330. *The Reaction of Methyl Radicals with Olefins. Part IV.*
The Reaction with Tetrafluoroethylene and Vinyl Fluoride.

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The rate of polymerisation of tetrafluoroethylene induced by acetaldehyde photolysis is very much greater than that of ethylene under the same conditions. An insoluble solid polymer is produced for which the kinetic results suggest a molecular weight corresponding to about 26 fluoroethylene units. In contrast to the behaviour with the lower olefins the rate of aldehyde photolysis is greatly increased by the presence of fluoroethylene. By analogy with the previous results a chain polymerisation is assumed to be initiated by methyl radicals from the aldehyde photolysis, a fluorinated radical which can initiate further polymerisation being eventually produced by chain transfer. The experimental results require that this radical should be able to induce the decomposition of a molecule of acetaldehyde into carbon monoxide and methane without itself suffering any change in the process.

Vinyl fluoride is also polymerised by aldehyde photolysis, the rate of which is unchanged. This can be explained if every polymerisation chain suffers chain transfer.

In the previous papers of this series (*J.*, 1949, 2219 *et seq.*) we have considered the reactions which occur when methyl radicals from the aldehyde photolysis interact with the lower olefins. As valuable information was obtained from measurements of the degree of inhibition of the photolysis by the olefin it was necessary to work at temperatures at which the chain length of the aldehyde photolysis was appreciable. At these temperatures (about 300° c.) the formation of high polymers from the lower olefins was not to be expected and the maximum degree of polymerisation observed corresponded to about three ethylene units per molecule. Polytetrafluoroethylene produced commercially by catalysed liquid-phase reaction is very stable to heat, being unchanged and still solid at temperatures at which polyethylene decomposes rapidly. It was therefore of interest to investigate the interaction of methyl radicals with fluoro-substituted olefins as it seemed probable that the propagation reaction might proceed further before the intervention of chain transfer or chain termination than with ethylene.

Experimental.

Methods.—The experimental methods were the same as those described in Part I. The rates of aldehyde photolysis and of olefin polymerisation were obtained separately by a combination of pressure measurements with chemical analysis for unchanged aldehyde. Tetrafluoroethylene and vinyl fluoride were obtained from Imperial Chemical Industries Limited, General Chemicals Division, in glass vessels at atmospheric pressure. They were displaced from the vessels with water, dried with phosphoric oxide, and fractionated between cooled traps, only the middle fractions being collected. Larger quantities of the tetrafluoroethylene polymer were produced in a simple flow apparatus. The gas was passed slowly through a bubbler containing acetaldehyde at −20° and the emerging stream containing about 50 mm. of acetaldehyde vapour allowed to flow through a quartz tube irradiated by a mercury lamp. The polymer formed as a white cloud in the gas, the greater part settling to the bottom of the tube and the remainder adhering to the cooler parts of the wall. About 4 g. of the polymer were obtained in this way.

Results.—(i) *Vinyl fluoride.* The rate of photolysis of 50 mm. of acetaldehyde at 300° in the presence of vinyl fluoride and the rate of the induced polymerisation of the latter are shown in Figs. 1 and 2 as a function of vinyl fluoride pressure. The rate of polymerisation is very similar to that of ethylene under the same conditions. In contrast to the behaviour with ethylene, the rate of aldehyde photolysis is unchanged by the presence of vinyl fluoride, though the latter is polymerised.

(ii) *Tetrafluoroethylene.* Figs. 1 and 2 also give the experimental results for the aldehyde-induced polymerisation of tetrafluoroethylene. Here the rate of polymerisation is almost ten times that of ethylene, and the rate of aldehyde photolysis is greatly accelerated instead of suffering inhibition.

(Owing to the rapid rates of pressure change the initial rates were obtained by plotting pressure–time curves for the early parts of the reaction and drawing tangents at the origin.) Figs. 3 and 4 give the corresponding results obtained with a constant pressure of tetrafluoroethylene (50 mm.) and variable

FIG. 1.

Rate of photolysis of 50 mm. of acetaldehyde in the presence of ethylene, vinyl fluoride, and tetra-fluoroethylene. Smooth curve for tetrafluoro-ethylene is that calculated from equation (I).

FIG. 2.

Rates of polymerisation of ethylene, vinyl fluoride, and tetrafluoroethylene induced by photolysis of 50 mm. of acetaldehyde. Smooth curve for tetrafluoro-ethylene is that calculated from equation (II).
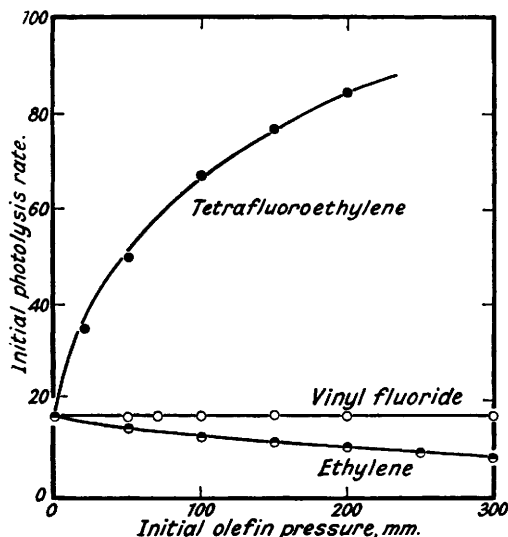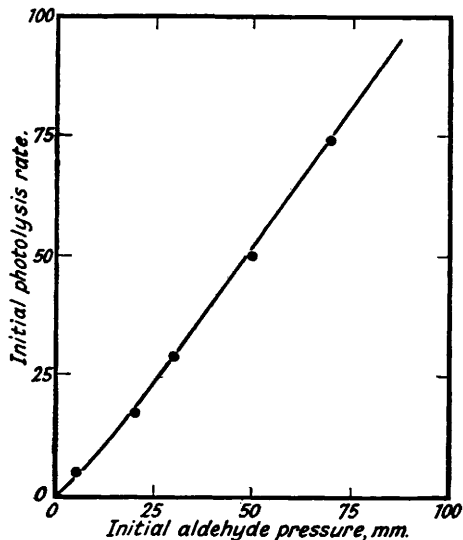

FIG. 3.

Rate of photolysis of acetaldehyde in the presence of 50 mm. of tetrafluoroethylene as function of alde-hyde pressure. Smooth curve is that calculated from equation (I).
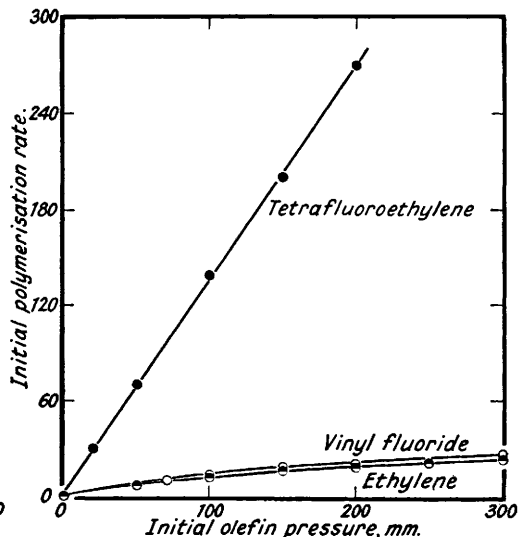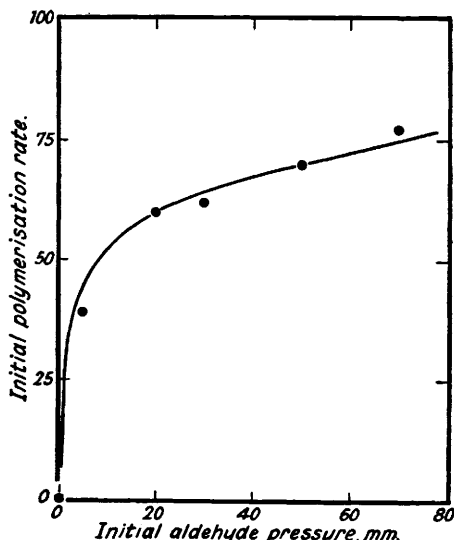

FIG. 4.

Rate of polymerisation of 50 mm. of tetrafluoroethyl-ene induced by acetaldehyde photolysis as function of aldehyde pressure. Smooth curve is that calculated from equation (II).

aldehyde pressures. The polymerisation of tetrafluoroethylene is also induced by the photolysis of acetone. The results given in Table I show that the rate of photolysis is not altered by the presence of the olefin.

The photolysis of propaldehyde induces the polymerisation, there being very marked acceleration of the rate of photolysis, as shown by the results in Table II.

TABLE I.

Photolysis of 50 mm. of acetone in presence of tetrafluoroethylene.

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

Initial C_2F_4 pressure, mm.	Overall pressure change, mm.	Rate of photo-lysis.	Rate of C_2F_4 poly-merisation.	Initial C_2F_4 pressure, mm.	Overall pressure change, mm.	Rate of photo-lysis.	Rate of C_2F_4 poly-merisation.
0	+ 0·5	1·0	—	60	−30·5	1·0	31·0
10	− 4·9	—	5·4	80	−40·0	—	40·5
30	−15·4	1·2	15·9	100	−46·1	1·2	46·6
50	−25·7	—	26·2				

TABLE II.

Photolysis of 50 mm. of propaldehyde in the presence of tetrafluoroethylene.

Initial C_2F_4 pressure, mm.	Rate of alde-hyde photolysis.	Rate of C_2F_4 polymerisation.	Initial C_2F_4 pressure, mm.	Rate of alde-hyde photolysis.	Rate of C_2F_4 polymerisation.
0	5·0	—	60	25·5	35·0
20	14·0	12·5	80	28·0	45·0
40	21·5	25·0	100	30·5	54·5

X-Ray diffraction photographs of the solid material were taken by Mr. C. W. Bunn who reports :
" The *X*-ray diffraction photographs show sharp, rather spotty, crystal reflections together with diffuse bands. The positions of the crystal reflections correspond to the side-spacings of high-molecular-weight polytetrafluoroethylene, indicating that the material is a linear polymer in which the chains are packed side-by-side in the same way as in the high polymer. The diffuse bands correspond to those given by the high polymer above 20°, and indicate that the crystals are disordered in the same way (Rigby and Bunn, *Nature*, 1949, **164**, 583). The degree of disorder is greater, and the transition point (if any) lower, than for the high polymer; these differences, and the spottiness of the crystal reflections, are consistent with the low molecular weight of the material. In short, the *X*-ray photographs suggest that the material is a linear polymer of tetrafluoroethylene of comparatively low molecular weight."
The solid reaction product had a diffuse melting point of about 220°, which is about 100° below that of the high polymer. The infra-red spectrum showed bands in the regions to be expected for CH and CH_3 vibrations which are absent from the high polymer, otherwise the spectra were rather similar.
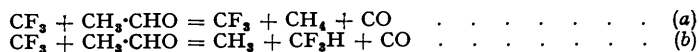
DISCUSSION.

It has previously been shown (Danby and Hinshelwood, *Proc. Roy. Soc.*, 1941, *A*, **179**, 169) that in the methyl-radical-induced polymerisation of ethylene the growing polymer radicals may undergo one of two alternative fates, either disproportionation to give a methyl radical and an olefin (chain transfer), or isomerisation to an inactive form (chain termination). The results obtained in the induced polymerisation of vinyl fluoride may be explained if the latter process does not occur at all, every polymer chain undergoing chain transfer. If every methyl radical removed by reaction with the olefin is regenerated in the chain-transfer step there will be no change in the stationary concentration of methyl radicals and no alteration in the rate of photolysis.

The marked acceleration of the rate of aldehyde photolysis in the presence of tetrafluoro-ethylene could be explained if the fluoroethylene, or an addition compound of it with aldehyde, absorbed in the ultra-violet region. Absorption spectra, however, showed no trace of any such additional absorptive process.
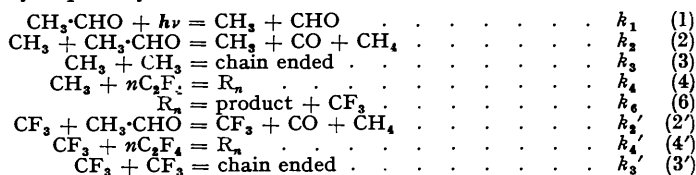
The quantum yield for radical production in the primary process of the aldehyde photolysis is about 0·2 at 3150 A. (Blacet, *J. Amer. Chem. Soc.*, 1942, **64**, 893). Four-fifths of the absorbed radiation is therefore lost by collisional deactivation. Nevertheless the observed acceleration cannot be accounted for by an interaction of fluoro-olefin with the activated aldehyde molecules before their energy is lost. The lifetime of activated aldehyde is too short for this process to be effective and in any case the maximum acceleration in rate theoretically possible is about five times compared with the observed limiting acceleration of over eight times.

The only alternative explanation is that fluoromethyl radicals are considerably more reactive than methyl radicals and that they are not lost in the process of causing aldehyde to react. From what we know of the reaction with ethylene, the induced polymerisation of the fluoro-ethylene must consist of the successive addition of olefin molecules to the initiating radical so as to build up a large radical. This radical in undergoing chain transfer may either regenerate the initial methyl radical or, alternatively, a radical such as CF_3 from the other end of the molecule.

If the latter, then this fluoromethyl radical might react with aldehyde by one of two alternative processes :

$$CF_3 + CH_3 \cdot CHO = CF_3 + CH_4 + CO \quad \ldots \ldots \ldots \quad (a)$$
$$CF_3 + CH_3 \cdot CHO = CH_3 + CF_3H + CO \quad \ldots \ldots \ldots \quad (b)$$

The experimental results require no loss of fluoromethyl radicals and preference is therefore given to (a). This reaction may be an induced predissociation of the kind suggested by Taylor and Burton (*J. Chem. Physics,* 1939, **7**, 414). It may also be significant that Morris (*J. Amer. Chem. Soc.,* 1944, **66**, 584) found that mixed deuteromethanes were not formed in the pyrolysis of mixtures of normal and deutero-aldehyde. This is consistent with reactions similar to (a) above. We therefore arrive at the following mechanism for the polymerisation of tetrafluoro-ethylene induced by acetaldehyde photolysis :

$$CH_3 \cdot CHO + h\nu = CH_3 + CHO \quad \ldots \ldots \ldots \quad k_1 \quad (1)$$
$$CH_3 + CH_3 \cdot CHO = CH_3 + CO + CH_4 \quad \ldots \ldots \quad k_2 \quad (2)$$
$$CH_3 + CH_3 = \text{chain ended} \quad \ldots \ldots \ldots \quad k_3 \quad (3)$$
$$CH_3 + nC_2F_4 = R_n \quad \ldots \ldots \ldots \ldots \quad k_4 \quad (4)$$
$$R_n = \text{product} + CF_3 \quad \ldots \ldots \ldots \ldots \quad k_6 \quad (6)$$
$$CF_3 + CH_3 \cdot CHO = CF_3 + CO + CH_4 \quad \ldots \ldots \quad k_2' \quad (2')$$
$$CF_3 + nC_2F_4 = R_n \quad \ldots \ldots \ldots \ldots \quad k_4' \quad (4')$$
$$CF_3 + CF_3 = \text{chain ended} \quad \ldots \ldots \ldots \quad k_3' \quad (3')$$

(The polymer radical R_n produced by the addition of fluoroethylene molecules to a *methyl* radical is assumed to be identical with that arising from a *fluoromethyl* radical.)

The usual stationary-state treatment of these equations leads to the following expressions for the rate of photolysis (ρ) of aldehyde in the presence of fluoroethylene and for the rate of the induced polymerisation (σ) :

$$\rho = C'[A]\left[\left\{[F]^2 + \frac{\rho_0{}^2}{(C')^2[A]^2}\right\}^{\frac{1}{2}} - [F]\right] + C''[A][F]^{\frac{1}{2}}\left[[F]^2 + \frac{\rho_0{}^2}{(C')^2[A]^2} - [F]\right]^{\frac{1}{2}} . \quad (I)$$

where $[A]$ = aldehyde pressure,
$\quad [F]$ = tetrafluoroethylene pressure,
$\quad \rho_0$ = aldehyde photolysis rate in absence of olefin,
$\quad C' = k_2 k_4 / 2k_3$,
and $\quad C'' = k_2' k_4 / (2k_3 k_3')^{\frac{1}{2}}$

$$\sigma = \tfrac{1}{2}nK'[F]\left[\left\{[F]^2 + \frac{\rho_0{}^2}{(C')^2[A]^2}\right\}^{\frac{1}{2}} - [F]\right] + nK''[F]^{3/2}\left[\left\{[F]^2 + \frac{\rho_0{}^2}{(C')^2[A]^2}\right\}^{\frac{1}{2}} - [F]\right]^{\frac{1}{2}} . \quad (II)$$

where $\quad n$ = average number of olefin molecules incorporated in product,
$\quad K' = (k_4)^2/k_3$,
and $\quad K'' = k_4 k_4' / (2k_3 k_3')^2$.

The values for the constants C', C'', $\tfrac{1}{2}nK'$, and nK'' which give the best agreement with experiment when substituted in equations (I) and (II) are :

$$C' = 2 \cdot 00 \times 10^{-4}; \quad C'' = 2 \cdot 56 + 10^{-3}; \quad \tfrac{1}{2}nK' = 8 \cdot 40 \times 10^{-4}; \quad nk'' = 2 \cdot 12 \times 10^{-4}.$$

The curves calculated from these equations are given in Figs. 1—4 for comparison with the experimental measurements.

From the above definitions of C' and K', we have

$$\tfrac{1}{2}nK'/C' = nk_4/k_2$$

From the values of $\tfrac{1}{2}nK'$ and of C' which give the best agreement with the experimental results when substituted in equations (I) and (II) we can obtain a value for the ratio nk_4/k_2. The results presented in Part II showed that there was only limited variation in the value of the ratio k_4/k_2 for a series of different olefins. If we assume that the ratio k_4/k_2 in the polymerisation of tetrafluoroethylene induced by acetaldehyde photolysis has the same value as that for the polymerisation of ethylene, we arrive at the value 26 for the number of tetrafluoroethylene molecules incorporated into each molecule of product. This is in general agreement with the melting point of the polymer, with the fact that C–H linkages (from the initiating methyl radicals) are still detectable by infra-red spectra, and with the X-ray diffraction data.

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