The Effect of Additives on the Thermal Decomposition of Benzoyl Peroxide in Benzene

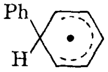
By G. R. CHALFONT, D. H. HEY, KATHERINE S. Y. LIANG, and M. J. PERKINS
(*Department of Chemistry, King's College, London*)

THE thermal decomposition of benzoyl peroxide in benzene[1] generates benzoyloxy-, and thence phenyl, radicals. The latter react with the solvent to form phenylcyclohexadienyl radicals (I). The ensuing radical reactions lead to a complex mixture of products from which biphenyl and benzoic acid can be isolated, each in yields of up to *ca.* 0·5 mole/mole peroxide. Much of the remaining product is a mixture of involatile substances, arising initially from dimerisation reactions of the radical (I).

Substantial modification of the product mixture is observed when the reaction proceeds in the presence of various additives. Thus small quantities of aromatic nitro-compounds result in yields of biphenyl and benzoic acid of as much as 0·9 mole/mole peroxide, with correspondingly less involatile product.[2] It has been suggested that the nitro-compounds accept a hydrogen atom from the radical (I), and transfer it to a benzoyloxy-radical, or to a benzoyl peroxide molecule.[3] Alternatively, an electron-transfer mechanism has been invoked, and supported by observation of similar effects with other electron acceptors as additives.[4]

Evidence is now presented consonant with a further, tentative, hydrogen-transfer mechanism outlined below. The suggested hydrogen acceptor is a nitroxide radical.

$$\begin{tikzcd} PhNO_2\ (II) \arrow[d] & \\ PhNO\ (III) \arrow[d, "Ph\cdot"] & PhNH{\cdot}OH\ (IV) \arrow[l] \\ Ph_2NO\cdot & \end{tikzcd}$$



(I)

$$(PhCO_2)_2 \rightarrow 2PhCO_2\cdot \qquad \text{(i)}$$

$$PhCO_2\cdot \rightarrow Ph\cdot + CO_2 \qquad \text{(ii)}$$

$$Ph\cdot + PhH \rightarrow \text{(I)} \qquad \text{(iii)}$$

$$\text{(I)} + Ph_2NO\cdot \rightarrow Ph_2 + Ph_2N{\cdot}OH\ \text{(V)} \qquad \text{(iv)}$$

$$\text{(V)} + (PhCO_2)_2 \rightarrow PhCO_2\cdot + PhCO_2H + Ph_2NO\cdot \qquad \text{(v)}$$

$$PhCO_2\cdot + Ph_2N{\cdot}OH \rightarrow Ph_2NO\cdot + PhCO_2H \qquad \text{(vi)}$$

The key to this scheme resides in the known stability of nitroxide radicals. A relatively high stationary-state concentration of these radicals may effectively oxidise phenylcyclohexadienyl radicals [eq. (iv)] before the latter may dimerise or disproportionate. There have been several recent examples of arylation reactions in which a stable radical intermediate participates in a similar fashion.[5,6] Also significant is the postulated induced decomposition of benzoyl peroxide by diphenylhydroxylamine [eq. (v)]. This finds some analogy in the reaction of benzoyl peroxide with dimethylaniline.[7]

Although it is a radical-propagating process, step (vi) must be regarded as the chain-ending reaction in the above scheme. This is because diphenyl nitroxide enters the induced (or chain) component of the reaction only *after* a molecule of peroxide has decomposed.

The following observations are in agreement with the scheme. [Where quantities of additive are given they refer to the reaction of benzoyl peroxide (1 g.) with benzene (100 ml.) at 80°; the data are summarized in the Table.]

(a) For the additives nitrobenzene (II), nitrosobenzene (III), phenylhydroxylamine (IV), and diphenylhydroxylamine (V), all of which give pronounced increases in yield of benzoic acid and biphenyl, electron spin resonance (e.s.r.) spectrometry indicates the presence of a stable radical, probably a nitroxide (a_N *ca.* 10 gauss). In the case of additives (III) and (V), proton splitting has been resolved, and is identical with that exhibited by diphenyl nitroxide. The implied addition of phenyl radicals to nitrosobenzene recalls other radical reactions of nitrosobenzene reported recently.[8] Conversion of (IV) into (III) during the reaction is demonstrated by optical spectrometry.

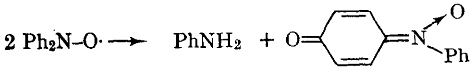
Two other effective additives for which similar schemes may be written are di-t-butyl nitroxide, and 2-methyl-2-nitrosopropane. In the latter case the e.s.r. spectrum of t-butyl phenyl nitroxide has been observed.

(b) An extremely rapid reaction occurs at room temperature between diphenylhydroxylamine and benzoyl peroxide in dilute benzene solution. The products are principally benzoic acid and diphenylnitroxide. There is no similarly rapid reaction between benzoyl peroxide and diphenyl nitroxide at these temperatures.

(c) To reach optimum yields of acid and biphenyl, as much as 300 mg. of nitrobenzene must be present. Less than 15 mg. of (III) or (IV) and *ca.* 20 mg. of (V) have comparable effect, but these compounds are destroyed during the reaction. On the other hand, in a reaction with 1 g. of nitrobenzene all but 30—40 mg. remains after complete decomposition of the peroxide. Allowing for some loss of nitrobenzene by phenylation, sufficient has been consumed to have been reduced to the effective quantity of, for instance, nitrosobenzene. Reduction of nitro-aromatics in radical reactions is well known.[9] A probable reducing agent here is the phenylcyclohexadienyl radical (I). It is possible that reduction of the nitro-compound is inhibited after the initial stages of the reaction by removal of phenylcyclohexadienyl radicals in reaction (iv). This seems consistent with the fact that the apparent first-order rate constant for the reaction increases with the quantity of added nitrobenzene up to the optimal 300 mg., but thereafter it is independent of the concentration of nitro-compound. There is no comparable limit to the rate of the nitrosobenzene-promoted reaction.

The results presented, together with unpublished observations on reactions in chlorobenzene,[10] suggest that the same intermediates are formed from nitrobenzene as are obtained in reactions of the other additives now discussed. This cannot, however, be regarded as proven.

The known disproportionation of diphenyl nitroxide[11] merits comment.



$$2\,Ph_2N\text{–}O\cdot \rightarrow PhNH_2 + O{=}C_6H_4{=}N(\rightarrow O)Ph$$

(VI)

Diphenylamine has been identified as a by-product of reactions with diphenylhydroxylamine as additive, and the N-oxide (VI) may be a strong electron-acceptor (see above[4]). Synthetic (VI) is indeed an effective additive, but the reaction mixtures once again give an e.s.r. signal suggestive of a stable nitroxide.

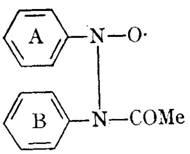
One further additive which is moderately effective is N-methyl-N-nitrosoaniline. In this case also, a relatively stable radical has been observed. The spectrum has a major nitrogen splitting (a_N *ca.* 12 gauss), but no fine structure has yet been resolved. It may be noted here that the spectrum of a stable radical (a_N 11·61 and 1·67 gauss) has been observed during the thermal decomposition in benzene of N-nitrosoacetanilide, another source of phenyl radicals.[12] This spectrum was assigned to the phenyldiazotate radical (Ph·N:N·O·). It now seems that a more conventional nitroxide structure [such as (VII)] derived from the reaction of the nitroso-group of nitrosoacetanilide, might constitute a defensible alternative. The recent assignment[12b] of the larger nitrogen coupling to the nitrogen originating as the nitroso-group is consistent with this alternative structure, and the hydrogen hyperfine couplings of phenyl (B) may well have been too small for detection.

TABLE

Yields of benzoic acid and biphenyl from the decomposition of 1 *g. of benzoyl peroxide in* 100 *ml. of benzene at* 80° *in the presence of additives**

Additive (mg.)	Yields (mole/mole peroxide) Benzoic acid	Biphenyl
Nil	0·22	0·36
$PhNO_2$ (100)	0·75	0·65
$PhNO_2$ (300)	0·93	0·83
PhNO (12)	0·92	0·86
PhNH·OH (7)	0·99	0·88
Ph_2N·OH (20)	0·96	0·78
PhN(NO)Me (100)	0·53	0·61

* Protection of the reaction mixture from atmospheric oxygen is unnecessary *provided that the solution is boiling.*



(VII)

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