

THE MECHANISM  
OF  
DIACYL PEROXIDE DECOMPOSITION

By

Robert J. Linhardt

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## ABSTRACT

Various substituted 4-X-diphenylacetyl Y-benzoyl peroxides have been prepared and characterized in situ by low temperature NMR and IR spectroscopy. These peroxides decompose in non-nucleophilic solvents below  $-20^{\circ}\text{C}$ , with net retention (13%,  $\text{X}=\text{CH}_3$ ,  $\text{Y}=\text{NO}_2$  in methylene chloride), forming ester in high yields. No evidence of radical involvement, such as solvent-derived products, radical coupling products or CIDNP, was observed in this decomposition. The corresponding carboxy inversion compounds (benzhydryl 4-nitrobenzoic carbonic carboxylic anhydrides) were not obtained as products of, nor were they intermediates in, diacyl peroxide decomposition.

Three 4-X-benzhydryl 4-nitrobenzoic carbonic carboxylic anhydrides ( $\text{X}=\text{Cl}$ ,  $\text{H}$ ,  $\text{CH}_3$ ) were prepared and characterized. These compounds decompose with net retention (29%;  $\text{X}=\text{CH}_3$ ; methylene chloride) in nonnucleophilic solvents to afford ester in high yield. Decomposition in chloroform at  $26^{\circ}\text{C}$  occurs with a Hammett  $-\sigma^+$   $\rho = -3.84$  and in nitromethane- $\text{d}_3$  with  $\rho = -4.36$

The activation parameters for these decompositions in chloroform- $d_6$  were calculated for X=H and X=Cl:  $\Delta E_{act}$  13-14 Kcal/mol,  $\Delta S_{36}^{\ddagger} = 37-39$  cal/°mol.

The decomposition of these diacyl peroxides in 90% aqueous acetone afforded only alcohol, acid and ester. The fraction ester (R) produced was similar to that obtained in the solvolysis of substituted benzhydryl-N-nitrosoamides, indicating a similar spectrum of ion pair intermediates. The R value could be increased by the addition of common ion (4-NO<sub>2</sub>-benzoate) from R=0.54 to R=0.95. This common ion effect, coupled with the formation of alcohol as a major product, is conclusive evidence for the intermediacy of ion pairs in this decomposition. Preliminary results obtained in the photodecomposition of diphenylacetyl 4-nitrobenzoyl peroxide in methanol-tetrahydrofuran suggests some decomposition is occurring via a radical pathway.

The mixed carbonic carboxylic anhydrides underwent two modes of decomposition in 90% aqueous acetone: 1) decomposition to ion pair intermediates which gave alcohol, acid, and ester as products; and 2) decomposition by nucleophilic attack at the carbonyl giving alcohol and 4-nitrobenzoic

anhydride. These pathways were easily distinguished when the mixed carbonic carboxylic anhydrides were decomposed in methanol. This showed the ion pair pathway to be the major one (80-100%) with  $R=0.20$ . This is somewhat lower than the  $R$  value obtained for benzhydryl-N-nitrosonaphthamide decomposition in methanol.

These data are consistent with a new mechanism for diacyl peroxide decomposition where the branching of radical, carboxy inversion, and ion pair pathways takes place directly from the diacyl peroxide.