energy if it is in fact stabilized internally there is reason to favor the more endothermic value (+2.4 kcal/mol) for $\delta\Delta H_s$.

Conclusion

We have developed a simple, accurate, and precise method for determining heats of formation of alkyl chlorides. When combined with other readily available data this allows determination of the heats of formation of the derived carbonium ions in SO_2ClF and in the gas phase. The close correspondence of relative heats of formation in the two media supports our earlier claim that differential solvation energies of carbonium ions are small in superacid media.

We have reported a close correlation between energies of activation for solvolysis rates and heats of ionization in superacid and those in the gas phase.[1] Heats of formation of carbonium ions are now accessible to ab initio calculations.[7,8] Since we have shown that differential solvation energies for carbonium ions in nonnucleophilic solvents are small or negligible, theoretical values for ΔH_f should apply approximately to SO_2ClF solution and hence be translatable into solvolysis rates. This would be the achievement of a long-sought goal of organic chemistry—the prediction of relative reaction rates in solution from quantum-mechanical calculations. Its success here cannot be generalized but is a good step in the right direction.

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Heats of Formation of Gaseous Free Radicals via Ion Cyclotron Double Resonance Spectroscopy

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Abstract: An ion cyclotron double resonance bracketing experiment combined with the previously determined gas-phase basicity scale has been employed to determine heats of formation (kcal mol^{-1}) for eight free radicals: phenoxy, 11.6 ± 2.3; benzyl, 48.0 ± 2.2; cycloheptatrienyl, 69.0 ± 3.1; cyclopentadienyl, 63.2 ± 2.2; cyclopropenyl, 105.1 ± 4.1; allyl, 43.7 ± 2.2; cyclopropyl, 66.5 ± 2.7; vinyl, 71.5 ± 2.2.

Introduction

It has recently been demonstrated that pulsed ion cyclotron double resonance bracketing techniques[1] used in conjunction with the quantitative gas-phase basicity scale[2] are capable of determining the enthalpies of formation of a wide variety of transient neutral molecules.[3] This paper reports the application of these techniques to the determination of the thermochemical stabilities of eight free radicals. Since most of the systems studied have published heats of formation, this work serves as a critical test of the double resonance bracketing techniques. It also represents the exposition of an experimental technique which could prove to be an important source of thermochemical data for molecules which are too short lived to be amenable to other experimental probes.

Experimental Section

Experiments were performed with a pulsed ion cyclotron resonance (ICR) spectrometer having a one-region trapped ion cell and a capacitance bridge detector.[4,5] Gaseous positive ions were formed by low-energy electron impact (ca. 12 eV) and efficiently trapped for many tenths of a second by static electric and magnetic fields. In the pulsed mode of operation, the electron beam is gated on for 10 ms, and the ions thus formed are trapped and allowed to react for a set delay time of typically 200 ms. This is followed by an 8-ms detection period during which time ions of a given mass-to-charge ratio are accelerated at their cyclotron frequency, $\omega_c = qB/m$, by a radio-frequency pulse from the capacitance bridge detector in order to measure their abundance in the ICR cell. Finally, all ions are removed from the cell by a quench pulse which neutralizes them by collison with the side plates of the cell.

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Table I. Thermochemical Data and Free-Radical Heats of Formation (kcal mol^{-1})

radical R·	IP(RH)[a]	$\Delta H_f{}^\circ{}_{298}$(RH)[b]	PA(R·)	DH°$_{298}$(R–H)	$\Delta H_f{}^\circ{}_{298}$(R·)	$\Delta H_f{}^\circ{}_{298}$(R·) lit.
$C_6H_5O\cdot$ (phenoxy)	196.0 ± 0.2	−23.1 ± 0.1	204.4 ± 2	86.8 ± 2.2	11.6 ± 2.3	11.4 ± 2.0[c] 12.8 ± 2.1[d] 9[e]
$C_6H_5CH_2\cdot$ (benzyl)	203.4 ± 0.2	11.95 ± 0.01	198.3 ± 2	88.1 ± 2.2	48.0 ± 2.2	47.8 ± 1.5[f] 45[g] 45.0 ± 1[h] 45 ± 1[i]
c-$C_7H_7\cdot$ (cycloheptatrienyl)	190 ± 1	44.5 ± 0.1	200.2 ± 2	76.6 ± 3.0	69.0 ± 3.1	64.8[j]
c-$C_5H_5\cdot$ (cyclopentadienyl)	197.7 ± 0.2	32.44 ± 0.01	198.8 ± 2	82.9 ± 2.2	63.2 ± 2.2	60.9 ± 1.2[k] 47 ± 4[l] 53 ± 3[m]
c-$C_3H_3\cdot$ (cyclopropenyl)	224 ± 2	66.6 ± 0.1	180.2 ± 2	90.6 ± 4.0	105.1 ± 4.1	
$C_3H_5\cdot$ (allyl)	224.3 ± 0.2	4.88 ± 0.01	180.2 ± 2	90.9 ± 2.2	43.7 ± 2.2	39.1 ± 1.5[n] 40.6[g] 39.6 ± 1.5[h] 41.5 ± 2[o]
c-C_3H_5 (cyclopropyl)	232 ± 0.7	12.74 ± 0.01	187.5 ± 2	105.9 ± 2.7	66.5 ± 2.7	66.9 ± 0.25[p] 66 ± 3[g] 61 ± 3[i]
$C_2H_3\cdot$ (vinyl)	242.1 ± 0.2	12.50 ± 0.01	182.6 ± 2	111.1 ± 2.2	71.5 ± 2.2	69 ± 2[g] 64 ± 2[i]

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The double-resonance experiments used to determine if a reactant ion, $RH^{+\cdot}$, is a precursor for a product ion, BH^+

$$RH^{+\cdot} + B \rightarrow BH^+ + R^\cdot \qquad (1)$$

have been described in detail.[6] They will only be briefly outlined here. The abundance of BH^+ is monitored at constant magnetic field and observation frequency, f_1, while the frequency of the double-resonance oscillator, f_2, is slowly scanned over a 4-amu region centered on the frequency necessary to eject $RH^{+\cdot}$ from the ICR cell. A decrease in the strength of the BH^+ signal at an f_2 corresponding to $RH^{+\cdot}$ is taken to indicate the occurrence of reaction 1. If, on the other hand, no change in the signal strength for BH^+ is observed, or if an increase is detected, then it is concluded that reaction 1 is not occurring at an appreciable rate. The assumption is made that, if double resonance indicates the occurrence of (1), the reaction is thermoneutral or exothermic; otherwise the process is assumed to be endothermic. The double-resonance experiments are repeated using a field sweep mode, wherein f_1 and f_2 are kept constant and the magnetic field is swept over the resonance for BH^+ twice, once with the double-resonance oscillator on, once with it off.[6] This experiment eliminates the possibility of detuning effects causing a spurious double resonance response.

Since the proton affinity (PA) of a molecule, B, is defined as $\Delta H°$ for

$$BH^+ \rightarrow B + H^+ \qquad (2)$$

$\Delta H°$ for reaction 1 is simply the difference between the proton affinity of B and that of R·. By determining by double-resonance techniques the sign of $\Delta H°$ for (1) for a series of bases, B, of known proton affinity, the PA for R· is bounded by the PA of the most basic compound for which (1) is endothermic and the PA of the least basic compound for which it is exothermic.

Most of the chemicals used in this study were obtained from commercial sources and their purity confirmed by ICR mass spectra at several delay times. Cyclopentadiene was prepared by the destructive distillation of dicyclopentadiene and stored at −20 °C.[7] Cyclopropene was synthesized using the method of Closs and Krantz,[8] purified via trap-to-trap distillation at −100 °C, and stored at liquid-nitrogen temperature. Except when limited by the magnetic field strength (the 9-in. electromagnet used has a maximum field of 14 kG), f_1 was chosen to be 307.14 kHz in order to minimize ion loss[4] and complications caused by trapping plate ejection.[9] Pressures were measured with a Bayard-Alpert ionization gauge and are reported uncorrected.

Calculations

The results of the present study, along with thermochemical data from the literature, are presented in Table I. The proton affinity of R is taken to be the mean of the proton affinities of the two bracketing reference bases. It is combined with the ionization potential (IP) of RH to provide the homolytic bond dissociation energy DH°$_{298}$(R–H) using the following scheme:

$$RH^+ = R^\cdot + H^+;\ \Delta H°_{298} = PA(R^\cdot)$$

$$RH = RH^{+\cdot} + e^-;\ \Delta H°_0 = IP(RH)$$

$$e^- + H^+ = H^\cdot;\ \Delta H°_0 = -IP(H^\cdot)$$

$$\overline{}$$

$$RH = R^\cdot + H^\cdot;\ \Delta H°_{298} = DH°_{298}(R\text{–}H)$$

$$DH°_{298}(R\text{–}H) = PA(R^\cdot) + IP(RH) - IP(H^\cdot)^{10} \qquad (3)$$

The combination of 0 K data with that obtained at room temperature is valid because the difference IP(RH) − IP(H·) is essentially temperature independent. The bond strength is readily combined with the heat of formation of RH to afford the desired free-radical heat of formation:

$$\Delta H_f{}^\circ{}_{298}(R^\cdot) = DH°_{298}(R\text{–}H) + \Delta H_f{}^\circ{}_{298}(RH) - \Delta H_f{}^\circ{}_{298}(H^\cdot)^{10} \qquad (4)$$

Scheme I

$$RH + e^- \rightarrow RH^{+\cdot *} + 2e^- \tag{5}$$

$$B + e^- \rightarrow B^{+\cdot *} + 2e^- \tag{6}$$

$$\{B,RH\} + e^- \rightarrow F^+ + 2e^- + \text{neutral fragments} \tag{7}$$

$$RH^{+\cdot *} + M \rightarrow RH^{+\cdot} + M^* \tag{8}$$

$$RH^{+\cdot *} \rightarrow RH^{+\cdot} + h\nu \tag{9}$$

$$RH^{+\cdot *} + RH \rightarrow RH^{+\cdot} + RH^* \tag{10}$$

$$RH^{+\cdot} + B \rightarrow BH^+ + R^\cdot \tag{11}$$

$$RH^{+\cdot} + B \rightarrow S^+ + \text{neutrals} \tag{12}$$

$$\{F^+, S^+, B^{+\cdot}\} + B \rightarrow BH^+ + \text{products} \tag{13}$$

$$RH^{+\cdot} + RH \rightarrow S^+ + \text{neutrals} \tag{14}$$

Results

The general sequence of reactions involved in the determination of the proton affinity of a free radical $R^\cdot$ is shown in Scheme I. Electron impact upon a mixture of RH, a reference base B, and an excess of an inert buffer gas M forms the radical cations $RH^{+\cdot}$ and $B^{+\cdot}$ (reactions 5 and 6) as well as various fragment ions F^+ (reaction 7). M is chosen to be N_2 or Ar and does not ionize at the low electron energies employed. In addition, protonation of the buffer gas, M, was not observed for any of the systems of this study. The initially formed $RH^{+\cdot}$ may be translationally, rotationally, and vibrationally excited. Relaxation, however, may occur via processes 8, 9, and 10: collision with the buffer gas, radiation, and resonant charge transfer.[11] For some combinations of RH and B, processes other than proton transfer (reaction 11) were observed (charge transfer and hydride transfer, for example); these have been represented by reaction 12. Process 13 represents other paths which may lead to BH^+. If $RH^{+\cdot}$ reacts with either RH or B (reactions 12 and 14) to form some ions S^+, S^+ may be subsequently deprotonated by B to form BH^+. Double resonance as described above would not be able to distinguish such a circuitous path from $RH^{+\cdot}$ to BH^+ from simple proton transfer (reaction 11). In cases where this was a possibility, double resonance was carried out to determine if any S^+ resulting from $RH^{+\cdot}$ was deprotonated by B.

The compounds studied may be broken into two categories based upon this scheme. Molecules in the first group, consisting of toluene, phenol, and cycloheptatriene, have radical cations which are stable at times longer than 200 ms except when the proton affinity of B is such that reaction 11 is exothermic. Because of the lack of side reactions, high pressures of RH and of B could be employed, providing large abundances of $RH^{+\cdot}$ This simplifies the double-resonance experiments. Partial pressures were typically 1×10^{-6} Torr for RH, 1×10^{-6} Torr for B, and 2×10^{-5} Torr for M; double resonance was done at a delay time of 200 ms. Molecules belonging to the second group of compounds consisting of cyclopentadiene, cyclopropene, propene, cyclopropane, and ethylene yield radical cations which react with their respective neutral precursors to give various product ions. Low pressures of RH and high filament currents were utilized in order to decrease the importance of reaction 14 relative to reaction 11. Partial pressures on the order of 3×10^{-7} Torr for RH, 1×10^{-6} Torr for B, and 2×10^{-5} Torr for M were typical as well as delay times of 30–80 ms for the double-resonance experiments.

For each compound studied at least four reference bases were examined to determine whether or not proton abstraction from $RH^{+\cdot}$ occurs. A list of those compounds whose proton affinities bracketed those of the radicals and thus put bounds on their PAs is presented in Table II. Below we provide the pertinent experimental details for each free radical studied as well as comparisons with the previous literature.

Table II. Proton Affinities of Bracketing Reference Bases[a]

base, B	PA, kcal mol^{-1}	base, B	PA, kcal mol^{-1}
$CH_2(CN)_2$	178.8	THF	198.8
CF_3CO_2Me	181.6	EtCOMe	199.4
MeOH	183.6	Et_2O	199.9
MeCHO	186.6	*i*-PrCOMe	201.1
EtOH	188.4	*i*-PrOEt	203.3
MeOAc	197.7	Et_2S	205.4

[a] Taken from ref 2 except for EtCOMe, *i*-PhCOMe, and Et_2S: R. W. Taft, private communication. The proton affinity of ammonia has been assigned a value of 205 kcal mol^{-1}.[2]

Phenoxy. Until recently, the only heat of formation available for this radical was the electron-impact value of 9 kcal mol^{-1} measured by Natalis and Franklin.[13] Two kinetic measurements have since appeared, giving values of 11.4 ± 2.0[14] and 12.8 ± 2.1 kcal mol^{-1}.[15] The ICR value of 11.6 ± 2.3 is in better agreement with the results of the kinetic measurements than it is with Franklin's early determination. Electron impact on phenol produces only the parent ion $C_6H_5OH^{+\cdot}$. Diethyl sulfide is the weakest base observed to abstract a proton from *m/e* 94. Double resonance showed two possible reaction pathways:

$$C_6H_5OH^{+\cdot} + EtS \rightarrow Et_2S^{+\cdot} + C_6H_5OH \tag{15a}$$

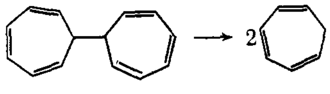
$$Et_2S^{+\cdot} + Et_2S \rightarrow Et_2SH^+ + C_4H_9S^\cdot \tag{15b}$$

$$C_6H_5OH^{+\cdot} + Et_2S \rightarrow Et_2SH^+ + C_6H_5O^\cdot \tag{16}$$

The occurrence of reaction 16 was confirmed through the use of C_6H_5OD and observation of double resonance between Et_2SD^+ and $C_6H_5OD^{+\cdot}$. Ethyl isopropyl ether is the weakest base unable to abstract a proton from *m/e* 94. However, in the absence of a buffer, proton transfer is observed, suggesting that as initially formed, under the conditions of the ICR experiments, the phenol radical cation is thermally excited.

Benzyl. Of the eight radicals studied in the present work, benzyl has received the most prior attention. All workers, save one, agree on a value of 45 kcal mol^{-1} for its heat of formation. A recent study by Rossi and Golden suggests a somewhat higher value of 47.8 ± 1.5 kcal mol^{-1},[16] in close agreement with the present ICR bracketing result of 48.0 ± 2.2 kcal mol^{-1}. Electron impact on toluene produces only the unreactive molecular ion $C_6H_5CH_3^{+\cdot}$, placing it in the first category of compounds. Methyl acetate is the strongest base which does not deprotonate *m/e* 92 while THF is the weakest one which does. The addition of the inert buffer gas has no effect on the observed proton affinity, implying that there is little or no internal excitation of $RH^{+\cdot}$.

Cycloheptatrienyl. The only available value for the heat of formation of this isomer of the benzyl radical comes from an electron spin resonance measurement of $\Delta H°$ for reaction 17.[17]



(17)

A limitation of the reliability of the result of this experiment lies in the use of group equivalence methods to derive the heat of formation of bitropenyl. In the ICR mass spectrometer, two ions are formed from electron impact on cycloheptatriene: the parent, $C_7H_8^{+\cdot}$, and an M − 1, $C_7H_7^+$. Double-resonance experiments confirm the occurrence of reaction 18. They also show that process 19 is not taking place on the time scale of the ICR experiment, and thus will not interfere with the bracketing experiments. Methyl ethyl ketone does not abstract a proton

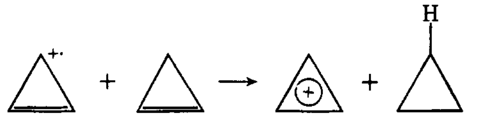
$$C_7H_8^{+\cdot} + C_7H_8 \rightarrow C_7H_7^+ + \text{neutrals} \tag{18}$$

$$C_7H_7^+ + C_7H_8 \rightarrow C_7H_8^{+\cdot} + \text{neutrals} \tag{19}$$

from *m/e* 92, whereas methyl isopropyl ketone does. There is little evidence for the radical cation being nonthermal. The fact that the benzyl radical and the tropyl radical have different proton affinities, and that their measured heats of formation agree with independent determinations from the literature, is good evidence that the radical cations of toluene and cycloheptatriene retain their identity and do not rearrange to some common ion. These results are consistent with conclusions reached from photodissociation experiments.[18]

Cyclopentadienyl. There are three values for $\Delta H_f°$ in the literature varying over a 14 kcal mol^{-1} span. The most recent and most precise value (60.9 ± 1.2 kcal mol^{-1}) derives from a kinetic measurement made by Benson;[20] it is in reasonable accord with the present ICR determination (63.2 ± 2.2 kcal mol^{-1}). The initially formed parent ion (*m/e* 66) in cyclopentadiene is observed to slowly protonate its own neutral to give $C_5H_7^+$. At low pressures of cyclopentadiene (5 × 10^{-7} Torr), $C_5H_7^{+\cdot}$ is stable to 200 ms, placing this compound on the borderline between the two general categories. Diethyl ether is the base with the lowest PA observed to abstract a proton from *m/e* 66 in the presence of a buffer gas. Methyl acetate is able to abstract a proton from the radical cation only in the buffer's absence. These experiments place a lower bound on the PA of cyclopentadienyl and also indicate the initial excitation of *m/e* 66.

Cyclopropenyl. This work appears to be the first experimental determination of the heat of formation of $c\text{-}C_3H_3\cdot$. With cyclopropene at 1 × 10^{-6} Torr, electron impact produced the radical cation $c\text{-}C_3H_4^{+\cdot}$ and the aromatic cyclopropenyl cation, $c\text{-}C_3H_3^+$ (20). Double resonance was used to show that the reverse reaction did not occur on the ICR time scale. Whereas malononitrile was found to be a weaker base than the cyclopropenyl radical, methyl trifluoroacetate is strong enough to remove a proton from *m/e* 40. There is no evidence for internal excitation of $c\text{-}C_3H_4^{+\cdot}$. Note, however, that our experiments do not preclude the possibility for ring opening upon ionization.



(20)

Allyl. Electron impact on propene at 5 × 10^{-7} Torr produces the parent, $C_3H_6^{+\cdot}$, as well as the allyl cation, $C_3H_5^+$, in a initial ratio of roughly 2:1. By 200 ms these ions have reacted almost completely to form $C_4H_7^+$ (*m/e* 55, probably the 2-methylallyl cation) and $C_5H_9^+$ (*m/e* 69). As shown by double resonance, malononitrile does not abstract a proton from the radical cation (*m/e* 42). Methyl trifluoroacetate was able to deprotonate $C_3H_6^{+\cdot}$, and the double-resonance experiments show that neither of the possible competitive paths, 21 and 22, was occurring.

$$C_3H_6^{+\cdot} \rightarrow C_4H_7^+ \quad (21)$$

$$C_4H_7^+ + CF_3CO_2Me \rightarrow C_4H_6 + CF_3CO_2MeH^+$$

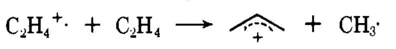
$$C_3H_6^{+\cdot} \rightarrow C_5H_9^+ \quad (22)$$

$$C_5H_9^+ + CF_3CO_2Me \rightarrow C_5H_8 + CF_3CO_2MeH^+$$

Our experiments lead to a value of 43.7 ± 2.2 kcal mol^{-1} for the heat of formation of the allyl radical. This is somewhat higher than values suggested by other workers. There was no evidence for a nonthermal $C_3H_6^{+\cdot}$

Cyclopropyl. With 1 × 10^{-6} Torr of cyclopropane, electron impact initially forms both the molecular ion $c\text{-}C_3H_6^{+\cdot}$ and $C_3H_5^+$. By 100 ms at this pressure the abundance of the radical cation decreases to approximately one-half of its initial value and ions at *m/e* 55 and 56 have appeared. However, at 3 × 10^{-7} Torr, the radical cation has decreased by only 10% at 100 ms. Double-resonance experiments show that *m/e* 42 is a precursor for both 55$^+$ and 56$^+$. In the absence of an inert buffer gas, acetaldehyde abstracts a proton from *m/e* 42; however, in the buffer's presence, this reaction does not occur. Ethanol is the weakest base observed to abstract a proton from thermalized $c\text{-}C_3H_6^{+\cdot}$. The resulting value of 66.5 ± 2.7 kcal mol^{-1} for the heat of formation of the radical agrees with values of 66 ± 3 and 66.9 ± 2.5 kcal mol^{-1} proposed recently by Benson,[20,21] but is in disagreement with Kerr's estimate of 61 ± 3 kcal mol^{-1}.[22] The difference in the proton affinities of the radical cations of cyclopropane and propene is evidence that the former does not open upon ionization.

Vinyl. As was the case with the cyclopropyl radical, Benson suggests a value for the heat of formation for the vinyl radical, 69 ± 2[20] kcal mol^{-1}, which is 5 kcal mol^{-1} higher than that suggested by Kerr, 64 ± 2[21] kcal mol^{-1}. The ICR bracketing technique arrives at a value of 71.5 ± 2.2 kcal mol^{-1}, in very good agreement with the Benson determination. In the ICR spectrometer at 2 × 10^{-7} Torr, ethylene gives an *m/e* 28 radical cation which has decreased by about 60% of its initial abundance by 200 ms with the concomitant appearance of *m/e* 41. Reasonable products for this reaction of $C_2H_4^{+\cdot}$ with ethylene are the allyl cation and methyl radical (reaction 23). Assuming this, we can calculate a $\Delta H°$ of +34 kcal mol^{-1} for reaction 23, implying that the ethylene parent ion is excited, even in the presence of 2 × 10^{-5} Torr of an argon buffer where *m/e* 41 is still observed as a product ion. Proton transfer is not observed to occur to CF_3CO_2Me, while it is observed to occur to methanol without any complications from alternate reaction paths.



(23)

Phenyl. Unfortunately, the double resonance bracketing technique failed when applied to determine the proton affinity of this species. The reason for the failure lies primarily in the reactivity of the radical cation. Although unreactive toward benzene itself, $C_6H_6^{+\cdot}$ reacts with many other bases, proton transfer usually not being the major reaction channel. For example, charge transfer occurs readily to *t*-BuCOMe, EtSMe, $C_6H_5CO_2Me$, and *i*-Pr_2S; with THF, *i*-Pr_2O, or *t*-BuOEt hydride transfer is the dominant reaction. When mixed with Me_2CO or MeCOEt, a product ion at *m/e* 117 was observed which double resonance showed to come from $C_6H_6^{+\cdot}$

C_6D_6 was utilized in an attempt to distinguish the proton-transfer pathways from those involving other mechanisms. Proton transfer was found to be too slow to provide a consistent series of no–yes results with a sharp cutoff. The experiments were also hampered by a scarcity of compounds in the necessary region of the proton-affinity scale.

Discussion

In both the ICR and the kinetic methods, the thermodynamic stability of a molecule is determined in systems removed from equilibrium. In the ICR experiments the assumptions made are that an exothermic reaction will proceed at a detectable rate (most exothermic proton transfer reactions have rates which approach the collision frequency) and that an endothermic process will not lead to any appreciable abundance of the product ion. The endothermicity of an ion–molecule reaction appears as an activation energy. Thus, a highly endothermic process will not proceed to any appreciable extent on the time scale on the experiment. It is possible, however, for an ion–molecule reaction which is endothermic by several kilocalories per mole to have an appreciable rate. This would lead to an underestimation of the proton affinity of the free radical. On the other hand, there could be a barrier to a process which is slightly exothermic, leading to a small degree of reactant-to-product conversion and an overestimation of the PA of the free radical. Such considerations put a limit on the accuracy with which this method can determine the basicity of a free radical, even given an infinitely dense basicity scale. We estimate this error to be ±2 kcal mol^{-1}, which is comparable in magnitude to the error introduced into the kinetic method by the approximation of radical-radical recombination activation energies.[3]

Conclusion

It has been demonstrated that the ion cyclotron double resonance bracketing experiment yields reliable values for the heats of formation of free radicals. In addition, our experience provides evidence for the validity of the general method for the determination of the thermochemical stabilities of transient neutral molecules.

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Study of Complexation of Polydentate Amido Ethers with Lithium Ions by Nuclear Magnetic Resonance Spectroscopy. 1. Solvent Effects

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Abstract: The complexation of lithium ions with polydentate amido ethers was investigated by ^1H and ^7Li magnetic resonance spectroscopy, including studies of spin-lattice relaxation times. Methylene chloride, nitromethane, acetonitrile, and pyridine were used as solvents. The tetradentate amido ether *N,N'*-diheptyl-*N,N'*,5,5'-tetramethyl-3,7-dioxanonanediamide (NDA) and the bidentate *N*-methylheptyl-3-oxapentanamide (PMA) were used as ligands. It was found that NDA acts as a much more effective complexing agent of lithium ions than its bidentate analogue PMA. For NDA the 1:1 complex represents the dominant species. However, it was shown that "sandwich"-type as well as bislithiated complexes may also be formed. The exchange rate between various forms is fast on the NMR scale. The stability constants, chemical shifts, and relaxation times of various complexes were calculated. The stability constants increase in the order of decreasing "donicities" of the solvent media. Inspection of ^1H NMR spectra revealed that conformation of amidic groups of the ligands is not affected by the complexation. The rotation around the C-N bond of NDA is, however, considerably restricted in the complexed species. It was found that the deviation from cubic symmetry is much less pronounced in a "sandwich"-type complex than in the 1:1 complex of NDA. Conductivity measurements were conducted for the latter complex in order to determine the degree of association of the complexed lithium with the perchlorate counterions. It was found that, even in such a high dielectric constant solvent as nitromethane, a large fraction of the complexed lithium ions was associated with their counterions, at the concentration range investigated by NMR.

Introduction

Tetradentate amido ethers were designed by Simon and his co-workers[1-3] as ionophores for alkali and alkaline-earth cations. The high complexing ability of these ligands is apparently due to cooperative interactions involving the ethereal and the amidic groups Their selectivity is strongly affected by minor differences in the molecular structure.[4]

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