

radicals in the  $3\ \mu\text{m}$  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 ( $\text{N}_3\text{Cl}$ ):  $\text{Cl} + \text{N}_3\text{Cl} \rightarrow \text{N}_3 + \text{Cl}_2$ ;  $\text{Cl} + \text{N}_3 \rightarrow \text{NCl}^* + \text{N}_2$ . The  $a\ ^1\Delta$  and  $b\ ^1\Sigma^+$  states of NCl were observed using the  $a\ ^1\Delta-X\ ^3\Sigma^-$  ( $1.07\ \mu\text{m}$ ) and  $b\ ^1\Sigma^+-X\ ^3\Sigma^-$  (665 nm) transitions. On the addition of  $\text{O}_2$ , the excited  $\text{NCl}^*$  radicals were quenched to the ground state. The formation of  $\text{NCl}_2$  radicals was also observed in the  $\text{Cl} + \text{N}_3\text{Cl}$  system. The addition of  $\text{Cl}_2$  increased the  $\text{NCl}_2$  concentration. However, the formation of  $\text{NCl}_2$  could be completely suppressed by the addition of  $\text{O}_2$ . It was deduced that the  $\text{NCl}_2$  radicals were formed in the state-selective reaction of metastable excited state  $\text{NCl}^*$  radicals with  $\text{Cl}_2$ :  $\text{NCl}^* + \text{Cl}_2 \rightarrow \text{NCl}_2 + \text{Cl}$ ;  $\text{NCl}(X\ ^3\Sigma^-) + \text{Cl}_2 \not\rightarrow \text{NCl}_2 + \text{Cl}$ . Thus the kinetics of ground state NCl could be studied in the absence of excited  $\text{NCl}^*$  and  $\text{NCl}_2$  by the addition of  $\text{O}_2$ . Rate constants for the reactions  $\text{NCl} + \text{NCl} \rightarrow \text{N}_2 + 2\text{Cl}$  and  $\text{NCl} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{Cl}$  were determined, e.g.  $k^{295}(\text{NCl} + \text{NO}) = (1.3 \pm 0.1) \times 10^{-11}\ \text{cm}^3\ \text{s}^{-1}$ .

### 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  $\text{P}(3\ ^4\text{S}_{3/2})$  with the molecules  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{PCl}_3$  were studied by using the vacuum UV atomic resonance fluorescence technique in a flow system.  $\text{P}(3\ ^4\text{S}_{3/2})$  was generated by microwave discharge of  $\text{PCl}_3$  in the presence of excess helium carrier gas and the atomic resonance fluorescence was monitored using the 178.77, 178.29 and