Another reaction of commercial importance is the nitration of alkanes to give nitroparaffins. Such reactions usually are carried out in the vapor phase at elevated temperatures using nitric acid (HNO₃) or nitrogen tetroxide (N₂O₄) as the nitrating agent:

\[
RH + HNO_3 \xrightarrow{\sim 425^\circ} RNO_2 + H_2O
\]

All available evidence points to a radical mechanism for nitration, but many aspects of the reaction are not fully understood. Mixtures are obtained; nitration of propane gives not only 1- and 2-nitropropanes but nitroethane and nitromethane:

\[
\begin{align*}
CH_3CH_2CH_3 + HNO_3 \rightarrow & \quad \begin{cases} 
CH_2CH(NO_2)CH_3 & \text{1-nitropropane (25\%)} \\
CH_2CH(NO_2)CH_2CH_3 & \text{2-nitropropane (40\%)} \\
nitroethane (10\%) & \text{nitromethane (25\%)}
\end{cases} \\
\end{align*}
\]

In commercial practice, the yield and product distribution in nitration of alkanes is controlled as far as possible by the judicious addition of catalysts (e.g., oxygen and halogens), which are believed to raise the concentration of alkyl radicals. The products are separated from the mixtures by fractional distillation.

Contributors