

Oxidation of carbon monoxide by methoxy-radicals

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The thermal decomposition of dimethyl peroxide (DMP) in a static system was investigated over the temperature range 123-153°C at varying pressures of carbon monoxide. The reaction of methoxy-radicals with carbon monoxide produces carbon dioxide and methyl radicals. The rate constant of reaction (2) $\text{CH}_3\text{O}\cdot + \text{CO} \xrightarrow{k_2} \text{CO}_2 + \text{CH}_3$ (2) was determined to be: $k_2/\text{l. mol}^{-1} \text{ s}^{-1} = 10^{10.2 \pm 0.6} \exp(-11.800 \pm 1500/RT)$ (R in cal mol⁻¹ K⁻¹). At low carbon monoxide pressures production of carbon dioxide is first order in carbon monoxide and half order in DMP while at high carbon monoxide pressures (> 120 Torr) it is zero order in carbon monoxide and first order in DMP. At high pressures of carbon monoxide and at 127°C reaction (2) is the main reaction of methoxy-radicals. These data are rationalized by a simple free-radical mechanism.