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 to 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 nitrite (ClNO) and nitrosyl chloride (ClONO).

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.

- Evidence for Cl:solvent charge-transfer complex formation

Discussion

The results presented here represent the first detailed measurements of ClNO photochemistry. The measured evolution in optical density following ClNO photolysis is consistent with the production of a photoproduct having an absorption band centered at 231 nm. In contrast, the photolysis results in production of a photoproduct with an absorption maximum at 311 nm. There are two possible assignments for the photoproduct: the Cl:solvent charge-transfer complex or the structural isomer, ClON.

Figure 1. Absorption spectrum of ClNO and its possible photoproducts. The major absorbance bands are for ClNO dissolved in acetonitrile.[2] The absorption spectrum of the structural isomer, ClON, is for this species isolated in an argon matrix.[6] The similarity of ClNO photochemistry to that of OClO and ClONO, namely direct dissociation in the gas phase and photodissociation 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 photolyzed at 266 nm and the transient spectra are probed throughout the UV.

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.

Figure 4. The transient absorption spectrum of (A) ClNO, (B) ClONO, and (C) ClNO dissolved in dichloromethane. 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 ClONO and ClNO produced from the photolysis of ClNO dissolved in dichloromethane.

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

Figure 7. Time-resolved pump-probe dynamics of ClNO, ClONO, and ClNO dissolved in dichloromethane for 266 nm pump and 360 nm probe. A sum of exponentials convolved with the instrument response provides the best fit to the data as shown by the solid line.

Acknowledgements

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

References


Conclusion and Future Work

In order to test the above photoproduct assignments, we plan to employ time-resolved vibrational spectroscopy. Time-resolved UV pump-RF 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.