about 15% of the monomer is converted directly to cleavage products as compared with only 3% for styrene. These cleavages are independent of oxygen pressure, and while they are represented by reactions 11 or 12, their mechanisms are unknown. Comparison of Figs. 1 and 9 shows that, as the oxygen pressure is reduced, epoxide formation and cleavage become important and reach maxima at higher pressures with α-methylstyrene than with styrene. This difference will be discussed in section 17.3. The effective value of the ratio, k_e/k_{po} increases with oxygen pressure in the oxidation of α-methylstyrene (Table IX), as also found in the oxidation of styrene (equation 32 and Fig. 5). At 50°, these ratios are 9–14 times larger for α-methylstyrene than for styrene. Thus, in the latter oxidation, monomer radicals are not only more prevalent (at the same pressure) than in styrene, but they also rearrange relatively faster.

MENLO PARK, CALIFORNIA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND STANFORD RESEARCH INSTITUTE]

The Oxidation of Unsaturated Compounds. VII. The Oxidation of Methacrylic Esters[1,*]

BY FRANK R. MAYO[3] AND A. A. MILLER

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The reaction of methyl methacrylate with oxygen has been studied at 50° in the presence of 0.01 M ABN at oxygen pressures from 0–3100 mm. Above about 500 mm. of oxygen, the rate of reaction of monomer (0.006 mole/l./hr.) and the products of oxidation (80% polyperoxide, $(C_5H_8O_4)_n$, and 20% methyl pyruvate and formaldehyde) are nearly independent of oxygen pressure. As the oxygen pressure approaches zero, the rate of reaction of oxygen decreases, and the rate of reaction of monomer approaches 0.40 mole/l./hr. Thus oxygen strongly retards polymerization of methyl methacrylate. The relative reactivity of monomer and oxygen toward monomer radicals, and the tendency toward crossed termination, are nearly independent of the composition of monomer radicals. Butyl methacrylate is about as reactive as the methyl ester. The over-all activation energy for its oxidation is 26.5 kcal./mole.

10. Introduction

Barnes, Elofson and Jones[62] found that methyl methacrylate absorbed oxygen at 40° to give a polymeric peroxide analyzing for $[(C_5H_8O_2)_{1.18}O_2]_n$. Further study of the oxidation of this monomer was undertaken to provide standards for study of its co-oxidation with styrene or α-methylstyrene (paper IX). When a substantial proportion of a cleavage product, methyl pyruvate, was found, the effect of pressure on this cleavage reaction was investigated.

11. Experimental

11.1. **Materials.**—Methacrylic esters were obtained from various commercial sources. They were washed free from inhibitor with aqueous sodium hydroxide, then washed with water, dried and distilled at reduced pressure. They were stored at about 7° and redistilled before each group of experiments. Beginning with experiment Q in Table XII, the monomer was dried with calcium hydride. No improvement in reproducibility was noted.

11.2. **Procedures.**—Experiments 1, A-1 and 8 were carried out with 200, 150 or 100 ml. of methyl methacrylate, respectively. In expt. 1, samples containing 0.1–0.2 g. of polyperoxide were withdrawn at intervals and analyzed according to procedure C (section 2.2). In expt. 8, the oxidation was carried out according to procedure A, and 20 g. of product was then analyzed by procedure C. In this experiment, oxygen was admitted at the rate of 0.006 mole/hr., and consumed at about one-tenth of this rate. Experiment A-1 was carried out similarly, with duplicate analyses for pyruvate (±2%) and polymer (±0.7%). In A-1, oxygen was admitted at the rate of 0.0025 mole/hr. and consumed at one-fourth to one-fifth of this rate. All high pressure experiments were carried out in a closed system by procedure C, starting with 10 or 20 ml. of monomer or solution.

In procedure C, with methyl methacrylate, the reaction mixture was distilled at 0.5 mm. pressure, with final warming of the residue to 50°. This distillate was then concentrated to 1–2 ml. at a pressure of 150 mm. in a short jacketed distilling column with a nichrome spiral for packing. The ester distilled at about 53°. The concentrate apparently contained a trace of volatile peroxide or of ABN, for the residue polymerized partially during concentration. For example, 8 g. of distillate from expt. 1 gave 0.77 g. of dry polymer in a 1-hour concentration, while similar concentration of fresh monomer gave only 0.05 g. of polymer. In the example cited and in other cases when the concentrate became viscous, the liquid was distilled from the polymer at 50–70° and 0.5 mm. pressure, and concentration was continued with the distillate. The polymer thus obtained was discarded. It was dry, brittle, and in a porous or expanded state so that it should have contained little volatile material. The concentrate, mostly methyl methacrylate, was examined for its infrared absorption. Methyl pyruvate was determined by the absorption of its band at 13.9 μ, with the use of a series of standard solutions. The ability of the fractionating column to separate pyruvate from methacrylate was tested by reconcentrating a distillate from a concentration. The second concentrate was free from pyruvate.

The epoxide of methyl methacrylate, methyl 2-methyl-2,3-epoxypropionate, was prepared by Dr. J. R. Ladd. A 5% solution of this epoxide in methyl methacrylate exhibited strong and sharp absorption bands at 11.5 and 13.2 μ. If the rate of epoxide formation had approached 5% of the rate of pyruvate formation, epoxide would have been detected easily. However, there was no significant spectroscopic evidence of any oxidation product other than pyruvate in the concentrates of the volatile materials from the oxidations.

In experiments with 0.04 M ABN, removal of initiator by volatilization at 50° and 0.5 mm. pressure was tedious. The difficulty was partially overcome by extracting the peroxide–initiator mixture with cold carbon tetrachloride. A large fraction of the initiator and a small fraction of the polymer did not dissolve. Most of the ABN was sublimed out of the insoluble fraction and then the two fractions were combined and heated to constant rate of weight loss. An extreme example is Z, with 20 ml. of solution, and 0.135 g. of ABN initially. After heating the whole product for 135 min. and the ABN-rich residue for 165 min. additional, the final weight of peroxide was 0.1425 g. and the final rate of weight loss was 0.6 mg. per 30-minute heating. The extrapolated initial weight was taken as 0.1461 g.

11.3. **Calculations.**—Calculations of rates followed the procedures used with styrene. At 50°, the density[63] of

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[*] For numbering of footnotes, equations, etc., *cf.* note 2 of paper V.

[62] C. E. Barnes, R. M. Elofson and G. D. Jones, THIS JOURNAL, **72**, 210 (1950).

[63] E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 8–9.

methyl methacrylate is taken as 0.908 g./ml. The vapor pressure, by boiling point, was 119–120 mm. at 50.0°.

12. Results and Discussion

12.1. Rates and Products of Reaction of Methyl Methacrylate at 500–3100 Mm. of Oxygen.—Since the rates and products of oxidation at 0.01 *M* ABN are essentially independent of oxygen pressure at pressures over 500 mm. of oxygen, these experiments will be considered together. Figure 19 summarizes the oxidation of 200 ml. of methyl methacrylate in a slow stream of oxygen at a total pressure of 1 atm. The data show no significant induction period or autocatalysis, but there is some indication that the total rate decreases gradually as the initiator decomposes. The only products found were the polyperoxide of methyl methacrylate, and the cleavage products, methyl pyruvate and formaldehyde. Methyl pyruvate was determined by infrared absorption. Formaldehyde was noted by odor, but was not determined, and is assumed to have been formed in quantities equivalent to pyruvate. In the presence of 0.01 *M* ABN and in the absence of solvent, about 20% of the oxygen consumed appears in the cleavage products, the rest as polyperoxide, approximately $(C_5H_8O_4)_n$. Figure 19 suggests that the proportion of cleavage products may increase from 20 to 25% over 48 hours, which may be significant, but there is little or no difference between 8-hour and 16-hour experiments. Therefore, most, if not all, of the cleavage products are primary oxidation products, not secondary products from decomposition of polyperoxide. In the absence of added initiator, the rate of oxidation was immeasurably slow, well below 0.0003 mole/l./hr.

Table XII shows the effects of oxygen pressure, initiator concentration, and benzene as solvent on the rate and products of oxidation. Although the reproducibility of the results at about 4 atm. of oxygen is unsatisfactory, the major trends at this pressure are unmistakable. The over-all rate of the oxidation is proportional to $[\mathrm{ABN}]^{1/2}$ and to the first power of the concentration of monomer. The over-all mechanism is therefore described satisfactorily by reactions 1, 3, 4 and 7. Of particular interest are the effects of [ABN] and diluent on the proportion of cleavage, R_C/R_O. Increasing [ABN] fourfold increases the proportion of cleavage from an average of 19% (excluding expt. T) to an average of 28%, and dilution with an equal volume of benzene increases the proportion further to an average of 38%. These effects correspond to the relation

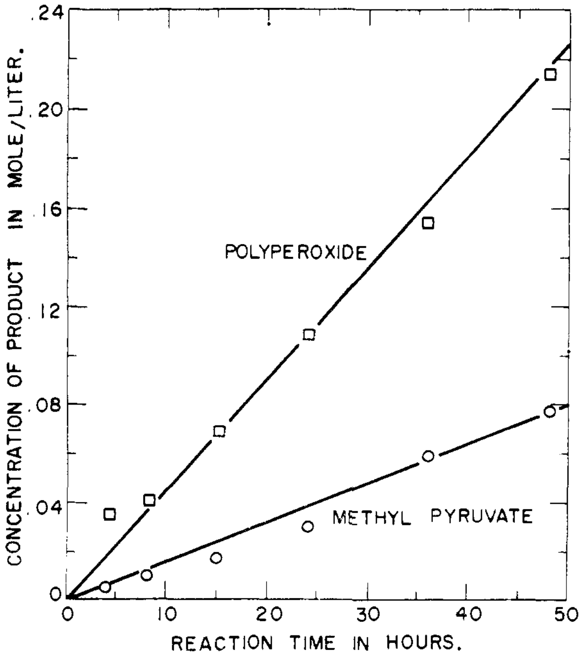

Fig. 19.—Oxidation of methyl methacrylate in expt. 1 (Table XII).

$$R_C/R_O = 1.77[\mathrm{ABN}]^{0.28}/[\mathrm{M}]^{0.44} \qquad (51)$$

The dependence of cleavage on concentration of initiator, the absence of epoxide, and the moderate molecular weight of the polyperoxide (1800[62]) all suggest that cleavage is not initiated by epoxide formation but by interaction of two peroxide radicals, reaction 14.

Further, equation 51 can be shown to represent a compromise between two reasonable limiting cases, both depending on reaction 14, followed by depolymerization to cleavage products (reaction 9). If the average number of $-\mathrm{MO_2}-$ units available for depolymerization in a peroxide radical is determined only by the competition between propagation 4 and termination 7, then R_C depends on the rate of interaction of peroxide radicals and on their average degree of polymerization. Then, for long kinetic chains, where end groups can be neglected

$$\frac{R_C}{R_O} = \frac{k_{chb}[\mathrm{MO_2}\cdot]^2 \times \dfrac{k_{pm}[\mathrm{MO_2}\cdot][\mathrm{M}]}{k_{to}[\mathrm{MO_2}\cdot]^2}}{k_{pm}[\mathrm{MO_2}\cdot][\mathrm{M}]} = \frac{k_{chb}}{k_{to}} \qquad (52)$$

On the other hand, if the number of $-\mathrm{MO_2}-$ units available for depolymerization is a constant, half the average number (n) of $-\mathrm{MO_2}-$ units accumulated between chain transfer reactions,[64] then

$$\frac{R_C}{R_O} = \frac{nk_{chb}[\mathrm{MO_2}\cdot]^2}{2k_{pm}[\mathrm{MO_2}\cdot][\mathrm{M}]} = \frac{nk_{chb}}{2k_{pm}[\mathrm{M}]}\left(\frac{R_i}{k_{to}}\right)^{1/2} \qquad (53)$$

Thus, the effects of both initiator and monomer concentration are consistent with the ideas that cleavage results from interaction of two peroxide radicals and that the extent of depolymerization is limited partly by a chain propagation and partly by a chain transfer process. That such a reaction of peroxide radicals should become evident with methyl methacrylate but not with styrene or methylstyrene is not surprising. Section 18 will show that peroxide radicals add much slower to methacrylate than to the styrenes; therefore the interaction of peroxide radicals with each other can compete better with the propagation reaction in the case of methyl methacrylate than in the case of styrene. Blanchard[65] has recently proposed a nonterminating reaction of two cumylperoxy radicals to give two cumyloxy radicals and oxygen. In this case also, reaction with solvent is relatively slow.

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[64] Since R_C/R_O is independent of oxygen pressure above 500 mm., the monomer–oxygen ratio in the copolymer is unimportant.

[65] H. S. Blanchard, Abstracts of New York Meeting of American Chemical Society, Sept., 1957, p. 75-P.

TABLE XII

THE AUTOXIDATION OF METHYL METHACRYLATE AT 50°

Expt.	O_2 pressure	Reaction time, hr.	Rates in moles/l./hr.[a] $(C_5H_8O_4)_n$	Methyl pyruvate (Rc)	Total O_2 (Ro)	Rc/Ro
			0.01 *M* ABN, no solvent			
A2	0	2.00			^{g}	
A1	14	7.0	0.0027^{b}	0.0012	0.0039^{h}	0.31
8	67	7.5	.0039^{c}	.0017	.0056^{i}	.30
1	630	8.0	.0049^{d}	.0013	.0062^{j}	.21
		48.0	.0044^{d}	.0016	.0061^{k}	.26
D	3000	8.0	.0041	.0010	.0051	.20
N	3130	16.0	.0044	.0009	.0053	.16
Q	3150	16.0	.0052	.0013	.0065	.20
V	3100	16.0	.0046^{e}	.0012	.0058	.21
T^{f}	3090	16.0	.0040	.0013	.0053	.25
			0.04 *M* ABN, no solvent			
L	3100	8.0	0.0086	0.0033	0.0119	0.28
M	3150	16.0	.0081	.0039	.0120	.33
R	2940	16.0	.0096	.0029	.0125	.23
U	3110	16.0	.0073	.0030	.0103	.29
Y	3040	8.0	.0077	.0029	.0106	.28
			0.04 *M* ABN, equal volumes of benzene and monomer			
W	3070	16.0	0.0037	0.0020	0.0057	0.35
X	3000	16.0	.0028	.0021	.0049	.43
Z	3080	16.0	.0035	.0022	.0057	.39
ZA	3070	16.0	.0036	.0020	.0056	.36

[a] Average for indicated reaction time. [b] The polymer contained 55.6% C, 7.8% H, corresponding to 30.3% by weight $C_5H_8O_4$ (45.5% C) and 69.7% polymethyl methacrylate (60.0% C). Thus the polymer contains 3.03 excess monomer per peroxide unit, and 0.0081 mole/l./hr. of monomer reacted in addition to that included in R_O. [c] This polymer contained 50.4% C, 66.0 wt. % $C_5H_8O_4$, 0.68 excess monomer per peroxide unit. 0.0026 mole/l./monomer reacted per hour in addition to that included in R_O. [d] *Cf.* Fig. 19. On the basis that $r_1 = 5.2 \times 10^{-5}$, and that 0.23 mole of pyruvate is formed for each mole of oxygen found as a peroxide, a polyperoxide made under 630 mm. of oxygen should contain 0.066 excess monomer per peroxide unit, 46.1% C. The polymer found by analysis is calculated as 95.2% by weight of $C_5H_8O_4$ and the rate of incorporation of methyl methacrylate is 6.6% greater than the stated rate of formation of polyperoxide. [e] Polymers prepared in similar 34-hour runs analyzed for 45.4 and 45.8% C, indistinguishable from the theoretical 45.5% C for $C_5H_8O_4$. [f] Monomer saturated with water at 30°; a little less than 1% water dissolved. [g-k] R_M in these experiments: 0.397 in sealed, evacuated tube,[g] 0.0120,[h] 0.0082,[i] 0.0065,[j] 0.0063.[k]

Experiment T in Table XII indicates that water is not responsible for the poor reproducibility of experiments at 3100 mm. pressure.

12.2. Rate of Oxidation of *n*-Butyl Methacrylate.—The temperature coefficient of the over-all oxidation was measured with *n*-butyl methacrylate, because of its lower vapor pressure. The procedure was that used originally on styrene.[4] Data are summarized in Table XIII.

The rates of oxidation of the methyl and butyl esters at 50° are essentially the same when corrected to the same concentration of monomer (Table XV). At one atmosphere of oxygen, the apparent over-all activation energy for the oxidation of the butyl ester is 26.5 kcal./mole, nearly the same as for styrene, 25.4 kcal./mole,[4] but the rate is much lower. With the butyl ester at 65°, the rate is independent of oxygen pressure over the range 25–740 mm.

TABLE XIII

INITIAL RATES OF OXIDATION OF BUTYL METHACRYLATE (0.01 *M* ABN)

Temp., °C.	O_2 pressure, mm.	Rates of oxidation, mole O_2/l. monomer/hr.
50	745	0.0039
65	740	.0254
80	730	.131
65	25	.026

12.3. Products of Reaction of Methyl Methacrylate below 500 Mm. of Oxygen.—The calculations in this and the next section neglect any contributions of residual alkoxy radicals to chain propagation and copolymer composition. This neglect is justified by the fact that the ratio of excess monomer to depolymerization residue is much more favorable than with styrene and α-methylstyrene and by the fact that satisfactory results are obtained.

The ratio $k_p/k_{po} = r_1$ has been determined by equation 20 for expts. A1 and 8. At 14 mm., r_1 is found to be 4.5×10^{-5}, at 67 mm., 4.9×10^{-5}. These values may agree within experimental error and they indicate little or no effect of penultimate units. Application of equation 27, with appropriate substitutions, gives quantitative support to this conclusion: r (for $\sim\!\!\sim MM\cdot$) $= 4.3 \times 10^{-5}$, and r' (for $\sim\!\!\sim MO_2M\cdot$) $= 5.2 \times 10^{-5}$. This value for r' is about 60 times the corresponding value for styrene, 8.9×10^{-7} (section 4.5). This difference means that low-pressure oxygen is not as readily incorporated into methyl methacrylate polymer as into styrene polymer.

Since the rate constant for reaction of methacrylate radicals with methyl methacrylate is 279 l./mole/sec. at 50°,[66] the rate constant for the reaction of methacrylate radicals ($\sim\!\!\sim MO_2M\cdot$) with oxygen is about 5.4×10^6 l./mole/sec. This rate constant is significantly smaller than that estimated for the reaction of a styrene radical with oxygen and is in the same range as the rate constants for reactions of two radicals in polymerizations. From the value of r' above, the composition of the polyperoxide prepared at 630 mm. of oxygen has been calculated in Table XII, probably more accurately than it could be determined by carbon analysis. The 1.066 ratio for methacrylate to oxygen calculated for this polyperoxide is considerably lower than the ratio 1.18 found by Barnes and co-workers.[62] They may not have provided sufficient agitation in their reaction mixture. Either ratio differs enough from the ratio of unity, assumed by Schulz and Henrici[67] for polyperoxides made under oxygen pressures at and below one atmosphere, to suggest modification of some of their equations and calculations.

12.4. Rates of Reaction of Methyl Methacrylate below 500 Mm. Pressure.—Data on the rates of reaction of methyl methacrylate and oxygen at several oxygen pressures are summarized in Table XII and Fig. 20. The rate of polymerization of methyl methacrylate in the presence of 0.01 *M* ABN at 50° checks the value, 0.41 mole/l./hr.,

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(66) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

(67) G. V. Schulz and G. Henrici, *Makromol. Chem.*, **18–19**, 437 (1956).

reported by Arnett.[68] The ratio of this rate to the rate of reaction of methacrylate at 1 atm. of oxygen, 61–62, agrees within experimental error with the ratio, 66, reported by Schulz and Henrici.[67]

The curves in Fig. 20 correspond to equations 19a, with the k_e term neglected, and 19b. For calculating these curves, $R_i^{1/2}/\delta_M = 0.0441$; $R_i^{1/2}/\xi_O = 0.000695$; $\xi_O/\delta_M = 63.4$; $[O_2] = 1.396 \times 10^{-5}\,p$(section 7.10); $[M] = 9.07$; $r_1 = 4.8 \times 10^{-5}$ (average value); $\phi = 20$. This value of ϕ is near the mean of the two values, 23.0 and 18.5, calculated for expts. A1 and 8 from the same constants.

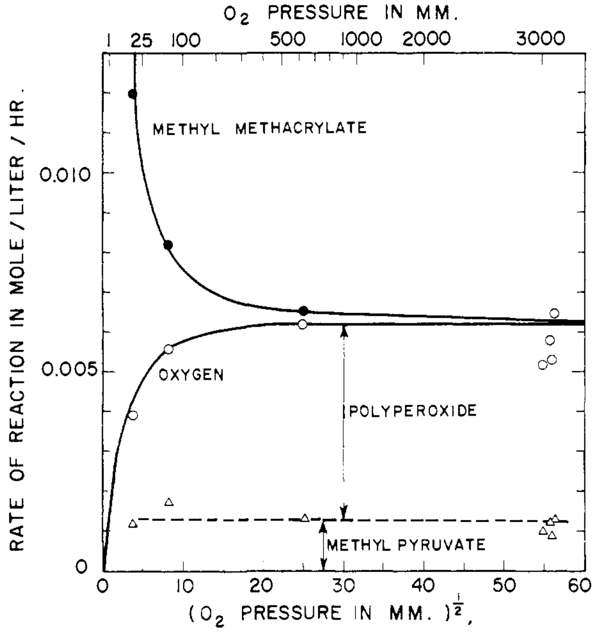

Fig. 20.—Rate of reaction of methyl methacrylate at 50° in presence of 0.01 *M* ABN as a function of oxygen pressure. Rate of polymerization is 0.40 mole/l./hr. in absence of oxygen.

The experimental points, and their excellent representation by equation 19, show clearly the effect of oxygen on the polymerization of methyl methacrylate. Above about 200 mm. pressure of oxygen, the product is nearly 1:1 peroxide and the rate of reaction of monomer is a small fraction of the rate in the absence of oxygen. Chain termination is by interaction of two peroxide radicals, consistent with the results of Schulz and Henrici[67] on induction periods. Below 200 mm. pressure, the rate of reaction of methacrylate increases steadily and the rate of reaction of oxygen decreases steadily, as less oxygen enters the copolymer and crossed termination becomes more important. The linear relation between R_O and $p^{1/2}$ below 25 mm. pressure shows that in this region, termination is almost exclusively by the favored interaction of unlike radicals.[69]

In this system, neither r_1 nor ϕ changes much as monomer radicals change from $\sim\!\!\sim MO_2M\cdot$ to $\sim\!\!\sim MM\cdot$. Apparently neither radical is a particularly good electron donor in the case of methyl methacrylate and polar effects are less important than with styrene. The failure of methyl methacrylate to exhibit a minimum rate at low pressure, as observed with styrene, is considered in section 16.3.

MENLO PARK, CALIFORNIA

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[68] L. M. Arnett, THIS JOURNAL, **74**, 2027 (1952).

[69] ADDED IN PROOF.—Correspondence with Prof. Schulz has brought out the good agreement between the work of Schulz and Henrici[67] and the present paper in the primary rate data, and in r_1 (and values derived from it). However, further comparison of the two papers now shows that the agreement in r_1 does not justify the theoretical assumptions in their paper; the agreement comes largely from compensation of errors.

In order to calculate r_1, they assume that methyl methacrylate and oxygen react at equal and constant rates during substantially all of the period of retardation by oxygen, *i.e.*, that an alternating copolymer is formed and that termination is by interaction of two peroxide radicals. In an experiment starting with 2.73 molar monomer in benzene and 160 mm. of oxygen (calculated to be 1.8×10^{-3} molar), they estimate that R_M has increased to one-tenth of the uninhibited rate one minute before the end of a 200-minute induction period. Here the oxygen concentration is assumed to be $1.8 \times 10^{-3}/200$ or 9×10^{-6} molar, and to reach zero in the next minute. From this concentration of oxygen, r_1 is calculated to be $<3 \times 10^{-5}$. Application of our equations (19a) and (19b) and the data in sections 12.3 and 12.4 shows that although their value of r_1 is nearly the same as ours (4.8×10^{-5}), the actual situation at the chosen instant is quite different. The calculations below are based on our uninhibited rate, corrected to 2.73 molar methacrylate, their initial concentration of oxygen, and 0.01 molar ABN (they give no concentration of ABN in their critical experiment, but this concentration seems to be immaterial). When R_M is one-tenth of the uninhibited rate, the concentration of oxygen is about 5.2×10^{-6} molar $^1/_{350}$ of the initial concentration, and R_O is only $0.038R_M$ (instead of $0.17R_M$). The crossed termination supplies 93% of the terminating steps, and R_M and R_O are only 0.24 as fast as if chain termination resulted only from interaction of two peroxide radicals. Thus, at the chosen instant, there is less oxygen present and it is disappearing more gradually than they assume. The sharp change in rate at the end of the induction period is due more to a temporary restraining effect of the crossed termination than to an abrupt exhaustion of oxygen.