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PHOTOLYSIS OF SOME AROYL PEROXIDES IN SOLUTION

J.D. Bradley and A.P. Roth

Department of Chemistry including Biochemistry
University of the Witwatersrand, Johannesburg,
South Africa

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Whilst the thermal decomposition of aroyl peroxides has been exhaustively studied [1], their photodecomposition has yet received little attention [2,3,4]. The recent revived interest in this area [5] and the steady interest in photoreactions in aromatic media [6] suggested to us that publication of some of our findings [7] might be of value to others.

In our experiments, 0.05 M solutions of benzoyl peroxide were irradiated for about 20 hours under nitrogen at 25° with a Hanau 300 W lamp through quartz in an apparatus similar to that used by Blair, Bryce-Smith and Pengilly [8] and Hey, Shingleton and Williams [9]. The yields (moles/mole peroxide) of the principal products determined when the photolysis was performed in various media are shown in Table 1. Biphenyl and phenyl benzoate were determined by GLC analysis. Benzoic acid was determined by weight after extraction and CO_2 by absorption in a weighed absorption tube (soda lime/anhydrone). Unchanged peroxide was destroyed and determined by treatment with sodium iodide in ethanol, followed by sodium thiosulphate titration.

TABLE 1. Yields of Photoproducts from Benzoyl Peroxide [10]

Product	Solvent			
	C_6H_6	CCl_4	$CCl_4/I_2/H_2O$ *	C_6H_{10} ≠
Ph_2	0.26	0.04	0.02	0.06
PhCOOPh	0.12	0.09	0.08	0.12
PhCOOH	0.29	0.07	0.52	0.19
CO_2	1.02	1.59	1.12	0.85

*7g I_2, 7 ml water, 250 ml CCl_4. The temperature employed did not permit iodine concentrations as high as those used by Hammond and Soffer [11].

≠Cyclohexene

These results suggest that the overall stoichiometry of the first step of these photoreactions is closely represented by

$$(PhCOO)_2 \xrightarrow{h\nu} Ph\cdot + CO_2 + PhCOO\cdot$$

whence cage combination yields about 0.1 moles/mole of phenyl benzoate [12]. About 0.04 moles/mole of biphenyl are also apparently formed in a cage reaction.

The origin of the biphenyl formed in benzene is an interesting matter, which experiments with bis-4-chlorobenzoyl peroxide and bis-4-methylbenzoyl peroxide sheds some light on. The results of photolysing these peroxides in benzene under the same conditions are shown in Table 2. These results were obtained by identical or analogous procedures to those already described.

TABLE 2. Yields of Photoproducts from Aroyl Peroxides, $(ArCOO)_2$

Products	$(4\text{-}ClC_6H_4COO)_2$	$(4\text{-}CH_3C_6H_4COO)_2$
Ar_2	0.02	0.013
ArPh	0.19	0.30
Ph_2	0.13	0.13
ArCOOAr	0.04	0.16
ArCOOPh	0.04	0.035
ArCOOH	0.43	0.29
CO_2	0.75	0.88

The biphenyl formed in these reactions presumably forms in comparable amounts by a comparable path in the photolysis of benzoyl peroxide in benzene. It seems reasonable to suggest that excited state molecules of peroxide bring about the formation of this purely solvent-derived biphenyl, from analogy with the action of benzophenone.[6] Thus perhaps about 0.1 moles/mole of biphenyl is formed from interaction of benzoyl peroxide-derived phenyl groups with benzene in those experiments. No dihydrobiphenyl or tetrahydroquaterphenyl could be found but it is possible that the work-up procedure could have caused losses of such hydroaromatics. It is noteworthy however that none of the very insoluble p-quaterphenyl was observed even after treatment of the reaction product mixture with o-chloranil.[13]

A full discussion of these and additional results will be submitted for publication shortly.

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