Hydrogen Atom Abstraction from Polystyrene by t-Butoxyl Radicals, Studied by Spin Trapping; Effect of Conformation on Reactivity

By **Norio Ohto, Etsuo Niki,*** and **Yoshio Kamiya,** Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan

A spin trapping technique was employed to examine the reactivity of polystyrene towards t-butoxyl radicals in solution at room temperature. with 2-methyl-2-nitrosopropane (MNP) and di-t-butyl peroxyoxalate (DBPO) as spin trapping reagent and t-butoxyl radical source, respectively. The polymer-derived radical produced by hydrogen atom abstraction was trapped by MNP: it was found that the polystyrene was selectively attacked at the tertiary positions. A comparison of the reactivities of polystyrene and anisole towards t-butoxyl radicals was made by direct integration of e.s.r. spectra of two spin adducts of radicals produced by hydrogen atom abstraction. The relative reactivity of polystyrene was found to increase with decreasing molecular weight and with dilution of the solution with benzene. These results suggest that the reactivity of polystyrene depends mainly on the nature of its coiled conformation in solution.

HYDROGEN atom abstraction from polymers by alkoxyl radicals is an important rate- and product-determining step in the oxidation of polymers by molecular oxygen. Polystyrene and polypropylene have been found to be less reactive toward t-butoxyl radicals than the corresponding monomers.[1,2] Although polystyrene has reactive tertiary benzylic hydrogen atoms, it is less reactive than polypropylene. The objective of the present work was to obtain additional data on the reactivity of polystyrene towards t-butoxyl radicals by a different technique, in order to elucidate reasons for the low reactivity of polystyrene toward radical attack. Previously, reactivities were determined from the results of competition between hydrogen atom abstraction and β-scission of the t-butoxyl radicals. In the present study a spin trapping technique was employed to determine the site and extent of radical attack on polystyrene. This technique has been developed recently for detection and identification of short-lived free radicals at concentrations too low for direct e.s.r. detection,[3-6] and has yielded quantitative information. Di-t-butyl peroxyoxalate (DBPO) and 2-methyl-2-nitrosopropane (MNP) were used as t-butoxyl radical source and spin trapping reagent, respectively.

EXPERIMENTAL

Materials.—Polystyrene with narrow molecular weight distribution was obtained from Pressure Chemical Co. DBPO was prepared and purified by the method of Bartlett *et al.*[7] MNP was prepared and purified by the method of Holman and Perkins.[8] Anisole was washed successively with 80% sulphuric acid and water, dried ($CaCl_2$), and distilled. Benzene was of the best quality available commercially.

Procedures.—DBPO was decomposed in the presence of substrate and MNP under vacuum in a sealed tube set in the e.s.r. cavity at 25 ± 1 °C. When the effect of molecular weight was studied, the molar ratio of polystyrene (RH) to anisole (AH) was varied, the concentration of polystyrene being kept constant at *ca.* 1M (in terms of monomer units). When the effect of dilution was examined, the molar ratio of polystyrene to anisole was maintained constant and the concentration of polystyrene was varied by addition of benzene.

---

[1] E. Niki and Y. Kamiya, *J. Org. Chem.*, 1973, **38**, 1403.

[2] E. Niki and Y. Kamiya, *J.C.S. Perkin II*, 1975, 1221.

[3] A. Mackor, Th. J. W. Wajer, Th. J. de Boer, and J. D. W. Voorst, *Tetrahedron Letters*, 1967, 385.

[4] G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 1968, **90**, 7141.

[5] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

[6] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.

[7] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **80**, 1762.

[8] R. J. Holman and M. J. Perkins, *J. Chem. Soc.* (*C*), 1970, 2195.

RESULTS AND DISCUSSION

Upon thermal decomposition, one molecule of DBPO produces two t-butoxyl radicals and molecules of carbon dioxide. The decomposition of DBPO in a solution of polystyrene in benzene with added MNP at room temperature gave two spin adducts, both of which exhibit triplet spectra. The hyperfine splitting constants (a_N) were 15.0 and 27.1 G, which were assigned to the tertiary alkyl spin adduct and the t-butoxyl spin adduct, respectively. No other spectra were observed during the reaction; we conclude that the tertiary hydrogen atoms of polystyrene are selectively removed by t-butoxyl radicals, and that little β-scission of the t-butoxyl radicals takes place under these conditions.

Reactions (1)—(6) represent the course of the decomposition of DBPO in the presence of polystyrene (RH), anisole (AH), and MNP (SA denotes a spin adduct). The reactivity of polystyrene relative to anisole towards t-butoxyl radicals can be calculated from equation (i).

$$\mathrm{DBPO} \longrightarrow 2\mathrm{Bu^tO\cdot} + 2\mathrm{CO_2} \quad (1)$$

$$\mathrm{Bu^tO\cdot} + \mathrm{RH} \xrightarrow{k_2} \mathrm{Bu^tOH} + \mathrm{R\cdot} \quad (2)$$

$$\mathrm{Bu^tO\cdot} + \mathrm{AH} \xrightarrow{k_3} \mathrm{Bu^tOH} + \mathrm{A\cdot} \quad (3)$$

$$\mathrm{R\cdot} + \mathrm{MNP} \longrightarrow \mathrm{R{-}SA}\ \ (\mathrm{II}) \quad (4)$$

$$\mathrm{A\cdot} + \mathrm{MNP} \longrightarrow \mathrm{A{-}SA}\ \ (\mathrm{III}) \quad (5)$$

$$\mathrm{Bu^tO\cdot} + \mathrm{MNP} \longrightarrow \mathrm{Bu^tO{-}SA}\ \ (\mathrm{I}) \quad (6)$$

$$[(\mathrm{II})]/[(\mathrm{III})] = k_2[\mathrm{RH}]/k_3[\mathrm{AH}] \quad (\mathrm{i})$$

A complication in the above procedure is that the spin adduct (I) undergoes cleavage to give t-butyl nitrite and t-butyl radicals [reaction (7)], which are trapped exclusively by MNP [reaction (8)], and the e.s.r. spectra of the t-butyl spin adduct and the spin adduct (II) are completely overlapped. The rate of fragmentation of the spin adduct (I) was measured in the absence of polystyrene and anisole so that a suitable correction could be made to the observed spectra.

$$(\mathrm{I}) \xrightarrow{k_4} \mathrm{Bu^t\cdot} + \mathrm{Bu^tONO} \quad (7)$$

$$\mathrm{Bu^t\cdot} + \mathrm{MNP} \longrightarrow \mathrm{Bu^t{-}SA}\ \ (\mathrm{IV}) \quad (8)$$

$$\mathrm{d}[(\mathrm{IV})]/\mathrm{d}t = k_4[(\mathrm{I})] \quad (\mathrm{ii})$$

The plot of $[(\mathrm{IV})]_t - [(\mathrm{IV})]_0$ against $\int_0^t [(\mathrm{I})]\mathrm{d}t$ (evaluated graphically) gave a straight line and the value of k_4 was calculated from the slope as 1.28×10^{-4} s^{-1} at 25 °C. This rate constant agrees well with the value (1.0×10^{-4}) calculated from the Arrhenius parameter determined by Perkins and Roberts.[9] Subtraction of $k_4 \int_0^t [(\mathrm{I})]\mathrm{d}t$ from the observed e.s.r. spectra of (II) gives the corrected value of [(II)]. In the presence of polystyrene and anisole, the relative reactivity can be calculated from equation (i) by using the corrected value of [(II)].

As shown in Figure 1, the plots of the left hand of equation (i) against [RH]/[AH] give a satisfactory straight line. The reactivities of polystyrene relative to anisole towards t-butoxyl radicals are summarized in the Table. Although the viscosity of the solution becomes higher with increasing molecular weight of polystyrene, it has been found [2] that the high macroscopic viscosity has little effect on the reactivities of simple hydrocarbons such as cumene toward t-butoxyl radicals.[2] Therefore the rate constant k_3 may be assumed to be constant, and the change in k_2/k_3 can be ascribed to change in k_2. Thus the Table shows that the relative reactivity of polystyrene decreases with increasing molecular weight, in agreement with the results obtained previously.[2]

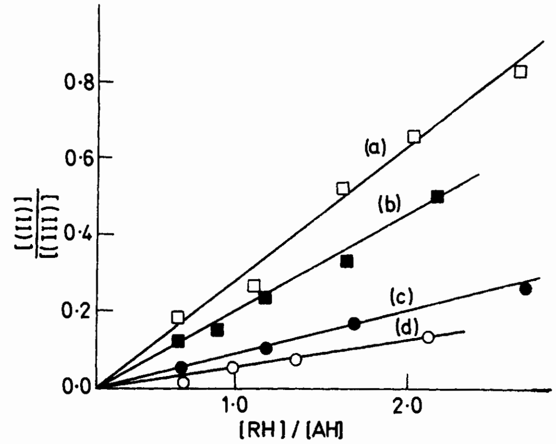

FIGURE 1 Plots of corrected [(II)]/[(III)] against [RH]/[AH] at various mol. wt. values: (a) 2 200, (b) 4 000, (c) 20 400, (d) 670 000

Effect of molecular weight on the reactivity of polystyrene relative to anisole towards t-butoxyl radicals at 25 °C in benzene

Mol. wt.	M_w/M_n	k_2/k_3 [a]
2 200	1.10	0.320
4 000	1.10	0.243
10 000	1.06	0.198
20 400	1.06	0.138
110 000	1.06	0.128
390 000	1.10	0.124
670 000	1.15	0.110

[a] Polystyrene concentrations expressed in mol l^{-1} in terms of monomer units.

In good solvents, the coiled configuration of polystyrene expands more than in poor solvents and it has been found [2] that the reactivity of polystyrene towards t-butoxyl radicals is higher in good solvents than in poor solvents.[2] This finding led us to examine the effect of dilution by benzene on the reactivity of polystyrene at room temperature. Values of k_2/k_3 were

---

[9] M. J. Perkins and B. P. Roberts, *J.C.S. Chem. Comm.*, 1973, 173.

calculated directly from equation (i) at several polystyrene concentrations. The molar ratio of polystyrene to anisole was kept constant. As shown in Figure 2, k_2/k_3 was found not to vary appreciably over the concentration range 0.2—1M, but it increased markedly at polystyrene concentrations below 0.2M. In this experiment, k_3 may be assumed to be constant; thus k_2 increases with dilution at low concentrations. Metz and Mesrobian [10] ascribed the low oxidizability of polystyrene to conformations that hinder the attainment of coplanarity of the developing *p*-orbital at the site of radical attack with π-electrons of the aromatic ring. However, this cannot be the sole reason for the low reactivity of polystyrene, since, as pointed out previously,[1] polystyrene is much less reactive than t-pentylbenzene.

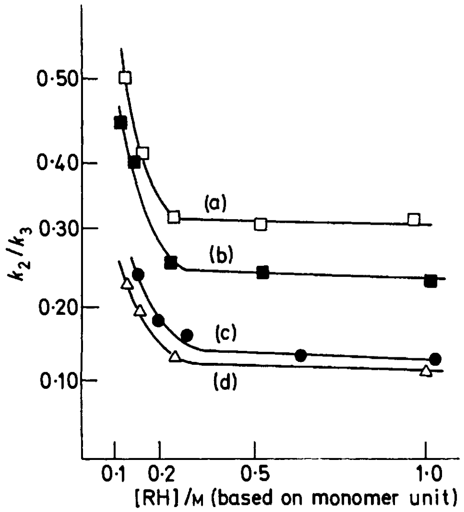

FIGURE 2 Plots of k_2/k_3 *vs.* [RH] at various mol. wt. values: (a) 2 200, (b) 4 000, (c) 20 400, (d) 110 000

On the other hand, the tertiary hydrogen atoms of 2,4-dimethyl- and 2,2,4-trimethyl-pentane are difficult to abstract because they are shielded from radical attack.[11] This suggests that the reactivity of tertiary hydrogen atoms of polystyrene is lowered by steric hindrance to approach of the attacking radical by the substituents on alternate carbon atoms.

The effects of molecular weight and solvent [2] suggest that chain conformation is another important factor. t-Butoxyl radicals probably cannot penetrate into a random coil of polystyrene, and the fraction of accessible tertiary hydrogen atoms will decrease with increasing molecular weight of polystyrene. However, total reactivity per polymer molecule increases with increasing molecular weight (Figure 3).

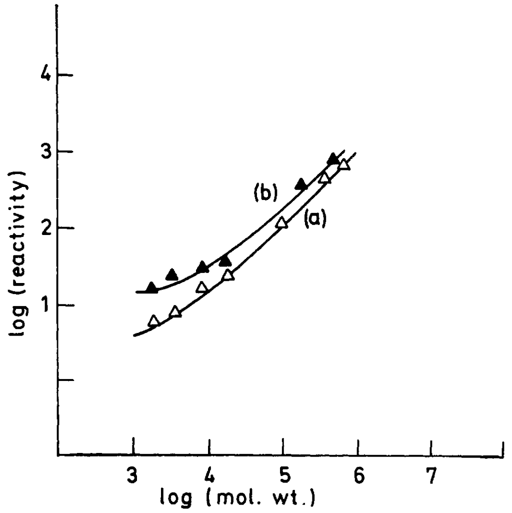

FIGURE 3 Plots of log (relative reactivity) of polystyrene per molecule against logarithm (mol. wt.): (a) this work; (b) ref. 2

In conclusion, the low reactivity of polystyrene may be ascribed to the steric inhibition of resonance, shielding from radical attack, and the presence of coiled conformations.

[6/1543 *Received*, 6*th August*, 1976]

---

[10] D. J. Metz and R. B. Mesrobian, *J. Polymer Sci.*, 1955, **16**, 345.

[11] G. A. Russell, in ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, ch. 7.