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A Study of two Bromine-Containing Peroxides as Initiators for the Radical Polymerization of Styrene

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(Eingegangen am 27. April 1959)

SUMMARY:

Styrene at various concentrations in benzene has been polymerized at 60° C. and 80° C. using bis(315- dibromo-4-methoxybenzoyl) peroxide and bis(m-bromobenzoyl) peroxide as initiators. Rates of initiation have been determined from analyses of the polymers for combined fragments from the initiators; the analyses were performed by radio-chemical techniques. It has been confirmed that with these peroxides, transfer to initiator is pronounced and further evidence on the mechanism of this reaction has been obtained. Values for the velocity constants for the dissociations of these peroxides have been derived.

ZUSAMMENFASSUNG:

Styrol wurde unter Verwendung von Bis(3,5-dibrom-4-methoxy-benzoyl)peroxyd und Bis(m-brombenzoyl)peroxyd als Initiatoren bei 60°C. und 80°C. in verschiedenen Konzentrationen in Benzol polymerisiert. Die Initiierungsgeschwindigkeiten wurden aus den Analysen der Polymeren für die kombinierten Fragmente der Initiatoren bestimmt; die Analysen wurden mit Hilfe radiochemischer Methoden ausgeführt. Es wurde festgestellt, daß bei diesen Peroxyden die Übertragung auf den Initiator verstärkt eintritt und ein weiterer Beweis für den Mechanismus dieser Reaktion erbracht. Werte für die Geschwindigkeitskonstanten des Zerfalls der Peroxyde werden angegeben.

Tracer studies¹) of polymerizations sensitized by aroyl peroxides have shown that the competition between the reactions

> (1) $\operatorname{RCOO} \rightarrow \operatorname{R} \bullet + \operatorname{CO}_2$ velocity constant = k_1 (2) $\operatorname{RCOO} \bullet + M \rightarrow \operatorname{RCOOM} \bullet$ k_2

where M represents a molecule of monomer, can be studied and that a value for the ratio of the velocity constants k_1/k_2 can be determined. The experimental method involves a comparison of the numbers of aroyloxy and aryl end-groups in polymers prepared under various conditions. With benzoyl peroxide, the value of k_1/k_2 depends upon the

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¹) J. C. BEVINGTON, J. Polymer Sci. 29 (1958) 235.

monomer and the reactivities of monomers towards the benzoyloxy radical can be compared quantitatively²). If methoxybenzoyl peroxides are used with styrene, the values of k_1/k_2 are considerably different from the corresponding value with benzoyl peroxide^{3, 4}); the magnitude of the effect depends upon the position of the substituent in the benzene ring.

The methoxy group is electron-releasing and in order to examine the effects of electron-attracting substituents upon the benzoyloxy radical, studies of bromine-containing peroxides were undertaken. It is not practicable to use ⁸²Br for labelling in work of this type since its half-life is only about 36 hours. An alternative procedure is to use unlabelled peroxide and then determine the bromine in the polymers by neutron activation analysis.

The first part of the work involved the use of bis(3:5-dibromo-4-methoxybenzoyl) peroxide. This initiator was labelled with ¹⁴C in the methoxy groups. End-group analyses by the ¹⁴C and neutron activation methods were in agreement; work with bis(m-bromobenzoyl) peroxide was then undertaken using only the neutron activation technique.

Certain anomalies in the behaviour of the bromo-peroxides were clearly revealed. Interpretation of the results is less certain than for the peroxides studied previously. Further work with these initiators is in progress but the results obtained so far are of interest in themselves and are presented here.

Experimental

Preparation of peroxides

The first peroxide was prepared by the following sequence of reactions:



- ²) C. A. BARSON, J. C. BEVINGTON, and D. E. EAVES, Trans. Faraday Soc. 54 (1958) 1678.
- ³) J. C. BEVINGTON, J. TOOLE, and L. TROSSARELLI, Trans. Faraday Soc. 54 (1958) 863.
- ⁴) J. C. BEVINGTON, J. TOOLE, and L. TROSSARELLI, Makromolekulare Chem. 28 (1958) 237.

In the preparations of the unlabelled and the ¹⁴C-peroxide, samples of all intermediates (except the acid chloride) were purified and their melting points agreed with values in the literature. The melting point of the purified peroxide was 158° C. -159° C., and its analysis 30.8% C, 52.0% Br, 1.56% H (calc. 31.1% C, 51.8% Br, 1.62% H). The specific activity of the ¹⁴C-peroxide was approximately 18μ c./g. of carbon. The bis(m-bromobenzoyl) peroxide was prepared by standard methods from m-bromobenzoic acid.

Preparation and assay of polymers

Procedures involved in the work with 14 C-peroxides have been described already³). For neutron activation analysis, small samples of the materials sealed in silica tubes were irradiated in the pile at A.E.R.E. HARWELL for 48 hours at a flux of 10^{11} slow neutrons/sec./cm². After the activity due to ⁸⁰Br had fallen to a low level, samples (about 2 mg.) of the materials were accurately weighed into aluminium cups of about 1 cm² cross section. A few drops of benzene were added and then allowed to evaporate, leaving thin films of polymer; these films were "infinitely thin" for assay purposes and self-absorption could be neglected.

The cups were placed at a fixed position beneath an end-window counter housed in a lead castle. Counting rates were measured at intervals over a period of a week. Corrections for lost counts and background were made. Measurements of $t_{1/2}$ and the maximum energy of the particles showed that the activity was due almost entirely to ⁸²Br. "Tails" in the decay curves, attributed to low levels of ¹⁴C activity induced in the polymers, were negligible compared with counting rates observed earlier in the decay. Methyl 3:5-dibromo-4-hydroxybenzoate was used as the primary standard for the bromine analyses. The bromine content of a specimen was taken as proportional to the corrected counting rate per mg. of sample at a standard time.

Blank experiments showed that unreacted peroxides could be removed completely from polymers by the usual re-precipitation procedure.

Results

Experiments with bis(3:5-dibromo-4-methoxybenzoyl) peroxide

At 60 °C. styrene at various concentrations in benzene was polymerized using ¹⁴C-peroxide. In similar experiments at 80 °C. both labelled and unlabelled specimens of peroxide were used; there was no detectable difference between the rates of polymerization observed with the two types of initiator. Polymers derived from the unlabelled peroxide were subsequently examined by neutron activation analysis.

For the polymerizations, the orders with respect to initiator and to monomer were respectively 0.5 and 1.1 and so the kinetic behaviour was normal. Kinetic chain lengths were calculated from the results of endgroup analysis by the ¹⁴C or neutron activation methods; from these chain lengths and the overall rates of polymerization, rates of initiation were calculated. For reasons explained later, the values for the kinetic chain length and rate of initiation are *apparent* values. Results for experiments at 80 °C. are presented in Figures 1 and 2; similar results were obtained from experiments at 60 °C. There are no systematic differences between the results obtained by the two methods of end-group analysis.



Fig. 1. Variation of apparent chain length with rate of polymerization for styrene in benzene with the dibromomethoxybenzoyl peroxide. Concentrations of styrene in moles/l. shown on curves



Fig. 2. Variation of apparent rate of initiation with concentration of initiator for systems referred to in Fig. 1. Concentrations of styrene in moles/I. shown thus: $(\bullet) = 4.07; (\neg) = 2.03; \bigotimes = 1.18; (\Phi) = 0.81$

Comparison of the ¹⁴C or bromine contents of polymers before and after hydrolysis leads to determination of the fraction (x) of the end-groups

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which are aroyloxy groups. Results for 80 °C. are collected in Table 1 and those for 60 °C. are displayed in Figure 3.

Concentration of monomer (mole/l.)	Concentration of initiator · 10 ³ (mole/l.)	x -1
4.07	13.2	1.07
	6.58	1.05*)
	2.63	1.07*)
2.03	13.1	1.05
	6.56	1.06*)
	2.62	1.09*)
1.18	13.1	1.07*)
	6.56	1.09
	2.62	1.08
0.81	13.1	1.07
	6.56	1.12*)
	2.62	1.10

Table 1. Aroyloxy end-groups in polymers at 80°C.

*) from bromine analyses.



Fig. 3. Dependence of fraction x upon concentration of monomer for polymerizations at 60°C. using the dibromomethoxybenzol peroxide

From Table 1, it can be seen that there is no systematic difference between the results from the two techniques for end-group analysis. For a particular concentration of monomer, there is a tendency for the value of x^{-1} to increase as the concentration of initiator is reduced.

Experiments with bis(m-bromobenzoyl) peroxide

At both 60 °C. and 80 °C., the dependence of rate of polymerization upon the concentrations of monomer and initiator was normal. From the analyses for bromine, apparent kinetic chain lengths and thence apparent rates of initiation were calculated. Results for polymerizations at 80 °C. with styrene at a concentration of 2.03 moles/l. in benzene, are presented in Table 2.

Rate of polymer · 10 ⁵ (mole/l./sec.)	Apparent kinetic chain length	Apparent rate of initiation · 10 ⁷ (mole/l./sec.)
2.18	144	1.51
1.92	114	1.68
3.03	95	3.17
3.18	89	3.58
3.64	46	7.97
	Rate of polymer · 10 ⁵ (mole/l./sec.) 2.18 1.92 3.03 3.18 3.64	Rate of polymer · 10 ⁵ (mole/l./sec.) Apparent kinetic chain length 2.18 144 1.92 114 3.03 95 3.18 89 3.64 46

Table 2. Experiments at 80°C.



Fig. 4. Dependence of fraction x upon concentration of monomer for polymerizations with bis(mbromobenzoyl) peroxide. Temperatures of reaction and concentrations of initiator (in moles/1. · 10³) shown thus: (•) = 80°C., 9.0; (★) = 80°C., 44.8; (-) = 60°C., 9.2; (•) = 60°C., 45.9

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A Study of two Bromine-Containing Peroxides as Initiators

The fraction x was calculated for the various polymers from the bromine contents of polymers before and after hydrolysis (see Fig. 4). There is considerable scatter in the results but it is evident that for a given concentration of monomer, the value of x^{-1} tends to increase as the concentration of initiator is reduced.

Discussion

It appears that the bromine-containing peroxides engage in transfer reactions when used with styrene, the chief evidence being the abnormal relationship between the apparent kinetic chain length and the rate of polymerization (see Fig. 1). The observations indicate that at high rates of polymerization, i.e. high concentrations of peroxide, more initiator enters the polymer than would be expected, since under these conditions low values of the kinetic chain length are found. For benzoyl peroxide and its methoxy derivatives, there were linear relationships between the reciprocal of the kinetic chain length (determined from end-group analysis) and the rate of polymerization suggesting that transfer to these initiators could be neglected. COOPER's⁵) value for the transfer constant for the polystyrene radical with bis(m-bromobenzoyl) peroxide at 70 °C. is 0.465 which is much greater than the corresponding values for benzoyl and anisoyl peroxides viz. 0.075 and 0.074 respectively.

From rates of initiation, determined by the tracer method, values for the velocity constants for the dissociation of initiators can be calculated. For the bromine-containing peroxides however these calculations are unsatisfactory because of the anomalous relationship between the apparent kinetic chain length and the rate of polymerization; rates of dissociation were calculated by an alternative procedure involving comparison with results for other initiators. There is no evidence for degradative transfer processes involving the initiators and so for fixed values of the rate of polymerization, concentration of monomer and temperature, the rate of initiation should be independent of the nature of the initiator. Assuming that two initiators have equal efficiencies, the relationship

$$k_{d_1}[I_1] = k_{d_2}[I_2]$$

should apply, k_{d_1} and k_{d_2} being the velocity constant for the dissociations, and $[I_1]$ and $[I_2]$ being the concentrations of the two initiators giving equal rates of polymerization. Average values for k_d obtained in

⁵) W. COOPER, J. chem. Soc. [London] 1952, 2408.

this way for the bromine-containing peroxides using benzoyl peroxide and its methoxy derivatives as standards, are given in Table 3. It is assumed, for reasons discussed previously⁶), that the efficiency of initiation for the peroxides is 100%.

	Bis(3:5-dibromo-4-methoxy- benzoyl) peroxide	Bis(m-bromobenzoyl) peroxide
$10^5 \cdot k_d$ (sec. ⁻¹) at 60 °C.	0.061	0.11
$10^5 \cdot k_d$ (sec. ⁻¹) at 80 °C.	0.94	1.22

Table 3. Rates of dissociation of initiators.

For bis(m-bromobenzoyl) peroxide at 80 °C., k_d has been given⁷) as 2.57 · 10⁻⁵ sec.⁻¹; the difference between the values of k_d for this peroxide is considerably greater than for the peroxides examined previously.

For bis(m-bromobenzoyl) peroxide, the dependence of x upon the concentration of initiator for a fixed concentration of monomer is a further indication of the importance of transfer to initiator. This transfer process must decrease in importance and the value of k_1/k_2 tend towards the real value as the concentration of initiator is reduced. The results so far available do not permit an extrapolation to be made, but it is suggested that the values for k_1/k_2 are at least 0.3 mole/l. at 60 °C. and at least 0.5 mole/l. at 80 °C.

At the higher concentrations of initiator, the value of the fraction x is large suggesting that transfer to initiator introduces hydrolyzable groups into the polymers. The transfer may be of a conventional type involving abstraction of an atom from the initiator, or it may be a reaction such as

 $P \bullet + (RCOO)_2 \rightarrow POCOR \bullet + R-COO \bullet$

where P• represents a polymer radical. The second reaction can be described as an induced decomposition and it would introduce additional aroyloxy groups into the polymer whatever the prevailing concentration of monomer; it could therefore be responsible for the observed variation of x with the concentration of initiator. The aroyloxy radical released during the induced decomposition would behave in the same way as an aroyloxy radical generated by thermal dissociation of the peroxide; it would stand the same chance of decomposing before being captured by

⁶) J. C. BEVINGTON, Proc. Roy. Soc. [London] A 239 (1957) 420.

⁷) C. G. SWAIN, W. H. STOCKMAYER, and J. T. CLARKE, J. Amer. chem. Soc. 72 (1950) 5426.

monomer and so it would cause no dependence of x upon the concentration of initiator. The radical induced decomposition

$$\begin{array}{ccc} P-CH_2-CH\bullet + (RCOO)_2 \rightarrow P-CH=CH+R-COOH+R-COO\bullet\\ & & & \\ & & C_eH_5 \end{array}$$

is rejected, since although it would cause abnormalities in the apparent rate of initiation, it would not cause x to depend upon the concentration of initiator.

In the experiments with bis (3:5-dibromo-4-methoxybenzoyl) peroxide, there was scatter of results but a definite indication that x decreases as the concentration of initiator is reduced while the concentration of monomer is held constant; the true value of k_1/k_2 could probably be found by an extrapolation procedure. From the limited results available, it is concluded that k_1/k_2 is at least 0.06 mole/l. at 60 °C. and at least 0.4 mole/l. at 80 °C.

Introduction of the methoxy group causes an increase in the stability of the benzoyloxy radical and a reduction in its reactivity towards styrene. The reduction in reactivity is thought to result from polar effects arising from the electron-releasing character of the methoxy group. Introduction of an electron-attracting substituent, such as bromine, in the meta position in the benzoyloxy radical should increase the reactivity of the radical towards styrene i.e. increase k_2 . The ratio k_1/k_2 is not much smaller for the bromine-containing radicals than for the benzoyloxy radical, so it can be concluded that k_1 also is increased to some extent. It is concluded tentatively therefore that introduction of an electronattracting group into the benzoyloxy radical increases its reactivity towards styrene and also reduces its stability.

J. T. thanks I. C. I. Ltd. (Dyestuffs Division) for study leave and L. T. thanks the INTERNATIONAL ROTARY CLUB of Italy for a Research Scholarship.