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Authors : Linhardt, Robert J. and Murr, B.L.

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MECHANISM OF DECOMPOSITION FOR DIACYL PEROXIDES AND
RELATED CARBOXY INVERSION COMPOUNDS IN AQUEOUS ACETONE

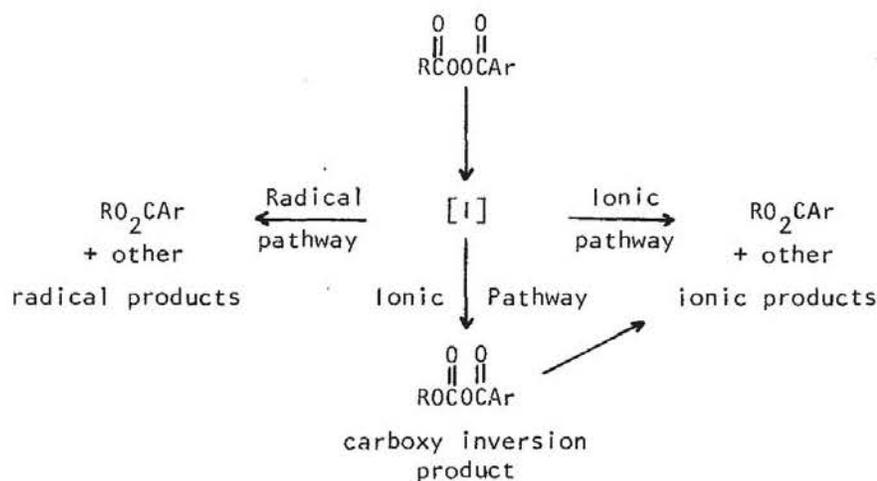
R. J. Linhardt and B. L. Murr*

Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland 21218

The recent report of CINDP during the decomposition of *t*-butylacetyl *m*-chlorobenzoyl peroxide, which was interpreted as arising from polarized, rearranged ion pair intermediates,¹ prompts us to report the behavior of ion pairs derived from substituted diphenylacetyl benzoyl peroxides in aqueous acetone. This solvolytic technique allows the study of the polar pathway of peroxide decomposition by comparing product compositions with well-defined energy surfaces established by related solvolytic studies.

It has been proposed that peroxide decompositions occur by radical and ionic mechanisms.² Recent results have been interpreted (Scheme 1) as involving a common resonance hybrid intermediate [I] leading to ion pairs and radicals.³

SCHEME 1



Ion pairs are intermediates in the solvolysis of benzhydryl esters,^{4a,b} halides,^{4a} thiocyanates,^{4a} diphenylmethane diazonium benzoate,^{4b,c} and benzhydryl nitrosobenzamide^{4d,e} in 90% aqueous acetone. We wish to examine the behavior of the ion pairs from diacyl peroxides in 90% aqueous acetone.

We report: 1) the preparation and characterization of the least stable unsymmetrical diacyl peroxide yet prepared (1, Scheme II); 2) the independent preparation of its "carboxy inversion compounds" (2); 3) the decomposition of the peroxide and inversion compound in dichloromethane with net retention of configuration; 4) the solvolysis of four diacyl peroxides and two related inversion compounds in 90% acetone. Our results provide definitive evidence for the ion pair intermediates from peroxides and inversion products that partition to ester and alcohol

Thermolysis in dichloromethane gave ester with net retention in >90% yield (by infrared).

TABLE I
Products of Solvolysis^{*a}
% Yield^{c, e}

Compound at .04M	Ester (4) + Alcohol (5) (or Acid (6))	Temp ^o C	R ^{b, c, d}
$p\text{CH}_3\text{PhPhCHCO}_2\text{O}_2\text{CPhpNO}_2$ (1b)	96%	15	0.38
$\text{Ph}_2\text{CHCO}_2\text{O}_2\text{CPhpNO}_2$ (1a)	79%	15	0.40
$p\text{ClPhPhCHCO}_2\text{O}_2\text{CPhpNO}_2$ (1d)	95%	15	0.46
$\text{Ph}_2\text{CHCO}_2\text{O}_2\text{PhmCl}$ (1c)	75%	15	0.50
$\text{PhCHOCOO}_2\text{CPhpNO}_2$ (2a)	>90% ^f	22	0.51
$p\text{CH}_3\text{PhPhCHOCOO}_2\text{CPhpNO}_2$ (2b)	>90% ^f	0	0.55

a) all compounds decomposed in 90% aqueous acetone v/v 25^oC; b) R = (Ester)/(Ester + Alcohol); c) peroxides analyzed by gas chromatography; d) inversion compounds analyzed by titration; e) isolated yield; f) minimum yield by infrared; g) amine·HCl present during peroxide decomposition.

The solvolysis of the diacyl peroxide and inversion compound afforded alcohol and ester. The fraction substrate leading to ester (R) gives a measure of total ion pair return.^{4b} The large fraction of alcohol requires that a correspondingly large fraction of ester arises via ionic intermediates. The solvolysis of benzhydryl benzoates and diphenylmethane diazonium benzoate both show partitioning of ca. R = 0.7.^{4a} The R values in the solvolysis of N-benzhydryl-N-nitrosobenzamides (ca. R = 0.5)^{4d} closely resemble those given for our compounds in Table I.

The kinetic data thus far obtained are approximate solvolysis rates, for compound 2a, $t_{1/2} = 50$ mins (T = 22^oC) and 2b, $t_{1/2} = 150$ mins (T = 0^oC). These rates are much faster than those of the corresponding ester,^{4b} but considerably slower than for the decomposition of peroxides.

No evidence for the involvement of radicals in the thermolysis of diacyl peroxides 1 or inversion compound 2 has been observed, the yields of ester are generally high and no solvent-derived products¹⁴ have been seen. The related p-bromobenzoyl phenylacetyl peroxide⁷ and p-nitrobenzoyl phenylethylacetyl peroxide¹⁵ do not give capturable radicals in their decomposition. We have not observed CIDNP during the decomposition of our peroxides.

These studies demonstrate the involvement of ion pairs in peroxide and inversion compound decomposition that behave like ion pairs generated by other systems. Furthermore, our results suggest the usefulness of the decomposition of diacyl peroxides in aqueous media. Work is continuing on this system in a search for special salt effects¹⁶ and to obtain detailed Hammett plots.

*The peroxide was prepared in 5 ml acetone at -78^oC from the acid chloride, peracid and tri-n-butylamine. After stirring 1 hr, the peroxide solution was allowed to warm to -50^oC and then solvolyzed with 20 ml of rapidly injected aqueous acetone (at 25^oC), bringing the final temperature to 15^oC and producing a 90% aqueous acetone solution where [ester] + [alcohol] = .04M.

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