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The dissociation energy of $Cl_2O_2^+$

John M. Bailey, Changtong Hao, Brian J. Johnson, Lee S. Sunderlin*

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA

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Abstract

Crystal structures containing a trapezoidal $Cl_2O_2^+$ cation, one of several structural isomers of $Cl_2O_2^+$, have been recently obtained by the Seppelt group. There is no experimental thermochemistry for this isomer, partly because the corresponding neutral structure has no significant interdiatomic bonding. We have measured the 0 K dissociation energy $D(Cl_2^+{-}O_2) = 57 \pm 7$ kJ/mol using energy resolved collision-induced dissociation experiments in a flowing afterglow-tandem mass spectrometer. This leads to $\Delta_f H_{298}(Cl_2O_2^+) = 1056 \pm 7$ kJ/mol. The calculated B3LYP/aug-cc-pVTZ dissociation energy is 13 kJ/mol higher than experiment, while CASPT2 calculations by Seppelt and coworkers give a result 8 kJ/mol below experiment. The agreement between experiment and theory is better than for the related X_4^+ (X = Cl, Br, and I) cations.

Keywords: Flowing afterglow; Collision-induced dissociation; Bond dissociation energy; ab initio calculations

1. Introduction

Seppelt and coworkers recently reported the crystal structures of $Cl_2O_2^+SbF_6^-$, $Cl_2O_2^+Sb_2F_{11}^-$, and $Cl_2O_2^+$-$HIr_2F_{12}^-$ [1,2]. These three compounds contain $Cl_2O_2^+$ cations with similar trapezoidal structures. As shown in Fig. 1, the experimental structure resembles O_2 and Cl_2 moieties with a long interdiatomic distance. Computations indicate that the trapezoid is the lowest-energy structure for isolated $Cl_2O_2^+$ [2]. The next-lowest isomer, $ClOOCl^+$, is the ionized form of the ClOOCl intermediate important in the atmospheric depletion of ozone [3,4].

In a separate study, Cacace et al. [5] prepared two isomers of $Cl_2O_2^+$ in the gas phase by chemical ionization, and characterized them by means of collision-induced dissociation (CID) in a mass spectrometer. The first isomer of $Cl_2O_2^+$ was prepared by the chlorination of ClO_2, and the following reaction sequence was given as the most probable.

$$Cl_2^+ + Cl_2 \rightarrow Cl_3^+ + Cl \quad (1)$$

$$Cl_3^+ + ClO_2 \rightarrow Cl_2O_2^+ + Cl_2 \quad (2)$$

The dissociation of $Cl_2O_2^+$ yielded peaks for Cl^+, ClO^+, and ClO_2^+. This supports an open chain structure of $[ClOClO]^+$ because all fragments can be traced to the simple fission of one bond in the chain.

Cacace prepared the second isomer of $Cl_2O_2^+$ by association of Cl_2^+ with O_2. Eqs. (3) and (4) show the most likely reactions.

$$Cl_2^+ + O_2 \rightarrow Cl_2O_2^+ \quad (3)$$

$$Cl_2 + O_2^+ \rightarrow Cl_2O_2^+ \quad (4)$$

Reaction (3) is believed to be dominant because of a higher abundance of Cl_2^+ (recombination energy 11.480 eV) compared to O_2^+ (recombination energy 12.071 eV). Cacace et al. [5] presented evidence that the isomer of $Cl_2O_2^+$ that was prepared by association of Cl_2^+ with O_2 had the connectivity of the $Cl_2O_2^+$ cation isolated in the solid phase. This was supported by the dominance of Cl_2^+ and O_2^+ in the CID spectrum. Because there is no experimental thermochemistry for this isomer of $Cl_2O_2^+$, we performed energy-resolved CID measurements on this ion.

Trapezoidal $Cl_2O_2^+$ is related to the X_4^+ (X = halogen) radical cations. The Seppelt group has also determined a crystal structure for Cl_4^+, and our group has measured

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* Corresponding author. Tel.: +1 815 753 6870; fax: +1 815 753 4802.
E-mail address: sunder@niu.edu (L.S. Sunderlin).

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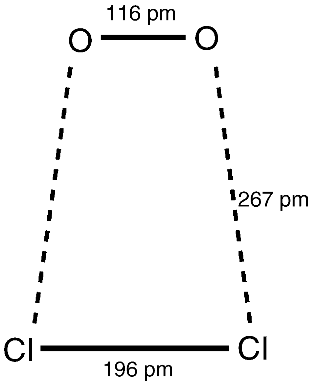

Fig. 1. Computed (B3LYP/aug-cc-pVTZ) geometry for $Cl_2O_2^+$.

dissociation enthalpies for X = Cl, Br, and I [6]. $Cl_2O_2^+$ is a weakly bound radical cation, like X_4^+. However, $Cl_2O_2^+$ has less symmetry (C_{2v} instead of D_{2h}), and one of the dissociation products (O_2) has a triplet ground electronic state. Computational difficulties with spin contamination have been noted for F_4^+, particularly in conformations with less symmetry [7]. Such problems are also likely for $Cl_2O_2^+$.

Li and Ng [8] performed G2 calculations of several isomers of Cl_2O_2 and $Cl_2O_2^+$. However, because their main concern was species of atmospheric interest, they did not report results for the neutral or cationic trapezoidal systems. Schwell and coworkers performed photoionization mass spectrometry studies of ClOOCl, determining $\Delta_fH(ClOOCl^+) = 1203 \pm 12$ kJ/mol [9].

2. Methods

2.1. Experimental

The strength of the Cl_2^+–O_2 interaction was measured using the energy-resolved collision-induced dissociation (CID) technique [10,11] in a flowing afterglow-tandem mass spectrometer (MS) [12]. The instrument consists of an ion source region, a flow tube, and the tandem MS. The dc discharge ion source used in these experiments is typically set at 2000 V with 2 mA of emission current. The flow tube is a 92 cm × 7.3 cm i.d. stainless steel pipe that operates at a buffer gas pressure of 0.35 Torr, a flow rate of 200 standard cm^3/s, and an ion residence time of 100 ms. The buffer gas is helium with up to 10% argon added to stabilize the dc discharge.

The $Cl_2O_2^+$ ions used in this study were prepared in the flow tube using the procedure of Cacace et al. [5] shown in Eqs. (3) and (4). Approximately 10^5 collisions with the buffer gas cool the resulting metastable $Cl_2O_2^+$ cluster ions to room temperature.

The tandem MS includes a quadrupole mass filter, an octopole ion guide, a second quadrupole mass filter, and a detector, contained in a stainless steel box that is partitioned into five differentially pumped interior chambers. During CID experiments, the ions are extracted from the flow tube and focused into the first quadrupole for mass selection. The reactant ions are then focused into the octopole, which passes through a reaction cell that contains a collision gas. After the dissociated and unreacted ions pass through the reaction cell, the second quadrupole is used for mass analysis. The detector is an electron multiplier operating in pulse-counting mode.

The energy threshold for CID is determined by modeling the cross section for product formation as a function of the reactant ion kinetic energy in the center-of-mass (CM) frame, E_{cm}. The octopole is used as a retarding field analyzer to measure the reactant ion beam energy zero. The ion kinetic energy distribution for the present data is typically Gaussian with a full-width at half-maximum of 0.9 ± 0.2 eV (1 eV = 96.5 kJ/mol). The octopole offset voltage measured with respect to the center of the Gaussian fit gives the laboratory kinetic energy, E_{lab}, in eV. Low offset energies are corrected for truncation of the ion beam [13]. To convert to the center-of-mass (CM) frame, the equation $E_{cm} = E_{lab}m(m+M)^{-1}$ is used, where m and M are the masses of the neutral and ionic reactants, respectively. All experiments were performed with both mass filters at low resolution to improve ion collection efficiency and reduce mass discrimination. Average atomic masses were used for all elements.

One complication with $Cl_2O_2^+$ is that another ion with a similar mass, Cl_3^+, is also created in the ion source. The main isotopic peaks of $Cl_2O_2^+$ are at 102, 104, and 106 amu, while the main peaks of Cl_3^+ are at 105, 107, 109, and 111 amu. In the present experiments, the first quadrupole was set to low resolution at a relatively low mass setting such that no ions heavier than 104 were transmitted. This avoided interference from Cl_3^+. The average reactant mass used was adjusted to account for the actual distribution of the transmitted ions.

Collision-induced dissociation data collected for weakly bound ions can give data that is difficult to fit because several of the assumptions made in the fitting procedure are less valid near zero energy in the laboratory frame [13]. These effects can cause measured thresholds to be too low. This problem can be alleviated by using a lighter collision gas. On the other hand, energy transfer during collisions with light collision partners like Ne can be less efficient, giving thresholds that are too high [14,15]. Therefore, CID experiments with $Cl_2O_2^+$ were done with both Ar and Ne as collision gases.

The total cross section for a reaction, σ_{total}, is calculated using $I = I_0 \exp(-\sigma_{total} nl)$, where I is the intensity of the reactant ion beam, I_0 is the intensity of the incoming beam ($I_0 = I + \sum I_i$), I_i is the intensity of each product ion, n is the number density of the collision gas, and l is the effective collision length, 13 ± 2 cm. Individual product cross sections σ_i are equal to $\sigma_{total}(I_i/\sum I_i)$. Data taken at several pressures is extrapolated to a zero pressure cross section before fitting the data to avoid the effects of secondary collisions [16].

Threshold energies are derived by fitting the data to a model function given in Eq. (5), where $\sigma(E)$ is the cross section for formation of the product ion at center-of-mass energy E, E_T is the desired threshold energy, σ_0 is the scaling factor,