475. *The Reaction of Methyl Radicals with Olefins. Part I. The Temperature Coefficient of the Induced Polymerisation of Ethylene.*

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When a mixture of acetaldehyde vapour and ethylene is irradiated with ultra-violet light at temperatures between 200° and 350° c., methyl radicals from the aldehyde photolysis induce a chain polymerisation of the olefin. From the temperature coefficient of the reaction the activation energy for the step, $CH_3 + C_2H_4$, is estimated to be 6·8 kcals.

THE rate of photolysis of acetaldehyde vapour by ultra-violet light at temperatures of about 300° is, in general, reduced by addition of olefins, which may undergo induced polymerisation. These reactions have been studied by Danby and Hinshelwood (*Proc. Roy. Soc.*, 1941, *A*, **179**, 169), who showed that they gave a particularly convenient method of following the interactions of methyl radicals with olefins and of investigating the kinetics of the induced polymerisation. The experiments have now been extended and the present paper describes an investigation into the influence of temperature on the methyl-radical-induced polymerisation of ethylene.

EXPERIMENTAL.

Methods.—The experimental methods employed were identical with those used by Danby and Hinshelwood. The mixture of acetaldehyde vapour and olefin was irradiated in a quartz vessel with plane-parallel windows by the unfiltered light from a mercury arc radiating principally at about 3600 A. The reaction vessel was maintained at the required temperature in an electric furnace. The reactions were followed by direct measurement of the overall pressure change on a mercury manometer and by chemical analysis for unchanged acetaldehyde in gas samples by the method of Friedemann, Cotonio, and Shaffer (*J. Biol. Chem.*, 1927, **73**, 342).

Acetaldehyde was dried and carefully fractionated through a long column. Commercial ethylene was dried by passage through P_2O_5 and distilled from a trap cooled in liquid air, only the middle fraction being collected.

Results.—Experiments were made at temperatures between 200° and 350°, within which limits the reactions proceeded at conveniently measurable rates under the experimental conditions employed. At each temperature the rate of photolysis of a constant amount of acetaldehyde (50 mm.) and the rate of polymerisation of the ethylene were measured for a series of ethylene pressures between zero and 400 mm. The amounts of photolysis and of polymerisation were nearly linear with respect to time over the early part of the reaction, and initial rates were therefore obtained by measuring the extent of reaction in a standard period of 8 minutes. When the rate of reaction decreased rapidly with time, the data were plotted and initial rates obtained by drawing tangents. The results are given in Table I.

TABLE I.

The Effect of Temperature on the Rate of Photolysis of 50 *mm. of Acetaldehyde in the Presence of Ethylene, and on the Rate of the Induced Polymerisation.*

(Rates are initial rates and are expressed in terms of the number of mm. of gas reacting in 8 minutes.

Initial C_2H_4 pressure, mm.	Rate of photolysis.					Rate of polymerisation.				
	200°.	250°.	300°.	325°.	350°.	200°.	250°.	300°.	325°.	350°.
0	5·3	10·4	16·5	20·2	25·0	—	—	—	—	—
50	4·0	8·5	14·2	17·5	22·3	2·4	4·5	7·3	7·9	8·3
100	3·3	7·5	12·6	15·6	19·9	4·0	8·6	12·3	13·6	14·1
150	2·6	6·8	11·3	13·8	18·3	5·9	11·8	16·3	17·6	19·5
200	2·4	6·2	10·4	13·1	17·1	7·2	14·2	19·8	22·0	23·9
250	2·2	5·7	9·3	11·7	16·0	7·7	15·6	21·6	23·5	27·0
300	1·8	5·0	8·3	10·6	14·4	8·0	17·0	24·4	26·9	31·4
350	—	—	7·6	—	—	—	—	27·0	—	—
400	1·2	4·1	7·0	9·5	12·8	9·0	19·8	29·5	32·5	38·3

DISCUSSION.

Danby and Hinshelwood found that the kinetics of the photolysis of acetaldehyde in the presence of olefin were consistent with the following reaction mechanism :

$$\begin{array}{llll}
CH_3\cdot CHO + h\nu & = CH_3 + CHO & k_1 & (1) \\
CH_3 + CH_3\cdot CHO & = CH_3 + CH_4 + CO & k_2 & (2) \\
CH_3 + CH_3 & = \text{chain ended} & k_3 & (3) \\
CH_3 + C_2H_4 & = R_1 & k_4 & (4) \\
R_1 + C_2H_4 & = R_2 & k_5 & (5) \\
R_2 + C_2H_4 & = R_3 & k_{5'} & (5') \\
R_{n-1} + C_2H_4 & = R_n & k_{5*} & (5*) \\
R_n & = \text{product} + CH_3 & k_6 & (6) \\
R_n & = \text{chain ended} & k_7 & (7)
\end{array}$$

The usual stationary-state treatment of these equations leads to the expressions for the rate of photolysis of acetaldehyde in the presence of ethylene (ρ), and for the rate of the induced polymerisation (σ), which are given below :

$$\rho = C[CH_3\cdot CHO](\{[C_2H_4]^2 + \rho_0^2/C^2[CH_3\cdot CHO]^2\}^{\frac{1}{2}} - [C_2H_4]) \quad . \quad . \quad . \quad . \quad (I)$$

$$\sigma = \tfrac{1}{2}nK[C_2H_4](\{[C_2H_4]^2 + \rho_0^2/C^2[CH_3\cdot CHO]^2\}^{\frac{1}{2}} - [C_2H_4]) \quad . \quad . \quad . \quad . \quad . \quad (II)$$

where $C = k_2k_4\beta/2k_3$, $K = (k_4)^2\beta/k_3$, and $\beta = 1 - k_6/(k_6 + k_7)$. n is the average number of ethylene molecules incorporated in the product and ρ_0 is the rate of photolysis of pure acetaldehyde under the conditions of the experiment.

The kinetic chain length of the polymerisation was considerable, but the average molecular weight of the product was small. This was shown to be due to a chain-transfer reaction (reaction 6). The kinetics require that the rate-determining chain-ending step should be unimolecular with respect to the growing polymer radical (reaction 7). This can arise if reaction 7 represents the isomerisation of the radical to a form for which both the addition of further ethylene and the splitting-off of a methyl radical to give chain transfer are unlikely. The precise mechanism of the eventual fate of the polymer radical—either bimolecular recombination or adsorption and reaction on the vessel wall—would then not affect the kinetics of the main process. The marked diminution in the rate of polymerisation in the series ethylene, propylene, *iso*butylene was shown to be due to increasing ease of this reaction.

FIG. 1.

Effect of temperature on photolysis rate of 50 *mm. acetaldehyde in the presence of varying amounts of ethylene. The curves are* calculated *from equation* (I) *with the values of the constant* C *given in Table II.*

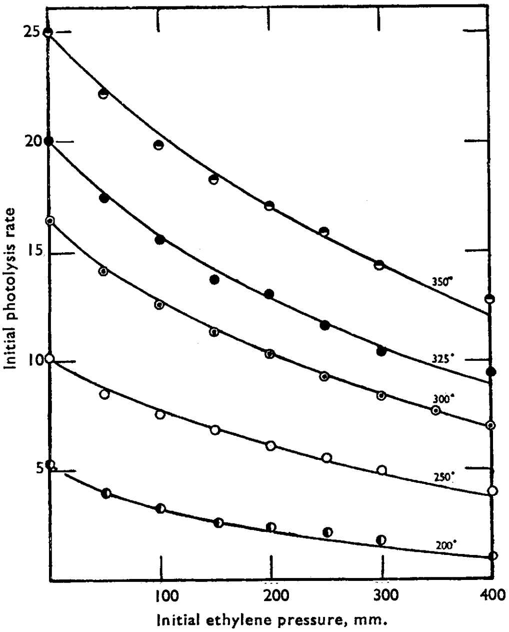


FIG. 2.

Effect of temperature on polymerisation rate of varying amounts of ethylene induced by photolysis of 50 *mm. acetaldehyde. The curves are* calculated *from equation* (II) *with the values of the constants* C *and* $\frac{1}{2}$nK *given in Table II.*

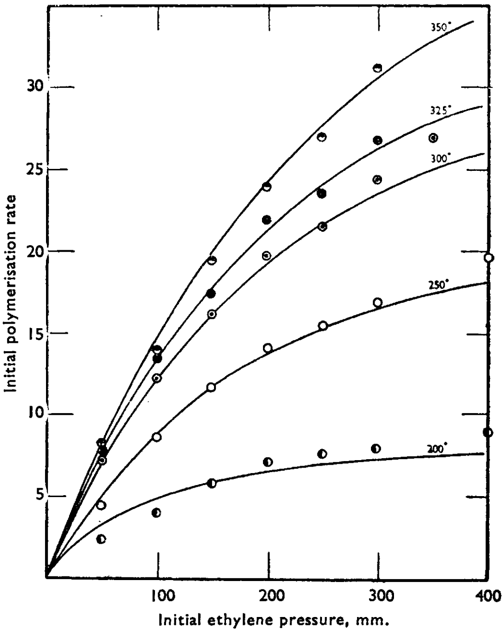


Table II give values of the constants C and $\frac{1}{2}nK$ which, when substituted in equations I and II, give curves in close agreement with the experimental results. Fig. 1 shows the curves obtained in this way for the rate of photolysis of 50 mm. of acetaldehyde at different temperatures as a function of the ethylene pressure. The experimental points are given for comparison. Fig. 2 shows the corresponding results for the polymerisation rate.

TABLE II.

Temp., ° K.	C ($\times 10^4$).	$\frac{1}{2}nK$ ($\times 10^4$).	nk_4/k_2.
473	4·82	3·68	0·764
523	6·12	3·62	0·591
573	8·01	3·85	0·481
598	9·24	3·82	0·413
628	10·0	3·58	0·358

In equations I and II, $C = k_2k_4\beta/2k_3$, and $K = (k_4)^2\beta/k_3$. Hence $\frac{1}{2}nK/C = nk_4/k_2$. If n is independent of temperature over the range involved, then

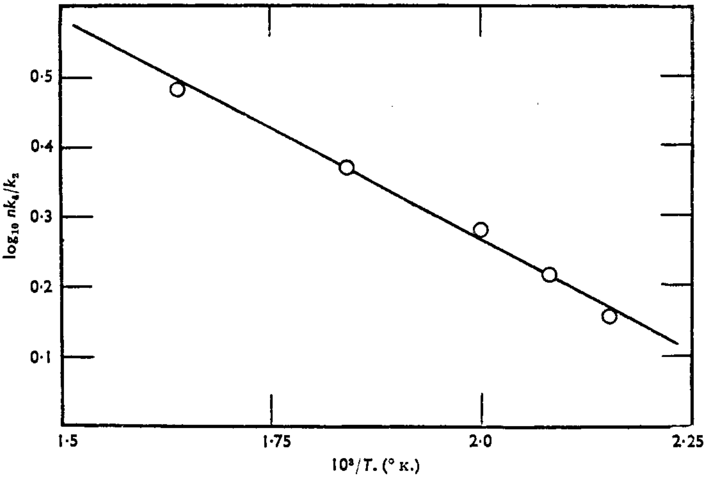
$$\frac{\mathrm{d}\ln(nk_4/k_2)}{\mathrm{d}T} = \left[\frac{\mathrm{d}\ln k_4}{\mathrm{d}T} - \frac{\mathrm{d}\ln k_2}{\mathrm{d}T}\right] = \frac{E_4}{\boldsymbol{R}T^2} - \frac{E_2}{\boldsymbol{R}T^2}$$

where E_4 and E_2 are the activation energies of reactions 4 and 2, respectively. The difference in the activation energy for the reaction of methyl radicals with acetaldehyde and with ethylene may therefore be obtained from the slope of the graph of $log_{10}(nk_4/k_2)$ against the reciprocal of the absolute temperature (Fig. 3). The slope is equal to $-(E_4 - E_2)/2{\cdot}303\boldsymbol{R}$, whence $E_4 - E_2 = -2{\cdot}9$ kcals.

The temperature coefficient of the acetaldehyde photolysis gives a value of 9·7 kcals. for the reaction, $CH_3 + CH_3{\cdot}CHO$ (Mitchell and Hinshelwood, *Proc. Roy. Soc.*, 1937, *A*, **159**, 32; Akeroyd and Norrish, *J.*, 1936, 890). We therefore arrive at the value of 6·8 kcals. for the activation energy of the reaction, $CH_3 + C_2H_4$.

FIG. 3.

Temperature coefficient of the ratio nk_4/k_2.



The value of 9·7 kcals. for the activation energy of the reaction of a methyl radical with acetaldehyde assumes that the activation energy, E_3, for the recombination of methyl radicals is negligible. This assumption may not be quite justified, in which case a correction of $\frac{1}{2}E_3$ should be added to both E_2 and E_4. The conclusion that methyl radicals react with ethylene with an activation energy 2·9 kcals. smaller than that for their reaction with acetaldehyde is unaffected.

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