Time-Resolved Studies of Nitrosyl Halide Photoreaction Dynamics

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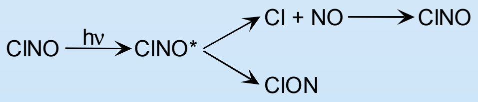
Introduction

The photochemistry of chlorine-containing compounds is an important area in atmospheric chemistry due the participation of these species in chemical cycles involving atomic chlorine (Cl), a central species in stratospheric ozone depletion.[1] One such class of compounds are halooxides such as chlorine dioxide (OClO) and dichlorine monoxide (ClOCl). Transient absorption and time-resolved resonance Raman studies[2] of aqueous OClO have found that the dominant photochemical pathway is dissociation to form ClO and O followed by geminate recombination of these photoproducts resulting in reformation of OClO. The minor photochemical pathway is isomerization to form ClOO which appears with a time constant of ~30 ps and decays on the sub-nanosecond timescale. In comparison, transient absorption studies of ClOCl dissolved in perfluorohexane[3] have found that the dominant photochemical pathway is production of the isomer ClClO, with little evidence for Cl and ClO production and geminate recombination. The appearance and decay time constants of ClClO, ~10 ps and ~100 ps respectively, are similar to those of ClOO suggesting that photoisomerization is a general feature of halooxide photochemistry in condensed environments.

To extend our understanding of the condensed phase photochemistry of chlorine-containing molecules, we have initiated a series of studies involving nitrosyl halides, and in particular nitrosyl chloride (ClNO).[4] In the gas phase, photoexcitation of ClNO results in dissociation to form Cl and NO with a quantum yield near unity.[5] Matrix-isolation studies of ClNO have found that photoexcitation results in formation of the isomer, ClON.[6] The similarity of ClNO photochemistry to that of OClO and ClOCl, namely direct dissociation in the gas phase and photoisomerization in low-temperature matrices, suggests that the photochemistry of ClNO in solution should be similar as well. To see if this is the case, we have performed transient absorption studies of ClNO dissolved in two solvents, acetonitrile and chloroform. ClNO is photoexcited at 266 nm and the subsequent dynamics are probed throughout the UV. The absorption spectra for ClNO and its possible photolysis species are shown in Figure 1.



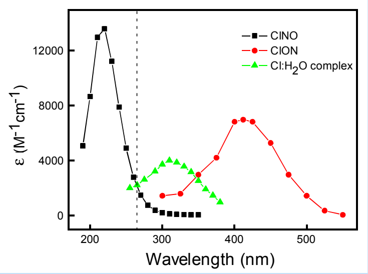


Figure 1. Absorption spectrum of ClNO and its possible photoproducts. The molar absorptivity values are for ClNO dissolved in acetonitrile.[7] The absorption spectrum of the structural isomer, ClON, is for this species isolated in an argon matrix[6] and the absorption spectrum of the $Cl:H_2O$ charge-transfer complex is taken from the literature.[8] The dashed line indicates the excitation wavelength used in this study.

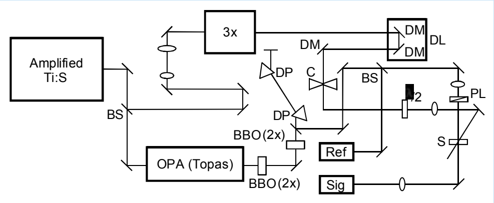


Figure 2. Schematic of the pump-probe spectrometer used in this study. The following abbreviations have been used: BS: beam splitter, OPA: optical parametric amplifier, BBO: frequency-doubling crystal, DP: Brewster dispersion prism, PL: calcite polarizer, S: sample, 3x: frequency tripler, DM: dichroic mirror, DL: optical delay line, C: chopper, l/2: zero-order half-wave plate.

References

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Results

- Photolysis of ClNO in both solvents results in an initial decrease in optical density at 256 nm and 266 nm consistent with ground state depletion of ClNO. An increase in optical density at longer probe wavelengths is also observed, with the maximum change in optical density occurring at ~295 nm in acetonitrile and at ~331 nm in chloroform.

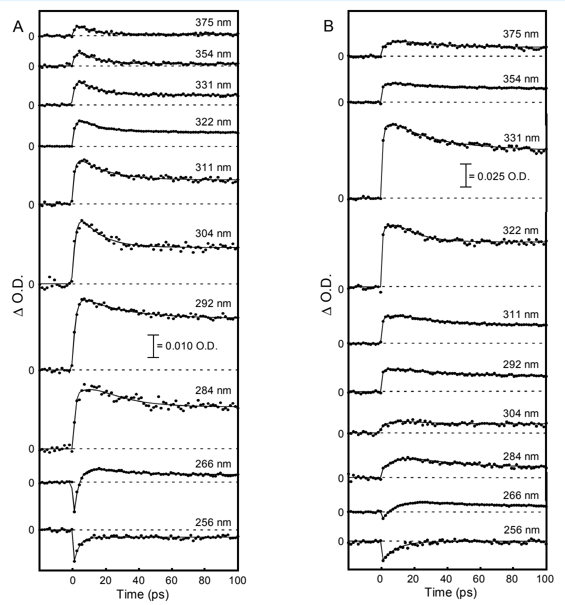

Figure 3. Time-resolved pump-probe dynamics of ClNO dissolved in (A) acetonitrile and (B) chloroform for 266 nm pump. Probe wavelengths and optical density scale are indicated in the figure. A sum of exponentials convolved with the instrument response provides the best fit to the data as shown by the solid line.

- The absolute change in optical density following ClNO photolysis demonstrates that photoproduct formation in chloroform results in a significantly larger change in optical density compared to acetonitrile. In addition, the photoproduct produced in acetonitrile appears to be undergoing vibrational relaxation where similar evolution is not observed in acetonitrile.

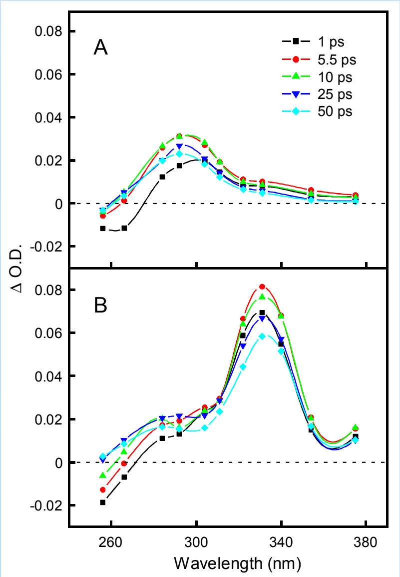

Figure 4. The transient absorption spectrum of ClNO dissolved in (A) acetonitrile and (B) chloroform. The time delay for each spectrum is given in the figure.

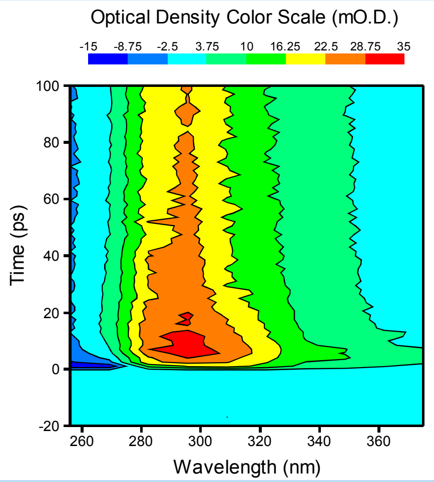

Figure 5. Contour plot of the transient absorption spectrum of ClNO dissolved in acetonitrile. The absolute change in optical density is indicated by the contour lines, with the color scale shown above the plot. The plot shows the blue-shifting and band narrowing typical of vibrational relaxation. This behavior is not observed for the 330 nm band produced from the photolysis of ClNO dissolved in chloroform.

Acknowledgements

This work was supported by the NSF and ACS-PRF. CCC gratefully acknowledges support from the Ford Foundation.

Discussion

The results presented here represent the first detailed measurements of ClNO photochemistry in solution. The measured evolution in optical density following ClNO photolysis in acetonitrile is consistent with the production of a photoproduct having an absorption band centered at 295 nm. In contrast, photolysis of ClNO dissolved in chloroform results in production of a photoproduct with an absorption maximum at 331 nm. **There are two possible assignments for the photoproduct: the Cl:solvent charge-transfer complex or the structural isomer, ClON.**

- **Evidence for Cl:solvent charge-transfer complex formation**

1. To determine the location of the absorption band for the Cl:solvent charge transfer complex in chloroform, we performed a transient absorption study of methyl hypochlorite (MeOCl) in dichloromethane (Figure 6). The ionization potentials of dichloromethane and chloroform are roughly the same; therefore, the absorption maximum for the charge transfer complex in these solvents should be similar. Following photoexcitation of MeOCl in dichloromethane, a broad absorption band is observed centered at 340 nm, similar to the 331-nm band observed following ClNO photoexcitation in chloroform. However, the photoproduct absorption band derived from ClNO is significantly different in comparison to that formed from MeOCl. Also, the appearance and decay kinetics of the ClNO photoproduct band are slower in comparison to MeOCl.

2. The $Cl:H_2O$ charge-transfer complex has maximum absorption at 310 nm. The similarity of the ionization potentials for water and acetonitrile suggests that the Cl:acetonitrile charge-transfer complex would have a similar absorption maximum consistent with the observation of the photoproduct absorption at 295 nm.

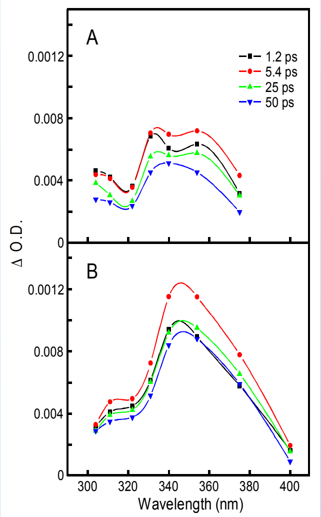

Figure 6. The transient absorption spectrum of (A) CH_3OCl and (B) ClNO dissolved in dichloromethane. The time delay for each spectrum is given in the figure.

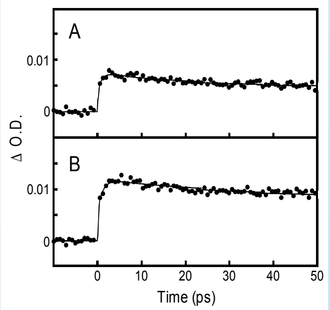

Figure 7. Time-resolved pump-probe dynamics of (A) CH_3OCl and (B) ClNO dissolved in dichloromethane for 266 nm pump and 340 nm probe. A sum of exponentials convolved with the instrument response provides the best fit to the data as shown by the solid line. Visual inspection as well as comparison of the time constants indicate that the kinetics for appearance and decay are slower for ClNO/dichloromethane.

- **Evidence for ClON production**

1. Infrared spectroscopy confirmed the formation of ClON following photolysis of ClNO trapped in Ar and N_2 matrixes.[6] In addition, both theoretical and matrix isolation studies have suggested that the cross section for ClON is significantly larger than that of ClNO.[6a,9] The maximum optical density change observed for the photoproduct is consistent with a molar absorptivity for this species that is at least 3 times larger than that of ClNO at 256 nm given the depletion intensity observed at this wavelength. Therefore, the molar absorptivity of the photoproduct is ≥ 10,000 $M^{-1}cm^{-1}$ (Figure 4).

2. UV absorption spectra taken before and after photolysis of ClNO in a low-temperature matrix are consistent with a ClON absorption-band maximum at 417 nm (Figure 1). Both photoproduct bands in this experiment are considerably blue-shifted relative to this value. However, theoretical calculations predict that the Cl-O bond in ClON is quite weak, and modification of this bond length in solution may have a substantial impact on the absorption spectrum. Therefore, it is possible that the ClON absorption band is shifted in solution relative to the matrix results.

Conclusion and Future Work

In order to test the above photoproduct assignments, we plan to employ time-resolved vibrational spectroscopy. Time-resolved UV pump-IR probe can be used to probe the Cl:solvent charge transfer complex complementary pair, NO. In addition, production of the structural isomer, ClON, can be monitored with time-resolved resonance Raman spectroscopy.