A KINETIC STUDY OF THE

THERMAL DECOMPOSITION OF ETHANE AND NEOPENTANE

DURING THEIR INDUCTION PERIODS

by

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ABSTRACT

In this study, a non-spectroscopic technique has been developed for the determination of independent rate constants of individual radical reactions.

The first system investigated was the flow pyrolysis of neopentane. Induction periods for the formation of methane and 2-methyl-1-butene were observed at 822 K. The induction period found for 2-methyl-1-butene indicates that it is a secondary product and that the reaction involving the vicinal methyl radical shift, $(CH_3)_3CCH_2 \longrightarrow (CH_3)_2CC_2H_5$, does not contribute appreciably to the formation of this product. The rate constants for the reactions, neo-$C_5H_{12} \longrightarrow CH_3$ + t-C_4H_9 and CH_3 + neo-$C_5H_{12} \longrightarrow CH_4$ + neo-C_5H_{11}, were found to be pressure independent. The values, $(1.7\pm0.1)\times10^{-5}$ s^{-1} and $(1.7\pm0.1)\times10^6$ l $mol^{-1}s^{-1}$, respectively, were observed. The methyl radical recombination rate constant increased with increase in pressure. The data obtained from 4-335 torr were extrapolated to determine the high pressure limiting rate constant, $(2.2\pm0.5)\times10^{10}$ l $mol^{-1}s^{-1}$. The rate constant for the reaction, CH_3 + $(CH_3)_2CCH_2 \longrightarrow CH_4$ + $CH_3C(CH_2)_2$, was found to be 2.2×10^6 l $mol^{-1}s^{-1}$.

The second system investigated was the pyrolysis of ethane at 902 K. The formation of ethylene exhibited an induction period. The rate constants for the reactions, $C_2H_6 \longrightarrow 2CH_3$ and $C_2H_5 \longrightarrow C_2H_4$ + H, were found to be pressure dependent. The data were extrapolated to find the high pressure limiting values, $(1.8\pm0.1)\times10^{-5}$ s^{-1} and $(2.6\pm0.3)\times10^4$ s^{-1}, respectively. The ethyl radical recombination rate constant was independent of pressure with a value $(1.3\pm0.2)\times10^{10}$ l $mol^{-1}s^{-1}$. The rate constant for the reaction, CH_3 + $C_2H_6 \longrightarrow CH_4$ + C_2H_5, was found to be equal to 4.2×10^6 l $mol^{-1}s^{-1}$ which further confirmed that this reaction exhibits a curved Arrhenius plot. The rate constants for the reactions, C_2H_5 + $C_2H_4 \longrightarrow C_3H_6$ + CH_3 and C_2H_5 + $C_2H_4 \longrightarrow$ 1-C_4H_8 + H, were determined to be 5.9×10^4 l $mol^{-1}s^{-1}$ and 5.6×10^4 l $mol^{-1}s^{-1}$, respectively. It was observed that the rate of formation of methane decreases as the reaction progresses, an observation which was not made in other studies.

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