227. *Radical-sensitised Polymerisation of Vinyl Acetate Vapour.*

By H. W. MELVILLE and R. F. TUCKETT.

The kinetics of the polymerisation of vinyl acetate vapour initiated by hydrogen atoms and by methyl radicals has been investigated, with the following results. Owing to the fact that the direct photochemical polymerisation does not occur at room temperatures below 20 mm., the free-radical reaction can be studied alone by working at pressures below this limit. The reaction rate is proportional to the first power of the vinyl acetate pressure and to the square-root of the rate of production of radicals. The kinetic chain length of the reaction has been measured by the method of end-group analysis. The reaction has a high negative temperature coefficient.

These results show that the direct photo-reaction also proceeds by means of a radical mechanism, the correlation between the two reactions being close. The direct reaction initially involves the production of di-radicals which are subject to deactivation spontaneously or by collision with inert added gases. These gas-phase reactions exhibit the so-called gel effect to a maximum degree and thus the termination velocity coefficients are reduced to small values. This gives rise to overall apparent negative energies of activation.

IN the previous paper it has been shown that vinyl acetate does not apparently undergo photochemical polymerisation at room temperature at pressures below 20 mm. In this respect it is unique but the phenomenon can be put to good use in the following way. With some molecules, *e.g.*, methyl methacrylate, it is comparatively easy to study the kinetics of the free-radical polymerisation without complications arising out of the occurrence of the direct photo-reaction; with other molecules like methyl acrylate this cannot conveniently be done for a variety of reasons. It is, however, important to study the kinetics of the radical reaction and thus characterise the type of polymerisation for purposes of reference so that by comparison it is possible to say whether or not the direct reaction, for example, goes by way of free radicals. At pressures below 20 mm. it proves to be possible to induce radical polymerisation and to study it to the complete exclusion of the direct reaction. The present paper describes the results obtained in this way.

The apparatus used was identical with that described in the previous paper. Special methods and modifications are described in the appropriate places.

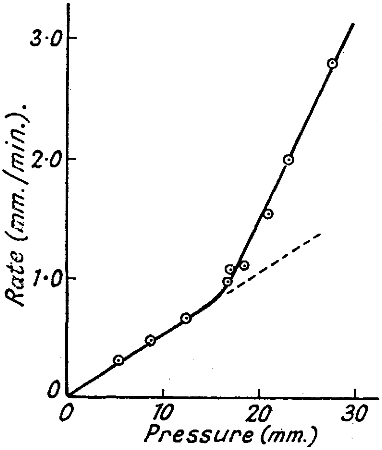
Hydrogen-atom-sensitised Reaction.—Although molecular hydrogen is an inhibitor for the direct photo-polymerisation, it indirectly becomes a sensitiser if mercury vapour is present and instead of a high-pressure mercury lamp a low-pressure type emitting unreversed 2537 A. radiation is employed. This phenomenon is well marked below the limiting pressure where, of course, no direct reaction can be detected. There is no doubt the accelerating effect of hydrogen is due to its sensitised dissociation to atomic hydrogen, which adds on to vinyl acetate to give a free radical, thus initiating polymerisation. There are some complications in the use of this indirect method. Excited mercury atoms will be deactivated by vinyl acetate molecules as well as by hydrogen and thereby start off a mercury-sensitised polymerisation, as has been shown in the previous paper. Fortunately, there is a pressure limit to this reaction (below) and hence its contribution to the total observed rate of polymerisation can easily be eliminated. Even at low pressures, mercury atoms will still be deactivated by vinyl acetate. The fraction f_{H_2} of excited mercury atoms deactivated by hydrogen molecules is simply given by

$$f_{H_2} = \frac{\sigma_{H_2}^2[H_2]\mu_{H_2-Hg}^{-\frac{1}{2}}}{\sigma_{H_2}^2[H_2]\mu_{H_2-Hg}^{-\frac{1}{2}} + \sigma_{VA}^2[VA]\mu_{VA-Hg}^{-\frac{1}{2}}}$$

where σ is the sum of the quenching radii and μ is the reduced mass of the pairs of molecules concerned; $\sigma_{H_2}^2 = 6{\cdot}0 \times 10^{-16}$ cm.^{2} and σ_{VA}^2 is not known: it is probably about 20×10^{-16} cm.^{2}, for methyl methacrylate, for example, has $\sigma^2 = 25 \times 10^{-16}$ cm.^{2} (Bolland, unpublished experiments). This value being taken, it is calculated that $f_{H_2} = 0{\cdot}8$ for $H_2 : VA = 2{\cdot}3 : 1$, and $f_{H_2} = 0{\cdot}9$ for $H_2 : VA = 5{\cdot}8 : 1$. Consequently, high hydrogen pressures were invariably used to eliminate complication of the kinetics in the above manner. The reproducibility of the free-radical reaction is much better than that of the direct photo-reaction, mainly because of the shorter chain lengths involved. Although the rate of reaction does not immediately attain its maximum value in a clean tube, a very light coating suffices to prevent completely any wall termination. Corrections due to absorption of monomer by polymer are practically absent.

The mixtures of hydrogen and vinyl acetate were prepared in two ways. In one procedure the reaction vessel was filled with vinyl acetate to a given pressure. This was condensed out, the side tube cooled in liquid air, and then hydrogen admitted. In the second procedure vinyl acetate was admitted first, followed by hydrogen, the pressure of which was maintained at a high value in its reservoir so that little if any vinyl acetate vapour could diffuse out into the hydrogen reservoir. The former method was the more convenient where it was necessary to measure accurately the initial pressure of the hydrogen rather than the total pressure of the mixture.

Fig. 1.



Variation of total rate of polymerisation with vinyl acetate pressure.

A pressure of 30 mm. of hydrogen being used, the variation of initial rate of polymerisation with pressure of vinyl acetate is shown in Fig. 1. In the first place it will be seen there is a marked acceleration in presence of hydrogen which can only occur because of the free-radical reaction induced by atomic hydrogen. Secondly, quite a fast reaction occurs at vinyl acetate pressures when the mercury-sensitised polymerisation of vinyl acetate does not proceed at all. At a pressure of 15 mm., however, this type of reaction seems to proceed in parallel with the hydrogen atom sensitised reaction. Below 15 mm. the free-radical reaction rate is proportional to the first power of the concentration of the acetate. Fig. 2 is a plot of the log of this rate as a function of radiation intensity. The slope of the line is 0·7, showing that quite a large proportion of the free radicals combines in the gas phase. Thus the kinetics are approximately expressed simply by

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = \text{const. } [\mathrm{M}]I^{\frac{1}{2}}$$

characteristic of a normal reaction in which mutual termination occurs and in which the rate of initiation is independent of monomer concentration. When individual runs are examined, however, and allowance is made for the disappearance of the appropriate amount of hydrogen, the first-order " constant " decreases with decreasing pressure as shown in Table I. Even a second-order " constant " exhibits a slight tendency to decrease. It is evident that this diminution in velocity must be due to the accumulation of some rate-retarding molecule produced as a result of secondary reactions.

Table I.

Temp. 15°. Hydrogen pressure 27·2 mm.

Time (mins.)	0.	1.	2.	3·5	5.	7.	9.	10.
Press. (mm.) of vinyl acetate, uncorr.	18·6	15·5	13·1	10·9	9·5	8·1	7·0	6·5
Press. (mm.) of vinyl acetate, corr. for loss of H_2	18·6	15·6	13·4	11·4	10·3	9·2	8·4	8·1
k (min.$^{-1}$) (1st order)	—	0·177	0·164	0·140	0·118	0·100	0·088	0·083
k (min.$^{-1}$ mm.$^{-1}$) (2nd order)	—	0·0100	0·0105	0·0095	0·0086	0·0079	0·0072	0·0070

The addition of hydrogen actually inhibits the mercury photosensitised polymerisation since the hydrogen molecule deactivates quite a proportion of the excited mercury atoms. In fact it is possible to obtain an approximate estimate of the quenching radius of the vinyl acetate molecules from such data. Table II gives the relevant data for low vinyl acetate pressures.

Table II.

Monomer pressure (mm.)	18·0	22·3
Rate of mercury-sensitised reaction	0·9	2·2
Total rate of reaction with 30 mm. of hydrogen	1·00	1·85
Estimated rate of Hg-sensitised reaction in presence of hydrogen	0·79	0·66
Fraction of H_2 molecules deactivating excited Hg atoms (f_{H_2})	0·79	0·69

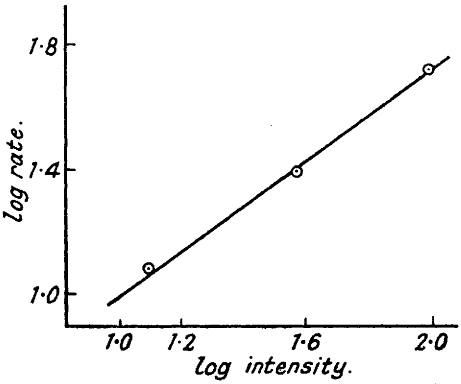
At a pressure of 18·0 mm. the mercury-sensitised rate is reduced from 0·9 to 0·19 mm./min., since a fraction f_{H_2} of the mercury atoms is deactivated by hydrogen. The value of f_{H_2} at 22·3 mm. is 0·69. But f_{H_2} is given by the equation

$$f_{\mathrm{H}_2} = \frac{\sigma_{\mathrm{H}_2}[\mathrm{H}_2]/[\mathrm{VA}]\,.\,\mu_{\mathrm{H}_2-\mathrm{Hg}}^{-\frac{1}{2}}}{\sigma_{\mathrm{H}_2}[\mathrm{H}_2]/[\mathrm{VA}]\mu_{\mathrm{H}_2-\mathrm{Hg}} + \sigma_{\mathrm{VA}}{}^2\mu_{\mathrm{Hg}-\mathrm{VA}}^{-\frac{1}{2}}}$$

If σ_{H_2} is taken as $6{\cdot}0 \times 10^{-16}$ mm.^{2}, then since $[H_2]/[VA]$ is known, σ_{VA-Hg} may be computed. The figures are 20 and 25×10^{-16} mm.^{2}, respectively, in good agreement with the experimentally determined value of 25×10^{-16} mm.^{2} for methyl methacrylate.

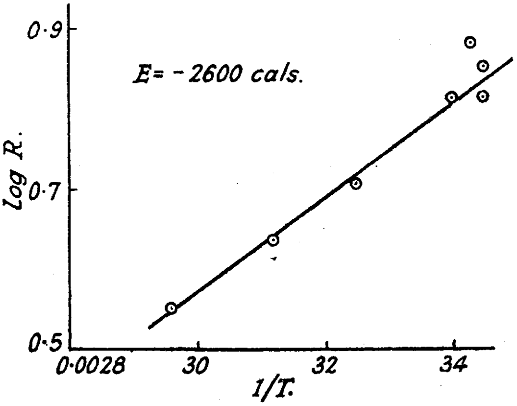
Inhibitors.—Although an examination of the course of an individual run showed unmistakable evidence of the production of an inhibitor, more direct evidence was desirable. This was obtained in the following manner. Unfortunately, the constant pressure–variable volume method cannot be used, but a modification is possible. A mixture of monomer and hydrogen at a suitable pressure is irradiated for such a time that 2 mm. of vinyl acetate are polymerised. The gases are then thoroughly mixed by moving the mercury in the gas burette, and the pressure is adjusted so that the original vinyl acetate pressure is obtained. Next, another 2 mm. of vinyl acetate are polymerised and the time is noted. If no inhibitor had been produced the time should have been slightly shorter because of the slight diminution in volume of the system. Table III shows that, in fact, these times for 2 mm. polymerisation increased continually.

FIG. 2.



Effect of intensity on the rate of the free radical reaction.

FIG. 3.



Temperature coefficient of the free radical reaction.

TABLE III.

Vinyl acetate 18·8 mm. Hydrogen 24·2 mm.

Initial vol. of system (c.c.) ...	210	198	187	176	167	159	150
Time (mins.) for $-\Delta p = 2$ mm.	1·23	1·18	1·63	2·58	3·50	4·75	6·75

Further conclusive proof of the presence of an inhibitor can be obtained by examining the intensity exponent, which should increase as inhibitor accumulates. This is best done by carrying out two runs with different intensities and comparing the ratio of times required for the same pressure decrease throughout the course of the reaction. The following results were obtained in two such runs.

Ratio of intensities 8·0 : 1. Vinyl acetate 19·0 mm. Hydrogen 27·5 mm.

Pressure range (mm.)	18—11	6·0—3·5	4·5—3·5
Ratio of times	2·3	3·16	3·8

The increase in ratio shows that the exponent is increasing from about 0·5 towards unity at the end of the run.

The inhibitor is not produced by short-wave radiations from the 2537 A. lamp, for an acetic acid filter does not cut down inhibitor production. It is condensable in liquid air and solid carbon dioxide. This was shown by condensing the contents of the reaction vessel after a run into a suitable trap and pumping off all non-condensable gas. Fresh hydrogen was then added, and the run continued. At — 183° and — 80° the inhibitor was retained in the trap.

Temperature Coefficient.—The temperature coefficient of the free-radical reaction can only be studied over a comparatively small range since at higher temperatures the direct reaction begins to make its appearance and thus complicates the interpretation of the kinetics. Fig. 3 shows how the rate varies with temperature, the rate being measured by taking the reciprocal of the time for the pressure of vinyl acetate to fall 4 mm. It will be seen that the temperature coefficient is negative, with a value of — 2600 cals. So far as is known, the addition of atomic hydrogen to an unsaturated molecule proceeds with such a small energy of activation that the temperature coefficient of the polymerisation process must certainly be due to that of the propagation and termination reactions. Since the polymerisation ends by mutual destruction of active molecules, the apparent energy of activation is equal to $E_p - \frac{1}{2}E_T$, E_p and E_T being the energies of activation for propagation and termination. These temperature coefficients were measured at different intensities and the results are given in Table IV.

TABLE IV.

Chain length at 17°:

8.		12.		50.	
Temp.	τ (mins.) for $\Delta p = 4$ mm.	Temp.	τ (mins.) for $\Delta p = 4$ mm.	Temp.	τ (mins.) for $\Delta p = 4$ mm.
17·5°	4·00	17·0°	6·25	18·0°	10·0
19·5	3·6	18·6	5·3	19·0	11·4
25·0	5·2	21·3	6·2	32·0	19·7
35·5	4·3	34·5	7·9	48·0	38·4
55·0	5·5	47·6	9·3	—	—
—	—	65·0	11·2	—	—
$E = -$ 1900 cals.		$E = -$ 2600 cals.		$E = -$ 8200 cals.	

This reaction thus falls into line with the direct photo-polymerisation and with the polymerisation of methyl acrylate and of methyl vinyl ketone in the gas phase in that negative energies of activation are observed. With the free-radical reaction it is probable that the value would not change with further increase in chain length. The mere fact that the value is negative would imply that E_T is greater than E_p by a substantial amount. This fact is anomalous since it would imply that the two free radicals must become activated before they react with each other; in other words, more activation energy is required for the interaction of two radicals than is required for the interaction between a radical and a double bond. Such a state of affairs is hardly conceivable, but there appears to be no valid alternative explanation. The variation of the apparent energy of activation with chain length may quite well be due to a variation in E_p or E_T, especially when the chain length is so short.

Chain Length.—If after a hydrogen-atom-sensitised polymerisation all the vinyl acetate vapour is condensed out by passing the mixture through a trap cooled in liquid air, the hydrogen pressure is less than that at the start of the run. For example, with 18·6 mm. of vinyl acetate and 27·15 mm. of hydrogen a time of illumination of 10 mins. gives a total pressure decrease of 12·3 mm., the hydrogen pressure being now 25·85 mm. The reason for the small fall in pressure is that the hydrogen atom responsible for starting polymerisation is incorporated in the polymer itself. Thus the decrease may be made the basis of measuring the kinetic chain length of the reaction and therefore the number average molecular weight of the polymer.

Owing to the small pressure decrease certain precautions have to be taken. Only tubes lightly coated with polymer may be used since atomic hydrogen may reduce the polymer and so be removed in a non-polymerisation reaction. The most convenient method of measuring the decrease in hydrogen pressure consists in admitting the appropriate amount of vinyl acetate, freezing this out, and then admitting hydrogen. After the run the vinyl acetate is once more frozen out, and the hydrogen pressure measured. After correction for the cooling of the trap, the decrease in pressure of hydrogen is subtracted from the total observed pressure decrease to give the diminution in vinyl acetate pressure.

In considering the kinetics of the reaction as a whole it is necessary first to determine whether there is any possibility of a hydrogen atom terminating polymerisation as well as starting it. If this kind of termination occurred exclusively, then it can be shown (Melville, *Proc. Roy. Soc.*, 1937, *A*, **163**, 511) that $R \sim$ const. $[M]^2$, the rate being independent of intensity. Since the observed kinetics are $R \sim$ const. $[M]I^{\frac{1}{2}}$, it is evident that this kind of termination does not enter into the question. As has been seen in Table IV, the kinetic chain length is comparatively short, and this introduces a slight complication. The general expression for the concentration of the active polymer is

$$d[P]/dt = I - k_t[P]^2 = 0$$

where $I = k[H][M]$, k being the bimolecular coefficient for the reaction of hydrogen atoms with the monomer. For short chains, then

$$-d[M]/dt = I + I^{\frac{1}{2}}[M]k_p/k_t$$

Thus the rate will not be strictly proportional to the square-root of the intensity. The deviation may be computed in the following way. Suppose $-\,d[M]/dt \sim I^x$; then for two intensities

$$x = [\log R_2/R_1)]/[\log (I_2/I_1)]$$

Let $I_2/I_1 = 8$, as was used in some experiments, then, if $\delta = k_t/k_p$,

$$x \log 8 = \log \frac{I_2 + [M]\delta^{-1}I_2^{\frac{1}{2}}}{I_1 + [M]\delta^{-1}I_1^{\frac{1}{2}}}$$

$$= \log \sqrt{8} + \log \frac{\nu_2}{\nu_2 - 0{\cdot}65}$$

where ν_2 is the chain length at intensity I_2; or

$$x = 0{\cdot}50 + 1{\cdot}11 \log \nu_2/(\nu_2 - 0{\cdot}65)$$

Hence x may be obtained for various different values of ν_2 as follows :

$\nu_2 =$	4	5	6	12	∞
$x =$	0·586	0·567	0·55	0·53	0·500

For example, with a vinyl acetate pressure of 19 mm. and H_2 = 27·5 mm. at 17°, the chain length is greater than 10 for full intensity and over 30 at the 0·125 full intensity x (*experimental*) = 0·47.

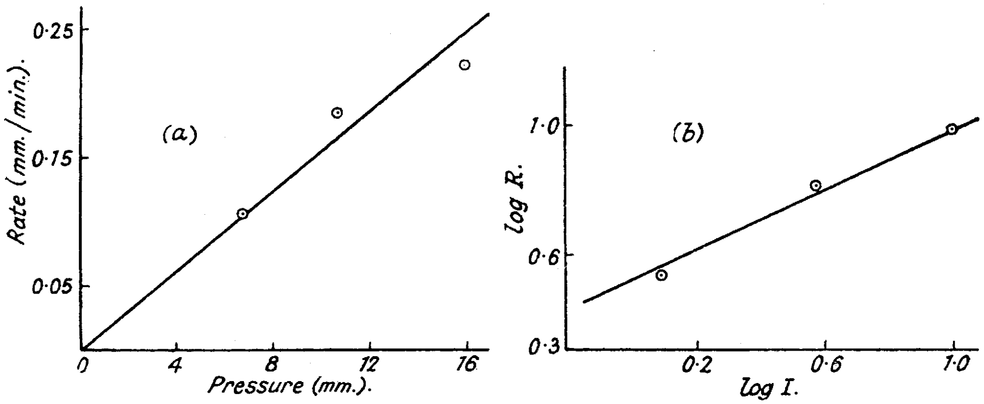
Independent evidence also indicates mutual termination of polymer growth. In such a mechanism the chain length should be inversely proportional to the square-root of the intensity of incident light. Instantaneous values of the chain length cannot, of course, be computed because of the impossibility of measuring accurately small decreases in hydrogen pressure; hence the following procedure was adopted. The hydrogen–vinyl acetate mixture is illuminated, and the chain length measured by the above-mentioned method. A second measurement is made by resuming the run. In this way the corrected vinyl acetate pressure–time curve is constructed. The rate of polymerisation at say two given pressures can then be read off. The rate of hydrogen loss is assumed to be the average rate of loss over the run. The whole procedure is then repeated at a lower intensity. The results in Table V show the expected dependence of chain length on intensity, and the observed figures are in reasonably good agreement with the theoretical values calculated from the ratio of the intensities.

TABLE V.

Intensity.	Chain length at vinyl acetate pressures (mm.) of :		Ratio of chain lengths obs. at vinyl acetate pressures (mm.) of :		Calculated ratio of chain lengths.
—	13·0	6·0	13·0	6·0	—
1·00	13·5	2·7	3·6	2·5	2·83
0·125	49	6·8	—	—	—

Methyl-radical-sensitised Reaction.—Hydrogen atoms are not always the most suitable type of initiator for a free-radical reaction. In addition, it has been shown with butadiene, for example (Jones and Melville, *Proc. Roy. Soc.*, 1946, *A*, **187**, 87), that whereas methyl radicals initiate polymerisation, hydrogen atoms lead to hydrogenation of the butadiene. It was therefore desirable to see whether methyl radicals from photodecomposing acetone could effect polymerisation of vinyl acetate vapour and so find whether the kinetics of the two reactions are identical. With acetone as a source of methyl radicals there is a very marked acceleration of polymerisation, for at 22 mm. vinyl acetate pressure the rate was 0·02 mm./min. but on addition of 40 mm. of acetone the rate jumped to 0·45 mm./min. Even well below the critical limit with VA = 16 mm., the rate was 0·22 mm./min., the rate of the direct reaction being negligible. In Fig. 4 the kinetics are briefly summarised. In Fig. 4(*a*) it will be seen that the rate is proportional to pressure, the upper limit of pressure being fixed by the limit for the direct reaction. In Fig. 4(*b*) log rate is plotted against log intensity. The slope of the straight line is 0·46. Thus the kinetics of the hydrogen-atom- and of the methyl-radical-sensitised reaction are exactly similar. There is, however, a further interest in this similarity. If matters are so adjusted that the two reactions occur at the same speed, then the chain length must be identical and the rate of initiation must also be identical. But the rate of production of hydrogen atoms is known, and hence it should in principle be possible to measure the rate of production of methyl radicals from acetone, and thus throw some further light on the photochemistry of this molecule. Much has already been written about the photochemistry of acetone, and it is usually presumed that when the molecule does dissociate the first act is the production of acetyl and methyl radicals and that the former subsequently decompose to methyl and carbon monoxide, though under some conditions they may combine to diacetyl. In a recent paper evidence is presented to show that apparently the excited acetone molecule may decompose to fragments of ethane and carbon monoxide *without* the production of radicals. The production of acetyl does complicate matters. In some acetone-catalysed polymerisations (Jones and Melville, *loc. cit.*) it has been found that the rate of production of carbon monoxide from acetone is diminished when monomer is present. This would imply that the acetyl radical reacts with the monomer before it has time to decompose. Similar experiments were made with acetone and vinyl acetate, pressures of 16—17 mm. of vinyl acetate and 35·40 mm. of acetone being used; thus, in 5 mins. 11·7 × 10^{-3} mm. of carbon monoxide were produced with acetone alone; with vinyl acetate present, 4·6 mm. of gas were polymerised and the pressure of monoxide was 11·2 × 10^{-3} mm. In another series of experiments, carbon monoxide production was 29 × 10^{-3} and 28 × 10^{-3} mm., respectively, in presence and in absence of vinyl acetate. Thus acetyl radicals do not initiate polymerisation, unless, of course, the carbon monoxide molecule is eliminated just when the acetyl radical meets a vinyl acetate molecule, an unlikely state of affairs.

FIG. 4.



(a) *Effect of pressure on the methyl-radical-sensitised reaction.*
(b) *Effect of intensity on the radical-sensitised reaction.*

The experimental procedure is somewhat complicated. First of all two lamps are used, the first a low-pressure lamp emitting the 2537 A. line to dissociate the hydrogen, the second a high-pressure lamp to dissociate the acetone. The distances of these lamps from the reaction vessel are so adjusted that with a given acetone pressure the rates of polymerisation are the same. First, a hydrogen atom run is made, the chain length being measured at two points. Next another hydrogen atom run is made for approximately half the period, and the chain length re-measured. Acetone is then admitted to a pressure of 50 mm. The hydrogen pressure is then measured again since a small amount escapes on introduction of the acetone. The hydrogen–vinyl acetate–acetone mixture is then irradiated with the high-pressure lamp for a time such that polymerisation occurs to the same extent as with the first hydrogen atom run. The data from the first run then give the hydrogen molecule consumption during the second part of the run. Finally, the vinyl acetate and acetone are condensed out, and the total pressure due to hydrogen and to carbon monoxide is measured.

By this method it was found over the same range of vinyl acetate pressures, *viz.*, 17·5—12·5 mm., that the carbon monoxide produced from the photodecomposing acetone was equal to volume of hydrogen consumed in the corresponding part of the hydrogen run. The data for a run of this type are given below.

Vinyl acetate = 22·0 mm. Hydrogen 35·0 mm. Acetone 50·0 mm.

Type of run.	Rate of 1st half of polymerisation.	Rate of 2nd half of polymerisation.	
Me	1·38	0·80	0·25 mm. CO produced
H	1·32	0·73	0·30 mm. H_2 consumed
Me	1·46	0·98	0·25 mm. CO produced

General Discussion of the Vinyl Acetate Reaction.

It now remains to discuss and compare the free-radical and the direct polymerisation reactions. The former is at first sight the simpler, for the mechanism consists in the addition of the hydrogen atom or methyl radical to the vinyl acetate molecule to form another free radical, to which are subsequently added further vinyl acetate molecules until two of these comparatively large free radicals interact. It is not yet certain whether this results in combination or disproportionation. The anomalous feature of this and other gas-phase reactions is the negative temperature coefficient. This may be due to a variety of factors. First, even if the radical polymers are small, it may be that in course of growth a new solid phase appears with the consequence that monomer will presumably be adsorbed on this growing particle as a necessary preliminary to addition. The rate of polymerisation will then be proportional to the concentration of monomer in the polymer particle. Increase of temperature will consequently decrease this concentration so that this factor alone will give rise to an apparent negative temperature coefficient. Second, quite a different factor may also give rise to a diminished temperature coefficient. It has now been established (Burnett and Melville, *Nature*, 1946, **158**, 553) that when polymerisation of vinyl acetate occurs in a solvent such as hexane in which the polymer is not very soluble, the effect of precipitating out the growing polymer is to diminish the magnitude of the bimolecular reaction coefficient for the termination of polymer growth. The coefficient which is not normally affected by temperature acquires in these circumstances a positive temperature coefficient. A similar precipitation will occur even more readily in the gas phase. It is not therefore suprising that an overall negative temperature coefficient is observed, and that the larger the kinetic chain length the higher the value of the negative energy of activation. It is possible that both factors operate together.

With the direct reaction at sufficiently high pressures, the general kinetics are similar to those of the pure radical reaction. For comparable rates of initiation the overall polymerisation velocities of the radical and of the direct reaction are quite similar. It would therefore seem probable that the direct reaction also proceeds by a free-radical mechanism. The problem then is to understand why the critical pressure limit and inert gas effects make their appearance. The matter is most satisfactorily accounted for if it is assumed that absorption of ultra-violet light by monomer results in the production of a di-radical. Such a radical is simply an electronically excited molecule. The results show clearly that such a molecule can spontaneously give up its electronic energy or give it up to an inert gas at quite low pressures. At high enough pressures, however, further monomer molecules will add on to both ends of this di-radical. It is unfortunate that the photopolymer is made insoluble by some secondary reactions and thus its molecular weight cannot be compared with that of the free-radical polymer. The negative temperature coefficient of the direct reaction then is explained in a similar manner to that of the radical reaction.

Experimental evidence has been given elsewhere to suggest that the polymerisation of vinyl acetate in the liquid phase or in solution goes by way of free radicals. Here there should be an exact correlation between the reaction in the two phases. The obstacle to establishing a numerical correlation is due wholly to the so-called gel effect, *i.e.*, to the influence of environment or polymer shape on the velocity coefficient for the termination of molecular growth. In the liquid phase precisely similar overall kinetics are observed, but it is evident that the magnitudes of the velocity coefficients cannot be compared. For the gas phase the termination coefficient will not have its maximum value but some lower and ill-defined value. For these reasons the liquid-phase reaction with either pure monomer or monomer in a good solvent is far simpler than the gas-phase reaction.

The experiments described in this and the preceding paper were carried out in 1938—39 in the Colloid Science Department, The University, Cambridge. We should like to thank Professor E. K. Rideal for his great encouragement and interest in this work. These researches were made possible owing to the generosity of Aero Research Limited, Duxford, Cambridgeshire, who kindly provided a maintenance grant to one of us (R. F. T.).

THE UNIVERSITY, ABERDEEN.

[*Received, December 5th*, 1946.]