radicals in the 3 μm region. By following the decay of this transient IR absorption, the rate coefficients for the combination and disproportionation reactions between *tert*-butyl radicals were deduced.

State-selective chemistry: the NCl radical

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The kinetics of the NCl radical were studied in a discharge flow system by molecular beam mass spectrometry. Ground X $^3\Sigma^-$ state and metastable excited a $^1\Delta$ and b $^1\Sigma^+$ state NCl radicals were generated via the reaction of excess chlorine atoms with chlorine azide (N_3Cl): $Cl + N_3Cl \rightarrow N_3 + Cl_2$; $Cl + N_3 \rightarrow$ $NCl^* + N_2$. The a $^1\Delta$ and b $^1\Sigma^+$ states of NCl were observed using the a $^1\Delta$–X $^3\Sigma^-$ (1.07 μm) and b $^1\Sigma^+$–X $^3\Sigma^-$ (665 nm) transitions. On the addition of O_2, the excited NCl* radicals were quenched to the ground state. The formation of NCl_2 radicals was also observed in the $Cl + N_3Cl$ system. The addition of Cl_2 increased the NCl_2 concentration. However, the formation of NCl_2 could be completely suppressed by the addition of O_2. It was deduced that the NCl_2 radicals were formed in the state-selective reaction of metastable excited state NCl* radicals with Cl_2: $NCl^* + Cl_2 \rightarrow NCl_2 + Cl$; $NCl(X\ ^3\Sigma^-) + Cl_2 \not\rightarrow NCl_2 + Cl$. Thus the kinetics of ground state NCl could be studied in the absence of excited NCl* and NCl_2 by the addition of O_2. Rate constants for the reactions $NCl + NCl \rightarrow N_2 + 2Cl$ and $NCl + NO \rightarrow N_2O + Cl$ were determined, *e.g.* $k^{295}(NCl + NO) = (1.3 \pm 0.1) \times 10^{-11}$ cm^3 s^{-1}.

Direct determination of the rate constants of elementary reactions of atomic phosphorus using high sensitivity resonance fluorescence detection

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The reactions of ground state phosphorus atoms P(3 $^4S_{3/2}$) with the molecules O_2, Cl_2, NO, NO_2 and PCl_3 were studied by using the vacuum UV atomic resonance fluorescence technique in a flow system. P(3 $^4S_{3/2}$) was generated by microwave discharge of PCl_3 in the presence of excess helium carrier gas and the atomic resonance fluorescence was monitored using the 178.77, 178.29 and

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, 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