

Branching Ratio for the Self-Reaction of Acetonyl Peroxy Radicals

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Mixtures in air of chlorine, acetone, nitrogen dioxide, and nitric oxide (partly) were photolysed at 330 nm wavelength to produce acetonyl peroxy radicals and to determine the fraction of acetonoxo radicals formed in one of the two branches of the self-reaction of acetonyl peroxy, $2\text{CH}_3\text{COCH}_2\text{OO}\cdot \rightarrow \text{CH}_3\text{COCHO} + \text{CH}_3\text{COCH}_2\text{OH} + \text{O}_2$ (3a) and $2\text{CH}_3\text{COCH}_2\text{OO}\cdot \rightarrow 2\text{CH}_3\text{COCH}_2\text{O}\cdot + \text{O}_2$ (3b). In these experiments the decomposition of acetonoxo gives rise to acetyl peroxy radicals, which react with NO_2 to form peroxy acetyl nitrate (PAN). The quantum yield of PAN was measured as a function of time. Computer simulations were used to explore the effect of acetonyl peroxy nitrate as an unstable intermediate formed in the reaction $\text{CH}_3\text{COCH}_2\text{OO}\cdot + \text{NO}_2 \rightleftharpoons \text{CH}_3\text{COCH}_2\text{OONO}_2$ (9). The experimental data were evaluated to derive for the rate coefficients associated with reaction (3) the branching ratio $k_{3b}/(k_{3a} + k_{3b}) = 0.50 \pm 0.05$ and for the reverse path of reaction (9) the rate coefficient $k_{-9} = 10.0 \pm 3 \text{ s}^{-1}$.

Key words: Acetonyl Peroxy; Peroxy Radical; Self-Reaction Branching Ratio; Acetonyl Peroxy Nitrate.