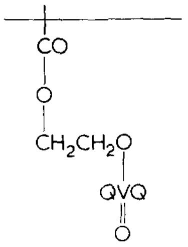
Photoactive polymers containing vanadium: 2. Kinetics of photodecomposition

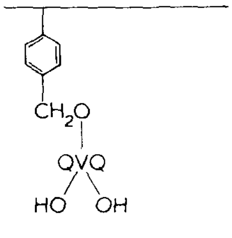
S. M. Aliwi and C. H. Bamford
Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK
(Received 13 October 1976)

Kinetic investigations of the photolysis of the copolymers VA_1, VA_2 and VA_3, characterized in Part 1, are described. These copolymers have side-chains carrying vanadium (V) chelate residues of structure $-OV(Q_2)=O$ (Q = 8-quinolyloxy) and also side-chains with hydroxyl groups. At $\lambda = 365$ nm the copolymers photoinitiate polymerization of methyl methacrylate and values of the rates of initiation and photodecomposition have been determined. When the V^V content is monitored at $\lambda = 330$ nm linear first-order plots are obtained, but at $\lambda = 500$ nm the initial reaction appears to be unusually fast. The final slopes in the two types of experiment are the same and permit evaluation of the first-order rate coefficient k_d. The latter increases with the OH content of the polymer for a given light intensity. Rates of photodecomposition and initiation are equal. To elucidate the mechanisms of reaction, experiments were carried out with VOQ_2OCH_3 as a model. In methyl methacrylate and benzene solutions, addition of methanol increases k_d. U.v.–visible spectroscopy indicates (thermal) complex formation between VOQ_2OCH_3 and CH_3OH, which occurs apparently instantaneously in benzene, but relatively slowly in methyl methacrylate. It is proposed that photochemical complex formation between hydrogen bonded$-OV(Q_2)=O$ and $-OH$ groups occurs in the polymer and is responsible for the apparent anomalies observed with a monitoring wavelength of 500 nm.

INTRODUCTION

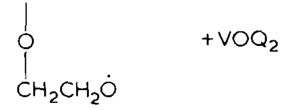
In Part 1[1] we showed that photoactive polymers can be prepared by introducing vanadium chelate residues into suitable preformed polymer molecules carrying hydroxyl groups in the side chains. Two types of preformed polymers were examined: (A) copolymers of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA); and (B) a styrene/*p*-hydroxymethyl styrene copolymer. It was concluded that the photoactive groups in the final copolymers VA, VB, had structures (I) and (II):


(I)
In copolymers VA

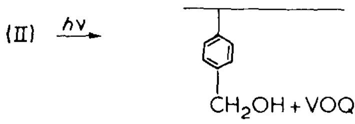

(II)
In copolymer VB

Here Q represents the 8-quinolyloxo ligand.

On irradiation with light of $\lambda = 365$ nm, (I) and (II) photolyse according to equations (1) and (2) respectively:


(III)

(1)



(2)

Copolymers VA can participate in photografting and cross-linking reactions in the presence of a vinyl monomer by virtue of the macroradical product (III); evidently no similar processes are available for copolymer VB since this produces detached hydroxyl radicals on photolysis.

In this paper we describe a kinetic investigation of the photolysis of copolymers VA.

EXPERIMENTAL

Preparations (when necessary) and purification of the starting materials were carried out as described by Aliwi and Bamford[2]. Copolymers A_1, A_2, A_3 and VA_1, VA_2, VA_3 were prepared, purified and characterized as described in the previous paper[1].

The rate coefficients for photodecomposition of the polymers in various media were determined by the techniques described in an earlier paper[2].

RESULTS AND DISCUSSION

Photoinitiation of polymerization

Copolymer VA_1 (see previous paper[1] for characterization) photoinitiates the polymerization of methyl methacrylate as shown in *Figure 1*, which presents the dependence of the rate of polymerization ω as a function of the incident light intensity I_0 ($\lambda = 365$ nm). The low quantum yield (see *Table 1*) and the maximum intensity available limit the accessible range of ω; we believe the data indicate that ω is proportional to $I_0^{1/2}$, so that retardation is effectively absent under these conditions ($[V] = [C] = 3.58 \times 10^{-5}$ g atoms 1^{-1} or mol 1^{-1}, C representing a chelate residue in the copolymer.

The dilatometric contraction vs. time plots obtained in these experiments were always linear; the significance of this observation will be considered later.

Rate coefficients of photodecomposition

The photodecomposition of copolymer VA_1 was monitored at $\lambda = 500$ and 330 nm. At the latter wavelength, $\log(A_t - A_\infty)$ (A_t representing the absorbance at time t) is linear in reaction time (*Figure 2B*; however, at $\lambda = 500$ nm the corresponding plot generally shows an initial steep portion before becoming linear (*Figure 2A*).

The form of the plot for $\lambda = 500$ nm has been shown to depend on two factors: (i) the mole fraction of HEMA in the preformed copolymer; and (ii) the concentration of the photoactive copolymer. The departure from linearity decreases with decrease in (i) or (ii).

Figure 3 shows the relevant plots for a copolymer VA_3 containing a mole fraction 0.103 HEMA at three different copolymer concentrations $c(\text{g } 1^{-1})$ and demonstrates the dependence of the shape of the plot on c. Note that for $c = 0.571$ the plot is linear throughout. Corresponding plots have been obtained for copolymers VA_1 and VA_2 with mole fractions of HEMA of 0.314 and 0.207, respectively. With VA_1 the plot still shows initial curvature at the lowest concentration which could be examined ($c = 0.125$). In the case of VA_2, linearity is achieved with $c = 0.25$, but initial curvature appears for $c > 0.75$. These data substantiate the generalization made above.

Values of the first-order rate coefficient of photodecomposition k_d derived from the linear plots of $\log(A_t - A_\infty)$ vs. t obtained by monitoring at $\lambda = 330$ nm are similar to those obtained from the final slopes of the corresponding plots at $\lambda = 500$ nm.

The coefficient k_d, while naturally independent of the vanadium content of a copolymer derived from a given preformed polymer, depends on the HEMA content of the latter, as illustrated in *Table 1*. The mole fractions of HEMA in the copolymers were calculated from reactivity ratios [r_1 (HEMA) = 1.267, $r_2 = 0.141$] previously determined by us.

Comparisons between the rates of initiation of free-radical polymerization $\mathscr{I}$ and photodecomposition have been

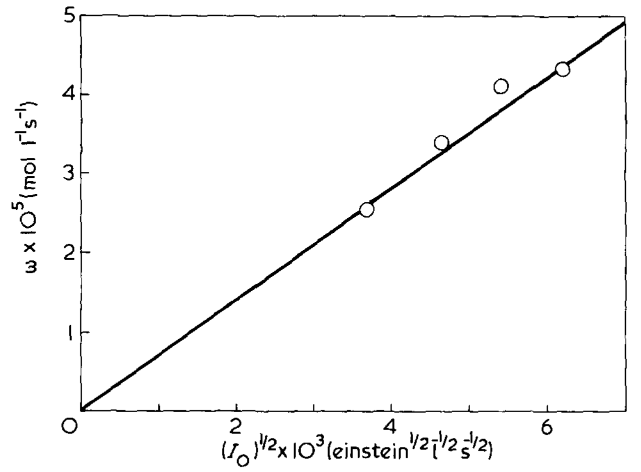


Figure 1 Dependence of rate of polymerization ω on $I_0^{1/2}$. Copolymer VA_1, 0.625 g 1^{-1}. Methyl methacrylate, 25°C, λ = 365 nm

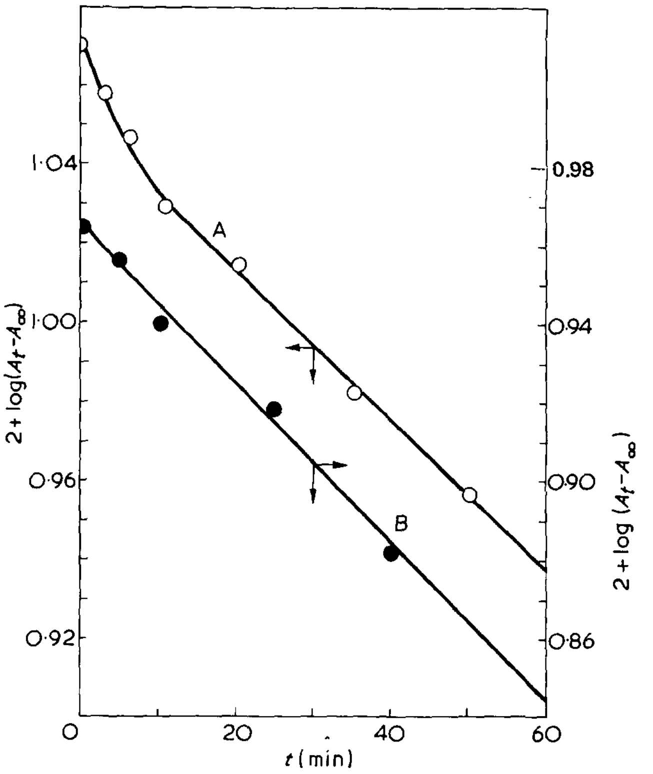


Figure 2 Plot of $\log(A_t - A_\infty)$ vs. t for irradiation (λ = 365 nm) of copolymer VA_1 (0.625 g 1^{-1}) in MMA solution. $I_0 = 1.18 \times 10^{-5}$ einstein 1^{-1} s^{-1}. Monitoring wavelengths: A, 500; B, 330 nm

Table 1 Values of k_d and Φ[a]: dependence on HEMA content of preformed copolymer. $I_0 = 1.21 \times 10^{-5}$ einstein 1^{-1} s^{-1}. Bulk methyl methacrylate, 25° C, λ = 365 nm

	Mole fraction HEMA											
	0.103 VA_3				0.207 VA_2				0.314 VA_1			
t(min)[b]	$[V] \times 10^5$ (g-atom 1^{-1})	c (g 1^{-1})	$k_d \times 10^5$ (s^{-1})	$\Phi \times 10^4$	$[V] \times 10^5$ (g-atom 1^{-1})	c (g 1^{-1})	$k_d \times 10^5$ (s^{-1})	$\Phi \times 10^4$	$[V] \times 10^5$ (g-atom 1^{-1})	c (g 1^{-1})	$k_d \times 10^5$ (s^{-1})	$\Phi \times 10^4$
15	1.48	0.571	4.15	3.30	1.49	0.250	6.90	5.47	0.81	0.125	6.81	5.20
30	2.15	0.857	4.51	3.72	3.08	0.500	5.43	4.70	1.69	0.250	6.37	5.13
60	3.50	1.143	4.97	4.40	4.29	0.750	5.06	4.67	3.05	0.500	7.66	6.62
150	–	–	–	–	5.97	1.000	5.52	5.5	3.42	0.625	6.93	6.11
	Means		5.4	3.8			5.7	5.1			6.9	5.8

[a] In calculating Φ the value of I_{abs} at the beginning of irradiation has been used. Since small changes in absorption at λ = 365 nm occur early in the reaction, as will be explained later, corresponding errors may be introduced into Φ, especially for VA_1 and VA_2

[b] Times for refluxing with VOQ_2OH

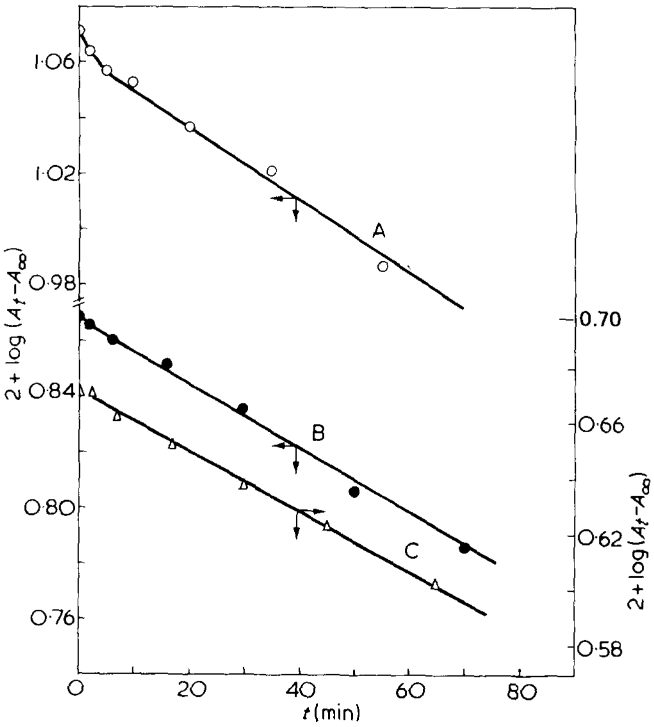


Figure 3 Plots of log $(A_t - A_\infty)$ vs. t for irradiation (λ = 365 nm) of copolymer VA_3 in MMA solution: effect of copolymer concentration. Concentrations: A, 1.143; B, 0.857; C, 0.571 g l^{-1}

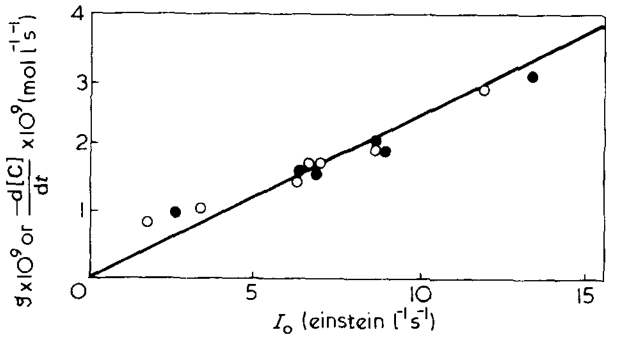


Figure 4 Rates of photodecomposition (–d[C]/dt) and photoinitiation ($\mathscr{I}$) for copolymer VA_1 (0.625 g l^{-1} as functions of incident light intensity (λ = 365 nm)

made for copolymers VA_1 and VA_3. Values of $\mathscr{I}$ were calculated from the conventional relationship:

$$\omega = k_p k_t^{-1/2}[M]\mathscr{I}^{1/2} \tag{3}$$

in which k_p, k_t are the rate coefficients of propagation and second-order termination, respectively, and M represents monomer. For methyl methacrylate at 25°C we have taken $k_p k_t^{-1/2} = 0.056$ mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$. *Figure 4* shows that for copolymer VA_1 the rates of initiation and chelate decomposition are equal, within the limits of experimental error. Similar results were found to hold for copolymers VA_2 and VA_3. Further, *Figure 4* illustrates that for VA_1 both $\mathscr{I}$ and –d[C]/dt are proportional to I_0 for weak light absorption. (The errors involved in measuring the low rates corresponding to low I_0 are relatively large.) In general, we conclude that:

$$\mathscr{I} = -\frac{d[C]}{dt} = k_d[C] = \Phi I_{abs} \tag{4}$$

where Φ is the quantum yield for photodecomposition or photoinitiation. Values of Φ are presented in *Table 1*, from which it will be seen that Φ increases with increase in the mole fraction of HEMA in the preformed polymer.

Experiments with methoxo-oxobis (8-quinolyloxo)-vanandium (V)

The results already described reveal that the hydroxyl groups in the photoactive polymers exert a significant influence on the photolysis. To assist interpretation of the data we have investigated the influence of methanol on the photolysis of the monomeric analogue VOQ_2OCH_3 in various media.

Spectral observations. When a solution of VOQ_2OCH_3 in benzene or methyl methacrylate is mixed with methanol a change in the near u.v.–visible spectrum occurs as indicated in *Figures 5* and *6*, respectively. With benzene the process is relatively rapid, being effectively complete in about 3.5 min while with MMA the change is much slower and is incomplete after 30 min under similar conditions (25°C). In the region 340–550 nm there is a considerable reduction in absorbance, but outside this region the effect is very small. We interpret these observations to indicate that complex formation between methanol and the vanadium chelate occurs and is subject to a marked medium effect.

The spectral changes occurring during irradiation of solutions of VOQ_2OCH_3 in MMA containing methanol are identical with those found for copolymers VA in MMA solution (see Part 1[1]).

Photodecomposition of VOQ_2OCH_3. The chelate was photolysed in degassed benzene and MMA solutions in the presence of methanol: typical plots of log$(A_t - A_\infty)$ vs. t (at λ = 500 nm) are given in *Figure 7*.

The plots are linear for benzene solutions but have an initial curved portion for MMA solutions reminiscent of

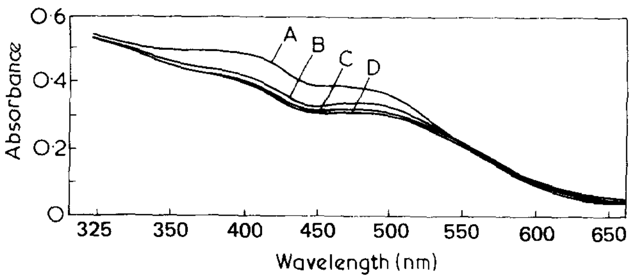


Figure 5 Effect of methanol on visible–near u.v. spectrum of VOQ_2OMe in benzene solution. [MeOH] = 1.48 mol l^{-1}. A, Before addition of methanol. Times after addition: B, 1; C, 3.5; D, 9 min

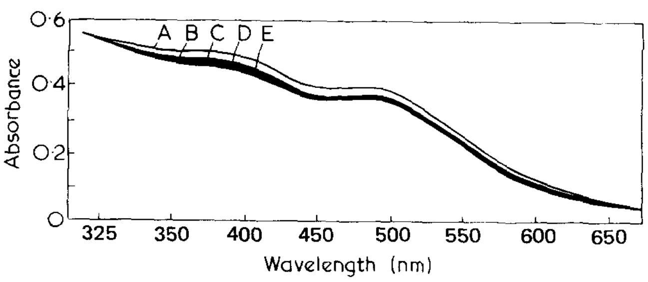


Figure 6 Effect of methanol on visible–near u.v. spectrum of VOQ_2OMe in MMA solution. [MeOH] = 1.48 mol l^{-1}. A, Before addition of methanol. Times after addition: B, 4; C, 8; D, 15; E, 30 min

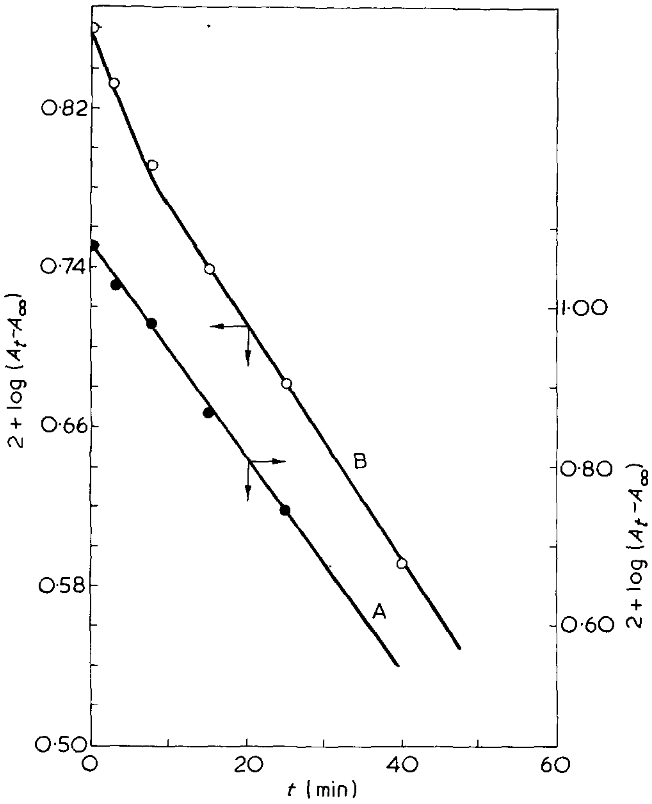
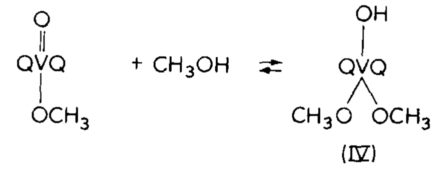


Figure 7 Photodecomposition of VOQ$_2$OMe in A, benzene + methanol (3.08 mol l^{-1}); B, MMA + methanol (0.31 mol l^{-1}). Monitoring wavelength 500 nm. I_0 (λ = 365 nm) = 9.56 x 10^{-6} einstein l^{-1} s^{-1}

those found for solutions of the VA$_1$ copolymers in this solvent (compare *Figures 2* and *3*). It is natural to correlate these observations with the chelate–methanol complex formation already discussed. In benzene solution, the process is so rapid that it is effectively complete by the time irradiation is started, but with MMA as solvent the slow complex formation extends into the early part of the period of irradiation. As already demonstrated (*Figure 6*), complex formation brings about a marked decrease in optical density at 500 nm, so that the initial steep portion of the curve in *Figure 7* is readily understandable. This interpretation is strongly supported by the data in *Figure 8*. During standing of the solution in MMA + CH$_3$OH in the dark at 25°C the absorbance decays as shown by curve A; irradiation of the solution after 30 min standing then gives the linear plot in B. Curve C shows that (in a separate experiment) irradiation without appreciable standing produces a plot with initial curvature (compare *Figure 7B)*. The similarity in the timescales of the initial steep portions of curves A and C is evident.

We have made several different types of experiment in an attempt to elucidate these observations. (i) Vanadium (IV) derivatives in general give well-documented 8-line e.s.r. spectra (I = 7/2 for ^{51}V). No e.s.r. spectrum was detectable from solutions of VOQ$_2$OCH$_3$ in MMA + CH$_3$OH which has been allowed to stand in the dark at 25°C [corresponding to *Figure 8A*]. Weak spectra were obtained after 10 min irradiation with intensities which were effectively unaffected by preliminary standing of the solution in the dark(curves B and C). We conclude that insignificant reduction of V^V occurs in the dark at 25°C. (ii) The absence of abnormally rapid photoreduction in the early stages of irradiation is also consistent with experiments on the photoinitiation of polymerization of MMA by VOQ$_2$OCH$_3$ in the presence of methanol. Within the limits of experimental error, linear dilatometric contraction–time plots were obtained so that there is no evidence of unusually rapid initial radical generation. (iii) Monitoring the chelate photodecomposition at λ = 330 nm leads to linear plots of log(A_t–A_∞) vs. reaction time, an observation which clearly supports the view that the curvature in the corresponding plots for λ = 500 nm is not connected with photoreduction.

Thus it appears that the process represented in *Figure 8C* is not connected with chemical reduction of vanadium (V); in the experiment of *Figure 8C* photoreduction of vanadium (V) occurs from the onset of irradiation and is superimposed on the process of *Figure 8A*. We propose that the latter is the reversible formation of a complex (IV) between VOQ$_2$OCH$_3$ and CH$_3$OH, e.g.:



$$\mathrm{Q_2V(=O)OCH_3} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{Q_2V(OH)(OCH_3)_2} \tag{5}$$

(IV) is a derivative of 7-coordinate vanadium (V); complexes of the latter type are well known[3,4]. We believe that the reaction in *Figure 8A* is too slow to be simple hydrogen

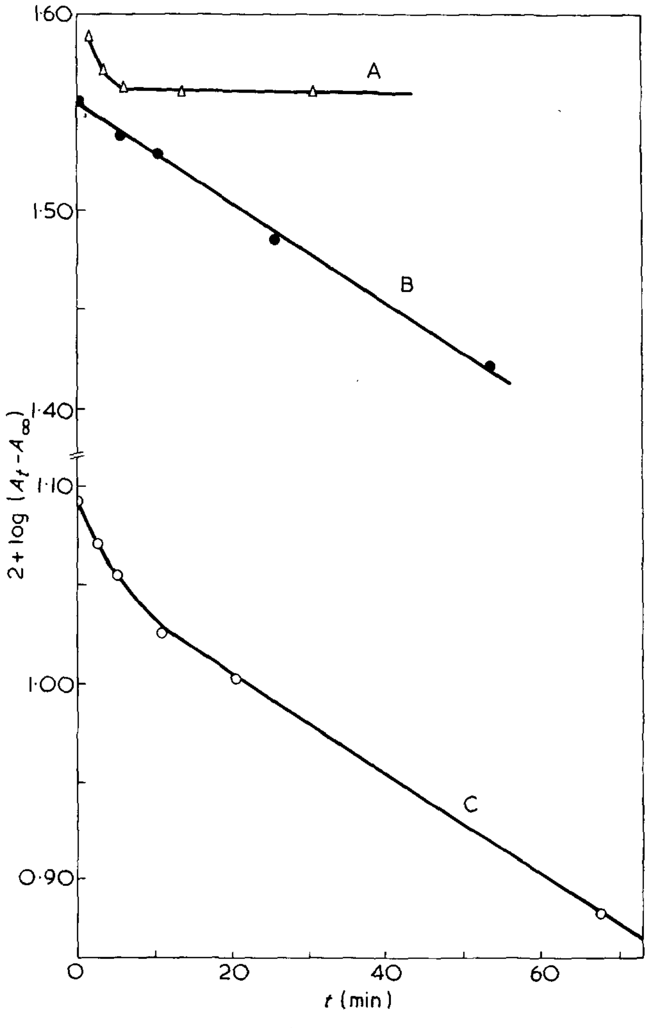


Figure 8 Dependence of log (A_t – A_∞) on t for VOQ$_2$OMe in MMA + methanol (3.08 mol l^{-1}): A, on standing in dark; B, on irradiation (λ = 365 nm) after standing in dark for 30 min; C, on irradiation (λ = 365 nm) without previous standing in dark. Monitoring wavelength 500 nm

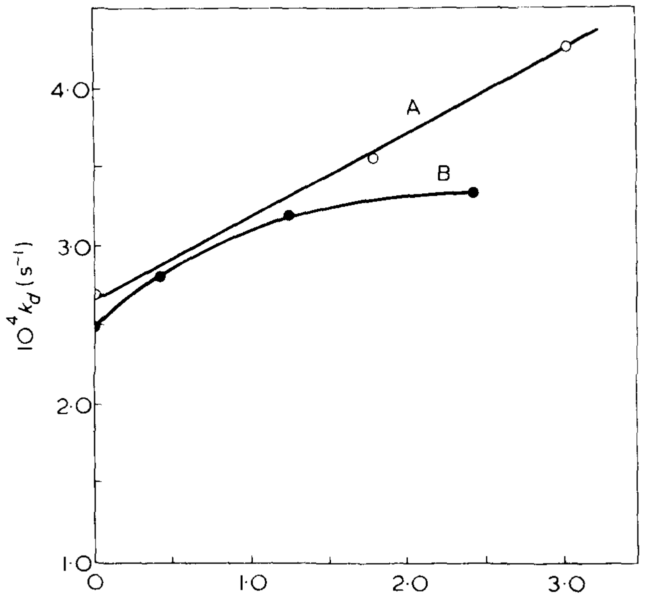


Figure 9 Photodecomposition (λ = 365 nm) of VOQ_2OMe: dependence of rate coefficient on methanol content. [VOQ_2OMe] = 3.52×10^{-5} mol l^{-1}: A, benzene solution; B, MMA solution. Monitoring wavelength 330 nm

bond formation between the vanadyl oxygen and methanol (there appears to be good evidence for this[5]); hydrogen bonding may, of course, be a preliminary to the formation of (IV).

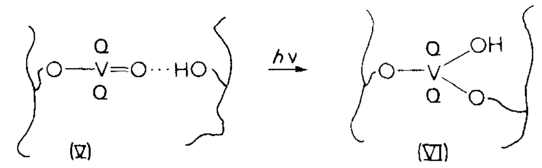
We have shown (*Table 1*) that the rate coefficient of photodecomposition of the VA copolymers increases with increasing mole fraction of HEMA. Accordingly, we have examined the dependence of k_d for VOQ_2OCH_3 on the methanol content of solutions in benzene + methanol and MMA + methanol. In both media k_d increases with [CH_3OH], as demonstrated by *Figure 9*. In bulk methanol, k_d has a value approximately 4-fold that in MMA solution. Low concentrations (< 2.5 mol l^{-1}) of methanol increase the rate of initiation in MMA solutions to an extent compatible with the observed increase in k_d. Under all conditions, therefore, it seems that the rates of photodecomposition and initiation are equal for a given light intensity. The results in *Figure 9* are qualitatively understandable in terms of reaction (5) if the quantum yield of photodecomposition of complex (IV) is greater than that of VOQ_2OCH_3. *Figure 9* does not give a quantitative picture of the variation of Φ with [CH_3OH] since the extinction coefficient at 365 nm decreases somewhat with [CH_3OH] (*Figure 6*) so that changes in Φ are greater than would appear from *Figure 9*.

Photolysis of VA copolymers

Clearly there is a resemblance between the results presented for the photolysis of copolymers and their monomeric analogue and we believe that the behaviour of the two types of system may be interpreted in similar terms. We are particularly concerned with the data in *Figures 2* and *3*.

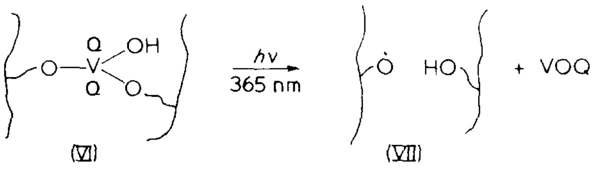
From the earlier discussion it seems likely that the initial steep portion of the plot in *Figure 2B* is attributable to complex formation between vanadium chelate residues and hydroxyl groups in the copolymer leading to a species analogous to (IV), with a lower extinction coefficient. However, this process, unlike the corresponding one in systems containing VOQ_2OCH_3 + CH_3OH, must be photochemical in nature since no changes in optical density are detectable when solutions of the VA copolymers are kept in the dark. In conformity with the earlier discussion, complexation is considered to reduce the optical density but to be without effect on the oxidation state of vanadium.

A close inspection of the absorption spectrum of copolymer VA_1 in MMA (Part 1, Figure 1(a) with that of VOQ_2 OCH_3 in the same solvent (Figure 6(a) of ref 2) reveals some differences, notably a reduction in extinction coefficient in the visible region. It is probable that these are the result of hydrogen bonding between vanadyl oxygen atoms and hydroxyl groups in the copolymer, as indicated diagrammatically:



(6)

Irradiation of (V) produces complex (VI), analogous to (IV). Whereas reaction (5) is facile and occurs thermally, reaction (6) (which involves different species) has a higher activation energy and proceeds at 25°C only with photochemical activation. This view is consistent with the observation that after a short (10 min) irradiation (λ = 365 nm) of copolymer VA_1 in MMA, no change in optical density occurs on switching off the light, as would be expected if reaction (6) were reversible. The end of the initial steep part of a curve such as *Figure 2A* corresponds to the more-or-less complete conversion of (V) into (VI). Photolysis of (VI) proceeds according to (7), in conformity with the results reported in Part 1.



(7)

Both *intra-* and *inter*-molecular complexes may be formed, although extensive formation of the latter could lead to photogelation after short periods of irradiation, which has not been observed. Observations typified by *Figure 3* show that complexation depends on VA copolymer concentration, decreasing in extent as the concentration decreases. This result is naturally explained if the complexes are intermolecular, but it could also arise from concentration-dependent chain conformations in the case of intramolecular complexes. In view of the low overall concentrations of hydroxyl groups in these experiments, intramolecular hydrogen bonding and complexing is most likely. The observed increase in Φ with increasing HEMA content of the copolymer (*Table 1*) is understandable on steric grounds; the decreasing separation of hydroxyl (and therefore chelate) groups with increasing HEMA content of the copolymer, apparent from the mean sequence lengths given in Table 1 of Part 1[1], would be expected to be accompanied by an increasing probability of the formation of an intramolecular hydrogen bonded species (V).

One further point remains for consideration. If the complex (VI) has a higher quantum yield of photolysis we might expect that the rate of initiation $\mathscr{I}$ and the rate of photodecomposition would increase after the commencement of irradiation, as the conversion to complex proceeds. At first sight the linear dilatometric plots and the linear character of *Figure 2B* do not seem to substantiate these expectations. However, the lower extinction coefficient in the region of λ = 365 nm (assuming the effect of complex formation is similar to that in *Figures 5* and *6*) would compensate the increased quantum yield to some extent, although (on the basis of *Figures 5* and *6* which, however, refer to the $VOQ_2OCH_3 + CH_3OH$ systems) perhaps not completely. In the case of *Figure 2B* the initial linearity may be misleading, and the early portion may be distorted by spectral features similar to, but much smaller than, those observed at a monitoring wavelength of 500 nm. Further, dilatometric experiments are not very sensitive to small changes in the rate of initiation since the rate of photolysis enters into the contraction as the one-half power.

We have considered several other mechanisms which might account for the shape of the curve in *Figure 2A*. These include: (i) an abnormally rapid photodecomposition (e.g. involving exciplex formation) of two chelate groups situated on neighbouring sites; and (ii) photochemical conversion of initial *cis* chelate residues[6,7] to *trans*, followed by hydrogen bonding of the latter. None of these was satisfactory. Thus, calculation from the reactivity ratios shows that the number of suitable pairs of chelate residues available for (i) to occur is insignificant (approximately a fraction 8×10^{-4} of the total vanadium atoms) while postulate (ii) is inconsistent with the existence of some hydrogen bonding before irradiation, since all the chelate residues initially have the *cis* configuration[6,7].

REFERENCES

1 Aliwi, S. M. and Bamford, C. H. *Polymer* 1977, **18**, 375
2 Aliwi, S. M. and Bamford, C. H. *JCS Faraday Trans. I* 1975, **71**, 1733
3 Drew, R. E. and Einstein, F. W. B. *Inorg. Chem.* 1973, **12**, 829
4 Dewan, J. C. Kepert, L. D., Raston, C. L., Taylor, D. and White, A. H. *JCS Dalton Trans.* 1973, p 2082
5 Guzy, C. M., Raynor, J. B. and Symons, M. C. R. *J. Chem. Soc. (A)* 1969, p 2791
6 Scheidt, W. R. *Inorg. Chem.* 1973, **12**, 1758
7 Savitskii, A. V., Skachilova S. Ya. and Kokoreva, S. Yu. *Russian J. Inorg. Chem.* 1967. **12**, 435