

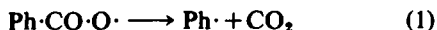
## SOME HYDROGEN ABSTRACTIONS INVOLVING THE BENZOYLOXY RADICAL

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**Abstract**—The reactivities of triphenylmethane and various penta-arylethanes towards hydrogen abstraction by the benzyloxy radical are compared. The procedure involved study of the effects of these hydrocarbons upon the yields of carbon dioxide during the decomposition in benzene of benzoyl peroxide suitably labelled with carbon-14. Triphenylmethane is less reactive than pentaphenylethane towards the benzyloxy radical but the reactivity difference is less than might have been predicted from the behaviour of the hydrocarbons with the polystyrene radical. The reactivities of the penta-arylethanes are correlated with the Taft  $\sigma^*$  constants for the substituents.

Various methods<sup>1-4</sup> involving tracer techniques have been used to compare the reactivities of olefins towards benzyloxy radical addition. The present paper is concerned with the adaption of one of these methods,<sup>3,4</sup> to studies of the relative reactivities of certain substances in hydrogen abstraction reactions involving this radical. The ratio of the velocity constants for the reactions



is determined; SH represents a hydrogen donor.

When benzoyl peroxide decomposes in very dilute solutions in benzene at 60°, almost all the derived benzyloxy radicals dissociate to give CO<sub>2</sub>.<sup>5</sup> If the solution contains a substance which is reactive towards the benzyloxy radical, the yield of CO<sub>2</sub> is depressed and the equation

$$W^*/W = 1 + k_2s/k_1 \quad (3)$$

is satisfied,  $W^*$  being the weight of CO<sub>2</sub> produced in pure benzene and  $W$  being the weight produced in a similar experiment with the additive at a concentration  $s$ . The additives used in this work were: pentaphenylethane, 1,1,1,2-tetraphenyl-2-*p*-tolylethane, 1,1,1-triphenyl-2,2-di-*p*-tolylethane, 1,1,1,2-tetraphenyl-2-*p*-anisylethane, 1,1,1-triphenyl-2,2-di-*p*-anisylethane and triphenylmethane.

Derivation of equation (3) assumes that the additive does not affect the rate of decomposition of the peroxide. One method for checking this assumption is to measure also the yields of benzoic acid. If the scheme is valid, the sum of the molar yields of CO<sub>2</sub> and benzoic acid should be independent of the nature and concentration of the additive.

### RESULTS

Fig 1 indicates how CO<sub>2</sub> production from benzoyl peroxide is affected by 1,1,1-triphenyl-2,2-di-*p*-anisylethane and by pentaphenylethane and how equation (3) is satisfied; the equation is satisfied also for decompositions in the presence of triphenylmethane, 1,1,1,2-tetraphenyl-2-*p*-tolylethane, 1,1,1-triphenyl-2,2-di-*p*-tolylethane and 1,1,1,2-tetraphenyl-2-*p*-anisylethane. The Table shows the values of  $k_2/k_1$  deduced from the slopes of lines such as those in Fig 1. Triphenylmethane was used at concentrations up to 0.82 mole/l; the corresponding value of  $k_2/k_1$  was considerably less than those for the various penta-arylethanes.

Isotope dilution analyses for benzoic acid were also performed. Results for decompositions in the presence of 1,1,1-triphenyl-2,2-di-*p*-anisylethane have been used to construct Fig 2. It can be seen that the sum of the numbers of moles of CO<sub>2</sub> and benzoic acid is, within experimental error, independent of the concentration of the additive; similar results were found for the other additives.

### DISCUSSION

The results presented in Fig 2 confirm that reduction in the yield of CO<sub>2</sub> brought about by the additive is balanced by an increase in the yield of benzoic acid. It is clear therefore that the rate of production of benzyloxy radicals is unaffected by the presence of the additive and that the radicals either dissociate to give CO<sub>2</sub> or abstract hydrogen to produce benzoic acid. The values of  $k_2/k_1$  deduced by application of equation (3) may therefore be taken as reliable measures of the reactivities of the various hydrocarbons towards the benzyloxy radical.

Schemes based on the Hammett or similar correlation have been used<sup>6</sup> to assess the effects of substituents upon the relative reactivities of series of compounds towards radicals. In the present

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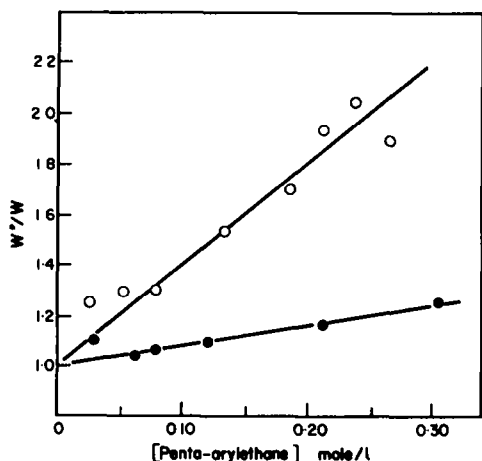


Fig. 1. Effect of penta-arylethanes upon the production of  $\text{CO}_2$  from benzoyl peroxide in benzene at  $60^\circ$ . Initial weight of peroxide = 1 mg. Initial concn. of peroxide = 0.50 g/l.  $W^*$  = weight of  $\text{CO}_2$  produced in absence of additive.  $W$  = weight of  $\text{CO}_2$  produced in presence of additive ● = pentaphenylethane ○ = 1,1,1-triphenyl-2,2-di-*p*-anisylethane.

Table 1. Relative reactivities towards the benzoyloxy radical and Taft substituent constants

Compound	$k_2/k_1$ mole $^{-1}$ h $^{+1}$	$\sigma^*$
pentaphenylethane	0.79	0.00
1,1,1,2-tetraphenyl-2- <i>p</i> -tolylethane	0.75	-0.10
1,1,1-triphenyl-2,2-di- <i>p</i> -tolylethane	0.69	-0.20
1,1,1,2-tetraphenyl-2- <i>p</i> -anisylethane	1.69	+0.64
1,1,1-triphenyl-2,2-di- <i>p</i> -anisylethane	4.00	+1.28
triphenylmethane	0.05	—

Errors in  $k_2/k_1$  are considered to lie between 5% and 8% for the penta-arylethanes and to be about 15% for triphenylmethane.

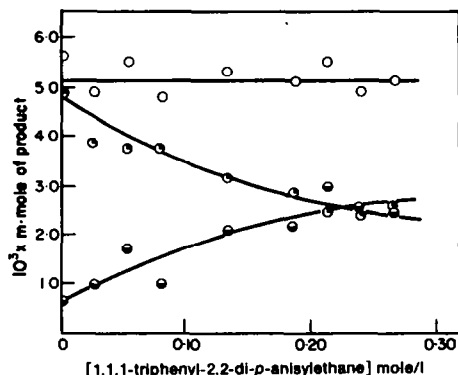


Fig. 2. Yields of benzoic acid and carbon dioxide in experiments involving 1,1,1-triphenyl-2,2-di-*p*-anisylethane and referred to in Fig. 1. ○ = yield of  $\text{CO}_2$ , ● = yield of benzoic acid ○ = combined yields of  $\text{CO}_2$  and benzoic acid.

work, it was found that the reactivities of the penta-arylethanes towards the benzoyloxy radical correlated well with the Taft  $\sigma^*$  constants<sup>10</sup> for the substituent groups. The  $\sigma^*$  value for a substituent X is often taken<sup>11</sup> as  $\sigma^*$  for  $\text{X-CH}_2$  and this procedure has been followed. Data for this correlation of  $\sigma^*$  values<sup>12</sup> with reactivities are given in the Table; for di-*para* substitution, the algebraic sum of the  $\sigma^*$  values was taken. The plot of  $\log k_2/k_1$  against  $\sigma^*$  (Fig 3) contains only five points but it is reasonably linear and leads to  $\rho^* = +0.51$ . This positive value for  $\rho^*$  indicates that the abstraction is favoured by electron withdrawal. This result contrasts with that for the addition of the benzoyloxy radical to unsaturated compounds where withdrawal of electrons from the double bond results in low reactivity.<sup>1</sup> The reactivities of the penta-arylethanes towards the benzoyloxy radical correlate much better with Taft  $\sigma^*$  values for the substituents than with Hammett  $\sigma$  values. This finding suggests that resonance effects of the substituents are likely to be only small in the transition state for the hydrogen abstraction since the  $\sigma^*$  constants are measures of inductive effects alone whereas the  $\sigma$  constants include both resonance and inductive effects. The labile hydrogen atom in a penta-arylethane is most probably that directly attached to carbon-2 of the ethane so that the present results probably mean that the two benzene rings also attached to this carbon atom cannot achieve a coplanar configuration which would lead to resonance interaction of the substituents with the developing radical centre on this carbon atom.

In the treatment of radical reactivity developed by Bamford *et al.*<sup>13,14</sup> the reactions of radicals with hydrocarbons are regarded as processes in which polar effects are absent. The treatment then predicts that the value of  $k/k'$  (where  $k$  and  $k'$  are the velocity constants for the reaction of a

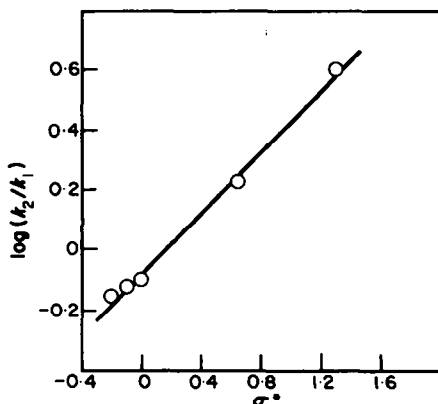


Fig. 3. Correlation between the relative reactivities of penta-arylethanes towards the benzoyloxy radical and the Taft  $\sigma^*$  constants for the substituent groups.

radical with two particular hydrocarbons) should be independent of the nature of the radical. Transfer constants<sup>15</sup> for pentaphenylethane and triphenylmethane in the polymerization of styrene at 60° indicate that the former is nearly 6000 times more reactive than the latter towards the polystyrene radical; for the case of the benzoyloxy radical, however, the factor is only 16. The present results indicate that polar effects are significant in the reactions of the benzoyloxy radical so that deviations from the scheme<sup>13,14</sup> are to be expected. Poor agreement between the predictions of the scheme and the reactivities of the benzoyloxy radical towards unsaturated substances has already been noted.<sup>1</sup>

#### EXPERIMENTAL

Procedures are similar to those described<sup>3-5</sup> with only minor modifications. Materials were assayed for carbon-14 by gas-counting.

Reaction mixtures containing <sup>14</sup>C-benzoyl peroxide were kept for 96 h at 60° in completely air free sealed tubes. All the reaction mixtures contained initially 1 mg of benzoyl peroxide at a concentration of 0.50 g/l in benzene at 60°. CO<sub>2</sub> and benzoic acid produced during decompositions were determined by isotope dilution analysis.

Pentaphenylethane was prepared by two procedures described by Bachmann. In the first,<sup>6</sup> a mixture of triphenylmethyl bromide and diphenylmethyl bromide in benzene was treated with Cu powder; in the second,<sup>7</sup> the Grignard reagent from triphenylmethyl bromide was prepared and made to react with diphenylmethyl bromide. The preparations gave products with identical IR and NMR spectra.

The preparations of the substituted penta-arylethanes can be illustrated by the case of 1,1,1,2-tetraphenyl-2-*p*-anisylethane. The Grignard reagent from bromobenzene was caused to react with *p*-anisaldehyde to form phenyl-*p*-anisyl carbinol which was converted to phenyl-*p*-anisylmethyl chloride by reaction with HCl gas. This product was made to react with triphenylmethyl sodium (formed

from triphenylmethyl chloride and sodium amalgam) to give 1,1,1,2-tetraphenyl-2-*p*-anisylethane. Other penta-arylethanes were prepared by this method using triphenylmethyl sodium and the appropriate substituted diarylmethyl chloride. Triphenylmethane was a commercial product, recrystallised twice from EtOH. The penta-aryl ethanes were characterised chiefly by their NMR and IR spectra. M.p. is not a good criterion of purity for these compounds due to thermal decomposition, especially in air. However, m.ps performed under vacuum were in agreement with, or several degrees higher than, those reported in the literature.<sup>7</sup>

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