177.50 nm ($3p^2 4s$ ($^4P_{1/2,3/2,5/2}$) → $3p^3$ ($^4S_{3/2}$)) 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 → PO + O($^3P_1$). Second-order rate constants (k_R, cm^3 $molecule^{-1}$ 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