Molecular Structure and Photochemical Reactivity. XII.
The Vapor-Phase Photochemistry of Acrolein at 3130 Å

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Abstract: The vapor-phase photochemistry of acrolein has been studied at 3130 Å between 35 and 200°. The major photodecomposition products were CO ($\Phi \sim 5 \times 10^{-3}$) and C_2H_4 ($\Phi \sim 3 \times 10^{-3}$). C_2H_2 and C_4H_6 (butadiene) were minor products ($\Phi < 10^{-6}$), and small amounts of CO_2 were formed in a bimolecular dark reaction. These results, and those of previous workers, are explained by a mechanism involving the primary steps for decomposition of excited acrolein: $CH_2{=}CHCHO^* \rightarrow C_2H_3 + HCO$ and $CH_2{=}CHCHO^* \rightarrow C_2H_4 + CO$. The relative importance of the two processes varies with the pressure of the irradiated gas.

This paper reports part of a study to determine the effect of molecular structure upon the mode of photochemical decomposition and reactivity of simple organic molecules.[1]

Previous workers have shown that aldehydes and ketones which have unsaturated side chains conjugated with the carbonyl group are more stable to photodecomposition than their saturated aliphatic counterparts.[2] However, the results of, and conclusions from, studies of the photochemistry of acrolein by Thompson and Linnett,[3] Blacet, *et al.*,[4] Harrison and Lossing,[5] and Weir[6] seem mutually inconsistent. For this reason, and because acrolein is one lachrymator in Los Angeles type smog,[7,8] it seemed desirable to reexamine the photochemistry of acrolein using more advanced methods of purification and analysis.

Experimental Section

Materials. Degassed acrolein (Matheson Coleman and Bell) was separated from traces of polymer by two bulb-to-bulb distillations. A middle cut was stored over hydroquinone in a blackened side arm to prevent polymerization.[9] Before each run the aldehyde was further purified by glpc using a 20 ft × 0.25 in. 1,2,3-tris(cyanoethoxy)propane (TCEP) on 60–80 Chromosorb P (HMDS) washed column at 75° with helium as carrier gas. No impurity could be detected in this chromatographed acrolein by ir or mass spectrometry. Nitric oxide (Matheson Gas Co.) was thoroughly degassed and then transferred to the first of two Ward-Leroy stills in series. A middle cut of the fraction volatile with the stills at −137 and −160° was stored. CO_2 (Matheson Gas Co.) was degassed and used without further purification. Piperylene (Matheson Coleman and Bell) was better than 99% pure by glpc and was used without further purification. 3-Pentanone (Matheson Coleman and Bell) was purified immediately before use on a 20 ft × 0.25-in. TCEP–Chromosorb P column at 160°.

All purified compounds were analyzed by ir and/or mass spectrometry. No impurity was detected.

(1) J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).
(2) J. G. Calvert and J. N Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 368.
(3) H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, 1452 (1935).
(4) F. E. Blacet, G. H. Fielding, and J. G. Roof, *J. Amer. Chem. Soc.*, **59**, 2375 (1937).
(5) A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **37**, 1696 (1959).
(6) N. A. Weir, *J. Chem. Soc.*, 6870 (1965).
(7) E. A. Schuck and G. T. Doyle, Report 29, Air Pollution Foundation, San Marino, Calif.
(8) E. R. Stephens, E. F. Darley, O. C. Taylor, and W. E. Scott, *Intern. J. Air Water Pollution*, **4**, 79 (1961).
(9) C. W. Smith, "Acrolein," John Wiley and Sons, Inc., New York, N. Y., 1962, p 240.

Apparatus and Procedure. A conventional high-vacuum system was used. The apparatus was connected *via* two Ward-Leroy stills, a mercury diffusion pump, and a combined gas buret–Toepler pump to an Aerograph 500D gas chromatograph with a flame ionization detector. It was also possible to completely transfer samples from the gas buret to a removable sample bulb for mass spectrometric, ir, and other analyses.

The cylindrical quartz reaction vessel (length 20 cm, diameter 3.5 cm, volume 181 cm³) was situated inside an aluminum cylinder wound with electrical heating tape. This was insulated with asbestos. The temperature of the oven was controlled to better than ±1° by a Leeds and Northrup type H recorder fitted with a control device. The oven and Ward-Leroy still temperatures were measured with copper–constantan thermocouples.

The reaction vessel was completely filled by a parallel beam of the collimated emission from a PEK Labs 110 high-pressure-point source arc. The 3130-Å radiation was isolated by a Schott-Jena 3130-Å interference filter system. This filter transmitted light of wavelengths 3080–3200 Å. The transmitted light intensity was measured with an RCA 935 phototube connected to a galvanometer. The light intensity was checked, at least every six runs, using the photolysis of ~25 torr of 3-pentanone at 125° as an actinometer ($\Phi_{CO} = 1.0$).

Pressure in the reaction vessel was measured with a Statham PA707TC-5-350 pressure transducer which had a linear response from 0 to 250 torr. The pressure in the remainder of the apparatus was measured with a mercury manometer.

After irradiation, the reaction mixture was passed through a trap at −196° and the volatile fraction collected in the gas buret. The condensate was warmed and refrozen. Any remaining noncondensable products were added to those already in the gas buret and the total amount was measured. This fraction was wholly CO. Its composition was checked by transferring it to the removable sample bulb and then injecting onto an 8 ft × 0.25 in. molecular sieve (13X) column. The chromatograph had a Carle thermal conductivity detector and was used to analyze for H_2, CO, and CH_4.

The condensate in the trap was then transferred to the Ward-Leroy stills and the fraction volatile with the stills at −100 and −140° collected. The total pressure was measured and then the whole sample analyzed for C_2H_4, C_2H_2, and C_4H_6 (butadiene) on the Aerograph 500D chromatograph using a 25 ft × 1/8 in. column of 20% hexadecane on 30–60 firebrick at 25° with helium as carrier gas. The column was calibrated immediately after the analysis of each product sample by the injection of a known amount of C_2H_4. In the earlier experiments and at frequent intervals throughout the work, this fraction was analyzed by mass spectrometry instead of glpc to check that CO_2 was the only compound not detected by glpc. The amount of CO_2 formed in a run was thus equal to the total amount of the fraction minus the hydrocarbons detected by glpc.

The residue in the Ward-Leroy stills was analyzed by either ir or mass spectrometry or both.

Results

The results are given in Table I. Preliminary experiments at 125° showed that the major products of

Table I. Photochemistry of Acrolein at 3130 Å

CH₂CHCHO, torr[a]	NO, torr[a]	Piperylene, torr[a]	CO₂, torr[a]	Temp, °C	Irradiation time, sec	I_{abs}, quanta cm⁻³ sec⁻¹	Φ_{CO} × 10³	$\Phi_{C_2H_4}$ × 10³
17.8	...	...	...	125.0	3,600	5.1×10^{12}	5.8	3.3
17.6	...	...	10.7	125.0	3,600	5.1×10^{12}	3.9	1.7
17.6	...	...	23.1	124.5	3,600	5.1×10^{12}	3.2	1.6
17.6	...	...	79.4	124.5	3,600	5.1×10^{12}	2.6	0.7
19.0	...	...	307.0	124.5	3,600	5.7×10^{12}	2.6	0
18.5	1.5	...	...	124.5	900	5.7×10^{12}	...	3.3
18.2	...	...	...	125.9	900	5.4×10^{12}	6.2	2.8
18.2	...	...	...	124.0	1,800	5.4×10^{12}	6.1	2.9
17.8	...	...	...	126.5	3,600	5.1×10^{12}	5.9	3.0
18.8	...	...	...	126.0	17,400	3.4×10^{11}	6.4	3.1
18.7	...	...	...	126.0	10,800	1.0×10^{12}	6.5	2.6
4.6	...	...	...	126.0	3,600	1.6×10^{12}	16.7	10.5
4.6	...	0.1	...	124.0	3,600	1.6×10^{12}	16.2	9.9
4.6	...	0.3	...	124.5	3,600	1.6×10^{12}	15.3	8.4
4.6	...	1.2	...	124.5	3,600	1.6×10^{12}	15.0	8.3
4.7	...	1.9	...	124.5	3,600	1.6×10^{12}	12.8	6.4
34.0	...	2.2	...	126.0	3,600	8.3×10^{12}	2.2	0
17.8	...	...	...	126.5	3,600	5.1×10^{12}	5.9	3.6 }[b]
					3,600	5.1×10^{12}	5.6	3.1

[a] Pressures are at run temperatures. [b] In this experiment, the residue from the Ward stills at the end of the run was reirradiated. The results agree, within experimental error, with those for pure acrolein.

irradiation were CO ($\Phi_{CO} \sim 5 \times 10^{-3}$), C₂H₄ ($\Phi_{C_2H_4} \sim 3 \times 10^{-3}$), and CO₂ ($\Phi_{CO_2} \sim 5 \times 10^{-4}$). The only other products detected were C₂H₂ ($\Phi_{C_2H_2} \sim 10^{-6}$) and C₄H₆ (butadiene) ($\Phi_{C_4H_6} \sim 10^{-6}$). These figures represent total yields of ~ 0.15 μmole of CO, C₂H₄, and CO₂ and $\sim 10^{-4}$ μmole of C₂H₂ and C₄H₆. With our apparatus it was possible to measure CO to ±0.005 μmole, but the low-temperature fractionations in the analysis for C₂H₄, CO₂, C₂H₂, and C₄H₆ reduced the accuracy for these compounds to ±0.02 μmole. Thus it was not possible to obtain reliable quantum yields for C₂H₂ and C₄H₆ production.

There was no evidence for polymer formation, and no pressure change was detected during any run. Any disappearance of acrolein was too small to measure; it was impossible to obtain a materials balance and some polymer may have gone undetected.

A number of "dark" runs were carried out. The only detectable product was CO₂. Its rate of formation was the same in both "dark" and "light" reactions and was proportional to [CH₂=CHCHO].[2] As CO₂ was the product of a bimolecular "dark" reaction, its occurrence was ignored in the interpretation of the photochemical results.

Φ_{CO} and $\Phi_{C_2H_4}$ were measured over a pressure range of 1.0–64.0 torr of acrolein at 125°. The results are shown in Figure 1. At 64 torr, no C₂H₄ could be detected and the value of Φ_{CO} was 3.6×10^{-3}. Similar results were obtained by irradiating 17.6 torr of CH₂=CHCHO at 125° with between 10.0 and 307.0 torr of CO₂ added. With 307.0 torr of CO₂, no C₂H₄ was detected and $\Phi_{CO} = 2.6 \times 10^{-3}$.

The addition of up to 10% NO to the system at 125° did not cause a reduction in $\Phi_{C_2H_4}$. However, the addition of small amounts of piperylene at the same temperature caused an equal reduction of Φ_{CO} and $\Phi_{C_2H_4}$ within experimental error. The irradiation of 2.2 torr of piperylene and 34.0 torr of acrolein gave no C₂H₄ and $\Phi = 2.2 \times 10^{-3}$ for CO production.
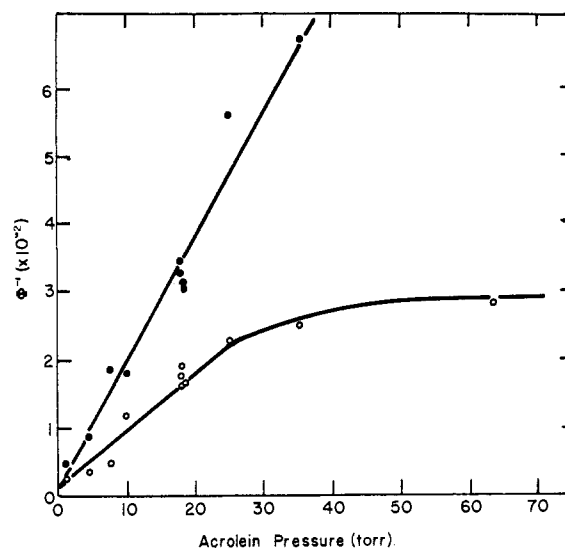
The quantum yields were independent of light

Figure 1. Variation of Φ^{-1} with acrolein pressure at 125°: ●, C₂H₄; ○, CO.

intensity over the range 9.6×10^{11}–1.6×10^{13} quanta cm⁻³ sec⁻¹. Φ_{CO} and $\Phi_{C_2H_4}$ were also independent of irradiation time.

Plots of log Φ (~ 30 torr of acrolein) for CO and C₂H₄ against $1/T$ were good straight lines over the range 35–200°. By least squares
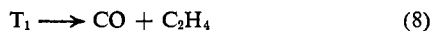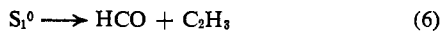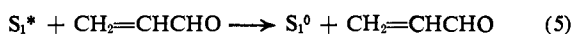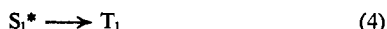
$$\log \Phi_{CO} = (0.63 \pm 0.20) - (1164 \pm 75)/T$$
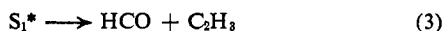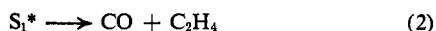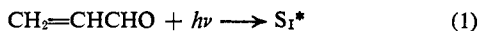
and

$$\log \Phi_{C_2H_4} = (-1.04 \pm 0.32) - (672 \pm 115)/T$$

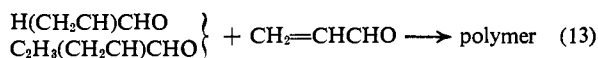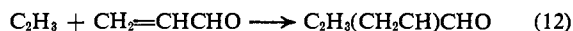The error limits quoted here, and elsewhere in the paper, are the standard deviation.

Discussion

The results can be explained most satisfactorily by the simplified mechanism

$$CH_2=CHCHO + h\nu \longrightarrow S_1^* \qquad (1)$$

$$S_1^* \longrightarrow CO + C_2H_4 \qquad (2)$$

$$S_1^* \longrightarrow HCO + C_2H_3 \qquad (3)$$

$$S_1^* \longrightarrow T_1 \qquad (4)$$

$$S_1^* + CH_2=CHCHO \longrightarrow S_1^0 + CH_2=CHCHO \qquad (5)$$

$$S_1^0 \longrightarrow HCO + C_2H_3 \qquad (6)$$

$$S_1^0 \longrightarrow CH_2=CHCHO \qquad (7)$$

$$T_1 \longrightarrow CO + C_2H_4 \qquad (8)$$

$$T_1 \longrightarrow CH_2=CHCHO \qquad (9)$$

S_1 and T_1 are the first excited singlet and triplet states of acrolein and S_1^* and S_1^0 are vibrationally excited and zero level singlets.

Although no H_2 was found in the products and the addition of NO to the system did not reduce $\Phi_{C_2H_4}$, the inclusion of reactions 3 and 6 would be justified if HCO and C_2H_3 were totally consumed by the reactions

$$HCO \longrightarrow H + CO \qquad (10)$$

$$H + CH_2=CHCHO \longrightarrow H(CH_2CH)CHO \qquad (11)$$

$$C_2H_3 + CH_2=CHCHO \longrightarrow C_2H_3(CH_2CH)CHO \qquad (12)$$

$$\left.\begin{array}{l} H(CH_2CH)CHO \\ C_2H_3(CH_2CH)CHO \end{array}\right\} + CH_2=CHCHO \longrightarrow polymer \qquad (13)$$

The maximum measured difference between Φ_{CO} and $\Phi_{C_2H_4}$ in any run was 6.2×10^{-3} when 4.6 torr of acrolein was irradiated. If our hypothesis is correct then $\Phi_{polymer} = 6.2 \times 10^{-3}$; this is too small for us to detect. There is no information in the literature concerning the competitive reactions

$$C_2H_3 + RHC=CHR \nearrow^{C_2H_3RHC-\dot{C}RH}_{\searrow C_2H_4 + RHC=\dot{C}R}$$
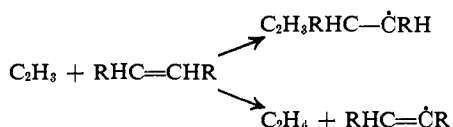
Weir[6] produced vinyl radicals by the CH_3-sensitized decomposition of acrolein and of vinyl formate at 175°. He measured the ratio of rate constants for like- and cross-disproportionation to like- and cross-combination. However, results for other reactions of vinyl radicals were not given. In our work we did find traces of C_2H_2 and C_4H_6. If vinyl radicals were present possible routes for formation would be

$$2C_2H_3 \nearrow^{C_2H_2 + C_2H_4 \quad (14)}_{\searrow C_4H_6 \quad (15)}$$
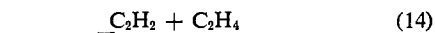
The amount of C_2H_4 formed in reaction 14 would be too small for us to see its disappearance in the NO experiments. For the reactions between H atoms and propylene, Jennings and Cvetanović[10] found that the rate constant for addition to the double bond was approximately 30 times greater than that for hydrogen abstraction. If the ratio k_{add}/k_{abs} were similar for H + acrolein, then $\Phi_{H_2} \sim 1.6 \times 10^{-4}$ in our work. This is a total yield of $\sim 10^{-2}$ μmole under our experimental conditions, whereas our lower limit for H_2 detection was $\sim 5 \times 10^{-2}$ μmole. Volman, et al.,[11] showed the

(10) K. R. Jennings and R. J. Cvetanović, J. Chem. Phys., 35, 1233 (1961).

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

presence of radicals in the vapor-phase photolysis of acrolein at 2537 and 2810 Å by the Paneth mirror technique. However, while they performed experiments with other compounds at 3130 Å, it is not clear whether they studied the behavior of acrolein at this wavelength. Therefore, the inclusion of reactions 3 and 6 seems reasonable, and Blacet, et al.,[4] proposed similar reactions for polymer formation in their work.

Only reactions 6 and 7 are proposed for S_1^0 as sufficiently high reactant pressures completely inhibit C_2H_4 formation. Reaction 8 is justified by the observation that piperylene causes an equal reduction in Φ_{CO} and $\Phi_{C_2H_4}$. The two modes of decomposition for S_1^*, reactions 2 and 3, are included because at low pressures of acrolein adding piperylene only partly suppresses C_2H_4 formation.

All attempts to detect fluorescent or phosphorescent emission from acrolein[3,4,12] have been unsuccessful, and so no steps involving radiative decay to the ground state have been included.

A steady-state treatment of the reaction scheme gives

$$\Phi_{CO} = \frac{1}{k_2 + k_3 + k_4 + k_5[Acr]} \times \left(k_2 + \frac{k_3 + k_5[Acr]}{k_6 + k_7} + \frac{k_4 k_8}{k_8 + k_9} \right) \qquad (16)$$

where Acr ≡ acrolein. As acrolein absorbs radiation strongly at 3130 Å and the quantum yield for decomposition is so low, it is reasonable to assume that k_7 is large. Thus at low pressures of acrolein the term $(k_3 + k_5[Acr])/(k_6 + k_7)$ in eq 16 becomes insignificant and Φ_{CO}^{-1} is proportional to [Acr]. However, at higher pressures of acrolein $(k_3 + k_5[Acr]) \sim (k_6 + k_7)$ and the relationship between Φ_{CO}^{-1} and [Acr] changes. At very high pressures of acrolein only reactions 1, 5, 6, and 7 will be of importance and

$$\Phi_{CO} = [1 + (k_7/k_6)]^{-1}$$

These effects are shown in Figure 1.

For C_2H_4 production, a steady-state treatment gives

$$\Phi_{C_2H_4} = \frac{1}{k_2 + k_3 + k_4 + k_5[Acr]}\left(k_2 + \frac{k_4 k_8}{k_8 + k_9} \right)$$

$\Phi_{C_2H_4}^{-1}$ should be proportional to [Acr] at all pressures of acrolein. Also, when [Acr] = 0 the term $(k_3 + k_5 \cdot [Acr])/(k_6 + k_7)$ in eq 16 becomes very small and Φ_{CO}^{-1} should be equal to $\Phi_{C_2H_4}^{-1}$. A least-squares treatment of the results in Figure 1 from 1 to 25 torr gave $\Phi_{CO}^{-1} = 29.4 \pm 4.5$ and $\Phi_{C_2H_4}^{-1} = 27.9 \pm 8.1$ at [Acr] = 0. There is agreement within experimental error.

At a pressure of 30 torr of acrolein, Φ_{CO} is independent of [Acr] (Figure 1) and so

$$\Phi_{CO} = k_6/(k_6 + k_7)$$

However, it has already been argued that $k_7 \gg k_6$ so that $\Phi_{CO} \simeq k_6/k_7$. From the experiments where 30 torr of acrolein was irradiated at temperatures between 35 and 200°

$$\log \Phi_{CO} = (0.63 \pm 0.20) - (1164 \pm 75)/T \simeq \log(k_6/k_7)$$

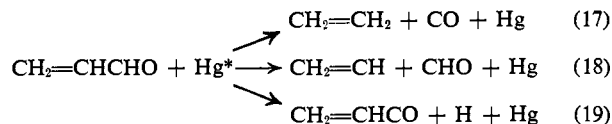(12) K. Inuzuka, Bull. Chem. Soc. Japan, 34, 6 (1961).

Thus

$$k_6/k_7 = 4.3 \pm 2.0 \exp(-5360 \pm 345)/RT$$

Reactions 6 and 7 are both unimolecular and the similarity in A factors is expected. The result that $E_6 - E_7 = 5.36 \pm 0.34$ kcal mole^{-1} is also reasonable.

The results for the variation of $\Phi_{C_2H_4}$ with temperature have not been treated in this manner because the expression for $\Phi_{C_2H_4}$ is more complicated and dependent upon [Acr] so that no useful information can be derived.

Thompson and Linnett[3] found that the gaseous photodecomposition products of 145 torr of acrolein at 3130 Å consisted of 98.6% CO and 1.4% ethylene. These authors proposed that the ethylene deficiency was caused by acrolein polymer on the reaction vessel walls absorbing ethylene. Blacet, et al.,[4] working with 200 torr of acrolein, found that the gaseous products were 91% CO, 6% unsaturated hydrocarbons, and 3% H$_2$; they suggested reactions 10–13 could cause the imbalance between Φ_{CO} and $\Phi_{C_2H_4}$. Our mechanism is consistent with these results. At pressures greater than 100 torr of acrolein one would expect reactions 1 and 5–7 to be most important and that C$_2$H$_3$ and H would disappear mainly via reactions 10–13. As the quantum yield for polymer formation at 3130 Å is less than 5×10^{-3}, it seems unlikely that Thompson and Linnett's explanation is correct.
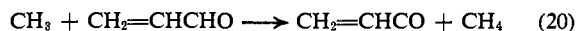
Harrison and Lossing[5] (HL) studied the Hg(^{3}P$_1$)-photosensitized decomposition of acrolein. The products, identified by mass spectrometry, were CO, butadiene, ethylene, acetylene, and a trace of H$_2$. The addition of methyl radicals to the system led to the formation of propylene and a small amount of a compound of molecular weight 70 which was thought to be methyl vinyl ketone. HL proposed that the primary steps were

$$\begin{array}{r} \text{CH}_2\text{=CH}_2 + \text{CO} + \text{Hg} \quad (17) \\ \text{CH}_2\text{=CHCHO} + \text{Hg*} \longrightarrow \text{CH}_2\text{=CH} + \text{CHO} + \text{Hg} \quad (18) \\ \text{CH}_2\text{=CHCO} + \text{H} + \text{Hg} \quad (19) \end{array}$$
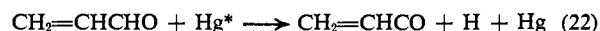
followed by various radical reactions to give the hydrocarbon products. Equation 17 is identical with the reaction we propose for the decomposition of triplet acrolein. However, we found no evidence for the vinyl–formyl split of triplet acrolein proposed in reaction 18. A possible explanation of reaction 18 is that the energy given to the acrolein molecule by Hg(^{3}P$_1$) is sufficiently greater than the energy required to give the first triplet (65.7 kcal mole^{-1})[12] so that the reverse of reaction 4 may occur. C$_2$H$_3$ and HCO could then be formed by reactions 3 or 6. Inuzuka[12] gives the energy of S$_1^0$ as 85.6 kcal mole^{-1}. Alter-

natively the exent of reaction 18 may be too small for us to detect. HL did not give the relative importance of reactions 17–19.
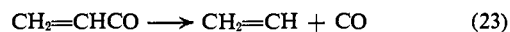
It is possible that reaction 19 was not a primary step in the Hg(^{3}P$_1$)-sensitized decomposition of acrolein. Products formed from the acrylyl radical, CH$_2$=CHCO, were only detected when CH$_3$ radicals were added. Methyl vinyl ketone could have been formed by

$$\text{CH}_3 + \text{CH}_2\text{=CHCHO} \longrightarrow \text{CH}_2\text{=CHCO} + \text{CH}_4 \quad (20)$$

$$\text{CH}_3 + \text{CH}_2\text{=CHCO} \longrightarrow \text{CH}_3\text{COCH=CH}_2 \quad (21)$$

Reaction 20 is probably $\sim$16 kcal mole^{-1} exothermic. Castro and Rust[13] and Volman and Brinton[14] studied the methyl-sensitized thermal decomposition of acrolein and proposed that the acrylyl radical was an unstable intermediate in the reaction chain. HL used high concentrations of CH$_3$ to trap out other radicals. It is possible that reactions 18 and 19 should be combined to give one primary step

$$\text{CH}_2\text{=CHCHO} + \text{Hg*} \longrightarrow \text{CH}_2\text{=CHCO} + \text{H} + \text{Hg} \quad (22)$$

followed by

$$\text{CH}_2\text{=CHCO} \longrightarrow \text{CH}_2\text{=CH} + \text{CO} \quad (23)$$

If reaction 22 is a primary step it must be of minor importance compared to reaction 17.

The experimental conditions under which Weir[6] photolyzed acrolein are unclear. His observation that the products consisted mainly of CO and C$_2$H$_4$ with only traces of C$_2$H$_2$ and C$_4$H$_6$ is in accord with our reaction mechanism.

Weir[6] also investigated the photolysis of divinylmercury with the unfiltered output of a medium-pressure Hg arc at 275°. Only negligible amounts of hydrocarbons were formed although, at this temperature, most mercury alkyls readily decompose. It appears that the vinyl group confers exceptional stability toward photodecomposition on compounds of the type C$_2$H$_3$XR where X = CO or Hg and R = H or C$_2$H$_3$, respectively.

Osborne and Pitts[15] found that acrolein is also extremely resistant to photooxidation. This photochemical stability explains why acrolein is a day- and night-time lachrymator in Los Angeles smog.

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