

ing competing modes of decomposition. On the second view, the isomerization would be thought of as a relatively slow unimolecular change arising from some electronically activated state but requiring some additional thermal (vibrational) activation. The activated state would be quenched by the presence of nearby pentane molecules. Reduction in temperature decreases the isobutane yield more than the isopentane yield, indicating that a higher vibrational activation energy is required for isomerization with splitting than for

isomerization without splitting, which seems reasonable.

These attempts to rationalize our observations are of course far from definitive. In fact, practically every change we made in the nature of the solid or the irradiation conditions resulted in some unexpected change in the radiolysis yields. The distribution of products in the radiolysis of an organic compound is certainly far from fixed and can show tremendous variations with apparently minor changes in the molecular environment.

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The Photochemical Decomposition of Acetaldehyde in Aqueous Solutions of Allyl Alcohol at 2537 Å.¹

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The photochemical decomposition of acetaldehyde at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol in the temperature range from 27 to 73°. The quantum yields of the gaseous products, methane, ethane, carbon monoxide and hydrogen, were determined. The results are consistent with a combination of a free-radical intermolecular reaction and an intramolecular reaction which may be a "geminate" free-radical process.

Introduction

Recent studies in this Laboratory have been directed at obtaining information about photochemical decomposition in aqueous solutions by the use of allyl alcohol as scavenger.^{2,3} In our earlier work on hydrogen peroxide² and acetone,³ the compounds studied were known to undergo photochemical decomposition at 2537 Å. entirely by free-radical mechanisms in the gas phase. In this study the object was to extend our previous investigations to a compound which was known to undergo photolysis in the gas phase by other than a free-radical process.

Acetaldehyde at 3130 Å. decomposes in the gas phase by primary decomposition into free-radicals. At 2804 Å. and shorter wave lengths, two primary photodecompositions occur: the intramolecular formation of methane and carbon monoxide and the formation of methyl and formyl free-radicals.⁴ The most recent study of the photochemistry of acetaldehyde in aqueous solutions⁵ indicated that under radiation from the full light of a mercury arc gaseous products were not formed and that acetaldol is the principal product.

Experimental

The reaction cell, gas train, gas analysis methods and actinometry were similar to those described previously for our acetone studies.³ Hydrogen, which was not previously a product, was oxidized together with carbon monoxide over cupric oxide. The water thereby formed was measured at low pressures in the gas buret.

Light Source.—The helical mercury resonance arc, normally supplied for a.c. operation, was converted to d.c. operation by a half-wave rectification unit capable of supplying 4 kv. With a 20,000 ohm resistance in series with the lamp, the arc current could be stabilized from less than 1 to over 100 mamp.

Reaction Solution.—Acetaldehyde was prepared by the sulfuric acid depolymerization of paraldehyde in a nitrogen atmosphere. The aldehyde was removed by distillation and then redistilled. The middle fraction was retained and stored at Dry Ice temperature over anhydrous calcium sulfate and hydroquinone *in vacuo*. A sample of acetaldehyde of known volume, pressure and temperature was distilled into a known volume of degassed water or allyl alcohol solution at Dry Ice temperature and the initial concentration of acetaldehyde was calculated.

Solution Products.—Quantitative determinations of solution products were not made. However, formaldehyde was found by the use of fuchsin reagent,⁶ and aldol was identified by the use of Dische reagent.⁷

Results

Aqueous Acetaldehyde Photolysis.—Experiments were conducted at three temperatures, 27.6, 49.5 and 73.0°. In Fig. 1 the quantum yields for the gaseous products as a function of temperature for three different intensities are shown. For clarity in representation, the experimental points are not given but, since the same three temperatures were used in all experiments, they occur at both ends of each curve and at the intersection of the straight lines used to connect the experimental points. The concentration of acetaldehyde was 0.05 M for all the experiments shown here. In Fig. 2 the quantum yields for three different acetaldehyde concentrations, 2.9, 7.6 and 24.6 mM, at 73.0° are shown.

Aqueous Acetaldehyde-Allyl Alcohol Photolysis.—The results obtained for solutions of acetaldehyde and allyl alcohol in water at 27.6 and 73.0° are shown in Figs. 3 and 4. It should be noted that the concentration of acetaldehyde and intensity are the same for both temperatures. Within experimental error,⁸ hydrogen was not found at either temperature in the presence of even the lowest allyl alcohol concentration used.

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) D. H. Volman and J. C. Chen, *THIS JOURNAL*, **81**, 4141 (1959).

(3) D. H. Volman and L. W. Swanson, *ibid.*, **82**, 4141 (1960).

(4) F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

(5) Y. Hirshberg and L. Farkas, *ibid.*, **59**, 2453 (1937).

(6) W. J. Blaedel and F. E. Blacet, *Ind. Eng. Chem., Anal. Ed.*, **13**, 449 (1941).

(7) R. E. Deriaz, M. Stacey, E. G. Teece and L. F. Wiggins, *J. Chem. Soc.*, 1222 (1949).

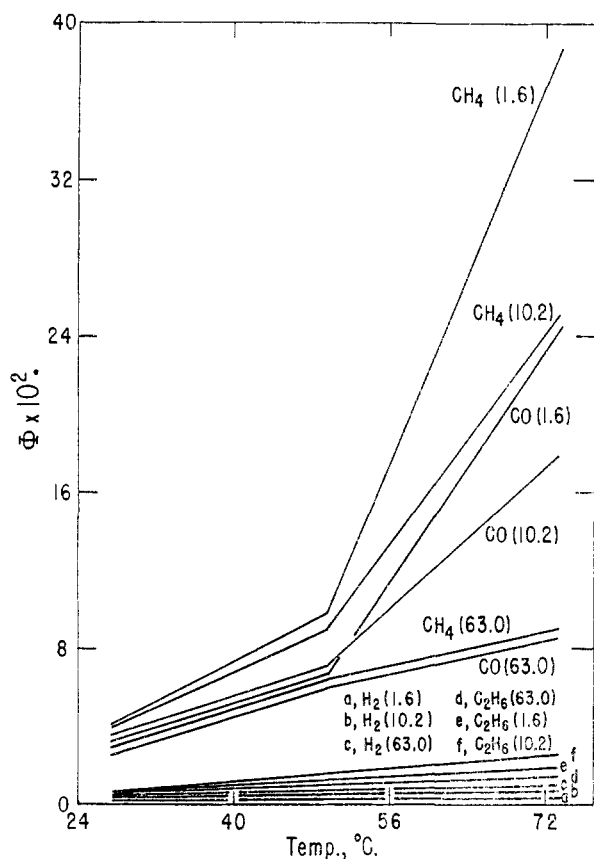


Fig. 1.—Quantum yields as a function of temperature at intensities of 1.6, 10.2, and 63.0×10^{-8} einst. cc.⁻¹ min.⁻¹ absorbed for an initial acetaldehyde concentration of 0.05 *M*.

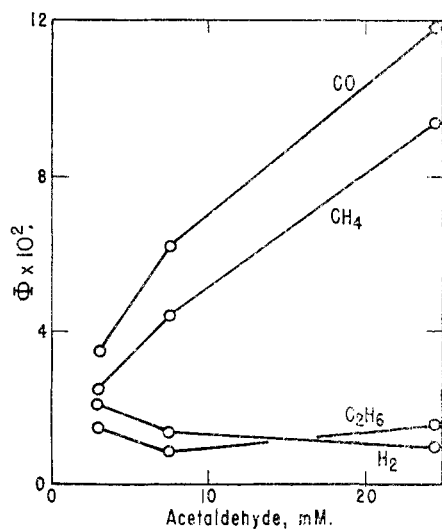


Fig. 2.—Quantum yields as a function of acetaldehyde concentration at 73.0° and an intensity of 4.9×10^{-8} einst. cc.⁻¹ min.⁻¹ absorbed.

Discussion

The results are consistent with the mechanism

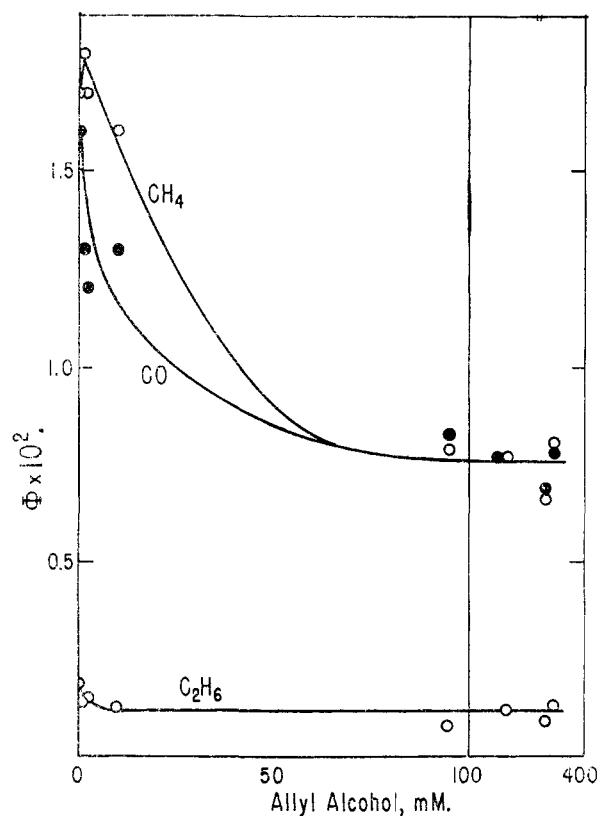
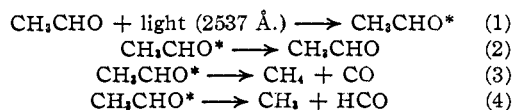


Fig. 3.—Quantum yields with added allyl alcohol at 27.6°, 0.025 *M* acetaldehyde and 4.7×10^{-8} einst. cc.⁻¹ min.⁻¹ absorbed.

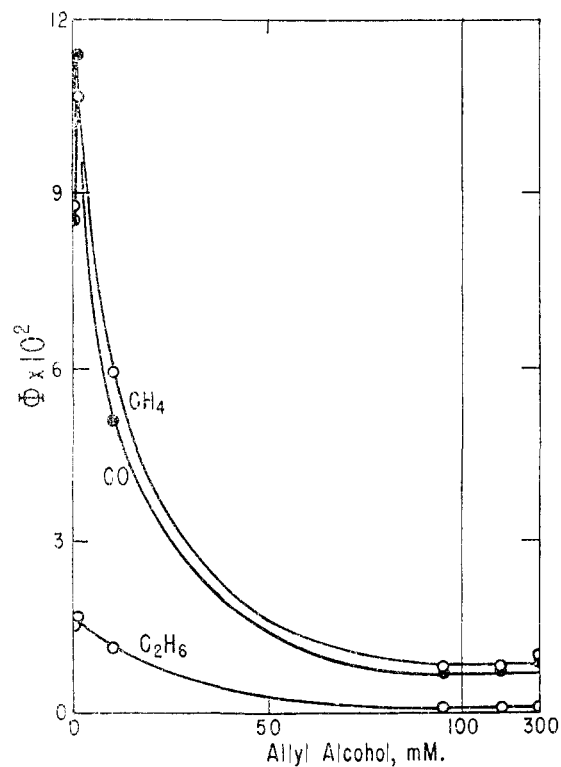
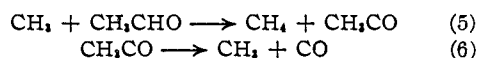
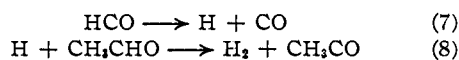


Fig. 4.—Quantum yields with added allyl alcohol at 73.0°, 0.025 *M* acetaldehyde and 4.7×10^{-8} einst. cc.⁻¹ min.⁻¹ absorbed.

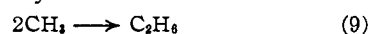
where CH_3CHO^* may represent either an activated molecule or free radicals in a solvent cage. In the absence of allyl alcohol, the quantum yields of all the gaseous products increase with increasing temperature. This is readily understandable for methane and carbon monoxide as they may be produced by a chain reaction



Lower intensities would also favor higher quantum yields for these products as Fig. 1 also shows. The increase in hydrogen quantum yield with temperature is probably not due to chain formation of hydrogen but may be explained by the reactions usually given for the gas phase mechanism⁸



In addition an increase in the rate of reaction 4 with increasing temperature would contribute to an increase in hydrogen formation as well as all of the other products. Since ethane can most logically be formed by



this reaction would also account for the temperature effect on the ethane quantum yield. The effects of intensity on the quantum yields of methane, carbon monoxide and hydrogen are those expected from the foregoing reactions. The mixed order of the ethane curves may be explained by noting that ethane formation is favored by low intensity through the formation of methyl radicals in reaction 6 while at the same time reaction 9 is favored by high intensity.

The effect of acetaldehyde concentration on the quantum yields of carbon monoxide and methane at 73.0°, Fig. 2, is explicable on the basis of their formation by the chain mechanism. The decrease in the hydrogen quantum yield with increasing acetaldehyde concentration may be explained by the reaction

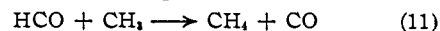


competing with reaction 7. This appears likely since we have identified formaldehyde in the solution products. The ethane yield is least affected as would be expected from the mechanism which tends to maintain the steady state concentration of methyl radicals relatively constant. These results are quite similar to those we have found for

(8) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954, p. 284 ff.

the methyl radical induced decomposition of acetaldehyde.⁹

In the presence of allyl alcohol, the quantum yields of the gaseous products reach limiting values which are approximately the same at 27.6 and 73.0°. Since chain decomposition is not important at 27.6°, these values are approximately half the values found in the absence of scavenger for carbon monoxide and methane. The values are proportionately much less at 73.0° since chain decomposition is here much more important. These findings are quite similar to those of Blacet and Loeffler⁴ in the gas phase using iodine as scavenger. One could use the explanation they have used, that the limiting value in scavenger represents a non-free-radical intramolecular decomposition. However, we would like to point out that in solution an alternative explanation is possible. One could assume that all of the non free-radical process occurring in the gas phase proceeds by formation of excited molecules which are completely quenched in solution. The intramolecular solution process may be, in fact, a "geminate" reaction¹⁰ between methyl and formyl radicals from the same aldehyde molecule in the solvent cage.



The limiting value for the quantum yield of ethane formation in the presence of allyl alcohol is about 0.001 both at 27.6 and 73.0°. This represents about 60% of the value for the uninhibited reaction at 27.6° and about 6% of the value for the uninhibited reaction at 73.0°. This would indicate that some ethane may be formed by a non free-radical process. Although such a mechanism has not been proposed previously for ethane formation in acetaldehyde photolyses, there is evidence from gas phase studies that all of the ethane is not formed by combination of methyl radicals. Ausloos and Steacie¹¹ have shown that in the chain decomposition of CH_3CDO induced by CH_3 radicals from the photolysis of azomethane, only non-deuterated ethanes are obtained. However, they also found that about 40% of the ethane formed in the photolysis of CH_3CDO was a mixture of $\text{C}_2\text{H}_5\text{D}$ and $\text{C}_2\text{H}_4\text{D}_2$ and that only CH_3D and no CH_2D_2 was formed. If the deuterated ethanes were formed from reactions involving CH_2D radicals, CH_2D_2 should have been found also.

(9) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952).

(10) Term suggested by R. M. Noyes, *THIS JOURNAL*, **77**, 2042 (1955).

(11) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).