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Thermal decomposition of H_3O^- produced in reaction of OH^- with H_2CO

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The ion–molecule reaction $OH^- + H_2CO \rightarrow H_3O^- + CO$ has been studied at 300 K with isotopic labeling of reactants. The H_3O^- product is only observed in small abundance because the ion dissociates into $OH^- + H_2$ upon multiple collisions in a helium buffer gas. Without isotopic labeling, the pseudo-first-order kinetics plots for the reactions of OH^- with H_2CO and $OD^- + D_2CO$ were found to be curved as a result of the regeneration of OH^- or OD^- reactant. A scavenger technique was used to remove the H_3O^- (or D_3O^-) produced prior to dissociation, to reveal the true first-order attenuation of OH^- (or OD^-) in reaction with H_2CO (or D_2CO). The rate constant for the $OH^- + H_2CO$ reaction is 7.6×10^{-10} cm^3 s^{-1}, and for $OD^- + D_2CO$ is 5.7×10^{-10} cm^3 s^{-1}. For the isotopically mixed cases $OH^- + D_2CO$ and $OD^- + H_2CO$, the rate constants are equal to 1.3×10^{-9} cm^3 s^{-1}, about twice as large as those for the reactions involving only a single hydrogen isotope, indicating that isotopic exchange is an important process. The rate constants for the thermal dissociation of H_3O^- and D_3O^- in helium were found to be 1.6×10^{-12} and 1.1×10^{-12} cm^3 s^{-1}, respectively, within a factor of 2. The results are discussed in terms of other thermal dissociation reactions of ions.

INTRODUCTION

Many studies of unimolecular[1] and collision-induced dissociations of ions have been carried out owing to their importance in mass spectrometry. In contrast, only a small number of experiments on the thermal decomposition of ions has been reported.[2-9] Most of the vast amount of information on thermal reactions of ions involves bimolecular and termolecular reactions.[10] There is little direct information on *thermal* unimolecular processes involving ions. Indirect information can be obtained through termolecular association and the equilibrium constant, i.e., $K = k_f/k_r$.

The reason for the dearth of information on thermal decomposition of ions is simple—no universal and straightforward technique has been devised to study thermal decomposition. As a consequence, decomposition remains a problem that is easily overlooked in the interpretation of thermal experiments. For example, in the reaction of $OH^-(H_2O)$ with CH_3CN, we have found that one of the primary product ions $CH_2CN^-(H_2O)$ as well as the secondary ion $CH_2CN^-(CH_3CN)$ undergo thermal decomposition.[2] This secondary process made the determination of the primary branching fraction difficult; in fact, if the thermal decomposition were somewhat faster, it would have totally obscured the existence of the cluster product. Thermal decomposition occurred even though the bond strengths of these cluster ions are estimated to be in the 13–15 kcal mol^{-1} range, i.e., decomposition occurred at thermal energies far below the bond energy. We now find that the ion H_3O^-, with a dissociation energy[11,12] of 5 kcal mol^{-1} for breakup into OH^- and H_2, also undergoes thermal decomposition in a 300 K helium buffer, and we are able to estimate the rate constant for this process.

A decade ago, in an ion-cyclotron resonance (ICR) study, Kleingeld and Nibbering[13] reported that the reaction of OH^- with formaldehyde produces H_3O^-,

$$OH^- + H_2CO \rightarrow H_3O^- + CO. \tag{1}$$

The reaction is exothermic by about 0.2 eV. Their results involving isotopic substitution indicated that the reaction proceeded by proton transfer followed by hydride transfer within the collision complex. Following Kleingeld and Nibbering's work, we used a selected ion flow tube (SIFT) apparatus to examine reaction (1).[14] The OH^- decay plot was distinctly nonexponential. We did not observe H_3O^-, but rather observed the production of H_3CO^- and $H_3CO_2^-$, which are the secondary ions noted by Kleingeld and Nibbering

$$H_3O^- + H_2CO \begin{cases} \rightarrow H_3CO^- + H_2O \\ \rightarrow H_3CO_2^- + H_2. \end{cases} \tag{2}$$

[The ions H_3CO^- and $H_3CO_2^-$ may have the structures $H^-(H_2CO)$ and $OH^-(H_2CO)$.] At first, the lack of H_3O^- signal seemed puzzling, but we later realized that reaction (2) competes with the thermal decomposition of H_3O^-,

$$H_3O^- + He \rightarrow OH^- + H_2 + He \tag{3}$$

thereby reforming OH^-. Reaction (1) (or isotopic variant) has also been studied in flow tube experiments by Bohme *et al.*[15] and Grabowski *et al.*,[16] and in both works, the H_3O^- product (or isotopic variant) was unobservable.

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Process (3) is not significant in the low pressure ICR experiments. In the present work, sufficiently high primary ion intensities were used that the H_3O^- signal could be observed (at a maximum level typically 1% of the initial OH^- intensity). We report here rate constants for reactions (1)–(3) as well as those for the combinations of perdeuterated species. This is part of a larger study involving the chemical reactivity of H_3O^- with various neutrals, the results of which will be reported elsewhere.[12]

EXPERIMENTAL METHOD AND DATA ANALYSIS

The measurements were made using the Phillips Laboratory SIFT apparatus. The apparatus has been described in detail,[17,18] and only those aspects that are relevant to the present study are discussed here. OH^- and OD^- were made in a high pressure ion source from a mixture of N_2O and NH_3 or ND_3. Electron attachment to N_2O produces O^-, which then abstracts a H atom from NH_3 to form OH^-.

OH^- or OD^- was injected into a fast flow of He and allowed to react with H_2CO 50 cm from an ion sampling orifice. The He pressure in the flow tube was 0.4 Torr and the temperature was 300 K. H_2CO or D_2CO was made by heating *para*-formaldehyde or perdeuterated *para*-formaldehyde to 100 °C. The flow rate of formaldyhyde vapor was measured by an MKS Instruments, Inc., flow controller. Some formaldyhyde was seen to have polymerized on the inlet to the flow meter, but not on the low-pressure side. In experiments with CO scavenger to be described below, the OH^- decay vs measured H_2CO flow rate was distinctly exponential, implying (but not proving) negligible nonlinear flow problems. Furthermore, the kinetics data obtained with H_2CO have been remarkably independent of time, even in comparison with our 1983 effort using a capillary tube to determine the H_2CO flow rate.[14] In earlier research at the National Oceanic and Atmospheric Administration, flow meter measurements of H_2CO flow rates were estimated accurate to ±40%.[19] In the present work, we consider the flow meter accuracy to be the major uncertainty in the reaction rate coefficients, but estimate an overall uncertainty of ±35%. Ion signals of OH^- or OD^- and the various product ions were monitored as a function of the formaldehyde flow rate. Normally, reaction rate constants are derived from the exponential decay of the primary ion intensity. In this case, however, reaction (3) prevented a rate constant for reaction (1) from being measured in the standard manner since thermal decomposition of H_3O^- reforms OH^-. In order to circumvent the thermal decomposition problem, we used a scavenger reaction

$$H_3O^- + CO \rightarrow HOCO^- + H_2. \qquad (4)$$

The rate constant for reaction (4) has been measured only at 93 K. At that temperature, the rate constant is 6.2×10^{-10} cm^3 s^{-1}.[12] The fast nature of the reaction meant that we were able to add enough CO so that the scavenger reaction (4) for all practical purposes preempted thermal decomposition as a process destroying H_3O^- and therefore prevented OH^- from reforming. With CO added, we were therefore able to measure the rate constant for reaction (1) directly. The CO was added upstream of the reaction region and does not react with OH^-. Normally, 100 std. cm^3 min^{-1} of CO scavenger was added to 9000 std. cm^3 min^{-1} of He buffer; adding two or three times as much CO had no effect on the results.

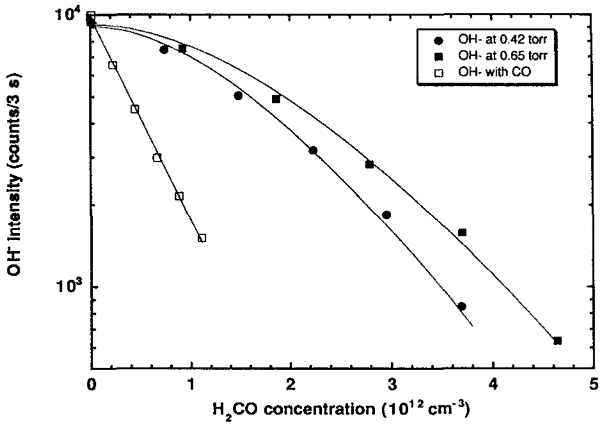

FIG. 1. The decay of the OH^- count rate as a function of H_2CO concentration, with and without CO scavenging of the H_3O^- product. The decay at 0.42 Torr He (no scavenger) (solid circles); the decay at 0.65 Torr He (no scavenger) (solid squares); the decay with CO scavenger (open squares). The solid lines are fits to the data using Eq. (6). The reaction time was 2.4 ms.

Without CO added, the semilogarithmic plot of the decay of OH^- intensity as a function of H_2CO [reaction (1)] was distinctly nonlinear (Fig. 1). The nonlinearity stems from reactions (1)–(3) all occurring in the flow tube. Reaction rate constants for reactions (2) and (3) were derived by fitting the observed decay to solutions of rate equations governing these processes. The rate equations and solutions[20] are given below using time-dependent functions $\mathrm{X}=[OH^-]$, $\mathrm{Y}=[H_3O^-]$, $\mathrm{Z}=[H_3CO^-]+[H_3CO_2^-]$, and neutral concentrations $\mathrm{B}=[\mathrm{He}]$, and $\mathrm{R}=[H_2CO]$. Let k_1 be the primary ion decay constant [reaction (1)], k_2 be the secondary rate constant [reaction (2)], and k_3 be the thermal decomposition rate constant [reaction (3)]. The rate equations are

$$d\mathrm{X}/dt = k_3\mathrm{BY} - k_1\mathrm{RX}, \qquad (5a)$$

$$d\mathrm{Y}/dt = k_1\mathrm{RX} - k_2\mathrm{RY} - k_3\mathrm{BY}, \qquad (5b)$$

$$d\mathrm{Z}/dt = k_2\mathrm{RY}, \qquad (5c)$$

and the solutions are

$$\mathrm{X} = [I_0/\Delta\gamma][(k_2\mathrm{R}+k_3\mathrm{B}-\gamma_1)\exp(-\gamma_1 t) - (k_2\mathrm{R}+k_3\mathrm{B}-\gamma_2)\exp(-\gamma_2 t)], \qquad (6a)$$

$$\mathrm{Y} = [I_0 k_1\mathrm{R}/\Delta\gamma][\exp(-\gamma_1 t) - \exp(-\gamma_2 t)], \qquad (6b)$$

$$\mathrm{Z} = I_0 - \mathrm{X} - \mathrm{Y}, \qquad (6c)$$

where

$$\Delta\gamma = [(k_1\mathrm{R}+k_2\mathrm{R}+k_3\mathrm{B}\}^2 - 4\mathrm{R}^2(k_1k_2)]^{1/2}, \qquad (7)$$

$$\gamma_1 = (1/2)(k_1\mathrm{R}+k_2\mathrm{R}+k_3\mathrm{B}-\Delta\gamma), \qquad (8)$$

$$\gamma_2=(1/2)(k_1\mathrm{R}+k_2\mathrm{R}+k_3\mathrm{B}+\Delta\gamma). \quad (9)$$

Note that

$$\Delta\gamma=\gamma_2-\gamma_1. \quad (10)$$

In fitting the experimental data, we were careful to check that the total ion intensity was constant (I_0) as the H_2CO flow rate was increased. Mass discrimination effects thus did not appear to be a problem over the small mass range involved in the experiment (17–47 amu).

Before settling on reaction (3) as the cause of the curvature, we considered the possibility that H_3O^- could decompose during sampling. Tests were carried out in which the sampling potentials were varied over wide ranges and no change was observed in the shape of the OH^- decay curve. The data presented here were taken with extremely low voltages on the sampling orifice plate and first sampling lens. These settings have been used in our laboratory previously to detect weakly bound cluster ions, and we are confident that the dissociation did not occur during sampling.

RESULTS AND DISCUSSION

Figure 1 shows the semilogarithmic decay curves for the reaction of OH^- with H_2CO with and without CO scavenger added. A fit to the data using Eq. (6) is also shown in the figure. For the case with CO added to the buffer, the semilogarithmic decay is linear and the least-squares line fits the data well, indicating that all H_3O^- reacted with CO before it had time to decompose. The OH^- decay with no CO added is quite nonlinear and considerably weaker than when CO is added. The decay rate increases with increasing H_2CO flow so that the data plot has a downward bow. The bow shape can be explained thusly: At low H_2CO flow rates, most of the H_3O^- formed thermally decomposes back into OH^-, but at larger H_2CO flows, reaction (2) begins to scavenge H_3O^-, i.e., H_2CO reacts with H_3O^-, competing with thermal decomposition. This competition causes the OH^- decay rate to increase since less reformation of OH^- occurs. Finally, at very high H_2CO flows, the OH^- decay approaches the decay rate we observe when CO is added, since nearly all the H_3O^- formed reacts with H_2CO before it thermally decomposes. A similar situation is found for the fully deuterated reaction (Fig. 2).

When only one reactant is deuterated, e.g., $OD^- + H_2CO$, an important channel of the reaction is isotope exchange,[13,21] and the kinetics plots are very nearly linear since the main product, e.g., OH^-, cannot reform OD^-. While the primary ion decay plot is not noticeably curved (on a semilogarithmic scale), in this case, the apparent rate coefficient is still slightly in error because the other product ion, e.g., H_2DO^-, is present equally[13] in two forms $HOD\cdot H^-$ and $DOH\cdot H^-$, one of which will thermally decompose to regenerate the primary ion. Thus, even in the mixed-isotopic case, the CO scavenger is needed to obtain a correct result.

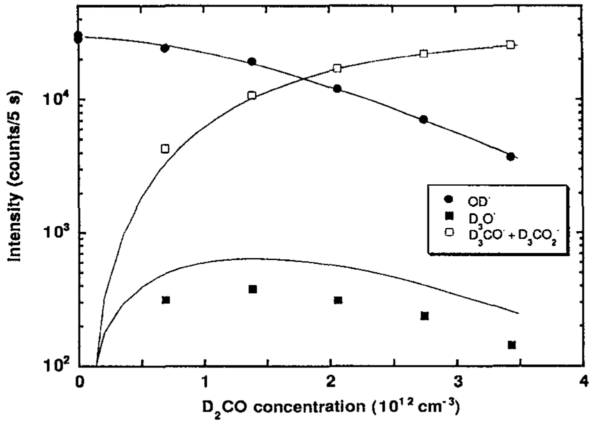

FIG. 2. Ion count rates for the reaction of OD^- with D_2CO in 0.4 Torr helium. The decay of OD^- intensity as a function of D_2CO flow rate (solid circles); D_3O^- product (solid squares); secondary ions D_3CO^- and $D_3CO_2^-$ summed (open squares). The solid lines are fits to the data using Eq. (6). The reaction time was 2.6 ms.

The primary reaction rate constant k_1 can be measured directly using the scavenger technique. We were unable to produce H_3O^- in the SIFT ion source, which might have enabled a more direct measurement of k_2 and k_3. Instead, the secondary rate constant k_2 and thermal decomposition rate constant k_3 must be derived by fitting data with evaluations of Eq. (6). The value of the collisional rate constant k_2 can be calculated[22] from the polarizability (2.45×10^{-24} cm^3) (Ref. 23) and dipole moment (2.332 D) (Ref. 24) of H_2CO. The result of this calculation is $k_2 = 3.56\times 10^{-9}$ and 3.41×10^{-9} $cm^3\,s^{-1}$, respectively, for the nondeuterated and fully deuterated reactions; the polarizability and dipole moment are assumed to be the same for D_2CO, so the difference in the two k_2 values is solely a mass effect. H_3O^- has the structure of either H^- clustered to H_2O (the ground state) or OH^- clustered to H_2 (no more than 0.2 eV above the ground state), so both channels of reaction (2) can be thought of as ligand exchange. Most ligand exchange reactions are fast, and a first guess at the rate constant for reaction (2) would be the collisional value. If the collisional value for k_2 is used in Eq. (6), the thermal decomposition rate constant k_3 must be 1.6×10^{-12} or 1.1×10^{-12} $cm^3\,s^{-1}$ to achieve a fit to data for the nondeuterated or fully deuterated reactions, respectively. Data at 0.42 and 0.65 Torr He (see Fig. 1) yielded the same value of k_3. A total of nine data sets were analyzed in this manner; five included product data and four did not. There are two caveats.

(a) Trial fits showed that within certain bounds, the OH^- or OD^- data could be fit by a wide range of values of k_2 and k_3 as long as the ratio k_2/k_3 was approximately unchanged. Thus, should k_2 happen to be half its collisional value, the OH^- or OD^- data can be fit well using a k_3 value of about half the 1.6×10^{-12} or 1.1×10^{-12} $cm^3\,s^{-1}$ figure given immediately above. However, if k_2 is taken to be lower than about 1×10^{-9} $cm^3\,s^{-1}$, the resulting OH^- or OD^- decay curve has the wrong shape and cannot fit the data regardless of the value of k_3. The H_3O^- (and D_3O^-) intensities also imply that k_2 is indeed large (next paragraph).

TABLE I. Rate constants for reactions involving production and destruction of H_3O^-. The k_1 values are accurate to 35%. The k_2 and k_3 values are good to within a factor of 2.

Reaction	Rate constant ($cm^3\ s^{-1}$)
$OH^- + H_2CO \rightarrow H_3O^- + CO$	$k_1 = 7.6 \times 10^{-10}$
$OD^- + D_2CO \rightarrow D_3O^- + CO$	$k_1 = 5.7 \times 10^{-10}$
$OH^- + D_2CO \rightarrow OD^- + HDCO(\sim 50\%)$	$k_1 = 1.3 \times 10^{-9}$
$\rightarrow HD_2O^- + CO(\sim 50\%)$	
$OD^- + H_2CO \rightarrow OH^- + HDCO(\sim 50\%)$	$k_1 = 1.3 \times 10^{-9}$
$\rightarrow H_2DO^- + CO(\sim 50\%)$	
$H_3O^- + H_2CO \rightarrow H_3CO^- + H_2O(\sim 65\%)$	$k_2 = 3.56 \times 10^{-9}$
$\rightarrow H_3CO_2^- + H_2(\sim 35\%)$	(calculated collisional value)
$D_3O^- + D_2CO \rightarrow D_3CO^- + D_2O(\sim 65\%)$	$k_2 = 3.41 \times 10^{-9}$
$\rightarrow D_3CO_2^- + D_2(\sim 35\%)$	(calculated collisional value)
$H_3O^- + He \rightarrow OH^- + H_2 + He$	$k_3 = 1.6 \times 10^{-12}$
$D_3O^- + He \rightarrow OD^- + D_2 + He$	$k_3 = 1.1 \times 10^{-12}$

(b) The H_3O^- (or D_3O^-) intensity is overestimated by the collisional value of k_2 and the corresponding "best fit" k_3, as shown in Fig. 2. The observed H_3O^- (or D_3O^-) intensity can be fit exactly only by increasing k_2 beyond the calculated collisional value and increasing k_3 by a similar factor. This discrepancy in the product ion intensity, and the inability to determine k_2 and k_3 independently, leads us to expect that our k_2 and k_3 are accurate only at the factor-of-2 level.

We should also note that the difference in the thermal dissociation rate constants for H_3O^- and D_3O^- $k_3 = 1.6 \times 10^{-12}$ and $1.1 \times 10^{-12}\ cm^3\ s^{-1}$, respectively, is almost entirely attributable, in the fitting process at least, to the difference in the primary rate constants $k_1 = 7.6 \times 10^{-10}$ and $5.7 \times 10^{-10}\ cm^3\ s^{-1}$, respectively, for the reactions $OH^- + H_2CO$ and $OD^- + D_2CO$. If, for any reason, such as different handling or heating of H_2CO and D_2CO samples, the two primary rate coefficients k_1 are in fact closer in value than we measured, then the thermal rate constants k_3 will likewise be closer in value.

Table I lists the rate constants derived for reactions (1)–(3) for both hydrogenated and deuterated reactants. Product branching fractions given in the table are considered accurate to within ten percentage points.

The most interesting result found here is that H_3O^- and D_3O^- thermally decompose in a 300 K helium bath. The second-order rate constant was found to be 1.6×10^{-12} or $1.1 \times 10^{-12}\ cm^3\ s^{-1}$, respectively, for H_3O^- or D_3O^- decomposition, with an estimated uncertainty of a factor of 2. These rate constants correspond to a decomposition for about every 2500 He collisions. At the pressures used in our experiment, this corresponds to a lifetime on the order of 0.1 ms. This may be compared with the reaction time of 2.5 ms.

We may compare the thermal dissociation of H_3O^- with the few other decomposition systems studied to date. A related, but fundamentally different case, is found in the thermal detachment of NO^-.[25,26] The electron is bound in this system by only 0.026 eV,[27] an energy comparable to room temperature kT. This reaction is classed as collisional detachment rather than thermal detachment, i.e., it is a one-step process rather than a multistep statistical process. Detachment for this ion occurs even at temperatures as low as 142 K, and activation energies are in the 100 meV range. In all likelihood, it is only the small size and high vibrational frequency of this ion that allows it to be observed at room temperature at all.

H_3O^- has a much larger electron binding energy (1.5 eV) (Ref. 28) than NO^-, and does not collisionally detach at room temperature. The dissociation energy[11,12] of H_3O^- (into $OH^- + H_2$) is 0.2 eV, which is still much greater than kT. The maximum rate of collisional dissociation that can occur is given roughly as the collision rate constant times a Boltzmann factor. This yields a rate constant over an order of magnitude too small to explain the decomposition observed here. Therefore, the mechanism for this decomposition must be thermal, i.e., the process is one involving dissociation of the high energy portion of the internal energy distribution of the ions. H_3O^- has only six vibrational degrees of freedom. According to calculations,[29] only two modes are low enough in frequency to have population in excess of 1% at 300 K.

Hierl *et al.*[2] have studied the thermal dissociation of $CH_2CH^-(H_2O)$ and $CH_2CN^-(CH_3CN)$ as a function of temperature. For these two ions, it is the cluster bond that breaks. The bond strengths are on the order of 13–15 kcal mol^{-1}. These ions are relatively large species with many vibrational degrees of freedom, including low frequency modes. This allows for the energy to be pumped readily into the molecule and for relatively large amounts of internal energy to be stored. Hierl *et al.* found activation energies of 0.22 and 0.35 eV, respectively, for the dissociation. These activation energies are considerably lower than the bond strengths involved (0.55–0.65 eV). Activation energies lower than the relevant bond dissociation energies are typical for thermal dissociations in the low pressure limit if the reverse association reaction is barrierless.[30]

French and Kebarle[7] have measured the decomposition of $C_2H_7^+$ into $C_2H_5^+$ and H_2 as a function of temperature. They found an activation energy of 0.43 eV, which is again considerably lower than the dissociation energy of 0.72 eV (17 kcal mol^{-1}). As with the CH_2CN^- clusters discussed above, the $C_2H_7^+$ system has many internal degrees of freedom to store large amounts of internal energy, which allows for the breaking of a bond of this strength even in a room-temperature buffer gas.

Meot-ner, Sieck, and Field[3–6] have studied the thermal decomposition of a number of organic positive ions at higher temperatures. The ions which were observed to decompose are protonated dimethoxyethane, *bis*(2-methoxyethyl) ether, *tert*-butyl methyl ether, ethanol, and diethyl ether as well as carbonium ions in the C_7–C_{10} range. Temperature, pressure, and collision gas were varied for some of the decomposition reactions. Decomposition was seen only at elevated temperatures, ~500 K and above. However, the bond strengths for many of these compounds are larger (as strong as 1.4 eV) than those of the species discussed in paragraphs above. Activation energies for thermal decomposition of the organic positive ions were found to be smaller than the endothermicities. Smith *et al.* have also studied the quasithermal decomposition of $CH_3CH_2OH_2^+$ in a drift tube.[8]

A recent set of experiments by McMahon and colleagues[9] has demonstrated the unimolecular dissociation of cluster ions in an ultralow pressure ICR with a high pressure mass spectrometer as an ion source. The ions they studied were $H^+(H_2O)_n$, $H^+(H_2O)_n(C_2H_5OH)_m$, and $Cl^-(H_2O)_n$. They attribute the dissociation to blackbody radiation from the cell walls. They also found that buffer gases increase the dissociation rates. The ionic bond strengths varied from 12 to 21 kcal mol^{-1}. The data reported in their paper involves only radiative dissociation, though the method appears applicable to the study of thermal dissociation reactions on a routine basis.

While the data set for thermal decomposition of ions is limited, it does indicate that the thermal dissociation process may occur often and at thermal energies much below the bond dissociation energy. Most of the observations of thermal dissociation in the literature have been fortuitous in that the process was observed as a byproduct of a reaction sequence being studied for other reasons, such as in the present work on H_3O^-. It leads one to speculate how many similar cases have been overlooked.

CONCLUSIONS

Reaction rate coefficients for isotopic variants of the $OH^- + H_2CO$ reaction have been measured and imply that H/D exchange occurs in about half the collisions. Use of a scavenger reaction was required to circumvent regeneration of the primary OH^- from thermal dissociation of the product ion H_3O^-. An estimate of the thermal decomposition rate coefficient has been obtained by fitting the data to solutions of the relevant rate equations.

Thermal dissociation of a molecular ion can be observed only when there is a balance between its rate and that of other competing processes such as the ion residence time in the apparatus and further reaction. If the rate of decomposition is fast enough, the ion will be unobservable in all but very low pressure experiments. In more marginal cases, where the ionic dissociation energy is in the neighborhood of 5–15 kcal mol^{-1}, thermal dissociation presents problems in determining product branching ratios and, as in the present work, in measuring the primary reaction rate constant. Product thermal decomposition may be especially important for reactions involving clusters where the bond strengths are relatively weak and there exist low frequency modes of vibration, as well as for large organic systems where low energy decomposition pathways exist. Thermal decomposition will be more important in high pressure apparatus such as flow tubes and high pressure mass spectrometers and less important in ICR spectrometers.

It appears that the first apparatus suitable for the study of unimolecular gas phase ion–molecule reactions on a routine basis are finally becoming available. The Fourier transform (FT)-ICR coupled to a high pressure mass spectrometer ion source discussed above is an example. Furthermore, Kass has now shown that a flowing afterglow triple quadrupole can be used to study unimolecular isomerization reactions.[31,32]

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