5); ●, 2.5(−4):1.1(−5). (11) EtCN:*i*-C_4H_8; ■, 3.0(−4):1.8(−5); ●, 2.5(−4):1.5(−5); ○, 3.0(−4):3.8(−5). (12) EtCN:$(Me)_2CO$; ○, 6.6(−4):1.5(−5); ■, 4.3(−4):9.9(−6); ●, 3.8(−4):9.2(−6). (14) *i*-C_4H_8:$(Me)_2CO$; ▲, 2.4(−4):2.8(−5); ●, 5.4(−4):1.3(−4); ○, 3.6(−4):5.9(−5).

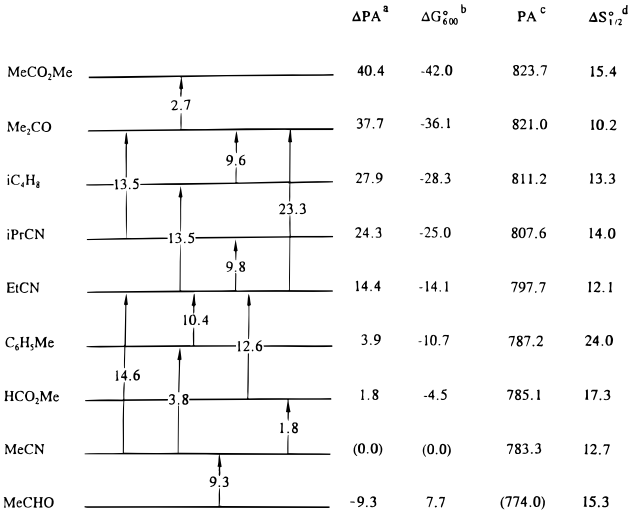

Figure 3. Experimental and normalized proton-transfer thermochemistry. Values in an arrow give the experimental $-\Delta H°$, in kJ/mol, for the reaction $AH^+ + B \rightleftarrows BH^+ + A$ between the indicated bases A and B. (a) Measured PA difference between various bases and MeCN (kJ/mol). (b) $\Delta G°$ for proton transfer between MeCN and various bases at 600 K (kJ/mol). (c) Absolute PA scale at 600 K referenced to PA(MeCHO) = 774.0 kJ/mol. (d) Protonation half-reaction entropies at 600 K for the indicated bases [J/(mol•K)]. See text for description.

the networks between the various bases are given in Figure 3relative to MeCN. Although essentially all pairs were well-behaved in the sense that the derived equilibrium constants were independent of total pressure and concentration under conditions where clustering reactions were minimized (elevated temperatures), there were two exceptions: $HCO_2Me-C_7H_8$ (toluene) and MeCHO−MeCN mixtures.

HCO_2Me−Toluene Mixtures. Measurements were taken over the temperature range 504−645 K. The basic observation was that the terminal "equilibrium" ion ratio, $C_7H_8H^+/HCO_2MeH^+$, exhibited a subtle but steady decrease with increasing total pressure in a mixture of constant composition. This effect was particularly pronounced below 600 K. For example, the apparent $-\Delta G°$ decreased from 5.4 kJ/mol at 3.3 mbar to 4.9 kJ/mol for a 4:1 HCO_2Me/C_7H_8 mixture in CH_4 at 518 K and showed no evidence of asymptotically approaching a pressure-independent value at higher densities (up to 6 mbar). This artifact was not traceable to limited observation times since constant ion ratios were tracked for several milliseconds after the initial reactions involved in the approach to equilibrium had gone to completion. Although we have no specific explanation for the behavior found in this system, we note that C_7H_8 is unique among the molecules studied in that the $C_2H_5^+$ ion generated in the initial chemical ionization reaction involving the CH_4 carrier gas ($CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$) efficiently forms a covalently bonded addition product with C_7H_8 (protonated methylethylbenzene) at lower temperatures under our conditions rather than transferring a proton, although the protonation reaction is exothermic by some 100 kJ/mol. The formation and subsequent chemistry of the arenium ions produced by alkyl cationic addition to C_6H_6 and C_7H_8 have been reported in detail from Stone's[12] and Kebarle's[13] laboratories, but in those cases the reactant was t-$C_4H_9^+$ and the proton-transfer channel was endothermic. Whatever the reasons, a reliable van't Hoff plot could not be constructed for HCO_2Me/C_7H_8 mixtures. However, we did derive a $\Delta G°$ for this system at 600 K, where the pressure effect on K_{equil} was minimal (see Table 1). No pressure dependence of K_{equil} was detected for the other two proton donor/acceptor partners investigated here in comixtures with C_7H_8 (MeCN, EtCN), although addition of $C_2H_5^+$ to C_7H_8 was also observed in those measurements and a negative temperature dependence was again noted for the insertion/addition reaction.

MeCHO/MeCN Mixtures. The van't Hoff plot for this pair is given as 1 in Figure 1. At temperatures > 630 K ($10^3/T < 1.56$) the data for this system exhibited extensive scatter, with the general effect being an increase in K_{equil} (circled section of plot). No new ions corresponding to impurity or self-reaction were detected in the composite spectrum at these temperatures, and the measurements appeared to be otherwise quite normal. A low-level signal (<3% of total ionization) was noted at m/z 43 over the entire temperature range, and its relative intensity did not increase with observation time. This species is presumably protonated ketene, CH_3CO^+, produced in the initial chemical ionization reactions by dissociative proton transfer to MeCHO. The increase in K_{equil} and associated scatter in the high-temperature data suggest pyrolysis of CH_3CHOH^+, but separate diagnostics in very dilute $MeCHO/CH_4$ mixtures failed to reveal the decomposition products. In any event, the thermochemical information for the MeCHO/MeCN pair was derived from the data taken below 630 K, where the system was well-behaved.

Discussion

The present ΔPA between MeCHO and $MeCO_2Me$ from the ladder is 49.7 ± 1.3 kJ/mol (combined total uncertainty in precision) compared with the earlier NIST value of 56.5 kJ/mol. The corresponding $\Delta G°_{600}$'s are 49.7 kJ/mol (present) and 56.9 kJ/mol (previous). Consequently, the experimental NIST scale was expanded by approximately 14% in both ΔPA ($\Delta H°$) and $\Delta G°$ based on the current data. Comparison of the thermochemistry for individual reaction pairs common to both studies indicates that this expansion was systematic throughout and not specific to any particular bridging pair. Random experimental spot-checks of $\Delta H°$ and $\Delta G°$ for reaction pairs with PAs above $(Me)_2CO$ verified our overall previous results for the upper scale, indicating that the expansion was confined to the subset below i-C_4H_8. During construction of the upper section of the earlier NIST scale[3] we also generated an experimental interlocking $\Delta H°$ ladder of relative ionization energies (IEs) for aromatic molecules based on variable-temperature equilibrium measurements.[14] Over the span of the ladder, from 1,2,3,5-tetramethylbenzene to C_6F_6, the equilibrium results yielded a ΔIE of 170.3 kJ/mol compared with the optical and photoionization spectroscopic ΔIE of 177.0 kJ/mol. The segment between C_3H_6 and i-C_4H_8 was added as an afterthought in our original study and involved a separate set of experimental procedures as well as equipment interchanges. We can only speculate that the expansion resulted from an error in temperature measurement, possibly traceable to a faulty dc comparator reference voltage in the DVM used to monitor the outputs of the source thermocouples in those particular measurements. Irrespective of the exact reason(s), the present data supersede and correct the earlier results in this region and should be substituted for them.

Kinetic measurements cannot define either absolute PAs or entropies of protonation since only relative values are obtained experimentally. The average temperature in the present study was 584 K; consequently we have normalized our relative PAs to a PA(MeCHO) of 774 kJ/mol (185.0 kcal/mol) at 600 K. This value has been based[15] on an evaluation of many sets of independent data, including the recent photoionization measurements of Ruscic and Berkowitz[16] and Bogan et al.[17] The entropy changes associated with the half-reaction $B \rightarrow BH^+$ [$\Delta S_{1/2} = S°(BH^+) - S°(B)$] for all of the bases studied have also been derived from the data of Table 1. In this case the values have been anchored to a $\Delta S_{1/2}$ for MeCN protonation of 12.7 J/(mol·K) at 600 K, which is taken from the average of the directly computed 600 K value by East et al. [12.6 J/(mol·K)][18] and that from the JANAF tables [12.8 J/(mol·K)][19] assuming $MeCNH^+$ has the same entropy as the isoelectronic neutral MeCCH at 600 K. The resultant PAs and half-reaction entropies are given in Figure 3.

Several scales exist for the PA subset between MeCHO and $(Me)_2CO$/$MeCO_2Me$. In a series of articles Radom and coworkers[7] have reported computational results at various levels of theory for several molecules common to the experimental studies at both 298 and 600 K. Hunter and Lias[15] have also maintained a PA database which includes all available experimental and theoretical results at various temperatures and have recently completed a comprehensive reevluation of the entire gas-phase PA scale.[20] The general observation is an increase of 3.8 ± 1 kJ/mol in absolute PA(600 K) values relative to those at 300 K, with the entire scale shifting upward more or less uniformly except for certain classes of compounds such as amines. The existing subsets within the range of interest here are given in Table 2. For the purpose of comparison data obtained in the present study and referenced to the recommended PA(MeCHO) at 600 K of 774.0 kJ/mol in Table 1 have been uniformly scaled down by 4.0 kJ/mol to match the recommended[20] 298 K value of 770.0 kJ/mol. The extensive SM scale was originally anchored to a PA(600 K) for CO of 141.9 kcal/mol (593.7 kJ/mol), essentially identical with the current recommended value[20] at 300 K (593.7 kJ/mol vs 593.0 kJ/mol). Therefore their values are presented as reported, after converting to kJ/mol.

Experimentally, the assignment of accurate relative protonation entropies in variable-temperature equilibrium measurements can present a significant challenge. While $\Delta H°$ values separating base pairs depend only on the slopes of van't Hoff plots, $\Delta S°$ values derived from the intercepts are affected by random and systematic errors in sample makeup as well as discrimination factors associated with the ion transmission and detector response characteristics of the mass specrometer. Small errors in $\Delta H°$ are also magnified in the corresponding $\Delta S°$ value. For example, a 1 kJ/mol error in measuring a $\Delta H°$ for a proton-transfer equilibrium involving two bases with PAs differing by 10.0 kJ/mol (2.4 kcal/mol) induces an absolute error of 1.9 J/(mol·K) in the overall $\Delta S°$ for the reaction when the raw data are taken between 520 and 650 K (approximate range covered in the present study). A listing of available $\Delta S_{1/2}$ values for the bases under study is given in Table 2. Included are (i) values at 584 K derived in the present study, (ii) computed values by East et al.[18] (600 K), (iii) the SM data (quoted as 500 K, but

TABLE 2: Comparison of Thermochemical Values from Various Sources

	proton affinities[a]				half-reaction entropies ($\Delta S_{1/2}$)[b]			
base	present results (300 K)[c]	Hunter and Lias[d] (300 K)	computational (300 K)	SM (300 K)[e]	present results (600 K)	computational (600 K)[f]	SM (570 K)[c]	JANAF (600 K)[g]
$MeCO_2Me$	819.7	823		815.9	15.4		16.7	
$(Me)_2CO$	817.0	812	811.9[h]	810.4	10.2	14.0	18.8	
i-C_4H_8	807.2	802.0	802.1[i]	802.1	13.3	16.3	23.0	
i-PrCN	803.6	803.6		808.3	14.0		0.0	13.3
EtCN	793.7	794.1	794.3[j]		12.1	14.0		12.3
toluene	783.2	784.0		785.3	24.0	18.4−24.7	12.6	
HCO_2Me	781.1	782.5	782.2[h]	787.0	17.3		2.1	
MeCN	779.3	779.2	780.1[j]		(12.7)	12.6		12.8
MeCHO	(770.0)	770	770.2[i]		15.3	7.8		

[a] In units of kJ/mol. [b] In units of J/(mol·K). [c] Values at 300 K derived by subtracting 4.0 kJ/mol from the 600 K values given in Table 1. See text for details. [d] Reference 20. [e] Reference 6. The temperature quoted in the SM study was 500 K for $\Delta S_{1/2}$ values. However, their measurements within this subset, excluding bridges to toluene from bases with PA's below this subset, were taken at an average temperature of 570 K. [f] Reference 18. [g] Values for $\Delta S_{1/2}$(600 K) assuming AH^+ has the same entropy as the geometrically equivalent isoelectronic neautral. See text for details. [h] Reference 7c. [i] Reference 7a. [j] Reference 7b.

see footnote to Table 2), and (iv) 600 *K* values taken from the JANAF tables assuming BH^+ has the same entropy as the structurally equivalent isoelectronic neutral.

In our opinion, a strong argument can be made against the use of *i*-C_4H_8 as a reference standard in constructing an experimentally derived relative gas-phase PA scale. East et al.[18] have computed third-law entropies for 42 molecules and their protonated forms spanning the PA range between H_2 and $(Me)_3N$ at 298, 500, and 600 K. All rotational barriers, as well as torsional contributions in multirotor situations, have been included in the calculations. The $\Delta S_{1/2}$ values for protonation half-reactions may be directly calculated from their data, and eight of the molecules considered fall within the PA range covered in this study. Although absolute entropies of the various A and AH^+ systems vary considerably from molecule to molecule at a given temperature, a remarkable consistency is found in the change in $\Delta S_{1/2}$ ($\Delta\Delta S_{1/2}$) as a function of temperature (excluding *i*-C_4H_8). For the lone-pair bases MeCHO, MeSH, MeCN, C_2H_3CN, $(Me)_2O$, EtCN, and $(Me)_2CO$, $\Delta\Delta S_{1/2}$ is 7.1 ± 1.1 J/(mol·K) as the temperature is increased from 298 to 600 K. Between 500 to 600 K, the increase is 2.2 ± 0.4 J/(mol·K). In sharp contrast, the computed $\Delta\Delta S_{1/2}$ for protonation of *i*-C_4H_8 is 0.1 J/(mol·K) between 298 and 600 K and 0.6 J/(mol·K) from 500 K-600 K. These data translate into the following interpretive dilemma for the experimentalist. If one assumes a hypothetical molecule (X) with the same PA and $\Delta S_{1/2}$ as *i*-C_4H_8 at 298 K, a proton-transfer equilibrium measurement at 298 K involving X and *i*-C_4H_8 would yield $K_{\mathrm{equil}} = 1.0$ ($\Delta G°$, $\ln K = 0.0$). Since the ΔS for the proton-transfer reaction is projected to be approximately 7 J/(mol·K) at 600 K, the experimental measurement at 600 K would yield a K_{equil} of 2.3, and the resultant van't Hoff plot based on the 298 and 600 K ln *K* values would indicate a $\Delta H°$ (ΔPA) of 4.2 kJ/mol and a $\Delta S°$ of 14 J/(mol·K) even though $\Delta\mathrm{PA} = 0.0$. The same treatment for an experimental measurement taken between 500 and 600 K, again taking $\Delta\mathrm{PA} = 0.0$ but with $\Delta\Delta S_{1/2} = 1.6$ J/(mol·K), would give $K_{\mathrm{equil}}(600\ \mathrm{K}) = 1.2$ and an apparent $\Delta H°$ from the slope of the van't Hoff plot of −4.8 kJ/mol and a $\Delta S°$ of 9.7 J/(mol·K) from the intercept. The overall result would be the assignment of a ΔH (ΔPA) of 4.5 ± 0.3 kJ/mol to a thermoneutral proton-transfer reaction, with $\Delta S°$ strongly dependent upon the temperature range covered in the equilibrium measurements.

In view of the potential uncertainties associated with *t*-$C_4H_9^+$ kinetics, we consider the position of *i*-C_4H_8 in the experimental PA scale to be unreliable. However, it is useful as a bridge for connecting bases with lower and higher PAs since thermochemical anamolies associated with any given *i*-C_4H_8/base combination cancel out in constructing an interlocking ladder provided all of the measurements were taken within a reasonably constant temperature window. A side-by-side comparison of the existing thermochemical scales within the MeCHO/$MeCO_2Me$ subset is given in Table 2. The absolute values quoted for PAs and $\Delta S_{1/2}$ from both the present and SM experimental scales are not as important in the present context as the relative numbers since the conversion to an absolute scale in these cases assumes a reference value for anchoring the individual ladders.

Protonation Enthalpies. Both the SM and Radom scales include only five entries in the range of interest (excluding *i*-C_4H_8), with the Radom scale necessarily limited to small molecules in order to avoid the computational demands imposed by excessively large basis sets. From top to bottom ($MeCO_2Me$ to MeCHO), the overall ΔPA from the present data (49.7 kJ/mol), agrees well with that recommended in the updated NIST[20] scale (53 kJ/mol) although the agreement between $(Me)_2CO$ and MeCHO is less satisfactory at 47.0 kJ/mol (present) vs 42.0 kJ/mol (NIST) and 41.7 kJ/mol (Radom). The individual absolute values obtained in the present work after scaling down the PAs listed in Table 1 to PA(MeCHO) = 770.0 kJ/mol at 300 K also agree within 1 kJ/mol with both the ab initio and NIST database numbers with the exception again being $(Me)_2CO$, where the difference is 5 kJ/mol. The widest comparison possible with the SM scale is the ΔPA from HCO_2Me to $MeCO_2Me$. The present data give 38.6 kJ/mol, consistent with the NIST database ΔPA of 40.5 kJ/mol. Alternatively, the SM scale appears to be considerably compressed, with a ΔPA of 28.9 kJ/mol over this same range. A depression is also evident in their smaller subset between HCO_2Me and $(Me)_2CO$, with ΔPA(SM) = 23.4 kJ/mol, while the independent computational and NIST recommended scales suggest 29.7 and 29.5 kJ/mol, respectively.

Protonation Entropies. Comparison of the relative/absolute protonation entropies reveals substantial deviations in some cases, reflecting the experimental difficulties associated with such measurements. As discussed earlier, our data have been referenced to an absolute $\Delta S_{1/2}$ of 12.7 J/(mol·K) at 600 K for the half-reaction $MeCN \rightarrow MeCNH^+$. Since third-law entropies are available for neutral nitriles as well as alkylacetylenes, which are isoelectronic with protonated nitriles, an independent set of data for $\Delta S_{1/2}$ can be generated for this class of molecules. Unfortunately the analogous information does not exist for oxygen bases when protonation occurs on a carbonyl function. Comparison of the present experimental $\Delta S_{1/2}$ values for the nitriles with those derived from the isoelectronic equivalency calculations and those computed by East et al. reveals remarkable agreement (Table 2). The single SM entry for alkylnitriles (*i*-PrCN) of $\Delta S_{1/2} = 0.0$ J/(mol·K) is not consistent with the other data, which suggest a value of 13.0 ± 1.0 J/(mol·K) for this class of molecules at approximately 600 K.

As a rough approximation, and only for the purpose of discussion, we will consider all of the bases with carbonyl functions as a single class of molecules. Although an obvious oversimplification since each carboxylic acid, aldehyde, ketone, and ester will exhibit distinct vibrational and rotational modes, moments of inertia, and symmetry changes due to isomeric forms upon protonation which will influence heat capacities and $\Delta S°$ values, this assumption does not affect the following analysis. The experimental $\Delta S_{1/2}$(600 K) values derived in the present study for oxygen bases range from 10.2 J/(mol·K) [$(Me)_2CO$] to 17.3 J/(mol·K) (HCO_2Me) after referencing to MeCN, with an average value of 14.6 J/(mol·K). East et al. predict 8.0 J/(mol·K) for MeCHO and 14.0 J/(mol·K) for $(Me)_2CO$, while the SM study reports 2.1, 18.8, and 16.7 J/(mol·K) for HCO_2Me, $(Me)_2CO$, and $MeCO_2Me$, respectively. Both our and the SM values for the carbonyl bases within this subset are based on experimentally derived entropy bridges incorporating measurements with other molecules (all are network-derived “consensus” values). We note that the SM ladder predicts an overall $\Delta S°$ at 570 K (see footnote to Table 2) of 14.6 J/(mol·K) for proton transfer from HCO_2Me to $MeCO_2Me$, while the present data give -1.9 J/(mol·K) (essentially zero) within the same temperature window. The two data sets connecting these simple esters are in substantial disagreement. This disparity is magnified in the $HCO_2Me-(Me)_2CO$ bridge (Table 2).

Basicity Scales. A $\Delta G°$ ladder derived from equilibrium constants measured at a single constant temperature constitutes a separate thermodynamic scale. As we discussed earlier, our original NIST value for the $\Delta\Delta G°_{600}$ between MeCHO and $MeCO_2Me$ was 56.9 kJ/mol compared with the present value of 49.7 kJ/mol, representing a 12.7% compression. Although the SM study did not include MeCHO, they did report a complete $\Delta G°_{600}$ protonation scale which indicated a $\Delta\Delta G°$ between HCO_2Me and $MeCO_2Me$ of 37.2 kJ/mol. The present data for this particular pair gives a 37.5 kJ/mol difference (Figure 3), essentially identical with their value. However, this agreement is apparently fortuitous since significant differences exist in individual and overall ΔPA and $\Delta S°$ values.

Conclusions. The present experimental and recently published computational data, taken together with the updated NIST database values, suggest the following for the PA subset between MeCHO and $MeCO_2Me$. Considering all of the available information, it would appear that this experimentally difficult section of the total gas-phase scale is characterized by a ΔPA span of approximately 51 kJ/mol (12.2 kcal/mol), with a composite uncertainty of ±2 kJ/mol (0.5 kcal/mol). With respect to entropies of protonation ($\Delta S_{1/2}$ values), the present experimental measurements are very consistent with both ab initio calculations and those derived indirectly from isoelectronic neutrals in those cases where comparisons are possible. We also find no evidence that a hindered rotor is created upon protonation of acetone resulting in an abnormally high $\Delta S_{1/2}$ value as suggested earlier.[6]

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