The Reaction of Protonated Dimethyl Ether with Dimethyl Ether: Temperature and Isotope Effects on the Methyl Cation Transfer Reaction Forming Trimethyloxonium Cation and Methanol

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Abstract: Fourier transform ion cyclotron resonance mass spectrometry has been used to study the temperature and deuterium isotope effects on the methyl cation transfer reaction between protonated dimethyl ether and dimethyl ether to produce trimethyloxonium cation and methanol. From the temperature dependence of this bimolecular reaction it was possible to obtain thermodynamic information concerning the energy barrier for methyl cation transfer for the first time. From the slope of an Arrhenius plot, a value for $\Delta H^{\ddagger}$ of -1.1 ± 1.2 kJ mol^{-1} was obtained, while from the intercept a value for $\Delta S^{\ddagger}$ of -116 ± 15 J K^{-1} mol^{-1} was derived. This yields a $\Delta G^{\ddagger}(298)$ value of 33.7 ± 2.1 kJ mol^{-1}. All thermodynamic values were in good agreement with ab initio calculations. Rate constant ratios for the unimolecular dissociation forming trimethyloxonium cation and the dissociation re-forming reactants were extracted from the apparent bimolecular rate constant. Attempts at modeling the temperature dependence and isotope effects of the unimolecular dissociation forming trimethyloxonium cation were also made.

Introduction

Much work in the area of gas-phase ion chemistry focuses on the mechanisms and energetics of ion/molecule reactions.[1] Numerous techniques involving the observation of equilibria[2,3] or kinetics[4,5] of ion/molecule reactions have been devised to obtain thermochemical information pertaining to minima on potential energy surfaces. In particular, many studies on the energetics of proton transfer[6,7] and clustering energetics, mainly around protonated species,[7] have been carried out. Considerably less work has been done on the energetics of intermolecular transfer of larger groups such as alkyl cations,[8] mainly due to the slowness of these reactions compared to proton transfer and association reactions. For example, low-pressure FTICR mass spectrometry was used to determine that the rate of proton transfer between protonated methyl chloride and methyl chloride is approximately 5 times faster than methyl cation transfer between these two species.[9] Similarly, methyl cation transfer between protonated methanol and methanol to produce protonated dimethyl ether and water has been shown to be fairly slow, with a rate constant of ~1×10^{-10} cm^3 s^{-1}.[10] Despite the sluggishness of these reactions, high-pressure mass spectrometry has been used to measure equilibrium constants for methyl cation transfer which were then used to derive a methyl cation affinity scale for various bases.[11−13]

Of equal importance to thermochemical information on stable ionic species and ion/molecule complexes is that pertaining to the maxima on the potential energy surfaces known as transition states. Except for ab initio calculated barrier heights, thermochemical information pertaining to these maxima is quite scarce. Using a combination of collision-induced dissociation mass spectrometry and RRKM calculations Mayer has estimated the barrier height for isomerization of the proton-bound complex of methanol and acetonitrile to a complex between *N*-methylated acetonitrile cation and water to be 115 kJ mol^{-1}.[14] This corresponds to a barrier for methyl cation transfer between methanol and protonated acetonitrile of −6 kJ mol^{-1}. More recently, this work was extended to the ethyl cation transfer between ethanol and acetonitrile to produce *N*-ethylated acetonitrile and water.[15] The barrier for this reaction was deduced to be −22 kJ mol^{-1}.

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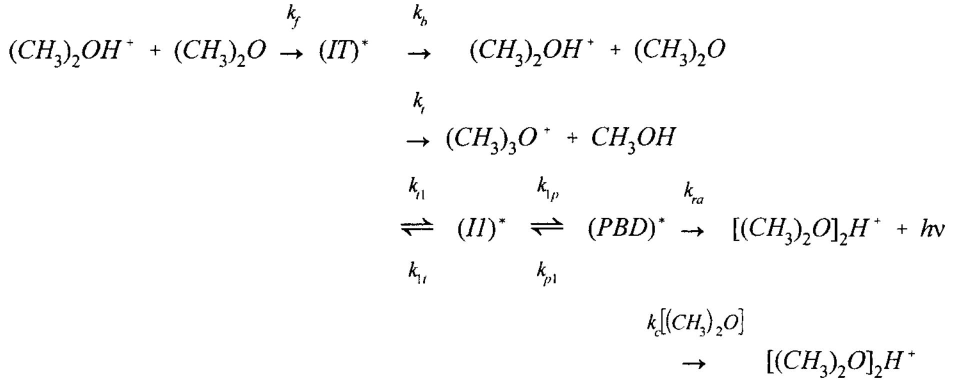
Scheme 1



$$(CH_3)_2OH^+ + (CH_3)_2O \xrightarrow{k_f} (IT)^* \xrightarrow{k_b} (CH_3)_2OH^+ + (CH_3)_2O$$

$$(IT)^* \xrightarrow{k_t} (CH_3)_3O^+ + CH_3OH$$

$$(IT)^* \underset{k_{1t}}{\overset{k_{t1}}{\rightleftharpoons}} (I1)^* \underset{k_{p1}}{\overset{k_{1p}}{\rightleftharpoons}} (PBD)^* \xrightarrow{k_{ra}} [(CH_3)_2O]_2H^+ + h\nu$$

$$(PBD)^* \xrightarrow{k_c[(CH_3)_2O]} [(CH_3)_2O]_2H^+$$

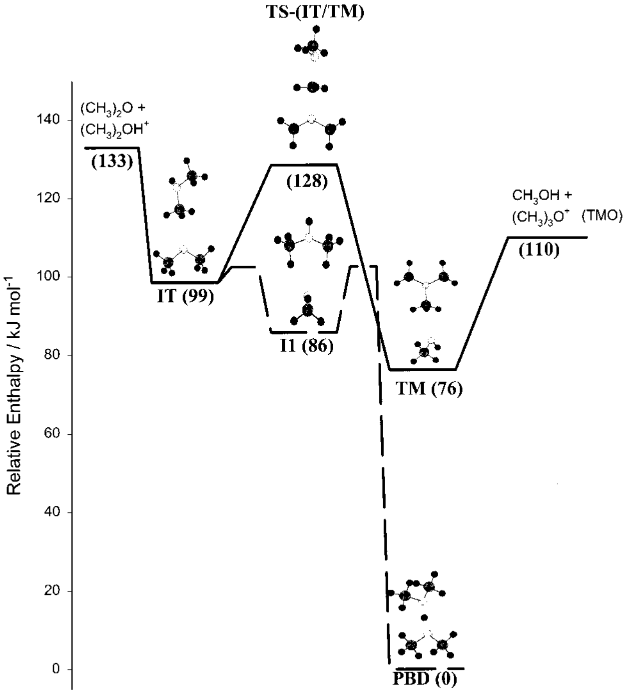


Figure 1. B3LYP/6-311G** calculated potential energy diagram relevant to the reaction of protonated dimethyl ether and dimethyl ether producing trimethyloxonium cation and methanol.

Recently, we have observed that the low-pressure radiative association reaction between dimethyl ether and protonated dimethyl ether was in competition with a side reaction which produced trimethyloxonium cation and water.[16] This side reaction became more pronounced at increased temperature and, at the highest temperatures studied, became the dominant reaction pathway. One of the results of the temperature dependence on the low-pressure radiative association reaction between dimethyl ether and protonated dimethyl ether was the deduction that the mechanism shown in Scheme 1, which involves dissociation through higher-energy isomers of the proton-bound dimer, was required to correctly model the temperature dependence.

In Scheme 1 IT and I1 are isomers of the nascent proton-bound dimer of dimethyl ether PBD. It should be noted that the isomer IT may dissociate into reactants or may eliminate methanol to form the trimethyloxonium cation. That the proton-bound dimer dissociates through isomers I1 and IT was also demonstrated by ab initio calculations. By systematically lengthening and constraining one of the O−H bonds in the proton-bound dimer (PBD) it was found that it isomerized to structure I1. Further stretching of this bond resulted in isomerization of I1 to IT. The B3LYP/6-311G** calculated potential energy surface with the structure of the previously mentioned species is shown in Figure 1.

In the present work we report the temperature dependence of the bimolecular rate constant for the reaction of protonated dimethyl ether with dimethyl ether to form the trimethyloxonium cation. The temperature dependence of this bimolecular reaction, occurring in an FTICR cell at low pressures, has been analyzed to obtain the energy, enthalpy, and entropy of activation for formation of trimethyloxonium cation from dimethyl ether and protonated dimethyl ether. Thermochemical information pertaining to this type of energy barrier has never been obtained from direct experimental determination in the past. The values experimentally obtained are compared to those calculated by ab initio means.

Experimental Section

The experimental procedure has been described in detail previously.[16] Briefly, all experiments were carried out with a Bruker CMS 47 FT-ICR mass spectrometer equipped with a 4.7 T magnet. The 6 cm × 6 cm cylindrical ICR cell is mated to a home-built high-pressure external ion source which has also been described in detail previously.[17]

Protonated dimethyl ether was formed directly in the ICR cell by proton transfer from protonated benzene to neutral dimethyl ether. Protonated benzene was generated in the external high-pressure ion source in a roughly 400:100:1 mixture of CH_4:N_2:C_6H_6 and was transferred to the ICR cell via a system of electrostatic ion optics. After an appropriate delay time to allow for a sufficient extent of proton transfer, all ions except protonated dimethyl ether were ejected from the ICR cell by using standard radio frequency (rf) ejection techniques. A second delay ensured thermalization of the ions, after which all ions except for the original precursor were once again ejected. The FT-ICR pulse sequence is shown in Figure 2.

Neutral dimethyl ether was introduced into the ICR cell via precision leak valves at calibrated pressures from 7.0×10^{-9} mbar to 1.4×10^{-6} mbar.

The intensities of protonated dimethyl ether, the proton-bound dimer, and the trimethyloxonium cation $(CH_3)_3O^+$ were monitored at various reaction times up to about 90% conversion of protonated dimethyl ether. Between four and fifty six scans were accumulated and Gaussian multiplied (apodized) to enhance the accuracy of the ion abundance measurements. Observed rate constants, k_{obs}, for reaction of protonated dimethyl ether were obtained from a least-squares curve-fitting of a semilogarithmic plot of normalized protonated dimethyl ether intensity versus time such as that shown in Figure 3. The apparent bimolecular

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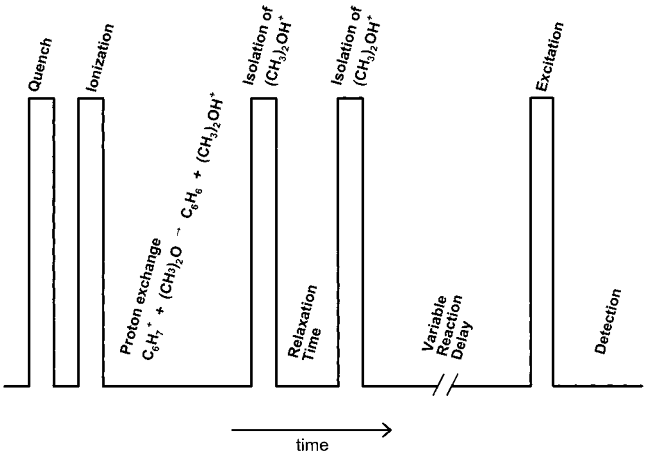

Figure 2. Scan function used for the FT-ICR experiments reported in this work.

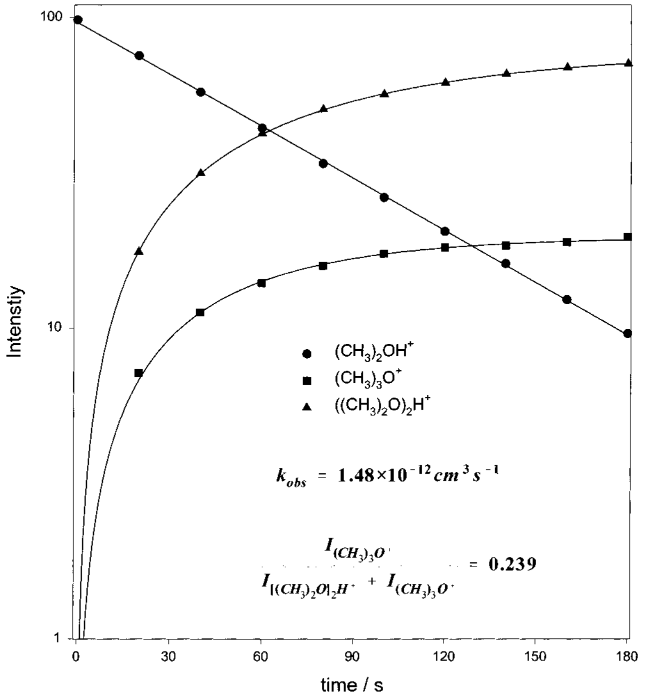

Figure 3. Semilogarithmic plot of intensity of protonated dimethyl ether, trimethyloxonium cation, and proton-bound dimer of dimethyl ether vs time for the reaction of protonated dimethyl ether with dimethyl ether at 306 K and dimethyl ether pressure of 4.2 × 10^{-7} mbar.

rate constant for the formation of trimethyloxonium cation $k_{\mathrm{app,tmo}}$ was obtained from k_{obs} by using the multiplicative factor obtained from the branching ratio shown in eq 1

$$k_{\mathrm{app,tmo}} = k_{\mathrm{obs}} \times \frac{I_{(CH_3)_3}\mathrm{O}^+}{I_{[(\mathrm{CH_3})_2\mathrm{O}]_2\mathrm{H}^+} + I_{(\mathrm{CH_3})_3\mathrm{O}^+}} \qquad (1)$$

where the I's are the intensities of the subscripted species. The pressure-independent values of $k_{\mathrm{app,tmo}}$ for a given temperature were averaged to obtain pressure-independent rate constants at each temperature.

The temperature inside the ICR cell was measured using iron−constantan thermocouples.

Computational Methods

Ab inito structures, energies, and vibrational wavenumbers were all calculated using the B3LYP/6-311G** level of theory and basis set. Calculations were performed using the Gaussian 94[18] computational package. The B3LYP/6-311G** calculated vibrational frequencies were scaled by 0.95 for use in the RRKM calculations.[19] Corrections suggested by Scott and Radom[19] were used for zero-point energies and for contributions to the thermal enthalpy and entropy due to vibrational degrees of freedom. Minima and maxima on the potential energy surface were verified by zero and one imaginary frequency, respectively.

The collision rate constants k_f and k_c were estimated using parametrized trajectory calculations which required the dipole moment and polarizability of the neutral reactant.[20]

The unimolecular rate constants for the dissociation reaction forming trimethyloxonium cation and methanol were modeled using the simple RRKM theory given by eq 2

$$k_{\mathrm{uni}} = \frac{\sigma}{h}\frac{N^{\ddagger}(E - E_0)}{\rho(E)} \qquad (2)$$

where σ is the symmetry number, h is Planck's constant. The sum ($N^{\ddagger}$) and density (ρ) of states for the transition state and reacting ion, respectively, were calculated using the Beyer−Swinehart direct count algorithm employing the B3LYP/6-311G** vibrational wavenumbers. The calculated unimolecular rate constants reported here were averaged over a Boltzmann internal energy distribution of the reacting species.

The unimolecular dissociation rate constants for the dissociation reaction to re-form reactants were obtained from master equation modeling using the VARIFLEX program[21] which uses variational transition state theory (VTST) in order to minimize the RRKM unimolecular dissociation rate constant due to the absence of a well-defined transition-state structure for dissociation. B3LYP/6-311G** calculated geometries, vibrational wavenumbers, and intensities were also utilized for these calculations.

Results and Discussion

Temperature Effect. Apparent bimolecular rate constants ($k_{\mathrm{app,tmo}}$) for the formation of trimethyloxonium cation from dimethyl ether and protonated dimethyl ether are summarized in Table 1 at the various temperatures studied. An analysis of the mechanism shown in Scheme 1, results in an expression for $k_{\mathrm{app,tmo}}$ given by eq 3

$$k_{\mathrm{app,tmo}} = \frac{k_f k_t}{k_b} \qquad (3)$$

where the rate constants are those for the reactions given in Scheme 1. From $k_{\mathrm{app,tmo}}$ and a calculated value of k_f, it is possible to obtain a ratio of the rate constants for formation of trimethyloxonium cation to the rate of dissociation into reactants. The values for the ratio, k_t/k_b are given in Table 1. Both dissociations originate from the species (IT)* which is a high-energy isomer of the proton-bound dimer of dimethyl ether. Complexes similar in structure to IT have been predicted to precede methyl cation transfer in the past for the reaction of methanol and protonated methanol to produce protonated dimethyl ether and water.[22−24] That re-dissociation of the proton-bound dimer proceeds through structures I1 and IT was verified by both ab initio calculations (stretching of one of the O−H

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Table 1. Summary of Rate Constants for Reaction of Dimethyl Ether and Protonated Dimethyl Ether Producing Trimethyloxonium Ion and Methanol at Various Cell Temperatures

	294 K[a]	306 K	313 K	322 K	326 K	333 K
$k_{app,tmo}/10^{-13}$ cm^3 s^{-1}	3.45 ± 0.09	3.68 ± 0.09	3.85 ± 0.14	3.91 ± 0.18	3.99 ± 0.09	4.25 ± 0.15
$k_t/k_b/10^{-4}$	1.97 ± 0.06	2.13 ± 0.06	2.24 ± 0.10	2.30 ± 0.10	2.34 ± 0.11	2.51± .09
$k_t^{b,c}/10^7$ s^{-1}	3.70 ± 0.11	5.20 ± 0.15	6.34 ± 0.28	7.87 ± 0.38	8.73 ± 0.22	10.87 ± 0.39
$k_t^{b,d}/10^7$ s^{-1}	1.24 ± 0.04	1.75 ± 0.05	2.16 ± 0.14	2.69 ± 0.17	2.99 ± 0.08	3.73 ± 0.17

[a] Reported also in Table 3. [b] Obtained by multiplying the value of k_t/k_b by the value of k_b calculated by VTST. [c] Dissociation energy in calculation of k_b was 34 kJ mol^{-1}. [d] Dissociation energy in calculation of k_b was 39 kJ mol^{-1}.

bonds in the proton-bound dimer resulted in structure I1, and further stretching resulted in structure IT) and by modeling the dissociation kinetics of nascent protonated dimers of dimethyl ether.[16]

That k_t/k_b is of the order 10^{-4} means that re-dissociation of nascent IT is 4 orders of magnitude faster than the methyl cation transfer reaction, even though the energy requirement for the latter is lower (see Arrhenius analysis of $k_{app,tmo}$ below). The entropic barrier is expected to be significantly higher for the methyl cation transfer reaction compared to simple re-dissociation into reactants which may explain this observation.

Also in Table 1 are values of k_t obtained by multiplying the k_t/k_b ratio by the value of k_b which was calculated by VTST using a dissociation energy for IT of 34 kJ mol^{-1}. In Figure 4 the quasi-experimental values of k_t obtained in this manner are plotted against temperature (solid line and squares) illustrating the positive temperature dependence. Also in Figure 4, the values for k_t which were obtained by RRKM calculations are plotted against temperature. These values were obtained using an enthalpy of activation of −2.3 kJ mol^{-1} from (IT)* (this is the lower limit to the experimental enthalpy of activation, vide infra) and a dissociation energy for IT of 34 kJ mol^{-1} (solid lines and circles).

The calculated values of k_t are larger than the "experimental" values at lower temperatures and higher at the highest temperature studied. To try to obtain better agreement between the calculated and "experimental" values of k_t, the dissociation energy of IT was varied in the VTST and RRKM determinations of k_b and k_t, respectively. In the last row of Table 1 are the values of k_t obtained by multiplying the experimental k_t/k_b by the value of k_b calculated using a dissociation energy for IT of 39 kJ mol^{-1}. These values are also plotted in Figure 4 (dashed lines and squares) along with the RRKM determined k_t (dashed lines and circles). It is apparent that the agreement between the calculated and "experimental" values of k_t is much better using 39 kJ mol^{-1} as the dissociation energy.

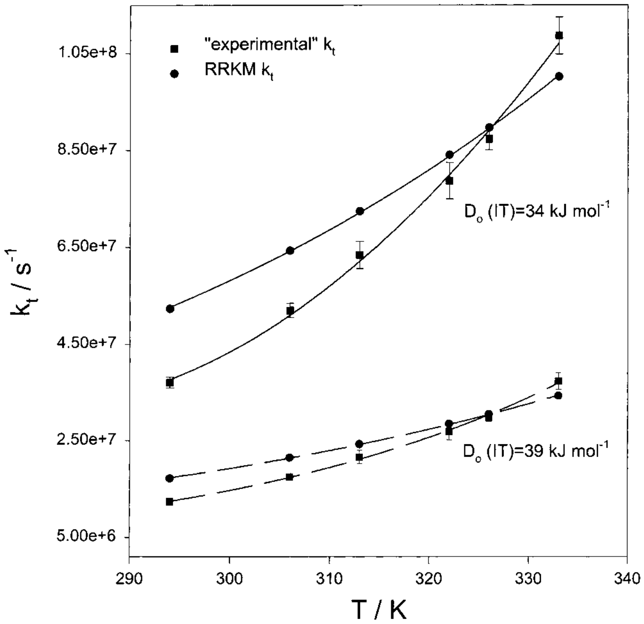

Figure 4. Plot of "experimental" and RRKM calculated k_t vs temperature. Experimental k_t was extracted from the k_t/k_b ratio by multiplying by VTST calculated k_b as described in the text. The solid lines denote "experimental" and theoretical values of k_t obtained with a value for the dissociation energy of IT of 34 kJ mol^{-1}, while the dashed lines denote that a dissociation energy of IT of 39 kJ mol^{-1} was used.

Table 2. Comparison of Experimental Thermodynamic Values for the Formation of Trimethyloxonium Ion from Dimethyl Ether and Protonated Dimethyl Ether Derived from the Slope and Intercept of the Arrhenius Plot in Figure 5 with ab Initio Values at 298 K

	experimental	B3LYP/6-311G**
$\Delta H^\ddagger$/kJ mol^{-1}	−1.1 ± 1.2	−4.6
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	−116 ± 15	−132
$\Delta G^\ddagger$/kJ mol^{-1}	33.7 ± 2.1	34.8
[a]D_{298}/kJ mol^{-1}	128[b]	133
$\Delta_r H(298)$	−28[c]	−23

[a] 298 K dissociation energy of the proton-bound dimer of dimethyl ether, [b] Reference 25. [c] Reference 26.

Arrhenius Analysis of $k_{app,tmo}$. The apparent rate constant for production of trimethyloxonium cation from dimethyl ether and protonated dimethyl ether shows a positive temperature dependence and the Arrhenius plot is presented in Figure 5

From the slope of the Arrhenius plot one can obtain the activation energy E_a and the enthalpy change going from reactants to the transition state according to eqs 4 and 5, respectively

$$E_a = - m \times R \tag{4}$$

$$\Delta H^\ddagger = E_a - 2RT \tag{5}$$

where m is the slope of the Arrhenius plot, R is the ideal gas

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Table 3. Summary of Rate Data for the Reactions of Protonated or Deuteronated Dimethyl Ether (or d_6) and Dimethyl Ether (or d_6) Producing Trimethyloxonium Cation and Methanol (294 K)

	dimethyl ether H^{+a}	dimethyl ether D^+	dimethyl ether-d_6 H^+	dimethyl ether-d_6 D^+
$k_{app,tmo}/10^{-13}$ cm^3 s^{-1}	3.45 ± 0.09	4.25 ± 0.27	7.80 ± 0.49	11.46 ± 0.98
$k_t/k_b/10^{-4}$	1.97 ± 0.06	2.44 ± 0.15	4.76 ± 0.30	6.99 ± 0.60
$k_t(\text{exp})^{b,c}/10^7$ s^{-1}	3.70 ± 0.11	4.09 ± 0.25	4.95 ± 0.31	6.79 ± 0.58
$k_t(\text{calc})^{c,d}/10^7$ s^{-1}	5.23	4.57	2.57	2.63
$k_t(\text{exp})^{b,e}/10^7$ s^{-1}	1.24 ± 0.04	1.38 ± 0.08	1.66 ± 0.16	2.32 ± 0.19
$k_t(\text{calc})^{d,e}/10^7$ s^{-1}	1.72	1.49	0.78	0.79

[a] Also reported in Table 1. [b] Obtained by multiplying k_t/k_b by k_b calculated by VTST. [c] Calculated using a dissociation energy for IT of 34 kJ mol^{-1}. [d] RRKM see text [e] Calculated using a dissociation energy for IT of 39 kJ mol^{-1}.

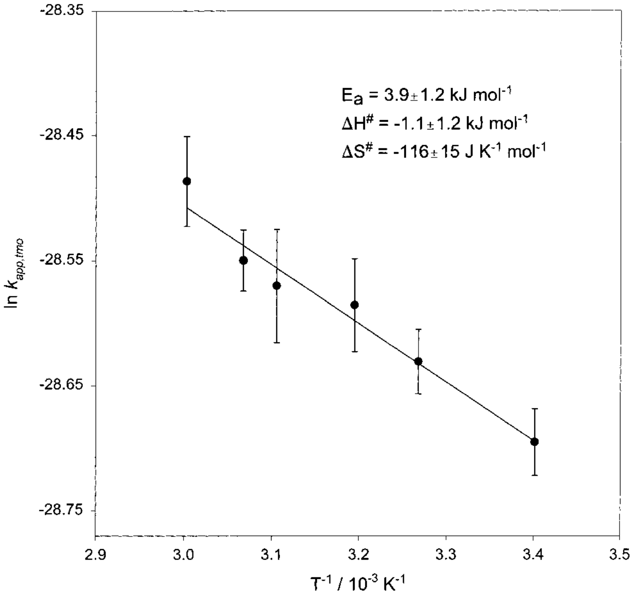

Figure 5. Arrhenius plot for the bimolecular reaction of protonated dimethyl ether and dimethyl ether producing trimethyloxonium cation and methanol. The slope and intercept as well as the errors associated with them were obtained from a weighted least-squares analysis from SigmaPlot.

constant, and T is the temperature. The slope of the Arrhenius plot in Figure 5 yields a value for E_a of 3.9 ± 1.2 kJ mol^{-1} and a $\Delta H^\ddagger$ of -1.1 ± 1.2 kJ mol^{-1}. From the thermodynamic formulation of transition state theory, the intercept of the Arrhenius plot A can be written in terms of the entropy of activation, $\Delta S^\ddagger$,

$$A = \frac{k_B T}{h} e^2 e^{\Delta S^\ddagger / R} \tag{6}$$

where k_B is the Boltzmann constant and all other terms have been defined above. Thus from the intercept of the Arrhenius plot and eq 6, a $\Delta S^\ddagger$ of -116 ± 15 J K^{-1} mol^{-1}, is obtained. These values, obtained experimentally, are in accord with what is expected intuitively.

The experimental values, together with $\Delta G^\ddagger$, are compared with ab initio values reported in Table 2. The experimental values are in fairly good agreement with the calculated values. It is known that density functional theory typically underestimates energies of transition states which is apparent from Table 3. There is some disagreement between the calculated and experimental entropy difference which is discussed further below.

Isotope Effect. The bimolecular apparent rate constants, $k_{app,tmo}$, for the formation of trimethyloxonium cation from dimethyl ether and protonated dimethyl ether are summarized in Table 3 for the isotopomeric reactions given by eqs 7 through 10.

$$(CH_3)_2O + (CH_3)_2OH^+ \rightarrow (CH_3)_3O^+ + CH_3OH \tag{7}$$

$$(CH_3)_2O + (CH_3)_2OD^+ \rightarrow (CH_3)_3O^+ + CH_3OD \tag{8}$$

$$(CD_3)_2O + (CD_3)_2OH^+ \rightarrow (CD_3)_3O^+ + CD_3OH \tag{9}$$

$$(CD_3)_2O + (CD_3)_2OD^+ \rightarrow (CD_3)_3O^+ + CD_3OD \tag{10}$$

Experimental values of k_t/k_b for the isotopomeric reactions as well as "experimental" values of k_t obtained by multiplying k_t/k_b by k_b calculated by VTST are also given. The experimental values of k_t are also compared with theoretical values, calculated the same way as above, in Table 3. The experimental values of k_t increase slightly when substituting the proton by a deuteron for both the h_6 and d_6 reactions and there is an even more pronounced effect on going from h_6 to d_6 in the reactants. The isotope effects are very much underestimated by the theoretical calculations.

This disagreement between experiment and theory is most likely due to the calculation of k_t which may be rationalized by looking at the structure of the transition state on going from IT to TM in Figure 1. The C−O bond lengths for the methyl cation to be transferred are both approximately 2 Å. This would suggest that each of the "fragments" making up the transition state (methanol, methyl, and dimethyl ether) are actually internal free rotors. Assuming that each of these fragments is an internal rotor, deuteration acts to increase the entropy of the transition state which decreases the entropic barrier to formation of trimethyloxonium cation and methanol. A decrease in the entropic barrier would increase the sum of states associated with the transition state and would have a more substantial effect for the fully deuterated species. Neglect of the internal rotors in the transition state may then be the most probable source of disagreement between the experimental and theoretical values of k_t.

The fact that the free rotors do affect the entropic barrier can be verified by comparing the experimental and calculated entropy differences between reactants and the transition state to formation of trimethyloxonium cation and methanol in Table 2. The ab initio entropy difference is significantly greater than the experimental since the former does not rigorously include the entropy from internal rotations.

Conclusions

It has been shown that the temperature dependence of the bimolecular reaction of protonated dimethyl ether with dimethyl ether to form trimethyloxonium cation and methanol can be used to obtain meaningful transition-state energetics. Here, the changes in enthalpy and entropy from reactants to transition state which are obtained, compare favorably to values predicted by ab initio calculations. In gas-phase ion chemistry, experimental relative enthalpy values for clustering reactions are quite abundant, but information pertaining to transition-state energies are quite rare. It is clear from this work that low-pressure ICR temperature-dependent studies can provide a valuable means for the experimental determination of transition-state energies.

It is not possible to ascertain the experimental rate constant for the elementary unimolecular dissociation of the isomer dissociating to trimethyloxonium cation but, a ratio k_t/k_b of the two dissociation channels, both stemming from the high-energy isomer, IT, of the proton-bound dimer of dimethyl ether can be obtained. From VTST estimates of k_b,k_t was extracted from this ratio and compared with modeled rate constants. A dissociation energy for the high-energy isomer of the proton-bound dimer of dimethyl ether of approximately 39 kJ mol^{-1} gives much better agreement between the "experimental" and RRKM estimates of k_t than the ab initio value of 34 kJ mol^{-1}. The difference in the magnitude of the experimental and theoretical isotope effects in k_t have been rationalized as being due to neglect of internal rotations. The differences are consistent with an increase in the entropy of the transition state, upon deuteration, due to presence of internal free rotations.

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