477. *The Reaction of Methyl Radicals with Olefins. Part III. Reaction with Mixtures of Ethylene and Higher Olefins.*

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Addition of ethylene to higher olefins antagonises the inhibitory action which these exert on the photolysis of acetaldehyde. This is due to an increased possibility of chain transfer; radicals derived from the higher olefins add on C_2H_4 and regenerate CH_3 groups under conditions where they would normally isomerise and therby terminate the chain.

The rates of polymerisation under the influence of methyl radicals from acetaldehyde being known from previous work for ethylene and propylene separately, and the effect of these two gases in inhibiting the photolysis of the aldehyde having been measured, an obvious extension of the investigation was to study the behaviour of mixtures of the two.

The experimental methods were those already described. All experiments were carried out at 300° c. with an initial acetaldehyde pressure of 50 mm. The rate of photolysis of the aldehyde was measured as a function of the composition of the binary ethylene–propylene mixture, and the total rate of consumption of olefin determined at the same time.

The results are shown in Figs. 1—4.

The most significant effects of mixing the two olefins are:

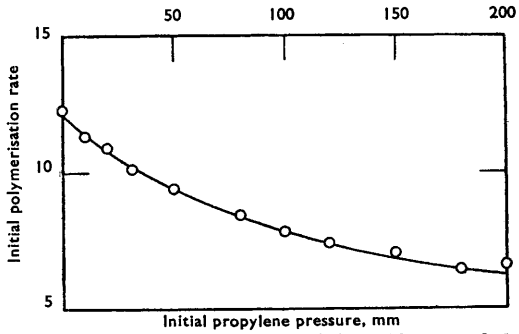
(1) The rates of polymerisation are far from additive (Figs. 1 and 2).

(2) With a constant ethylene pressure the addition of propylene causes a steep decrease in the rate of photolysis (Fig. 3).

(3) With constant propylene pressure, however, the addition of the first amounts of ethylene

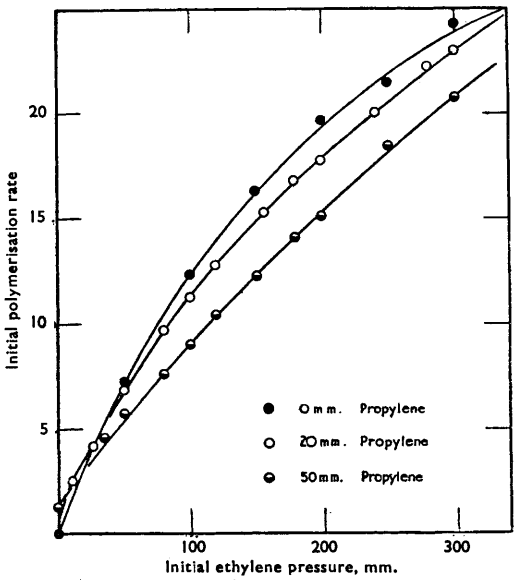
causes an increase in the photolysis rate, that is, the ethylene, although itself an inhibitor, antagonises the effect of the propylene (Fig. 4).

FIG. 1.



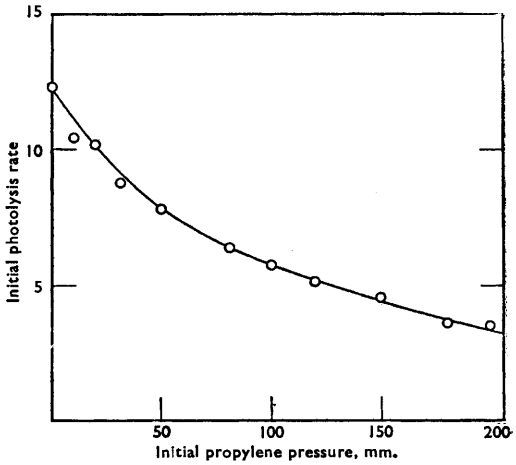
Polymerisation rate of ethylene–propylene mixtures containing 100 *mm. ethylene and various propylene pressures. Marked points are experimental. Curve is calculated from equation IV.*

FIG. 2.



Polymerisation rates of ethylene–propylene mixtures as function of ethylene pressure. Marked points are experimental. Curve is calculated from equation IV.

FIG. 3.



Photolysis of 50 *mm. acetaldehyde in presence of* 100 *mm. ethylene and various propylene pressures. Curve is calculated from equation III.*

The theoretical treatment of these effects is somewhat complicated, and we may approach it in the following way.

The reactions written below will be expected to occur from what is known of the behaviour of the individual gases.

1.	$CH_3{\cdot}CHO + h\nu = CH_3 + CHO$	k_1
2.	$CH_3{\cdot}CHO + CH_3 = CH_3 + CH_4 + CO$	k_2
3.	$CH_3 + CH_3 = C_2H_6$	k_3
4.	$CH_3 + C_2H_4 = R_e$	k_4^e
	$CH_3 + C_3H_6 = R_p$	k_4^p
5.	$R_e + C_2H_4 = R_{ee}$	k_5^{ee}
	$R_p + C_3H_6 = R_{pp}$	k_5^{pp}
	$R_{ee} + C_2H_4 = R_{eee}$	k_5^{eee}
6.	R_{eee} = product + CH_3	k_6^{eee}
	R_{pp} = product + CH_3	k_6^{pp}
7.	R_{eee} = product (chain ended)	k_7^{eee}
	R_{pp} = product (chain ended)	k_7^{pp}

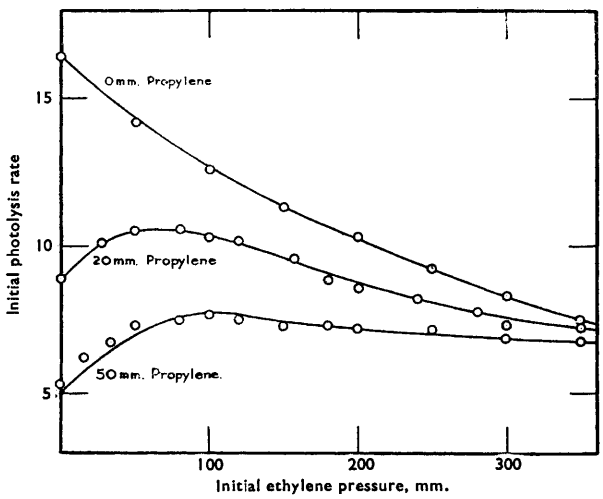
Here the polymerisation is assumed to proceed to the same degree as with the separate gases.

Additional steps rendered possible by the presence of both olefins simultaneously are:

$$(a)\ R_e + C_3H_6 = R_{ep}$$
$$(b)\ R_p + C_2H_4 = R_{pe}$$
$$\ldots\ldots \text{ etc.}$$

in a rather complex array.

FIG. 4.



Photolysis of acetaldehyde in presence of ethylene–propylene mixtures as function of ethylene pressure. Curves are calculated from equation III.

Before adding these to the set numbered 1—7, we may make a preliminary investigation in an indirect manner. Let a given ethylene–propylene mixture be regarded as equivalent to a single olefin of appropriate properties. Its behaviour should then be describable by a series of terms such as the above in which the letters with the subscript p or those with the subscript e are omitted. The rates of polymerisation, σ, and of photolysis, ρ, will then be given as in the earlier investigations by

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

and

$$\rho = C[CH_3{\cdot}CHO](\{[X]^2 + \rho_0^2/C^2[CH_3{\cdot}CHO]^2\}^{\frac{1}{2}} - [X]) \quad \ldots\ldots \quad (II)$$

where $[X]$ = concentration of "olefin,"
ρ_0 = photolysis rate in absence of olefin,
$C = k_2k_4\,\beta/2k_3$, $K = k_4^2\beta/k_3$,
$\beta = k_7/(k_6 + k_7)$
and n = average number of olefin molecules added before the chain ends.

β is the characteristic measure of the probability that the chain ends, whilst $(1 - \beta)$ is that of chain transfer.

For the fictitious "olefin" of the mixture we now determine β and plot it as a function of composition for mixtures in which the total pressure is kept constant. Since n varies from 3 for ethylene to 2 for propylene, a linear interpolation is taken for the mixtures. In this way the graph shown in Fig. 5 is obtained.

We may now consider what form this graph would be likely to have if the interpolymerisation of the ethylene and propylene were random. Suppose at a given step of the chain the probability of addition of ethylene to a growing radical is r and that of the addition of propylene w. Suppose further that after the addition of three successive molecules of ethylene there is a very high probability of chain transfer, according to a reaction of the type characterised above by the constant k_6, and that after the addition of two successive propylene molecules there is a high probability of chain ending. These assumptions are suggested by the results found with the individual gases. The chain may now end in many ways: for example, after the addition of two propylenes alone; after the addition of ethylene, propylene, ethylene, propylene, propylene;

and so on. The total probability of ending (rather than transfer) is given by a convergent series of which the earlier terms are:

$$w^2(1 + r + r^2 + wr + 2wr^2 + 2wr^3 + w^2r^2 + 3w^2r^3 + wr^4 + 4w^2r^4 + w^3r^3 + 3w^2r^5 + 4w^3r^4 + 7w^3r^5 + w^2r^6 + w^4r^4 \ldots\ldots).$$

Now since it is known from previous work that there is a much greater difference between different olefins than between different radicals in respect of the same olefin, it is not unreasonable to estimate r and w from the known rates of reaction of methyl radicals with ethylene and propylene, respectively. k_4 for propylene is 2·2 times as great as for ethylene.

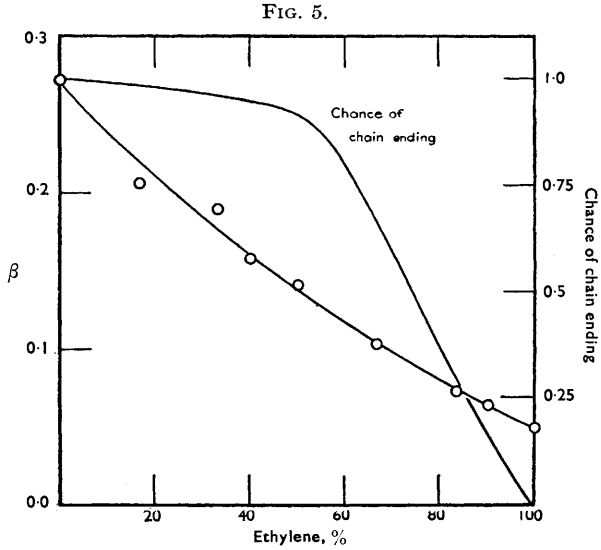
Thus $$w/[C_3H_6) \div r/[C_2H_4] = 2{\cdot}2$$

whence $$w = 2{\cdot}2/(2{\cdot}2 + x) \text{ and } r = x/(2{\cdot}2 + x)$$

where $$x = \frac{\text{ethylene concentration}}{\text{propylene concentration}}.$$

The probability of chain-ending plotted against composition for a series of ethylene–propylene mixtures is also shown in Fig. 5. The values obtained range necessarily from unity to

FIG. 5.



zero, since no transfer was allowed for with propylene and no ending with ethylene, though in fact β varies from 0·055 with ethylene to 0·30 with propylene. Nevertheless, the general shapes of the curves for the probability of chain-ending according to the above calculation and for the variation of β should be similar if the assumptions are generally correct.

Comparison of the curves in Fig. 5, however, shows that some quite special factor is operative. According to the calculation just made, the probability of chain-ending should decrease only very slowly as the composition changes from pure propylene by addition of ethylene, and should not show a serious fall until about 50% of the latter is present. In fact β decreases rapidly with the first additions of ethylene. It seems clear, therefore, that the ethylene has a very marked specific effect in preventing chain-ending. This is reflected in its action in antagonising the inhibitory effect of the propylene on the photolysis.

Since this effect now appears as a major factor in the observed behaviour, we express it by the following equation:

$$8.\ R_{pp} + C_2H_4 = \text{product} + CH_3 \qquad k_8$$

R_{pp} is assumed to regenerate a methyl radical if it meets ethylene before it has time to isomerise and become inactive.

This last equation is now added to the set 1 . . . . . .7.

The question now arises as to the part played by the reactions labelled (*a*), (*b*) . . . . . above.

As far as the photolysis rate is concerned they will play little part, the inhibitory action being principally determined by the competition of the reactions numbered 6, 7, and 8.

Ignoring, therefore, (*a*), (*b*) . . . . , and solving the usual stationary state equations for the reactions characterised by k_1 to k_8, we obtain for the photolysis rate :

$$\rho = C[CH_3{\cdot}CHO]\left[\left\{\left([C_2H_4] + \frac{W[C_3H_6]}{1 + S[C_2H_4]}\right)^2 + \frac{\rho_0^2}{C^2[CH_3{\cdot}CHO]^2}\right\}^{\frac{1}{2}} - \left([C_2H_4] + \frac{W[C_3H_6]}{1 + S[C_2H_4]}\right)\right] \quad \text{(III)}$$

where $C = k_2k_4^e\beta^e/2k_3$, $W = k_4^p\beta^p/k_4^e\beta^e$,

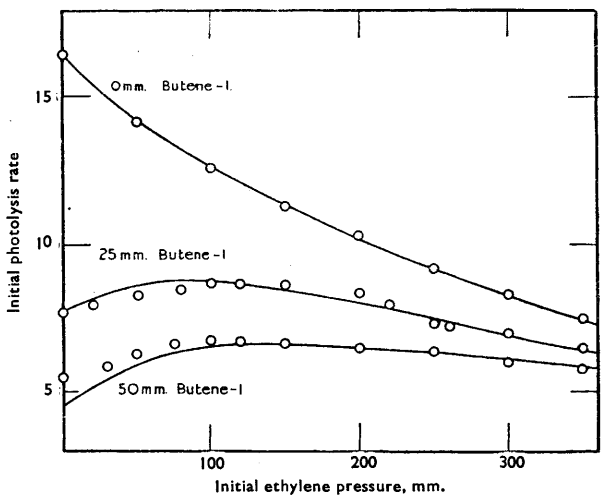
and $S = k_8/(k_6^{pp} + k_7^{pp})$.

C and W are known from the measurements on ethylene and propylene alone, whilst S must be determined from the experiments themselves.

Figs. 3 and 4 show that equation III expresses the results for the photolysis rates satisfactorily.

In considering the polymerisation rates the matter is less simple.

FIG. 6.



Photolysis of acetaldehyde in presence of ethylene–butene-1 mixtures. Curves are calculated from equation III.

Fig. 1 shows that for high proportions of propylene the reaction rate is low in any case. Most of the contribution to σ in a mixture comes from the ethylene. As far as the rate goes the influence of the terms derived from (*a*), (*b*) . . . will be small. These reactions may exert some influence but not a very large one, since the value of n is always small.

The polymerisation rate derived from equations 1—8 alone is given by :

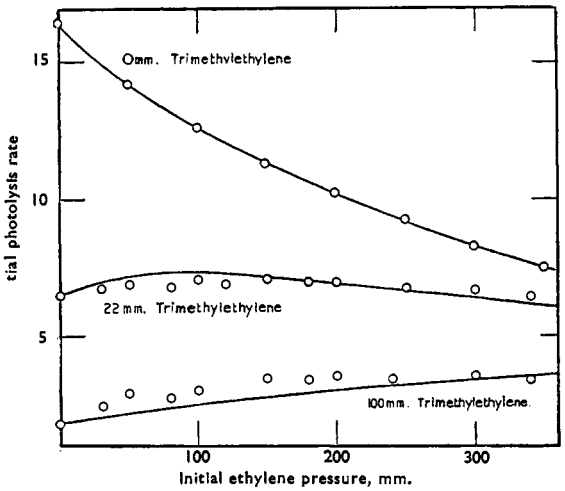
$$\begin{aligned}\sigma &= n^ek_4^e[CH_3][C_2H_4] + n^pk_4^p[CH_3][C_3H_6] \\ &= \tfrac{1}{2}n^eK\{[C_2H_4] + \delta[C_3H_6]\}\left[\left\{\left([C_2H_4] + \frac{W[C_3H_6]}{1 + S[C_2H_4]}\right)^2 + \frac{\rho_0^2}{C^2[CH_3{\cdot}CHO]^2}\right\}^{\frac{1}{2}}\right. \\ &\qquad \left. - \left([C_2H_4] + \frac{W[C_3H_6]}{1 + S[C_2H_4]}\right)\right] \quad . \quad . \quad \text{(IV)}\end{aligned}$$

where $\delta = n^pk_4^p/n^ek_4^e$, and $K = (k_4^e)^2\beta^e/k_3$.

Now n_p is approximately 2 and n_e approximately 3. This would give $\delta = 1{\cdot}5$. In the mixed system δ will be modified, and it seems quite likely that an empirical modification will be enough to express the changed kinetics. In fact if the above equation is tested with $\delta = 0{\cdot}45$, quite an adequate representation of the results is possible, as is shown in Figs. 1 and 2. That δ is below the value calculated above is probably to be attributed to the extra consumption of ethylene in the new chain-transfer step 8. However, the conditions of the experiment are far less suitable for the drawing of detailed conclusions about the polymerisation than they are for the study of the reactions of the radicals from the aldehyde with the mixed olefins.

Similar experiments were made on mixtures of ethylene with butene-1, butene-2, and trimethylethylene respectively. The results were generally in conformity with those described for the ethylene–propylene system, the most significant effect being the antagonism by small amounts of ethylene of the strong inhibitory action of the higher olefins on the photolysis of the aldehyde (see Figs. 6 and 7).

FIG. 7.



Photolysis of acetaldehyde in presence of ethylene–trimethylethylene mixtures. Curves are calculated from equation III.

The values of β are reproduced with the constants shown in the table, *C* and *W* being found from experiments with the pure gases, and *S* being determined from the experiments with a single mixture.

Mixture of ethylene with :	*C*.	*W*.	*S*.
Propylene	8×10^{-4}	12·0	$1{\cdot}65 \times 10^{-2}$
Butene-1	8×10^{-4}	13·0	$1{\cdot}02 \times 10^{-2}$
Butene-2	8×10^{-4}	14·0	$7{\cdot}0 \times 10^{-3}$
Trimethylethylene	8×10^{-4}	19·0	$6{\cdot}6 \times 10^{-3}$

The effectiveness of the chain transfer which occurs where a radical of the type R_{xx} reacts with ethylene decreases, but not at all markedly, with increasing complexity of the olefin.

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