

## Reactions of Methyl Radicals with (*Z*)-2-Butene near 1000 K

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Methyl radicals are important intermediates in the combustion of hydrocarbon fuels and there are few kinetic studies of their reactions at higher temperatures. The single pulse shock tube technique has been used to study the hydrogen abstraction reactions of methyl radicals with (*Z*)-2-butene at temperatures of (873 to 1031) K and pressures in the range of (1.5 to 2.2) bar with argon as the bath gas. Thermal decomposition of *tert*-butyl peroxide was used as the source of methyl radicals in the system. Products were analyzed in post-shock analyses using dual-column gas chromatography with simultaneous flame-ionization and mass-spectrometric detection. The primary observed stable products are methane and ethane, together with smaller amounts of butadiene, propene, (*Z*)-2-pentene, (*E*)-2-pentene, and 3-methyl-1-butene. The ethane/methane ratio is sensitive primarily to the relative rates of methyl recombination and abstraction of H from (*Z*)-2-butene by methyl radicals. Absolute rate constants for the latter process have been derived on this basis. Abstraction of H from (*Z*)-2-butene occurs mainly from the allylic sites and leads to methane and but-2-en-1-yl (1-methylallyl) radicals. The ensuing decomposition and radical recombination processes of 1-methylallyl account for the other olefins observed. A detailed chemical kinetic model that quantitatively describes the product distribution has been created. An analysis of the radical recombination products shows that that recombination of methyl and 1-methylallyl radicals occurs preferentially at the terminal position, which is favored by a factor of about 1.9 near 1000 K. Our data also lead to the rate constant for ejection of H from the 1-methylallyl radical, which does not appear to have been previously reported. The present results for abstraction of H by methyl radicals are compared with literature data from studies at lower temperatures.