FSU | DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY

Professor Jack Saltiel's 60-Year Celebration Symposium

[Contribution No. 3059 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California]

Mechanisms of Photochemical Reactions in Solution. XXII.[1] Photochemical *cis–trans* Isomerization

By George S. Hammond, Jack Saltiel, Angelo A. Lamola,[2] Nicholas J. Turro,[3] Jerald S. Bradshaw,[4] Dwaine O. Cowan, Ronald C. Counsell, Volker Vogt,[5] and Christopher Dalton[6]

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We report a detailed study of the photochemical isomerization of four pairs of *cis–trans* isomers, the stilbenes, the 1,2-diphenylpropenes, the piperylenes (1,3-pentadienes), and ethyl maleate–ethyl fumarate. Principal emphasis has been placed on isomerization in the presence of photosensitizers although the results have been correlated with those obtained by direct excitation in the case of the stilbenes and diphenylpropenes. The composition of the mixtures in the photostationary states is a complicated, but rational, function of the nature of the photosensitizers. All results can be understood if it is assumed that transfer of triplet excitation may involve excitation of acceptors to nonspectroscopic as well as spectroscopic states. We infer that the stilbene triplet exists in two interconvertible states, one transoid and one twisted. Probably the only stable triplet in the 1,2-diphenylpropene system is a twisted form. Self-quenching of stilbene triplets by ground-state *trans*-stilbene is significant. Sensitizers having low excitation energies function as true "photocatalysts," *i.e.*, in the presence of excited states of the sensitizers the composition of the photostationary mixture approaches that at thermal equilibrium.

Many studies of photochemical *cis–trans* isomerization have been reported and the mechanisms of these processes have been the subject of frequent, lively discussions.[7] Most of the work has involved irradiation with light absorbed directly by the substrate molecules or under conditions such that the primary absorption process is undefinable. Recent work[14–17] has shown that the reaction can also be effected by irradiation in the presence of suitable photosensitizers. Since the sensitized reaction is in some ways more amenable than the direct process to study in depth, we have investigated several systems in detail. The results not only clarify the specific photochemical process but also give useful information concerning the mechanisms of triplet excitation transfer and the properties of electronically excited states of molecules.

(1) Part XXI: G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, submitted.
(2) National Science Foundation Predoctoral Fellow, 1961 to present.
(3) National Science Foundation Predoctoral Fellow, 1960–1963.
(4) National Science Foundation Postdoctoral Fellow, 1962–1963.
(5) National Science Foundation Undergraduate Research Participant, 1962.
(6) National Science Foundation Undergraduate Research Participant, 1963.
(7) Thorough documentation of the literature is impractical because of its volume. Considerable pertinent discussion has recently been focused on the stilbenes.[8–13] Reference 9 gives a representative treatment.
(8) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Am. Chem. Soc.*, **63**, 2973 (1940).
(9) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).
(10) H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).
(11) S. Yamashita, *Bull. Chem. Soc. Japan*, **34**, 490 (1961).
(12) H. Stegemeyer, *J. Phys. Chem.*, **66**, 2555 (1962).

General Theory

We presume the *a priori* hypothesis that most photosensitized reactions involve transfer of electronic excitation from the sensitizer to an acceptor. Transfer of either triplet or singlet excitation can be realized. Triplets are generally much longer-lived than singlets. Consequently triplets are more likely than singlets to live long enough to encounter potential acceptors. All available evidence indicates that triplet transfer requires close contact of the partners in energy exchange. On the other hand, it has been shown[18]

April 19, 2025

Kroto Auditorium, Chemical Sciences Building (CSL), Florida State University

Conference Schedule

Breakfast & Check-In (CSL Lobby): 9:30 – 10:00 AM

Morning Session

10:00 – 10:10 AM

Opening Remarks

Prof. Wei Yang

Chair, Department of Chemistry and Biochemistry, Florida State University

10:10 – 10:25 AM

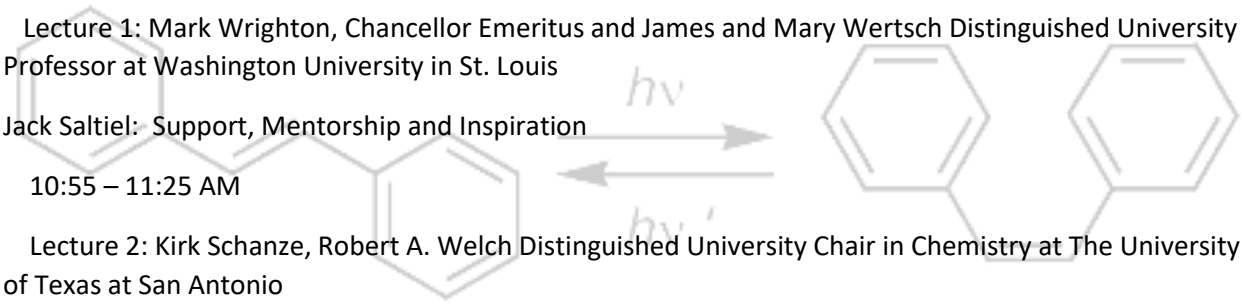
Prof. Richard McCullough,

President, Florida State University

10:25 – 10:55 AM

Lecture 1: Mark Wrighton, Chancellor Emeritus and James and Mary Wertsch Distinguished University Professor at Washington University in St. Louis

Jack Saltiel: Support, Mentorship and Inspiration



10:55 – 11:25 AM

Lecture 2: Kirk Schanze, Robert A. Welch Distinguished University Chair in Chemistry at The University of Texas at San Antonio

Conjugated Polyelectrolytes: Bridging the Gap Between Fundamental Properties and Applications to Biosensing and Antimicrobial Defense

11:25 – 11:55 AM

Lecture 3: V. Ramamurthy, Professor of Chemistry at the University of Miami.

Free Space as a Tool in Chemistry: Photochemistry in Restricted Environments

11:55 – 12:25 PM

Saltiel Group Research Presentation – Sulthana Fehroza (Graduate Student – 25 minutes)

The Photodimerization of 9-Deuterioanthracene. Nuclear Hyperfine and Unprecedented Kinetic Isotope Effects

Lunch Break

12:25 – 1:30 PM

Lunch (CSL)

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Afternoon Session

1:40 – 2:10 PM

Lecture 4: Elizabeth Gaillard, Presidential Research Professor in the Department of Chemistry and Biochemistry at Northern Illinois University.

Aging and the Human Visual Cycle: A Narrative of Cis-Trans Photoisomerizations

2:10 – 2:40 PM

Lecture 5: Kevin O'Shea, Professor of Chemistry and Biochemistry at Florida International University

Ultrasonic-Induced Destruction of Perfluorinated Alkyl Substances

2:40 – 3:10 PM

Bob McMahon, Professor of Chemistry at the University of Wisconsin–Madison

Photochemistry and Spectroscopy of Relevance to Astrochemistry

3:10 – 3:40 PM

Ya-Ping Sun, Frank Henry Leslie Chair Professor in the Department of Chemistry at Clemson University

Carbon "Carbon "Quantum" Dots: Zero-Dimensional Carbon of Characteristic Optical Transitions and Unique Photoexcited States

3:40 – 4:00 PM

Zoom Messages from Friends and Colleagues (David Schuster, Olga Dmitrienko, Steve Fleming, 20 minutes): https://fsu.zoom.us/j/92561198103

4:00 – 4:20 PM

Messages from Guests (Lucas Watkins, Robert Topper, David West, 20 minutes)

4:20 – 5:00 PM

Professor Jack Saltiel (40 minutes)

Surviving the Holocaust. Why I turned to Science

5:30 – 6:30 PM

Dinner (CSL)

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