LONG-WAVELENGTH PHOTOCHEMISTRY OF MATRIX-ISOLATED BIACETYL

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Visible irradiation (520 nm$>$ λ $>$485 nm) of matrix-isolated biacetyl ($C_4H_6O_2$) results in the formation of a complex of *cis*-methylhydroxycarbene (CH_3COH) and ketene (CH_2CO), as well as other products. The wavelengths used in this study are longer than those necessary for the S_0-S_1 ($\tilde{X}^1A_g$ -$\tilde{A}^1A_u$) transition, indicating that the photolysis is the result of a multiphoton process. One such process is sequential, where the spin-forbidden S_0-T_1 ($\tilde{X}^1A_g$ -$\tilde{a}^3A_u$) transition is followed by the allowed T_1-T_2 ($\tilde{a}^3A_u$ -$\tilde{b}^3B_g$) transition, with photoproducts emerging from the higher triplet (or following a radiationless transition to another state). A simultaneous two-photon process is also possible through the symmetry-forbidden S_0-S_2 ($\tilde{X}^1A_g$ -$\tilde{B}^1B_g$) transition. Photoproduct formation as a function of irradiation flux and wavelength was used to sort out the relative contributions of each of these processes.