NOTES

Photodissociation of Cl_2O at 248 and 308 nm

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INTRODUCTION

Studies of the photodissociation dynamics of Cl_2O (dichlorine monoxide) can aid in understanding the photochemistry of the more complex chlorine oxides which play a major role in stratospheric ozone depletion. As we reported in a previous publication,[1] the formation of Cl+ClO products (ΔH_0^o=33.8 kcal/mol)[2] is the only channel observed for Cl_2O photolysis at 308 nm and is the major channel at 248 nm. We have repeated the Cl_2O photolysis experiment at 248 and 308 nm and present here a refinement of the analysis for the Cl+ClO channel. At 248 nm, three distinct dissociation pathways that led to Cl+ClO products were resolved. At 308 nm, the angular distribution is slightly more isotropic than previously reported.

The experimental method and apparatus are described elsewhere.[3] Briefly, a molecular beam was crossed with an excimer laser beam at the center of rotation of a rotatable mass spectrometer detector. Collisionless conditions allowed for the detection of primary dissociation products recoiling away from the beam direction. Photoproduct time-of-flight (TOF) distributions were measured as a function of the detector angle.

The new data were recorded on the same apparatus under similar conditions that differed primarily in source conditions and laser polarization. For the new experiment, a continuous molecular beam of Cl_2O was formed by passing a gas mixture of 2% SF_6 in helium over the surface of liquid Cl_2O at −73 °C and expanding the mixture through a 0.1 mm quartz nozzle held at or below −60 °C with a stagnation pressure of 190 Torr. In all experiments, the laser beam was nearly randomly polarized in a plane perpendicular to the scattering plane and parallel to the molecular beam axis. In the current experiment, there was a slight net polarization (~58%) perpendicular to the scattering plane, whereas previously there was a slight net polarization parallel to that plane. The differences in the beam conditions and the laser polarization were taken into account in the analysis.

Analysis of product TOF and angular distributions were carried out by the forward convolution technique used previously. For each channel, center of mass (c.m.) translational energy $P(E_T)$ and angular $w(\theta)$ distributions were transformed to the LAB frame and adjusted iteratively until the predicted LAB TOF distributions agreed with the observed distributions at all LAB angles. The c.m. angular distributions were fit to $w(\theta) \propto 1 + \beta P_2(\cos\theta)$, where the anisotropy parameter β varies from −1 to 2 for dissociation with the recoil vector perpendicular and parallel to the transition dipole, respectively.

248 nm

Representative TOF distributions of products from 248 nm photolysis are shown in Fig. 1. The m/z=51 (ClO^+) data could not be fit at all angles with a single $P(E_T)$ distribution as was done in the previous work. Instead, the three observed peaks at m/z=51 were fit with three separate components in the $P(E_T)$ distribution (Fig. 2), each with different anisotropy parameters. The fastest component had a large translational energy release with a maximum at 49 kcal/mol (E_{int}=33 kcal/mol). The angular distribution was fit by β=0.7±0.2, indicating a prompt, parallel dissociation. The middle component had an average translational energy release of $\langle E_T\rangle$=36 kcal/mol ($\langle E_{int}\rangle$=46 kcal/mol) and anisotropy of β=1.5±0.2. A fit to the slowest component gave β=1.2±0.2 and a $P(E_T)$ distribution with a sharp cutoff

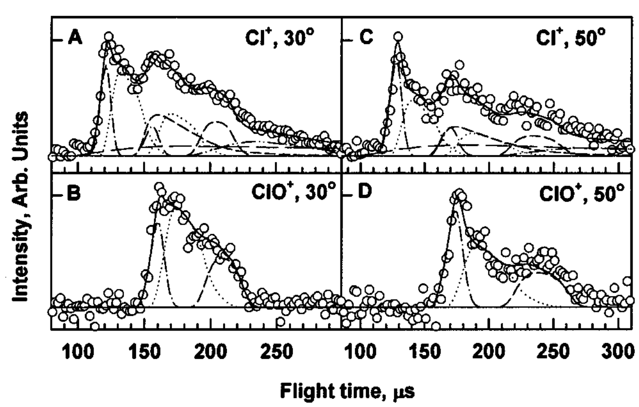

FIG. 1. TOF number density distribution $N(t)$ from Cl_2O photolysis at 248 nm for (A) Cl^+ products collected at a detector angle of 30°, (B) ClO^+ products at 30°, (C) Cl^+ products at 50°, and (D) ClO^+ products at 50°. The solid line is the overall fit to the data. The dashed, dotted, and dot–dashed lines correspond to the three components in the c.m. $P(E_T)$ distribution (Fig. 2). The long-dashed line in (A) and (C) is a hypothetical fit based on photolysis of Cl_2O clusters in the beam. The dot–dot–dashed line in (A) and (C) corresponds to the spontaneous secondary dissociation of ClO. Stimulated secondary dissociation of ClO is not included.

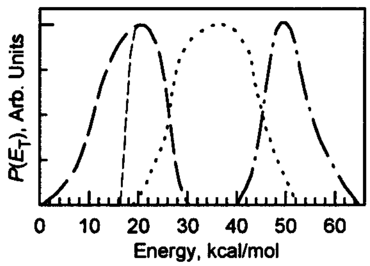

FIG. 2. Optimized c.m. $P(E_T)$ distributions for the Cl+ClO channel from Cl_2O photolysis at 248 nm. The light-dashed line in the slowest component shows the cutoff from the $m/z=51$ data, corresponding to internal energies beyond the ClO dissociation limit. The anisotropy parameters and average translational energies for each component are dashed line, $\beta=1.2\pm0.2$, $\langle E_T\rangle=17.8$ kcal/mol; dotted line, $\beta=1.5\pm0.2$, $\langle E_T\rangle=35.9$ kcal/mol; and dot–dashed line, $\beta=0.7\pm0.2$, $\langle E_T\rangle=51.1$ kcal/mol. The scaling factor for each component is independent of angle.

with a minimum E_T of 14±1 kcal/mol. The cutoff was due to opening of the $Cl_2O\rightarrow Cl+Cl+O$ channel, because the internal energy of the ClO product exceeded the bond dissociation energy ($D_0=63.4$ kcal/mol) for products with $E_T>19.0$ kcal/mol. The 5 kcal/mol discrepancy could be attributed to (a) spin–orbit excitation (2.5 kcal/mol) of one or both Cl atom products,[4] (b) a centrifugal barrier to dissociation of rotationally excited ClO products (in the rigid radical approximation,[5] the ClO centrifugal barrier could be as high as 7.3 kcal/mol), or (c) a combination of these causes.

The $m/z=35$ signal (Figs. 1A, C) comprised direct Cl photoproducts, Cl atoms from secondary dissociation of ClO, ClO fragments which cracked in the ionizer, and background from cluster photolysis. In order to fit the Cl counterfragment, we extended the slowest $P(E_T)$ distribution to lower translational energies. We concluded that ≈4% of the ClO underwent spontaneous dissociation. The secondary Cl signal from this dissociation was modeled and included in the fit. Contributions from primary ClO products were fit assuming 32%, 37%, and 49% of the ClO fragmented to Cl^+ in the ionizer with the extent of fragmentation increasingly linearly with ClO internal energy. Photodissociation of ClO was also observed at higher laser power, but was minimized by keeping laser fluences low. A small underlying signal remained, which we assigned to products from photolysis of Cl_2O clusters.

In summary, we have now resolved three components in the $P(E_T)$ distribution with differing anisotropies, each leading to Cl+ClO products. These results support our conjecture that the formation of Cl+ClO products involves several excited state potential energy surfaces.

308 nm

At 308 nm, the $m/z=51$ (ClO^+) TOF spectra were fit by a $P(E_T)$ distribution very similar to the one published previously, with a peak at 33 kcal/mol and a slow shoulder extending down to 6.5 kcal/mol. The angular distribution, fit with $\beta=0.4\pm0.3$, was slightly less anisotropic than previously reported.

A long-lived excited state of Cl_2O was recently proposed by Nickolaisen *et al.*[6] to explain quenching at high pressures of the ClO yield from Cl_2O photolysis at $\lambda>300$ nm in flow tube studies. They postulated a metastable excited state which must live longer than the mean collision time at 5 Torr of ~50 ns. Such a lifetime would lead to complete rotational averaging of the anisotropic angular distribution, resulting in $\beta\leqslant0.19$ if Cl_2O dissociates from its ground state geometry.[7] This value of β is half of the observed value, but within our uncertainty. Our results thus indicate that $\tau<9$ ps at 308 nm, but our uncertainties preclude us from ruling out a longer-lived state.

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