

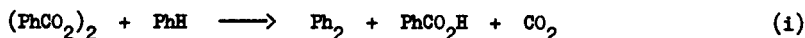
THE EFFECT OF COPPER SALTS ON THE THERMAL DECOMPOSITION
OF BENZOYL PEROXIDE IN BENZENE

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The extensive literature concerning the modification of free radical reactions by transition metal salts prompted an investigation into the influence of copper salts on the thermal decomposition of benzoyl peroxide in benzene. In the absence of additive, the thermal decomposition of benzoyl peroxide in benzene gives biphenyl and benzoic acid as major products (eqn. 1) in yields usually below 50%, together with much high-boiling material. The higher-boiling products are formed in side reactions (particularly dimerisation) of the intermediate



phenylcyclohexadienyl radical (formula 1 in Scheme I, below) (1). The yield of biphenyl may, however, be increased by oxidising the phenylcyclohexadienyl radical by oxygen (2) or other additives (3).

Table 1 gives some of the results obtained using cupric benzoate and copper bronze, and it is seen that cobalt naphthenate produces similar improvements in yields of benzoic acid and biphenyl. Table 2 shows the results of similar experiments carried out with chlorobenzene and with an equimolar mixture of benzene and chlorobenzene. In the experiments with chlorobenzene alone no unsubstituted biphenyl was detected among the products.

In related work, Kochi and Gilliom (4) have already reported the effect of copper salts on the decomposition of di-o-phenylbenzoyl peroxide. This reaction was shown to give almost quantitative yields of o-phenylbenzoic acid and benzocoumarin, compared with yields of ca 40% in the absence of copper ions. By analogy with their proposed mechanism, it is suggested that in the thermal decomposition of benzoyl peroxide in benzene the resonance-stabilised phenylcyclohexadienyl radicals (1) may be oxidised by the paramagnetic divalent copper, as shown in Scheme I.

TABLE 1

Products from the Decomposition of Benzoyl Peroxide
(1 g.) in Benzene (100 ml.) at 80° in the Presence of Additives *

Additive	Products	
	Biphenyl Mole/mole peroxide	Benzoic Acid Mole/mole peroxide
Nil	0.36	0.22
Cupric Benzoate (50 mg)	0.88	1.06
Cobalt Naphthenate (130 mg)	0.66	0.92
Copper Bronze † (15 mg)	0.83	0.90

Reactions were carried out under reflux for 36 hr. Exclusion of air from above the boiling solutions had no effect on the products.

† Diaoyl Peroxides are known to react with copper to give the corresponding copper salts: e. g. G. A. Razuvaev and V. N. Latyaeva, J. Gen. Chem. U.S.S.R., 28, 2233 (1958).

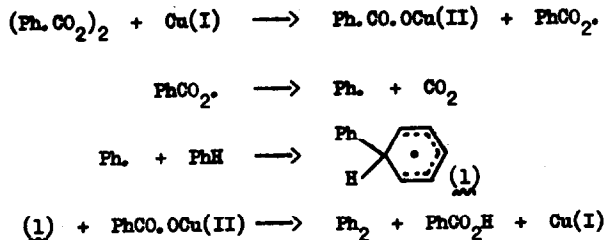
TABLE 2

Products from the Decomposition of Benzoyl Peroxide (1 g.) in Chlorobenzene or Equimolar Benzene-Chlorobenzene Mixtures at 80° in the Presence of Cupric Benzoate and of Air. *

Solvent (100 ml.)	Additive	Benzoic Acid Mole/mole Peroxide	Biaryl Mole/mole Peroxide [Ratio of Chlorobiphenyls to Biphenyl]	Isomer
				Distribution of Chlorobiphenyls % o-; m-; p-
PhCl	Nil	0.42	0.45	53.5; 25.8; 20.7
PhCl/PhH	Nil	not determined	0.46[1.13]	54.3; 24.7; 21.0
PhCl	(PhCOO) ₂ Cu (50 mg)	"	0.78	58.9; 23.1; 18.0
PhCl/PhH	(PhCOO) ₂ Cu (50 mg)	"	0.79[1.47]	58.0; 24.1; 17.9
PhCl	Nil (under air)	0.35	ca 1.0 [†]	55.5; 27.3; 17.2
PhCl/PhH	Nil (under air)	not determined	ca 0.95 [†] [1.30]	55.4; 27.4; 17.2

* Duplicate reactions were carried out under reflux for 36 hr. Oxygen was rigorously excluded, except in the last two experiments in which no special precautions were taken and the reaction mixtures were exposed to dry air.

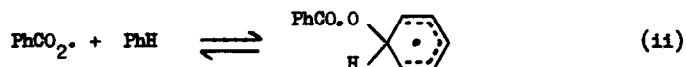
† The biaryl yield in these experiments showed poor reproducibility; however the isomer ratios and relative reactivity remained sensibly constant.



Scheme I

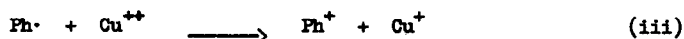
Benzoyloxylation of toluene by benzoyl peroxide in the presence of copper salts has been reported recently by Kovacic and Kurz,(5) who used acetonitrile as solvent. Toluyl benzoates were formed in fair yield (ca. 0.4 mole/mole peroxide), and the typically electrophilic substitution pattern (56% o; 18% m; 26% p) led to the suggestion that the reactive species is PhCO_2^+ (formed by $\text{PhCO}_2\cdot + \text{Cu}^{++} \longrightarrow \text{PhCO}_2^+ + \text{Cu}^+$). In view of the reported electrophilic nature of hydroxyl (6), and of *p*-nitrobenzoyloxy (7) radicals, the alternative mechanism, also discussed by Kovacic and Kurz, and which is analogous to that proposed by Kochi and Gilliom for the formation of benzocoumarin, seems equally possible.

With aromatic hydrocarbons and their halogeno-derivatives as the sole solvent, the concentration of copper salt in solution is limited by its solubility, and is presumably inadequate to intercept a high proportion of benzoyloxy radicals or their adducts with benzene with which they may be in equilibrium (8) (eqn. ii). Hence decarboxylation occurs, and it is



the resonance-stabilised phenylcyclohexadienyl radical (1) which is intercepted by the cupric salts.

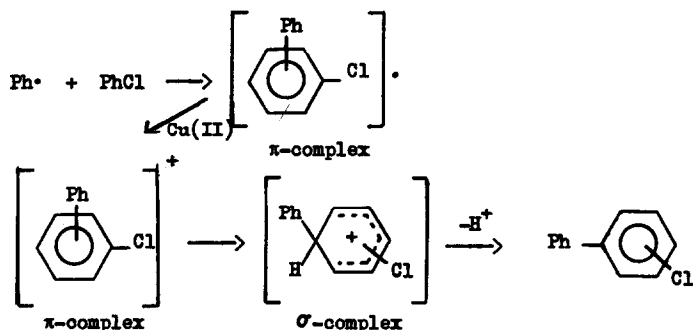
The partial rate factors for chlorobenzene are consistent with attack by phenyl radicals, but do not totally exclude participation of the phenylation (eqn. iii), as the latter species formed during certain diazonium salt decompositions has much radical character, and, for



instance, with mixtures of benzene and nitrobenzene, has been reported to favour reaction with

benzene by a factor of only 2 (9). However, at the present time a wholly radical mechanism appears preferable for the title reaction.

The importance of π -complex formation in aromatic substitution has been the subject of much discussion. The possibility that a radical π -complex is a long-lived intermediate which may be oxidised to a cationic π -complex, as in Scheme II, also appears to be ruled out by the isomer distribution patterns.* However, such a mechanism is perhaps less easily dismissed for the benzoyloxylation experiments of Kovacic and Kurz (5), and it may also be significant that transition metal salts were present in the hydroxylation experiments of Smith and Norman (6). On the other hand, electron spin resonance data are consistent with the radical adduct of HO \cdot and ArH being a σ -complex (10).



Scheme II

The small changes in the observed isomer ratios of the chlorobiphenyls which are found in the copper promoted reactions now reported may be significant when compared with the results of Morrison and his collaborators (11). The latter workers showed that oxygen, while increasing the yields of biaryl as much as three-fold, had no effect on the isomer distribution of the products. The present series of experiments included a number in the presence of air, as shown in Table 2; the small effects noted seem to be outside the limits of experimental error,** and are of the same order as those caused by cupric benzoate. No mechanistic interpretation appears justified at this juncture.

* We are grateful to Professor Kochi for making this point.

** All analyses of biaryls were by gas chromatography of total reaction products, and the method was checked by analysis of standard mixtures.

ACKNOWLEDGEMENT

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