Oxalyl Chloride, $(COCl)_2$, UV Spectrum and Cl Quantum Yields at 193, 248 and 351 nm, and the Kinetics of the ClCO + M Reaction

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Oxalyl chloride, $(COCl)_2$, is commonly used in laboratory studies as a photolytic precursor of Cl atoms. Here, we report the UV-Vis absorption spectrum of $(COCl)_2$ between 200 and 450 nm at 298 K measured using diode array spectroscopy and the Cl quantum yield, $\Phi(\lambda)$, in the pulsed laser photolysis of $(COCl)_2$ at 193, 248, and 351 nm measured at 298 K using atomic resonance fluorescence. Oxalyl chloride UV photolysis occurs via an impulsive three-body dissociation mechanism into CO, Cl, and ClCO*

$$(COCl)_2 + h\nu \rightarrow ClCO^* + Cl + CO \quad (1)$$

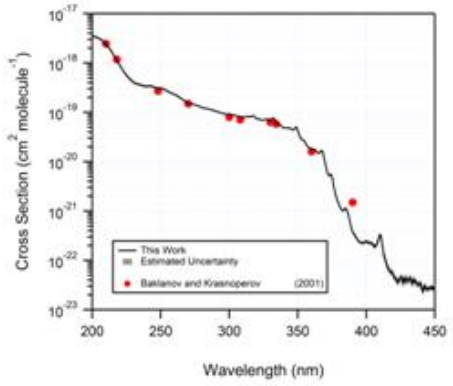
where excited ClCO, ClCO*, can subsequently dissociate or stabilize

$$ClCO^* \rightarrow Cl + CO \quad (2a)$$
$$\rightarrow ClCO \quad (2b)$$

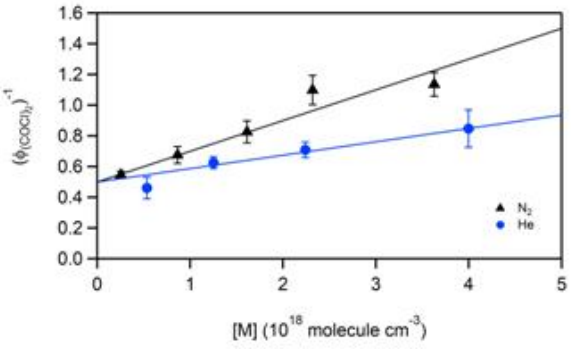
ClCO is thermally unstable under the temperatures and pressures of our experiments

$$ClCO + M \rightarrow Cl + CO + M \quad (3)$$

leading to the formation of a Cl atom, which was resolvable in the Cl atom temporal profile. At 193 nm, $\Phi(\lambda)$ was found to be 2.07 ± 0.37 and consistent with a branching ratio for channel 2a greater than 0.9. At 248 nm, a branching ratio of 0.80 for channel 2a was determined, while the overall Cl atom quantum yield, following the completion of reaction 3, was found to be 1.98 ± 0.26, independent of bath gas pressure (15-70 Torr). The photolysis quantum yield at 351 nm was pressure dependent suggesting the involvement of a long-lived excited electronic state. In the low-pressure limit the overall Cl atom quantum yield was 2 ± 0.22. The $\Phi(\lambda)$ measurements and interpretation will be discussed. The thermal decomposition rate coefficient of ClCO was measured as part of this work over the 13-128 Torr pressure range at temperatures between 253 and 298 K with He and N_2 bath gas. Our results will be compared with results from previous studies.



UV-Vis spectrum of oxalyl chloride.



Stern-Volmer plot for the 351 nm photolysis of oxalyl chloride.

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