

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

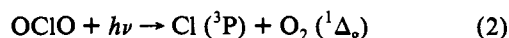
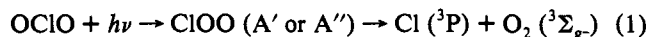
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Chlorine and bromine oxides play an important role in the destruction of stratospheric ozone over Antarctica. Recent reports indicate that more than 20% of the ozone decline is caused by the coupling of chlorine and bromine oxide cycles.¹ Among other 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 co-workers established the existence of a parallel photochemical channel, producing Cl and O₂.^{3,4}

The photodecomposition of OClO occurs from the ²B₂ electronic state.^{5,6} Reactions from the ²B₂ 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



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 O₂ (³Σ_g⁻).⁷ The second mechanism involves symmetric dissociation (along a C_{2v} reaction coordinate) producing Cl + O₂ (¹Δ_g). These are the only two allowed symmetry channels of Cl production from the ²B₂ excited state.⁸ The electronic state of the product oxygen molecule provides an

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(5) There are three closely spaced excited states of OClO (²A₂, ²A₁, and ²B₂).⁶ Excitation of ground-state OClO populates the ²A₂ excited electronic state. Calculations by Peterson and Werner⁶ reveal barriers on the exit channels for formation of ClO and O from both the ²A₂ and ²A₁ states. However, the ²B₂ state is dissociative along this coordinate. These results support the conclusion that the competing photoreactions of this molecule occur from the ²B₂ state. Spin-orbit coupling and vibronic mixing enable the molecule to relax to the reactive ²B₂ state (presumably via ²A₂ → ²A₁ → ²B₂; however, direct relaxation from the ²A₂ state to the ²B₂ state cannot be ruled out).

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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 OClO¹¹, Cl¹², ClO¹², and O₂¹³ 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 O₂ (¹Δ_g) or O₂ (³Σ_g⁻) is needed.¹⁶

The ³Σ_g⁻ → ¹Δ_g emission of O₂ was observed following excitation of OClO at 355 nm in D₂O, C₆D₆, and CCl₄. 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 O₂ (¹Δ_g) formation in D₂O 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 + O₂ (¹Δ_g) production in C₆D₆ (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 D₂O (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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(8) Gas-phase studies of OClO indicate mode specificity in the reaction products. Excitation of the bending vibration enhances the yield of Cl + O₂.⁹ Excitation of the asymmetric stretch enhances the production of ClO + O.¹⁰ The production of Cl + O₂ along an asymmetric reaction coordinate that does not involve ClOO as a reactive intermediate is not considered in this discussion.

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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.

(16) The apparatus was nearly identical to that previously described in the following: Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886. The only change was that the detector was a 0.25-cm² Ge diode/preamplifier unit (North Coast EO-817P) operating at a bias of -250 V, supplied by a North Coast Model 823 bias supply.

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(18) Quantum yields of singlet oxygen were determined by extrapolation of the emission intensities to zero time, which were corrected to 100% absorption (from absorbances varying from 0.2 to 0.6). These were compared to the singlet oxygen quantum yields of the standard sensitizers *meso*-tetrakis(4-sulfonatophenyl)porphine in D₂O¹⁹ or acridine in C₆D₆ and CCl₄.²⁰ All measurements were carried out under air-saturated conditions.

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