

Quenching of organic triplet donors by fluorinated β -diketonates of Cr(III)

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The influence of fluorine substitution on the quenching behaviour of ligand-fluorinated Cr(III) β -diketonates was examined in fluid solution by flash photolysis. Rate constants for quenching of the triplet state of selected organic molecules were measured in benzene solution at room temperature. The results indicate that the mechanism of quenching is electronic energy transfer. The quenching rate constants were found to be dependent on the energy of the donor and the accessible energy levels of the complex. The contribution of the undistorted doublet states and the distorted quartet states to the quenching efficiency is modified by spin statistical factors. Comparison of the results with data already published indicates that the $-\text{CF}_3$ group enhances the quenching efficiency by causing expansion of the metal t_{2g} orbitals.

Photochemical oxidation of XCFCF_2 ($\text{X} \equiv \text{H, F, Cl, Br, I}$)

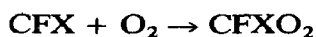
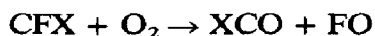
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The oxidation of XCFCF_2 ($\text{X} \equiv \text{H, F, Cl, Br, I}$) initiated by $\text{O}(^3\text{P})$ and chlorine atoms was studied at room temperature. In the reactions of CF_2CFCl and CF_2CFBr with $\text{O}(^3\text{P})$ the only product was CF_2O . With CF_2CFH a small amount of CFHO was also produced.

In the chlorine-atom-sensitized oxidation a long chain reaction with quantum yields larger than 100 was observed at low total pressure in the five olefins. For $\text{X} \equiv \text{Cl, Br}$ and I the corresponding $\text{CF}_2\text{XCF}(\text{O})$ compound was the main product. In the other two cases CF_2O and CFXO were the oxidation products.

The key reactions to explain the oxidation products in the system with $\text{O}(^3\text{P})$ in the presence of O_2 are



followed by a biradical chain reaction for C_2HF_3 , biradical and monoradical simultaneous chain reactions for $\text{C}_2\text{F}_3\text{Cl}$ and a monoradical chain reaction for $\text{C}_2\text{F}_3\text{Br}$.

A complete oxidation scheme is given and discussed.