EXCITED RADICALS IN THE GAS PHASE PHOTOLYSIS OF BUTENE ISOMERS IN THE VACUUM UV REGION

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A systematic study of the pressure effects on the quantum yields of some products between 0.1 and 600 Torr (13 and 80,000 Nm^{-2}) was carried out in the 7.6 and 8.4 eV photolysis of normal, iso and *cis*-2-butenes. The propylene quantum yield ($s\text{-}C_4H_9^* \rightarrow C_3H_6 + CH_3$) decreased with the increase in the n-butene pressure and a good linearity of S/D versus pressure plot, over a broad pressure region, was observed. It is concluded that hydrogen atoms involved in the $s\text{-}C_4H_9^*$ radical formation are produced with a relatively narrow energy distribution. The slope of S/D versus pressure lines decreased with the increase in photon energy, indicating the trend in the kinetic energy of the H-atoms.

In the case of isobutene and *cis*-2-butene photolysis the Stern-Volmer plots for allene formation were nonlinear. It is concluded that the formation of two different allene precursors is needed to account for this result. By the use of a simple RRK-type formalism we also conclude that the excess energy of the photon in the primary photoexcited butene molecules is far from being randomized before their fragmentation occurs.

$$C_4H_8 + h\nu \rightarrow C_4H_8^{**} \rightarrow C_3H_5^* + CH_3$$