

177.50 nm ($3p^24s (^4P_{1/2,3/2,5/2}) \rightarrow 3p^3 (^4S_{3/2})$) transitions. Excitation was with a microwave-powered atomic resonance lamp. The density of $P(3 ^4S_{3/2})$ atoms was estimated by measuring the concentration of $O(^3P_1)$ atoms formed in the titration reaction $P(^4S_{3/2}) + O_2 \rightarrow PO + O(^3P_1)$. Second-order rate constants (k_R , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1σ); 300 K) are reported for the reactions of $P(3 ^4S_{3/2})$ with O_2 ($(1.01 \pm 0.05) \times 10^{-13}$), Cl_2 ($(6.8 \pm 0.2) \times 10^{-13}$), NO ($(3.3 \pm 0.1) \times 10^{-14}$) and NO_2 ($(1.80 \pm 0.05) \times 10^{-11}$). Similar results were also obtained with a different source of phosphorus atoms, PBr_3 .

The photolysis of azomethane in carbon monoxide and reaction kinetics of acetyl radicals

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The photolysis of azomethane in carbon monoxide leads to a series of markedly interdependent reactions involving methyl and acetyl radicals. We used a molecular modulation spectrometer to monitor each of these radical species directly in the same spectral region and in the same experiment. The kinetic information from the molecular modulation spectrometer was complemented by product analysis studies, conducted under similar experimental conditions, that confirm the reactions involved and reduce the number of unknowns. A computer-based parameter estimation routine was used to determine several rate constants and the absorption cross section for the acetyl radical. The effect of pressure was investigated and, where appropriate, unimolecular rate theory based on Kassel integrals was used to determine limiting low and high pressure rate constants.

Intramolecular relaxation of vibrational energy in alkyl radicals

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Alkyl radicals may be chemically activated at room temperature to the level of about 45 kcal mol^{-1} by the addition of hydrogen atoms to various olefins. This level is about 75 kcal mol^{-1} below that used in previous chemical activation

studies on cyclopropanes and butanes from which picosecond relaxation times have been reported. Hydrogen atoms are produced by the mercury-photosensitized decomposition of H_2 . The critical thresholds for alkyl radical decomposition processes occur in the region 30 - 33 kcal mol⁻¹. Decomposition of the initially produced non-randomized species competes with internal relaxation followed by decomposition by other pathways. A number of systems are described. For 3-hexyl radicals, a relaxation rate of $5 \times 10^{12} \text{ s}^{-1}$ was found.

Vinylidene radicals in photolysis and reactions of hydrocarbons

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Vinylidene radicals ($H_2C=C$): are proposed as important intermediates in the vacuum UV photolysis of C_2H_2 as well as the combination of two triplet CH_2 radicals. The interpretation is based on the vacuum UV absorption spectrum of a long-lived transient observed in these systems as well as mass spectrometric determinations of the yields of deuterated acetylenes produced from the reaction of two triplet $CH_2(CD_2)$ radicals in the presence of large quantities of inert gas. The $CH_2(CD_2)$ radicals were produced from the flash photolysis of CH_2CO-CD_2CO mixtures. The results are discussed both with respect to the mechanisms for dissociation of the combined C_2H_4 and with respect to the energetics of the overall process which, it is proposed, involves an excited triplet of the vinylidene radical.

Photochemical study of peroxy radical interactions in hydrocarbon oxidation

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Measuring the chemiluminescence light level in suitable reaction mixtures and utilizing computer modelling techniques we studied the following processes: (1) the cross-combination of peroxy radicals; (2) the interaction of peroxy radicals with inhibitors; (3) the interaction of peroxy radicals with metal com-