# Gas-phase Reaction of OH with Alkyl Iodides

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*Summary* Reaction between OH radicals and alkyl iodides is shown to proceed rapidly in the gas-phase; the absolute rate for reaction with $CF_3I$ is determined to be $k = (1{\cdot}2 \pm 0{\cdot}2) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

HYDROXYL radical reactions have been studied extensively in the gas-phase, owing to their importance in combustion processes and in atmospheric chemical cycles. Absolute rate data have been reported for a large number of H atom abstraction reactions; however, there has been no report of halogen atom abstraction. This is somewhat surprising as halogen abstraction reactions by $O(2^3P_J)$, $O(2^1D_2)$, F, Br, I, $CF_3$, and $CH_3$ from RI, RBr, and molecular halogens are well known.

We have studied the reaction of OH radicals with alkyl iodides using flash photolysis with time-resolved absorption photometry and here report the absolute rate constant for reaction of OH with $CF_3I$. Hydroxyl radicals were produced by photolysis of dilute mixtures of $O_3$ in the presence of $H_2O$ vapour. Photolysis of $O_3$ in the ultraviolet ($\lambda \leqslant 310$ nm) produces $O(2^1D_2)$ atoms which react rapidly with $H_2O$ yielding two OH radicals. The kinetics of OH ($X^2\Pi$, $v = 0$) were monitored[1] by time-resolved absorption of the $Q_13$ spectral line at 308·15 nm. Addition of $CF_3I$ to this mixture caused a rapid increase in the rate of decay of OH. These decays were found to be pseudo-first-order, as the reagent concentrations are large relative to that of OH (typically $10^{12}$—$10^{13}$ radicals cm$^{-3}$). By plotting the pseudo-first-order rate coefficients obtained from such decay traces against the partial pressure of $CF_3I$ present, the absolute second-order rate constant can be obtained. The rate constant for reaction of OH with $CF_3I$ at 295 K was determined as $(1{\cdot}2 \pm 0{\cdot}2) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The product HOI was not observed in this work, but it could probably be detected using mass spectrometry combined with flow tube techniques. As some photolysis of $CF_3I$ will also occur in our system, the measurements were repeated at low flash energies, but no variation in the rate data was observed and it can be concluded that the small degree of $CF_3I$ photolysis is of no consequence in the decay kinetics of OH.

We have also carried out preliminary experiments with other alkyl iodides including $CH_3I$, $C_2F_5I$, and $C_3F_7I$, all of which react rapidly with OH.

Reactions of $O(2^3P_J)$ and $F(2^2P_J)$ with alkyl iodides have been studied in some detail by molecular beam techniques[2,3] and it has been shown that the attacking atom first forms a complex with the iodide and that this then breaks up to yield products, the overall reaction being abstraction of an iodine atom: $X + RI \rightarrow RIX^{\ddagger} \rightarrow IX + R$. As OH reactions parallel halogen atom reactions in many respects, we would expect the dominant reaction channel to be abstraction following attack of OH on RI, which contrasts with the displacement reactions observed in solution.

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