

Final Report

DOE Award No. DE-FG02-86ER13504

Project Period: 4/15/86 – 4/15/99

Research Site: Department of Chemistry, University of Rochester, Rochester, NY 14627

Principal Investigator: David G. Whitten

Summary of Research Results:

The research conducted under this award has focused on the study and development of useful chemical reactions initiated via photoinduced electron transfer events. Specifically the research was initiated with a goal of determining whether the energy "harvested" in a photoinduced electron transfer process could be used to selectively break relatively strong carbon-carbon bonds in organic molecules that otherwise might be relatively unreactive. Since most of the photoinduced electron transfer reactions studied involved a single electron transfer event, the reactions invariably involved bond cleavage processes occurring from odd electron radical ions or ion-radical pairs. Our first results, summarized in publications 1-5 (see list below) showed that amines, amino alcohols and related compounds, subjected to photoinduced one-electron oxidation, undergo selective fragmentation at rates rapid enough to compete with return electron transfer within a contact radical ion pair. Importantly, these results showed that both partners in the contact ion-radical pair – the oxidized amine and the reduced electron acceptor – are essential for rapid reaction. Subsequent work revealed that quite different donor and acceptor substrates could be used in these reactions (publications 6-14). The studies of fragmentation reactions was extended to a series of different substrates and media (publications 14-18, 19-23) and gradually a focus was developed on potential applications. One particularly interesting application was the development of small molecules and polymers containing both a light absorbing acceptor and a fragmentable donor (publications 19, 21, 24). The polymers constructed in this manner exhibit light induced decomposition and offer some promise as useful photodegradable materials. The last few years of the project focused on photoinduced electron transfer fragmentations occurring as chain processes. Thus in a typical situation organic halide acceptors and electron rich pinacols as donors were found to undergo a double fragmentation reaction that in certain cases occurred as an ion-radical chain fragmentation (publications 26, 27, 31). These reactions, particularly those in which donor and acceptor pinacols both can fragment, (publications 31 and 32) can result in large amplifications of an initial photoprocess and consequent quantum yields much greater than unity. The possibility that these reactions can be used in dosimetry for both ultraviolet and visible light or for ionizing radiation has been carried out by investigators subsequent to their leaving Rochester.

DOE Patent Clearance Granted

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Office of Intellectual Property Law

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Publications:

1. X. Ci, L. Y. C. Lee, and D. G. Whitten. "Photoinduced Electron-Transfer Fragmentation of Amino Alcohols: Stereochemical Effects and Connectivity between One- and Two-Electron Events". *J. Am. Chem. Soc.*, 109, 2536 (1987).
2. X. Ci and D. G. Whitten. "Light-Induced Redox Reactions of Dyes, Metal Complexes and Amines: One- vs. Two-Electron Transfer Reactions and C-C Bond Cleavage Processes" in *Photoinduced Electron Transfer*, M. A. Fox and M. Chanon, editors; Elsevier, Amsterdam; Part C, pp. 553-577 (1988).
3. X. Ci and D. G. Whitten. "Photochemical Dehydrofragmentation Reactions: Importance of Donor and Acceptor Structure in Determination of Reactivity in

Radical Ion Pairs Formed in Electron Transfer Photoreactions". *J. Am. Chem. Soc.*, **109**, 7215 (1987).

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9. W. R. Bergmark and D. G. Whitten. "Cooperative Reactivity in Photogenerated Radical Ion Pairs: Photofragmentation of Amino Ketones". *J. Am. Chem. Soc.* **112**, 4042 (1990).
10. X. Ci, M. A. Kellett and D. G. Whitten. "Oxidative Photofragmentation of α,β -Amino Alcohols via Single Electron Transfer: Cooperative Reactivity of Donor and Acceptor Ion Radicals in Photogenerated Contact Radical Ion Pairs." *J. Am. Chem. Soc.*, **113**, 3893 (1991).
11. W. R. Bergmark and D. G. Whitten. "Fragmentation of Amino Ketones by Photoinduced Electron Transfer." *Mol. Cryst. Liq. Cryst.*, **194**, 239 (1991).
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13. X. Ci and D. G. Whitten. "Exciplex Emission and Photofragmentation Reactions of Contact Ion Pairs Generated via Quenching of Cyanoaromatic Singlets by Amino Alcohols." *J. Phys. Chem.*, **95**, 1988 (1991).
14. W. R. Bergmark, I. R. Gould, M. A. Kellett and D. G. Whitten. "Surprising Differences in the Reactivity of Cyanoaromatic Radical Anions Generated by Photoinduced Electron Transfer." *J. Am. Chem. Soc.*, **113**, 358 (1991).
15. D. G. Whitten, C. Chesta, X. Ci, M. A. Kellett and V. W. Yam. "Photoinduced Single Electron Transfer Fragmentation and Cyclization Reactions. Medium and Interfacial Effects." Proceedings of the Conference on Photochemical Processes in Organized Molecular Systems, K. Honda, ed., Elsevier, Amsterdam, pp. 213-236 (1991).
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Excited State Single Electron Transfer Processes, NATO Workshop Proceedings, *J. Photochem. & Photobiol. A: Chem.*, **82**, 211 (1994).

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25. H. Gan, U. Leinhos, I.R. Gould, D.G. Whitten Photochemical Electron Transfer Initiated Oxidative Fragmentation of Aminopinacols. Factors Governing Reaction Rates and Quantum Efficiencies of C-C Bond Cleavage, *J. Phys. Chem.* **99**, 3566 (1995).
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