

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-

plexes. Our results include absolute values for some of the rate constants involved and relative chemiluminescence quantum efficiencies of peroxy radical cross-combinations.

Adiabatic photoreactions in dilute solutions of *p*-substituted *N,N*-dialkylanilines and related donor-acceptor compounds

ERNST LIPPERT, A.A. AYUK, W. RETTIG and G. WERMUTH

Stranski-Institut für Physikalische und Theoretische Chemie, Technische Universität Berlin, Strasse des 17. Juni 112, D-1000 Berlin (F.R.G.)

Twisted intramolecular charge transfer (TICT) stable excited states can occur in molecules in which two chromophores are separated by one (twisted) single bond. The TICT state is achieved after absorption to the lowest-lying Franck-Condon excited state of that molecule by an adiabatic photoreaction. This lower-lying TICT state potential minimum in the hypersurface of the lowest-lying excited state of the total π electronic system comes from higher-lying excited states in the ground state molecular geometry and gives rise to the effect of dual fluorescence which allows us to study the kinetics of the twist mechanism. If the *para* substituent to the *N,N*-dialkylaniline is large (9-anthryl or sulphone) the aniline twists around that substituent, but if the substituent is small (nitrile) or flexible (ester) the dialkylamino group twists around its phenyl ring. The population of the TICT state is favoured by (1) the dialkylamino group ionization potential, (2) the substituent electron affinity, (3) the lifetime of the excited state, (4) its dipole-dipole interaction with the solvent and (5) a low viscosity.

Triplet excimer formation with phenanthrene: the importance or relative chromophore configuration

R. BUSSE and K.A. ZACHARIASSE

Max-Planck-Institut für Biophysikalische Chemie, Göttingen (F.R.G.)

Triplet excimers were detected in dilute solution with 1,3-di(9-phenanthryl)propane (99P3P) by triplet-triplet (T-T) absorption spectroscopy in the nanosecond time domain. From an analysis of the T-T absorption spectra as a function of time, the kinetics of the intramolecular triplet excimer formation were resolved as a function of temperature and solvent viscosity. For the triplet excimer