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Zero-Pressure Thermal-Radiation-Induced Dissociation of Gas-Phase Cluster Ions: Comparison of Theory and Experiment for $(H_2O)_2Cl^-$ and $(H_2O)_3Cl^-$

Robert C. Dunbar,[*,†] **Terrance B. McMahon,**[‡] **Detleff Thölmann,**[‡] **D. Scott Tonner,**[‡]
Dennis R. Salahub,[§,||] **and Dongqing Wei**[||]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, Départment de Chimie, Université de Montréal, C.P. 6128, succursale Centre-ville, Montréal, Québec H3C 3J7, Canada, and Centre de Recherche en Calcul Appliqué, 5160 boul. Decarie, Bureau 400, Montréal, Québec H3X 2H9, Canada

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Abstract: The kinetics of dissociation of $(H_2O)_2Cl^-$ and $(H_2O)_3Cl^-$ at essentially zero pressure by absorption of infrared photons from the background radiation field (ZTRID) are compared with theoretical expectations and kinetic modeling. New experimental dissociation results as a function of temperature are reported for $(H_2O)_3Cl^-$. Density functional calculations of the complex structures and the normal mode frequencies and integrated infrared absorption intensities are described. A master equation approach was used to model the dissociation rates predicted from these molecular properties. Using literature dissociation enthalpies in the modeling, order-of-magnitude agreement between experimental and predicted dissociation rates with no adjustable parameters was found. Alternatively, taking the ZTRID measurements as independent determinations of the dissociation enthalpies, values of $\Delta H_{\text{diss}}{}^{298}$ of 11.6 kcal ($(H_2O)_2Cl^-$) and 9.5 kcal ($(H_2O)_3Cl^-$) were derived, in modest disagreement with literature. Redetermination of the $(H_2O)_2Cl^-$ dissociation enthalpy by high-pressure mass spectrometry gave 11.9 kcal mol^{-1}, in excellent accord with the ZTRID value. The ZTRID $\Delta H_{\text{diss}}{}^{298}$ value for $(H_2O)_3Cl^-$ was confirmed by analysis of the temperature dependence, and we consider it to be reliable. The success of this modeling is taken as a strong validation of our picture of the ZTRID process, and this is suggested as a promising new approach to estimation of ion dissociation thermochemistry.

I. Introduction

Recently McMahon et al. reported the thermal dissociation of several gas-phase cluster ions at pressures so low that collisional energy deposition was negligible.[1] It was assumed that these dissociations were driven by absorption of infrared radiation from the ambient thermal black-body radiation field in the ion trap. These reactions thus appear to take us back to the original hypothesis of Perrin in 1919[2] that absorption of ambient radiation drives unimolecular dissociations (a mechanism which was soon recognized to be overwhelmed under usual conditions by the dominant collision-mediated dissociation mechanism). There hardly seems any alternative to this interpretation, but it is such a strikingly novel idea that it seems important to show that the dissociation kinetics are in quantitative accord with our expectations for the radiation-induced process. One important recent confirmation was provided by the demonstration that the deuterium isotope effects in several cases followed expectations based on the combined effects of changes in the vibrational mode frequencies and the variation in black-body spectral density at different IR frequencies.[3] The present work offers a confirmation of a different sort, by showing that the observed dissociation kinetics are quantitatively predictable based on known and calculable properties of the ions. For two ions showing such dissociations it has been possible to calculate the IR emission/absorption intensities with fair confidence, giving us the exceptional opportunity to compare observed and calculated dissociation rates in a very satisfactory way.

We want to show here, for these two computationally tractable cases, that the observed rates and temperature dependences are quantitatively predictable from quantum chemistry-derived molecular properties, using exact kinetic modeling in the ambient black-body radiation field. After using the agreement of theory and experiment to establish confidence in the radiation-induced dissociation picture of these reactions, we will go on to derive rather precise values of the dissociation thermochemistry for the two cluster ions. We will refer to our presumed picture of these reactions as driven by ambient IR radiation using the abbreviation ZTRID (zero-pressure thermal radiatively induced dissociation). In our approach to these questions, we will draw heavily on the analysis recently published[4] which considered kinetic and thermochemical aspects of ZTRID for a model set of generic hydrocarbons; the cases considered there are closely similar to the situation for the present pair of actual ions.

We may note some previous work on thermal dissociations of ions under conditions (pressures of the order of 1 mbar) such that only collisional, and not radiative, energy exchange could be relevant. These include work by Meotner and Field[5] on C_7 carbonium ion dissociations (480−600 K), a study by Sieck and Meotner of protonated ether dissociations (400−640 K)[6] and dissociations of protonated *tert*-butyl methyl ether ions,[7]

[†] Case Western Reserve University.

[‡] University of Waterloo.

[§] Université de Montréal.

[||] Centre de Recherche en Calcul Appliqué.

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and several studies of protonated ethanol dissociation.[8-10] Interpretation of these collision-induced thermal dissociations is difficult because they are typically in the fall-off pressure regime where quantitative relations between reaction thermochemistry and kinetics are difficult to establish. An attractive feature of the ZTRID experiment, where collisions are negligible, is that the uncertainties surrounding collisional energy transfer statistics are avoided, while the energy input and removal by infrared radiation is quite well understood and susceptible to kinetic modeling with considerable confidence.

The theoretical basis for relating thermal dissociation kinetics to bond strengths in this experiment was explored in detail in ref 4, which described two approaches to solving this problem. These two methods, detailed master-equation modeling and Tolman's theorem estimation, were illustrated as applied to a generic molecular model. The first of these methods, master equation modeling, is well suited to the present specific cases, since it gives a framework for direct use of the detailed molecular information provided by the quantum chemistry calculations and is exact within broad assumptions. The second method, applicable when ZTRID temperature dependence data are available, provides a basically independent measurement of the dissociation energy, offering a valuable redundancy in the assignment of this energy. Quantitative consistency between the two approaches, as will be illustrated for the $(H_2O)_3Cl^-$ case in the present study, should provide a high degree of confidence to dissociation thermochemical values derived from ZTRID data.

While normal mode frequencies are often easy to estimate with calculations of even modest scale, optical absorption intensities of vibrational transitions are notoriously difficult to calculate accurately, especially if absolute, rather than relative, values are required as they are here. Two dissociation reactions were singled out for the detailed scrutiny of this study, based on the consideration that the two parent ions involved are small enough to allow quantum chemical calculations of the vibrational properties at a sufficiently high level to give some confidence in the results. The two dissociations chosen were

$$(H_2O)_2Cl^- \rightarrow (H_2O)Cl^- + H_2O \qquad (1)$$

and

$$(H_2O)_3Cl^- \rightarrow (H_2O)_2Cl^- + H_2O \qquad (2)$$

The ZTRID kinetics are highly sensitive to the dissociation enthalpies of the ionic complexes. Hiraoka and Misuze[11] reported values of $\Delta H_{\mathrm{diss}}{}^{298}$ from equilibrium measurements in the source region of a high pressure mass spectrometer (HPMS). The thermochemical values derived here from ZTRID are significantly different from these. This discrepancy motivated a remeasurement of the equilibrium dissociation thermochemistry for the $(H_2O)_2Cl^-$ case, which resulted in a confirmation of our ZTRID value. This gives us further confidence in the promise of ZTRID as a thermochemical measurement technique.

II. Experimental Section

Measurements of the rates of unimolecular dissociation for the cluster ions of interest were carried out on a Bruker-Spectrospin CMS 47 FTICR spectrometer which has been modified at the University of Waterloo by the addition of an external high pressure source. The construction of this FTICR-high pressure external source combination as well as the process of ion transport from the source to the FTICR cell have been described in detail elsewhere. The instrument has been recently modified by increasing the pumping speeds of pumps in the source housing and ion flight regions to 510 L s^{-1} and 330 L s^{-1}, respectively.

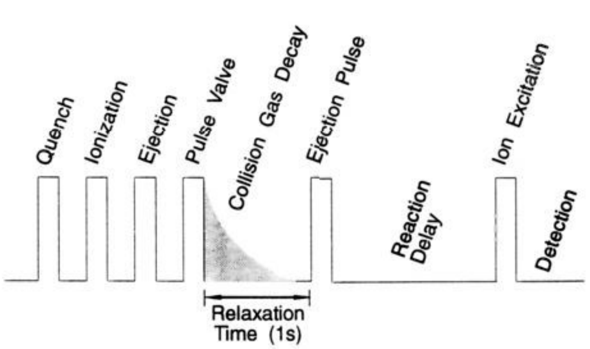

Figure 1. Pulse sequence used for ZTRID measurements.

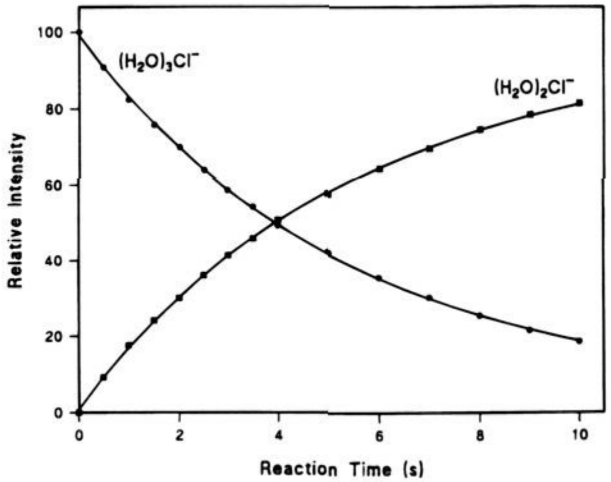

Figure 2. Illustrative kinetic plot for reaction 2 under ZTRID conditions.

The hydrated chloride ions are generated at pressures between 3 and 5 torr of CH_4 in the high pressure source by means of a sequence of ion molecule clustering reactions. CCl_4 is added in trace amount to the CH_4 to act as a dissociative electron capture reagent resulting in the formation of chloride ion. Several different pressures of H_2O in the gas mixture are then used to generate the degree of association desired in the adduct. Arrival of the ion of interest at the FTICR is accomplished at very low ion kinetic energies through use of the cylindrical deceleration assembly described previously. The ion kinetic energy is sufficiently low that the $(H_2O)_3Cl^-$ ion, which is bound by <12 kcal mol^{-1} undergoes no significant collision-induced dissociation even with a pressure of 1.0×10^{-6} torr of Ar in the FTICR cell. Similarly, it has been shown that ions bound by as little as 8 kcal mol^{-1} (*e.g.* $(CH_4)H_3O^+$) can be successfully introduced into the cell with only minimal extents of dissociation. To relax the small residual kinetic energy due to the ion transfer completely, a high pressure pulse of CH_4 is employed prior to the first ejection sequence used to isolate the cluster ion of interest. Following isolation of the well thermalized desired ion a series of experiments is performed in which the subsequent relaxation delay is randomly varied among ten values selected at regular fractions of the maximum delay time in order to eliminate any possibility of erroneous kinetics arising from a slow monotonic pressure variation. A typical pulse sequence for these kinetics experiments is shown in Figure 1. No significant peaks appeared in the spectra other than those corresponding to reactants and products of reactions 1 and 2, so there are no complications from other reactive processes. As illustrated in Figure 2 the normalized relative ion abundances plotted

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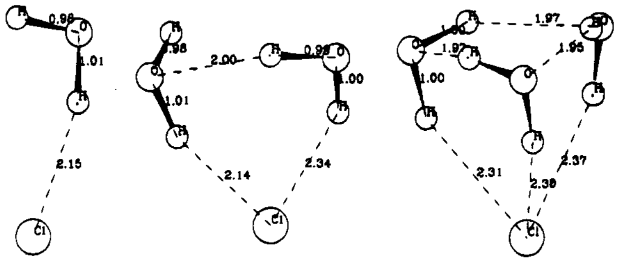

Figure 3. Calculated minimum-energy structures for the first three hydrates of Cl^-.

as a function of reaction time give smoothly single exponential decay curves from which the first order rate constant is readily extracted.

Temperature measurements were carried out by means of a Pt resistance thermometer mounted in the space between transmitter and receiver plates of the FTICR cell. Temperature was varied in two different ways. The first involved turning on the bake-out heaters until the desired temperature was reached and then turning off the heaters and carrying out the kinetics experiment. Typically no temperature change was observed during this experiment. The second method involved turning on the internal ionization filament to a set current value with the nominal electron energy maintained sufficiently low that no electrons entered the cell. The measured cell temperature was then directly related to the filament current used and could be maintained constant over sufficiently long periods of time to carry out the slower kinetics experiments. No differences were found in measured rate constants resulting from the two different heating methods. Although calculations suggested the possibility of radiative heating of the ions by direct radiation from the hot filament (located 9 cm distant from the cell center), the agreement of results using these two different methods showed that this was not a significant effect.

Kinetics experiments were also carried out as a function of the pressures of argon, methane, and *n*-butane to investigate the contributions due to conventional bimolecular thermal activation. Absolute pressure calibrations of the gauge readings were done on the basis of known rate constants for ion-molecule reactions involving each neutral molecule.

III. Quantum Chemical Calculations

Calculations were carried out using the deMon-KS software package[12] which is based on the Kohn–Sham density functional theory (DFT).[13,14] The DZVP basis set[15] which is of double-ζ quality with polarization functions on heavy atoms was used. Reliable results for geometries and vibrational frequencies and intensities for water clusters[16] and hydrated proton clusters[17] have been achieved by employing gradient-corrected nonlocal functionals, for example, that due to Perdew,[18] which has been used in the current study.

To study the vibrational spectroscopic properties of hydrated Cl^- clusters one has to optimize their structures. A geometry was considered as optimized when the gradient was less than 0.0001 atomic units. The optimized structures are shown in Figure 3. The structures are similar to those of post-Hartree–Fock (HF) calculations.[19] The Cl^- is weakly attached to the H_2O molecules via electrostatic interactions. Apparently the Cl^-–H_2O interaction is weaker than the hydrogen bond between water molecules, so that "surface" type structures have been obtained. Such a structure can be viewed clearly from the plot for $(H_2O)_3Cl^-$, where Cl^- lies below the plane defined by the water cluster. Unlike in the water cluster, three "free" hydrogens all point toward Cl^- to achieve maximum attraction. Due to the presence of Cl^-, the hydrogen bond length between two water molecules is longer than in water clusters. The weak interactions (hydrogen bonds and Cl^-–H_2O) are generally stronger compared with the results of the post-HF calculations.[19]

Table 1. Quantum Chemical Calculations of Cluster Ion Vibrational Properties

mode number	$(H_2O)Cl^-$ frequency (cm^{-1})	$(H_2O)Cl^-$ intensity (km mol^{-1})	$(H_2O)_2Cl^-$ frequency (cm^{-1})	$(H_2O)_2Cl^-$ intensity (km mol^{-1})	$(H_2O)_3Cl^-$ frequency (cm^{-1})	$(H_2O)_3Cl^-$ intensity (km mol^{-1})
7	221	29	103	7	101	8
8	320	60	167	69	141	6
9	763	172	230	63	174	14
10	1703	184	263	30	243	13
11	3160	1014	328	62	248	16
12	3686	10	496	49	312	3
13			574	27	492	2
14			777	177	496	1
15			838	181	557	72
16			1686	148	634	33
17			1755	227	637	49
18			3122	781	772	52
19			3391	432	806	365
20			3531	191	813	387
21			3676	20	1051	1
22					1726	155
23					1729	156
24					1761	223
25					3307	136
26					3327	186
27					3352	68
28					3425	647
29					3439	356
30					3445	368

The harmonic vibrational frequencies and IR intensities of various vibrational modes were generated for all the structures optimized. Due to a cancelation of errors, the DFT harmonic vibrational frequencies and intensities agree well with the experimental anharmonic results for water molecules, water clusters,[16] and hydrated proton clusters.[17] Our DFT results, listed in Table 1, are of quantitative value for the following kinetic modeling. One can see from Table 1 that the frequencies above 3400 cm^{-1} decrease when the cluster size increases. Those frequencies are due to the asymmetric stretching of H_2O. Clearly, this shows that the O–H bond becomes weaker as the cluster grows. The frequencies and intensities for $(H_2O)Cl^-$ are also given; its frequencies were used to make the vibrational enthalpy correction to zero Kelvin for reaction 1.

IV. Results

Dissociation Kinetics Measurements. The rate constants for unimolecular dissociation of both $(H_2O)_2Cl^-$ and $(H_2O)_3Cl^-$ at 295 K have been previously reported in reference 1. These measurements have been extended in the current manuscript to include the temperature dependence, shown in Figure 4, of the unimolecular dissociation of $(H_2O)_3Cl^-$ from 295 K to 320 K. Two sets of data were obtained, one for 2.5 × 10^{-9} mbar of CH_4 in the FTICR cell and the second for 6.6 × 10^{-8} mbar of CH_4. It can be seen that at the higher pressure the increase in the dissociation rate due to contributions from bimolecular collisional activation of the cluster is less than 10%. Thus we can be confident that at methane pressures less than 10^{-8} mbar bimolecular Lindemann-type activation of the ions will be negligible. As a further confirmation that distinct radiative and collisional mechanisms are involved, note that in ref 1 the dissociation rate was measured as a function of pressure for three different buffer gases (argon, methane, and butane), with the same zero-pressure intercept being observed in all three cases. The kinetic data derived from these experiments are summarized in Table 2.

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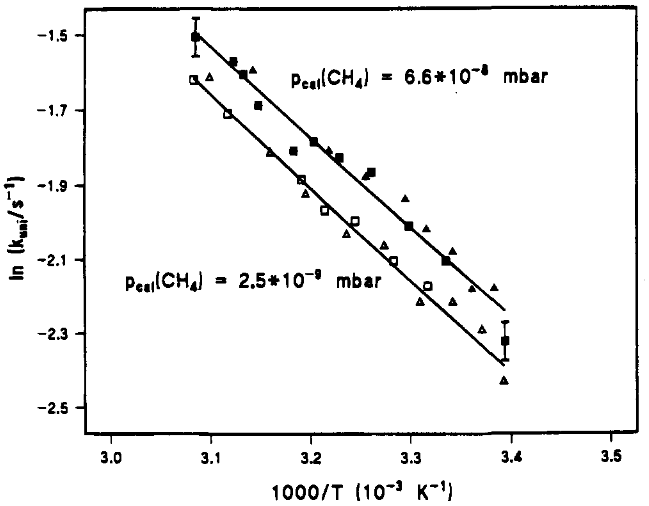

Figure 4. Temperature dependence of the $(H_2O)_3Cl^-$ dissociation rate. Results are shown for methane pressures of 2.5×10^{-9} and 6.6×10^{-8} mbar in the ion trap.

Table 2. Experimental Dissociation Kinetics Results

	dissociation rate constant (s^{-1})	$E_a = -d(\ln k)/d(1/RT)$ (kcal mol^{-1})
$(H_2O)_2Cl^-$	2.4×10^{-3} (295 K)	
$(H_2O)_3Cl^-$ [a]	0.11 (300 K)	5.0
$(H_2O)_3Cl^-$ (buffer gas)[b]	0.122 (300 K)	4.8

[a] Methane pressure 2.5×10^{-9} mbar. [b] Methane buffer gas at 6.6×10^{-8} mbar.

Kinetic Modeling. Ways to make the link between the computed vibrational properties of the cluster ions and their dissociation kinetics were discussed in ref 4. Both the dissociation rate and its temperature dependence are strongly dependent on the dissociation energy E_0. Assuming that the cluster dissociations are barrierless processes, E_0 is the same as $\Delta H_{\text{diss}}°$, which in turn can be estimated from the room temperature enthalpy values measured by equilibrium HPMS. We will follow the approach of finding the value of $\Delta H_{\text{diss}}°$ which most closely corresponds to the observed ZTRID kinetics and then comparing these $\Delta H_{\text{diss}}°$ values with HPMS values. We anticipate the main utility of ZTRID to be the estimation of otherwise unknown dissociation thermochemistry, so these comparisons will be an interesting test.

Using the calculated IR intensities and master-equation modeling of the kinetics, we can calculate the ZTRID dissociation rate of the ion at a given temperature with no adjustable parameters except E_0. Comparison with experiment then gives a parameter-free determination of the dissociation energy. An important point of the present paper is that this is the first time this rigorous approach has been possible, since these are the first ions for which both vibrational calculations and ZTRID data have been available. Complementary to this, the temperature dependence of ZTRID can be analyzed by the Tolman theorem approach to give an independent E_0 assignment which hardly depends at all on the calculated vibrational properties of the ion and offers a useful check on the master-equation result.

Coarse-grained master-equation modeling is well suited to the present purpose.[20] The molecule is pictured as moving up and down along the internal energy axis as it absorbs and emits infrared photons. Master-equation modeling of such a picture is appropriate if all the activation, deactivation, and reaction processes of the molecules are taken to be random processes whose rate constants depend only on the internal energy. Our application of this method to low-pressure dissociation kinetics of polyatomic ions has been described.[21-23] In summary, the transport matrix, or **J** matrix, is set up containing all the detailed rate constants. The lowest eigenvalue of the **J** matrix is the dissociation rate constant for the long-time, steady-state situation where all the initial transients related to the particular initial preparation of the population have died out.

We have frequently assigned the individual rate constants for IR absorption and emission using a weakly-coupled harmonic oscillator picture of the molecule,[24,25] using the convenient device of assigning an internal temperature to the ion corresponding to any given value of internal energy. The IR active vibrational modes, assumed to be thermally equilibrated with the internal temperature, are treated individually to yield rate constants for absorption, induced emission, and spontaneous emission. The validity and ease of application of this approach for molecules with more than three or four atoms has been discussed at length.[25]

Since collisional energy transfer is assumed to be negligible, up-pumping occurs by photon absorption and down-pumping by photon emission. These processes are governed by the Einstein A and B coefficients,

$$A = 2.88 \times 10^{-9}\, \bar{\nu}^2 I_n \tag{3}$$

where A is in s^{-1}, $\bar{\nu}$ is in cm^{-1}, I_n is the integrated IR absorption intensity (in practical units[26,27]) for the ($n \rightarrow n + 1$) transition of the normal mode in question, and

$$B = \frac{c^3 A}{8\pi h\nu^3} \tag{4}$$

with ν in Hz and B in cm^3 Hz s^{-1} J^{-1}. The I_0 values were taken from the calculations as given in Table 1, using a factor of 43.4 to convert from km mol^{-1} to practical integrated intensity units. As usual, the harmonic oscillator approximation $I_n = (n + 1)I_0$ was used.

The entry in the master equation transport matrix **J** for the rate of up-pumping from energy level i to level j is

$$\text{absorption } (i \rightarrow j) = \sum_{E(i,j)=h\nu(m)} \rho(h\nu) B P_m^n \tag{5}$$

where P_m^n is the probability of occupation of the nth quantum level of normal mode m, the summation is over all quantum states of all normal modes for which the mode frequency $h\nu(m)$ equals the energy difference between level i and level j, and $\rho(h\nu)$ is the radiation density, given by the Planck black body formula

$$\rho = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^u - 1} \tag{6}$$

where ρ is the radiation density in energy per unit volume per unit frequency, ν is the frequency, T is the ambient temperature, and $u = h\nu/kT$. The **J** matrix entry for down-pumping from level j to level i is the sum of the induced emission rate, given by an expression similar to eq 5, plus the spontaneous emission rate

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$$\text{spontaneous emission } (j \rightarrow i) = \sum_{E(i,j)=h\nu(m)} AP_{\mathrm{m}}^{n+1} \qquad (7)$$

where, again, the summation is over all quantum levels of all modes whose frequency equals the energy difference between level i and level j.

In general dissociation rate values must be put into the **J** matrix for energies above E_0. However, for both of these small cluster ions, RRKM[28] modeling indicates that the dissociation rate at the first level above E_0 is very fast ($>10^7$ s^{-1}), so that the actual dissociation rate values put in the matrix are irrelevant as long as they are large. (Or the matrix can be terminated at the E_0 level.)

An energy graining of 100 cm^{-1} was used. The **J** matrix was diagonalized, and its lowest eigenvalue was taken to be the steady-state dissociation rate. Tables 3 and 4 show the calculated dissociation rates and temperature dependences (E_a values) as a function of the assumed value of E_0.

V. Discussion

It is apparent straight away by comparing Table 2 with Tables 3 and 4 that our picture of these reaction processes is quantitatively sensible. If we accept the literature values for the dissociation thermochemistry,[11] as noted in Tables 3 and 4, the observed rates of dissociation and the temperature dependence of the $(H_2O)_3Cl^-$ case are in order of magnitude accord with the expectations from the theoretical modeling of the ZTRID process. There are no adjustable parameters whatsoever in this comparison. This should dispel any lingering doubt about the quantitative ability of the radiation hypothesis to account for the observed dissociation processes.

The rate of ZTRID depends very strongly on the dissociation energy E_0, and most of the rest of our discussion will be concerned with using ZTRID data as a way to determine E_0. The less than perfect agreement between the observed ZTRID rates for these two ions (Table 2) and those predicted on the basis of literature E_0 values (Tables 3 and 4) suggests that the thermochemistry assigned in ref 11 may not be quite right, and we will reevaluate these numbers. As we discuss the application of ZTRID to estimate the dissociation enthalpies of dissociation reactions, we will be careful to distinguish several energy quantities. E_0 is the height of the zero-Kelvin potential energy hill which must be surmounted to reach products. $\Delta H_{\mathrm{diss}}{}^\circ$ is the zero-Kelvin enthalpy difference between products and reactants and will be equal to E_0 for a barrierless dissociation. $\Delta H_{\mathrm{diss}}{}^{298}$ is the dissociation enthalpy at 298 Kelvin. E_a is the Arrhenius activation energy $-\mathrm{d}(\ln k_{\mathrm{diss}})/\mathrm{d}(1/RT)$ for dissociation (at 298 Kelvin). We will assume that E_0 and $\Delta H_{\mathrm{diss}}{}^\circ$ are equal, and obtain $\Delta H_{\mathrm{diss}}{}^{298}$ from the standard thermochemical relation

$$\Delta H_{\mathrm{diss}}{}^{298} = \Delta H_{\mathrm{diss}}{}^{\circ} + (H^{298} - H^{\circ})_{\mathrm{products}} - (H^{298} - H^{\circ})_{\mathrm{reactants}} \qquad (8)$$

For the reactions of interest here, the contribution of the last two (warming) terms largely consists of $4RT$ for the translational and rotational enthalpy of the water molecule, plus the difference in vibrational enthalpy of products and reactants at 298 K, which can be calculated from the calculated vibrational frequencies.

To illustrate the relation between these quantities, Table 5 shows the expected values, based on the literature values for the 298 K enthalpy of dissociation measured by HPMS. (Values for $(H_2O)_3Cl^-$ are given for illustration, but it should be noted that we are fairly sure the HPMS measurement on which they are based is too high.) Note that the expected Arrhenius activation energy is substantially smaller than the dissociation enthalpy, as was stressed in ref 4.

Table 3. Calculated Dissociation Kinetics for $(H_2O)_2Cl^-$

assumed E_0 (kcal mol^{-1})	dissociation rate constant (s^{-1}) 300 K	330 K	$E_a = -\mathrm{d}(\ln k)/\mathrm{d}(1/RT)$ (kcal mol^{-1})
8.6	1.2×10^{-2}	3.6×10^{-2}	7.2
9.7	4.3×10^{-3}	1.5×10^{-2}	8.2
10.8	1.4×10^{-3}	5.6×10^{-3}	9.3
11.5[a]	6.6×10^{-4}	3.0×10^{-3}	9.9
12.0	3.9×10^{-4}	1.9×10^{-3}	10.4
13.1	9.3×10^{-5}	5.3×10^{-4}	11.4

[a] This enthalpy value corresponds to the dissociation enthalpy assigned in ref 11 which is believed to be too high.

Table 4. Calculated Dissociation Kinetics for $(H_2O)_3Cl^-$

assumed E_0 (kcal mol^{-1})	dissociation rate constant (s^{-1}) 300 K	330 K	$E_a = -\mathrm{d}(\ln k)/\mathrm{d}(1/RT)$ (kcal mol^{-1})
6.3	0.25	0.48	4.3
7.4	0.124	0.28	5.4
8.6	0.057	0.15	6.4
9.5[a]	0.028	0.086	7.3
9.7	0.024	0.076	7.5
10.8	0.0095	0.035	8.5

[a] This enthalpy value corresponds to the dissociation enthalpy assigned in ref 11.

Table 5. Dissociation Energetics Based on Measured HPMS Equilibrium Thermochemistry

	$\Delta H_{\mathrm{diss}}{}^{298}$ (HPMS)	$\Delta H_{\mathrm{diss}}{}^{\circ}$ [a]	$\langle E' \rangle$[b]	E_a[c]
$(H_2O)_2Cl^- \rightarrow (H_2O)Cl^-$	11.9 (13.0[d])[e]	10.4 (11.5[d])	2.1	9.1 (10.2[d])
$(H_2O)_3Cl^- \rightarrow (H_2O)_2Cl^-$	(11.8[d])	(9.5[d])	2.6	(7.7[d])

[a] Experimental enthalpies corrected to 0 *K* by eq 8. [b] Correction term for predicting the Arrhenius activation energy via eq 9. [c] Predicted Arrhenius activation energy based on the HPMS thermochemistry. [d] Based on the HPMS thermochemistry given in ref 11. Note that we consider these values to be significantly too high. [e] Unparenthesized values correspond to the remeasured dissociation enthalpy reported here, while the parenthesized values correspond to the assignment of ref 11.

Table 6. Thermochemistry Derived from the ZTRID Experimental Numbers[a]

	$\Delta H_{\mathrm{diss}}{}^{298}$	$\Delta H_{\mathrm{diss}}{}^{0}$	E_a
$(H_2O)_2Cl^- \rightarrow (H_2O)Cl^-$	11.6	10.1	b
$(H_2O)_3Cl^- \rightarrow (H_2O)_2Cl^-$	9.5	7.2	5.0

[a] It is not straightforward to assign uncertainties to these values, but we believe the ΔH_{diss} values to be confident within ±0.5 kcal mol^{-1}. [b] Not experimentally determined. Predicted from modeling to be 8.5 kcal.

For $(H_2O)_2Cl^-$, with only one data value to fit, E_0 can obviously be chosen to give agreement of experiment and theory. The resulting E_0 is seen from comparing Tables 2 and 3 to be about 10.1 kcal mol^{-1}. For $(H_2O)_3Cl^-$ we need to choose E_0 to match simultaneously the observed rate and the observed temperature dependence. These requirements are satisfied using E_0 values differing by only 0.4 kcal. Comparing Tables 2 and 4, we choose a value of $E_0 = 7.2$ kcal mol^{-1} as the average of the two fitted values (7.4 and 7.0). The final thermochemical assignments and the resulting values of the room temperature dissociation enthalpies are listed in Table 6.

The Tolman theorem estimate resulting from the truncated Boltzmann approximation to the kinetics[4] gives an alternative and less laborious way of interpreting the observed activation

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(28) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972. Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973.

Table 7. Photon Emission and Absorption Properties in the Thermal Radiation Field at 300 K

	$(H_2O)_2Cl^-$ ($E_0 = 3600$ cm^{-1})	$(H_2O)_3Cl^-$ ($E_0 = 3000$ cm^{-1})
k_{abs} ($E = 0$) (s^{-1})[a]	1.7	2.0
k_{abs} ($E = E_0$) (s^{-1})[a]	3.4	2.5
$\langle h\nu\rangle_{abs}$ ($E = 0$) (cm^{-1})[b]	519	770
k_{emit} ($E = 0.75E_0$) (s^{-1})[a]	14	6.3
k_{emit} ($E = E_0$) (s^{-1})[a]	26	10.4
$\langle h\nu\rangle_{emit}$ ($E = 0.75E_0$) (cm^{-1})[b]	892	841
$\langle h\nu\rangle_{emit}$ ($E = E_0$) (cm^{-1})[b]	1411	862

[a] Rates of absorption or emission of photons (without regard to the photon energy), for ions having the designated amount of internal energy, sitting in the thermal 300 K photon field. [b] Average energy of the absorbed or emitted photons.

energy for $(H_2O)_3Cl^-$. In ref 4 it was suggested that to an excellent approximation E_a and E_o can be related by a corrected Tolman theorem relation

$$E_o = E_a + \langle E' \rangle - 0.85 \text{ kcal mol}^{-1} \qquad (9)$$

Here $\langle E' \rangle$ is the average energy of the parent ion population under conditions of reactive depletion, as discussed in detail in ref 4. Equations 8 and 9 provide a link that leads from the observed temperature dependence of the dissociation rate to an estimate of the room temperature dissociation enthalpy for reaction 2. Using $\langle E' \rangle = 2.6$ kcal mol^{-1}, the measured E_a of 5.0 kcal leads to $E_o = 6.8$ kcal mol^{-1}, which in turn gives $\Delta H_{diss}^{298} = 9.1$ kcal mol^{-1}. This is in good agreement with the master-equation result of 9.5 kcal mol^{-1} derived above.

Since the kinetic modeling is quantitatively successful, it is of interest to display the picture it gives of photon emission and absorption for these cluster ions in the thermal radiation field. In Table 7 are shown several modeled quantities for the two cluster ions. k_{abs} is the rate at which photons are absorbed (without regard to the photon frequency; that is, the absorption rate summed over all the vibrational modes). This is given for two hypothetical ion populations: the case where all the ions are in their vibrational ground state and the case where all the ions have an internal energy equal to the dissociation threshold E_0. It is seen that the absorption rate is not a strong function of the ion internal energy. Also given is the average energy of the absorbed photons, $\langle h\nu\rangle_{abs}$. The photon emission rate (again without regard to the photon energy) is given as k_{emit}, also at two internal energies. It is seen that the emission rate is quite a strong function of internal energy, as is well understood for radiative cooling.[25,27] The average emitted photon energies are given as $\langle h\nu\rangle_{emit}$. As expected from the discussion of ref 4, the average emitted and absorbed photon energies are of the same order of magnitude as the blackbody radiation peak (1040 cm^{-1}), although there are variations depending on the detailed molecular properties. It is interesting to observe that the emission rates are faster than the absorption rates near the dissociation threshold: the fact that ions can nevertheless acquire enough energy to dissociate reflects the statistical fluctuations associated with the discrete quantized nature of the heating and cooling processes.

The present study was not focussed on collisionally driven thermal dissociation kinetics, but the effect of methane buffer gas on the $(H_2O)_3Cl^-$ dissociation rate was observed as a function of temperature (Table 2) and also previously as a function of methane pressure (ref 1). From Figure 2 of ref 1 we see that the collision-induced dissociation rate is double the zero-pressure (ZTRID) rate at a methane pressure of 6×10^{-7} mbar, which corresponds to a collision rate for the ion of 13 collisions per second (assuming the collision rate equals the Langevin orbiting rate). This is consistent with the observation from the present Table 2 that the methane buffer increased the thermal dissociation rate by about 10% at a methane pressure corresponding to about 2 collisions per second. Looking at Table 7, we see that the number of radiative energy transfer opportunities (photon emission plus photon absorption) is about 13 per second, so that equal contributions of collisional and radiative dissociation are observed when the photon exchange rate is about equal to the collision rate. Without going into a detailed quantitative analysis, this indicates that the average energy transferred to or from methane per collision is approximately the same as the average photon-mediated energy transfer to or from the cell walls, namely 850 cm^{-1} (from Table 7). We conclude, not surprisingly, that methane functions as a moderately efficient energy-transfer collider, with an average energy transfer of about 850 cm^{-1} when colliding with a $(H_2O)_3Cl^-$ complex containing 3000 cm^{-1} of internal energy.

Table 8. Dissociation Enthalpies from Several Density-Functional Calculations

	ΔH_{diss}^{298} (Perdew;[a] DZVP)	ΔH_{diss}^{298} (Perdew;[a] Sadlej)	ΔH_{diss}^{298} (Becke;[b] Sadlej)	ΔH_{diss}^{298} (expt[c])	ΔH_{diss}^{298} (expt[d])
$(H_2O)_2Cl^- \rightarrow (H_2O)Cl^-$	17.68	16.91	12.25	11.6	13.0
$(H_2O)_3Cl^- \rightarrow (H_2O)_2Cl^-$	20.18	14.18	13.03	9.5	11.8

[a] Perdew–Perdew nonlocal correction (ref 18). [b] Becke–Perdew nonlocal correction (ref 30). [c] Present results. [d] Results given in ref 11.

The exchange of water molecules between the cluster and the background water vapor provides another mechanism for energy exchange between the complex and its environment. However, this mechanism is far too slow to be significant in the present work. The background water pressure is of the order of 5×10^{-11} mbar, corresponding to a collision rate of about 0.001 s^{-1}. Even if *every collision* with water resulted in dissociation, the rate would still be less than the slowest observed rate (Table 2). However, this is far from a realistic picture. Actually collision with water molecules is expected to partition energy randomly between the departing water molecule and the exchanged complex, and activation of the complex to an internal energy above the dissociation threshold depends on the same random walk along the energy axis as with photon exchange or energy exchange with a colliding buffer gas. Since a water exchange is more efficient at randomizing energy than collision with, say, a methane molecule, this mechanism should be a few times more efficient than methane buffer gas activation. Assuming that it is 5 times more efficient than methane activation and making use of the discussion of methane collisional activation efficiency in the preceding paragraph, it is readily seen that it would require a water pressure of the order of 1×10^{-8} mbar to activate dissociations by water exchange at a rate as great as 10% of the photon-activated rates observed here at 300 K. This is more than two orders of magnitude greater than the known background water pressure.

As has been seen, the dissociation enthalpies derived from the ZTRID approach are slightly lower than those from the HPMS equilibrium study of ref 11. This motivated the redetermination of the HPMS equilibrium in the case of $(H_2O)_2Cl^-$, using the high pressure instrument at Waterloo. The new results were $\Delta H = 11.9$ kcal mol^{-1}, $\Delta S = 17.8$ cal mol^{-1} K^{-1}. This is in very acceptable agreement with the ZTRID result and suggests that the measurements of ref 11 had a certain amount of systematic error. Unfortunately interfering contaminant ions made a similar redetermination impossible for $(H_2O)_3Cl^-$.

Since the ZTRID determination for the $(H_2O)_3Cl^-$ dissociation is reinforced by the agreement of the two different approaches to ZTRID data analysis, we believe this number to be even more secure than the $(H_2O)_2Cl^-$ result. In particular, the temperature dependence determination does not depend on the accuracy of the quantum chemical IR intensity calculations, whose absolute accuracy is not well established. We suggest that the ZTRID value of $\Delta H_{diss}{}^{298} = 9.5$ kcal mol^{-1} for reaction 2 should be the preferred value, and the value in ref 11 should be regarded as too high by 2.3 kcal mol^{-1}.

While it was not a principal goal of this work to compute the dissociation energies for these two ions, it is still interesting to note the values coming from the density-functional calculations, as shown in Table 8. The first column is the dissociation enthalpies calculated using the DZVP basis set as described above. It appears that these values are significantly too high. For comparison, further calculations were carried out using the larger Sadlej basis set[29] and using both the Perdew–Perdew functional[18] (second column) and the Becke–Perdew functional[30] (third column). It is seen that the larger basis set gives lower dissociation energies, and for the $(H_2O)_2Cl^-$ case it seems that the calculated value may be converging toward the experimental value. For the $(H_2O)_3Cl^-$ case, it appears that the calculated values are still significantly above experiment.

Measurement of bond strengths in covalent molecular ions has been dominated by dissociation methods, such as threshold appearance determination, and extrapolation of the rate-energy curve to zero dissociation rate.[31] In contrast, bond strengths for protonated molecules and ionic clusters have largely come from equilibrium and equilibrium bracketing measurements in high-pressure mass spectrometer sources and ion trapping instruments. Recent developments have suggested new dissociation-based tools for thermochemistry of the latter kinds of ions. One of these, useful for relative if not absolute binding energy determinations, is the competitive dissociation method for proton affinity comparison.[32] Another emerging useful approach for medium-to-large clusters is the analysis of kinetic energy releases (KER's).[33] While it does not yield dissociation energetics directly, photoelectron spectroscopy also gives some kinds of thermochemical insight for anion clusters and has contributed to understanding the energetics of $(H_2O)_nCl^-$ clusters.[34] The ZTRID approach described here using low-pressure thermal dissociation promises to add a particularly direct dissociation-based tool for measuring absolute cluster ion dissociation thermochemistry.

VI. Conclusions

It may seem surprising that the very slow absorption of infrared photons from the thermal background, at a rate of 2 or 3 photons per second (Table 7), can result in dissociation of a cluster ion at an observable rate, given that the bond strength is several times larger than the photon energy. Nevertheless, the validity of this picture is clearly demonstrated by the success of the quantitative modeling described here in matching the observed kinetics using no adjustable parameters.

When the dissociation enthalpies were considered as adjustable, relatively small corrections to the literature values were sufficient to give agreement of the observed kinetics with the modeled predictions. The fit is so sensitive to the chosen dissociation enthalpy that ZTRID is suggested as a promising new route to determining dissociation thermochemistry. The newly remeasured HPMS dissociation energy for $(H_2O)_2Cl^-$ was in completely acceptable agreement with the ZTRID assignment. The resulting new recommended dissociation enthalpy values for these two cluster ions are given in Table 6.

It seems that the measurement of thermal dissociation kinetics, which is so widespread and useful for neutral systems, may be ready for more extensive development in ionic systems. The present results and the success of the thermochemical analysis show the promise of the low-pressure ZTRID approach as a well controlled and quantitative dissociation-based tool for bond strength determination in ions like these chloride–water clusters.

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