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Thermokinetic Determination of Gas-Phase Basicities. Application to Ketene, Methylketene, and Formaldimine

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Rate constants have been determined for proton transfer reactions of the type $[MH]^+ + B \leftrightarrows M + [BH]^+$, where M is ketene, methylketene, and formaldimine and B is a reference base. A quantitative relationship between the rate constant and the free energy (or enthalpy) of the reaction allows the determination of the gas-phase basicity, GB, (or proton affinity, PA) of M. This thermokinetic method gives results comparable to that obtained from equilibrium constant measurements. The values derived for ketene, methylketene, and formaldimine follow: GB(ketene) = 788 ± 3 kJ/mol, PA(ketene) = 817 ± 3 kJ/mol; GB(methylketene) = 809 ± 3 kJ/mol, PA(methylketene) = 842 ± 3 kJ/mol; GB(formaldimine) = 830 ± 3 kJ/mol and PA(formaldimine) = 860 ± 5 kJ/mol. Heats of formation of methylketene and of formaldimine that may be deduced from a combination of these results with literature data are as follows: $\Delta H_f°_{300}$ (CH_3CHCO) = −97 ± 5 kJ/mol and $\Delta H_f°_{300}$ ($CH_2{=}NH$) = 75 ± 5 kJ/mol.

Introduction

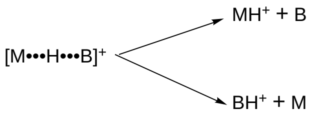
Gas-phase acidities and basicities of molecules provide important keys to the understanding of ion/molecule chemistry, both in the gas phase and in solution. Their precise determination is consequently of interest, and several methods are currently used whereby these thermochemical quantities may be obtained, each of them possessing its proper advantages and limits.

A large amount of the presently available data[1−4] is coming from the measurement of the equilibrium constant of the proton transfer reaction:

$$[MH]^+ + B \leftrightarrows M + [BH]^+ \qquad (I)$$

The equilibrium constant for reaction I, K_I, directly leads to the corresponding free enthalpy change which is also equal to the gas-phase basicity difference: $\Delta G°_I = -RT \ln K_I = GB(M) - GB(B)$. When the entropy variation $\Delta S°_I$ can be reasonably estimated, a value for the enthalpy change $\Delta H°_I = \Delta G°_I + T\Delta S°_I$, i.e., the proton affinity difference $\Delta H°_I = PA(M) - PA(B)$, may be also deduced. Moreover, if the equilibrium constant can be measured at various temperatures, both $\Delta H°_I$ and $\Delta S°_I$ may be obtained from a van't Hoff plot of $\ln K_I$ against $1/T$.

The second source of thermochemical information concerning acidities and basicities of gaseous molecules is given by the so-called "kinetic method".[5] In these experiments the dissociation of a series of proton bound bimolecular clusters $[M\cdots H\cdots B]^+$



is examined in order to deduce the relative basicities (or proton affinities) through the relationship:

$$\ln([MH]^+/[BH]^+) \approx \Delta GB/RT \text{ (or } \Delta PA/RT)$$

A more qualitative technique, the "bracketing method", consists of the appreciation of the occurrence/nonoccurrence of the proton transfer reaction (I) when the base B is varied. This method was first expected to give a bracketing of the proton affinity of M, but it seems more likely that it provides information on the gas-phase basicity.[6,7]

Finally, we recently[7] observed that the correlation between the experimental rate constant for the proton transfer reaction I, k_{exp}, and its free enthalpy change, $\Delta G°_I$, may be described by a relationship of the type

$$\frac{k_{exp}}{k_{coll}} = \frac{1}{1 + e^{(\Delta G°_I + \Delta G°_a)/RT}} \qquad (1)$$

where k_{coll} is the collision rate constant and $\Delta G°_a$ an apparent energy barrier for reaction I. It has been demonstrated[7] that the reaction efficiency RE = k_{exp}/k_{coll} may be fitted by the parametric function

$$RE = \frac{a}{1 + e^{[b(-GB(B)+c)]}} \qquad (2)$$

with a being a normalizing factor, $c = GB(M) + \Delta G°_a$, and $b = 1/RT^*$ (T^* is the "effective" temperature of the system). After examination of several series of proton transfer reactions, it has been observed that $\Delta G°_a$ is of the same order of magnitude as the term RT^*. Consequently the gas-phase basicity of M may be approximated by $GB(M) \approx c - 1/b$. It has been shown that the preceding relationship allows the determination of unknown gas-phase basicities with good precision (±5 kJ/mol), either by fitting of the experimental data and extraction of the parameters $a-c$ or by an extrapolation procedure.[7]

Relation 2 may be extended to the proton affinity determination by using eq 3, with again $b = 1/RT^*$ but, that time, $c' = PA(M) + \Delta G°_a - T\Delta S°_I$.

$$RE = \frac{a}{1 + e^{[b(-PA(B)+c')]}} \qquad (3)$$

The proton affinity of M may thus be approximated by $PA(M) \approx c' - 1/b + T\Delta S°_I$. The precision of this latter relationship is

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limited by the range of $\Delta S°_I$ values; clearly a good precision is obtained only in the cases where a set of reactions (I) possessing similar entropic variations $\Delta S°_I$ is considered.

Another way to use expression 2 or 3, which avoids the approximation $\Delta G°_a \approx RT^*$, consists of comparing the relative efficiency curve of the unknown M with that of a standard; this procedure will be used later on in this paper.

Each of these four methods of determination of gas-phase basicity possesses their domain of applicability. The "equilibrium method" needs the equilibration of $[MH]^+$ and $[BH]^+$ ions in a mixture of neutrals M and B; this procedure obviously necessitates that the two latter molecules are stable species but also that the structures of M and B are conserved during the protonation/deprotonation process. Thus, the equilibrium method is not appropriate if an isomerization or a dissociation process is induced by the protonation. The "kinetic method" is subjected to the formation of the primary proton bound cluster which may also depend upon the stability of M and B and the possibilities of unwanted isomerization or dissociation processes.

The "bracketing" and the "thermokinetic" methods are not subjected to the above mentioned constraints intrinsic to the equilibrium or the kinetic techniques. In particular thermochemical information on unstable neutral species, or simply of neutrals hardly amenable to experiments, may be obtained. Moreover, the basicity of a neutral corresponding to the deprotonated form of a fragment ion may be also established by these methods as it will be illustrated thereafter.

In the present study, we report the data obtained using the thermokinetic method to determine the basicity of ketene, methylketene, and formaldimine. Experiments were conducted in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source. The $[MH]^+$ ions are produced in the external ion source by dissociative ionization of a suitable neutral and then allowed to react in the ICR cell with the reference bases B.

Experimental Section

Three sets of proton transfer reactions have been studied which involved (i) acetyl cation, (ii) propanoyl cation, and (iii) immonium $[CH_2NH_2]^+$ cation with several reference bases B. Experiments were performed on a Bruker Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source.[8] The acetyl cation, propanoyl cation, and $[CH_2NH_2]^+$ cations were generated by dissociative ionization of acetone, 3-pentanone, and propylamine, respectively, in the external ion source (typical conditions were as follows: filament current, 4 A; electron energy, 30−70 eV; ionizing pulse duration, 10 ms). All of the ions resulting from electron ionization were transferred to the reaction cell located inside the 4.7 T superconducting magnet. Selection of the ion of interest was done by ejection of unwanted ions by a combination of chirp and soft radio frequency (rf) pulses. The reactants were relaxed to thermal energy ($T = 300$ K) by introducing argon inside the ICR cell at a pressure approximatively 1 order of magnitude greater than the pressure of the neutral reactant and by imposing a relaxation delay of 2−6 s after selection of the reacting ions.

Next, the ions were allowed to react for a variable time with neutral bases B. Experiments were conducted at a constant pressure in the range of 10^{-8} to 10^{-7} mbar, as indicated by the ionization gauge (Balzers-IMR-132) located between the high-vacuum pump and the cell housing. The intensities of the peaks were determined in the frequency domain after Fourier transformation of the corresponding time domain signal.

The bimolecular rate constants k_{exp} were deduced from the slope of the logarithmic plot of reactant ions versus reaction time. The concentration of the neutral was determined from its indicated pressure (P_B) after calibration of the ionization gauge with the reaction $[CH_3OH]^{\bullet+} + CH_3OH \rightarrow [CH_3OH_2]^+ + {}^{\bullet}OCH_3$ ($k = 2.53 \times 10^{-9}$ cm^3·molecule^{-1}·s^{-1} [9]). The relative gauge sensitivity was corrected by taking into account the polarizability, α, of the neutrals.[10] The accuracy of the so derived experimental rate constant values is ca. ±10%. The collision rate constants, k_{ADO}, were calculated using the average dipole orientation theory.[11] Tables 2−4 contain the k_{exp} and k_{ADO} so determined for the reactions $[MH]^+ + B \leftrightarrows M + BH]^+$ under investigation together with the polarizability and the dipole moment of B. Since only relative values of the reaction efficiencies are of interest here, these quantities are normalized, for each set of data, by defining the relative efficiency as RE $= (k_{exp}/k_{ADO})/(k_{exp}/k_{ADO})_{max}$.

TABLE 1: Summary of the Experimental Determinations of the Gas-Phase Basicity of Ketene

ref	method	base B	$\Delta G°$ [a]	GB(B)[b]	GB(CH_2CO)[c]
12	equilibrium (ICR)	acetone	+0.8	783.3	782.5
		isobutene	−6.6	776.3	782.8
13	equilibrium (ICR)	tetrahydrofuran	+5.0	(795.2)	790.2
		methyl acetate	−1.7	788.2	789.9
		acetone	−6.3	783.3	789.6
14	equilibrium (HPMS)	acetone	−0.8	783.3	784.1
		isobutene	−7.1	776.3	783.4
		ethyl formate	−15.1	771.2	786.3
		diethyl oxide	+15.0	800.5	785.5
15	bracketing	dimethyl oxide	−	766.2	767 ± 2
		isopropanyl alcohol	+	769[d]	
this work	thermokinetic	see Table 2			788 ± 3

[a] $\Delta G°$ (kJ/mol) of the reaction $[CH_3CO]^+ + B \rightarrow CH_2CO + [BH]^+$. [b] GB values (kJ/mol) from $GB(B) = PA(B) + T[\Delta S°_{1/2}(B) - S°_{H^+}]$, with $T = 300$ K and $S°_{H^+} = 109$ kJ/mol. PA(B) and $\Delta S°_{1/2}$(B) are taken from ref 3. [c] $GB(CH_2CO) = GB(B) - \Delta G°$ (kJ/mol). [d] From ref 1a. GB(i-C_3H_7OH) = GB(NH_3) − 49 = 769 kJ/mol.

Results and Discussion

Ketene. Protonation of the ketene molecule is expected to occur preferentially on the terminal carbon atom. Accordingly, the acetyl cation $[CH_3CO]^+$ is predicted by molecular orbital calculations, at the MP3/6-31G**/HF/4-31G + ZPE level,[28] to lie 181 kJ/mol below the oxygen protonated form $[CH_2COH]^+$; these two structures are the most stable in the $[C_2H_3O]^+$ system.

The protonation thermochemistry of ketene has been investigated experimentaly by several groups in 1977−1978.[12−15] A brief survey of these studies will be done before considering the effects due to the reevaluation of the standards in the basicity scale.

Ausloos and Lias studied[12] the equilibrium involving protonated acetone and ketene in a pulsed ICR spectrometer. From the equilibrium constant measurement and estimate of the $\Delta S°$ correction they concluded that PA(ketene) = PA(acetone) + 0.7 kJ/mol. The authors further reevaluate the PA value of acetone from the proton transfer equilibrium between acetone and isobutene, and they finally propose PA(ketene) = 811 ± 4 kJ/mol. In a comparable experiment using a trapped ICR spectrometer, Vogt et al.[13] explored the equilibria involving ketene and (i) protonated tetrahydrofuran or (ii) protonated methyl acetate to deduce GB(ketene) = 790 kJ/mol and PA(ketene) = 820 ± 8 kJ/mol. In the same study, and in contrast with Ausloos and Lias,[12] it is found that ketene is more basic than acetone. High-pressure mass spectrometry was also used to measure the proton affinity of ketene.[14] Proton transfer equilibria involving ketene with acetone, ether, isobutene, and ethyl formate lead to a proton affinity value of PA(ketene) =

TABLE 2: Efficiencies of Proton Transfer Reactions Involving $[CH_3CO]^+$ and Several Bases B

base B	PA(B) (kJ/mol)	GB(B)[c] (kJ/mol)	$\Delta S°_{1/2}$(B)[d] (J/(mol K))	α[e] (Å^3)	μ (D)	P_B (mbar)	k_{exp}[h]	k_{ADO}[h]	RE[i]
dimethyl ether	793.3[a]	766.2	18.8	5.16	1.31[f]	1×10^{-7}	0.6	15.59	0.0004
isobutene	802.1[a]	776.3	23.0	7.92	0.50[f]	1×10^{-7}	0.16	13.81	0.014
isopropylcyanide	808.3[a]	775.6	0	8.05	4.04[g]	8×10^{-8}	0.38	30.50	0.015
acetone	810.4[a]	783.3	18.8	6.37	2.88[f]	1×10^{-7}	1.48	24.07	0.078
methyl acetate	815.9[a]	788.2	16.7	6.81	1.71[f]	2.0×10^{-8}	4.19	17.13	0.301
ethyl acetate	828.9[a]	800.6	14.6	8.62	1.78[f]	1.14×10^{-8}	12.2	18.05	0.827
3-pentanone	833.9[a]	804.3	10.5	9.93	2.72[g]	1.0×10^{-8}	18.4	23.28	0.974
diisopropylketone	852 ± 1[b]	821.1	(6)	13.53	2.67[g]	1.8×10^{-8}	19.3	23.68	1

[a] From ref 3; the more recent value PA(isobutene) = 801.7 ± 1.4 kJ/mol [36] fully confirms the anchoring of this basicity scale. [b] From ref 33. [c] GB(B) = PA(B) + $T[\Delta S°_{1/2}(B) - S°_{H^+}]$, with $T = 300$ K and $S°_{H^+} = 109$ J/(mol·K). [d] From ref 3. $\Delta S°_{1/2}$(B) is the standard entropy difference between the protonated and the neutral form of B. When the experimental data are not available, as $\Delta S°_{1/2}$(B) equal to $R \ln(\sigma_B/\sigma_{BH^+})$ (where σ is the relevant symmetry number) has been assigned; this estimate is indicated in parentheses. [e] Polarizabilities from ref 10b. [f] Dipole moment from ref 33. [g] Dipole moment calculated by the AM1 semiempirical procedure.[35] [h] $\times 10^{-10}$ cm^{-3}·molecule^{-1}·s^{-1}. [i] Relative reaction efficiency: RE = $(k_{exp}/k_{ADO})/(k_{exp}/k_{ADO})_{max}$.

816 ± 2 kJ/mol. The ion chemistry of ketene was studied using an ion trap device.[15] The proton affinity of ketene was estimated to lie between PA(CH_3OCH_3) and PA(CH_3OCH_3) and PA(C_3H_7-OH) by the bracketing technique, thus leading to PA(ketene) = 798 ± 5 kJ/mol.

The range of published values for the proton affinity of ketene (798−820 kJ/mol) must be now reconsidered in view of the most recent anchoring of the basicity scale. Table 1 summarizes the various experimental, objective data and the GB(ketene) values that may be deduced using the GB scale of Szulejko and McMahon.[3]

It may be seen that the GB values derived from the published data are in fact situated in the range 767−790 kJ/mol. Significantly enough, a mean value of GB(ketene) = 786 ± 3 kJ/mol is obtained if one considers only the nine results obtained by the equilibrium technique.[12−14] The value of 767 kJ/mol deduced using the bracketing technique from ion trap experiments[15] appears to be seriously underestimated.

The thermokinetic method has been applied to the ketene molecule by considering the deprotonation reactions:

$$[CH_3CO]^+ + B \rightarrow CH_2CO + [BH]^+ \qquad \text{(II)}$$

occurring into the ICR cell of the Bruker FT-ICR spectrometer. The acetyl cation has been produced in the external source of the instrument by dissociative ionization of acetone, and various bases B have been used for reaction II. The experimental rate constant, k_{exp}, and the theoretical rate constant, k_{coll}, are collected in Table 2 together with the relevant thermochemical data.

The curve corresponding to the relative efficiency of reaction II with respect to GB(B) is reported in Figure 1. The fit is characterized by a normalizing factor a of 1.01 ± 0.05 and by values of parameters b and c of 0.22 ± 0.07 kJ^{-1}·mol and 792.6 ± 0.8 kJ/mol respectively. Using the observation[7] that GB(M) $\approx c - 1/b$, we derive GB(ketene) = 788.1 kJ/mol.

As already mentioned in the Introduction, another way to use the relative efficiency curve consists of comparing the unknown to a standard. The fitted curves RE versus GB(B) corresponding to isobutene and acetone have been reported earlier.[7] For these two compounds the parameters a−c are equal to 0.95/0.96 ± 0.03 and 0.27/0.22 ± 0.03 kJ^{-1}·mol and 782.4/785.9 ± 0.7 kJ/mol, respectively. If, as is the case here, the parameters a and b are nearly identical to one fit to another, the difference in c values represents the difference in gas-phase basicities; it appears thus that GB(ketene) = GB(acetone) + 6.7 kJ/mol (i.e., precisely the relationship obtained by Beauchamp and co-workers[13]) and that GB(ketene) = GB(isobutene) + 9.4 kJ/mol (i.e., a difference comparable to that observed in refs 12 and 14). Thus, using GB(acetone) = 783.3 kJ/mol and GB(isobutene) = 776.3 kJ/mol,[3] we conclude that GB(ketene) = 787.9 ± 2.5 kJ/mol.

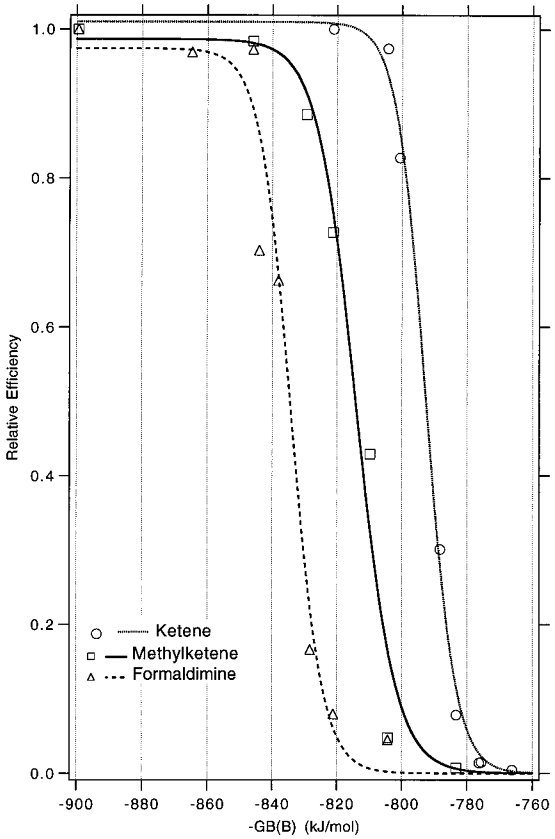

Figure 1. Representative curves of proton transfer reaction efficiency versus GB(B) for reaction $[MH]^+ + B \leftrightarrows M + [BH]^+$ (M = ketene, methylketene, and formaldimine).

In summary the experimental data coming from the thermokinetic method point to a gas-phase basicity of ketene being GB(ketene) = 788 ± 3 kJ/mol in excellent agreement with the results of the equilibrium method, but higher by no more than 21 kJ/mol from the value obtained by ion trapping experiments.[15]

The determination of the proton affinity, PA(ketene), may be similarly done by considering relationship 3. It has been pointed out that a good correlation of RE with PA(B) is expected only for a series of reactions characterized by a comparable $T\Delta S°_I$ term. This is indeed the case for the data collected in Table 2 if one excludes the isopropylcyanide molecule (see Table 2 and ref 7 for acetone and isobutene). The resulting curve is presented in Figure 2. The parameters a−c are equal to 1.01 ± 0.02 and 0.21 ± 0.02 kJ^{-1}·mol and 820.6 ± 0.7 kJ/

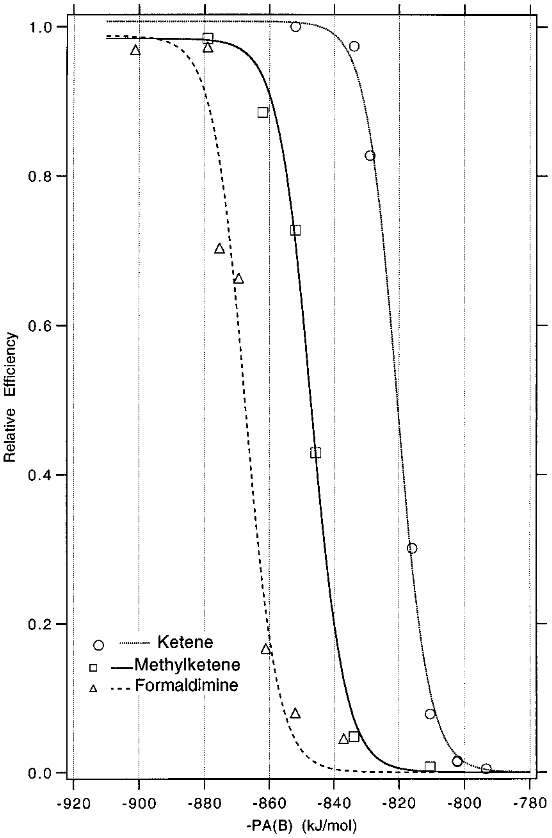

Figure 2. Representative curves of proton transfer reaction efficiency versus PA(B) for reaction $[MH]^+ + B \rightarrow M + [BH]^+$ (M = ketene, methylketene, and formaldimine).

mol for ketene and 0.96/0.96 ± 0.02 and 0.21/0.20 ± 0.02 kJ^{-1}·mol and 808.9 ± 0.9/813.4 ± 0.7 kJ/mol for isobutene and acetone, respectively.

When the two standards, isobutene and acetone, are considered, a mean value of PA(ketene) = 817 ± 3 kJ/mol is obtained.

The proton affinity may be also deduced from the GB value and the usual entropic correction:

$$PA(M) = GB(M) - T[\Delta S_{1/2}(M) - S^\circ_{H^+}]$$

where $\Delta S_{1/2}(M) = S^\circ_{MH^+} - S^\circ_M$ and $S^\circ_{H^+}$ being the translational entropy of the proton. In the case of the couple $[CH_3CO]^+/CH_2CO$ the $\Delta S_{1/2}(M)$ term may be approximated by $\Delta S_{1/2}(M) \approx R \ln \sigma_M/\sigma_{MH^+} = -3.4$ $J \cdot mol^{-1} \cdot K^{-1}$. Consequently, with $S^\circ_{H^+} = 109.0$ $J \cdot mol^{-1} \cdot K^{-1}$ at 300 K, we deduce PA(ketene) = GB(ketene) + 34 kJ/mol = 822 kJ/mol. Finally, the direct use of the approximation PA(ketene) = $c' - 1/b + T\Delta S^\circ_I$ leads to PA(ketene) = 820.9 ± 5.0 kJ/mol. These two estimates, subjected to the uncertainties inherent in the derivation of $\Delta S_{1/2}(M)$ and to the range of ΔS°_I values are, however, in reasonable agreement with the experimental determination of 817 ± 3 kJ/mol.

To conclude this part, one must mention that these PA values are comparable to, but slightly lower than, the proton affinity value, PA(ketene) = 825 ± 3 kJ/mol, which may be deduced from the presently accepted 300 K heats of formation of $[CH_3CO]^+$ (657 ± 1.5 kJ/mol;[16] a comparable theoretical evaluation of 658 kJ/mol has been proposed[17]), CH_2CO (−47.7 ± 1.6 kJ/mol [18]), and $[H]^+$ (1530 kJ/mol).

Methylketene. The most stable protonated form of methylketene is the propanoyl cation, $[CH_3CH_2CO]^+$; the two other possible structures, namely, $[CH_3CHCOH]^+$ and $[CH_3CHCHO]^+$, are higher in energy by 170 and 250 kJ/mol, respectively, according to correlated molecular orbital calculations.[29]

The protonation of methylketene, prepared by pyrolysis of propionic anhydride, has been studied using an ion trap mass spectrometer.[19] The equilibrium constant determination of reaction

$$(AcOMe)H^+ + CH_3CHCO \leftrightarrows AcOMe + [CH_3CH_2CO]^+ \qquad (III)$$

leads to $\Delta G^\circ_{III} = -6.5 \pm 3.2$ kJ/mol. With use of PA (AcOMe) = 839 kJ/mol and with the assumption, justified by the conservation of the symmetry number upon protonation, that $\Delta S^\circ_{1/2} = 0$ for the couple $[CH_3CH_2CO]^+/CH_3CHCO$, the authors then deduced that PA(methylketene) = 845 kJ/mol but with use of PA(MeOAc) = 839 kJ/mol. With the more recent basicity determination for methyl acetate: GB(MeOAc) = 788.2 kJ/mol and PA(MeOAc) = 815.9 kJ/mol,[3] the GB(methylketene) and PA(methylketene) values must be shifted downward to 794.7 ± 3.2 kJ/mol and 822.4 ± 3.2 kJ/mol, respectively.

We investigate the following reactions involving propanoyl cation, produced by ethyl loss from ionized diethylketone,[30] and various bases B in FT-ICR experiments:

$$[CH_3CH_2CO]^+ + B \leftrightarrows [BH]^+ + CH_3CHCO \qquad (IV)$$

The relevant data are gathered in Table 3, and the relative efficiency curves as a function of either GB(B) or PA(B) are reported in Figures 1 and 2. The parameter values *a*−*c* of eq 2 are 0.99 ± 0.03/0.98 ± 0.02 kJ^{-1}·mol, 0.16 ± 0.02/0.19 ± 0.03 kJ/mol, and 814.0 ± 1.1/847.0 ± 0.5 kJ/mol for GB(methylketene)/PA(methylketene), respectively.

From these data, by reference to acetone and isobutene, one obtains GB(methylketene) = 807.7 ± 2.1 kJ/mol and PA(methylketene) = 840.8 ± 2.7 kJ/mol. On the other hand one may deduce a gas-phase basicity GB(methylketene) = 807.9 kJ/mol and a proton affinity PA(methylketene) = 844.1 kJ/mol using the approximations GB(M) = $c - 1/b$ and PA(M) = $c' - 1/b + T\Delta S^\circ_I$.[7] We can thus confidently propose that the most meaningful experimental values are GB(methylketene) = 808 ± 2 kJ/mol and PA(methylketene) = 842 ± 3 kJ/mol. One may note that the $T\Delta S^\circ$ difference associated with the GB and PA values of methylketene (34 kJ·mol) is very close to what is calculated for the couple $[CH_3CH_2CO]^+/CH_3CHCO$ when taking ΔS° equal to zero (i.e., 33 kJ/mol), as expected from a simple consideration of the symmetry number of both species. It is noteworthy that, again, our estimates for GB or PA are greater by no less than 16 kJ/mol than the values deduced from the ion trapping experiments,[19] as also observed above for the ketene itself in similar experiments.

The heat of formation of the propanoyl cation has been determined from photoionization experiments $\Delta H_f{}^\circ{}_{300}[CH_3CH_2CO]^+ = 591.2 \pm 2.3$ kJ/mol.[20] Combining this value with $\Delta H_f{}^\circ[H]^+ = 1530$ kJ/mol and PA(methylketene) = 842 ± 3 kJ/mol, we deduce a heat of formation for neutral methylketene of $\Delta H_f{}^\circ{}_{300}(CH_3CH{=}C{=}O) = -97 \pm 5$ kJ/mol. The tabulated value for this quantity[22] is −105 kJ/mol, and, recently, a very different value of −65 kJ/mol has been suggested on the basis of theoretical G2 calculations.[21] This point may be commented on further. First the tabulated $\Delta H_f{}^\circ{}_{300}(CH_3CHCO)$ value of −105 kJ/mol [22] is only an estimate based on the observation that reactions involving redistribution of substituents at an sp^2 carbon are nearly thermoneutral. For example the reaction $CH_2O + (CH_3)_2CO \rightarrow 2CH_3CHO$ is associated with a ΔH° of only −6 kJ/mol. The authors thus assume that the reaction $CH_2CO + CH_3CHO \rightarrow CH_3CHCO + CH_2O$ is essentially thermoneutral, and, using the heats of formation values of −48, −166, and −109 kJ/mol for CH_2CO, CH_3CHO, and CH_2O, respec-

TABLE 3: Efficiencies of Proton Transfer Reactions Involving $[CH_3CH_2CO]^+$ and Several Bases B

base B	PA(B) (kJ/mol)	GB(B)^c (kJ/mol)	$\Delta S°_{1/2}(B)^d$ (J/(mol K))	α^e (Å^3)	μ (D)	P_B (mbar)	$k_{exp}{}^i$	$k_{ADO}{}^i$	RE^j
acetone	810.4^a	783.3	18.8	6.37	2.88^f	1×10^{-7}	0.14	22.21	0.007
3-pentanone	833.9^a	804.3	10.5	9.93	2.72^g	4.4×10^{-8}	0.85	21.28	0.048
benzylacetone	845.6^a	809.7	−10.5	16.0	2.72^g	6.4×10^{-8}	7.91	22.03	0.429
diisopropylketone	852 ± 1^b	821.1	(6)	13.53	2.67^g	2.8×10^{-8}	13.1	21.46	0.727
cyclohexenone	862 ± 2^b	829.3	(0)	10.89	3.75^f	7.3×10^{-8}	19.3	26.07	0.885
mesityl oxide	879^b	845.9	(0)	9.12	3.9^h	1.6×10^{-8}	22.2	26.15	0.984
tert-butylamine	934.7^a	899.5	−8.4	9.51	1.29^f	4.1×10^{-8}	43.1	15.65	1

[a] From ref 3. [b] From ref 34. [c] GB(B) = PA(B) + $T[\Delta S°_{1/2}(B) - S°_{H^+}]$, with $T = 300$ K and $S°_{H^+} = 109$ J/(mol·K). [d] From ref 3. $\Delta S°_{1/2}(B)$ is the standard entropy difference between the protonated and the neutral form of B. When the experimental data are not available, a $\Delta S°_{1/2}(B)$ equal to $R \ln(\sigma_B/\sigma_{BH^+})$ (where σ is the relevant symmetry number) has been assigned; this estimate is indicated in parentheses. [e] Polarizabilities from ref 10b. [f] Dipole moment from ref 33. [g] Dipole moment calculated by the AM1 semiempirical procedure.[35] [h] Dipole moment of mesityl oxide has been considered equal to that of 3-penten-2-one. [i] $\times 10^{-10}$ cm^{-3}·molecule^{-1}·s^{-1}. [j] RE = $(k_{exp}/k_{ADO})/(k_{exp}/k_{ADO})_{max}$.

TABLE 4: Efficiencies of Proton Transfer Reactions Involving $[CH_2NH_2]^+$ and Several Bases B

base B	PA(B) (kJ/mol)	GB(B)^c (kJ/mol)	$\Delta S°_{1/2}(B)^d$ (J/(mol K))	α^e (Å^3)	μ (D)	P_B (mbar)	$k_{exp}{}^i$	$k_{ADO}{}^i$	RE^j
cyclohexanone	837 ± 2^a	804.3	(0)	11.11	2.87^f	2.5×10^{-8}	0.9	27.45	0.045
diisopropylketone	852 ± 1^a	821.1	(6)	13.53	2.671^g	3×10^{-8}	1.6	27.15	0.080
diisopropyl ether	861 ± 1^a	828.3	(0)	12.37	1.13^f	6.5×10^{-8}	2.4	19.51	0.166
acetylacetone	869.4^b	838.0	4.6	10.11	3.03^f	3.3×10^{-8}	13.3	27.79	0.663
pyrrole	875.3^b	843.9	4.2	7.94	1.74^f	2×10^{-8}	10.7	20.62	0.703
mesityl oxide	879^a	845.9	(0)	9.12	3.9^h	2.0×10^{-8}	24.2	33.76	0.973
methylamine	901.2^b	864.7	−12.6	3.98	1.30^f	1.5×10^{-8}	12.4	17.44	0.969
tert-butylamine	934.7^b	899.5	−8.4	9.51	1.29^f	2×10^{-8}	14.1	19.23	1

[a] From ref 34. [b] From ref 3. [c] GB(B) = PA(B) + $T[\Delta S°_{1/2}(B) - S°_{H^+}]$, with $T = 300$ K and $S°_{H^+} = 109$ J/(mol·K). [d] From ref 3. $\Delta S°_{1/2}(B)$ is the standard entropy difference between the protonated and the neutral form of B. When the experimental data are not available, a $\Delta S°_{1/2}(B)$ equal to $R \ln(\sigma_B/\sigma_{BH^+})$ (where σ is the relevant symmetry number) has been assigned; this estimate is indicated in parentheses. [e] Polarizabilities from ref 10b. [f] Dipole moment from ref 33. [g] Dipole moment calculated by the AM1 semiempirical procedure.[35] [h] Dipole moment of mesityl oxide has been assumed to be equal to that of 3-penten-2-one.[33] [i] $\times 10^{-10}$ cm^{-3}·molecule^{-1}·s^{-1}. [j] Relative reaction efficiency: RE = $(k_{exp}/k_{ADO})/(k_{exp}/k_{ADO})_{max}$.

tively, they deduced $\Delta H_f°_{300}(CH_3CH{=}C{=}O) = -105$ kJ/mol. We believe that the thermoneutrality hypothesis must apply, more closely, to reactions V and VI, in which the substitution

$$CH_3CH{=}CH_2 + CH_2{=}C{=}O \rightarrow CH_2{=}CH_2 + CH_3CH{=}C{=}O \quad (V)$$

$$CH_3CH{=}C{=}CH_2 + CH_2{=}C{=}O \rightarrow CH_2{=}C{=}CH_2 + CH_3CH{=}C{=}O \quad (VI)$$

concerns an ethylenic sp^2 carbon atom; with $\Delta H_f°_{300}(CH_2{=}CH_2) = 52$ kJ/mol, $\Delta H_f°_{300}(CH_3CH{=}CH_2) = 20$ kJ/mol, $\Delta H_f°_{300}(CH_2{=}C{=}CH_2) = 191$ kJ/mol, and $\Delta H_f°_{300}(CH_3CH{=}C{=}CH_2) = 162$ kJ/mol, it follows that $\Delta H_f°_{300}(CH_3CH{=}C{=}O) = -80$ and −76 kJ/mol from reactions V and VI, respectively. This is indeed a first argument in favor of a reevaluation of the presently used heat of formation of methylketene. The second evidence is that the heat of formation of neutral methylketene we can derive from its experimental ionization energy, 8.95 eV,[1b] combined with the estimated heat of formation of methylketene radical cation of 779 kJ/mol derived by Traeger et al.[31] leads to $\Delta H_f°_{300}(CH_3CH{=}C{=}O) = -85$ kJ/mol. Consequently, experiments and structural thermochemical relationships point to a $\Delta H_f°_{300}(CH_3CH{=}C{=}O)$ value in the range −96/−76 kJ/mol. The higher value obtained from G2 calculations,[21] $\Delta H_f°_{300}(CH_3CH{=}C{=}O) = -65$ kJ/mol, let an opened question as long as this method usually gives accurate heat of formation values (±5 kJ/mol); it may be noted for example that the $\Delta H_f°_{300}$ of ketene itself is very well-estimated at the G2 level[32] (−47 kJ/mol as opposed to the experimental value of −48 kJ/mol).

Formaldimine. Formaldimine is a highly unstable species in the condensed phase and is thus not amenable to a direct determination of its basicity by the equilibrium method. The first tentative determination of the basicity of $CH_2{=}NH$ has been done by the bracketing technique involving immonium ion $[CH_2{=}NH_2]^+$ in an FT-ICR spectrometer.[23] It has been observed that the $[CH_2{=}NH_2]^+$ cation is deprotonated by diisopropyl ether but not by styrene, while an intermediate situation is observed with ammonia; after considering these results, the authors proposed a proton affinity value PA($CH_2{=}NH$) = 854 ± 8 kJ/mol.

We similarly studied the reaction

$$[CH_2{=}NH_2]^+ + B \leftrightarrows CH_2{=}NH + BH^+ \qquad (VII)$$

with immonium ions produced in the external source of the Bruker FT-ICR instrument and a set of eight bases B (Table 4). The relative efficiencies correlate satisfactorily with either GB(B) or PA(B) as indicated in Figures 1 and 2.

From the curve fitting we derive the parameter values $a-c$ of 0.99 ± 0.06/0.98 ± 0.05 and 0.195 ± 0.045/0.207 ± 0.045 kJ^{-1}·mol and 835.4 ± 1.5/867.0 ± 1.3 kJ/mol, respectively for GB($CH_2{=}NH$)/PA($CH_2{=}NH$). With the approximation GB(M) = $c - 1/b$ and PA(M) = $c' - 1/b + T\Delta S°_I$ [7] (and $\Delta S_{1/2}$(M) = −5.8 J/(mol·K)), we deduce GB($CH_2{=}NH$) = 830.3 ± 1.5 kJ/mol and PA($CH_2{=}NH$) = 862.2 ± 3 kJ/mol. Now, by reference to acetone and isobutene, one obtains GB($CH_2{=}NH$) = 830.0 ± 3.0 kJ/mol and PA($CH_2{=}NH$) = 858.9 ± 2.7 kJ/mol, leading finally to the rounded values GB($CH_2{=}NH$) = 830 ± 3 kJ/mol and PA($CH_2{=}NH$) = 860 ± 5 kJ/mol.

Although the error limits are overlapping, our estimate is slightly higher than that obtained by Peerboom et al. by the bracketing method,[23] PA($CH_2{=}NH$) = 854 ± 8 kJ/mol. In fact, this shift was expected because, according to relationship 3, the PA(M) does not correspond to the beginning of the rising part of the RE curves.[7] In the present case the shift led to an underestimate of the PA(M) as estimated by the bracketing method of about 10 kJ/mol.

The determination of the heat of formation of formaldimine, $CH_2{=}NH$, is still an actual question; the various estimates span a wide range of values (69−135 kJ/mol) with seemingly a recent consensus offered by a theoretical estimate of 86 ± 10 kJ/mol [24,25] and an experimental determination of 88 ± 8 kJ/mol [26] based on the appearance energy measurement. Our PA($CH_2{=}NH$) determination, combined with the well-established heat of formation of immonium ion, $\Delta H_f{}^\circ{}_{300}[CH_2NH_2]^+ = 745$ kJ/mol,[27] allows us to propose a heat of formation of formaldimine of $\Delta H_f{}^\circ{}_{300}$ ($CH_2{=}NH$) = 75 ± 5 kJ/mol. Owing to the experimental and theoretical uncertainties, the agreement between this value and the two previously recalled most recent estimates is excellent.

Conclusion

The recently developed thermokinetic method[7] has been applied to the determination of gas-phase basicities and proton affinities of three important neutral molecules: ketene, methylketene, and formaldimine. The method gives results with an accuracy of ±3 to ±5 kJ/mol and in excellent agreement with data obtained from the measurement of the equilibrium constant of proton transfer reaction. Moreover, the method proves to be useful when the neutrals are unstable or reactive species.

From a combination of the above results and literature data we derive the following heat of formation values of neutral methylketene and formaldimine: $\Delta H_f{}^\circ{}_{300}(CH_3CHCO) = -97 \pm 5$ kJ/mol and $\Delta H_f{}^\circ{}_{300}(CH_2{=}NH) = 75 \pm 5$ kJ/mol.

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