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AASERT-92 A NOVEL PHOTOCHEMICAL AND INTERFACIAL APPROACH TO THE DEGRADATION OF HAZARDOUS MATERIALS

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Approved for public release;
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13. ABSTRACT (Maximum 200 words)

An intriguing proposal is that the intramolecular hydrogen bond of 3Bz "locks" the species into a conformation unfavorable to reaction. We have begun to study this reaction with many of the techniques used previously to study 3BP and 3DBK. Recently, theorists have studied the use of coherent laser excitation to select pathways for chemical reactions -- to use light to shape the wavefunctions of the molecules' excited states. With this work, we advance a more mundane, but, perhaps, also a more practical method to shape these wavefunctions and thereby control chemical reaction pathways. We have shown that by controlling the conformation of a molecule one may sometimes control the shape of the excited state as well.

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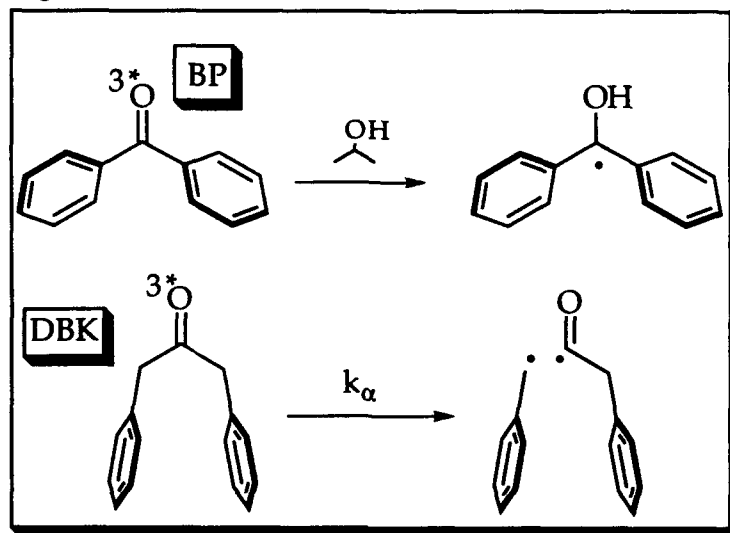
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*A NOVEL Photochemical and Interfacial approach to
the Degradation of Hazardous Material*

B. Annual Technical Report for AASERT Award F49620-93-I-0292

Triplet benzophenone (^3BP), in the absence of quencher, has a lifetime of many microseconds and is thus amenable to bimolecular chemistry. Triplet dibenzyl ketone (^3DBK)'s lifetime, though it cannot be measured directly, can be indirectly estimated as less than one nanosecond, probably nearer 100 picoseconds. The molecules are shown in their approximate ground state conformations.

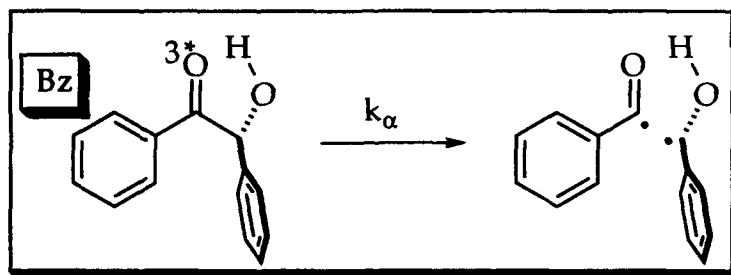


With a combination of classical photochemistry (transient quenching followed by product analysis), UV spectroscopy (emission and absorption, time resolved and steady state), electron spin resonance (of the triplet states frozen in glasses and of the radicals formed in solution at room temperature), and calculations (molecular mechanics and semi-empirical quantum mechanics), we have recently completed studies that show the reactivity of these two disparate triplet states to be remarkably sensitive to conformation.

Planar conformations of ^3BP appear to have no enthalpic barrier to hydrogen abstract from methylcyclohexane. As ^3BP moves from planarity, the enthalpic barrier to reaction grows and the reactivity of the triplet state decreases. Certain conformations of ^3DBK also appear to cleave with no activation barrier. Perhaps surprisingly for an aliphatic carbonyl triplet state, the reactivity of ^3DBK is not controlled by the conformation at the carbonyl moiety (i.e. extent of sp^2 hybridization at the carbonyl carbon), but by the conformation of the phenyl rings relative to the carbonyl.

The methyl ether of triplet benzoin (^3Bz) has been reported¹ to react at least an order of magnitude faster than ^3Bz , too fast, in fact, for its rate to be measured by

¹F. D. Lewis, R. T. Lauterbach, H.-G. Heine, W. Hartmann, and H. Rudolph, *J. Am. Chem. Soc.*, **97**, 1519, (1975)



quenching. An intriguing proposal is that the intramolecular hydrogen bond of ${}^3\text{Bz}$ "locks" the species into a conformation unfavorable to reaction. We have begun to study this reaction with many of the techniques used previously to study ${}^3\text{BP}$ and ${}^3\text{DBK}$.

Recently, theorists have studied the use of coherent laser excitation to select pathways for chemical reactions -- to use light to shape the wavefunctions of the molecules' excited states. With this work, we advance a more mundane, but, perhaps, also a more practical method to shape these wavefunctions and thereby control chemical reaction pathways. We have shown that by controlling the conformation of a molecule one may sometimes control the shape of the excited state as well.