thermore, we have made the approximation that an MO level ordering valid for one molecule is also valid for a number of related molecules in the same structure. While this appears to be true more times than one might have supposed, certainly there are many exceptions.

While the theme of this article has been the prediction of structure from MO level diagrams, it is more realistic to turn the problem about. That is, since reliable structures are often known, we should test assumed or calculated MO schemes to see if they are compatible with the known structures. The test is to show stability with respect to second-order Jahn–Teller distortions.

Acknowledgment. We thank the U. S. Atomic Energy Commission and the National Science Foundation for support of this work under Grants No. At(11-1)-1087 and 6341X, respectively.

Molecular Structure and Photochemical Reactivity. XIV. The Vapor-Phase Photochemistry of *trans*-Crotonaldehyde

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Abstract: The vapor-phase photochemistry of *trans*-crotonaldehyde has been studied at wavelengths longer than 2550 Å between 70 and 130°. The major photodecomposition products were CO and propylene. Small amounts of C_2H_4, allene, methylacetylene, cyclopropane, ethylketene, and *enol*-crotonaldehyde were also formed. The results are explained by a mechanism involving decomposition from, and multistage collisional deactivation of, a vibrationally excited upper singlet state, intersystem crossing to an unstable upper triplet state, and internal conversion to the ground state *via* isomerization of the upper singlet state to unstable intermediates.

The vapor-phase photochemistry of *trans*-crotonaldehyde has been the subject of many investigations. Blacet and Roof[2a] found that the molecule was extremely resistant to photodecomposition at room temperature when irradiated with any of the mercury lines between 3660 and 2399 Å. Subsequently, Blacet and Luvalle[2b] showed that photodecomposition did occur at 2380 Å and 265° to give CO, unidentified unsaturated hydrocarbons, and methane. Tolberg and Pitts[3] found $\phi_{CO} \simeq 1.5$ at 2380 Å and 265°, and identified the hydrocarbon products as CH_4, propylene, and 2-butene. Allen and Pitts[4] studied the methyl radical sensitized decomposition of *trans*-crotonaldehyde and showed that 2-butene was formed by methyl radical displacement of the formyl group. McDowell and Sifniades[5] reported that in the vapor phase at ~30°, and with the wavelength range 2450–4000 Å, *trans*-crotonaldehyde isomerized to but-3-en-1-al, but neither Yang[6] nor later workers[7,8] could detect this isomer. Using a long-path-length ir spectrophotometer, Coomber, *et al.*,[7] found that ethylketene and *enol*-crotonaldehyde were unstable intermediates in the photolysis at 3130 and 2537 Å. Subsequently, Allen and Pitts[8] proposed that the photodecomposition at 2537–2654 Å involved the formation of an electronically excited molecule of crotonaldehyde which isomerized to ethylketene. This isomer then photodecomposed to propylene and CO. Although this is an attractive proposition, we felt their mechanism was not proven and so undertook the present study.

Experimental Section

Materials. *trans*-Crotonaldehyde (Matheson Coleman and Bell) was purified immediately before each run by glpc on a 15 ft × 0.25 in. Carbowax 20M (20%) column at 75° with helium as carrier gas. No impurity could be detected in the chromatographed aldehyde by ir or mass spectrometry. Nitric oxide (Matheson Gas Co.) was thoroughly degassed at −210° and then transferred to the first of two Ward-Leroy stills in series. A middle cut of the fraction volatile with the stills at −170 and −180° was stored in a blackened bulb on the vacuum line. CO_2 (Matheson Gas Co., "Bone Dry" grade) was degassed and used without further purification. 2,3-Dimethylbutene-2 (Chemical Procurement Laboratories Inc.) was better than 99% pure by glpc and was used without further purification. 3-Pentanone (Aldrich Chemical Co.) was purified immediately before use by glpc on a 20 ft × 0.25 in. 1,2,3-tris(cyanoethoxy)propane (TCEP)–Chromosorb P column at 160°. CO, C_2H_4, CH_4, allene, methylacetylene, cyclopropane, and propylene (all Matheson Gas Co.) were used for gas chromatographic calibration. Each compound, except CO and CH_4, which were used directly, was purified by low-temperature distillation in the Ward-Leroy stills. CF_3I (Peninsular Chem Research), O_2 (Matheson, Research Grade), and N_2 (American Cryogenic, prepurified quality) were used without further purification. All purified compounds were analyzed by ir or mass spectrometry or both. No impurity was detected.

Apparatus. Two apparatuses were used. One, a conventional high-vacuum system, has been described before[9] except for the following modifications. The combined gas buret–Toepler pump was connected *via* a microvolume gas-sampling valve (Carle Instruments Inc.) to a gas chromatograph with a 10 ft × 0.25 in. column of 40–60 mesh 13X molecular sieves and a Gow Mac

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[1] Address inquiries to Dr. J. W. Coomber, Physical Chemistry Section, Central Electricity Research Laboratories, Leatherhead, England.

[2] (a) F. E. Blacet and J. G. Roof, *J. Am. Chem. Soc.*, **58**, 73 (1936); (b) F. E. Blacet and J. E. Luvalle, *ibid.*, **61**, 273 (1939).

[3] R. S. Tolberg and J. N. Pitts, Jr., *ibid.*, 80, 1304 (1958).

[4] E. R. Allen and J. N. Pitts, Jr., *J. Phys. Chem.*, 70, 1691 (1966).

[5] C. A. McDowell and S. Sifniades, *J. Am. Chem. Soc.*, **84**, 4606 (1962).

[6] N. C. Yang, private communication.

[7] J. W. Coomber, J. N. Pitts, Jr., and R. R. Schrock, *Chem. Commun.*, 190 (1968).

[8] E. R. Allen and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **91**, 3135 (1969).

[9] J. W. Coomber and J. N. Pitts, Jr., *ibid.*, **91**, 547 (1969).

thermal conducting detector. This unit was used to analyze for H_2, CO, and CH_4.

The reaction vessel was completely filled by a parallel beam of the collimated emission from a Hanovia Type A (637 A) medium-pressure mercury arc. Two filter combinations were used. Filter A consisted of 6 mm of Corning CS7-54 glass and 3 cm of Cl_2 at atmospheric pressure. Filter B was 4 mm of CS7-54 plus 3 cm of Cl_2. The mercury lines, and their relative intensities, passed by these filters were checked by analyzing the filtered light using a Bausch and Lomb monochromator with a mechanical wavelength changer. The emergent radiation passed through 1 cm of fluoroscein solution to a photomultiplier. For filter A the resultant spectrum showed that 98% of the transmitted light was of wavelength longer than 2537 Å and 93% was longer than 2550 Å (the minimum of the trough between the π–π^* and n–π^* regions of the *trans*-crotonaldehyde absorbtion spectrum[2a,10]). The relative intensities of the lines were 2804 Å, 11.5%; 2753 Å, 5.6%; 2699 Å, 11.2%; 2652 Å, 31.9%; and an asymmetric peak with its maximum at 2580 Å, 39.7%. For Filter B, 20% of the light was of shorter wavelength than 2550 Å. The relative intensities were 2804 Å, 5.8%; 2753 Å, 4.1%; 2699 Å, 6.5%; 2652 Å, 23.8%; 2576–2537 Å, 53.9%; 2482 Å, 5.8%; and 2399 Å, 1.0%. Light intensity was checked, at least every six runs, using the photolysis of ~20 Torr of 3-pentanone at 130° as an actinometer ($\phi_{CO} = 1.0$).

The second apparatus was used to investigate the role of intermediates in the photochemistry of *trans*-crotonaldehyde. A conventional high-vacuum system was connected to the 20-m path length gas cells of a modified Perkin-Elmer 221 ir spectrophotometer. The cell in the analyzing beam was isolable from the one in the reference beam. The whole system could be evacuated to $\sim 10^{-5}$ Torr. Pressure in the apparatus was measured with either a Statham pressure transducer or an RCA 1946 vacuum tube gauge.

Six 7 × 6 cm quartz windows in the top of the analysis cell allowed the contents to be irradiated perpendicular to the ir beam. Two lamp and filter combinations were used. A Hanovia 1200-W medium-pressure lamp with a water-cooled quartz jacket and 2-mm Pyrex as a filter was used for wavelengths longer than 3000 Å. Two low-pressure resonance lamps (Hanovia) plus 5 cm of Cl_2 at atmospheric pressure were used for wavelengths below 2800 Å.

Procedure. In the conventional apparatus the reactants were degassed and expanded into the reaction vessel. Pressure in the reaction vessel was measured and monitored with a Statham pressure transducer. This was calibrated with dry air against a mercury manometer and a McLeod gauge. The calibration was checked frequently throughout the work. When the fraction of light absorbed by the reactants was greater than 3%, it was measured directly with an RCA 935 phototube and galvanometer. For smaller absorptions, the fraction was calculated using an extinction coefficient determined in the photolysis apparatus. The value of the decadic extinction coefficient, $\epsilon = 1.80$ l. mole^{-1} cm^{-1} for the band passed was calculated using the equation given by Blacet, *et al.*,[10] and agrees well with their value of $\epsilon = 1.70$ l. mole^{-1} cm^{-1} at 2654 Å. Conversion of the aldehyde was kept below 1.5% in all experiments.

After irradiation in runs not involving NO, the reaction mixture was passed through a trap at −196°. The volatile fraction was collected in the gas buret and the condensate warmed and refrozen. Any remaining noncondensable products were added to those already in the gas buret and the total amount was measured. The fraction was then analyzed for CO, H_2, and CH_4 by glpc or mass spectrometry. In runs with NO the trap was first at −210° and the volatile fraction treated as before. Then with the trap at −196°, NO was removed. The treatment of the residue at −196° was the same whether or not NO had been a reactant.

The residue was transferred to the Ward-Leroy stills. The fraction volatile with the stills at −115 and −140° was collected, measured, and analyzed for C_2H_4, propylene, allene, methylacetylene, and cyclopropane on a 25 ft × 1/8 in. column of 20% hexadecane on 30-60 firebrick at 30°. The column was calibrated immediately after the analysis of each product sample by the injection of a known amount of a calibration mixture of these gases. The composition of the product sample was also checked by mass spectrometry; no other product was found. The residue in the Ward stills was analyzed by glpc on a 20 ft × 1/4 in. TCEP-Chromosorb P column or by mass spectrometry. This fraction was entirely crotonaldehyde.

For the long-path-length ir apparatus (LPIR), purified *trans*-crotonaldehyde was degassed and admitted to both cells (usually pressures $\leq 10^{-1}$ Torr were used) followed by inert gas if required. The system was allowed to equilibrate and the cells were isolated from each other. During and after irradiation, the rates of formation and disappearance of ethylketene and *enol*-crotonaldehyde were obtained from the growth and decay of the absorptions at 2132 cm^{-1} and 3630 and 1100 cm^{-1}, respectively.[7] An estimate of the quantum yields for production of these compounds was made by comparing the results with those obtained from the photooxidation of CF_3I in the LPIR. The rate of appearance of COF_2 was followed from its absorption at 1923 cm^{-1}; $\phi_{COF_2} = 1.0$ and is independent of wavelength and pressure of O_2 and CF_3I.[11] Quantum yields were calculated using the approximation

$$\frac{\phi_{COF_2}}{\phi_x} \simeq \frac{R_{COF_2}}{R_x} \frac{\epsilon_{crot}P_{crot}}{\epsilon_{CF_3I}P_{CF_3I}}$$

where x is ethylketene or *enol*-crotonaldehyde, crot is *trans*-crotonaldehyde, R is the rate of formation, ϵ is the extinction coefficient, and P is the reactant pressure.

Results

Preliminary experiments showed that when *trans*-crotonaldehyde was irradiated at 100° with light of wavelength longer than 2550 Å (filter A) the major products were CO ($\phi \sim 0.3$) and C_3H_6 ($\phi \sim 0.15$). The only other products detected in these and subsequent runs with filter A were C_2H_4, methylacetylene, allene, and cyclopropane. The quantum yields for these compounds were all $\sim 10^{-4}$. With filter B, CH_4 and 2-butene were detected in addition to the previous products. A number of "dark" runs showed that the thermal decomposition of *trans*-crotonaldehyde could be ignored for irradiation times of less than 3 hr at 100°. Unless otherwise stated, all runs were at 100° and with filter A.

In the preliminary runs the optical density of the reaction vessel and contents increased during irradiation. A similar effect was noted by Allen and Pitts.[8] This decrease in transmission was partly due to deposition of polymer on the vessel walls. However, a decrease in transmission also occurred when the empty cell was irradiated after a run. This variation ceased after approximately 1200 sec and small amounts of noncondensable gas were found in the cell. This suggests that the increase in optical density was caused partly by the deposition of polymer on the vessel walls and partly by photolysis of this polymer. The cell was always preirradiated before photolysis began. Because of this effect and the small conversion (<1.5%) of *trans*-crotonaldehyde, no attempt was made to measure the quantum yield for polymerization.

The light used in this study was not strictly monochromatic and the quantum yields are only suitable for mechanistic interpretation. The accuracy of our analyses has been discussed before,[9] and within these limitations our quantum yields for CO and propylene are probably accurate to better than ±10%. Because of the small amounts produced ($\sim 10^{-3}$ μmole), quantum yields were not calculated for the other products.

The quantum yields for CO and C_3H_6 were constant when the incident light intensity was varied using neutral density screens: $I_0 = 3.2 \times 10^{13}$ quanta cm^{-3} sec^{-1}, $\phi_{CO} = 0.23$, $\phi_{C_3H_6} = 0.10$; $I_0 = 1.1 \times 10^{13}$ quanta cm^{-3} sec^{-1}, $\phi_{CO} = 0.25$, $\phi_{C_3H_6} = 0.09$; $I_0 = 3.8 \times 10^{12}$ quanta cm^{-3} sec^{-1}, $\phi_{CO} = 0.22$, $\phi_{C_3H_6} = 0.09$. The quantum yields were also constant with irradiation time: $t = 1000$ sec, $\phi_{CO} = 0.25$, $\phi_{C_3H_6} = 0.09$; $t =$

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[10] F. E. Blacet, W. G. Young, and J. G. Roof, *J. Am. Chem. Soc.*, **59**, 608 (1937).

[11] J. Heicklen, *J. Phys. Chem.*, 70, 112 (1966).

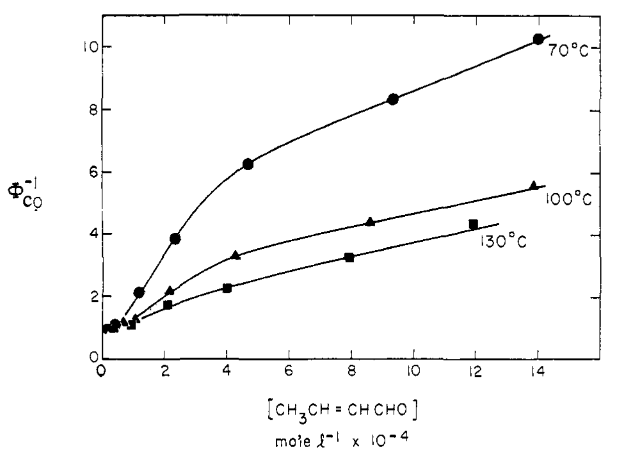


Figure 1. The variation of ϕ_{CO}^{-1} with *trans*-crotonaldehyde concentration at 70, 100, and 130°.

3600 sec, $\phi_{CO} = 0.23$, $\phi_{C_3H_6} = 0.10$; $t = 5000$ sec, $\phi_{CO} = 0.22$, $\phi_{C_3H_6} = 0.10$.

Substitution of filter B for filter A involved changing both intensity and wavelength. For 16.0 Torr of aldehyde with filter A, $I_0 = 3.2 \times 10^{13}$ quanta cm^{-3} sec^{-1}, $\phi_{CO} = 0.25$ and $\phi_{C_3H_6} = 0.11$, while for filter B with the same pressure of aldehyde, $I_0 = 6.8 \times 10^{13}$ quanta cm^{-3} sec^{-1}, $\phi_{CO} = 0.40$, $\phi_{C_3H_6} = 0.17$, and $\phi_{CH_4} \simeq 0.02$.

The addition of 0.4 Torr of NO to 2.9 Torr of aldehyde, and 1.0 Torr of NO at 16.0 Torr of aldehyde did not reduce the quantum yields of CO or C_3H_6 within experimental error.

ϕ_{CO} and $\phi_{C_3H_6}$ decreased when 20.0 Torr of *trans*-crotonaldehyde was irradiated in the presence of up to 1.0 Torr of 2,3-dimethylbutene-2 (DMB). Plots of ϕ/ϕ_0 (where ϕ_0 is the quantum yield without DMB) against DMB pressure for CO and C_3H_6 were identical straight lines with slope of -0.25 Torr^{-1}.

Variation of temperature and pressure had a pronounced effect on the quantum yields. The effect of aldehyde pressure on ϕ_{CO}^{-1} at 70, 100, and 130° is shown in Figure 1. The variation of $\phi_{C_3H_6}^{-1}$ with aldehyde pressure at 100° is shown in Figure 2; similar curves were obtained at 70 and 130°. Extrapolation of the curves in Figure 1 to [CH$_3$CH═CHCHO] = 0 shows that within experimental error $\phi_0 = 1.0$ for CO at all three temperatures. The value of ϕ_0 (C_3H_6) varied with temperature, at 70°, $\phi_0 = 0.50$; 100°, $\phi_0 = 0.44$; and 130°, $\phi_0 = 0.40$. At pressures greater than 10 Torr of *trans*-crotonaldehyde $\phi_{C_3H_6}(130°) > \phi_{C_3H_6}(100°) > \phi_{C_3H_6}(70°)$.

Experiments with the LPIR showed that the quantum yield for ethylketene formation was higher at λ <2800 Å ($\phi \sim 0.02$) than at λ >3000 Å ($\phi \sim 0.001$). The quantum yield was inversely proportional to aldehyde and inert gas pressure. No ethylketene was detected at the longer wavelengths when more than 25 torr of N_2 was present. *enol*-Crotonaldehyde behaved in an opposite manner; its quantum yield (ϕ_{enol}) was larger for λ >3000 A (ϕ_{enol} ~0.01) and became constant when more than 50 torr of N_2 was present. Only traces of *enol*-crotonaldehyde were detected at λ <2800 Å. When the absorptions due to *enol*-crotonaldehyde and ethylketene had disappeared, no new peaks corresponding to their decomposition products could be found. The addition of small pressures of O_2 to *trans*-crotonaldehyde had no effect on either ϕ_{ketone} or ϕ_{enol}.

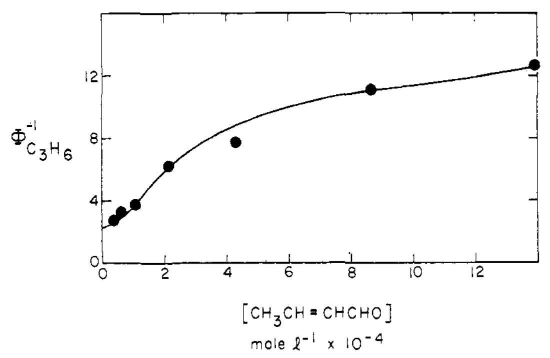


Figure 2. The variation of $\phi_{C_3H_6}^{-1}$ with *trans*-crotonaldehyde concentration at 100°.

The low quantum yields for formation, the instability of these intermediates ($t_{1/2}$(*enol*) ~ 10 min, $t_{1/2}$(ketene) ~ 60 min at 0.5 Torr), and our method of analysis probably account for the fact that neither isomer was detected in the conventional photolysis apparatus.

Discussion

The results of the experiments with filter A (where essentially all the radiation was being absorbed by the carbonyl group) indicate a mechanism such as

$$A + h\nu \longrightarrow A_1^{n} \tag{1}$$

$$A_1^{n} \longrightarrow C_3H_6 + CO \tag{2a}$$

$$A_1^{n} \longrightarrow C_3H_5 + HCO \tag{2b}$$

(2)

$$A_1^{n} \longrightarrow \text{ethylketene} \tag{3}$$

$$A_1^{n} + A \longrightarrow A_1^{0} + A \tag{4}$$

$$A_1^{0} \longrightarrow A \tag{5}$$

$$A_1^{0} \longrightarrow A_3^{0} \tag{6}$$

$$A_1^{0} \longrightarrow \textit{enol}\text{-crotonaldehyde} \tag{7}$$

$$A_3^{0} \longrightarrow C_3H_6 + CO \tag{8a}$$

$$A_3^{0} \longrightarrow C_3H_5 + HCO \tag{8b}$$

(8)

$$A_3^{0} \longrightarrow A \tag{9}$$

$$\text{ethylketene} \longrightarrow A \tag{10}$$

$$\textit{enol}\text{-crotonaldehyde} \longrightarrow A \tag{11}$$

A is a ground-state molecule of *trans*-crotonaldehyde, A_1^{n} is a vibrationally excited molecule in the first excited singlet state, A_1^{0} is a molecule in that state with insufficient vibrational energy for dissociation, and A_3^{0} is a molecule in the first excited triplet state in thermal equilibrium with its surroundings.

Although NO did not reduce the quantum yield of either CO or C_3H_6 and H_2 was not detected, the inclusion of reactions 2b and 8b is justified if the radicals all react as follows

$$HCO \longrightarrow H + CO \tag{12}$$

$$H + A \longrightarrow CH_3\dot{C}HCH_2CHO \tag{13}$$

$$C_3H_5 + A \longrightarrow CH_3\dot{C}HCH(C_3H_5)CHO \tag{14}$$

$$\left.\begin{array}{l} CH_3\dot{C}HCH_2CHO \\ CH_3\dot{C}HCH(C_3H_5)CHO \end{array}\right\} + A \longrightarrow \text{polymer} \tag{15}$$

Polymer is certainly formed in the system, and Skirrow and Osborne[12] have postulated the oxidation of the

(12) G. Skirrow and A. D. Osborne, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides*, **13**, 378 (1958).

$CH_3\dot{C}HCH(C_3H_5)CHO$ radical as leading to the formation of considerable amounts of acetaldehyde in the photooxidation of *trans*-crotonaldehyde. These authors also proposed that oxidation of the propenyl radical led to ethylene formation. They showed that when [*trans*-crotonaldehyde]/[O_2] ~ 0.9, roughly twice as much CH_3CHO as C_2H_4 was formed in spite of acetaldehyde being consumed during the oxidation. This argues strongly that reaction 14 is fast compared to the abstraction reaction

$$C_3H_5 + CH_3CH{=}CHCHO \longrightarrow C_3H_6 + CH_3CH{=}CHCO \quad (16)$$

There is no other datum on the relative rates of reactions 14 and 16. Neither is there any published datum on the relative rates of reactions 13 and 17.

$$H + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCO + H_2 \quad (17)$$

However, Cvetanović and Jennings[13] have found that the rate constant for addition of H atoms to the double bond of propylene is 30 times greater than that for abstraction. Although the nature of the hydrogen to be abstracted in *trans*-crotonaldehyde is different from that in propylene, this ratio is probably a good approximation. Volman, *et al.*,[14] showed by removal of a tellurium mirror that radicals were formed in the vapor-phase photolysis of *trans*-crotonaldehyde at 2537 Å. Further evidence for radical formation comes from the results of Harrison and Lossing[15] on the Hg($6\,^3P_1$)-photosensitized decomposition of *trans*-crotonaldehyde. These authors proposed that crotonyl and propenyl radicals were involved in the decomposition.

The decrease in ϕ_{CO} and $\phi_{C_3H_6}$ caused by DMB and the equality of ϕ/ϕ_0 for CO and C_3H_6 indicate that intersystem crossing to the triplet state occurs (reaction 6) and that A_3^0 decomposes by both reaction 8a and 8b.

The absence of fluorescent and phosphorescent emission from crotonaldehyde has been previously recorded,[2] and consequently only reactions 5 and 9 are included for the direct return of the electronically excited molecules A_1^0 and A_3^0 to the ground state.

The low quantum yield for ethylketene formation and the fact that its extinction coefficient at 2600 Å is probably similar to those of ketene and methylketene,[16,17] and hence *trans*-crotonaldehyde, make it unlikely that any is lost by photolysis in our system. The LPIR experiments showed only CO, C_3H_6, and the other previously mentioned compounds as products, so reaction 10 appears reasonable. Reaction 11 may be justified by a similar argument. Noyes, *et al.*,[18] have suggested isomerization to one or more unstable intermediates as a means for electronically excited molecules to lose some of their energy and return to the ground state during photolysis. The dependence of ϕ_{ketene} and ϕ_{enol} on pressure and wavelength fit reactions 3 and 7.

Applying steady-state approximations, this mechanism predicts that

$$\phi_{CO} = \frac{k_2 + k_4[A]\phi_\infty}{k_2 + k_3 + k_4[A]} \quad (18)$$

where [A] is aldehyde concentration, $\phi_\infty = k_6k_8/(k_5 + k_6 + k_7)(k_8 + k_9)$, $k_2 = k_{2a} + k_{2b}$, and $k_8 = k_{8a} + k_{8b}$. At zero pressure of aldehyde, $\phi_0 = k_2/(k_2 + k_3)$. However, from Figure 1, $\phi_0 = 1.0$ within experimental error. This is reasonable as the low value of ϕ_{ketene} compared to ϕ_{CO} requires that $k_2 \gg k_3$. Thus eq 18 becomes

$$\phi_{CO} = \frac{k_2 + k_4[A]\phi_\infty}{k_2 + k_4[A]}$$

Thus

$$(\phi_0 - \phi) = \phi_0 - \left\{\frac{k_2 + k_4[A]\phi_\infty}{k_2 + k_4[A]}\right\}$$

which on rearranging and substituting the experimental value $\phi_0 = 1.0$ becomes

$$(1 - \phi)^{-1} = (1 - \phi_\infty)^{-1} + (1 - \phi_\infty)^{-1}\frac{k_2}{k_4[A]} \quad (19)$$

$(1 - \phi)^{-1}$ is plotted against $[A]^{-1}$ in Figure 3. Equation 19 requires the plots to be straight lines, whereas they curve upward at pressures below 5 Torr of aldehyde.

Similarly, for C_3H_6 production

$$\phi_{C_3H_6} = \frac{k_{2a} + k_4[A]\phi^1_\infty}{k_2 + k_4[A]}$$

where $\phi^1_\infty = k_6k_{8a}/(k_5 + k_6 + k_7)(k_8 + k_9)$. This may be rearranged to

$$(\phi_0 - \phi)^{-1} = (\phi_0 - \phi^1_\infty)^{-1} + (\phi_0 - \phi^1_\infty)^{-1}\frac{k_2}{k_4[A]}$$

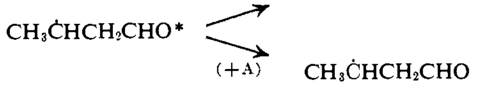
where $\phi_0 = k_{2a}/k_2$. Substituting the experimental values of $\phi_0(C_3H_6)$ in the equation gives curved plots similar to those from eq 19 in Figure 3.

One possible explanation of this curvature involves the radicals produced in reactions 13 and 14. If these radicals decompose at low pressures to give CO and propylene, this would account for the curvature shown in Figures 1–3. Reaction 13 might be expected to give a "hot" $CH_3\dot{C}HCH_2CHO$ radical because a C–C π bond is ruptured and a C–H bond formed. Benson[19] has discussed the strengths of bonds in radicals, and it seems reasonable that the enthalpy of reaction 20 would

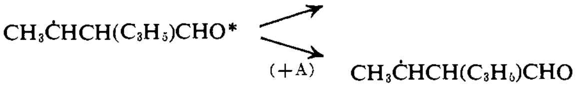
$$CH_3\dot{C}HCH_2CHO \rightleftharpoons CH_3CH{=}CHCHO + H \quad (20)$$

be ~22 kcal mole^{-1}. For C_3H_5 radicals adding to the aldehyde an exothermicity of ~7 kcal mole^{-1} seems likely.

The reaction sequence would be



$$CH_3\dot{C}HCH_2CHO^* \begin{cases} \longrightarrow CH_3CH{=}CH_2 + HCO & (21) \\ \xrightarrow{(+A)} CH_3\dot{C}HCH_2CHO & (22) \end{cases}$$



$$CH_3\dot{C}HCH(C_3H_5)CHO^* \begin{cases} \longrightarrow CH_3CH{=}CHC_3H_5 & (23) \\ \xrightarrow{(+A)} CH_3\dot{C}HCH(C_3H_5)CHO & (24) \end{cases}$$

followed by reactions 12 and 15. The asterisk denotes a "hot" radical.

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[13] R. J. Cvetanović and K. R. Jennings, *J. Chem. Phys.*, **35**, 1233 (1961).

[14] D. H. Volman, P. A. Leighton, F. E. Blacet, and R. K. Brinton, *ibid.*, **18**, 203 (1950).

[15] A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **37**, 1696 (1959).

[16] D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, **68**, 1793 (1964).

[17] G. B. Kistiakowsky and B. H. Mahan, *J. Am. Chem. Soc.*, **79**, 2412 (1957).

[18] W. Noyes, D. Phillips, J. LeMaire, and C. S. Burton, *Advan. Photochem.*, **5**, 329 (1968).

[19] S. W. Benson, *J. Chem. Educ.*, **42**, 509 (1965).

No 2,4-hexadiene was found in the products of low-pressure runs; neither did the addition of NO reduce the quantum yields. This would be expected if the above mechanism were correct.[20-22]

Porter and Connelly[23] have discussed the effect that multistage deactivation of a vibrationally excited upper electronic state will have on the shape of ϕ^{-1} against pressure plots for a system. These authors showed that for a mechanism involving decomposition from, and cascade deactivation of, a vibrationally excited upper singlet plus decomposition from an upper triplet state, the plot of ϕ^{-1} against pressure would pass through a point of inflection. The data displayed in Figures 1 and 2 display this characteristic.

Kutschke, *et al.*,[24-26] found similar curves for hexafluoroacetone photolyses and derived further graphical tests for detecting multistage deactivation. Our mechanism now becomes

$$\mathrm{A} + h\nu \longrightarrow \mathrm{A_1}^n \tag{1}$$

$$\left.\begin{aligned} \mathrm{A_1}^n &\longrightarrow \mathrm{C_3H_6} + \mathrm{CO} && (2\mathrm{a},n) \\ \mathrm{A_1}^n &\longrightarrow \mathrm{C_3H_5} + \mathrm{HCO} && (2\mathrm{b},n) \end{aligned}\right\} \quad (2,n)$$

$$\mathrm{A_1}^n \longrightarrow \text{ethylketene} \tag{3,n}$$

$$\mathrm{A_1}^n + \mathrm{A} \longrightarrow \mathrm{A_1}^{n-1} + \mathrm{A} \tag{4,n}$$

$$\left.\begin{aligned} \mathrm{A_1}^{n-1} &\longrightarrow \mathrm{C_3H_6} + \mathrm{CO} && (2\mathrm{a},n-1) \\ \mathrm{A_1}^{n-1} &\longrightarrow \mathrm{C_3H_5} + \mathrm{HCO} && (2\mathrm{b},n-1) \end{aligned}\right\} \quad (2,n-1)$$

$$\mathrm{A_1}^{n-1} \longrightarrow \text{ethylketene} \tag{3,n-1}$$

$$\mathrm{A_1}^{n-1} + \mathrm{A} \longrightarrow \mathrm{A_1}^{n-2} + \mathrm{A} \tag{4,n-1}$$

$$\vdots$$

$$\mathrm{A_1}^{m-1} + \mathrm{A} \longrightarrow \mathrm{A}^m + \mathrm{A} \tag{4,m-1}$$

$$\mathrm{A_1}^m + \mathrm{A} \longrightarrow \mathrm{A_1}^{m-1} + \mathrm{A} \tag{4,m}$$

$$\vdots$$

$$\mathrm{A_1}^1 + \mathrm{A} \longrightarrow \mathrm{A_1}^0 + \mathrm{A} \tag{4,1}$$

followed by reactions 5 through 15. $\mathrm{A_1}^{m+1}$ is chosen as the vibrational level of the upper singlet below which decomposition does not occur. Assuming $k_{2,i} \gg k_{3,i}$, this mechanism predicts that

$$\phi_{\mathrm{CO}} = \frac{\left\{\sum_{i=m+1}^{n} k_{2,i}[\mathrm{A_1}^i]\right\} + k_8[\mathrm{A_3}^0]}{I_\mathrm{a}} \tag{25}$$

and by applying steady-state approximations, eq 25 becomes

$$\phi_{\mathrm{CO}} = 1 - (1 - \phi_\infty)\left\{\prod_{i=m+1}^{n} (1 + a_i/[\mathrm{A}])^{-1}\right\} \tag{26}$$

where ϕ_∞ is as before and $a_i = k_{2,i}/k_{4,i}$. $\phi_{\mathrm{CO}} = 1.0$ at [A] = 0 so eq 26 may be rearranged to

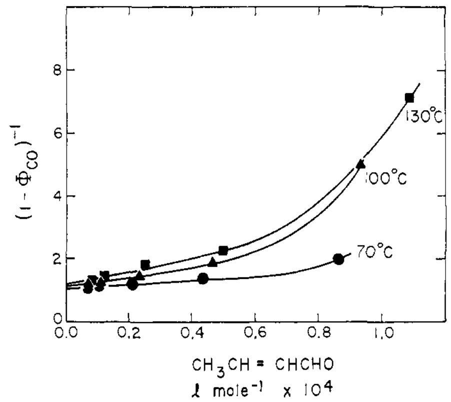

Figure 3. The variation of $(1 - \phi_{\mathrm{CO}})^{-1}$ with the reciprocal of *trans*-crotonaldehyde pressure at 70, 100, and 130°.

$$(1 - \phi)^{-1} = (1 - \phi_\infty)^{-1} + (1 - \phi_\infty)^{-1}\left\{\left[\prod_{i=m+1}^{n} (1 + a_i/[\mathrm{A}])\right] - 1\right\} \tag{27}$$

When $n = m + 1$

$$(1 - \phi)^{-1} = (1 - \phi_\infty)^{-1} + (1 - \phi_\infty)^{-1}\sum_{i=m+1}^{m+1}(a_i/[\mathrm{A}])$$

which is identical with eq 19.

One of the tests proposed by Kutschke, *et al.*,[26] involves the function

$$f_1 = (1 - \phi)[\mathrm{A}]^{-1} = (1 - \phi_\infty)/([\mathrm{A}] + a_i) \qquad \text{for } n = m + 1$$

$$= (1 - \phi_\infty)[\mathrm{A}]^{-1}\Big/\prod_{i=m+1}^{n}(1 + a_i/[\mathrm{A}]) \qquad \text{for } n > m + 1$$

If $n = m + 1$, plots of f_1 against [A] start at $f_1 = (1 - \phi_\infty)/a_i$ for [A] = 0 and decrease smoothly to zero as $[\mathrm{A}] \rightarrow \infty$; the slope is always negative and continuously decreases in magnitude as [A] increases. However, if $n > m + 1$, then $f_1 = 0$ when [A] = 0, the function increases with [A] when [A] is small, passes through a maximum when

$$\sum_{i=m+1}^{n} \{a_i/(a_i + [\mathrm{A}])\} = 1$$

then decreases to $f_1 = 0$ as $[\mathrm{A}] \rightarrow \infty$. Plots of f_1 against [A] for CO are shown in Figure 4. They show that for *trans*-crotonaldehyde $n > m + 1$. The relative values of f_1 for CO at 70, 100, and 130° are in the sense predicted by Kutschke, *et al.*[26] Expressions similar to eq 25 and 26 may be derived for $\mathrm{C_3H_6}$ production. At 100°, $\phi_0(\mathrm{C_3H_6}) = 0.44$ so that eq 27 and the function f_1 involve $(0.44 - \phi)$. A plot of $(0.44 - \phi)[\mathrm{A}]^{-1}$ against [A] is shown in Figure 5. Further evidence for multistage deactivation is that ϕ_{CO} and $\phi_{\mathrm{C_3H_6}}$ are smaller at longer wavelengths.

The variation of $\phi_0(\mathrm{C_3H_6})$ with temperature is presumably a result of the nonequality of the temperature dependence of $k_{2\mathrm{a}}$ and $k_{2\mathrm{b}}$. ϕ_0 decreases with increasing temperature showing the radical split (reaction 2b) is more important at higher temperature and that its acti-

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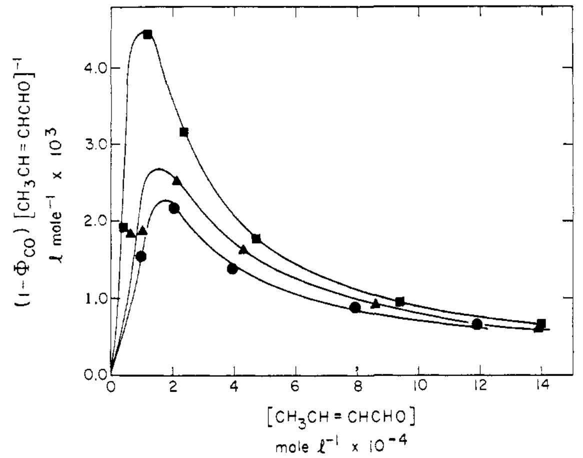

Figure 4. The function $f_1 = (1 - \phi_{CO})[CH_3CH{=}CHCHO]^{-1}$ plotted against *trans*-crotonaldehyde concentration at 70, 100, and 130°: ■, 70°; ▲, 100°; ●, 130°.

vation energy is greater than that of reaction 2a. At higher pressures, $\phi_{C_3H_6}$ increases with temperature which indicates that $E_{8a} > E_{8b}$.

Our observations and mechanism are radically different from those of Allen and Pitts.[8] These authors reported that ϕ_{CO} and $\phi_{C_3H_6}$ were dependent on I_0. We found them to be independent of light intensity. The most important difference between the two studies is that Allen and Pitts irradiated *trans*-crotonaldehyde with light which was absorbed in both regions of the aldehyde's spectrum whereas in our work 93% of the light fell in the carbonyl region. Allen and Pitts employed two 2-mm Corning CS7-54 glasses and a Br_2–Cl_2 filter. This corresponds to our filter B. With this combination 20% of the transmitted light falls in the π–π^* region of the *trans*-crotonaldehyde spectrum. The products and their quantum yields with filter B were significantly different from those found using filter A. ϕ_{CO} increased by 60% and CH_4 and 2-butene were found as additional products when filter B was substituted for filter A. Although the latter filter passed some light of shorter wavelength than 2550 Å, the differences in the photodecomposition for the two absorption regions are obvious.

It is debatable whether the intensity effect reported by Allen and Pitts is real. They report results of experiments where the band pass of the filter and the light intensity were varied together. They concluded that the resulting variation in quantum yield was due entirely to an intensity effect. Because of the wavelengths used by Allen and Pitts, it is not possible to interpret the temperature dependence of ϕ_{CO} and $\phi_{C_3H_6}$ in their work by our mechanism. However, we have already speculated that at higher temperatures reactions 21 and 23 would be more important. If a chain mechanism is involved, a dependence of quantum yield upon light intensity might be expected.

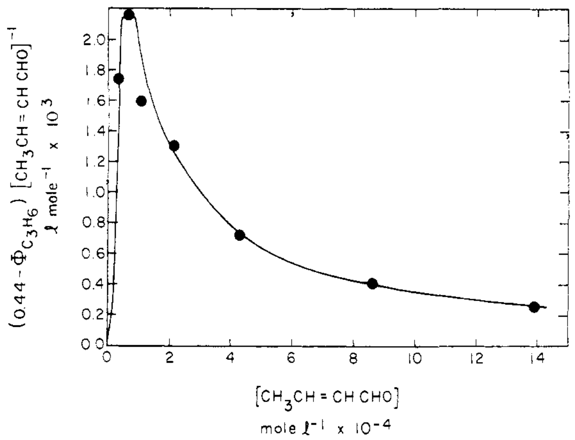

Figure 5. The function $f_1 = (0.44 - \phi_{C_3H_6})[CH_3CH{=}CHCHO]^{-1}$ plotted against *trans*-crotonaldehyde concentration at 100°.

Allen and Pitts proposed that the decrease in transmission by their reaction vessel and its contents during irradiation was due partly to polymer formation and partly to formation of a compound in the gas phase with an extinction coefficient 100 times greater than crotonaldehyde's. This compound was proposed to be ethylketene. We believe the increase of optical density was due entirely to the formation and photolysis of polymer. By analogy with ketene and methylketene, it seems that ethylketene will have approximately the same extinction coefficient as *trans*-crotonaldehyde at ~2600 Å.

In view of these comments, we feel it is more likely that the photochemistry of *trans*-crotonaldehyde in the carbonyl absorption region involves decomposition from, and multistage collisional deactivation of, a vibrationally excited upper singlet state, some intersystem crossing to an unstable triplet state, and some internal conversion to the ground state *via* unstable isomeric intermediates rather than the mechanism of Allen and Pitts.

Acknowledgment. We thank R. R. Schrock for assistance with the LPIR and D. G. Marsh for discussions. We acknowledge the support of this research by Grant AP 00109, Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U. S. Public Health Service.