159. *The Photolysis of Propaldehyde.*

By R. E. Dodd.

The photodecomposition of propaldehyde vapour at temperatures of 210—450° has been studied, both steady and intermittent illumination at 3132 Å being used. A pronounced curvature in the $\log_{10} K$–$1/T$ plot and a hitherto unobserved type of curve from the sector experiments suggest two independent reaction chains in this region of temperature in which the light-induced decomposition predominates.

THE kinetics of the photodecomposition of propaldehyde have not been widely studied and the work here described was initiated in an attempt to confirm and extend the few measurements by Mitchell and Hinshelwood (*Proc. Roy. Soc.*, 1937, *A*, **159**, 32) on the high-temperature photolysis. In particular, it was supposed that the stated similarity to the high-temperature photolysis of acetaldehyde would be confirmed and that a study of the effect of intermittent illumination would yield information about the individual rate constants, as in the case of acetaldehyde (Haden and Rice, *J. Chem. Physics*, 1942,

10, 445; Lucas and Rice, *ibid.*, 1950, **18**, 993; Dodd, *Trans. Faraday Soc.*, 1951, **47**, 56). It has been found, however, that the reaction is more complex and gives evidence of two simultaneous modes of decomposition.

EXPERIMENTAL

The apparatus for the determination of reaction rates and the determination of the ratio $\bar{r}/r_s$ (where $\bar{r}$ is the mean rate of decomposition under intermittent illumination, and r_s the steady rate under the same conditions of temperature and pressure but uninterrupted illumination) has been described (Dodd, *loc. cit.*). Initial rates of change of total pressure were measured over the temperature range 210—450°. Analyses of residual aldehyde were made by absorption in sodium hydrogen sulphite solution and titration with iodine.

For the reaction under steady illumination, at 3132 Å, the intensities of light absorbed ($I_{abs.} \sim 10^{-11} Nh\nu$ cm.$^{-3}$ sec.$^{-1}$) were measured directly by two selenium cells, screened by 2-mm. Chance OX7 filter glass. One cell, which could be switched out of circuit, observed transmitted light while the other observed the lamp through a variable gauze screen. They were connected, in opposition, to a spot galvanometer and were balanced to zero by means of the gauze screen when the reaction vessel was evacuated. Corrections were made for transmission losses and reflection (Hill and Hunt, *J. Chem. Physics*, 1947, **15**, 111). The calibration of galvanometer reading against light absorbed was made through the photolysis of acetaldehyde, whose absolute rate constant at 200° was taken to be 41·5 mole$^{-1/2}$ cm.$^{-3/2}$ sec.$^{-1/2}$ (Grahame and Rollefson, *ibid.*, 1940, **8**, 98).

Propaldehyde from various sources was used, from redistilled technical grade to Eastman Kodak white label. Various drying and distillation procedures were adopted, but in every case redistillation immediately preceded a vacuum-distillation into the aldehyde reservoir. No differences in behaviour were detectable in the various samples.

RESULTS

General Characteristics.—An appreciable dark reaction was observed. Initial rates of change of pressure varied with aldehyde pressure (Fig. 1) in a manner indicating a thermal

FIG. 1. *Pressure-dependence of thermal reaction at various temperatures.*
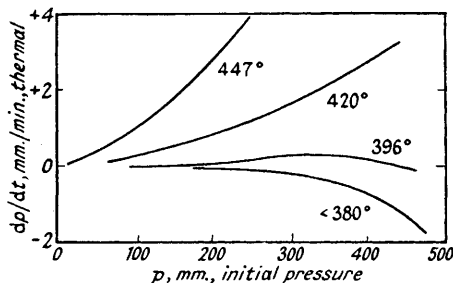
decomposition, which became appreciable at about 400°, and a competing condensation, with negligible temperature-dependence. This condensation may have occurred in the tubes leading to the reaction vessel or at the surface of the mercury manometer, though the dead space was kept at $\sim$60°.

The reaction rate under steady illumination was appropriately corrected for dark reaction and the function

$$y = r_s \text{ (mm./min.)}/60\,p \text{ (mm.) } I_{abs.}^{1/2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(expected to be constant by analogy with the acetaldehyde photolysis) was found to vary with initial pressure (see Fig. 2) according to

$$y = K - \alpha p^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This can be accounted for on the assumption that a competing light-induced polymerisation occurs, where

$$\sigma = 60\,\alpha p^{3/2}\,I_{abs.}^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These conclusions are supported by analysis for propaldehyde. In every case the loss of aldehyde ($-\Delta p_{ald.}$) exceeded the pressure increase ($\Delta p_{tot.}$): in the dark $-\Delta p_{ald.}/\Delta p_{tot.}$ varied

from zero at 395° (when condensation and thermal decomposition were practically balanced) to −0·55 at 310° : under illumination, $-\Delta p/\Delta p_{tot.}$ varied from 0·64 to 0·80, though 0·88 and 0·94 were obtained after prolonged (complete reaction) runs. The comparison of rates at 395° confirms the light-induced polymerisation extra to the dark condensation.

FIG. 2.   *Pressure-dependence of light-induced reaction : open points correspond to half incident light intensity.*
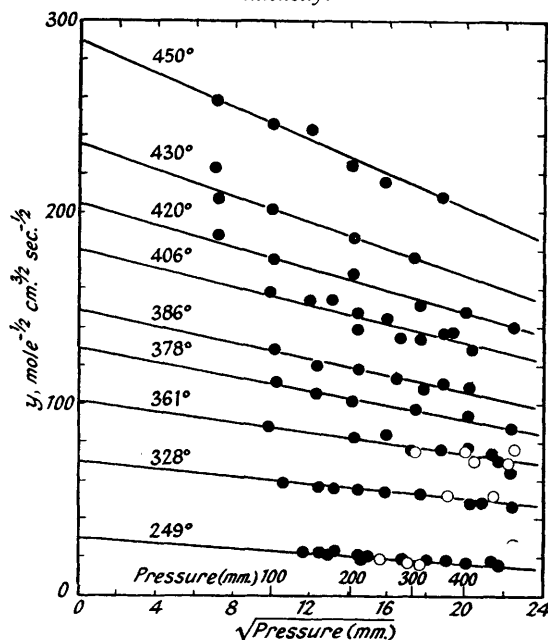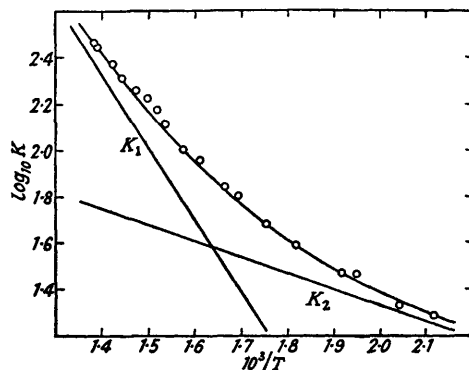

FIG. 3.   *Temperature-dependence of photodecomposition.*

Photodecomposition under Steady Illumination.—The principal contribution to the rate of change of pressure in the temperature range studied was the light-induced decomposition. The y–$\sqrt{p}$ curves (Fig. 2), extrapolated to zero, give the constant K [eqn. (2)], which should be that of the pure photodecomposition (rate, r_s) obeying the equation

$$r_s = K\ [C_2H_5\!\cdot\!CHO]\sqrt{I_{abs.}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

That the rate was proportional to $\sqrt{I_{abs.}}$ was shown within experimental error by halving the light intensity to give the open points in Fig. 2, and was further borne out by the sector experiments at 356° and above.

The plot of $\log_{10} K$ against the reciprocal of temperature (Fig. 3) did not, however, yield a

straight line but a curve suggesting two independent contributions to the reaction. By successive approximations these were estimated as :

$$K_1 = 10^{6 \cdot 7 \, \pm \, 0 \cdot 6} \exp \left[(-14 \cdot 4 \, \pm \, 1 \cdot 0) \ \text{kcal.}/\boldsymbol{R}T\right]$$

and

$$K_2 = 10^{2 \cdot 8 \, \pm \, 0 \cdot 6} \exp \left[(-3 \cdot 3 \, \pm \, 0 \cdot 4) \ \text{kcal.}/\boldsymbol{R}T\right]$$

where

$$K = K_1 + K_2 \qquad \qquad \qquad \qquad \qquad (5)$$

Fig. 4. *Sector results :* $\bar{r}/r_s$ *as a function of sector speed. The small points are derived values of* $\bar{r}_\alpha/r_{s\alpha}$, *and* $\bar{r}_\beta/r_{s\beta}$ *and the broken lines are fitted to them [eqn. (8)]. The full curves are calculated from fitted curves [eqn. (7)].*
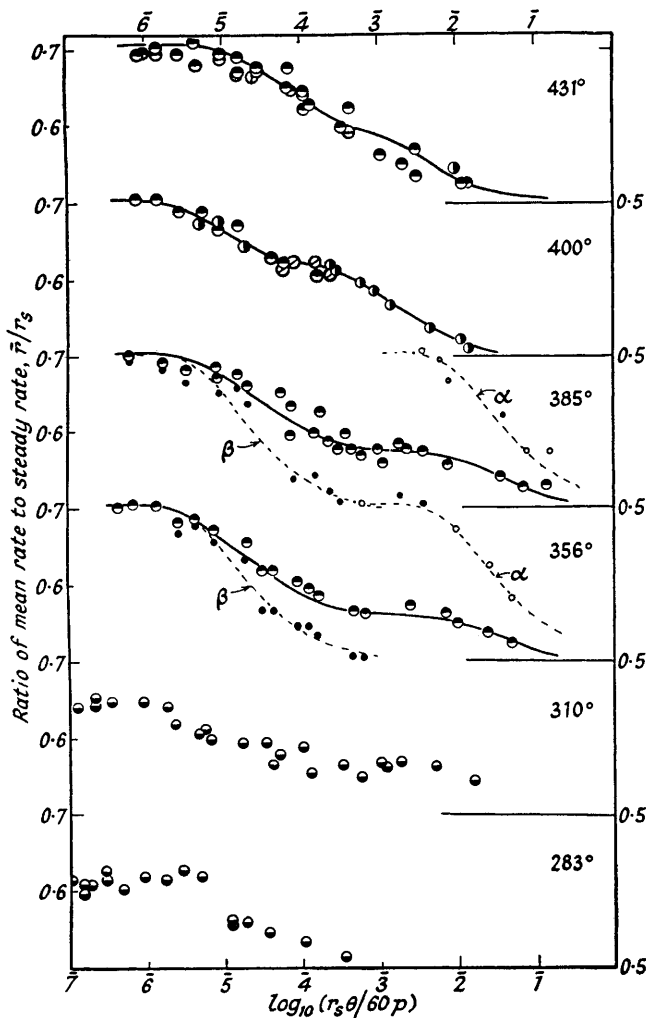
Photodecomposition under Intermittent Illumination.—Equation (4) can be explained, as for acetaldehyde, by a mechanism in which one of the free radicals found in the primary step (quantum yield, k_1) induces further decomposition in a regenerative chain reaction (k_2) and is destroyed in a bimolecular terminating step (k_3). If that explanation is to hold, the ratio of mean rate to steady rate determined in sector experiments should obey the equation

$$\frac{\bar{r}}{r_s} = f\left(\frac{k_3}{k_2} \cdot \frac{r_s \theta}{60p}\right) \qquad \qquad \qquad (6)$$

where θ is the duration of each light or dark period.

Accordingly, the values of $\bar{r}/r_s$ for propaldehyde at various temperatures were plotted against $\log_{10} (r_s\theta/60p)$ as in Fig. 4. Though the theoretical limits of $\bar{r}/r_s$ for a reaction rate proportional to $\sqrt{I_{abs.}}$, *viz.*, $1/\sqrt{2}$ and $\frac{1}{2}$, are reached at temperatures of 356° and above, the intermediate points do not conform to the function f which is applicable to a single chain-carrying radical (Melville and Burnett, *Proc. Roy. Soc.*, 1947, *A*, **189**, 470; Dodd, *loc. cit.*).

If it is supposed that two independent contributions are made to the reaction (subscripts α and β) each obeying eqns. (4) and (6) but with different chain-carrying species of different life-times and reaction constants, then

$$\frac{\bar{r}}{r_s} = \frac{K_\alpha}{K} \cdot \frac{r_\alpha}{r_{s\alpha}} + \frac{K_\beta}{K} \cdot \frac{\bar{r}_\beta}{r_{s\beta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\frac{r_\alpha}{r_{s\alpha}} = \text{f}\left(\frac{k_{3\alpha}}{k_{2\alpha}} \cdot \frac{r_{s\alpha}\theta}{60p}\right); \quad \frac{\bar{r}_\beta}{r_{s\beta}} = \text{f}\left(\frac{k_{3\beta}}{k_{2\beta}} \cdot \frac{r_{s\beta}\theta}{60p}\right) \quad . \quad . \quad . \quad . \quad . \quad (8)$$
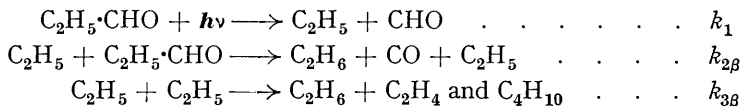
and

$$K = K_\alpha + K_\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From eqn. (7) it is apparent that at such values of θ that $\bar{r}_\alpha/r_{s\alpha}$ is already at its upper limit of 0·707, while $\bar{r}_\beta/r_{s\beta}$ is still at its lower limit of 0·500, the resultant $\bar{r}/r_s$ will be constant at a value $0·500 + 0·207 K_\alpha/K$. The marked plateaux at temperatures of 310°, 356°, and 385° are in accordance with this. In principle, the value of K_α, and hence K_β, can be deduced from the height of a plateau; $\bar{r}_\beta/r_{s\beta}$ and $\bar{r}_\alpha/r_{s\alpha}$ can then be calculated from the observed values of $\bar{r}/r_s$, it being assumed respectively that $\bar{r}_\alpha/r_{s\alpha} = 0·707$ to the left of the plateau and $\bar{r}_\beta/r_{s\beta} = 0·500$ to the right of the plateau. These ratios plotted against $\log_{10} (r_s\theta/60p)$ should now conform to function f [eqn. (8)]. Fig. 4 shows the derived ratios (smaller points) at 356° and 385°, the fitted curves (broken line) from eqn. (8), and the resultant curve for $\bar{r}/r_s$ calculated [eqn. (7)] from them. The fitted curves yield values for $\log_{10} K/\sqrt{k_1 k_{3\alpha}}$ and $\log_{10} K/\sqrt{k_1 k_{3\beta}}$. Hence at 356°, $K_\alpha = 28$, $K_\beta = 66$ (cf. $K_1 = 53$, $K_2 = 41$); at 385°, $K_\alpha = 45$, $K_\beta = 88$ (cf. $K_1 = 88$, $K_2 = 45$); and, at both temperatures, $k_1 k_{3\alpha} = 10^{8·7}$ and $k_1 k_{3\beta} = 10^{15}$. It is, however, not clear how far this is fortuitous. Similar procedure applied to results at 400° and 431° enables a tolerable fit of the calculated full curve, but the found values of K_α and K_β are less in agreement with K_1 and K_2 while $k_1 k_{3\alpha} = 10^{11·5}$.

At temperatures of 310° and 283° (as also at 325° and 245°, not shown) the value of $\bar{r}/r_s$ does not reach 0·707 at high sector speeds (up to 3000 r.p.m., corresponding to $\sim 8 \times 10^{-4}$ sec.). This is probably too far to the left to be another plateau and therefore indicates deviation from the $\sqrt{I_{abs.}}$ law, the apparent order at these temperatures being 0·63 and 0·66.
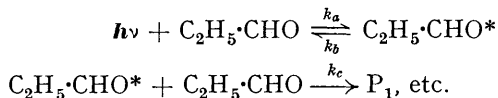
DISCUSSION

The sector experiments are a better indication of deviation from the square-root law at lower temperatures than are the measurements under steady illumination in which such deviation would be within experimental error; but for that reason the correction to the steady-rate results would be small and in any case not in the direction required to make a straight line of Fig. 3. Thus the evidence remains for two simultaneous reactions, obeying the same kinetics and of roughly the same magnitude. The reaction is undoubtedly a chain reaction (Mitchell and Hinshelwood, *loc. cit.*) and ethyl radicals have been detected by mirror methods (May, Taylor, and Burton, *J. Amer. Chem. Soc.*, 1941, **63**, 249; Garrison and Burton, *J. Chem. Physics*, 1942, **10**, 730). Ivin and Steacie (*Proc. Roy. Soc.*, 1951, *A*, **208**, 25) have shown that ethyl radicals react, both by disproportionation and by combination, with small activation energy and with collision efficiency approaching the maximum. This suggests mechanism β as :

$$C_2H_5 \cdot CHO + h\nu \longrightarrow C_2H_5 + CHO \quad . \quad . \quad . \quad . \quad . \quad k_1$$
$$C_2H_5 + C_2H_5 \cdot CHO \longrightarrow C_2H_6 + CO + C_2H_5 \quad . \quad . \quad . \quad k_{2\beta}$$
$$C_2H_5 + C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \text{ and } C_4H_{10} \quad . \quad . \quad k_{3\beta}$$

with the reasonable identification $K_\beta = K_1$, $k_{2\beta} \sim 10^{14} \exp (-14 \text{ kcal.}/\mathbf{R}T)$.

It may be conjectured that the other mechanism involves formyl radicals in a similar chain, though there is no direct evidence for their stability at these temperatures. Their participation in the acetaldehyde photolysis has been suggested though not confirmed (Haden and Rice, *loc. cit.*). Hydrogen atoms and "hot" molecules are also possible

species. It is possible that the latter are at least involved in the light-induced polymerisation, since eqn. (3) would be obeyed if the initiation took place according to

$$h\nu + C_2H_5 \cdot CHO \underset{k_b}{\overset{k_a}{\rightleftharpoons}} C_2H_5 \cdot CHO^*$$

$$C_2H_5 \cdot CHO^* + C_2H_5 \cdot CHO \xrightarrow{k_c} P_1, \text{ etc.}$$

if $k_b \gg k_c$, and if the termination were by mutual reaction (Gee and Melville, *Trans. Faraday Soc.*, 1944, **40**, 240).

Further speculation is not warranted by these data and it is not intended at present to continue the investigation. Yet there is good evidence for the composite mechanism in the pronounced curvature of the Arrhenius plot and in data from sector experiments of a type not previously remarked.

The Chemical Laboratories, King's College,
Newcastle-on-Tyne, 1.