203. *The Photolysis of Formaldehyde, Acetaldehyde, and Acetone at High Temperatures.*

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It is a matter of some interest that, whereas the photolysis of acetaldehyde at elevated temperatures takes on the character of a chain reaction, that of acetone does not. Leermakers (*J. Amer. Chem. Soc.*, 1934, **56**, 1537) showed that in the former case the quantum yield rises from unity at 100° to values of the order of 10^2 between 300° and 400° for light of wave-length 3130 A. With acetone, however, the quantum yield never rises appreciably above unity (Leermakers, *ibid.*, p. 1899; Winkler, *Trans. Faraday Soc.*, 1935, **31**, 761).

The chain mechanism proposed by Leermakers is based largely on the methyl radical as a carrier, as follows:

$$\begin{array}{llll}
(1)\ CH_3{\cdot}CHO + h\nu & = CH_3 + CHO & (5)\ CH_3 + CH_3{\cdot}CHO & = CH_4 + CH_3{\cdot}CO \\
(2)\ CHO & = CO + H & (6)\ CH_3 + CH_3 & = C_2H_6 \\
(3)\ H + CH_3{\cdot}CHO & = H_2 + CH_3{\cdot}CO & (7)\ CHO + CH_3{\cdot}CHO & = CH_4 + CO + CHO \\
(4)\ CH_3{\cdot}CO & = CH_3 + CO & (8)\ CH_3 + CHO & = CH_4 + CO
\end{array}$$

If this mechanism is correct, the reason for the marked difference between the behaviour of acetaldehyde and acetone must be ascribed to the reactive hydrogen in the aldehyde, and therefore to the absence of any reaction in the case of the acetone analogous to (5), *i.e.*,

$$(9)\ CH_3 + CH_3{\cdot}CO{\cdot}CH_3 = C_2H_6 + CH_3{\cdot}CO$$

There are, however, other possibilities which are not excluded, for Leermakers' kinetic results might be explained in either of the two following ways:

$$\begin{array}{ll@{\qquad}ll}
h\nu + R{\cdot}CHO & = R + H + CO & h\nu + R{\cdot}CHO & = R + H + CO \\
H + R{\cdot}CHO & = RH + CO + H & H + R{\cdot}CHO & = RH + CHO \\
H + H & = H_2 & CHO + R{\cdot}CHO & = RH + CO + CHO \\
R + R & = R_2 & R + R & = R_2 \\
R + H & = RH & CHO + CHO & = 2CO + H_2 \\
 & \text{(I.)} & & \text{(II.)}
\end{array}$$

In mechanism (I) the chain carrier is a hydrogen atom, but in (II) it is the CHO group. Each of these expressions leads to a kinetic equation identical with the empirical relationship obtained by Leermakers, *i.e.*, $dA/dt = I_{abs.} + kA\sqrt{I_{abs.}}$, where A represents the concentration of aldehyde. The inertness of acetone to chain propagation could then be explained by the relatively low reactivity of the methyl radical in comparison with the hydrogen atom.

In order to test these points we have carried out a series of comparative experiments on the effect of temperature on the photolysis of formaldehyde, acetaldehyde, acetone, and mixtures of the last two. Leermakers's experimental results are confirmed; in addition, we find that formaldehyde decomposes at elevated temperatures by way of a chain reaction which is kinetically similar to that of acetaldehyde, while with mixtures of acetaldehyde and acetone there is neither measurable inhibition by the acetone nor sensitisation by the aldehyde.

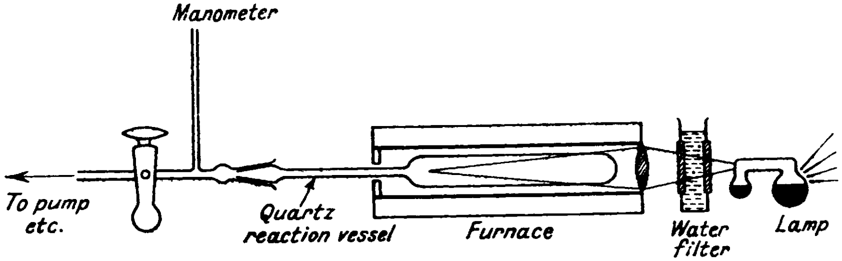
These results partly support Leermakers's mechanism, for if either of the alternative mechanisms given above were true, we should expect either an inhibition of the aldehyde chain by acetone due to the reaction $H + CH_3{\cdot}CO{\cdot}CH_3 = CH_4 + CH_3{\cdot}CO$, or alternatively a sensitisation of the decomposition of acetone, if the acetyl radical were further able to take part in the chain, *e.g.*, by a reaction analogous to (7) : $CH_3{\cdot}CO + CH_3{\cdot}CO{\cdot}CH_3 = C_2H_6 + CO + CH_3{\cdot}CO$. The fact that no such sensitisation occurs, however, also argues against the validity of reaction (7) itself, for with acetone present we should expect $CHO + CH_3{\cdot}CO{\cdot}CH_3 = CH_4 + CO + CH_3{\cdot}CO$ to occur, which, according to Leermakers, would be a chain-propagating reaction. For this reason we prefer to eliminate reaction (7) from Leermakers's scheme, and thus arrive at a simplification which has some bearing on the discussion of the kinetics (see p. 893).

EXPERIMENTAL.

The apparatus is shown in Fig. 1. The reaction vessel consisted of a clear silica tube of 240 c.c. capacity. This was enclosed in an electric furnace which was wound in four sections and could be kept at a temperature constant to ± 0·5° over a length of 20 cm. One end of the furnace was closed by a silica lens by means of which the light from a mercury lamp could be focused into the reaction vessel. The lamp was of special design; it was used " end-on " and gave a luminous area of 2 sq. cm. through a plane quartz end-plate. The light beam after passing through an infra-red water filter was rendered slightly convergent by the lens. The lamp was run from a battery of accumulators, and afforded a source of very constant intensity. Further, when the reaction system had been set up it was undisturbed throughout a series of measurements to ensure constancy of illumination. The reaction vessel was connected by a ground joint to a vertical mercury manometer, a mercury diffusion pump, and reservoirs of aldehydes and acetone. Rate measurements for acetone were made by means of the pressure change in the system, a sensitive glass Bourdon gauge being used. In the case of acetaldehyde and formaldehyde the volumes of $(CO + CH_4)$ and $(H_2 + CO)$ respectively were measured in a micro-burette to obviate errors due to polymerisation accompanying the decomposition. All the connecting tubing and the mercury manometer were wound with 32-gauge nichrome wire covered by a layer of asbestos string and heated electrically to 100° to prevent polymerisation of the formaldehyde. The reactants were purified by standard methods as follows : For acetaldehyde, Leighton and Blacet (*J. Amer. Chem. Soc.*, **1933**, **55**, **1766**) ; for formaldehyde, Trautz and Ufer (*J. pr. Chem.*, **1926**, **113**, 105) ; for acetone, Shipsey and Werner (J., **1913**, **103**, **1255**). No attempt was made to measure absolute quantum yields. Since the quantum yields of formaldehyde (Norrish and Kirkbride, J., 1933, 1578) and acetaldehyde (Leermakers, *J. Amer. Chem. Soc.*, **1934**, **56**, 1537) are known to be unity at 100°, and that of acetone to be 0·3 at 60°, all that was necessary was to carry out standard runs at these temperatures, with which the velocities at the higher temperatures could be compared on the assumption that no change in extinction coefficient with temperature occurred. The pressures employed at the different temperatures were chosen so as to yield a series of constant concentrations and are recorded as pressures reduced to 100°.

FIG. 1.

Reaction System.



Results.

In Table I(*a*) and (*b*), the rates of decomposition of aldehyde, measured in c.c. of aldehyde at *N.T.P.* decomposed per minute, have been divided by the pressure of aldehyde reduced to 100°. It is seen that at each temperature the velocity is proportional to the concentration of aldehyde.

TABLE I.

(*a*) *Acetaldehyde.*

(To convert rates to mm./min. at 100°, multiply by 3·63.)

Temp.		100°	150°	200°	250°	300°	350°
$\frac{\text{Rate} \times 10^{-4}}{[\text{R·CHO}]}$ at	100 mm.	1·86	6·61	21·5	64·0	131·0	241·0
	150 mm.	1·81	7·0	20·7	68·3	144·6	244·0
	200 mm.	1·17	7·0	23·1	71·5	124·0	242·0

(*b*) *Formaldehyde.*

(To convert rates to mm./min. at 100°, multiply by 4·84.)

Temp.		100°	200°	250°	300°	325°	350°
$\frac{\text{Rate} \times 10^{-4}}{[\text{R·CHO}]}$ at	100 mm.	1·65	4·81	13·2	58·0	89·0	165·0
	200 mm.	1·40	4·75	15·3	65·0	102·5	195·0
	400 mm.	0·9	4·15	13·1	65·0	110·5	214·0

The rates of decomposition of acetone were measured by the Bourdon gauge, and are shown below reduced to mm. of mercury at 60°.

Acetone: 70 mm. at 60°

Temp.	63°	99°	199°	300°	396°
Rate, mm. Hg at 60° per min. × 10^{-3}	3·95	6·15	6·52	8·5	9·91

In all cases blank runs were carried out in the dark; with acetone no measurable thermal decomposition was apparent in any case below 400°, but with formaldehyde and acetaldehyde a small amount of thermal decomposition occurred at the higher temperatures, for which the rates of photolysis were subsequently corrected.

In order to find if acetone exerted any inhibiting effect upon the rate of photolysis of acetaldehyde, a series of runs was carried out at 350° using acetaldehyde at about 167 mm. pressure with increasing quantities of acetone. The results are in Table II.

TABLE II.

Me·CHO, mm.	$COMe_2$, mm.	Rate (mm./min.) in		Rate of photolysis, mm./min.	Me·CHO, mm.	$COMe_2$, mm.	Rate (mm./min.) in		Rate of photolysis, mm./min.
		dark.	light.				dark.	light.	
167	0	0·1	5·60	5·50	169·5	4·2	0·1	5·46	5·36
165·5	0	0·11	5·72	5·61	166·3	8·6	0·09	5·36	5·27
166·1	0	0·1	5·74	5·64	167·1	17·4	0·11	5·44	5·33
169	0·6	0·1	5·28	5·18	168·3	83·3	0·12	5·04	4·92
166·8	2·3	0·1	5·76	5·66					

The slight falling off in velocity of photolysis with increasing pressure of acetone may be ascribed to the reduction in the effective light intensity by the absorption of part of the light by the acetone. It is thus clear that acetone does not act as an inhibitor to the aldehyde chain. These experiments, however, do not show whether acetone itself enters into the chain reaction; in order to test for such possible photo-sensitisation, three comparative runs were carried out at 350°, (1) with acetaldehyde alone, (2) with equal amounts of acetone and acetaldehyde, (3) with acetone alone. At the end of a given period of illumination the gas produced in each case was pumped away and analysed, with the results shown below:

Run.	Time of illuminaton (mins.).	C.c. at *N.T.P.*				
		CO.	CH_4.	C_2H_6.	Unsat.	H_2.
I. Me·CHO (128 mm.)	187	20·4	20·1	0·0	0·6	—
II. Me·CHO (128 mm.) + $COMe_2$ (128 mm.)	274	24·3	23·4	0·4	0·3	—
III. $COMe_2$ * (128 mm.)	284	1·0	0·8	0·4	0·15	0·1

* Only the total volume of gas was measured, and the composition calculated from the analyses of Winkler (*loc. cit.*) at this temperature.

It seems clear that, although at this high pressure the acetone acting as an " inner filter " again reduces the velocity of the photolysis of the aldehyde, yet there is no appreciable photosensitised decomposition of the acetone, judging from the quantity of ethane produced.

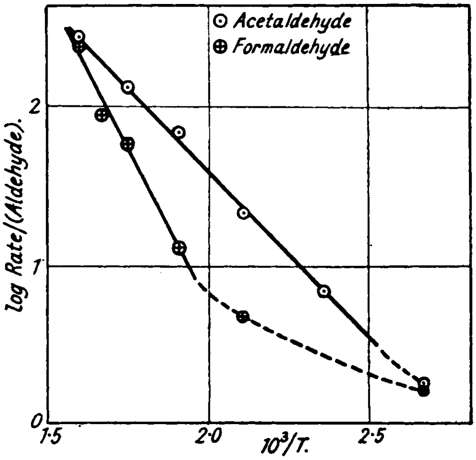
DISCUSSION.

At pressures between 100 and 200 mm. of acetaldehyde at 100°, a column of 25 cm., corresponding to the length of our reaction vessel, would absorb over 90% of the incident light between 3100 and 2500 A. Thus, with constant intensity, $I_{\text{abs.}}$ is approximately constant, and Leermakers's rate equation may be written :

$$\text{Rate}/[\text{Aldehyde}] = k_1/[\text{Aldehyde}] + k_2$$

Our results for acetaldehyde and formaldehyde recorded in Table I are in accordance with this expression. For temperatures greater than 150°, when the chain length becomes great, the second term is much larger than the first. In these cases Rate/[Aldehyde] is sensibly constant, although for formaldehyde it tends to increase slightly with the pressure as would be the case if $I_{\text{abs.}}$ were not quite constant but increased with the pressure. At lower temperatures the log (Rate/[Aldehyde])–$1/T$ graph deviates from the straight-line relation owing to the operation of the first term (Fig. 2).

FIG. 2.



In Table III the values of the quantum yields have been calculated, the values already recorded at 100° for acetaldehyde and formaldehyde and at 60° for acetone being assumed. Hence, while there are exactly similar chain reactions in formaldehyde and acetaldehyde, there is none in acetone; neither is there any inhibition of the aldehyde photolysis by acetone or sensitisation of the acetone photolysis by aldehyde in mixtures of the two. Further, although the absorption coefficient of acetone is of the same order as that of the acetaldehyde, yet there is only a small decrease in the rate of photolysis of acetaldehyde as the pressure of acetone is increased (Table II); this suggests that light absorbed by the acetone can generate chains in the aldehyde by the reaction of the methyl groups set free in the primary act. Such decrease as there is may be accounted for if the quantum yield of the primary decomposition of acetaldehyde is greater than that of acetone.

TABLE III.

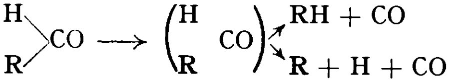
Mean quantum yields in the photolysis of aldehyde and acetone at constant concentration and at constant intensity of irradiation by mercury light through quartz. (Pressures reduced to 100°.)

Temp.	63°	100°	150°	200°	250°	300°	325°	350°	396°
H·CHO (100 mm.)	—	1·0	—	2·9	8·0	35·0	53·9	100·0	—
Me·CHO (100 mm.)	—	1·0	3·5	11·5	34·4	70·4	—	138·0	—
$COMe_2$ (70 mm.)	0·3	0·47	—	0·5	—	0·65	—	—	0·76

These facts dispose of the two mechanisms suggested as alternatives to that of Leermakers, and we conclude that the chains are indeed propagated by methyl radicals. Reaction (7) is omitted for reasons already stated, and this leads to a simplified kinetic equation for the velocity of photolysis at high temperatures when the first term is negligible, *viz.*, $d[\text{R·CHO}]/dt = (k_5/k_8)[\text{R·CHO}]\sqrt{I_{\text{abs.}}}$, the k's referring to the reactions on p. 890; k_8 refers to an atomic recombination and will be unaffected by temperature, so the measured temperature coefficient must refer to k_5. The energies of activation have been calculated from the slopes of the graphs in Fig. 2, giving 9·8 kg.-cals. for acetaldehyde (cf. 10 kg.-cals. obtained by Leermakers) and 16·2 kg.-cals. for formaldehyde. On the basis of the above deductions these must refer respectively to the reactions

$$\begin{aligned} CH_3 + CH_3\text{·}CHO &= CH_4 + CH_3\text{·}CO \\ H + H\text{·}CHO &= H_2 + H\text{·}CO \end{aligned}$$

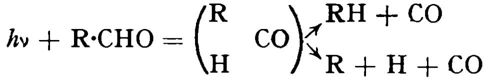
The Primary Reactions.—In our study of the primary processes operative in the photolysis of aldehydes and ketones, we have inclined to the view that both radicals are liberated either simultaneously or the one very quickly after the other (Bamford and Norrish, J., 1935, 1504):



$$\begin{matrix}H\\R\end{matrix}\!\!>\!CO \longrightarrow \left(\begin{matrix}H\\R\end{matrix}\;CO\right)\!\begin{matrix}\nearrow RH + CO\\ \searrow R + H + CO\end{matrix}$$

With aldehydes, a very high proportion of the hydrocarbon RH is produced in all cases; this has led us to the view that the hydrocarbon is formed directly in the process of disruption, and that free radicals and hydrogen atoms are only set free in small amounts (10% of the decomposition). This view has been confirmed by Pearson's experiments (*ibid.*, p. 1151); it is obvious that the occurrence of chain reactions at high temperatures can be readily explained as originating from the free radicals produced, but that it in no way demands that the whole of the primary change should occur in this way. This answers Leermakers's objection (*J. Amer. Chem. Soc.*, 1934, **56**, 1904) to our view. Furthermore, the primary mechanism which we have assumed above is equivalent kinetically to the combination of reactions (1) and (2) of Leermakers's scheme. In assuming the spontaneous decomposition of the CHO radical, he is adopting the conclusion already reached by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103); it is a small step from this to the virtual simultaneous rupture of both bonds. Thus, none of the results at high temperature is in disagreement with the theory based on those obtained at low temperatures, and the modified scheme for the chain photolysis of aldehydes may now be written

(1), (2)



$$h\nu + R{\cdot}CHO = \left(\begin{matrix}R\\H\end{matrix}\;CO\right)\!\begin{matrix}\nearrow RH + CO\\ \searrow R + H + CO\end{matrix}$$

(Primary reaction)

(3) $H + R{\cdot}CHO = H_2 + R{\cdot}CO$

(4) $R{\cdot}CO = R + CO$

(5) $R + R{\cdot}CHO = RH = R{\cdot}CO$

(6) $R + R = R_2$

In the case of formaldehyde the scheme is still further simplified by reactions (3) and (5) becoming identical.

SUMMARY.

1. The rate of photolysis of formaldehyde, acetaldehyde, and acetone has been measured at a series of temperatures between 400° and that of the room.

2. Confirming the results of previous workers, a chain reaction was found with acetaldehyde but not with acetone. Formaldehyde exhibited a chain reaction similar to that of acetaldehyde.

3. The temperature coefficients gave values of the heat of activation of 9·8 kg.-cals. for acetaldehyde and 16·0 kg.-cals. for formaldehyde.

4. A study of the rate of photolysis of mixtures of acetaldehyde and acetone has led to a slight simplification of the mechanism of Leermakers, and has confirmed the propagation of the chain by methyl radicals.

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