THE MECHANISM
OF
DIACYL PEROXIDE DECOMPOSITION

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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°C, with net retention (13%, X=CH₃, Y=NO₂ 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 carboxylic carboxylic anhydrides) were not obtained as products of, nor were they intermediates in, diacyl peroxide decomposition.

Three 4-X-benzhydryl 4-nitrobenzoic carboxylic carboxylic anhydrides (X=Cl, H, CH₃) were prepared and characterized. These compounds decompose with net retention (29%; X=CH₃; methylene chloride) in nonnucleophilic solvents to afford ester in high yield. Decomposition in chloroform at 26°C occurs with a Hammett $\sigma^+$ $\rho = -3.84$ and in nitromethane-$d_3$ with $\rho = -4.36$.
The activation parameters for these decompositions in chloroform-δ₆ were calculated for X=H and X=Cl:

\[ \Delta E_{act}^{1/2} = 13-14 \text{ Kcal/mol}, \quad \Delta S_{3{\text{Cal}}}^{1/2} = 37-39 \text{ cal/°mol}. \]

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-NO₂-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-\textit{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.