

PREDICTION OF THE PRODUCT CHANNELS IN THE REACTION OF THE METHYL RADICAL WITH FULMINIC ACID

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April 28, 2020

Abstract

The reaction of $\text{CH}_3 + \text{HCNO}$ was theoretically studied by both density functional theory and molecular orbital calculations and analyzed by quantum statistical methods. The potential energy surface was constructed at the $\text{UCCSD(T)}/\text{B3LYP}/6\text{-}311++\text{G}(3\text{df},2\text{p}) + \text{ZPE}$ level. Four entrance channels are opened relating to the interaction of the CH_3 radical with each of the four atoms of the HCNO molecule, giving rise to eighteen different product sets. The predicted geometries and heats of reaction are in good agreement with available experimental data. The major pathways involve addition of CH_3 to the C atom of HCNO with a small energy barrier of ~ 4 kcal/mol forming both Z and E- $\text{HC}(\text{CH}_3)\text{NO}$ (IS1 / IS1b) intermediates lying 45 or 44 kcal/mol, respectively, below the reactants. The nascent intermediates can collisionally be deactivated and subsequently decompose into $\text{H} + \text{CH}_3\text{CNO}$, or isomerize prior to decomposition giving other products. Kinetics calculations covering the temperature range of 400 – 2500 K, under pressures of 7.6×10^{-1} - 7.6×10^5 Torr for N_2 , He, and Ar as the third bodies show that at 760 Torr N_2 , the adducts including both IS1 and IS1b are the major products at temperature below 600 K, while $\text{H} + \text{CH}_3\text{CNO}$ and $\text{CNO} + \text{CH}_4$ are the major products at $T \gtrsim 1500$ K. The total high-pressure rate coefficient can well be expressed by the following 3-parameter equation: $k(T) = 7.75 \times 10^{-16} T^{1.69} \exp(-1480 \text{ K}/T)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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