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Solution Photochemistry of Chlorine Dioxide: Mechanisms for the Generation of Atomic Chlorine

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Chlorine and bromine oxides play an important role in the destruction of stratospheric ozone over Antarctica. Recent reports indicate that more than 20% of the ozone decline is caused by the coupling of chlorine and bromine oxide cycles.[1] Among other products, this coupling results in the formation of ClOO and OClO. While the former is known to destroy ozone through the formation of atomic chlorine and molecular oxygen, the role of OClO in the stratospheric ozone balance is currently a topic of debate. Early photochemical studies of OClO indicated that excitation dissociates the molecule into ClO and O.[2] If this were the sole photochemical process, OClO would not affect the balance of stratospheric ozone. However, recent work of Vaida and coworkers established the existence of a parallel photochemical channel, producing Cl and O_2.[3,4]

The photodecomposition of OClO occurs from the $^2B_2$ electronic state.[5,6] Reactions from the $^2B_2$ state can generate Cl by two reaction paths, given by eqs 1 and 2.[7] The electronic states of the products are determined by orbital correlation. The first

$$\mathrm{OClO} + h\nu \rightarrow \mathrm{ClOO}\ (\mathrm{A}' \text{ or } \mathrm{A}'') \rightarrow \mathrm{Cl}\ (^3\mathrm{P}) + \mathrm{O}_2\ (^3\Sigma_{g^-}) \quad (1)$$

$$\mathrm{OClO} + h\nu \rightarrow \mathrm{Cl}\ (^3\mathrm{P}) + \mathrm{O}_2\ (^1\Delta_g) \quad (2)$$

mechanism, eq 1, occurs by photoisomerization of OClO to ClOO, which can be produced either in the ground state, A′, or the first electronic excited state, A″. While thermodynamically more stable than OClO, ClOO is kinetically unstable and readily dissociates to form Cl and O_2 ($^3\Sigma_g^-$).[7] The second mechanism involves symmetric dissociation (along a C_{2v} reaction coordinate) producing Cl + O_2 ($^1\Delta_g$). These are the only two allowed symmetry channels of Cl production from the $^2B_2$ excited state.[8] The electronic state of the product oxygen molecule provides an experimental handle by which the relative importance of these two chlorine-producing mechanisms can be distinguished.

By taking advantage of the well-characterized spectroscopy of OClO[11], Cl[12], ClO[12], and O_2[13] in water solution, one can determine the relative roles of these reaction paths. In solution, unlike the gas phase, chlorine atoms are easily detected as they readily form charge-transfer (CT) complexes with solvent molecules. This gives rise to a CT absorption, which, for many solvents, occurs in the near-UV to visible spectral region.[14] Transient absorption studies of the photolysis of OClO at 355 nm in water solution reveal a quantum yield of 0.1 ± 0.01 for Cl production.[15] To determine the relative importance of the two allowed mechanisms for Cl generation, the quantum yield for formation of either O_2 ($^1\Delta_g$) or O_2 ($^3\Sigma_g^-$) is needed.[16]

The $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ emission of O_2 was observed following excitation of OClO at 355 nm in D_2O, C_6D_6, and CCl_4. By comparing the intensity of this emission (1270 nm) with that of sensitizers for which the yield is known,[13,17] the quantum yield of O_2 ($^1\Delta_g$) formation in D_2O was found to be 0.005 ± 0.003.[15,16] Thus, in water solution, 95% of the Cl is produced from the isomerization pathway, eq 1; the remaining 5% results from the symmetric dissociation, eq 2.[15] The importance of the symmetric C_{2v} dissociation increases with decreasing solvent polarity. The quantum yields of Cl + O_2 ($^1\Delta_g$) production in C_6D_6 (ET (30) = 34.5 kcal/mol) and carbon tetrachloride (ET (30) = 32.5 kcal/mol) are 0.02 and 0.07, respectively, much larger than in D_2O (ET (30) = 63.1 kcal/mol).[19] The increase in the amount of symmetric C_{2v} dissociation with decreasing solvent polarity suggests that this mechanism may be important in the gas phase chemistry of OClO.

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(5) There are three closely spaced excited states of OClO ($^2A_2$, $^2A_1$, and $^2B_2$).[6] Excitation of ground-state OClO populates the $^2A_2$ excited electronic state. Calculations by Peterson and Werner[6] reveal barriers on the exit channels for formation of ClO and O from both the $^2A_2$ and $^2A_1$ states. However, the $^2B_2$ state is dissociative along this coordinate. These results support the conclusion that the competing photoreactions of this molecule occur from the $^2B_2$ state. Spin–orbit coupling and vibronic mixing enable the molecule to relax to the reactive $^2B_2$ state (presumably via $^2A_2 \rightarrow {}^2A_1 \rightarrow {}^2B_2$; however, direct relaxation from the $^2A_2$ state to the $^2B_2$ state cannot be ruled out).

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(15) In our earlier study, spectroscopic and kinetic evidence was presented which established that ClOO was a precursor to Cl production for photolysis of OClO in water. This analysis used the gas-phase spectrum of ClOO for modeling the kinetics, as no solution spectrum has been reported. Without knowledge of the absorption cross sections in solution, the optical study is unable to establish whether or not all Cl is generated from ClOO.

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