

studies on cyclopropanes and butanes from which picosecond relaxation times have been reported. Hydrogen atoms are produced by the mercury-photosensitized decomposition of H_2 . The critical thresholds for alkyl radical decomposition processes occur in the region 30 - 33 kcal mol⁻¹. Decomposition of the initially produced non-randomized species competes with internal relaxation followed by decomposition by other pathways. A number of systems are described. For 3-hexyl radicals, a relaxation rate of $5 \times 10^{12} \text{ s}^{-1}$ was found.

Vinylidene radicals in photolysis and reactions of hydrocarbons

ALLAN H. LAUFER

Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Washington, DC 20234 (U.S.A.)

Vinylidene radicals ($H_2C=C$): are proposed as important intermediates in the vacuum UV photolysis of C_2H_2 as well as the combination of two triplet CH_2 radicals. The interpretation is based on the vacuum UV absorption spectrum of a long-lived transient observed in these systems as well as mass spectrometric determinations of the yields of deuterated acetylenes produced from the reaction of two triplet $CH_2(CD_2)$ radicals in the presence of large quantities of inert gas. The $CH_2(CD_2)$ radicals were produced from the flash photolysis of CH_2CO-CD_2CO mixtures. The results are discussed both with respect to the mechanisms for dissociation of the combined C_2H_4 and with respect to the energetics of the overall process which, it is proposed, involves an excited triplet of the vinylidene radical.

Photochemical study of peroxy radical interactions in hydrocarbon oxidation

TAMÁS VIDÓCZY, ROGER LAMPERT, JULIA LUKÁCS, GÁBOR VASVÁRI, ÁGNES KESZLER and DEZSŐ GÁL

International Laboratory, Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Pusztaszeri ut 59 - 67 H-1025 Budapest (Hungary)

Measuring the chemiluminescence light level in suitable reaction mixtures and utilizing computer modelling techniques we studied the following processes: (1) the cross-combination of peroxy radicals; (2) the interaction of peroxy radicals with inhibitors; (3) the interaction of peroxy radicals with metal com-