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SHORT COMMUNICATIONS

THE REACTIVITIES OF α-METHYLSTILBENE AND α,β-DIMETHYLSTILBENE TOWARDS THE BENZOYLOXY RADICAL

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ABSTRACT

The reactivities of the E isomers of α-methylstilbene (1,2-diphenylpropene) and α,β-dimethylstilbene (2,3-diphenylbut-2-ene) towards the benzoyloxy radical have been compared by procedures involving the analyses of the end-groups in polymers of methyl methacrylate, prepared using benzoyl peroxide as initiator in the presence of one of the stilbene-like compounds. Introduction of the methyl groups into stilbene causes marked reduction in reactivity towards the benzoyloxy radical; the results can be explained in terms of steric effects.

INTRODUCTION

The E isomer of 1,2-diphenylpropene (α-methylstilbene) (MSTL) is about 28 times as reactive as methyl methacrylate (MMA) in capturing the benzoyloxy radical at 60°C but it is less reactive than the E isomer of stilbene (STL) by a factor approaching two (1). This difference between STL and MSTL has been attributed to a steric effect; attachment of the radical to the carbon atom carrying both methyl and phenyl groups is regarded as seriously impeded. This explanation is now tested by studying the reaction of the E isomer of 2,3-diphenylbut-2-ene (α,β-dimethylstilbene) (DMSTL) with the benzoyloxy radical; for this substance, both ends of the olefinic bond could be regarded as shielded so that the overall reactivity might be quite low.

The reactivities of unsaturated substances towards the radical $C_6H_5.CO.O.$ can be examined through experiments in which benzoyl peroxide (BPO) is used to initiate polymerizations of a monomer, typically MMA, containing the substance under consideration. One method of working depends upon determination of the relative numbers of benzoate and phenyl end-groups derived from the initiator; the necessary end-group analyses can be performed if the BPO is labelled with carbon-14 in the carbonyl groups and with tritium in the rings ($^{14}C,^{3}H$-BPO) (1). The procedure leads to comparison of the rate constant for the addition of the benzoyloxy radical to an unsaturated substance with the rate constant for the decarboxylation of the radical. An alternative method involves use of BPO enriched with carbon-13 at the carbonyl sites (^{13}C-BPO) to initiate the polymerizations, followed by examination of the benzoate end-groups in the polymers by ^{13}C-NMR (2). The procedure allows direct comparison of the rate constants for the additions of the benzoyloxy radical to MMA and the unsaturated substance. Supplementary evidence on the reactivities of unsaturated substances towards aroyloxy radicals can be obtained by using p.fluorobenzoyl peroxide (FBPO) as initiator for polymerizations of, say, MMA containing the substances under investigation and then studying the p.fluorobenzoate end-groups by ^{19}F-NMR (3).

The reactivity of DMSTL has been assessed by the three methods involving respectively $^{14}C,^{3}H$-BPO, ^{13}C-BPO and FBPO. The results already published (1) for MSTL were obtained with $^{14}C,^{3}H$-BPO; they have been supplemented by application of the two other procedures.

EXPERIMENTAL

Most of the materials have been specified already (1). DMSTL was prepared by a modification of the method of Brasen et al. (4) in which 1-chloro-1-phenylethane was reacted with an excess of lithium diisopropylamide in dry tetrahydrofuran. After work-up, the resulting mixture of hydrocarbons was equilibrated with methanesulphonic acid and then with iodine, both in refluxing toluene. From the resulting mixture of two compounds, the E isomer crystallized and was purified by chromatography and by recrystallization from methanol (m.pt. 110-2°C; lit. value for the E isomer, 107°C).

Polymerizations were performed with toluene as diluent under air-free conditions at 60°C and were monitored dilatometrically; conversions were restricted to 8%. Polymers were recovered by precipitation in methanol and purified by reprecipitations. Radioactivities were measured by scintillation counting of solutions, using an LKB 'Spectral' 1219 Liquid Scintillation Counter (1). ^{13}C-NMR spectra were recorded on a BRUKER WH400 spectrometer operating at 100 MHz and ^{19}F-NMR spectra on a JEOL FX100 instrument operating at 93.7MHz.

RESULTS

For polymerizations initiated by ^{14}C,^{3}H-BPO, the values of [MMA] were 3.15 mol dm^{-3} for reactions nos. 1, 2 and 3 and 2.65 mol dm^{-3} for reaction no. 4; the corresponding values of $10^2 \times$ [DMSTL] were 8.32, 5.38, 1.70 and 10.90. For polymers 1, 2, 3 and 4, the values of (^{3}H-activity)/(^{14}C-activity) were 2.56, 2.52, 2.88 and 2.97 respectively; for the peroxide, the ratio of activities was 1.35.

Use was made of the relationships (1)

$$x = \frac{^{14}\text{C-activity of polymer}}{^{14}\text{C-activity of peroxide}} \times \frac{^{3}\text{H-activity of peroxide}}{^{3}\text{H-activity of polymer}}$$

$$\frac{x}{(1-x)\,[\text{MMA}]} = \frac{k_2}{k_1} + \frac{k_2'\,[\text{DMSTL}]}{k_1\,[\text{MMA}]}$$

where k_1 is the rate constant for decarboxylation of the benzoyloxy radical and k_2 and k_2' are the rate constants for its attachment to MMA and DMSTL respectively; k_2/k_1 is known to be 0.31 dm^3 mol^{-1}. There is some scatter of the points in Figure 1, largely because of great sensitivity to errors in the determination of x from four measurements of radioactivity. The line has been drawn as a result of a least squares analysis; the error bars correspond to ±5% uncertainty in the values of x. From the slope of the line, k_2'/k_1 is found to 0.75 dm^3 mol^{-1} so that k_2'/k_2 is 2.4.

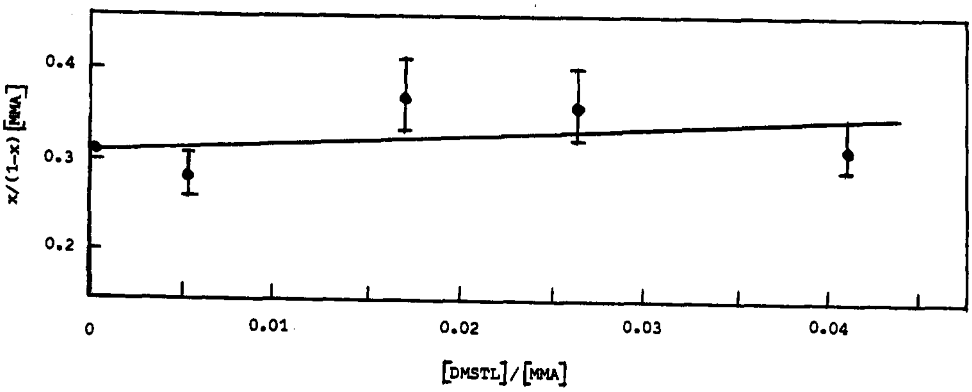

Figure 1. Plot of x/(1-x)[MMA] vs. [DMSTL]/[MMA] (see text).
x/(1-x) = (no. of benzoate end-groups)/(no. of phenyl end-groups).

Figure 2 shows part of the 100MHz ^{13}C-NMR spectrum of a polymer of MMA prepared using ^{13}C-BPO as initiator in the presence of MSTL; $10^2 \times$[MSTL]/[MMA] was 2.78. Benzoate groups attached to MMA units give rise to a pair of peaks between 165.5 and 166.5ppm (2), clearly visible in Figure 2. The prominent additional signals in the spectrum must be attributed to initiator fragments joined to units derived from MSTL. Integration of the spectrum and use of the relationship

$$\frac{\text{area for } C_6H_5.CO.O.MSTL\text{- peaks}}{\text{area for } C_6H_5.CO.O.MMA\text{- peaks}} = \frac{k_2''[MSTL]}{k_2[MMA]}$$

where the rate constant k_2'' refers to the addition of $C_6H_5.CO.O.$ to MSTL, leads to a value of 37 for k_2''/k_2. The spectrum of a polymer prepared with ^{13}C-BPO from a system in which $10^2 \times [DMSTL]/[MMA]$ was 3.26 showed signals due to benzoate groups adjacent to MMA units but none which could be assigned to the initiator fragments joined to units derived from DMSTL. Evidently k_2'/k_2 is much smaller than k_2''/k_2.

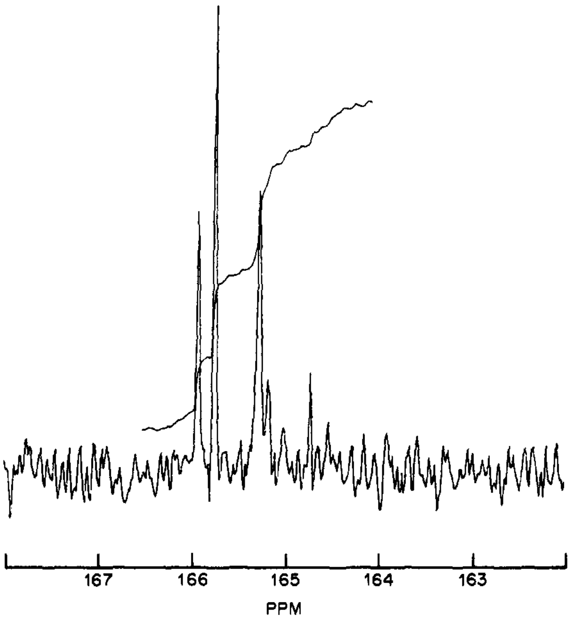

Figure 2. Part of the 100MHz ^{13}C-NMR spectrum of a polymer of MMA prepared using ^{13}C-BPO in the presence of MSTL.

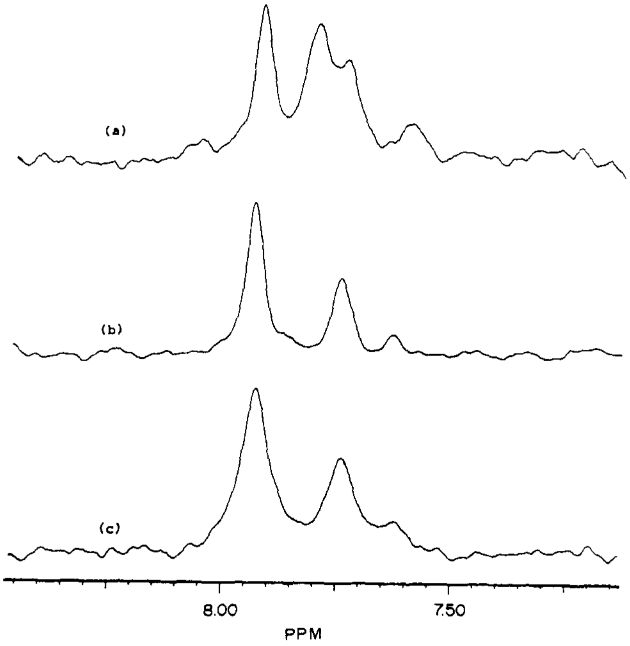

Figure 3. Parts of the 93.7MHz ^{19}F-NMR spectra of polymers of MMA prepared using FBPO (a) in the presence of MSTL (polymer 5) (b) in the presence of DMSTL (polymer 6) (c) without additive (polymer 7).

The ^{19}F-NMR spectra in Figure 3 refer to polymers of MMA prepared at 60°C using FBPO as initiator. Polymers 5 and 6 were obtained from systems in which $10^2 \times [MSTL]/[MMA]$ and $10^2 \times [DMSTL]/[MMA]$ were 3.17 and 2.20 respectively; polymer 7 was derived from MMA and FBPO without additive. The marked difference between the spectra for polymer 5 and 7 shows that the former must contain an appreciable proportion of benzoate end-groups attached to units derived from MSTL and that reaction between the p.fluorobenzoyloxy radical and MSTL occurs readily; on the other hand, the close similarity between the spectra for polymers 6 and 7 shows that the former polymer contains few benzoate end-groups attached to units formed from DMSTL.

DISCUSSION

The results obtained with ^{13}C-BPO confirm that MSTL is rather reactive towards the benzoyloxy radical and that, even at quite low concentrations, it can compete effectively with MMA for the capture of the radical. There is poor agreement between the value of k_2''/k_2 reported here and that found previously (1) by the use of ^{14}C,^{3}H-BPO but there is no doubt that, although MSTL is quite reactive, it is appreciably less so than STL with respect to the benzoyloxy radical. Both procedures show that MSTL is considerably more reactive than DMSTL towards the radical; a large difference is found also for the reactivities towards the p.fluorobenzoyloxy radical.

It has been shown (5) that, as expected, the benzoyloxy radical adds to styrene (STY) mainly at the methylene group but that the alternative of head-addition occurs in about 5% of the interactions. Attachment of the radical to STL can be regarded as head-addition; even allowing for the presence of two sites of equal reactivity in the molecule of STL, the rate constant for head-addition to STL is several times larger than that for tail-addition to STY. Radical-trapping experiments (6,7) indicated that at 60°C about 7% of the attachments of the benzoyloxy radical to MMA occur at the head of the molecule. This conclusion seems to con flict with the results of examination by ^{13}C-NMR of polyMMA made using ^{13}C-BPO (2); there was no evidence for the presence of end-groups $C_6H_5.CO.O.C(CH_3)(COOCH_3).CH_2-$.

It appears that the benzoyloxy radical can become attached to an olefinic carbon atom carrying a phenyl group, surprisingly readily so for STL-like compounds; the attachment is impeded if the carbon atom carries two groups viz. CH_3 and CH_3COO in the case of MMA and C_6H_5 and CH_3 in the cases of MSTL and DMSTL. Both olefinic carbon atoms in DMSTL are doubly substituted and so the overall reactivity is quite low.

Further work is in progress concerning steric effects in the reactions of initiating radicals with unsaturated substances; it is expected to give further information on the details of the initiating processes in radical polymerizations.

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