Kinetic Detection of Common Intermediates in Gas Phase Ion–Molecule Reactions

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Abstract: A kinetic method is proposed by which it is possible to establish whether or not separate ion–molecule reactions occurring in an ion cyclotron resonance spectrometer proceed through ionic intermediates of common geometrical structure. The procedure is tested on two sets of ion–molecule reactions, one exemplifying the situation in which different neutral molecules lead to a common product ion, the other the case of formation of different ions. Thus, protonation of 1-methylcyclopentene and of methylenecyclopentane is shown to lead to the methylcyclopentyl cation, while protonation of the C_7H_{12} isomers, 1-methylcyclohexene and 1,2-dimethylcyclopentene, is shown to result in the formation of different ions.

The question of the structures of carbocations has been an issue of major concern to chemists throughout the past several decades. It has received overwhelming attention, and has, at times, engendered much debate among workers in the field. Still, important matters remain to be satisfactorily resolved.[2]

At the present time most of the "hard" structural information available on carbocations comes from two sources: experimentally, from their proton and ^{13}C NMR (and to a lesser extent infrared and ultraviolet) spectra obtained in superacid media,[3] and theoretically by use of ab initio and semiempirical molecular orbital calculations.[4] The superacid NMR techniques, pioneered by Olah, have now been applied to the study of literally hundreds of carbocations under conditions of long life. It may be criticized only on the basis of what it is, a structural probe for ions immersed in a highly electrophilic solvent. It is possible, even likely, that the superacid media exerts a significant influence on the structural properties on the ions under scrutiny. The theoretical calculations, on the other hand, provide us with information about the ions as isolated (i.e., unsolvated) species. Of course, the findings of the quantum mechanical calculations are not to be treated as if they were experimental facts. Rather they should be viewed as part of an entire "chemistry" of the particular theoretical model from which they were derived. How much trust we choose to place in the predictions of the theory should depend primarily on our past experiences: the success or failure of the model to mimic known experimental data. Until recent years little was known experimentally about either the structure or the stability of ions in the gas phase. Thus, the critical assessment of theoretical approaches to the properties of isolated ions has been seriously hampered. With the advent of pulsed ion cyclotron resonance (ICR) spectroscopy,[5] however, reliable experimental data on the relative energies of ions is rapidly becoming available. Still, almost nothing is known from experiment about the geometrical structures of isolated ions. For the most part this simply reflects the difficulty of achieving high enough concentrations of ionic species such that their absorption or emission of radiation might be detected experimentally.[6,7] The scarcity of structural data on ions in the gas phase from direct spectroscopic means has encouraged the exploration of a number of indirect approaches to information about their geometry. These include the measurement of isotope effects,[8] the evaluation of the temperature dependence of equilibria established in an ICR spectrometer,[9] and the use of the energetic effects of substituents as probes to structure.[10] Another approach, involving a comparison of rates of ion-molecule reactions, is presented in the present paper.[11]

Consider an attempt to measure the relative basicities of two isomeric molecules of different thermodynamic stability, the protonation of which would be expected to lead to the same intermediate ion. The pair of equilibria
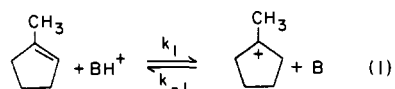
$$K_1 = [C_6H_{11}^+][B]/[endoC_6H_{10}][BH^+]$$
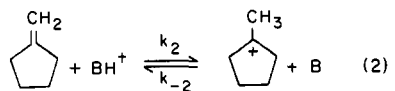
$$K_2 = [C_6H_{11}^+][B]/[exoC_6H_{10}][BH^+]$$

$$1 \gg K_1/K_2 = K_{isomerize} = k_1k_{-2}/k_2k_{-1}$$

where B is a suitable reference base, provide an adequate example. At first glance we would expect that because three molecules are common to each of the two reaction schemes, any difference in the measured basicities would simply equal the difference in the thermochemical stabilities of the neutral precursors, 1-methylcyclopentene and methylenecyclopentane. This being the case, we would then have a means of providing an absolute check on the ability of the ion cyclotron resonance experiment to properly account for the energetics of chemical equilibria. More careful scrutiny of the problem, however, reveals the obvious. There are two limiting conditions to consider. If $k_1 \simeq k_2$ (as our kinetic results indicate for this case), but $k_{-2} \ll k_{-1}$, then for the first reaction, involving 1-methylcyclopentene, the more stable of the two hydrocarbons, establishment of an equilibrium constant, $K = k_1/k_{-1}$, would lead to the correct measurement of its basicity relative to the standard base, B.

$$\Delta G° = -RT \ln (K)$$

On the other hand, consideration of reaction 2 for the thermodynamically less stable hydrocarbon, methylenecyclopentane, will *not* lead to a correct measurement of its basicity. For once the methylcyclopentyl cation has been formed, it will react with B, not to form methylenecyclopentane, but rather the more stable isomer 1-methylcyclopentene.
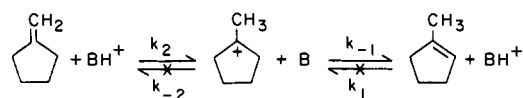
Under steady state conditions,

$$k_2[BH^+]_{ss}[exoC_6H_{10}] = k_{-1}[C_6H_{11}^+]_{ss}[B]$$

Consequently, a steady state situation rather than a true equilibrium for reaction 2 will be observed (i.e., that the

"equilibrium constant" which will actually be measured will correspond to k_2/k_{-1} rather than k_2/k_{-2}). It should be noted that the concentration of ions present in the ICR spectrometer is some five or six orders of magnitude less than that of their neutral precursors. This means that not enough of the more stable hydrocarbon, 1-methylcyclopentene, will be formed so that its reaction with the reference base will cause any significant contribution to the "back reaction". Further, none of the "normal" tests for equilibrium routinely performed during the course of an ICR experiment (e.g., double resonance and neutral pressure variation) will lead to an indication that anything is amiss.

It is possible to turn this undesirable situation around and to use it as a means of detecting situations where isomeric neutral molecules lead to the same intermediate ion. Instead of measuring equilibrium constants for the protonation reactions involving the isomeric hydrocarbons, let us instead proceed to determine the apparent reverse rate constants for the two processes. If they are measurably different (and the additional conditions mentioned below are satisfied) then we have established a case against the intervention of a common ion for the two processes. If, on the other hand, they are (within experimental error) the same, then the possibility exists that both reactions proceed through the same intermediate ion. Here caution must be exercised with respect to a second obvious limiting condition: $k_{-1} \simeq k_{-2}$, but $k_1 \ll k_2$. In this instance the measured gas phase basicities of both isomers will be in error. For processes such as (1) and (2) where isomeric compounds, I_1 and I_2, react with BH^+ to produce a common intermediate ion, I^+, assumption of steady state yields:

$$\frac{[I^+]_{ss}[B]}{[I_1][BH^+]_{ss}} = \frac{k_1}{k_{-1} + k_{-2}} \neq \frac{k_1}{k_{-1}}$$

$$\frac{[I^+]_{ss}[B]}{[I_2][BH^+]_{ss}} = \frac{k_2}{k_{-1} + k_{-2}} \neq \frac{k_2}{k_{-2}}$$

Our efforts at the present will be directed at establishing to what extent the simple kinetic technique described above may be of use in determining whether different reaction pathways lead to the same ion or to distinct species. Thus, we shall be concerned with situations where the result is already fairly certain. For example, we shall be interested to learn how nearly identical the measured reverse rate constants for reactions 1 and 2 are, where a common, methylcyclopentyl, cation is implicated. Equally important, we shall be concerned with establishing that reactions which could, but do not, result in the formation of a common ion might be distinguished as such. The pair of equilibria,

(3)

(4)
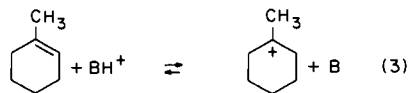
where, as before, B is some reference base common to both should provide an adequate example.

Methods and Results

The methods for determining equilibrium constants by ICR spectroscopy have been described at length previously[5] and will not be discussed here. The measured gas phase basicities of the compounds studied in this paper are presented in Chart I.[12] Specifically excluded from the chart is the "apparent" ICR value for the basicity of methylenecyclopentane ("ΔG^0" relative to $NH_3 = 6.5$ kcal/mol). We have, however, indicated an approximate value for this affinity ($\Delta G^0 = 3.0$ kcal/mol) based on our measured value for the proton affinity of 1-

Chart I
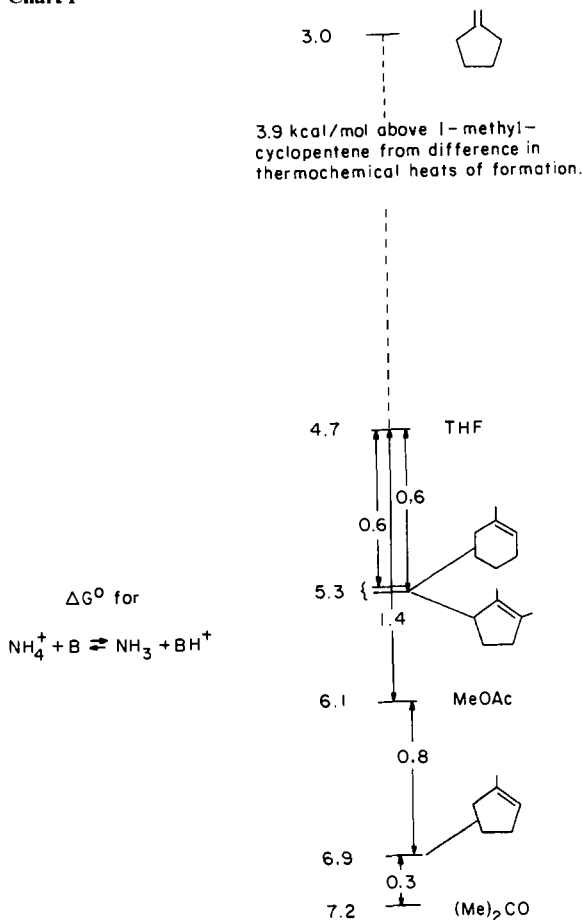
methylcyclopentene and the experimental difference in the heats of formation of the two hydrocarbons.[15] Following past practices, the gas phase basicities are relative to the value for ammonia (i.e., in terms of ΔG^0 for the reaction $NH_4^+ + B \rightleftarrows BH^+ + NH_3$) and are connected to the ICR basicity scale recently reported by Wolf et al.[13] by way of methyl acetate and tetrahydrofuran. The measurement of rate constants is straightforward, but, as it has received far less attention in the literature,[13,16] it will be briefly outlined. Consider the following equilibrium to be established in an ICR spectrometer.

$$A^+ + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A + B^+$$
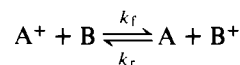
Removal of B^+, by double resonance ion ejection, will result in only the forward reaction being observed.

$$A^+ + B \overset{k_f}{\longrightarrow} A + B^+$$
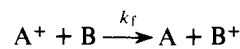
Since $[B] \gg [A^+]$ and $[B]$ is a constant, we may write the pseudo-first-order rate equation

$$-d[A^+]/dt = k_f[B][A^+]$$

or

$$[A^+] = [A_0^+]e^{-k_f[B]t}$$

Thus, k_f may be determined experimentally simply by fitting the observed decay of $[A^+]$ with time into exponential form, given an initial ion concentration, $[A_0^+]$, and the pressure of the neutral gas B. A typical time decay plot is displayed in Figure 1. Rate constants for all reactions considered in this paper and arrived at in the manner detailed above are presented in Table I. It should be noted that the accuracy of the absolute values for the bimolecular rate constants presented depend on calibration factors relating to the measurement of
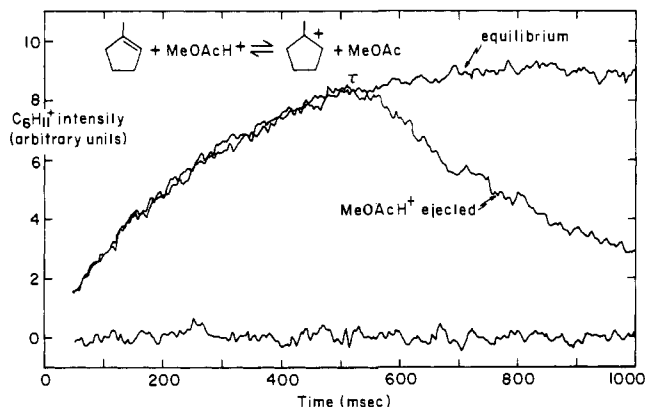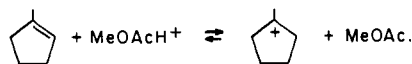
Figure 1. Time decay plot for reaction,

$$\text{(cyclopentene)} + \text{MeOAcH}^+ \rightleftarrows \text{(cyclopentyl}^+) + \text{MeOAc}.$$

Uppermost trace corresponds to equilibrium behavior of $C_6H_{11}^+$, middle trace to decay upon resonance ejection of $MeOAcH^+$ at time τ, and lower trace to baseline. Redrawn for clarity.

the absolute pressures of the neutral molecules. They are estimated to be reliable to ±25% or less. For example, we find the forward rate constant for the reaction,

$$\text{CH}_4\cdot^+ + \text{CH}_4 \xrightarrow{k_f} \text{CH}_5^+ + \text{CH}_3\cdot$$
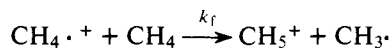
to be 1.33×10^{-10} cm^3 molecule^{-1}, to be compared with previous experimental values of 0.95,[17a] 0.99,[17b] 1.09,[17c] and 1.20[17d] $\times 10^{-10}$ cm^3 molecule^{-1}. The ratios of rate constants, such quantities as concern us here, are believed to be accurate within the stated limits.

1-Methylcyclopentene-Methylenecyclopentane. Reactions Leading to a Common Ion. Apparent equilibria were established between both 1-methylcyclopentene and methylenecyclopentane and the reference base methyl acetate.[18] What would appear from these data to be the difference in proton affinities (PA of 1-methylcyclopentene − PA of methylenecyclopentane) of the two cyclic alkenes ($\Delta\Delta G^\circ = -0.4$ kcal/mol) *does not* accurately reflect the observed difference in the heats of formation of the neutral molecules ($\Delta H^\circ = -3.9$ kcal/mol).[15] It should be noted that for both proton transfer reactions involving 1-methylcyclopentene and methylenecyclopentane, the ratio of the forward and reverse rate constants is, within the combined experimental error, numerically equal to the independently determined "equilibrium" constant for the respective process.

1-methylcyclopentene:

$$k_f/k_r = 0.19 \pm 0.11; \quad K_{eq} = 0.26 \pm 0.04$$

methylenecyclopentane:

$$k_f/k_r = 0.41 \pm 0.15; \quad "K_{eq}" = 0.49 \pm 0.08$$

This equality must necessarily hold for the equilibrium proton transfer process involving the more stable of the C_6H_{10} hydrocarbons, 1-methylcyclopentene. For reaction of the higher energy form, methylenecyclopentane, an approximate equality is to be expected, a result which follows directly from the assumption of a steady state concentration of the methylcyclopentyl cation, and the realization that $k_{-2} \gg k_{-1}$,

$$\frac{[C_6H_{11}^+]_{ss}[B]}{[\text{exo}C_6H_{10}][BH^+]_{ss}} = \frac{k_2}{k_{-1}}$$

More important for the discussion at hand is our observation that the apparent reverse rate constants for the two proton transfer processes 1 and 2 are the same, within experimental

Table I. Experimental Rate Constants[a]

Reaction	k, $\times 10^{10}$ cm^3 molecule^{-1} s^{-1}
(1-methylcyclopentene) + MeOAcH$^+$ → (methylcyclopentyl$^+$) + MeOAc	1.3 ± 0.4
(methylenecyclopentane) + MeOAcH$^+$ → (methylcyclopentyl$^+$) + MeOAc	2.7 ± 0.6
(methylcyclopentyl$^+$) + MeOAc → (1-methylcyclopentene) + MeOAcH$^+$	6.7 ± 1.6
(methylcyclopentyl$^+$) + MeOAc → (methylenecyclopentane) + MeOAcH$^+$	6.5 ± 1.0^b; 0.02^c
(1-methylcyclohexene) + THFH$^+$ → (methylcyclohexyl$^+$) + THF	2.1 ± 0.3
(1,2-dimethylcyclopentene) + THFH$^+$ → (dimethylcyclopentyl$^+$) + THF	1.5 ± 0.4
(methylcyclohexyl$^+$) + THF → (1-methylcyclohexene) + THFH$^+$	5.7 ± 1.6
(dimethylcyclopentyl$^+$) + THF → (1,2-dimethylcyclopentene) + THFH$^+$	2.7 ± 0.6

[a] Errors quoted correspond to two standard deviations. [b] Apparent value. [c] True value, calculated from k_1, k_2, and k_1 and from experimental difference in the heats of formation of 1-methylcyclopentene and methylenecyclopentane.

error, thus supporting, *but not necessarily proving*, the contention that the methylcyclopentyl cation returns to the same alkene, or the same equilibrium mixture of alkenes, independent of its origin. In this instance the experimental evidence in favor of both reactions proceeding through a common, methylcyclopentyl, cation is particularly strong. The fact that our data indicate the forward rate constants for the pair of proton transfer reactions to be identical within a factor of 2 requires that k_{-1} and k_{-2} be markedly different ($1 \gg k_1 k_{-2}/k_2 k_{-1}$).

1-Methylcyclohexene-1,2-Dimethylcyclopentene. Reactions Leading to Different Ions. As a test of our ability to distinguish between processes resulting in the formation of a common ion and reactions leading to distinct intermediate species, we have measured the forward and reverse rate constants and, independently, the equilibrium constants for the pair of reactions 3 and 4 involving the protonation of 1-methylcyclohexene and 1,2-dimethylcyclopentene, respectively. As indicated in Chart I, tetrahydrofuran, THF, was found to be a suitable reference base. For both compounds, the ratio of forward and reverse rate constants is found to be within experimental error of the measured value for K_{eq}, a necessary (but not sufficient) condition if the reactions being scrutinized are true equilibria.

1-methylcyclohexene-THF:

$$k_f/k_r = 0.37 \pm 0.16; \quad K_{eq} = 0.39 \pm 0.06$$

1,2-dimethylcyclopentene-THF:

$$k_f/k_r = 0.56 \pm 0.27; \quad K_{eq} = 0.40 \pm 0.02$$

In addition, the rates of reactions of the two carbocations with THF to form 1-methylcyclohexene and 1,2-dimethylcyclopentene are appreciably different.

Perhaps the major purpose which this case serves is to provide us with an indication of the reasonably wide variation in the rates of proton transfer reactions even among isomeric systems. (Rate constants for reactions of differing endothermicity are particularly likely to be markedly different.) It gives us some sense of confidence that, provided two rate constants

are actually established to be identical, within the limits of experimental accuracy currently attainable, then those rate constants probably pertain to the same reactive process. This point is important, for as indicated earlier, any prediction which might be made concerning the intervention of a common ion must be tempered by the possibility of the accidental numerical equality of rate constants describing different reactions.

Conclusion

We have demonstrated that it is possible to determine whether different reactions occurring within an ion cyclotron resonance spectrometer involves ions of common structure. The examples considered here have been chosen expressly to test the feasibility of the proposed kinetic procedure. Although the results of our investigations tell us little about the ion chemistry of these systems that we did not already know, they open the way to application of the kinetic technique to areas where definite queries about ion structure remain to be answered.

Experimental Section

All kinetic and equilibrium studies were performed on a trapped cell ion cyclotron resonance spectrometer described previously.[5a-c] Electron energies typically ranged from 15 to 17 eV and total neutral gas pressures from 2×10^{-7} to 5×10^{-7} Torr. Neutral pressure ratios (olefin:reference base) were varied from 9:1 to 5:1.

References and Notes

(1) (a) Earl C. Anthony Predoctoral Fellow, 1975–76; (b) Alfred P. Sloan Fellow, 1974–76.
(2) Nowhere is this more evident than in the case of the 2-norbornyl cation. For opposing viewpoints, see: H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); G. A. Olah, *ibid.*, **9**, 41 (1976).
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(12) The difference between the gas phase basicity of 1-methylcyclopentene reported here and that previously reported for isobutene,[13]

$$\Delta G^\circ = -1.7 \text{ kcal/mol}$$
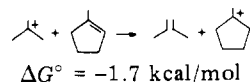
is in excellent accord with the value recently determined by Solomon and Field[14] using high-pressure mass spectrometry. These authors measured the free energy for the hydride transfer reaction

$$\Delta G^\circ = -5.5 \text{ kcal/mol}$$
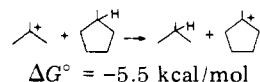
which when corrected for the differences in the heats of formation of the neutral saturated and unsaturated molecules[15] yields a proton affinity difference for the two olefins of −1.3 kcal/mol.

(13) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, submitted for publication.
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