

Comparative rates of radical autoxidation of acrylamide, methacrylamide and styrene

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(Received 17 March 1978)

The polymerization of acrylamide has been studied at 60°C in aqueous solution, in the presence of oxygen, with 4,4'-azobis-4-cyanopentanoic acid (ACV) as the initiator. It was found, that the rate of oxygen uptake was approximately directly proportional to the monomer and initiator concentrations, but was independent of the oxygen concentration. Oxygen uptake measurements have also been carried out on methacrylamide in aqueous solution at 60°C with ACV as the initiator. For this system the rate of oxygen uptake was found to be directly proportional to the monomer concentration, to the square root of the initiator concentration, and to the oxygen concentration to the power 0.40. Further oxygen uptake measurements were carried out using bulk styrene at 50°C with ACV as the initiator. For styrene, the rate of oxygen uptake was found to be directly proportional to the initiator concentration to the power 0.45. The significance of these results is discussed in terms of termination mechanisms, and the different rates of oxygen uptake of the three monomers are discussed in terms of the $Q-e$ scheme.

INTRODUCTION

It is commonly proposed¹ that at sufficiently high oxygen concentrations the autoxidation of many vinyl monomers proceeds by means of a chain reaction involving addition to the monomeric double bond and that polyperoxides are eventually produced by various termination reactions. For example, in the case of styrene, in bulk at 35°–85°C under 0.1–4 atm. oxygen², and also in emulsion³, termination involves the combination of two peroxy radicals RO_2 . A similar termination mechanism has also been proposed for acrylonitrile⁴, methyl methacrylate⁵, vinyl acetate⁶, and several other vinyl monomers⁷. Under low pressures of oxygen, for styrene⁸, α -methylstyrene⁹, and methyl methacrylate¹⁰, termination occurs by a cross-termination of peroxy radicals, RO_2 , and radicals having a terminal monomer unit, $R\cdot$. This paper reports a study of the kinetics of radical polymerization of acrylamide and methacrylamide in aqueous solution, in the presence of oxygen. Some oxygen uptake results obtained using bulk styrene as a model monomer, with ACV as initiator, are also reported.

EXPERIMENTAL

Reagents

Acrylamide. Acrylamide (Allied Colloids Ltd) was recrystallized twice from chloroform, and dried *in vacuo* at room temperature over anhydrous calcium chloride (m.p. 84.5°C).

Methacrylamide. Methacrylamide was recrystallized from methanol and dried *in vacuo* at room temperature over anhydrous calcium chloride (m.p. 110°C).

Styrene. Styrene (BDH) was washed 3 times with 10% w/v aqueous sodium hydroxide solution and 5 times with distilled water. After drying over anhydrous calcium sulphate, the monomer was distilled *in vacuo*. The middle frac-

tion was retained and stored under oxygen-free nitrogen over solid carbon dioxide until required.

4,4'-azobis-4-cyanopentanoic acid (ACV). ACV was prepared from levulinic acid (BDH) by the method of Bamford *et al.*¹¹.

Analysis

	Carbon (C)	Hydrogen(H)	Nitrogen (N)
Calculated %	51.40	5.75	20.10
Found %	51.35, 51.33	5.72, 5.74	19.83, 20.26

Water. Deionized water was used in all kinetic experiments.

Oxygen. Medical grade oxygen (British Oxygen Co.) was employed.

Other gas mixtures, such as 40% oxygen, 60% nitrogen, v/v, and air (British Oxygen Co.) were also used.

Oxygen uptake measurements

Oxygen uptake measurements were carried out on the monomers acrylamide, methacrylamide and styrene, with ACV as the initiator.

The uptake of oxygen of all three monomers was monitored using a Warburg manometer, and rates of oxygen uptake were found from the slopes of the oxygen uptake vs. time plots.

The oxygen electrode was also used to monitor oxygen uptakes of acrylamide and methacrylamide monomers in aqueous solution.

Warburg manometry

The Warburg respirometer is based on the principle that at a constant temperature and constant gas volume, any change in the amount of a gas can be measured by changes in its pressure. Further details of operation are reported elsewhere¹².

The appropriate solutions were pipetted into a previously

Table 1 Autoxidation of acrylamide in water at 60°C; oxygen uptake rates. The shaking rate was kept constant at 100 strokes/min. Constant initiator concentration = 5.0×10^{-3} mol/dm³. (4,4'-azobis-4-cyanopentanoic acid)

Monomer concentration [M] (mol/dm ³)	Rate of O ₂ uptake (mm ³ O ₂ /cm ³ solution h)
4.00	40.0
3.50	33.6
3.00	29.4
2.50	25.0
2.00	19.5
1.50	16.6
1.25	14.4
0.00	Slow release of nitrogen

calibrated flask, (1 cm³ of monomer solution, 1 cm³ of initiator solution) and the flask was then attached to the manometer, with every joint previously well lubricated with Apiezon grease.

The mixture was then thoroughly gassed for 15 min with the required gas with a pressure difference of 13 cm of Brodies liquid measured on the manometer. The flask and manometer were then connected and immersed in the thermostat. The stopcock on the manometer was left open during the 10 min equilibration period and the flask was shaken during this period to ensure thorough mixing of the oxygen and the solutions.

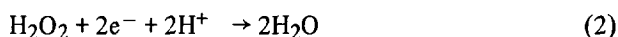
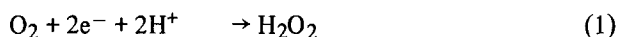
Two other flasks, containing deionized water (2 cm³), instead of monomer and initiator solutions served as reference thermobarometers.

After the initial 10 min equilibrium period, the stopcock on the manometer was closed, so that the flask was connected only to the manometer, and the changes in pressure were recorded at regular time intervals. The flasks were shaken between readings, at shaking rates of either 100 or 200 strokes/min. It was established by separate experiments that autoxidation rates were independent of shaking rates at these relatively high rates of shaking.

Oxygen electrode

The oxygen electrode system (Rank Brothers, Cambridge, England) consisted of a polarizing unit, the oxygen electrode, a magnetic stirrer and stirrer control, and a chart recorder.

The platinum electrode was mounted in perspex and was specifically designed for following the uptake of oxygen in aqueous solutions. The oxygen diffused through a thin teflon membrane and was reduced at the platinum surface immediately in contact with the membrane.



The other half-cell was also incorporated in the base of the incubation vessel and was composed of an Ag-AgCl electrode. Further details are described elsewhere¹³.

To study the dependence of the rate of oxygen uptake on monomer, initiator and oxygen concentration, the appropriate solutions were gassed for 10 min with medical grade oxygen, 2 cm³ of the gassed solutions transferred to the incubation vessel, and the reaction followed using the recorder. The rates of oxygen uptake are given by the slopes of the uptake-time plots, expressed in mV/h.

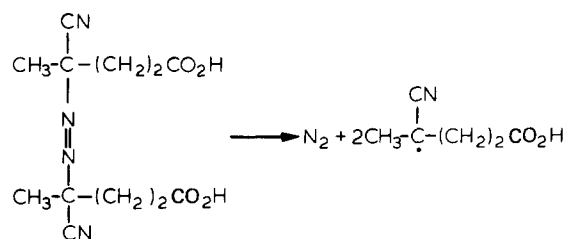
RESULTS

The dependence of rates of oxygen uptake upon monomer, initiator and oxygen concentrations was thoroughly investigated, and are presented in this paper either in tubular form or graphically. Only a few typical plots are shown.

Warburg manometry

Acrylamide. In the measurement of oxygen uptake rates for acrylamide, methacrylamide and styrene, the monomer solutions were saturated initially with 100% medical oxygen by gassing for 15 min prior to each experiment. Typical results for acrylamide at 60°C, at fixed initiator concentration but with varied monomer concentration, are shown in *Table 1*.

When the experiment was carried out using only 2 cm³ of 5.0×10^{-3} mol/dm³ ACV initiator solution, there was no oxygen uptake observed, but a release of nitrogen. This is due to the azo initiator decomposing in solution at 60°C, to release nitrogen. The rates of uptake of oxygen, equal to the slope of oxygen uptake-time plots, were not significantly affected by the release of nitrogen.



4,4'-Azobis-4-cyanopentanoic acid

The plot of log(monomer concentration) vs. log(rate of oxygen uptake) at constant initiator concentration was linear and had a slope of 1.00 ± 0.05 .

The variation of oxygen uptake rates with initiator concentration at constant monomer concentration is shown in *Table 2*. The plot of log(rate of oxygen uptake), log*R*, vs. log(initiator concentration), at constant monomer concentration, was linear with a slope of 1.00 ± 0.05 . When a run was carried out with no initiator present, there was no uptake of oxygen.

The dependence of oxygen uptake rates upon the gas composition was also examined for acrylamide, and the results are shown in *Table 3*. Thus the rate of oxygen uptake appears to be independent of oxygen concentration, over the range of oxygen concentrations investigated.

Table 2 Autoxidation of acrylamide in water at 60°C. Oxygen uptake rates. The shaking rate was kept constant at 100 strokes/min. Constant monomer concentration = 2.5 mol/dm³

Initiator concentration 10 ³ [ACV] (mol/dm ³)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
5.0	25.2
4.5	23.0
4.0	17.5
4.0	14.4
3.5	18.0
3.0	15.8
2.5	13.4
2.0	10.0
2.0	12.0
1.5	7.8
1.0	6.2
0.0	No uptake

Table 3 Autoxidation of acrylamide in water at 60°C: variation of oxygen uptake rates with composition of gas. Monomer concentration = 4.0 mol/dm³; initiator concentration = 1.0 × 10⁻² mol/dm³, ACV; shaking speed = 100 strokes/min

Composition of gas (v/v)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
100% O ₂	86.4
80% O ₂ - 20% N ₂	78.0
60% O ₂ - 40% N ₂	84.0
40% O ₂ - 60% N ₂	84.0
20% O ₂ - 80% N ₂ (air)	84.0

Monomer concentration = 2.5 mol/dm³; initiator concentration = 1.0 × 10⁻³ mol/dm³; gassing time = 15 min; shaking speed = 100 strokes/min

Composition of gas (v/v)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
20% O ₂ - 80% N ₂ (air)	12.6
10% O ₂ - 90% N ₂	12.6
5% O ₂ - 95% N ₂	12.6

Table 4 Autoxidation of methacrylamide in water at 60°C. Constant monomer concentration = 1.0 mol/dm³; shaking speed = 200 strokes/min

Initiator concentration 10 ³ [ACV] (mol/dm ³)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
5.0	28.8
4.0	26.4
3.0	23.2
2.5	20.0
2.0	17.4
1.0	13.2

Table 5 Autoxidation of methacrylamide in water at 60°C. Constant initiator concentration = 5.0 × 10⁻³ mol/dm³ (ACV); gassing time = 15 min with 100% oxygen; shaking speed = 200 strokes/min

Monomer concentration (mol/dm ³)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
1.0	28.8
0.8	22.8
0.6	18.0
0.5	14.0
0.4	10.8

Thus for the polymerization of acrylamide in aqueous solution, at 60°C, the following kinetic result, to a close approximation, was observed:

$$\frac{-d[O_2]}{dt} \propto [M]^{1.0}[In]^{1.0} \quad (4)$$

Methacrylamide. Similar studies of the variation of oxygen uptake rates with both monomer and initiator concentrations for methacrylamide were performed and results are shown in Tables 4 and 5.

The plot of log(rate of oxygen uptake), log*R*, vs. log(initiator concentration), at constant monomer concentration, was linear with a slope of 0.51 ± 0.02 and the plot

of log*R* vs. log(monomer concentration), at constant initiator concentration, was linear with a slope of 1.00 ± 0.02. Thus to a near approximation, for the autoxidation of methacrylamide, by means of Warburg manometry, it was shown that:

$$\frac{-d[O_2]}{dt} \propto [M]^{1.0}[In]^{0.5} \quad (5)$$

The dependence of the oxygen uptake rates upon the gas composition was also examined using the oxygen electrode and these results are reported later.

Styrene. The autoxidation of styrene was also studied for comparative reasons at 50°C. Some rate results, obtained at different initiator concentrations, but with a constant monomer concentration, are shown in Table 6, and some typical oxygen uptake plots are shown in Figure 1. The oxygen uptake vs. time plots do not pass exactly through the origin due to the small time needed initially to establish temperature and reactant-oxygen equilibrium. The plot of log(rate of oxygen uptake), log*R*, vs. log(initiator concentration) had a slope of 0.45 ± 0.02.

Table 6 Autoxidation of bulk styrene at 50°C. Shaking speed = 200 strokes/min

Initiator concentration [ACV] (mol/dm ³)	Rate of oxygen uptake (mm ³ O ₂ /cm ³ solution h)
1.0 × 10 ⁻²	1380.0
7.5 × 10 ⁻³	1120.0
3.0 × 10 ⁻³	700.0
2.0 × 10 ⁻³	666.7
1.0 × 10 ⁻³	480.0
2.5 × 10 ⁻⁴	262.5
2.0 × 10 ⁻⁴	240.0

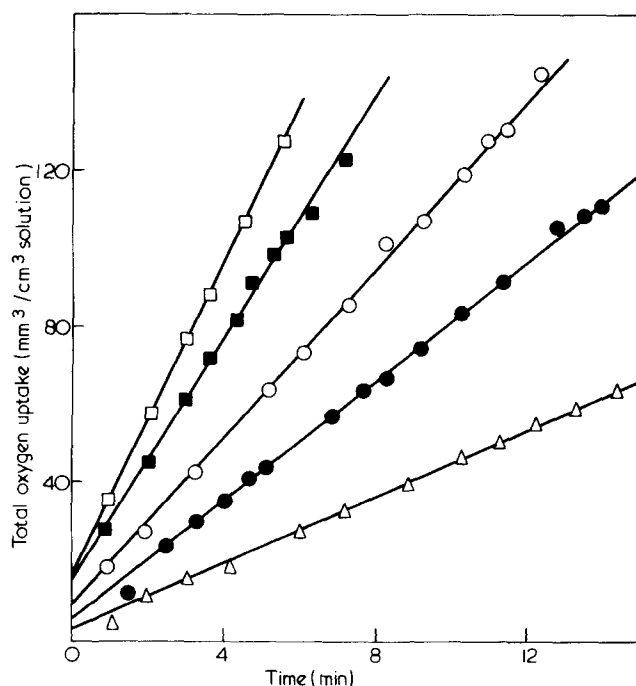


Figure 1 Typical plots of oxygen uptake vs. time for styrene at 50°C. Shaking speed = 200 strokes/min; gassing time = 15 min. Initiator concentrations: □, 10⁻² mol/dm³; ■, 7.5 × 10⁻³ mol/dm³; ○, 2.0 × 10⁻³ mol/dm³; ●, 1.0 × 10⁻³ mol/dm³; △, 2.5 × 10⁻⁴ mol/dm³

Table 7 Autoxidation of acrylamide in water at 60°C. Dependence of oxygen uptake on monomer concentration. Constant initiator concentration = 5.0×10^{-3} mol/dm³ (4,4'-azobis-4-cyanopentanoic acid); solutions were gassed for 10 min with 100% medical grade oxygen, before experiments; chart recorder speed = 10 in/h; full scale setting on recorder = 10 mV

Monomer concentration [M] (mol/dm ³)	Relative rate of oxygen uptake, R (mV/h)
0	0
0.50	1.3
1.00	2.7
1.25	3.2
1.50	3.6
2.00	5.3
2.50	6.5

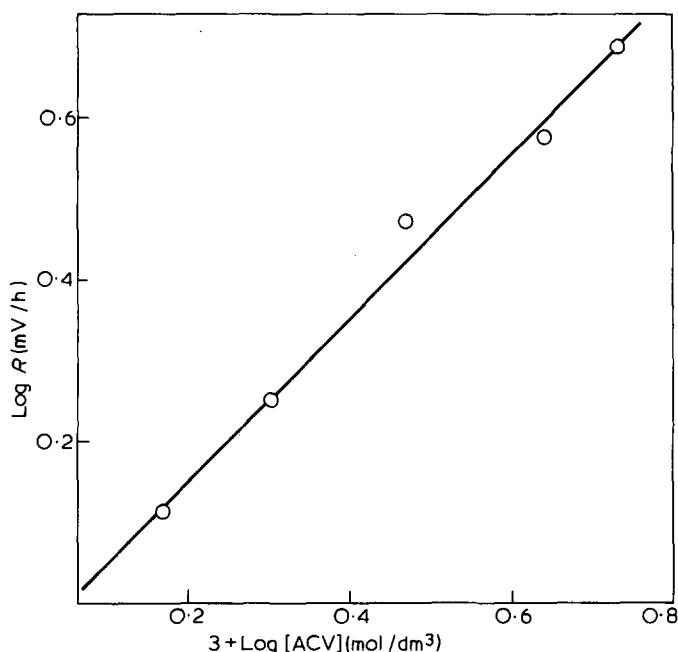


Figure 2 Plot of \log (rate of oxygen uptake), $\log R$, vs. \log (initiator concentration) at 60°C. Acrylamide is the monomer, monomer concentration 2.5 mol/dm³

Thus approximately for styrene, the results of the present study are in reasonable agreement with the relationship:

$$\frac{-d[O_2]}{dt} \propto [In]^{0.5} \quad (6)$$

which has been previously observed^{2,14}.

Oxygen electrode

Oxygen uptake measurements were also carried out at 60°C using aqueous solutions of acrylamide and methacrylamide, using an oxygen electrode. The rates of oxygen uptake measured by the oxygen electrode are all relative, and were measured in terms of the slope of the linear section of the uptake plot, expressed in mV/h.

The condition and age of the membrane was an important factor in the experimental technique and in order to obtain consistent results, the membrane had to be changed regularly.

Acrylamide. Some of the autoxidation results for acrylamide, showing the dependence of oxygen uptake rates on

the monomer concentration, at constant initiator concentration, are shown in *Table 7*. The plot of $\log R$ vs. \log (monomer concentration), at constant initiator concentration was linear and had a slope of 1.00 ± 0.02 . Thus to a near approximation, the rate of oxygen uptake is directly proportional to the monomer concentration.

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A plot of $\log R$ vs. \log (initiator concentration) at a constant monomer concentration of 2.5 mol/dm³ is shown in *Figure 2* and the slope was found to be 1.00 ± 0.02 . Hence, the rate of oxygen uptake is virtually directly proportional to the initiator concentration.

A series of experiments using the oxygen electrode was also carried out at 60°C with constant acrylamide and initiator concentrations of 2.5 and 5.0×10^{-3} mol/dm³, respectively, in which the gas compositions were varied. Within experimental error, the rates of oxygen uptake were independent of oxygen concentration, using pure medical oxygen and oxygen-nitrogen mixtures containing 60, 40, 20, 10, 5 and 2% v/v, of oxygen.

Methacrylamide. Similar types of measurement described in the previous section were carried out using methacrylamide instead of acrylamide and the results were analysed in the same way.

The plot of \log (rate of oxygen uptake) vs. \log (monomer concentration), at a constant initiator concentration, is linear and is shown in *Figure 3* and the slope was found to be 1.00 ± 0.02 .

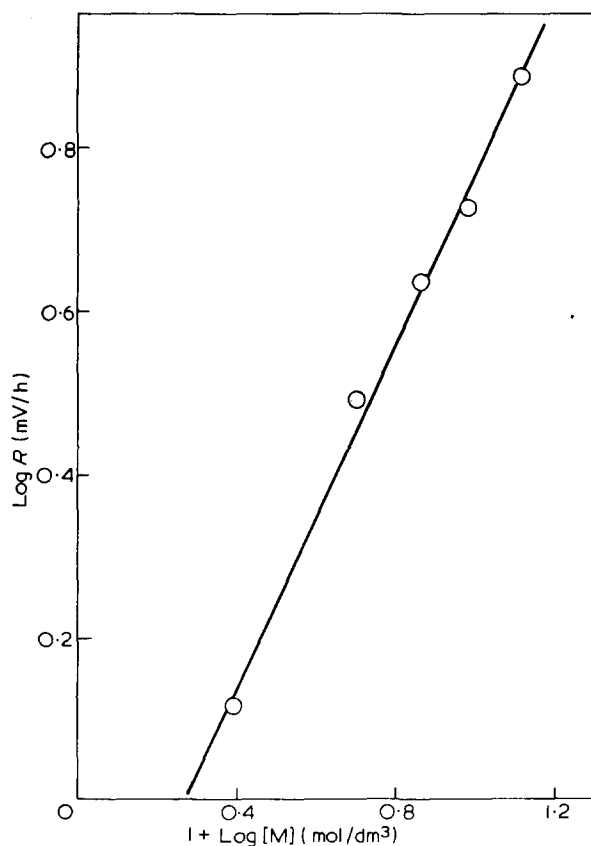


Figure 3 Plot of \log (rate of oxygen uptake), $\log R$, vs. \log (monomer concentration) at 60°C. Methacrylamide is the monomer, constant initiator concentration 5.0×10^{-3} mol/dm³

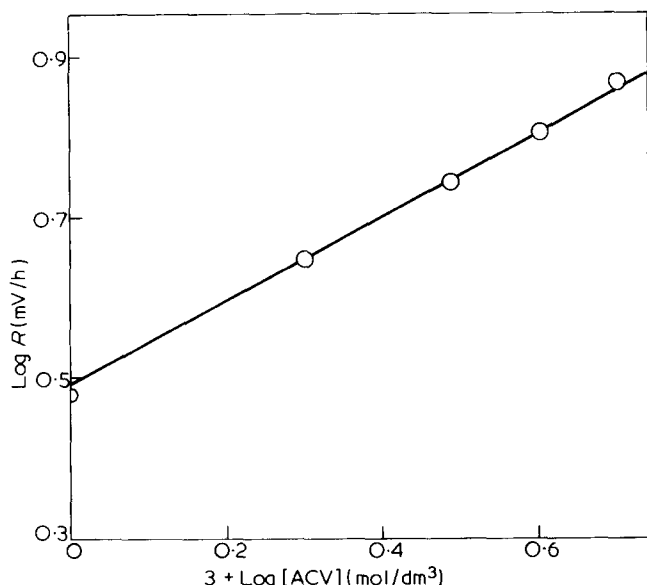


Figure 4 Plot of $\log(\text{rate of oxygen uptake})$, $\log R$, vs. $\log(\text{initiator concentration})$ at 60°C . Methacrylamide is the monomer, constant monomer concentration = 1.5 mol/dm^3

The plot of $\log(\text{rate of oxygen uptake})$ vs. $\log(\text{initiator concentration})$, at a constant monomer concentration, is also linear and is shown in Figure 4. The slope of the graph was found to be 0.49 ± 0.02 .

Thus to a near approximation, the rate of autoxidation of methacrylamide in aqueous solution at 60°C obeys the rate law:

$$-\frac{d[\text{O}_2]}{dt} \propto [\text{M}]^{1.0}[\text{In}]^{0.5} \quad (7)$$

The rate of autoxidation of methacrylamide, unlike that of acrylamide, was strongly dependent on the oxygen concentration as indicated by the results in Table 6.

For constant monomer and initiator concentrations, the plot of $\log(\text{rate of oxygen uptake})$ vs. $\log(\text{oxygen concentration})$ was linear with a slope of 0.40 ± 0.02 . Thus approximately, at constant $[\text{M}]$ and $[\text{ACV}]$:

$$-\frac{d[\text{O}_2]}{dt} \propto [\text{O}_2]^{0.40} \quad (8)$$

Kinetic aspects

The mechanism of the interaction of oxygen on polymerizing monomers is commonly assumed to be¹:

Initiation:



where In represents the initiator, ACV, and $\text{R}_i \cdot$ the primary radicals produced initially by decomposition of the initiator. M represents the monomer, and $\text{R} \cdot$ represents any radical with a terminal monomer unit.

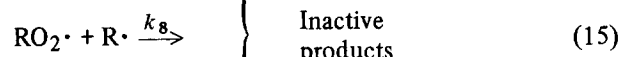
Propagation:



Radical decomposition:



Termination reactions:



Measurements of oxygen uptake for aqueous solutions of acrylamide. The kinetic conclusion derived from the oxygen uptake measurements in aqueous solution, using Warburg manometry and the oxygen electrode, can be summarized mathematically:

$$-\frac{d[\text{O}_2]}{dt} = K [\text{M}]^{1.0} [\text{In}]^{1.0} \quad (17)$$

where K is a proportionality constant, $[\text{M}]$ is the monomer concentration and $[\text{In}]$ is the initiator concentration.

The dependence of oxygen uptake on initiator concentration is unusual, in that it is first order and not half order, as is normally observed, and cannot be satisfactorily explained. Thus none of the three standard termination mechanisms, usually assumed, offer an explanation of the observed results.

Complications may arise in the acrylamide system in particular, but also partly in the methacrylamide system, due to association involving hydrogen bonding^{15,16}. The authors have dismissed any explanation of the acrylamide results based on monomolecular termination due to intramolecular hydrogen atom abstraction giving rise to inert stabilized radicals. There is, however, another complicating feature involving imidization of polyacrylamide radicals giving rise to stable radicals¹⁷, but again this does not provide a satisfactory explanation.

Measurement of oxygen uptake for styrene. Oxygen uptake measurements were carried out on styrene, with ACV as the initiator. This was done in order to check that the anomalous dependence of the rate of oxygen uptake, $-d[\text{O}_2]/dt$, on the initiator concentration to the first power

Table 8 Autoxidation of methacrylamide in water at 60°C .

Dependence of oxygen uptake on oxygen concentration. Constant monomer concentration = 1.5 mol/dm^3 ; constant initiator concentration = $5.0 \times 10^{-3} \text{ mol/dm}^3$ (ACV); solutions were gassed for 10 min before experiments; chart recorder speed = 10 in/h; full scale on recorder = 10 mV

Composition of gas (v/v)	Relative rate of oxygen uptake, R (mV/h)
100% O_2	8.00
80% O_2 - 20% N_2	7.50
60% O_2 - 40% N_2	7.20
40% O_2 - 60% N_2	6.00
20% O_2 - 80% N_2 (AIR)	5.00
10% O_2 - 90% N_2	3.75
5% O_2 - 95% N_2	2.75
2% O_2 - 98% N_2	2.00

for acrylamide was a basic feature of this monomer system and was not due to any inadequacies of the experimental methods employed.

The results of the present study of styrene autoxidation at 50°C, using Warburg manometry, were in reasonable agreement with equation (6), since the oxygen uptake rates at constant [M] and [O₂] varied with the [ACV] concentration to the power 0.45 ± 0.02.

This result suggests that the manometric technique was adequate and that the acrylamide monomer behaved in an unusual and unexpected manner.

Measurement of oxygen uptake for aqueous solutions of methacrylamide. Combining the kinetic results reached by Warburg manometry and the oxygen electrode, the present experimental studies have shown that for methacrylamide in aqueous solution at 60°C:

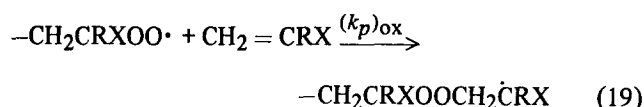
$$\frac{-d[O_2]}{dt} \propto [M]^{1.0} [In]^{0.5} [O_2]^{0.4} \quad (18)$$

This does not coincide with either crossed (equation 15) or mutual peroxy (equation 14) radical type termination and the actual termination mechanism appears to lie between these two distinct types.

Apart from the kinetic differences, methacrylamide takes up oxygen about twice as quickly as acrylamide. This can be partly explained in terms of hyperconjugation. More quantitative predictions of reactivity may be made by use of the Q-e scheme.

Q-e scheme

A theoretical assessment of the susceptibility of acrylamide and methacrylamide to oxidation, relative to that of styrene, can be made by analysing the data collected by Howard¹⁸ and applying the well-known Q-e scheme^{19,20} as outlined previously². Thus, when a series of monomers, CH₂ = CRX [where R = CH₃ or H and X = CN, C₆H₅, O(CO)CH₃ etc.] are radically autoxidized at 30°C with oxygen pressures > 150 torr, the rate-controlling propagation step becomes:



Absolute velocity constants (k_p)_{ox} have been determined by Howard and others¹⁸, at 30°C, for a series of monomers using rotating sector methods, together with the velocity constants, (2k_t)_{ox}, for mutual termination of the corresponding peroxy radicals.

For such a series of monomers, M, the rates of oxidation at 30°C at constant initiator and monomer concentration must be proportional to the $[k_p/(2k_t)^{1/2}]_{ox,M}$ values. If $[k_p/(2k_t)^{1/2}]_{ox,St}$ represents the corresponding velocity constant ratio for styrene, then, to a first approximation, George and Garton²¹ have shown that:

$$\frac{[k_p/(2k_t)^{1/2}]_{ox,M}}{[k_p/(2k_t)^{1/2}]_{ox,St}} = \text{Rate of autoxidation of M relative to styrene} \\ = Q \exp [-e_1'(e + 0.80)] \quad (20)$$

where e_1' represents the average polarity of the -CH₂CRXOO· radical, and Q and e are the parameters characteristic of M. Values of Q and e are conventionally assumed to be 1.00 and -0.80, respectively, for styrene²⁰.

Analysis of the known data indicated²¹ that the average value of e_1' for the radical -CH₂CRXOO· was +1.45 showing that such a polymeric peroxy radical is strongly electrophilic. This method of approach neglects to some extent the known differences in peroxy radical reactivity^{18,22} but permits a direct calculation of the predicted relative reactivities of acrylamide, methacrylamide, and styrene, towards autoxidation. Thus, the Q and e values for acrylamide are 1.18 and +1.30, respectively, while the corresponding values for methacrylamide are 1.46 and +1.24, respectively. Hence using equation (20), acrylamide would be expected to oxidize about 18 times slower, and methacrylamide about 13 times slower than styrene at 30°C under identical conditions.

In the present work, at 60°C, the experimental rate of autoxidation of methacrylamide was about twice that of acrylamide under identical conditions, in reasonable agreement with the above Q-e prediction. Clearly the difference in temperatures involved does not affect their relative reactivities greatly.

ACKNOWLEDGEMENTS

This project was supported by Allied Colloids Ltd, Bradford, England, and financial assistance is gratefully acknowledged.

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