The Detection of Ethylketen and *enol*-Crotonaldehyde in the Vapour-phase Photolysis of *trans*-Crotonaldehyde

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ISOMERISATION to one or more unstable intermediates has been suggested as a means for electronically excited molecules to lose some of their energy and return to their ground state during photolyses.[1] Using a long-path-length i.r. spectrophotometer we have identified two such isomers, with very low quantum yields ($\leqslant 0{\cdot}1$), during the photolysis of *trans*-crotonaldehyde. The isomers are ethylketen and *enol*-crotonaldehyde. It seems likely that *enol*-crotonaldehyde isomerises to crotonaldehyde and ethylketen is photolysed to propene and CO.

trans-Crotonaldehyde vapour has been photolysed in the 20 m. path-length cell of a Perkin Elmer 221 i.r. spectrophotometer at 25° using light of wavelengths 3130 and 2537 Å.

trans-Crotonaldehyde (0·6 ml.) was transferred to the evacuated sample and reference cells of the machine so that initially no absorption of i.r. radiation showed upon the recorder. The cells were isolated from each other and the aldehyde in the sample cell ($p \sim 0{\cdot}5$ mm. Hg) was irradiated, with either 3130 or 2537 Å light, perpendicular to the i.r. analysing beam. Products and intermediates formed during the reaction appeared as positive absorptions upon the recorder.

At both exciting wavelengths, i.r. absorptions were found at 3630, 2132, and 1100 cm.$^{-1}$ in addition to those due to CO, C_3H_6, CH_4, and the other established products of photolysis.[2,3] The rates of increase of these three peaks during irradiation and the rates of their subsequent decay in the dark, established that the 3630 and 1100 cm.$^{-1}$ absorptions arose from a different compound (A) from that (B) responsible for the 2132 cm.$^{-1}$ peak. Neither (A) nor (B) was stable in the dark. Plots of the optical density of (A) and (B) against time during irradiation were straight lines for low conversion of crotonaldehyde. This indicates that (A) and (B) are products of the primary photolytic step.

The absorption at 2132 cm.$^{-1}$ is typical of the C–O stretching vibration of a keten. Several ketens were prepared and their i.r. spectra recorded under conditions similar to those employed in the crotonaldehyde photolysis experiments. These spectra showed that the C–O stretching band was the only absorption detectable under the experimental conditions. The best fit to the absorption of (B) was ethylketen, which also absorbed at 2132 cm.$^{-1}$. CO and alkynes also absorb in this region. However, experiments showed that to give the required transmittance, more CO or alkyne would have to be formed during irradiation than the amount of aldehyde originally introduced to both cells. The intermediacy of ethylketen is compatible with the photochemistry of crotonaldehyde.[3]

We have yet to establish definitely the structure of (A). The absorption at 3630 cm.$^{-1}$ is typical of an O–H stretch whilst the 1100 cm.$^{-1}$ peak is characteristic of the C–O stretching band of a primary or secondary alcohol. McMillan, Calvert, and Pitts[4] found an absorption at 3628 cm.$^{-1}$ during the photolysis of pentan-2-one vapour in similar experiments. These authors established that this peak was caused by the *enol* form of acetone. The ratio of extinction coefficients of the 1100 cm.$^{-1}$ peak to that at 3630 cm.$^{-1}$ of (A) was $\sim$4. In butyl alcohol the C–O stretching vibration at 1060 cm.$^{-1}$ has ϵ 40 whilst the O–H absorption at 3665 cm.$^{-1}$ has ϵ 12. Therefore, we suggest that (A) is the *enol* form of *trans*-crotonaldehyde.

We acknowledge the support of this research by a grant from the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U.S. Public Health Service.

(*Received, December 15th*, 1967; *Com.* 1341.)

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