HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS PART VIII.* THE DECOMPOSITION OF BENZOYL PEROXIDE IN HEXAFLUOROBENZENE

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Summary

The decomposition of benzoyl peroxide in hexafluorobenzene proceeds by a spontaneous first-order process accompanied by an induced decomposition showing 1.5-order dependence upon the concentration of the peroxide. The induced decomposition is associated with the formation of 2,2′,3,4,5,6-hexafluorobiphenyl and benzoic acid. 2,3,4,5,6-Pentafluorobiphenyl is the main product at all concentrations of peroxide; small amounts of other compounds are formed, together with a high-boiling residue probably containing isomeric dodecafluorotetrahydroquaterphenyls. The mechanism is discussed.

Introduction

The decomposition of benzoyl peroxide in hexafluorobenzene gives 2,3,4,5,6-pentafluorobiphenyl [2] together with some benzoic acid, hydrogen fluoride and a high-boiling residue. 2,2′,3,4,5,6-Hexafluorobiphenyl has been reported [3,4] as a product from the phenylation of hexafluorobenzene, whether by benzoyl peroxide or by pyrolysis of nitrobenzene. We have also reported in a preliminary way the formation of this compound during the thermolysis of benzoyl peroxide in hexafluorobenzene [5], and a mechanism for the arylation reaction which takes account of this finding and at the same time avoids the thermodynamically improbable reactions which are implied by strict analogy with the corresponding processes in benzene has been suggested [6]. We now report a detailed investigation of the kinetics and products of the reaction of benzoyl peroxide with hexafluorobenzene.

Results and discussion

Rate measurements were made at a number of initial concentrations of peroxide ($[P]_0$). Although the reaction showed strict first-order kinetics over

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* For Part VII, see ref. 1.

the first half-life, the derived rate coefficients varied with the peroxide concentration. Similar dependences have been found in a number of homolytic arylation reactions involving peroxides and have been interpreted as evidence of a contribution by a term of 1.5 order with respect to peroxide. Although the observed rate coefficient $k_{obs.}$ certainly gives a linear graph when plotted against $([P]_0^{1/2}$, this was not absolute proof of the kinetic order since similarly good lines could be obtained with several functions of $[P]_0^x (0 < x < 1)$.

In the presence of the inhibitor "Galvinoxyl", the observed rate constant fell and its variation with $[P_0]$ was not as dramatic as in the absence of inhibitor. The lowest value of $k_{obs.}$ was obtained at the lowest value of $[P]_0$, suggesting that induced decomposition or its kinetic equivalent was still occurring to a small extent. However, we took a value of $k_1 = 1.22 \times 10^{-5} \text{ s}^{-1}$ (*cf*. Table 1) from these results, and attempted to find the order of the induced decomposition. Since

$$-d[P]/dt = k_{obs.}[P] = k_1[P] + k_{induced}[P]^{1 + x} \tag{1}$$

$$k_{obs.} = k_1 + k_{induced}[P]^x \tag{2}$$

and so

$$k_{obs.} - k_1 = k_{induced}[P]^x \tag{3}$$

from which x may be found by plotting $\log_{10}(k_{obs.} - k_1)$ against $\log_{10}[P]_0$, without presupposing any particular reaction order. The results in Table 1 give a graph of slope 0.53 ± 0.09 and it was therefore assumed that the order of the induced decomposition is indeed 1.5.

Detailed calculation of the instantaneous rates of consumption of peroxide at each time interval [7] confirmed that the 1.5-order contribution took place throughout the entire kinetic study and was not an artefact arising from a higher order mechanism making a steadily changing contribution during the reaction. From these analyses, values of $k_1 = 1.22 \times 10^{-5} \text{ s}^{-1}$ and $k_{induced} = 1.52 \times 10^{-5} \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ were obtained. The probable error in both constants was $\pm 3\%$.

The results establish rigorously the contributions of reactions of first and 1.5 order, which are assigned to the primary and induced decomposition, respectively, of the peroxide. The contribution of the primary homolysis of the peroxide to the total reaction can be expressed by the parameter f defined by the equation [4]

$$f = 2(K[P]_0^{1/2} - \ln\{1 + K[P]_0^{1/2}\})/K^2[P]_0 \tag{4}$$

where $K = k_{induced}/k_1$. This factor is simply a kinetic artefact which arises solely from the relative extents to which spontaneous (primary) and induced processes take place. Since f measures the proportion of primary to total decomposition of peroxide, $(1 - f)$ should parallel the yields of benzoic acid and of hexafluorobiphenyl if these compounds arise from induced decomposition processes. Although their formation almost certainly arises from these processes and their relative yields alter proportionately to $(1 - f)$, it cannot

TABLE 1

Kinetics of thermolysis of benzoyl peroxide in hexafluorobenzene[a]

$[P]_0$/mol l^{-1}	[Galvinoxyl]/mol l^{-1}	$10^5 k_{obs.}$/s^{-1}	$10^5(k_{obs.}-k_1)$[b]	$\log_{10}(k_{obs.}-k_1)$	$\log_{10}[P]_0$
0.00081	0.000152	1.25	0.03	−6.523	−3.092
0.00106	0.00142	1.30	0.08	−6.097	−2.872
0.00133	0.000193	1.35	0.13	−5.865	−2.866
0.00163	0.000233	1.33	0.11	−5.872	−2.855
0.00940	0	1.37	0.15	−5.824	−2.027
0.03187	0	1.50	0.28	−5.553	−1.500
0.05200	0	1.56	0.33	−5.467	−1.284
0.08383	0	1.60	0.38	−5.420	−1.077
0.1087	0	1.67	0.45	−5.347	−0.963
0.1482	0	1.76	0.54	−5.268	−0.829
0.2118	0	1.92	0.70	−5.155	−0.674

[a] At 78.2 °C.
[b] Taking $k_1 = 1.22 \times 10^{-5}$ s^{-1}.

account for all the induced processes since whereas $(1 - f)$ ranges between 11% and 23%, the yields of benzoic acid and of hexafluorobiphenyl are only 5 - 10%.

Another possible sequence which fits the requirements of the kinetics is the formation of the ester σ_F—OBz (σ_F = PhC$_6$F$_6$), *i.e.*

$$\sigma_F^{\cdot} + Bz_2O_2 = \sigma_F\text{—OBz} + BzO\cdot \qquad (5)$$

This may well account for the remainder of the peroxide decomposed by induced processes. It has been pointed out that such tertiary esters would be expected to be attacked by hydrogen fluoride to replace benzoic acid consumed in the formation of biaryl from $\sigma_F^{\cdot}$ and to give, concomitantly, products such as PhC$_6$F$_7$(σ_F—F) [6]. The absence of large amounts of products containing benzoyloxy groups does not therefore vitiate the above proposal.
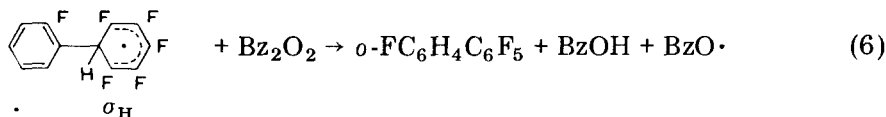
TABLE 2

Products of thermolysis of benzoyl peroxide in hexafluorobenzene[a]

| $[P]_0$/mol l^{-1}	0.0297	0.0500	0.0786	0.118	0.165
Reaction product (mol per mole peroxide consumed)					
2,3,4,5,6-Pentafluorobiphenyl	0.882	0.943	1.037	1.096	1.048
2,2′,3,4,5,6-Hexafluorobiphenyl	0.057	0.066	0.082	0.103	0.093
Benzoic acid	0.034	0.032	0.060	0.073	0.087
Pentafluorophenyl benzoate	0	0	0	0	0
Residue (as C$_{24}$H$_{10}$F$_{12}$)	0.540	0.482	0.363	0.296	0.273
$(1-f)$	0.118	0.144	0.183	0.209	0.236

[a] At 78.2 °C.

The rearrangement of the initially-formed intermediate $\sigma_F^{\cdot}$ to give the putative precursor $(\sigma_H^{\cdot})$ of 2,2′,3,4,5,6-hexafluorobiphenyl seems to involve a greater activation energy than its aromatisation through defluorination. A difference of about 3 kcal mol^{-1} accounts for the results of Fields and Meyerson, assuming that the aromatisation mechanisms are the same in both instances after $\sigma_F^{\cdot}$ has been generated [3].

$$\text{(structure } \sigma_H^{\cdot}) \quad + \text{ Bz}_2\text{O}_2 \rightarrow o\text{-FC}_6\text{H}_4\text{C}_6\text{F}_5 + \text{BzOH} + \text{BzO}\cdot \tag{6}$$

The only comparable rearrangement [9] appears to involve hydrogen and deuterium, and whilst exchange occurs readily in this system, it is not likely to have the profoundly different energetic contributions which would be expected for a rearrangement involving hydrogen and fluorine. There is no obvious route by which this exchange could be assisted. We have rejected a simple fluorination by some precursor of hydrogen fluoride since only the *ortho* atom is attacked; no 2,3,3′,4,5,6- or 2,3,4,4′,5,6-hexafluorobiphenyl have been detected although homolytic fluorination of the initially-formed pentafluorobiphenyl would be expected to give all three possible isomers. We therefore conclude that rearrangement of $\sigma_F^{\cdot}$ to $\sigma_H^{\cdot}$ must be the route by which 2,2′,3,4,5,6-hexafluorobiphenyl is formed.

We have reported earlier that aromatic carboxylic acids assist the formation of pentafluorobiphenyl in this reaction by providing a source of hydrogen to allow the defluorination of the intermediate $\sigma_F^{\cdot}$.

$$\sigma_F^{\cdot} + \text{BzOH} = \text{PhC}_6\text{F}_5 + \text{BzO}\cdot + \text{HF} \tag{7}$$
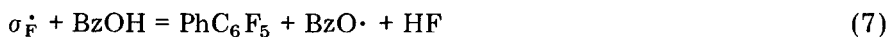
This appears to be a process of lower activation energy than the rearrangement since no 2,2′,3,4,5,6-hexafluorobiphenyl was formed in reactions in which improved yields of pentafluorobiphenyl were obtained by the addition of acids. Some of the benzoic acid formed concomitantly with the hexafluorobiphenyl in reaction (6) must be consumed by participating in reaction (7) in which a benzoyloxy radical is also formed. This may then undergo decarboxylation to give phenyl radicals or else attack other radicals or substrates, in just the same way as do benzoyloxy radicals derived from the parent peroxide. Possible other sources of benzoic acid to enable reaction (7) to proceed in the absence of added acids include reaction (6) and the attack of phenyl radicals upon benzoyl peroxide to give, ultimately, biphenyl-4-carboxylic acid [10].
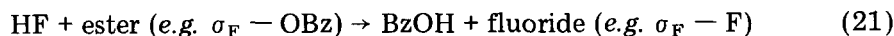
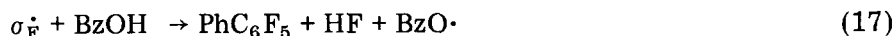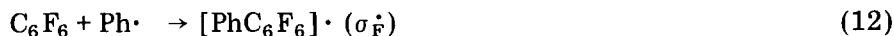There is no immediate reason why reaction (7) should be unique to the σ-intermediate. Other radicals which exist in the solution may similarly be capable of abstracting hydrogen from benzoic acid. There will not be a resultant loss of radicals, since an aroyloxy radical is generated as another is destroyed. The most obvious candidates for consideration in this context are the benzoyloxy radicals and phenyl radicals:

$$BzO\cdot \quad + BzOH \; = \; BzOH \; + \; BzO\cdot \tag{8}$$

$$Ph\cdot + BzOH = PhH + BzO\cdot \tag{9}$$
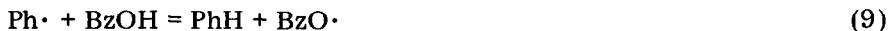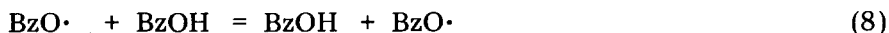
The reaction with benzoyloxy radicals is a simple exchange unless a foreign aroic acid is added; the reaction with phenyl radicals gives benzene. We have reported [2] that aromatic hydrocarbons are indeed formed in these reactions, and that they were derived from the peroxide. m-Toluyl peroxide (m-methyl-benzoyl peroxide) thus gave toluene, whereas benzene was found to be formed in the thermolysis of benzoyl peroxide. It therefore seems likely that hydrogen abstraction is occurring [reaction (9)] and that the aroic acid is the likely source of this hydrogen.

An assessment of the proposed mechanism

The main novelties of the mechanism which has been proposed for this reaction lie in the postulated functioning of benzoic acid as a defluorinating agent which allows the formation of pentafluorobiphenyl from the intermediate $\sigma_F^{\cdot}$ [reaction (7)] and the recognition that disproportionation is unlikely to be a significant source of the biaryl. This scheme, which includes some previously mentioned reactions, is set out fully below for clarity.

$$Bz_2O_2 \to 2BzO\cdot \tag{10}$$

$$BzO\cdot \; \to Ph\cdot + CO_2 \tag{11}$$

$$C_6F_6 + Ph\cdot \; \to [PhC_6F_6]\cdot (\sigma_F^{\cdot}) \tag{12}$$

$$C_6F_6 + BzO\cdot \to [BzOC_6F_6]\cdot (\sigma_F^{'\cdot}) \tag{13}$$

$$\sigma_F^{\cdot} \to \sigma_H^{\cdot} \tag{14}$$

$$\sigma_H^{\cdot} + Bz_2O_2 \; \to o\text{-}FC_6H_4C_6F_5 + BzOH + BzO\cdot \tag{15}$$

$$\sigma_F^{\cdot} + Bz_2O_2 \; \to \sigma_F - OBz + BzO\cdot \tag{16}$$

$$\sigma_F^{\cdot} + BzOH \; \to PhC_6F_5 + HF + BzO\cdot \tag{17}$$

$$Ph\cdot + BzOH \to PhH + BzO\cdot \tag{18}$$

$$2\sigma_F^{\cdot} \; \to \sigma_F - \sigma_F \tag{19}$$

$$2\sigma_F^{'\cdot} \; \to \sigma_F' - \sigma_F' \tag{20}$$

$$HF + ester \; (e.g. \; \sigma_F - OBz) \to BzOH + fluoride \; (e.g. \; \sigma_F - F) \tag{21}$$

The initiation reaction (10) is well known and needs no justification. The subsequent addition of radicals to the substrate is similarly proposed by analogy with aromatic hydrocarbon systems. The main driving force, here as with other aromatic systems, is the delocalisation of the unpaired electron over the cyclohexadienyl system to form a more stable radical. Of the reactions (14) - (16) comprising the induced decomposition of the peroxide by either $\sigma_F^{\cdot}$ or its rearrangement product, the processes (15) and (16) have exact parallels in the arylation of benzene by benzoyl peroxide. The rearrangement (14), unusual though it is, seems the simplest explanation of both

the hexafluorobiphenyl formed in the reaction and the maintenance of an induced decomposition of kinetic order 1.5 in conjunction with (16). The defluorination step (17) has two important consequences. It allows the formation of pentafluorobiphenyl by an energetically feasible route and it provides an additional route for the regeneration of benzoyloxy radicals. Secondly, there is no longer an upper limit of 2 mol of product per mole of peroxide expended, because in assessing the product yields and the kinetic form some components contribute more than once.

The termination processes (19) and (20) are those required for the kinetic form involving 1.5-order induced decomposition of the peroxide. Such termination reactions are not required exclusively; they need only represent the majority of termination processes for that section of the reaction proceeding by the induced mechanism. However, since this mechanism involves the formation of aroyloxy radicals which subsequently give aryl radicals and hence biaryl products, it is unlikely that one specific type of termination sequence is unique to a discrete part of the reaction. It therefore seems probable that most termination processes involved are of this type. However, reactions (22) and (23) are not excluded as minor contributors.

$$\sigma_H^{\cdot} + BzO\cdot \rightarrow o\text{-}FC_6H_4C_6F_5 + BzOH \tag{22}$$

$$\sigma_F^{\cdot} + BzO\cdot \rightarrow \sigma_F - OBz \tag{23}$$

The regeneration reaction (21) deserves especial mention. It provides a route for the recycling of a limited amount of benzoic acid through the reaction, until stopped by adventitious loss of hydrogen fluoride or of benzoic acid through processes such as (18) or by exhaustion of the ester residues. The requisite tertiary esters could arise either from further reactions of the $\sigma_F'\cdot$ formed in (13) or by processes such as (16). Since we detected no pentafluorophenyl benzoate which must arise if aroyloxylation of the substrate initiated by reaction (13) occurred, it is probable that all the esters necessary arise from radical—radical combination. One particular situation is important. The formation of σ_F—OBz is probably one of the major contributors in ester formation for it involves the interaction of two radicals, both present in quite high stationary concentrations. The particular reaction which this compound undergoes to generate benzoic acid, i.e.

$$\sigma_F - OBz + HF = \sigma_F - F + BzOH \tag{24}$$

also produces isomeric heptafluorodihydrobiphenyls. Since the biaryl arises from defluorination of the intermediate ($\sigma_F^{\cdot}$) which also gives hydrogen fluoride, this represents a sequence [(17), (16), (21)] in which the *effect* of disproportionation is achieved without the postulate of disproportionation itself. The distinction between this sequence and one-step disproportionation lies in the timing of the elementary reactions and in the competition possible with other processes. Disproportionation as a one-stage reaction requires (a) some transition state in which partial weakening of one C—F bond occurs and (b) that radical—radical combination to give the dimer does not proceed

exclusively. Since the two alternatives are kinetically equivalent (Rate = $k[\sigma_F^{\cdot}]^2$) and one of them has a lower activation energy than the other, a reaction between two radicals involving the abstraction of fluorine instead of direct pairing of electron spin is unlikely. In constrast, the abstraction of hydrogen from aromatic acids by a radical is apparently a general process in our system, for there is evidence that both aryl and σ-radicals do this. We have already discussed the formation of tertiary esters by reaction (16) and, to a small extent, reaction (23). The displacement of the benzoate function from the tertiary ester (σ_F—OBz) is a general reaction. Although such displacements may occur with other esters, the example of particular interest in this context is the reaction with σ_F—OBz.

Experimental

Hexafluorobenzene (I.S.C.) contained three impurities, two of which could be removed by treatment with concentrated sulphuric acid. The third impurity (*ca.* 0.1%) was unaffected by this treatment or by the thermolysis of benzoyl peroxide in such impure solvent, since its concentration was unaltered after reaction under our conditions. It appeared to be a polyfluorinated cyclohexane and, since it was not involved in the reaction and did not represent a major impurity, no further attempts were made to remove it. Benzoyl peroxide was purified by crystallisation three times from a chloroform/methanol mixture when, after lengthy drying under reduced pressure, it showed m.p. 105.5 °C and analysed iodimetrically as 99.9% pure.

The course of the reactions was followed by titrating aliquot portions, after their reaction with an excess of potassium iodide in aqueous acetone, with standard sodium thiosulphate by a variation of the dead-stop method involving polarised platinum electrodes. In the presence of free halogen depolarisation occurred rapidly, but when all the iodine was consumed the current flowing between the two electrodes dropped sharply [11]. Kinetic studies were made at 78.2 °C in a sealed apparatus under nitrogen; samples were ejected by positive pressure of nitrogen and were analysed for their peroxide content. The reaction products were identified by gas chromatography and also, where possible, by isolation.

2,2′,3,4,5,6-Hexafluorobiphenyl was obtained in 30% yield by the reaction of *o*-fluoroaniline and pentyl nitrite with hexafluorobenzene. After the initial evolution of gas, the mixture was boiled under reflux for 2 h. Crystalline 2,2′,3,4,5,6-hexafluorobiphenyl, m.p. 53 - 55 °C, was obtained by column chromatography (Al_2O_3) of the biaryl fraction of the reaction product, and was subsequently purified by preparative gas chromatography (Perkin—Elmer F21), m.p. 56 - 57 °C, (Found: C, 54.66; H, 1.78; F, 43.44%. $C_{12}H_4F_6$ requires C, 54.97; H, 1.54; F, 43.48%).

Attempts using either *o*-fluoroaniline and pentafluorobenzene, or *o*-fluorobenzoyl peroxide and hexafluorobenzene, did not give crystalline material.

Acknowledgements

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