The Vapor-Phase Photolysis of *trans*-Crotonaldehyde[1]

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Abstract: The vapor-phase photolysis of *trans*-crotonaldehyde (2-buten-1-al) has been investigated at 2654–2537 Å over a wide range of intensities, pressures, and temperatures. At 25° this α,β-unsaturated aldehyde was unusually stable, polymerization being the only significant reaction. Above 100°, reactions leading to the formation of gaseous products became important. The main products in decreasing order of abundance were carbon monoxide, propylene, hydrogen, and methane. Φ_{CO} was inversely proportional to the initial crotonaldehyde pressure and exceeded unity at 120° and pressures below 10 Torr. At 120°, Φ_{CO} was directly proportional to the incident light intensity; however, at temperatures greater than 200° the dependence was much less marked. A decomposition mechanism is suggested in which the absorption of radiation initially produced long-lived, thermodynamically unstable isomers, and subsequently a free-radical chain process was initiated by the secondary photolysis and/or thermolysis of one or more of these isomers.

The vapor-phase photolysis of *trans*-crotonaldehyde (2-buten-1-al) has been studied as part of a series of investigations designed to correlate the effects of structure on photochemical decomposition and reactivity.[3] Aldehydes and ketones with unsaturated side chains, especially those in conjugation with the carbonyl double bond, are enigmatic in their unusual stability to photodissociation when compared with their saturated aliphatic counterparts.

Early work by Blacet and coworkers showed that although crotonaldehyde is remarkably stable to light-induced decomposition into gaseous products in the wavelength range 3130–2380 Å at room temperature, photoinitiated dissociation does occur at 2380 Å and 265°.[4,5] The reaction products were mainly carbon monoxide with lesser amounts of unidentified unsaturated hydrocarbons and methane.

A more recent study by Tolberg and Pitts confirmed the presence of methane and identified 2-butene as a minor product.[6] It was suggested that the 2-butene was, at least in part, formed by the methyl radical displacement reaction

$$CH_3\cdot + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH_3 + CHO$$

Subsequently, Pitts, Thompson, and Woolfolk found additional strong evidence for this process[7] in the photolysis of crotonaldehyde–acetone mixtures at 120–350° and 2654–2537 Å. More recently the photoisomerization of crotonaldehyde to 3-buten-1-al has been proposed by McDowell and Sifniades[8] as a primary process.

None of the previous investigations reported a detailed study of the dissociation process, and the advent of more refined analytical techniques made a detailed reinvestigation of the problem desirable.

Experimental Section

Materials. Matheson Coleman and Bell crotonaldehyde was purified chromatographically, using a Carbowax 20M column at 80°. The eluted crotonaldehyde was condensed at 0° and finally transferred by vacuum distillation into a blackened storage reservoir. The purity was in excess of 99.5% and was checked at regular intervals. Acetone was Matheson Coleman and Bell "chromatoquality" reagent and was checked periodically.

Apparatus. Photolyses were carried out in a conventional static system described previously,[6] with minor modifications. The cylindrical quartz reaction vessel, 3 cm i.d., 20 cm long, and 140 cc volume, was just filled with a parallel beam of light from a Hanovia "Type A" Alpine Burner, a medium-pressure quartz mercury arc. With a combination of a gaseous Br_2–Cl_2 filter and two 2-mm path Corning CS 7-54 filters, more than 95% of the transmitted light was in the desired range 2654–2537 Å. This filter combination also passed some radiation above 4000 Å which was not absorbed by the crotonaldehyde or the reaction products.

The percentage transmission of the photolysis cell was measured by an RCA 935 phototube-galvanometer combination. Absolute light intensities were determined frequently using the photolysis of acetone at 125° ($\Phi_{CO} = 1.00$) as an internal actinometer.

Pressure measurements were made using a Statham PA707TC-5-350 pressure transducer with a linear range of 0–250 Torr, with the output fed to a millivolt recorder.

Analysis. After each experiment the products and unreacted crotonaldehyde were collected at −196° and fractionated at low temperature before gas chromatographic analysis. The fraction volatile at −196° was analyzed on a 13X molecular sieve column. The fractions volatile at −150° (mainly propylene) and −120° (butene) were analyzed with 20-ft hexadecane and 2,5-hexanedione columns, respectively, at room temperature. The condensables at −120° were analyzed on a Carbowax 20M column at 80°. Confirmation of the nature of the products was obtained by gas–liquid chromatography and qualitative analysis of the eluted components by mass spectrometry and infrared spectrophotometry.

Columns of dinonyl phthalate, Carbowax 20M, and Carbowax 1500 were employed in the analysis of the products of prolonged photolysis of crotonaldehyde.

To observe possible *trans–cis* photoisomerization the aldehyde vapor was irradiated in a cross-cell with suitable windows set in the sample beam of a Perkin-Elmer 221 infrared spectrophotometer.

Results

Photolyses in the range 3130–2380 Å have confirmed previous observations that crotonaldehyde is stable to photodissociation into gaseous products at room temperature.[4,5] It is also remarkably stable at elevated temperatures at 3130 Å, but at moderate intensities decomposition begins to be appreciable at 2654 Å and about 100°.

Photoisomerization. In contrast to *trans*-methyl propenyl ketone where photoisomerization to the *cis*

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[2] Author to whom communications should be addressed.

[3] J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957). For a recent review see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966.

[4] F. E. Blacet and J. G. Roof, *J. Am. Chem. Soc.*, **58**, 73 (1936).

[5] F. E. Blacet and J. E. LuValle, *ibid.*, **61**, 273 (1939).

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

[7] J. N. Pitts, Jr., D. D. Thompson, and R. W. Woolfolk, *ibid.*, **80**, 66 (1958).

[8] C. A. McDowell and S. Sifniades, *ibid.*, **84**, 4606 (1962).

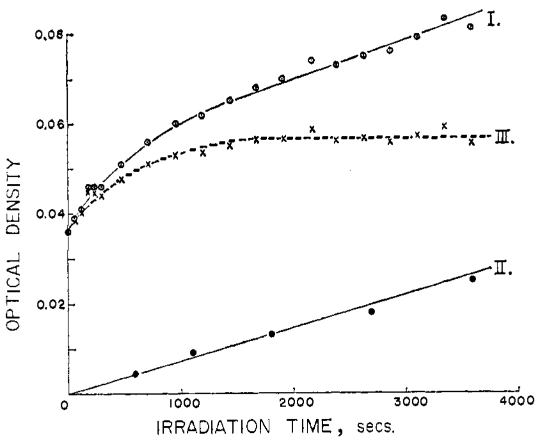

Figure 1. Variation of optical density with irradiation time during typical experiment. Curves I, II, and III show changes in over-all, solid- and vapor-phase optical densities, respectively. $I_0 = 2.8 \times 10^{13}$ quanta cc^{-1} sec^{-1}; crotonaldehyde concentration = 1.06×10^{-3} mole l.$^{-1}$ at 120°.

form was an important process at 3130 Å,[6] no such isomerization was observed with *trans*-crotonaldehyde. Furthermore, an exhaustive search using a variety of reaction conditions and gas chromatographic analyses failed to detect 3-buten-1-al as a product of the vapor-phase photolysis, although it has been reported to be an important product with a quantum yield of *ca.* 0.1.[8] Similarly, Yang was unable to detect $CH_3COCH_2CH=CH_2$ as a product[9] of the photolysis of liquid *trans*-methyl propenyl ketone ($CH_3COCH=CHCH_3$). However, it is possible that 3-buten-1-al was unstable under our chromatographic conditions.

In a recent communication Coomber, Pitts, and Schrock[10] have described the detection by long-path infrared spectrophotometry of two thermodynamically unstable isomers produced during the photolysis of *trans*-crotonaldehyde. They attribute the observed infrared absorptions to ethylketene and enol-crotonaldehyde, and suggest that both are products of the primary photolytic step with low quantum yields (≤ 0.1). It seems likely that one or both isomers may be intermediates in the photodissociation mechanism of *trans*-crotonaldehyde. Either or both of these isomers may be capable of absorbing the incident ultraviolet radiation which, in addition to their thermal instability, provides an alternate pathway for free-radical production.

Photopolymerization. At light intensities greater than 2.5×10^{12} quanta (abs) cc^{-1} sec^{-1} and room temperature, a strongly absorbing solid formed in the reaction cell. The chemical and physical behavior of the solid suggested it was a polymer similar to that found in acrolein photolysis.[11]

The variation of optical density with time of irradiation for a typical experiment is shown in Figure 1, curve I. This curve was easily reproducible and combines the effects of the decrease in optical density as crotonaldehyde was consumed and the increase in optical density due to the formation of absorbing gaseous products and the deposition of polymer on the cell windows. Curve II indicates the rate of deposition of polymer, estimated from the change in transmission through the evacuated vessel. Curve III, obtained by subtracting curve II from curve I, shows the change of absorbance in the gas phase during irradiation. Assuming the optical density of crotonaldehyde to remain constant at 0.036 (the conversion was less than 1%), it is seen that a strongly absorbing product was formed in the gas phase with an extinction coefficient about two orders of magnitude greater than that of crotonaldehyde at 2537 Å (ϵ 1.7 l. mole^{-1} cm^{-1}). Since the usual gaseous dissociation products are well known and none have extinction coefficients greatly in excess of that of crotonaldehyde, it seems reasonable to suggest that the strongly absorbing gaseous product may be the recently discovered isomer of crotonaldehyde, ethylketene.[10] It is unlikely, though by no means certain, that the enol-crotonaldehyde contributes significantly to this absorption since in general alcohols do not absorb radiation above 2000 Å. Curve III shows that the isomer in vapor phase attained a stationary concentration after 1200 sec. At steady state the removal processes are probably deactivation, isomerization, and thermal and photodecomposition. It is also apparent from curve II that the rate of deposition of polymer is independent of the strongly absorbing isomer but could be due to secondary radical addition and removal processes.

The polymeric material condensed on the reaction cell windows was irradiated for 5 hr. The only gaseous products were traces of H_2 and CO in roughly equal amounts. This suggests the presence of formaldehyde, which was verified later using the chromotropic acid test on the condensable reaction products. The small yield of gaseous products indicates that photolysis of the condensed polymer did not contribute significantly to the gaseous dissociation products during the average 1 hr experiment.

Dark Reaction. Although photopolymerization was observed at room temperature, no dark reaction producing polymer or noncondensable products was apparent, even over a 12-hr period. As the reaction temperature was raised above 150°, the dark reaction became significant, producing gaseous products, but there was no polymerization even at the elevated temperatures. The gaseous products were CO and C_3H_6 in about equal proportions, with traces of H_2 and CH_4, substantiating early pyrolysis studies.[5] The dark reaction is thought to be heterogeneous and not to involve free radicals.

Wavelength Effects. Undoubtedly, the largest single source of error in determining the absolute quantum yields was the use of acetone as an internal actinometer, since the absorption spectra of acetone and crotonaldehyde differ markedly and the radiation was not strictly monochromatic. It was difficult to estimate the magnitude of this error. However, the relative values of the quantum yields of the major products are probably good to within 5%.

Early experiments were performed using only the gaseous Br_2–Cl_2 filter, but because the quantum yields were much larger than those of past workers,[4–7] it was thought that this filter alone had too large a band pass. One, and finally two, Corning CS 7-54 2-mm filters were added to determine whether wavelengths other

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(9) N. C. Yang, private communication.

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

(11) F. E. Blacet, G. H. Fielding, and J. G. Roof, *J. Am. Chem. Soc.*, 59, 2375 (1937).

Table I. Effect of Filter Combination and Light Intensity on Quantum Yields and Ratios of Quantum Yields of Major Noncondensable Products[a]

Filter	Transmitted band width, Å (% T > 5%)	$I_{abs} \times 10^{-11}$ quanta cc^{-1} sec^{-1}	Quantum yield				Ratio of quantum yields to Φ_{CO}		
			CO	C_3H_6	H_2	CH_4	C_3H_6	H_2	CH_4
Br_2–Cl_2	2870–<2000	44.0	1.87	0.95	0.32	0.08	0.51	0.17	0.04
1(7–54)	4000–2300	21.7	0.92	0.44	0.18	0.03	0.48	0.20	0.03
Br_2–Cl_2 + 1(7–54)	2840–2330	12.5	0.57	0.28	0.10	0.02	0.49	0.18	0.04
Br_2–Cl_2 + 2(7–54)	2830–2400	8.0	0.32	0.15	0.05	0.01	0.47	0.16	0.03

[a] Photolyses at 120° and crotonaldehyde concentration of 1.06×10^{-3} mole l.$^{-1}$.

than 2654–2537 Å were affecting the mechanism of dissociation. The results are shown in Table I. The temperature and concentration of crotonaldehyde were constant in these experiments.

It is evident that although the absolute values of the quantum yields vary over a sixfold range, their ratios remain virtually constant. This suggests that changing the filters does not alter the reaction mechanism and that the observed large variation in the quantum yields is an intensity effect.

Pressure. The effect of initial pressure on quantum yields is shown in Figure 2. At 120° the quantum yields of the major products CO, C_3H_6, H_2, and CH_4 are proportional to the reciprocal of the initial pressure of crotonaldehyde, although their *ratios* remain constant from 90 to 5 Torr. Addition of 50 Torr of CO_2 to 25 Torr of crotonaldehyde decreased Φ_{CO} from 0.32 to 0.20, but did not affect the ratios of the quantum yields.

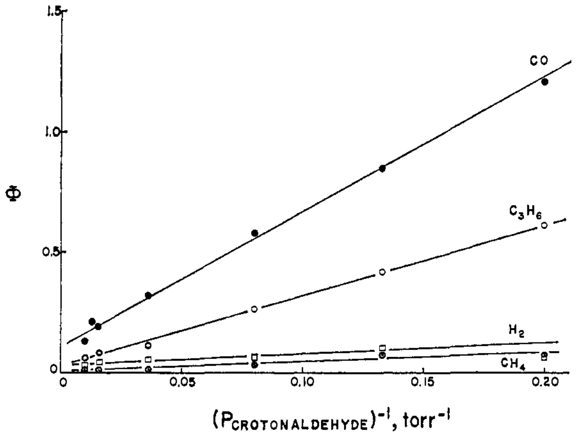

Figure 2. Variation of quantum yield with reciprocal crotonaldehyde pressure. $I_0 = 6.1 \times 10^{12}$ quanta cc^{-1} sec^{-1} at 120°.

Light Intensity. At 120°, the quantum yield of CO depended linearly on the intensity (Figure 3). At higher temperatures the dependence is less marked. Thus, at 225°, increasing the absorbed light intensity from 4.0 to 41.6 × 10^{11} quanta (abs) cc^{-1} sec^{-1} caused Φ_{CO} to increase only from 1.66 to 2.17. Absorbed light intensities were calculated using initial values for the incident intensity and the fraction of light absorbed by crotonaldehyde.

Temperature. The effect of temperature on CO and C_3H_6 is shown in Figure 4 for two light intensities, 4.9×10^{11} and 41×10^{11} quanta (abs) cc^{-1} sec^{-1}. It is evident that at the lower intensity both Φ_{CO} and $\Phi_{C_3H_6}$ increase approximately linearly until *ca.* 175–200° when they accelerate rapidly, particularly Φ_{CO}. At the high intensity, the situation is reversed with the quantum yields rising rapidly up to *ca.* 100–125° where the *rate* of increase of Φ_{CO} starts to decrease rapidly. Over the entire intensity range the ratio $\Phi_{C_3H_6}/\Phi_{CO}$ decreased on elevating the temperature.

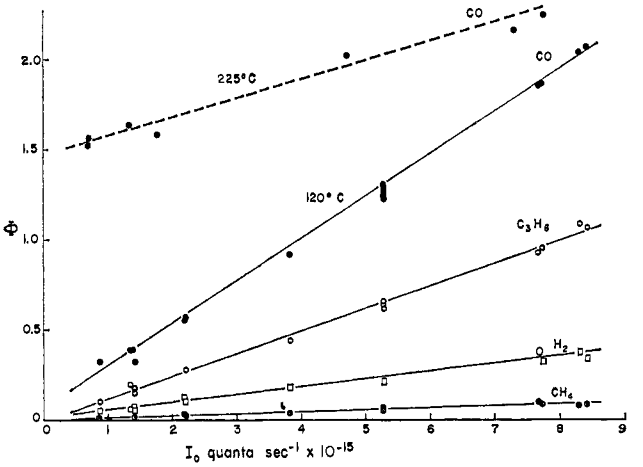

Figure 3. Variation of quantum yield with incident light intensity: solid lines at 120°; dashed line at 225°; crotonaldehyde concentration = 1.06×10^{-3} mole l.$^{-1}$; cell volume 140 cc.

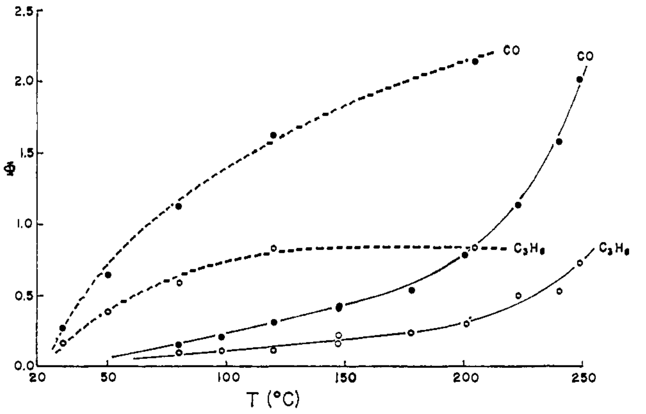

Figure 4. Variation of quantum yield with temperature: solid lines, low-intensity runs, $I_0 = 6.1 \times 10^{12}$ quanta cc^{-1} sec^{-1}; dashed lines, high-intensity runs, $I_0 = 4.7 \times 10^{13}$ quanta cc^{-1} sec^{-1}; crotonaldehyde concentration = 1.06×10^{-3} mole l.$^{-1}$.

Minor Products. A variety of minor products were isolated and identified. They include acetylene, ethylene, propane, methylacetylene, the four butenes 1,5-hexadiene, formaldehyde, acetaldehyde, *n*-butyraldehyde, and isovaleraldehyde. The quantum yields were generally very small and often difficult to determine accurately, and are thus not reported.

Discussion

A free-radical chain mechanism is proposed, based on the following observations. (1) Free radicals have been detected during the photolysis of crotonaldehyde at 2537 Å by tellurium mirror removal[12] and mass spectrometrically.[13] (2) The decomposition of crotonaldehyde sensitized by methyl radicals gave quantum yields of carbon monoxide greater than unity.[7,14] (3) The effect of temperature on the quantum yields of gaseous products is marked. (4) The minor products are more readily explained by a free-radical mechanism. (5) The photochemical stability of crotonaldehyde at room temperature may be partially explained as radical scavenging by the conjugated, unsaturated substrate. At low temperatures and low radical concentrations, radical addition to the double bond would be expected to predominate over the competing radical abstraction, recombination, disproportionation, and displacement reactions. Radical addition may produce longer lived, less active radicals which may subsequently react with other substrate molecules to yield polymer. The following mechanism, while not unique, appears to explain the yields and kinetic dependence of major products on wavelength, pressure, intensity, and temperature.

Simplified mechanism

$$\mathrm{RCHO} + h\nu \longrightarrow \mathrm{RCHO^*} \tag{1}$$

$$\mathrm{RCHO^*} + \mathrm{M} \longrightarrow \mathrm{RCHO} + \mathrm{M} \tag{2}$$

$$\mathrm{RCHO^*} + h\nu' \longrightarrow \mathrm{R_1} + \mathrm{R_2} \tag{3}$$

$$\mathrm{RCHO^*} \longrightarrow \mathrm{R_1} + \mathrm{R_2} \tag{4}$$

$$\mathrm{R_1} + \mathrm{RCHO} \longrightarrow \mathrm{R_1H} + \mathrm{R_3} \tag{5}$$

$$\mathrm{R_2} \longrightarrow \mathrm{R_1} + \mathrm{CO} \tag{6}$$

$$\mathrm{R_3} \longrightarrow \mathrm{R_1} + \mathrm{CO} \tag{7}$$

$$\mathrm{R_1} + \mathrm{RCHO} \longrightarrow \text{addition products } (<150°) \tag{8}$$

$$\mathrm{R_1} \longrightarrow \text{isomerization products } (>150°) \tag{9}$$

R_1 is H, CH_3, or $CH_3CH{=}CH$; R_2 is CHO or $CH_3CH{=}CHCO$; R_3 is $CH_3CH{=}CHCO$; RCHO is $CH_3CH{=}CHCHO$; and RCHO* is an unstable isomer.

The rate of formation of carbon monoxide is given by

$$R_{\mathrm{CO}} = \Phi_{\mathrm{CO}} I_{\mathrm{a}} = k_6(\mathrm{R_2}) + k_7(\mathrm{R_3})$$

where I_{a} is the initial absorbed intensity. Assuming steady-state conditions, we obtain below ~150°

$$\Phi_{\mathrm{CO}} = \frac{\varphi(k_3 + k_4)}{k_2(\mathrm{M}) + k_3 + k_4}\left[1 + \frac{2k_5}{k_8}\right]$$

The low quantum yield of isomer suggests that $k_2(\mathrm{M}) > k_3 + k_4$, and at low temperatures $k_3 > k_4$, therefore

$$\Phi_{\mathrm{CO}} \propto \frac{k_3}{k_2(\mathrm{M})}$$

Since k_3 is dependent on the incident light intensity, Φ_{CO} must also be dependent on the light intensity at constant crotonaldehyde concentration and temperature. Also at constant light intensity and temperature, Φ_{CO} is inversely proportional to crotonaldehyde concentration. Furthermore, since the ratios of the quantum yields of propylene, hydrogen, and methane to Φ_{CO} are essentially independent of temperature (see Table I), it follows that $\Phi_{\mathrm{C_3H_6}}$, $\Phi_{\mathrm{H_2}}$, and $\Phi_{\mathrm{CH_4}}$ should show the same dependence as Φ_{CO} (Figures 2 and 3).

Raising the temperature above about 250° increases the efficiency of thermal process 4 relative to the photolytic step 3 and enhances the radical abstraction and decomposition reactions 5–7 to such an extent that the kinetic scheme must be modified. Also at these higher temperatures a chain-terminating step involving radical isomerization is suggested to account for the absence of polymerization and the formation of new products. The rate of formation of carbon monoxide would then be

$$\Phi_{\mathrm{CO}} = k_5(\mathrm{R_1})(\mathrm{RCHO}) = \frac{2k_4k_5\varphi}{k_2k_9}$$

assuming that step 7 becomes the most important source of carbon monoxide and collisional deactivation of isomer by process 2 is still important. Above 250°, therefore, Φ_{CO} should be independent of intensity and crotonaldehyde pressure. At intermediate temperatures, however, the relative importance of the nonchain to the chain process will determine the observed kinetic dependence of the quantum yield. It may be seen in Figure 3 that the dependence of quantum yield on intensity is considerably less at 225°. The intercepts at $I_0 = 0$, however, suggest that the contribution to Φ_{CO} due to pyrolysis of the isomer is large at 225° and negligible at 120°. Thus at high light intensities photolysis of isomer is probably the dominant mode of free-radical production at least up to 200°, whereas at low light intensities pyrolysis becomes the dominant mode at a much lower temperature. The deactivation process 2 is probably temperature dependent which means that at high light intensities, as the temperature is raised, free-radical production becomes less efficient due to the increasing efficiency of process 2. At low light intensities, however, this decreasing efficiency in radical production on raising temperature is probably more than offset by the thermally controlled pyrolysis of isomer since the activation energy for thermal dissociation would be much greater than that for collisional deactivation to ground-state crotonaldehyde.

The change in the kinetics from 25 to 250° is shown in Figure 4. At 25° efficient scavenging of hydrogen atoms and propenyl radicals (R_1) by crotonaldehyde and the stability of the formyl (R_2) and crotonyl (R_3) radicals almost completely suppress the formation of gaseous products and initiate polymer formation. As the temperature is raised to 150° steps 4–6 become increasingly important compared to reaction 7, thus conferring a unique increasing intensity dependence on the quantum yield of gaseous products. It should be noted that as the reaction temperature is raised the yield of gaseous products increases and polymer formation becomes less apparent. Above 150°, where the quantum yields at high and low intensity converge, the reaction chain length becomes sufficiently large that the chain mechanism becomes dominant and the

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(12) D. H. Volman, P. A. Leighton, F. E. Blacet, and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

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

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

intensity dependence finally disappears. By extrapolation of the curves in Figure 4 this would appear to occur where the curves coincide, at about 250°, where the products should be independent of both pressure and intensity.

The nature of the molecule (RCHO*) involved in reactions 2–4 must be considered. There is no evidence to suggest that the absorption of radiation by a crotonaldehyde molecule does not produce initially an upper electronically excited singlet state. Since fluorescence has not been observed from crotonaldehyde irradiated at 2654 and 2537 Å,[4,5] it may be concluded that this state is extremely short-lived ($<10^{-8}$ sec). There is also no evidence for phosphorescence from crotonaldehyde irradiated at these wavelengths,[4,5] suggesting that the triplet state, if formed, is short-lived.

Hammond, Turro, and Leermakers[15] believe that a substantial energy barrier (*ca.* 50 kcal/mole) separates the first excited singlet state and the first triplet state in the conjugated dienes. Srinivasan[16] has pointed out the remarkable similarities between the photochemistry of conjugated dienes and that of unsaturated aldehydes and ketones. There is good reason, therefore, to believe that a similar large energy barrier exists between the first excited singlet state and the first triplet state of crotonaldehyde, which could effectively limit intersystem crossing. The observation that the quantum yield of photooxidation of crotonaldehyde at 2537 Å increased rapidly with increasing oxygen concentration and temperature,[17] and the lack of *trans* → *cis* isomerization in our system, may also be offered as evidence of the unimportance of the triplet state.

Since it appears that neither the first excited singlet nor the triplet state is directly involved in photochemical initiation, we conclude that (RCHO*) must be a long-lived thermodynamically unstable isomer of crotonaldehyde probably formed from the first excited singlet state initially produced. That such isomeric species exist with a lifetime sufficiently large to allow their substantial accumulation has already been shown.[10] The intermediacy of these isomers is supported by the inhibiting effect of nitrogen on the crotonaldehyde photooxidation at 2537 Å,[17] and the inhibiting effect of carbon dioxide in the present investigation suggesting that they are prone to collisional deactivation to ground-state crotonaldehyde. The collisional lifetime of these isomers, however, could be long enough to permit a relatively efficient initiation step by the secondary photolysis or thermolysis of either or both of them. At the present time this rather unusual initiation mechanism appears to us to be the most reasonable explanation of the observed dependence of quantum yields on intensity and pressure, although it must be regarded as tentative. This mechanism is consistent with the supposition proposed by Phillips, LeMaire, Burton, and Noyes[18] that isomerization provides a path for the radiationless relaxation of some electronically excited molecules.

The minor products, which became increasingly important at temperatures above 150°, may be readily explained by a free-radical mechanism. The formation of methane, isovaleraldehyde, and 2-butene indicates the presence of methyl radicals, while hydrogen and *n*-butyraldehyde suggest the participation of hydrogen atoms. These species may be produced by a spontaneous decomposition of energy-rich species formed in the primary step, or by the thermal decomposition of radicals. Because a large amount of energy is available in the initiation step (3), several processes are possible.

$$\begin{aligned}
\mathrm{RCHO^*} + h\nu' &\longrightarrow \mathrm{CH_3CH{=}CH + CHO} && (3)\\
&\longrightarrow \mathrm{CH_3CH{=}CHCO + H} && (3a)\\
&\longrightarrow \mathrm{CH_3CH{=}CH + CO + H} && (3b)\\
&\longrightarrow \mathrm{CH_3 + CH{=}CHCHO} && (3c)\\
&\longrightarrow \mathrm{C_3H_6 + CO} && (3d)
\end{aligned}$$

The last reaction (3d) must be of minor importance since at low temperatures yields are extremely low, although Φ_{CO} does approach $\Phi_{\mathrm{C_3H_6}}$. Energy-rich radicals might be expected in these processes since the energy available greatly exceeds that required to break a C–C or C–H bond. Such "hot" radicals could spontaneously decompose, and with decreasing wavelength and increasing excess energy a greater fraction could decompose in this way. Unimolecular decomposition of thermal carbonyl radicals must also be postulated to explain the increase of Φ_{CO} with temperature.

At low temperatures ($<150°$) the main loss of radicals would be by addition to the olefinic double bond of the substrate, producing relatively stable large radicals which subsequently react further with substrate molecules to yield polymer. At high temperatures ($>150°$) radical recombination reactions would become important. Propenyl radicals may disproportionate to propylene and allene or methylacetylene.[13] At these higher temperatures propenyl radicals may also isomerize to the relatively stable allyl radicals, which may add to crotonaldehyde or recombine to give 1,5-hexadiene. Both methylacetylene and 1,5-hexadiene were observed at the higher temperatures.

The decrease in the ratio $\Phi_{\mathrm{C_3H_6}}$ to Φ_{CO} as the temperature was raised may be due to the increasing importance of alkenyl radical isomerization followed by radical–radical combination.

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