THE MERCURY-PHOTOSENSITIZED DECOMPOSITION OF BENZALDEHYDE, ACROLEIN, AND CROTONALDEHYDE¹

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ABSTRACT

The Hg³P₁-photosensitized decomposition of benzaldehyde at low pressure and high radiation intensity forms predominantly a polymeric material. In the fraction of the reaction which forms the identifiable final products benzene and carbon monoxide, both a direct molecular rearrangement and a free radical split to phenyl and formyl radicals occur. The decomposition reactions of acrolein and crotonaldehyde involve the three primary processes:

 $\begin{array}{l} \text{RCHO} + \text{Hg}^* \rightarrow \text{RH} + \text{CO} + \text{Hg} \\ \rightarrow \text{R} + \text{CHO} + \text{Hg} \\ \rightarrow \text{RCO} + \text{H} + \text{Hg}. \end{array}$

INTRODUCTION

In the photolytic and mercury-photosensitized decompositions of aldehydes three possible primary processes can occur:

> $RCHO \rightarrow R + CHO$ [1]

$$RCHO \rightarrow RH + CO$$
 [2]

$$RCHO \rightarrow RCO + H.$$
 [3]

Where R is an alkyl group other than methyl, further primary processes involving rearrangements and bond splitting in this group are possible, and the course of the reaction may become quite complicated.

The direct photolysis and the mercury-photosensitized decomposition of acetaldehvde have both been studied in some detail. In the direct photolysis at 2537 to 3130 Å the main primary process is reaction [1], although part of the reaction appears to proceed by reaction [2] (1). In the reaction of acetaldehyde with $Hg(^{3}P_{1})$ atoms (2) the primary decomposition is almost exclusively to form methyl and formyl radicals, although the experimental results could not rule out the possibility that 5% of the reaction proceeded by reaction [2]. There was no evidence for the occurrence of reaction [3].

Very little work has been done on the relative importance of these primary processes when R is an unsaturated group capable of conjugating with the aldehydic function. In this case it might be expected that the proportions of the three possible steps would change. Blacet and Roof (3) studied the photolysis of crotonaldehyde in the 2400–2600 Å region and found no decomposition; however, Volman, Leighton, Blacet, and Brinton (4) found that during the photolysis of crotonaldehyde at 2537 Å tellurium mirrors were removed, indicating the presence of radicals. They postulated the following reaction:

$$CH_3 - CH = CH - CHO + h\nu \rightarrow CH_3 - -CH = CH + CHO.$$
 [4]

Blacet, Fielding, and Roof (5) studied the direct photolysis of acrolein and postulated that the primary process was to some extent the following:

$$CH_2 = CH - CHO + h\nu \rightarrow CH_2 = CH + CHO.$$
 [5]

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By mirror-removal experiments Volman and co-workers (4) showed that radicals were produced at 2537 and 2810 Å.

No work has been reported on the direct photolysis of benzaldehyde or on the mercuryphotosensitized decomposition of any of the three conjugated aldehydes: crotonaldehyde, acrolein, and benzaldehyde. In view of the few results available it was thought that some information on the relative importance of the three primary processes in the mercuryphotosensitized decomposition of these aldehydes would be of interest.

EXPERIMENTAL

The reactions were studied by passing the reactant at a few microns pressure, together with mercury vapor, in a stream of helium through a photochemical reactor attached to a mass spectrometer. The apparatus and procedure have been described previously (2, 6, 7).

In recent work (7, 8) the addition of methyl radicals, produced by the photosensitized decomposition of dimethyl mercury, to the reaction products has been found to be a convenient method of detecting free radicals, particularly those which are difficult to detect directly with low energy electrons. This method of detection of a radical R depends on the occurrence of the combination reaction

$$R + CH_3 \rightarrow RCH_3.$$
 [6]

It is worth while to consider briefly the conditions upon which the success of this method of radical detection and identification depends. The method will work only if conditions are such that radical recombination reactions predominate over radical attack on stable molecules. Although radical-radical reactions are several orders of magnitude faster than radical-substrate reactions, the concentration of radicals in conventional photochemical work is usually so small that radical-substrate reactions nevertheless predominate. However, as has been pointed out previously (7), conditions in the present reactor are considerably different. In the present system some 10-20% of the parent compound is decomposed in the order of 10^{-3} second with the result that the concentration of methyl radicals was approximately 1/10 that of the parent compound for most of the contact time. Under such conditions radical-radical reactions would be expected to predominate.

Of course, as the fraction of the reaction proceeding by a free radical mechanism decreases the occurrence of radical-radical reactions will also decrease. However, when using methyl radicals as a radical detector this effect can be counterbalanced by increasing the amount of methyl radicals added to the system.

The sensitivity of this method for the detection of a radical R is dependent on many variables: among others, the rate of recombination, the ratio of recombination to disproportionation, and the sensitivity of the mass spectrometer to the product RCH₃. It is therefore impossible to put the limits of radical detection by this method on an absolute scale.

Materials

The benzaldehyde, acrolein, and crotonaldehyde were all Eastman-Kodak "White-Label" materials purified by bulb-to-bulb distillation and degassed before use. The benzaldehyde- d_6 was prepared by Dr. L. C. Leitch and was 94.7% pure. The impurity was chiefly benzaldehyde- d_6 .

CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959 RESULTS AND DISCUSSION

Benzaldehyde

The only identifiable products found in the mercury-photosensitized decomposition of benzaldehyde were benzene and carbon monoxide. The major part of the reaction ($\sim 80\%$) appeared to proceed to the formation of a yellowish polymer which deposited on the walls of the reactor and rapidly caused a reduction in the amount of light transmitted. As the results in Table I show, the amounts of benzene and carbon monoxide produced were equal, suggesting that the deposit was a polymer of benzaldehyde and not of one of the reaction products.

TABLE I Benzaldehyde decomposition

Benzaldehyde decomposed		Proc	lucts	Yield (%)	
(μ)	(%)	C ₆ H ₆	CO	C ₆ H ₆	CO
0.92	11.7	0.166	0.172	18.1	18.8

No radicals could be detected at low electron energies. A search was therefore made for radicals by the addition of methyl radicals as previously discussed. Upon the addition of methyl radicals a peak at mass 92 of approximately 7 mm was produced. A peak was also produced at mass 91, the intensities at mass 92 and 91 being in the correct ratio for toluene. These results demonstrate the presence of the phenyl radical in the system, suggesting as a primary step the reaction:

$$C_6H_5CHO + Hg^* \rightarrow C_6H_5 + CHO + Hg.$$
^[7]

However, one cannot rule out the possibility that the primary reaction proceeds by the formation of the benzoyl radical, which then rapidly decomposes to form a phenyl radical and carbon monoxide.

$$C_{6}H_{5}CHO + Hg^{*} \rightarrow C_{6}H_{5}CO + H + Hg$$
[8]

$$C_6H_5CO \to C_6H_5 + CO$$
[9]

No formation of acetophenone, the addition product of C_6H_5CO and CH_3 , was observed, indicating that the C_6H_5CO concentration was very small. An estimate of the bond dissociation energy $D(C_6H_5-CO)$ can be made from the heat of formation of CO and recent estimates of the heat of formation of the phenyl radical ($\Delta H_t = 70$ kcal/mole) (9) and the benzoyl radical ($\Delta H_t = 15.6$ kcal/mole) (10). These values lead to $D(C_6H_5-CO) =$ 28 kcal/mole. Since the benzoyl radical should therefore be stable at 55° C, the failure to detect it either directly or by CH_3 addition must be taken as evidence that reaction [8] does not occur to a significant extent.

Reaction [7] undoubtedly occurs to some extent, the observed products benzene and carbon monoxide being formed by the subsequent reaction:

$$C_6H_5 + CHO \rightarrow C_6H_6 + CO.$$
^[10]

To determine the importance of reactions [7] and [10] relative to a possible direct molecular rearrangement to benzene and carbon monoxide:

$$C_6H_6CHO + Hg^* \rightarrow C_6H_6 + CO + Hg$$
[11]

experiments were carried out with $C_6H_5CHO-C_6D_5CDO$ mixtures. In the absence of the free radical processes [7] and [10] all the benzene produced in such mixtures should be

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either C_6H_6 or C_6D_6 . The amount of isotopically mixed benzenes relative to the C_6H_6 and C_6D_6 benzenes should therefore provide an index of the amount of benzene formed by reaction [11].

TABLE II
Decomposition of $C_6D_5CDO-C_6H_5CHO$ mixtures

Aldehyde de	e decomposed (µ)		roduct be	% free		
C ₆ D ₅ CDO	C₅H₅CHO	C ₆ D ₆	C₀D₅H	C ₆ H ₅ D	C ₆ H ₆	reaction
$1.46 \\ 0.599 \\ 0.646$	$1.36 \\ 0.569$	$\begin{array}{c} 0.257 \\ 0.078_7 \\ 0.090_7 \end{array}$	$\begin{array}{c} 0.026_{6} \\ 0.031_{4} \\ 0.017_{9} \end{array}$	$0.016_3 \\ 0.013_6$	$0.190 \\ 0.075_4$	34.0 32.0

In Table II are recorded the results obtained in the decomposition of benzaldehyde- d_6 and of two mixtures of benzaldehyde- d_6 and ordinary benzaldehyde. Because of the formation of polymer it was necessary to keep the period of illumination as short as possible, therefore the yield of carbon monoxide was not measured in these experiments. The small amount of C_6D_5H formed in the decomposition of benzaldehyde- d_6 alone arises from the small percentage of benzaldehyde- d_5 present in the original material. The results given for the two mixtures were corrected by this factor.

Assuming that for the isotopic aldehydes the same fraction of the total reaction proceeds by formation of free radicals, and similarily that the rate of reaction [10] is the same for all isotopic species, it is possible to calculate from the results of the two experiments the fraction proceeding by steps [7] and [10]. If these assumptions are valid the amount of the mixed benzenes, C_6D_5H and C_6H_5D , formed in each experiment should be equal. The observed agreement was not too satisfactory, presumably because the amounts formed were quite small compared to the experimental error. For purposes of calculation the amounts of C_6H_5D and C_6D_5H were averaged. The final column of Table II shows that of that fraction of the total reaction which produced benzene, 33% did so by a free radical mechanism. There was no evidence for the formation of mixed aldehydes suggesting that the recombination reaction

$$C_6H_5 + CHO \rightarrow C_6H_5CHO$$
 [12]

must be much slower than the disproportionation reaction [10].

Acrolein

Using low energy electrons no free radicals could be detected in the photosensitized decomposition of acrolein. From a comparison of the 50-v spectra with and without illumination the principal products were found to be ethylene, acetylene, carbon monoxide, and a small amount of hydrogen. At higher partial pressures of aldehyde a substance of mass 54 was formed. This was identified as 1,3-butadiene, presumably formed by the dimerization of vinyl radicals.

On the addition of methyl radicals to the system a compound of parent mass 42 was formed. This compound was identified as propylene and confirms the presence of the vinyl radical. This suggests the primary step:

$$CH_2 = CH - CHO + Hg^* \rightarrow CH_2 = CH + CHO + Hg.$$
[13]

In addition, a small amount of product of mass 70 was also formed. This compound was probably vinyl methyl ketone, suggesting the occurrence to some extent of the additional primary step:

$$CH_2 = CH - CHO + Hg^* \rightarrow CH_2 = CH - CO + H + Hg.$$
[14]

The product yields obtained by varying the length of the illuminated zone are given in Table III and shown graphically in Fig. 1. The carbon and oxygen balances were low,



FIG. 1. Mercury-photosensitized decomposition of acrolein.

TABLE III Acrolein decomposition (partial pressure acrolein 4.85 μ)

Length of illuminated zone (mm)	Acrolein decomposed		Products (µ)			Product balance	
	(μ)	(%)	CO	C_2H_4	C_2H_2	% C	% O
$38 \\ 18 \\ 10 \\ 5$	$ \begin{array}{r} 1.33 \\ 0.700 \\ 0.320 \\ 0.165 \end{array} $	$27.4 \\ 14.4 \\ 6.58 \\ 3.38$	$\begin{array}{c} 1.23 \\ 0.768 \\ 0.244 \\ 0.114 \end{array}$	$\begin{array}{c} 0.783 \\ 0.417 \\ 0.152 \\ 0.095 \end{array}$	0.282 0.095 0.037 0.00	$84.5 \\ 68.9 \\ 64.8 \\ 61.4$	$92.9 \\ (109.7) \\ 76.3 \\ 69.1$

probably as a result of the presence of radicals which were not included in the material balances. The curved nature of the plot of the acetylene yield versus the length of illuminated zone suggests that acetylene was not produced in a primary step. The only primary step producing acetylene which would be energetically possible is the reaction:

$$CH_2 = CH - CHO + Hg^* \rightarrow C_2H_2 + CH_2O + Hg.$$
[15]

The absence of formaldehyde as a product indicates that this reaction does not occur. Several secondary reactions can be postulated to explain the formation of acetylene

$$C_2H_3 + Hg^* \rightarrow C_2H_2 + H + Hg$$
^[16]

$$C_2H_3 \to C_2H_2 + H \tag{17}$$

 $2C_2H_a \rightarrow C_2H_2 + C_2H_4$ [18]

$$C_2H_4 + Hg^* \to C_2H_2 + H_2 + Hg.$$
 [19]

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From heats of formation, assuming $D(C_2H_3-H) \leq 110 \text{ kcal/mole}$, $D(H-C_2H_2)$ can be calculated to be $\geq 36 \text{ kcal/mole}$; therefore the decomposition reaction [17] should be very slow at the temperature of the reactor (55° C). It is possible that the acetylene could be produced by reaction [18]. However, most of the ethylene must arise by some other mechanism since in all cases more ethylene was produced than acetylene. The relatively large yield of ethylene, the apparent low concentration of vinyl radicals, and the absence of products containing the CHO group all suggest that a large proportion of the reaction proceeds by a molecular rearrangement mechanism:

$$CH_2 = CH - CHO + Hg^* \rightarrow CH_2 = CH_2 + CO + Hg.$$
^[20]

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The presence of the vinyl and acrylyl radical, as shown by the methyl addition products propylene and vinyl methyl ketone, strongly suggest the occurrence of two other primary processes:

$$CH_2 = CH - CHO + Hg^* \rightarrow CH_2 = CH + CHO + Hg$$
[13]

$$CH_2 = CH - CHO + Hg^* \rightarrow CH_2 = CH - CO + H + Hg.$$
^[14]

From the present experiments it is not possible to determine the relative importance of the three primary processes.

Crotonaldehyde

Difficulties were encountered in identifying the products formed in the mercuryphotosensitized decomposition of crotonaldehyde. For this reason an identification of all primary reactions and an estimate of their relative importance could not be made. The main products detected were carbon monoxide, propylene, a product of mass 40, a small amount of acetylene, and a very small amount of a product of mass 56. Use of low energy electrons led to detection of a radical mass 41. The addition of methyl radicals caused a small but definite increase at mass 84 indicating the presence of the crotonyl radical in small amounts and thus suggesting the occurrence of the primary reaction:

$$CH_{3}-CH=CH-CHO + Hg^{*} \rightarrow CH_{2}-CH=CH-CO + H + Hg.$$
[21]

The large amount of propylene produced suggested that the main primary step was the molecular rearrangement:

$$CH_{2}-CH=CH-CHO + Hg^{*} \rightarrow CH_{2}-CH=CH_{2} + CO + Hg.$$
[22]

It was not possible to determine whether the radical of mass 41 was formed by the primary reaction:

$$CH_{3}-CH=CH-CHO + Hg^{*} \rightarrow CH_{3}-CH=CH + CHO + Hg$$
[23]

or by the reaction of Hg* with propylene produced in reaction [22] as follows:

$$CH_2 = CH - CH_3 + Hg^* \rightarrow CH_2 = CH - CH_2 + H + Hg.$$
^[24]

Since a considerable amount of propylene was present, and since propylene has a large cross section for reaction with excited Hg atoms (6), the latter alternative appears more probable.

CONCLUSIONS

The mercury-photosensitized decomposition of benzaldehyde under the present conditions leads primarily to the formation of a polymeric material. However, that portion of the reaction which results in identifiable products has been shown to involve two primary processes, a molecular rearrangement to form benzene and carbon monoxide

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and a free radical split to form phenyl and presumably formyl radicals, with 33% of the reaction occurring by the free radical mechanism. No evidence was found for the formation of benzoyl radicals and hydrogen atoms. This mode of decomposition is quite different from that of acetaldehyde, in which no molecular rearrangement was found to occur, and free radicals only were formed.

The reactions of both acrolein and crotonaldehyde appear to involve three primary processes

$$RCHO + Hg ^{3}P_{1} \rightarrow RH + CO + Hg$$
[25]

$$\rightarrow$$
 R + HCO + Hg [26]

$$\rightarrow$$
 RCO + H + Hg. [27]

For both these compounds the results suggest that the main reaction is the molecular rearrangement [25], with reaction [26] occurring to a lesser extent and reaction [27] only to a very slight extent. The results for acrolein and crotonaldehyde do not permit quantitative determinations of the relative importance of the three steps.

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