Dynamics of Electron Transfer in Amine Photooxidation

Sir:

For the last 15 years, there has been an interest in elucidating the mechanism of the photoreduction of aromatic ketones by amines.[1] On the basis of photoreduction quantum yields and fluorescence quenching studies, Cohen has proposed[2] that the initial step in the carbonyl reduction is an electron transfer. Recently, we have initiated studies, utilizing picosecond (ps) absorption spectroscopy, to directly monitor the dynamics of electron transfer from 1,4-diazabicyclo[2.2.2]octane (Dabco) to the excited states of benzophenone and fluorenone; the choice of these two systems resulted from their contrasting photochemistry. The quantum yield for photoreduction of benzophenone in polar solvents is generally greater than 0.1, while that of fluorenone is zero. In polar solvents, the proposed mechanism[3,4] dictates that an electron is transferred to the excited singlet state of fluorenone, which then back-transfers the electron, regenerating ground-state fluorenone and amine. Photolysis of benzophenone in the presence of an amine transfers an electron to an excited triplet state, forming an ion pair that is stable relative to diffusional separation. Our results directly verify this proposal.

The experiments employ a ps absorption spectrometer consisting of a 10-Hz YAG (QI-YG400) with 20-ps time resolution and an OMA II Vidicon (PAR) interfaced to a 200-mm spectrograph (JY-UFS-200). The experimental design utilizes a light pulse of 355-nm wavelength to excite the sample, accompanied by simultaneous recording of the photoproduct spectra by a continuum extending from 450 to 660 nm at a variable time delay up to 2 ns. In the absence of amine, the triplet absorption of benzophenone (λ_{max} 525 nm) is observed[5] 20 ps after photolysis (Figure 1A). Upon the addition of 1 M Dabco, the radical anion of benzophenone (λ_{max} 655 nm) is observed with a formation half-life of 20 ± 10 ps (Figure 1B). The radical ion thus formed persists beyond 2 ns, without decay of the absorption maximum. The absorption spectrum of the first excited singlet state of fluorenone in the absence of amine is displayed in Figure 2A. In polar solvents, there is no measurable decay of the first excited singlet state during the first 200 ps. However, in the nonpolar solvent cyclohexane, we observed intersystem crossing with a triplet formation half-life of 120 ps. Similar behavior has been previously reported.[6,7] In the presence of 1 M Dabco, the radical anion of fluorenone is formed with a half-life of 20 ± 10 ps upon photolysis (Figure 2B); this species is not stable and decays within 60 ± 20 ps, presumably forming ground-state fluorenone and Dabco.

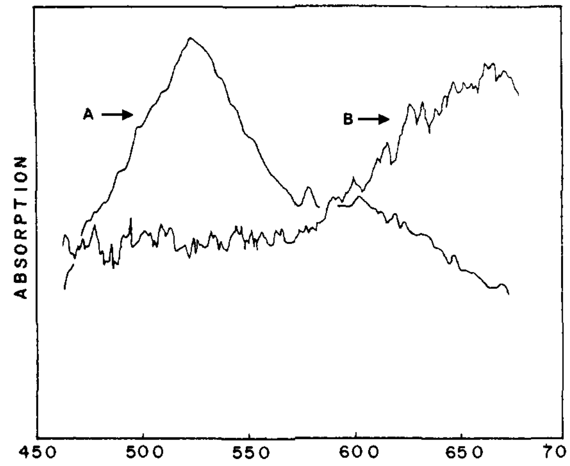

Figure 1. Transient absorption spectra: (A) 0.1 M benzophenone in acetonitrile at 20 ps; (B) 0.1 M benzophenone and 1 M Dabco in acetonitrile at 30 ps.

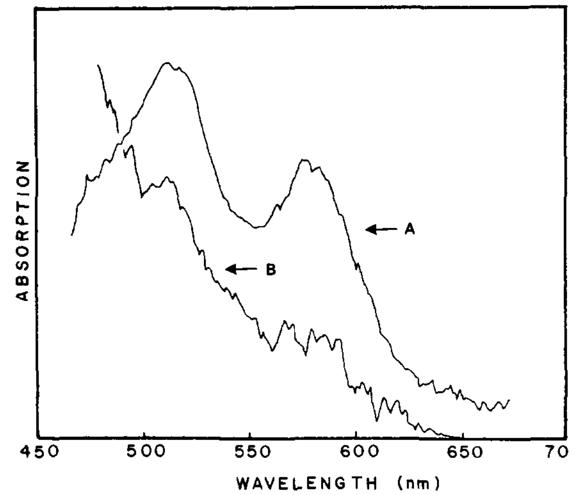

Figure 2. Transient absorption spectra: (A) 0.01 M fluorenone in 2-propanol at 20 ps; (B) 0.01 M fluorenone and 1 M Dabco in 2-propanol at 20 ps.

The mechanism of fluorescence quenching by electron transfer, as investigated by Rehm and Weller,[8] is assumed to occur by outer-sphere transfer where the rate-limiting step in the absence of diffusion involves solvation changes. The rate of electron transfer is expressed as

$$k = Z \exp(-\Delta G^*/RT) \qquad (1)$$

where Z is related to the reciprocal of the dielectric relaxation time, approximately 10^{11} s^{-1} and ΔG^* is the activation free enthalpy, which is a function of the overall free-enthalpy change for electron transfer (ΔG). Under the conditions of diffusion-controlled quenching, Rehm and Weller were not able to directly measure the rate constant for electron transfer, as the experiments are rate limited by the diffusion process, $k_{dif} = 2 \times 10^{10}$ M^{-1} s^{-1}. The results reported in this communication were obtained at 1 M amine; with this concentration of reductant, greater than 80% of the aromatic ketone molecules have an amine molecule within the first solvent sphere.[9] This eliminates translational diffusion such that the measured rate constant for electron transfer reflects only rotational diffusion and solvent reorganization. Rotational diffusion should not make a significant contribution to the rate-limiting process since under the assumption of adiabatic electron transfer, the resonance energy, $H = \langle A^*,D|H|A^-,D^+\rangle$, need be only on the order of 10^{-4} eV to allow transfer which can be achieved by van der Waals contact of the reacting pair without specific orientation.[8] Therefore, if the solvent reorganization model is correct, the rate constant for electron transfer is expected[10] to be approximately 16 ps for benzophenone/Dabco and 14 ps for fluorenone/Dabco, which is in good agreement with the experimental data (vide supra).

The stability of benzophenone radical anion relative to the fluorenone radical anion can be accounted for by the spin states of the systems.[11] Since there is electronic interaction between the radical anion and cation, the spin state for the benzophenone ion complex would be a triplet while that for fluorenone would be a singlet. As the rate of relaxation of a triplet state would be on the order of the electronic spin-lattice relaxation time, 10^7 s^{-1}

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(1) Cohen, S. G.; Parola, A; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.
(2) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.
(3) Caldwell, R. A. *Tetrahedron Lett.* **1969**, *26*, 2121.
(4) Guttenplan, J. B.; Cohen, S. G. *Tetrahedron Lett.* **1969**, *26*, 2125.
(5) The assignment of the various spectra will be presented in a forthcoming publication.
(6) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429.
(7) Andrews, L.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304.
(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(9) This assumes a packing of 16 acetonitriles around one molecule of benzophenone, based upon covalent radii models.
(10) Calculated, as in ref 6, by using $\Delta G = -15.0$ and -28.0 kcal/mol for benzophenone/Dabco and fluorenone/Dabco, respectively.
(11) Periasamy, N.; Linschitz, H. *Chem. Phys. Lett.* **1979**, *64*, 1979.

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or less, and the diffusional separation of the ion pair is of the order of 10^9 s^{-1},[8] the radical anion of benzophenone will be long-lived. Since the fluorenone ion complex is a singlet, relaxation to fluorenone and Dabco is not spin forbidden; thus, the ion pair is short-lived.

Acknowledgments. This research is supported by the Department of Energy (DE-AS02-79ER10349), the Cottrell Research Corporation, and the donors of Petroleum Research Fund, administered by the American Chemical Society.

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Received May 7, 1980

Book Reviews *

Molecular & Crystal Structure Models. By Anne Walton. Ellis Horwood Limited Publishers, Chichester, Sussex, England. 1978. 201 pp. $22.50.

This book is a comprehensive survey of currently available models, assembled, kit, and homemade. In addition to the usual crystal and molecular models, atomic and molecular orbital and macromolecular models are covered. There is also a chapter on construction devices and techniques. The descriptions of individual models include the theoretical basis of the model, materials of construction, ease of assembly, areas of application, relative cost, and more. With coverage of this scope, the individual descriptions are necessarily brief, but numerous literature references supplement the material in the book.

A useful feature is an appendix listing 70 manufacturers and distributers of models, kits, and construction materials, most located in the United States and England.

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Solution Chemistry of Surfactants. Volumes I and II. Edited by K. L. Mittal. Plenum Press, New York. 1979. Vol. I, xxvii + 515 pp. $45.00. Vol. II, xv + 443 pp. $39.50.

These two volumes include the proceedings of part of the 52nd Colloid and Surface Chemistry Symposium, namely those of the section on the solution chemistry of surfactants. The editor has also incorporated in these volumes several review papers dealing with topics not discussed at the Symposium, so as to improve the balance of coverage of the discussion. Volume I contains eight overview papers, twelve papers on micelle formation in aqueous media, and five papers on micelles and solvent effects in nonaqueous media. Volume II includes five papers on chemical and electrochemical reactions in micellar media, six papers on microemulsions, seven papers on surfactants at interfaces, and six other papers not fitting the above scheme. The volume closes with short biographic sketches of the contributors and an 11-page subject index. The papers range from the purely chemical to those treating commercial applications (e.g., J. C. Morgan et al., "Ultra-Low Interfacial Tension and its Implications in Tertiary Oil Recovery").

K. L. Mittal intended that these collections (together with his previous work "Micellization, Solubilization, and Microemulsions") serve as a general reference for researchers in the field of surfactant chemistry. These volumes are an excellent source of information on the current state of research in the field and reflect favorably the attention of their editor. A person entering the field might find it easier to begin with a shorter, few-author work, such as the "Micelles" volume from "Current Topics in Chemistry".

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High Pressure Chemistry. Edited by H. Kelm. Reidel Publishing Co., Dordrecht, Holland. 1978. vii + 600 pp. $59.00.

The book is a consequence of a NATO Advanced Study Institute in High Pressure Chemistry held in 1977. It contains 20 contributions from specialists in their fields. Seven chapters deal with discussions on the generation and measurement of pressure, a theoretical approach at computer simulation at high pressure, and various experimental techniques used at high pressure. A chapter is devoted to the effects of pressure on solids. Six chapters consider the liquid state at high pressure, and one chapter deals with the gaseous state. Organic molecules and polymers at high pressure are discussed in three chapters. Two chapters concern themselves with high-pressure effects on photophysical and photochemical processes and biochemicals.

The chapter on generation and measurement of pressure discusses the major types of hydrostatic pressure generation and components to achieve this. A chapter on computer simulation at high pressure using Monte Carlo or molecular dynamics methods to generate equations-of-state for various materials is presented. Theoretical results are compared with experimental data.

Reviews are presented on various experimental techniques undertaken at high pressure. For example, magnetic resonance spectroscopy, neutron scattering, infrared and Raman spectroscopy, Mössbauer spectroscopy, and X-ray diffraction methods are covered. In these reviews emphasis is placed on the experimental methods used to conduct the experiments as well as applications of the techniques.

The liquid state receives extensive attention in the book. The effects of pressure on fluids is covered in several chapters. The effects on the electronic structure of fluids as well as results of high pressures and high temperatures on the physical properties of fluids are discussed. Another chapter discusses the volume of activation as determined from the pressure dependence of the observed rate constants of a chemical reaction. Reviews are presented on the relaxation methods used to study fast reactions in solution under pressure, as well as pressure effects on rates of reaction of coordination compounds in solution.

Minimal attention is devoted to the solid and gaseous states. One chapter discusses the effects on pressure of order–disorder transitions and pressure-induced phase transitions. Kinetic phenomena in gases at high pressure are considered in terms of the influence of density variations.

Organic molecules and polymers under high pressure are also treated. Organic model reactions and organic problems under pressure, as well as pressure effects on the formation and properties of polymers, are described. Biochemicals and the effects of pressure on photophysical and photochemical processes are reviewed.

Some of the discussions can be considered minireviews and are useful starting points for further investigations. The chapters are generally pedagogical in their approach. It should be understood that some of the topics are treated superficially because of lack of space. Further, some of the topics are concentrated in the areas of interest to the authors, at the exclusion of other areas. Since this volume deals with a conference held in 1977, which has only recently been published (late 1979), it should be cited that the book cannot be considered a state-of-the-art treatment, particularly in fast moving areas.

A list of conference participants appears at the end of the book. An index of names of authors appearing in the references is included, as well as an index of chemical compounds discussed in the book. Finally a subject index appears.

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Nitrogen Oxides. Control and Removal. Recent Developments. By B. L. H. Yaverbaum. Noyes Data Corp., Park Ridge, N.J. 1979. xii + 388 pp. $42.00.

See the foregoing review on "Printing Inks". This volume covers the United States patent literature "since April 1975". It is divided into two parts: Industrial Processes for Stationery Power Plants, and Automotive Applications. Applications of catalytic conversion processes are predominant.

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*Unsigned book reviews are by the Book Review Editor.