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Gas-phase acidities and sites of deprotonation of 2-ketones and structures of the corresponding enolates

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Abstract

The gas-phase acidities of seven different 2-alkanone molecules have been investigated using pulsed ionization high pressure mass spectrometry (HPMS). From the temperature dependence of the equilibrium constant for proton-exchange reactions, the enthalpy and entropy changes for these reactions were determined. These experimental values agreed well with the G3(MP2) calculated values. From the thermochemistry of the proton-exchange reactions a gas-phase acidity scale, relative to acetone, was constructed for 2-ketones up to and including 2-decanone. Furthermore, an absolute gas-phase acidity scale is presented which is anchored to the gas-phase acidity value for acetone determined by Bartmess et al. [J. Am. Chem. Soc. 101 (1979) 6046]. The entropy changes associated with the proton-exchange reactions were all found to be very close to zero which suggests that there is no intramolecular solvation occurring in any of the enolate ions over the temperature range studied. The G3(MP2) calculations predict that the primary and secondary enolates of butanone, formed by deprotonation at either C1 or C3, respectively, have nearly identical basicities. However, as the 2-ketone chain length increases, the secondary enolate becomes more stable, with respect to the primary enolate. These theoretical predictions are in agreement with the stability ordering for enolates ($2^\circ \geq 1^\circ \gg 3^\circ$) found experimentally by Chyall et al. [J. Am. Chem. Soc. 116 (1994) 8681].

Keywords: Gas-phase acidity; 2-Ketones; HPMS

1. Introduction

The determination of gas-phase acidities and proton affinities has proven to be very useful, in conjunction with their solution phase analogues, to separate intrinsic substituent effects from solvent effects. Brauman and Blair [1] studied the effects of alkyl groups on the relative acidities of alcohols using bond dissociation energies and electron affinities to determine the relative enthalpy changes for proton transfer reactions. Assuming that the entropy changes for the ion–molecule reactions were zero, the relative gas-phase acidities for the substituted alcohols could be determined. Surprisingly, at that time, the ordering of relative gas-phase acidities was found to be *t*-butyl alcohol > *iso*-propanol > ethanol > methanol, which was exactly opposite to the trend found in the solution phase [2]. Wolfe et al. [3] compared the gas-phase basicities of tetrahydrofuran (THF) and diethyl ether (Et_2O) using proton transfer equilibrium constants in an ion cyclotron resonance (ICR) spectrometer. The results showed that THF had a lower proton affinity

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than Et_2O indicating that THF is the weaker base. Conversely, solution results establish that THF is a stronger base than Et_2O [4] These differences in the ordering of basicity between gas and solvent phase exemplify the strong effect the solvent has on these fundamental thermochemical properties.

Somewhat surprisingly, little research has been carried out to determine the gas-phase acidities of 2-alkanones. The only gas-phase acidity values that have been accurately determined for 2-alkanones are those for 2-butanone and acetone. However, those data were obtained only at a single temperature, and therefore no experimental values for entropy changes were determined. Cumming and Kebarle [5] determined equilibrium constants for deprotonation reactions of acetone and 2-butanone with many compounds, each at one temperature, using high pressure mass spectrometry (HPMS). From the equilibrium constant and known acidity values of the reference compounds, the gas-phase acidities of acetone and 2-butanone were determined. A statistical thermodynamic calculation was used to estimate the entropy change of the reaction, thereby obtaining an enthalpy change for deprotonation.

In the present work, the gas-phase acidities of a number of 2-ketones up to 2-decanone have been obtained by determining temperature dependent equilibrium constants with reference acids to obtain accurate gas-phase acidity values.

The two carbon atoms adjacent to the carbonyl group, at C1 and C3, are both acidic sites of 2-ketones. Deprotonation of the 2-ketones produces an enolate ion, the stability of which should decrease from primary to tertiary [6]. Thus, deprotonation of 2-ketones would be predicted to occur at C1 in the solution phase.

In the gas phase, the preferred site of deprotonation has been studied for butanone, 2-pentanone and 2-hexanone. Chyall et al. [7] initially deprotonated butanone using fluoride ions at 0.4 Torr of helium in the source of a flowing afterglow triple quadrupole instrument. Determination of the ratio of the isomeric enolate ions was accomplished using either CID or ion–molecule reactions with *n*-butylnitrite. From the ratio established for the enolate ions it was determined that butanone deprotonates at both C1 and C3 and the two species were present in a ratio of 47:53. By the same method, 3-methyl-2-butanone and 2-methyl-3-pentanone were determined to deprotonate at the less substituted site, producing either a primary enolate vs. a tertiary enolate or a secondary enolate vs. a tertiary enolate, respectively, both in a ratio of 95:5, in agreement with what is expected in solution. The ab initio calculated gas-phase acidities were in excellent agreement with their experimentally determined values [7]. The conclusion of Chyall et al. was thus that the gas-phase acidity ordering of acyclic, aliphatic ketone enolate ions is $2^\circ > 1^\circ \gg 3^\circ$.

The preferred sites of deprotonation for both 2-pentanone and 2-hexanone were determined using a different method. A ratio of the $[M–H]^-$ and $[M–D]^-$ peaks for isotopically labeled ketones was found using CID. Using $[OH]^-$ as the deprotonation reagent for 2-pentanone-1,1,1-d_3, Donnelly et al. [8] determined that 2-pentanone deprotonates at C1 or C3 in a ratio of 56:44. Similarly, Surig and Grutzmacher [9] used 2-hexanone-1,1,1-d_3 reacting with $[OH]^-$ to determine that 2-hexanone also produces a mixture of ions deprotonated at C1 or C3 in a ratio of 63:37. From these results it would seem that as the chain length increases the site of deprotonation for the 2-ketones will favor C1, resembling the result determined in solution. This is however contrary to the results of Chyall et al. [7].

Since the deprotonated 2-alkanones have a negative charge center near one terminus, it is possible that intramolecular solvation may be observed within the ion. This interaction could play an important role in the tertiary structure of the ion and, therefore, also in the thermochemistry. Some work has been conducted on this phenomenon with different anions including dithiols [10] and carboxylic acids [11] as well as in cations such as protonated peptides [12] and methoxyalkenes [13]. For example, Norrman and McMahon [11] investigated the occurrence of intramolecular solvation in gaseous carboxylate anions. This work was done using HPMS by making equilibrium proton transfer measurements between pairs of carboxylate ions in the gas phase. These experiments were accompanied by complementary ab initio calculations. Equilibrium constants for proton-exchange reactions (Eq. (1)) between various carboxylate anions, such as acetate, *n*-butanoate, *n*-decanoate and 2-ethylhexanoate, were measured over a range of temperatures from 440 to 660 K.

$$R_1COO^- + R_2COOH \leftrightarrows R_1COOH + R_2COO^- \quad (1)$$

The van't Hoff plot ($\ln K$ vs. $1/T$) for the proton-exchange reaction where R_1 = propyl and R_2 = nonyl was found to be non-linear and was described as a combination of two van't Hoff plots for two different isomers of the *n*-decanoate anion, each one dominating at either high or low temperature. It was assumed that the isomerization of these carboxylate ions was in fact a conformer change driven by intramolecular solvation. The dominant isomer at low temperature was characterized by a structure which was less favorable entropically, yet more favorable enthalpically, which displays intramolecular solvation, described as coiling, (R_2COO^--co in Eq. (2)). Conversely, the dominant isomer at higher temperature is less enthalpically favorable but, due to the uncoiled nature, has a significantly more favorable entropy associated with it (R_2COO^--un in Eq. (2)).

$$R_2COO^-(\text{un}) \leftrightarrows R_2COO^-(\text{co}) \quad (2)$$

The experimental results for *n*-butanoate ions show an intramolecular solvation entropy of around $0.0\,J\,K^{-1}\,mol^{-1}$, which suggests that there is no significant intramolecular solvation. The longer chain carboxylates, *n*-decanoate and 2-ethylhexanoate, showed much more unfavorable entropies of intramolecular solvation of -72.0 and $-70.3\,J\,K^{-1}\,mol^{-1}$, respectively. This large decrease in entropy for the coiled anions was attributed to the loss of internal rotational freedom about the methylene C–C bonds due to the interaction of the deprotonated carboxylate group of the anion with more than one hydrogen on the alkyl chain. The hydrogens involved appear to form a cavity around the carboxylate oxygens.

In the present work, as in that by Norrman and McMahon [11], equilibrium constants as a function of temperature were determined to permit the determination of enthalpy and entropy changes on deprotonation of 2-ketones. The occurrence or non-occurrence of intramolecular solvation was explored by examining the experimentally determined entropy values. The intramolecular solvated conformation of the interacting, or coiled, ion is expected to have a structure in which the alkyl tail of the ketone associates with the enolate moiety. Ab initio calculations were also used to compare with experimental thermochemical data and aid in its interpretation.

In another very interesting study by Craig and Brauman [14], it was found that remote substituents on an alkyl chain can stabilize the transition state of S_N2 reactions. For the series of S_N2 reactions shown in Eq. (3), CN is able to stabilize the transition state for these reactions

$$^{*}Cl^- + Cl(CH2)_nCN \rightarrow Cl^- + {}^{*}Cl(CH_2)_nCN \quad (3)$$

by promoting an intramolecular solvation interaction. This effect is expected to diminish as n becomes very large. The rate constants for these reactions for $n = 1$–5 were experimentally determined to be 3.2, 0.7, 2.5, 1.2 and $0.5 \times 10^{-10}\,cm^3\,s^{-1}$, respectively. The unexpected result is the quite large increase in the rate constant going from $n = 2$ to 3, where the latter is almost as high as for $n = 1$, indicating that this transition state is stabilized by some effect other than the through-bond inductive effect. This interaction was explained as an *intramolecular* hydrogen bond between the chloride ion and the acidic hydrogen α to the nitrile group. One of the motivations for the present work was to deduce, using the experimental thermochemistry, whether intramolecular solvation is significant in the enolate ions studied.

2. Experimental and computational methods

All experiments were carried out in the gas phase with a HPMS system operating in negative ion mode. The mass analysis was done using a VG Instruments MM 8-80 magnetic sector mass spectrometer. The instrument, constructed at the University of Waterloo, has been described in detail previously [15].

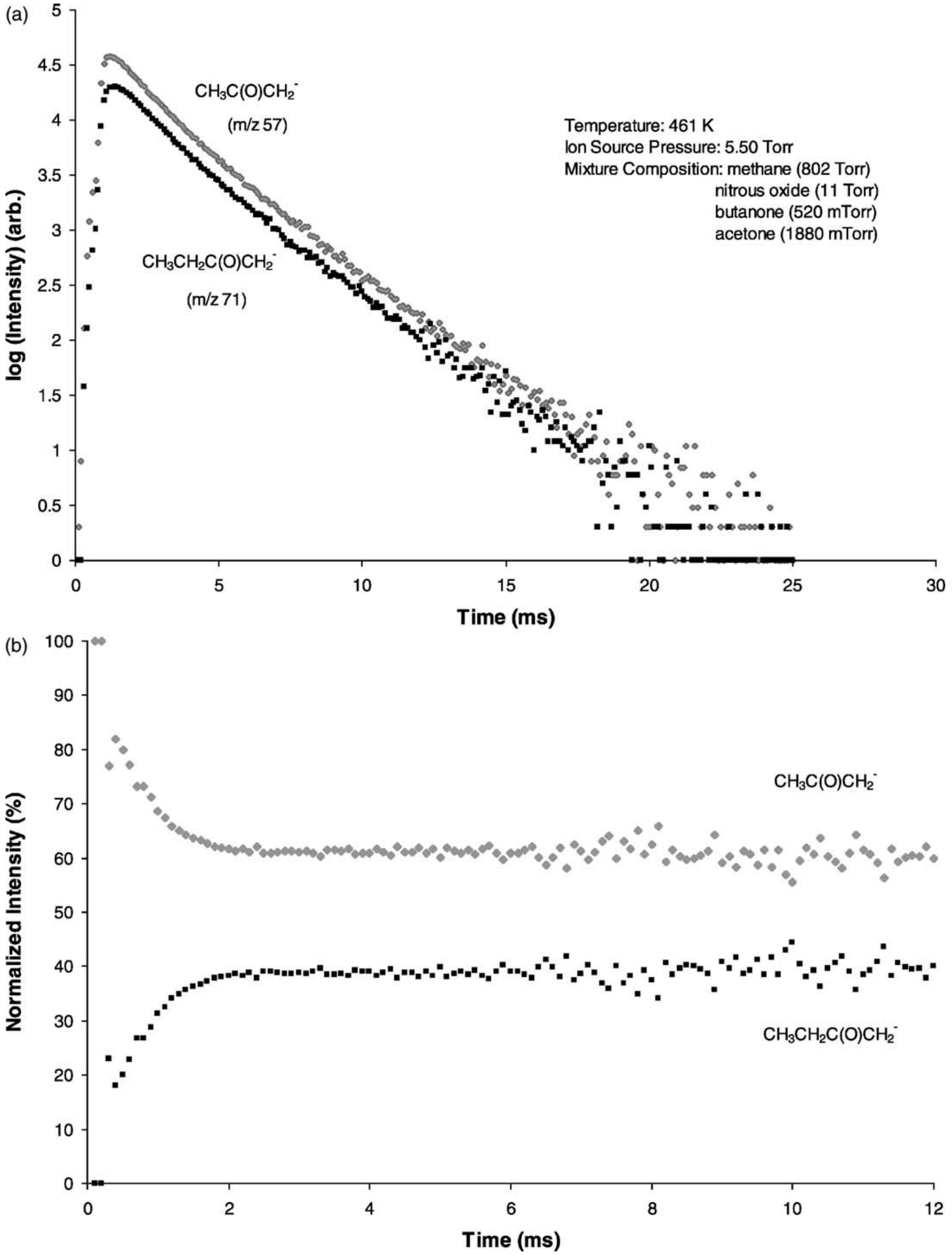

Fig. 1. Variation of (a) ion abundance and (b) normalized ion abundance of the enolates of acetone and butanone as a function of time after a 500-μs electron beam pulse. The results of 1000 electron gun pulses were accumulated. Experimental conditions are given in (a).

Gas mixtures were prepared in a 5 L stainless-steel reservoir. Methane was used as the bath gas at a pressure of about 800 Torr with about 10 Torr of nitrous oxide added to generate O^- by dissociative electron capture which then reacts with methane to form OH^- as the deprotonation chemical ionization reagent ion. The 2-alkanone components were present in very small amounts (∼0.5–2 Torr). All materials were commercial products used without further purification. The gas mixture was flowed into the ion source to a pressure of 5–6 Torr. Ionization was accomplished by a 500-μs pulse of 2 keV electrons directed onto a 200-μm aperture. A PC-based multichannel scalar (MCS) signal acquisition system configured at 60–200 μs dwell time per channel over 250 channels was used to monitor the reactions. The results of 1000–3000 electron gun beam pulses were accumulated to form time intensity profiles of mass selected ions. An example of ion intensity profiles as a function of time after ionization can be seen in Fig. 1a. The corresponding normalized time–intensity profile is given in Fig. 1b demonstrating that a steady-state abundance of ${A_1}^-$ and ${A_2}^-$ is established. The normalized profile is obtained by determining the percent of the total intensity for each of the anions. These intensities, $I_{A_1^-}$ and $I_{A_2^-}$, may be used to calculate an equilibrium constant from Eq. (4) where P_{A_1} and P_{A_2} are the relative partial pressures of the neutral ketones in the ion source. The Gibbs' free energy change is related to the equilibrium

$$K_{\mathrm{eq}} = \frac{I_{A_1^-}}{I_{A_2^-}}\frac{P_{A_2}}{P_{A_1}} \tag{4}$$

constant by Eq. (5), and to the entropy and enthalpy of the reaction by Eq. (6).

$$\Delta G^\circ = -RT\ln(K_{\mathrm{eq}}) \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{6}$$

Combining Eqs. (5) and (6) and dividing by RT yields the van't Hoff equation (Eq. (7)),

$$\ln(K_{\mathrm{eq}}) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{7}$$

and plotting $\ln(K_{\mathrm{eq}})$ vs. $1/T$ yields a van't Hoff plot. From the slope and intercept of the van't Hoff plot, the enthalpy change (ΔH°), and the entropy change for the reaction (ΔS°), respectively, can be obtained. The ΔH° and ΔS° values can then be used to obtain a ΔG° value at any given temperature using Eq. (5). The value of ΔH° for the proton-exchange reaction is also related to the proton affinity (PA) of the enolate ion. The proton affinity for a species is defined as the negative of the enthalpy change for the addition of a proton to that species. For negative ions, the proton affinity of the anion is the negative of the change in enthalpy (Eq. (9)) for the reaction given in Eq. (8).

$$A^- + H^+ \rightarrow AH \tag{8}$$

$$\Delta H^\circ(8) = -\mathrm{PA}(A^-) \tag{9}$$

The gas-phase acidity of AH is conventionally defined as the negative of the free energy change for Eq. (8). For the proton-exchange reaction of Eq. (10), the enthalpy change can then be related to the difference between the proton affinities of the two anions involved, as shown by Eq. (11).

$$AH + B^- \rightarrow A^- + BH \tag{10}$$

$$\Delta H^\circ(10) = \mathrm{PA}(A^-) - \mathrm{PA}(B^-) = \Delta\mathrm{PA} \tag{11}$$

All computational work was carried out at the G3(MP2) level of theory [16] using the Gaussian 98 [17] suite of programs.

3. Results and discussion

3.1. Gas-phase acidities and proton affinities

In the present study, the equilibrium constants for various proton-exchange reactions, Eq. (12), between 2-enolate ions and neutral 2-ketones were determined over a temperature range of 390–525 K.

$$\underset{[R_1CH_2C(O)CH_2{}^-]}{R_1CHC(O)CH_3{}^-} + R_2CH_2C(O)CH_3 \leftrightarrows R_1CH_2C(O)CH_3 + \underset{[R_2CH_2C(O)CH_2{}^-]}{R_2CHC(O)CH_3{}^-} \tag{12}$$

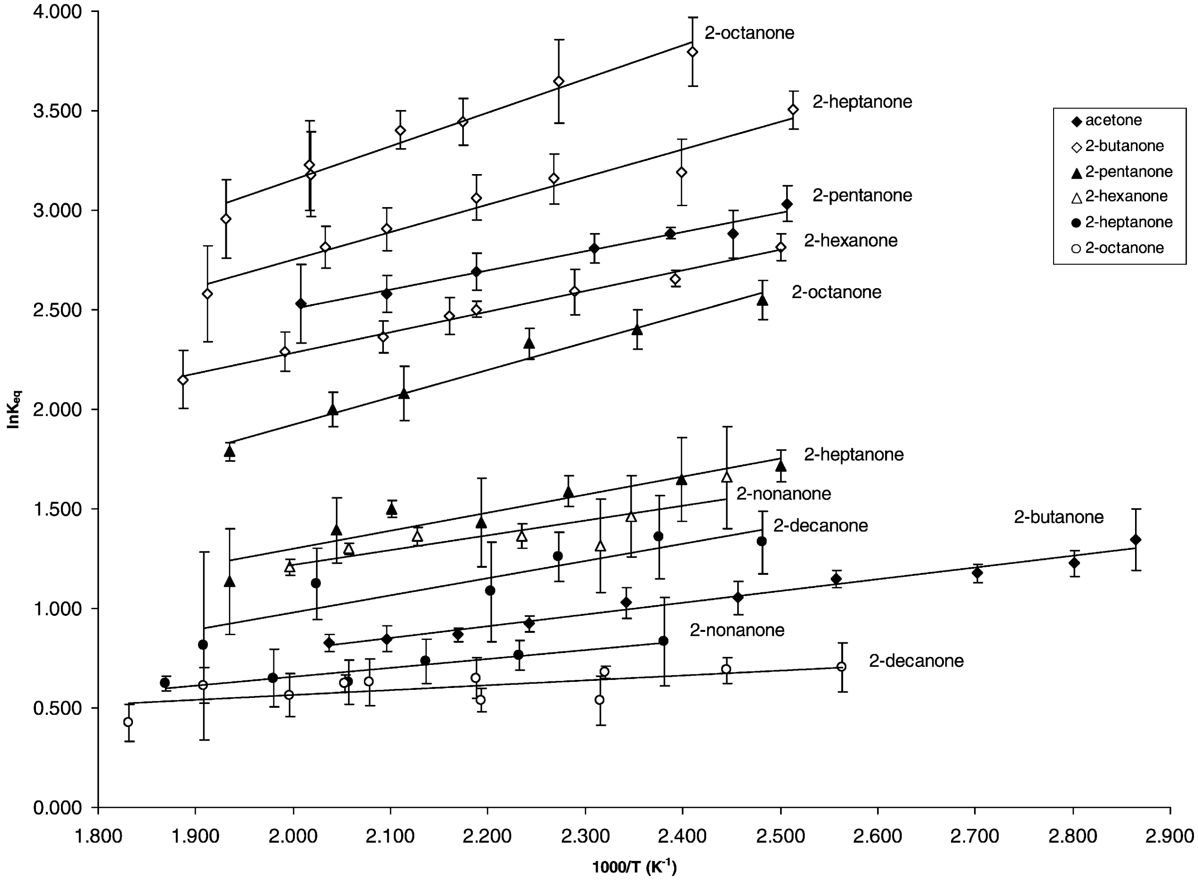

Fig. 2. van't Hoff plots for the various proton-exchange reactions between enolates and 2-ketones studied here. The symbols represent the ketone used to establish equilibrium with the ketone indicated on each line.

The van't Hoff plots for these reactions are shown in Fig. 2. Each line represents a proton-exchange equilibrium for two different ketones. The symbols in the legend indicate the compound used to establish equilibrium with the corresponding 2-alkanone indicated on the line itself. The van't Hoff plots are all linear, which indicates that there is very little or no change in ion structure over the experimental temperature range.

The experimental relative thermochemistries are shown in the form of a proton affinity ladder in Fig. 3. As expected, the anion proton affinities increase, and the relative acidities of the neutral ketones increase, as the chain length of the 2-alkanone molecule increases as can be seen in Fig. 4.

Cumming and Kebarle [5] determined that the gas-phase acidity for 2-butanone is 4 kJ mol^{-1} greater than that of acetone. Using a statistical mechanical estimation for the entropy change for the proton-exchange reaction of -3.3 J K^{-1} mol^{-1}, they determined the proton affinity of the butanone enolate to be 6 kJ mol^{-1} less than that of the acetone enolate. Their estimated entropy change for the reaction is in very good agreement with our experimental value of -3.0 (± 2.0) J K^{-1} mol^{-1}. Similarly, their relative gas-phase acidity and proton affinity values are in excellent agreement with the values determined in the present work.

The proton affinities and gas-phase acidities given in Fig. 3 are with respect to the proton affinity of deprotonated acetone and gas-phase acidity of acetone,

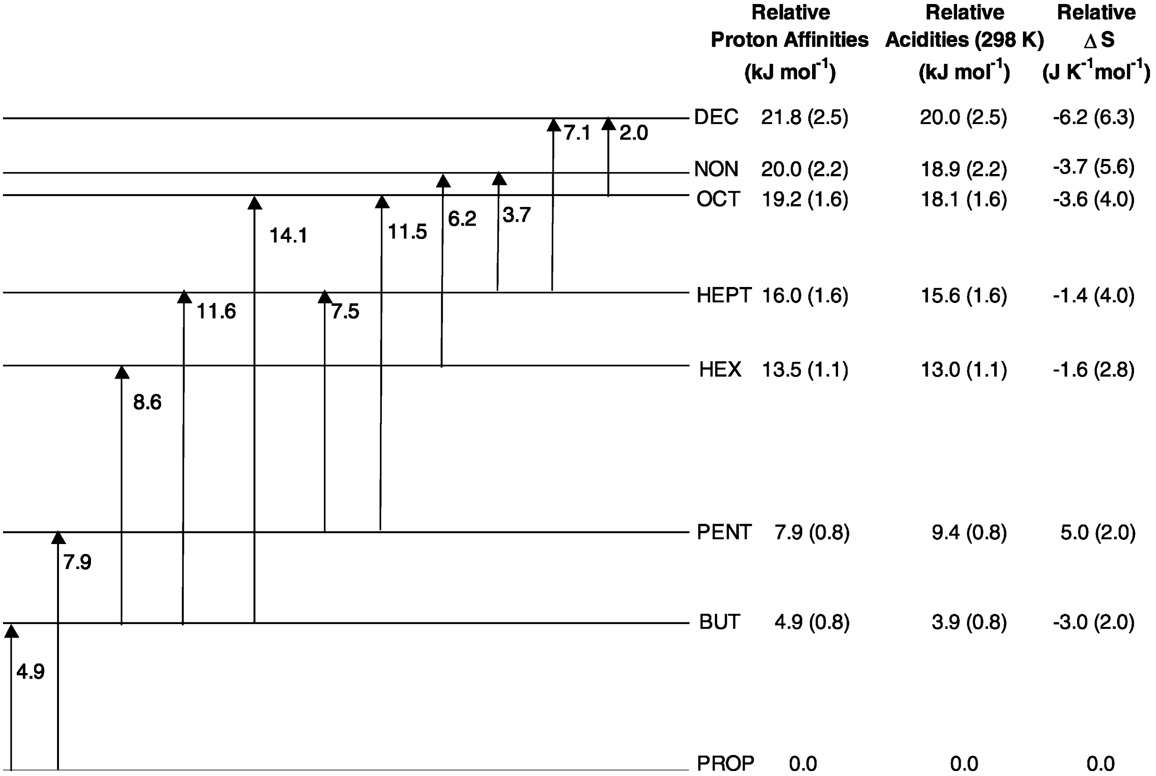

Fig. 3. Relative proton affinity scale of the enolate anions and relative acidity scale of the 2-ketones at 298 K. The relative proton affinities and gas-phase acidities are the negative of the reaction enthalpies and free energies associated with Eq. (12). The relative entropy is that associated with the reaction in Eq. (12).

respectively. There are three values for the proton affinity for deprotonated acetone listed in the NIST Chemistry WebBook [18]. The proton affinity value obtained by Cumming and Kebarle [5], 1546±11 kJ mol^{-1}, is very close to that determined by Bartmess et al. [18,19] 1544 ± 8.8 kJ mol^{-1}. There is very little difference between these two values, however, the Bartmess et al. [18,19] value has less error associated with it than the Cumming and Kebarle [5] value. Therefore, the proton affinity of deprotonated acetone determined by Bartmess et al. [18,19] has been used to anchor the proton affinity ladder in Fig. 3. The gas-phase acidity values were also anchored to the acetone value by Bartmess et al. [18,19] of 1514 ± 8.4 kJ mol^{-1}. The absolute enthalpy and gas-phase acidity values anchored to the values for acetone and its enolate of Bartmess can be found in Table 1.

Table 1
Absolute gas-phase acidities of the various 2-ketones and the proton affinities of the corresponding enolates

Compound	Absolute $-\Delta H^{\circ}$[a] (kJ mol^{-1})	Absolute $-\Delta G^{\circ}$ (298 K)[b] (kJ mol^{-1})
Acetone	1544.0 ± 8.8[c]	1514.0 ± 8.4[c]
Butanone	1548.9 ± 8.8	1518.0 ± 8.4
2-Pentanone	1551.9 ± 8.8	1523.4 ± 8.4
2-Hexanone	1557.5 ± 8.9	1527.0 ± 8.5
2-Heptanone	1560.0 ± 8.9	1529.6 ± 8.6
2-Octanone	1563.2 ± 8.9	1532.1 ± 8.6
2-Nonanone	1564.0 ± 9.1	1532.9 ± 8.7
2-Decanone	1565.8 ± 9.1	1534.0 ± 8.8

[a] For the reaction in Eq. (7), also denoted proton affinity (PA) of the enolate.

[b] For the reaction in Eq. (7), also denoted gas-phase acidity of the neutral ketone.

[c] Values determined in ref. [19] and taken from ref. [18].

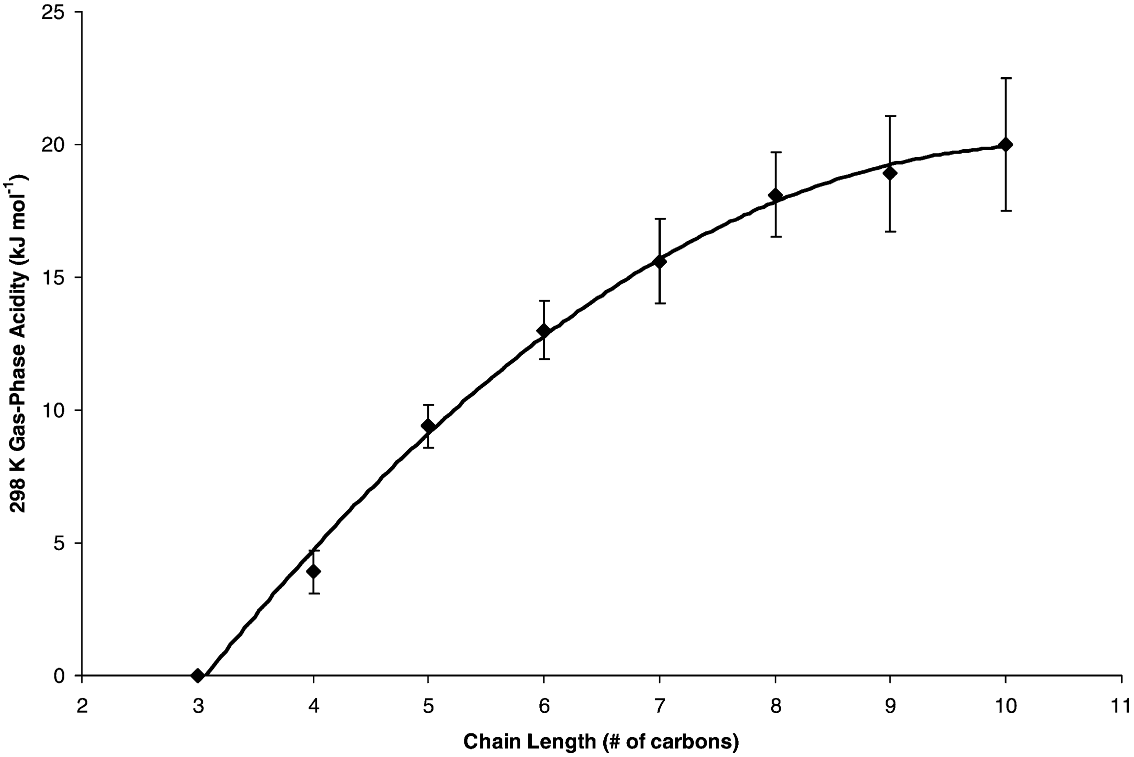

Fig. 4. Variation of the 298 K gas-phase acidities of the 2-ketones with chain length.

3.2. Entropies and intramolecular solvation

As shown in Fig. 3, the relative entropies with respect to acetone do not change significantly as the chain length increases, with the ΔS° values for proton transfer remaining virtually constant. Intramolecular solvation or coiling between the negatively charged enolate moiety and the carbon chain would constrain the geometry of the enolate anion resulting in a loss of internal rotation, which would manifest itself in a decrease in entropy since the enolate of acetone cannot coil to any significant extent. Therefore, since the entropy change associated with the reaction in Eq. (13), is effectively zero, even for the

$$\mathrm{CH_3C(O)CH_2^- + CH_3(CH_2)_nCH_2C(O)CH_3 \leftrightarrows CH_3C(O)CH_3 + CH_3(CH_2)_nCHC(O)CH_3^-} \quad (13)$$

largest 2-ketone investigated here ($n = 6$), over the entire temperature range studied, we conclude that there is no significant extent of coiling occurring in any of the enolate anions. One of the reasons that coiling is not important in these enolate ions can be deduced from the calculated charge distributions obtained from the natural population analysis (NPA). For the carboxylate ions, the charge on each of the oxygen atoms was found to be −0.90 [11]. For the enolate ions, the charge on the oxygen atom is not as high (−0.78) and that on C3, when deprotonation occurs at C3, is only −0.41. Since the charge density is not as large for the enolate ions, the intramolecular hydrogen bonds would not be expected to be as strong and, as seen experimentally, there appears to be no influence on the thermochemistry arising from intramolecular solvation.

3.3. Sites of deprotonation

Three different possible structures calculated for the deprotonated 2-butanone anion are shown in Fig. 5. Structures A and C are deprotonated at C1 while structure B is deprotonated at C3. The calculated enthalpies, entropies and free energies of the proton-exchange reaction with the enolate of acetone (Fig. 5) are all reasonably close to the experimental values. This may indicate that when the ion is deprotonated, at either C1 or C3, a mixture of at least structures A and B may exist. These computational results are in good agreement with the experimental results by Chyall et al. [7] who determined experimentally that 2-butanone deprotonates at C1 and C3 in a ratio of 47:53, roughly an equal mixture, indicating that the C1 and C3 sites are nearly equally acidic. Chyall et al. also reported results of MP4SDQ/6-31+G(d)//HF/6-31+G(d) calculations which showed that the primary enolate (deprotonation at C1, corresponding to Fig. 5A) was 0.4 kJ mol^{-1}, more stable than the secondary enolate (deprotonation at C3, corresponding to Fig. 5B), in excellent agreement with our G3(MP2) calculations which also predict a more stable primary enolate by 1.3 kJ mol^{-1}.

In Fig. 6, three different possible structures calculated for the deprotonated 2-pentanone enolate are presented. Structures A and C are deprotonated at C1 while structure B is deprotonated at C3. None of these structures can be totally disregarded since the calculated enthalpies, entropies and free energies of the proton-exchange reaction with the enolate of acetone (Fig. 6) are close to the present experimental values. Therefore, the system is most likely a mixture of at least three structures with both primary and secondary enolates being present. The calculations also predict that the secondary enolate is more stable by some 3 kJ mol^{-1} in agreement with the ordering of

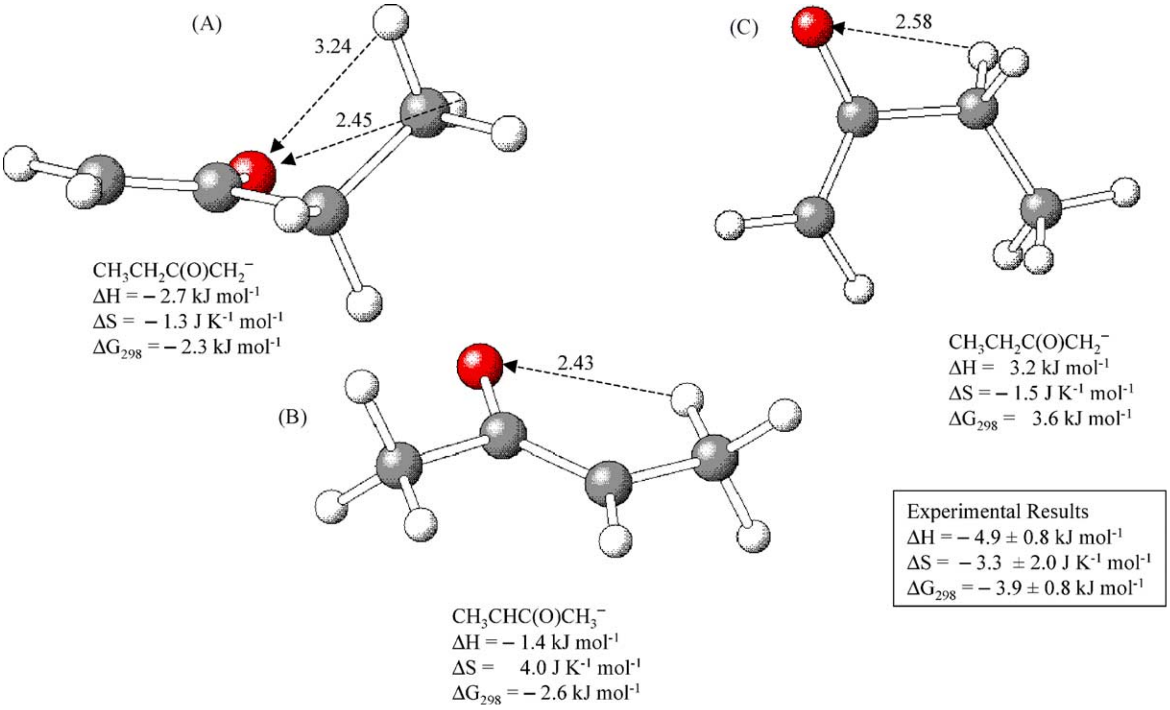

Fig. 5. Structures of primary, A and C; and secondary, B, enolates for deprotonated butanone calculated using G3(MP2) level of theory. Reaction energies are based on Eq. (12) where $n = 0$.

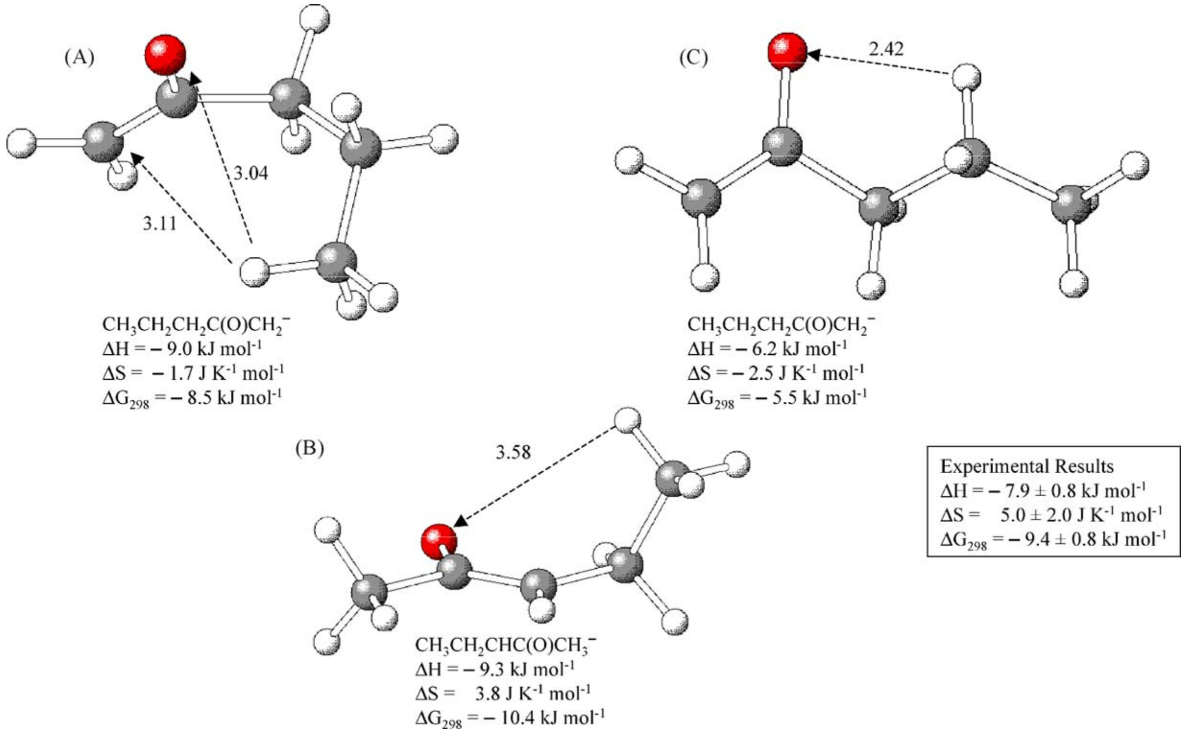

Fig. 6. Structures of primary, A and C; and secondary, B, enolates for deprotonated 2-pentanone calculated using G3(MP2) level of theory. Reaction energies are based on Eq. (12) where $n = 1$.

stability of enolate ions determined by Chyall et al. [7] which showed that secondary enolates are equally or more stable than primary enolates. CID experiments by Donnelly et al. [8] agree somewhat with our theoretical predictions in that the two acidic sites of 2-pentanone are comparable enthalpically. They showed that 2-pentanone deprotonates at C1 and C3 in a ratio of 56:44. If proton abstraction were statistical, a ratio of 60:40 should be obtained. Conclusions concerning the relative acidities of the C1 and C3 sites of 2-pentanone cannot be drawn from the experiments of Donnelly et al. [8] since deprotonation could be controlled kinetically rather than thermodynamically under the conditions of their experiments.

In Fig. 7, four different possible structures calculated for the deprotonated 2-hexanone anion are shown. Structures A and C are deprotonated at C1 while structures B and D are deprotonated at C3. The calculated enthalpies, entropies and free energies of the proton-exchange reaction with the enolate of acetone (Fig. 7) yielding the primary enolates (7A and 7C) are significantly different than those for the formation of the secondary enolates (7B and 7D) and the experimental results. However, the differences in the thermochemical values for the primary enolates are not sufficiently different from the experimental values to totally disregard the presence of either of these two possible structures. On the other hand, the calculated thermochemical values for the secondary enolates are in very good agreement with the experimental results. Clearly, the results of the calculations predict that the secondary enolate is energetically more favorable than the primary enolate in agreement with the ordering of Chyall et al. [7].

These theoretical predictions are in contradiction with the conclusions drawn by Surig and Grutzmacher [9] from their experiments on the deprotonation of various ketones. They found that the reaction of OH^-

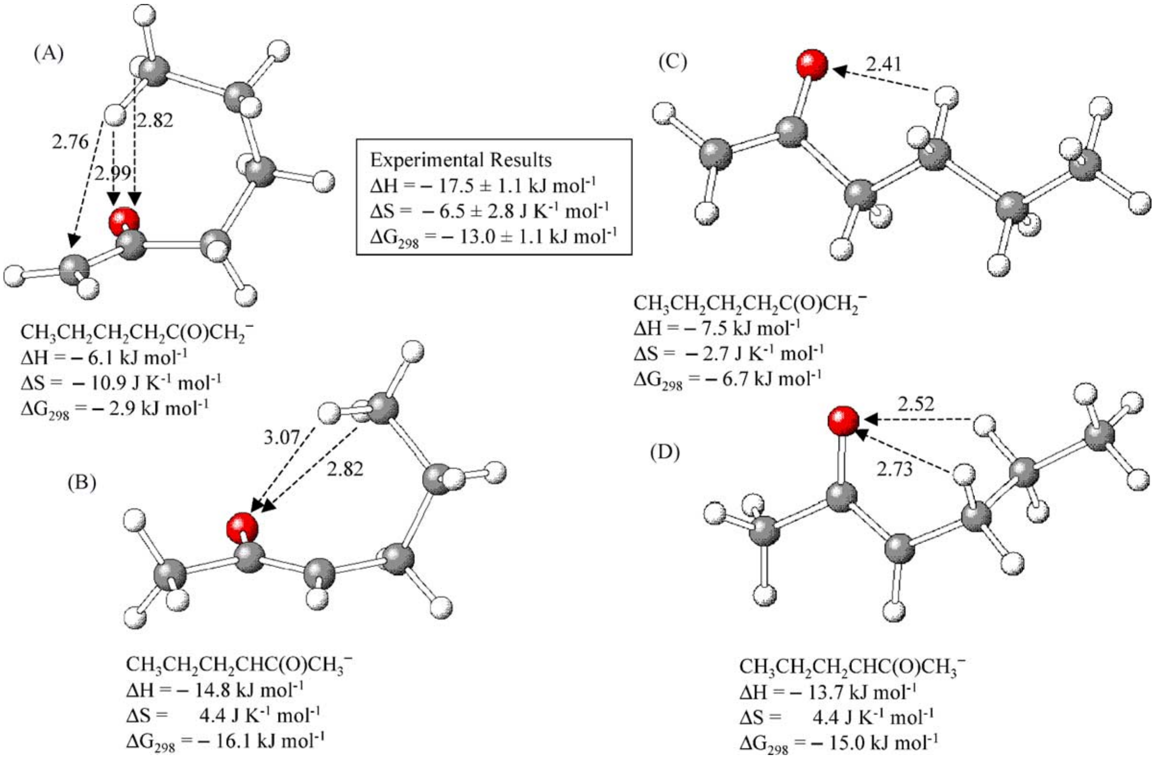

Fig. 7. Structures of primary, A and C; and secondary, B and D, enolates for deprotonated 2-hexanone calculated using G3(MP2) level of theory. Reaction energies are based on Eq. (12) where $n = 2$.

with 2-hexanone-1,1,1-d_3 yields 63% of the primary enolate and they concluded that the reaction was under thermodynamic control since they obtained the same ratio of primary to secondary enolate using F^- and NH_2^- as the chemical ionization agent. Stating that the reactions are under thermodynamic control indicates that the C1 site of 2-hexanone is more acidic than the C3 site. It can easily be argued that since the ratio obtained by their experiment is statistical (very close to 60:40) and that deprotonation by OH^-, F^- and NH_2^- are all exothermic that deprotonation is clearly *not* under thermodynamic control. Based on the results of our calculations and the good agreement with our experimental values as well as the experimental ordering of stabilities of enolates [7], we conclude that the secondary enolate of 2-hexanone is energetically more favorable than the primary enolate.

If this trend were to continue, that as the alkyl chain of the 2-ketone becomes longer, the acidity at the C3 site with respect to the C1 site becomes greater, then we would expect that for 2-decanone deprotonation would yield predominantly the secondary enolate. In light of this, and in comparison with the results of Norrman and McMahon results, where coiling was observed for the decanoate anion [11], it may be possible to observe coiling only in enolate anions which are larger than those corresponding to deprotonated 2-dodecanone. Such experiments were attempted but proved intractable due to the extremely low volatility of these large ketones.

4. Conclusions

Accurate relative experimental gas-phase acidities for seven different 2-alkanones up to and including

2-decanone have been observed. Using acetone to anchor the relative proton affinities, the absolute proton affinities of the enolate ions and gas-phase acidities of the parent ketones have been determined.

Neither the experimental nor the computational results indicate the occurrence of any significant extent of intramolecular solvation in any of the enolate anions studied. The computational results indicate that as the unbranched aliphatic 2-ketones increase in size, the C3 deprotonation site becomes more acidic with respect to the C1 position.

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