Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. VI. Binding Effects of Silica as a Mechanistic Probe in Systems of Photochemical Interest

Lawrence D. Weis,[1] Ted R. Evans, and Peter A. Leermakers[2]

Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received April 22, 1968*

Abstract: Quantitative studies of polar and steric effects of substrates adsorbed in silica gel–solvent matrices have been carried out. Such polar matrices have been utilized as a mechanistic tool in the detailed examination of (1) excimer and mixed excimer fluorescence, (2) stilbene *cis–trans* isomerization, and (3) photochromism in spiropyrans. It is clear that there is some controversy and ambiguity regarding mechanism in all three of these general areas. The present paper represents an attempt to clarify the behavior of these systems by a study of "super solvent effects," as observed in highly polar and optically transparent silica gel matrices. Several definitive observations are reported.

The classical series of investigations by de Boer and coworkers[3] involving the electronic spectroscopy of adsorbed molecules was the first pioneering work concerned with interactions of photons and molecular species bound to surfaces. In these early studies of surface field effects, halogens and phenols adsorbed from the gas phase onto sublimed salt films were observed to show strong perturbations of absorption maxima and molar absorption coefficients.[4] Subsequent investigations have found it convenient to utilize transparent microporous silicon materials with extremely large surface areas (200–600 m^2/g) as adsorbants, usually immersing them in inert solvents of similar refractive indices in order to increase transparency. Among recent investigations specifically concerned with the spectroscopic behavior of adsorbed molecules have been those of Robin and Trueblood.[5] Their technique of adsorbing aromatic anilines and nitro compounds in silicic acid–cyclohexane slurries produced pronounced shifts in absorption wavelength.

For the past 3 years an extended series of investigations has been conducted in these laboratories involving the spectra and photochemistry of organic molecules bound to silica gel surfaces. (We have previously published an expanded introduction to this topic.[6]) These initial studies of physical adsorption processes involved a variety of compounds and revealed quite characteristic spectroscopic behaviors. In general, red spectral shifts were observed to occur with adsorption of a compound onto the polar adsorbant silica gel if the excited state of the molecule experienced an increase in permanent dipole or if it was more polarizable than the ground state; blue shifts occurred if the reverse was true.[7] A more detailed examination of the reasons for those spectral changes[6] not only began to help elucidate the nature of physical adsorption processes, but also something of the configuration of excited electronic states. These initial studies have also suggested further utilization of silica gel surface binding as a means for influencing the course of photochemical processes and probing the reaction mechanisms involved. In fact, investigations in these laboratories as well as by other workers have already begun to confirm both the practical value and future promise of this tool. At least two groups[8,9] are presently using silica gel–solvent matrices for studying protein binding effects associated with biologically important chromophores, while Lamola[10] has recently found that such polar environments will significantly perturb the electronic spectral properties of acetophenone, inverting the relative energies of n,π^* and π,π^* triplet states. As a result of these investigations, the studies reported here have been directed toward an increased awareness of both the nature and utility of surface phenomena in photochemical investigations.

Results and Discussion

A. Silica Gel Surface Properties. The experiments which will be discussed below have employed almost exclusively silica gel–cyclohexane matrices to produce surface adsorption effects. Only nonpolar solvents (others include methylcyclohexane, methylpentane, etc.) can be utilized in these slurries since solvents of greater polarity will compete with the intended adsorbate for available binding sites and will result in incomplete substrate adsorption.

Silica gel is an activated form of powdered SiO$_2$, the surface area of which depends upon conditions of temperature, pressure or concentration, and mesh size. The silica gel used in these experiments (28–600 mesh; heated for 24 hr at 200° and atmospheric pressure; cooled and stored in an evacuated P$_2$O$_5$ desiccator) possesses a microporous surface, virtually free of adsorbed molecular water but still possessing many exposed SiOH groups.[11]

---

[1] National Science Foundation Undergraduate Research Participant, Summer 1967.

[2] Alfred P. Sloan Fellow.

[3] (a) J. H. de Boer, *Z. Phys. Chem.*, B14, 163 (1931); B15, 281 (1932); B16, 397 (1932); B17, 161 (1932); B18, 49 (1932); (b) J. H. de Boer and C. J. Dippel, *Z. Phys. Chem.*, B25, 399, 408 (1934); (c) J. H. de Boer and J. F. H. Custers, *Z. Phys. Chem.*, B25, 225 (1934); B21, 208, 217 (1933).

[4] A. Terenin, *Advan. Catal.*, 15, 227 (1964).

[5] M. Robin and K. N. Trueblood, *J. Amer. Chem. Soc.*, 79, 5138 (1957).

[6] P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *ibid.*, 88, 5075 (1966).

[7] P. A. Leermakers and H. T. Thomas, *ibid.*, 87, 1620 (1965).

[8] M. Buchwald and W. P. Jencks, *Biochemistry*, 7, 834 (1968).

[9] C. S. Irving and P. A. Leermakers, *Photochem. Photobiol.*, 7, 665 (1968).

[10] A. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1968).

[11] M. Baverez and J. Bastick, *Bull. Soc. Chim. Fr.*, 4070 (1967).

The basic effects of silica gel binding on organic molecules are clearly a function of many possible steric and electrical interactions.[6] However, the ultimate photochemical fate of bound molecules will depend importantly upon their specific physical orientations while adsorbed on the silica gel surface. In other words, photoreactivity depends upon which part or parts of the molecules are actually experiencing the adsorptive effects, the inhibitions to rotation and migration, the decreased availability of contacting other reactants, and which, if any, remain essentially solvated in the supernatant solution. It would thus seem quite desirable to have some quantitative estimate of both the extent to which a molecule is bound to silica gel and the capacity of silica gel surfaces for binding. From these data would accrue additional knowledge not only of the photochemical interactions allowable but of the nature of environmental influences associated with surface binding.

Surface Area. The surface areas of particulate solids are usually determined by BET procedures[12] which involve gas adsorption at cryogenic temperatures. Less strenuous methods, devised by Nelson and Eggertsen[13] for gas chromatographic applications and in good agreement with standard BET measurements, have been based upon changes in thermal conductivity exhibited by a gaseous adsorbate stream as it is passed over the solid. More recently Hoffmann, McConnell, List, and Evans[14] have developed an elegant technique for making such determinations in solution which simply utilizes Langmuir-type adsorption isotherms. The surface area of silicic acid (essentially a hydrated form of silica gel) was determined by adsorption of methanol (assumed to act analogously to a spherical gas molecule) from a hydrocarbon solvent. This method was found to give data in perfect agreement with BET areas previously established for silicic acid (540–640 m^2/g). Accordingly a similar determination was performed in these laboratories[15] on the silica gel which has been used for all the reported experiments. The result was a quite reasonable area of 200 m^2/g in view of the smaller mesh size used in the silicic acid measurements.

Functional Group Orientation. With the above information and an estimate of the number of molecules necessary to produce an adsorbed monomolecular layer on a given amount of silica gel, it is possible to estimate the physical area requirement of a molecule on the matrix surface and thus hopefully something about its bound spacial orientation. Table I lists a series of compounds for which such measurements were carried out. The data obtained here are not mechanistically definitive but are in good agreement with our previous speculations concerning adsorption mechanisms[6] and does provide some additional indications as to the specific surface phenomena involved.

Table I. Quantitative Adsorption Capacity of Silica Gel[a]

Compound	Monomolecular layer, adsorbed moles per gram of SiO_2
Acetone	5.5×10^{-4}
2-Butanone	4.0×10^{-4}
2-Hexanone	4.0×10^{-4}
2,2,4,4-Tetraphenylpentan-3-one	1.0×10^{-5}
Camphor	1.0×10^{-5}
Benzophenone	1.0×10^{-6}
Dicyclohexyl ketone	2.0×10^{-4}
Benzoic acid	2.0×10^{-5}
Naphthaldehyde	5.0×10^{-6}
Anthraldehyde	2.5×10^{-6}
Biacetyl	2.5×10^{-4}
2,2,5,5-Tetramethylhexane-3,4-dione	7.0×10^{-5}
1,1,3,3-Tetramethylcyclobutane-2,4-dione	7.0×10^{-5}
Bornanedione	1.0×10^{-4}
Diphenylamine	2.5×10^{-5}
Anthracene	2.0×10^{-7}
Azulene	5.0×10^{-8}
Benzanthracene	1.0×10^{-7}
Pyrene	5.0×10^{-8}
N,N-Dimethylanaline	2.0×10^{-7}
Nitrobenzene	5.0×10^{-6}

[a] Much of these data was obtained by Andrew F. Toth and David R. Van Alstine.

Small shifts and maintenance of vibrational structure in the electronic absorption spectra of bound aromatic compounds previously studied suggest that the adsorption process for benzenoid hydrocarbons involves weak dispersion interactions.[6] (Azulene, a nonbenzenoid aromatic hydrocarbon, is an exception in that it exhibits a somewhat more profound perturbation of absorption fine structure as a result of additional dipole–dipole interactions with the adsorbant surface.[6]) Thus to be bound effectively, polynuclear aromatic molecules must be oriented parallel to the silica gel surface in order to maximize interactions. For the large polynuclear aromatic compounds examined in these experiments one would expect a relatively small number of molecules to occupy all available binding sites simply from steric considerations. The measurements obtained are in complete agreement with this interpretation, as can be seen from the data in Table I for anthracene, benzanthracene, and pyrene.

The behavior of the series of ketones and diketones investigated seems to adhere conveniently to a simple explanation. The polar keto functional group is strongly bound to the matrix surface by what has been suggested earlier as a dipole–dipole interaction.[6] If the remainder of the molecule is only of a saturated hydrocarbon nature (*e.g.*, dicyclohexyl ketone), there will be no significant affinity for the surface binding forces and it will remain "floating" above the bound keto group in the nonpolar solvent. This situation will make available more surface binding sites and thus a monomolecular layer of increased concentration. On the other hand if the molecule is an aryl ketone (for instance, benzophenone), the aromatic nuclei will also be influenced by adsorption effects. This will cause the entire molecule to adhere more closely to the surface contour, and thus minimize the capacity of the adsorbant for binding large numbers of molecules.

In general, the conclusions to be drawn from this series of data are entirely reasonable: namely, polarizable or polar areas of an organic molecule will be bound to silica gel surfaces with a strength directly dependent upon whether hydrogen bonding, dipole–dipole interactions, or dispersion forces are involved, while any

---

[12] S. Brunauer, P. H. Emmet, and E. T. Teller, *J. Amer. Chem. Soc.*, 60, 309 (1938).

[13] E. M. Nelson and F. T. Eggertsen, *Anal. Chem.*, 30, 1387 (1958).

[14] R. L. Hoffmann, D. G. McConnell, G. R. List, and C. D. Evans, *Science*, 157, 550 (1967).

[15] C. S. Irving, N. J. Clendennin, and P. A. Leermakers, unpublished results.

Table II. Comparison of Spectral Shifts of Silica Gel and Silicic Acid

Compound	λ_{max}, Å		Spectral shift, cm^{-1}
	Cyclohexane solution	Silica gel matrix[a]	
Acetone	2781	2656	1720 (blue)
Biacetyl	$\left.\begin{matrix}4485\\4230\end{matrix}\right\}4375$	4025	3890 (blue)
Tetramethylcyclobutanedione	2268	2296	520 (red)
	3080	2915	1840 (blue)
	3510	3300	1820 (blue)
Azobenzene	4500	4840	1920 (blue)
Nitrobenzene	2567	2730	2330 (red)
4-Carbomethoxypyridinium iodides			
1-Methyl	4200	3200	7450 (blue)
1-Ethyl	4160	3250	6730 (blue)
1-Isopropyl	4260	3240	7390 (blue)
		Silicic acid matrix[b]	
Acetone	2781	2690	1216 (blue)
Biacetyl	$\left.\begin{matrix}4485\\4230\end{matrix}\right\}4375$	4205	926 (blue)
Tetramethylcyclobutanedione	2268	2274	114 (red)
	3080	2965	1251 (blue)
	3510	3393	999 (blue)
Azobenzene	4500	4250	1301 (blue)
Nitrobenzene	2567	2712	2151 (red)
4-Carbomethoxypyridinium iodides			
1-Methyl	4200	3450	5175 (blue)
1-Ethyl	4160	3500	4533 (blue)
1-Isopropyl	4260	3430	5563 (blue)

[a] See ref 6. [b] Spectra taken by Andrew F. Toth, this laboratory.

relatively "free" nonpolar areas will not be attracted to the matrix surface.

Silicic Acid Analog. Before examining the more elaborate effects of adsorption on secondary photochemical processes, the spectra for a number of compounds bound in silicic acid–cyclohexane slurries were recorded. This was done in order to observe the effect of a hydrated surface on electronic excitation and to provide some means of comparison between these two frequently used adsorbants. Table II shows some of the spectral shifts which can be associated with the surface field effects of each. It can be clearly seen that the direction of these effects is quite the same for both materials, with silicic acid in general exhibiting weaker interactions.

It would of course be highly desirable to have a wide range of varying surfaces which could be conveniently employed in these spectroscopic investigations. The possibility of using others, such as polyvinyl alcohol, has been explored somewhat but unfortunately no alternative has been encountered with the desirable optical properties of silica.

B. Effects of Silica Gel–Solvent Matrices on Excimer and Mixed Excimer Fluorescence. Excimer Emission. When the orientation of two closely associated planar molecules is roughly parallel, it may be expected that interactions between π-electron systems on the two molecules will lead to modifications of energies and ordering in the electronic states. Although experimental evidence for such associations among dye molecules in solution has existed for a number of years,[16] only recently have these interactions been observed with aromatic hydrocarbons. The phenomenon of excimer fluorescence has been studied extensively[17] since Förster and Kasper discovered concentration-dependent long-wavelength emission resulting from association of an electronically excited pyrene molecule with another pyrene molecule in its ground state.[18,19] The mechanism for excimer formation and emission can be most simply represented by

$$\begin{aligned} A + h\nu &\longrightarrow A^* \\ A^* + B &\longrightarrow (AB)^* \\ (AB)^* &\longrightarrow (AB) + h\nu \\ (AB) &\longrightarrow A + B \end{aligned}$$

(The term "excimer" applies to the interaction of a ground-state monomer and an excited-state monomer as distinguished from an excited ground-state dimer.) Initially excimer formation appeared restricted to pyrene, but subsequent studies have established behavior resembling excimer emission in a wide range of compounds, including many alkyl derivatives of aromatic hydrocarbons[20–23] and vinyl polymers.[24–28]

The formation of excimers in solution is a diffusion-controlled process in which a large fraction of the collisions between excited and unexcited monomers are

---

(16) For example, see T. Förster, "Fluorescence Organischer Verbindungen," Vandenhock and Ruprecht, Gottingen, Germany, 1951, pp 243, 251, 154; V. Zanker, *Z. Phys. Chem.*, **200**, 250 (1952); G. L. Levinson, W. T. Simpson, and W. Curtis, *J. Amer. Chem. Soc.*, **79**, 4314 (1957).

(17) E. L. Wehry and L. B. Rogers, "Fluorescence and Phosphorescence Analysis," Interscience Publishers, New York, N. Y., 1968, pp 113–118.

(18) T. Förster and K. Kasper, *Z. Phys. Chem.*, **1**, 275 (1954).

(19) T. Förster and K. Kasper, *Z. Electrochem.*, **59**, 976 (1955).

(20) J. B. Birks and L. G. Christophorou, *Nature*, **197**, 1064 (1963).

(21) J. B. Birks and L. G. Christophorou, *Proc. Roy. Soc.* (London), **A227**, 571 (1964).

(22) T. V. Ivanova, G. A. Mokeeva, and B. Y. Sveshnikov, *Opt. Spektrosk.*, **12**, 325 (1962).

(23) E. Döller and T. Förster, *Z. Phys. Chem.*, **31**, 274 (1962).

(24) S. S. Lehrer and G. D. Fasman, *Biopolymers*, **2**, 199 (1964).

(25) J. W. Longworth and F. A. Bovey, *ibid.*, **4**, 1115 (1966).

(26) J. W. Longworth, *ibid.*, **4**, 1131 (1966).

(27) S. S. Yanari, F. A. Bovey, and R. Lumry, *Nature*, 200, 242 (1963).

(28) M. T. Vala, Jr., T. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).

Table III. Monomer and Excimer Fluorescence Maxima[a]

Compound	Monomer fluorescence, λ_{max}, Å	Excimer fluorescence, λ_{max}, Å	Solvent
2,2′-Paracyclophane	. . .	3550	Cyclohexane
1,3-Diphenylpropane	2900	3300	Dichloroethane
1,2-Benzanthracene	4100	4700	Cyclohexane
Pyrene	3900	4650	Cyclohexane
Perylene	4700	5200	Cyclohexane
Isotactic polystyrene	2800	3400	Dichloroethane
Atactic poly-1-vinylnaphthalene	3400	4050	Dichloroethane
Atactic poly-2-vinylnaphthalene	3400	4050	Dichloroethane
Polyvinylbiphenyl	3100	3900	Dichloroethane

[a] All values here, with the exception of those for polyvinylbiphenyl, have been previously reported in the literature; see ref 28.

effective.[21,29,30] Excimer fluorescence competes favorably with both monomer fluorescence and internal quenching processes for the monomer excitation energy when the monomer lifetime is long. It has been clearly established that a "sandwich" or "face-on" configuration of the two interacting molecules is a necessary precondition for observation of excimer emission.[31–36] Also it has been deduced that the intermolecular distance in the excimer state is smaller than for the same configuration with both molecules in their electronic ground states.[31,37]

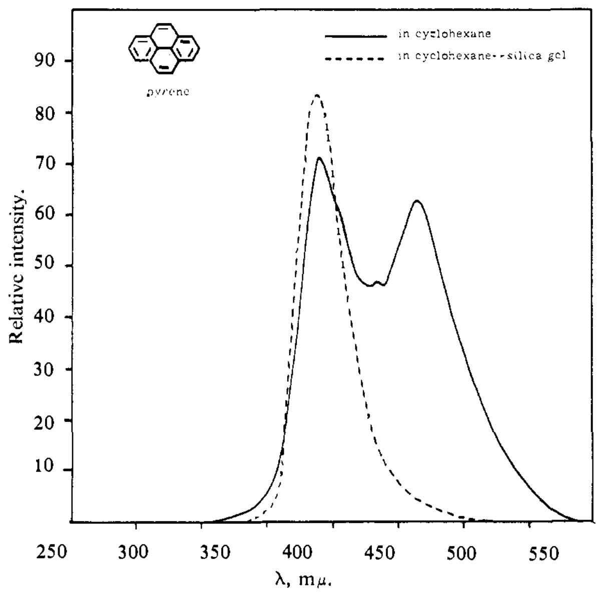


Figure 1. Fluorescence emission of 5×10^{-2} *M* pyrene in the media indicated in the legend.

Current work in these laboratories involving adsorption interactions has utilized excimer formation as a simple method for confirming the behavior and orientation of molecules bound to silica gel surfaces. Assuming a high enough substrate concentration and a sufficiently long monomer fluorescence lifetime, inhibition of excimer fluorescence may still occur for the following reasons: (1) the magnitude of the interaction between the excited and the unexcited monomer states may be so strong that chemical combination occurs, resulting in the formation of a stable photodimer; (2) steric hinderance due to substituent groups in the molecule may prevent the formation of stable dimer or excimer structures; and (3) the magnitude of the excimer interaction may be insufficient to overcome the repulsion potential so that the lowest excited singlet energy of the dimer exceeds that of the monomer and no excimer results.

In the present work it was reasoned that if adsorbed aromatic molecules behave as a two-dimensional ideal gas, postulated earlier,[38] then excimer fluorescence should be quenched by still a fourth process. If a surface-binding medium is employed to immobilize individual molecular species, then the required conjugate π system overlap could not (at low concentrations) be assumed in order to produce excimer emission. Figure 1 shows a very dramatic inhibition of the prominent pyrene excimer fluorescence as a result of employing silica gel–cyclohexane matrices for the adsorbing environment. In addition to pyrene, the series of excimeric hydrocarbons and polymers in Table III[39] has also been examined by an analogous use of physical adsorption. Although all these systems are observed to manifest excimer behavior, unfortunately no other such definitive example of fluorescence quenching could be observed (for reasons elaborated below).

Perylene and 1,2-benzanthracene molecules also produce the same type of concentration-dependent homoexcimeric emission as found with pyrene.[21,37] However, their low solubilities in nonpolar solvents have inhibited studies with adsorbent media. At best, fluorescence quenching of these molecules by silica only amounts to a slight intensity decrease observed in the long-wavelength excimer shoulders. Solvents of greater polarity, in which excimer behavior for these species is quite evident, unfortunately will only result in displacement of substrate from the matrix surface.

1,3-Diphenylpropane exhibits an excimerlike band in addition to normal fluorescence. This emission results from an excited state describable in terms of an intramolecular conformation mixture of charge-transfer and excitation-resonance states.[28] Conformational

---

(29) J. B. Birks, D. T. Dyson, and I. H. Munro, *Proc. Roy. Soc.*, (London), A275, 575 (1963).

(30) J. B. Birks, D. J. Dyson, and T. A. King, *ibid.*, A277, 270 (1964).

(31) J. Ferguson, *J. Chem. Phys.*, 28, 765 (1958).

(32) R. M. Hochstrasser, *ibid.*, **36**, 1099 (1962).

(33) B. Stevens, *Spectrochim. Acta*, 18, 439 (1962).

(34) J. Tanaka *Bull. Chem. Soc. Jap.*, **36**, 1237 (1963).

(35) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 3554 (1966).

(36) E. A. Chandross, *ibid.*, 43, 4175 (1965).

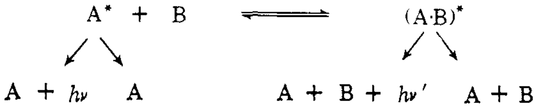
(37) J. Ferguson, *ibid.*, 44, 2677 (1966).

(38) A. Ron, M. Folman, and O. Schnepp, *ibid.*, **36**, 2449 (1962).

(39) Paracyclophane is included in the table but not discussed. The fixed configuration of the two benzene chromophores obviously precludes adsorption quenching of the normal excimer emission.

changes of the two phenyl groups permit an overlap of their conjugated π systems during the lifetime of the excited state, resulting in excimeric behavior. Hirayama's $n = 3$ rule[40] for diphenyl end-substituted alkanes, $C_6H_5(CH_2)_nC_6H_5$, empirically accounts for the lack of excimer emission in other diphenylalkanes since stable chain formations are possible only when two parallel benzenoid functions are separated by four saturated carbon–carbon bonds. When 1,3-diphenylpropane is physically adsorbed on a silica gel surface, a comparative indication of the energetics involved in intramolecular excimer formation is deduced. The dispersion forces responsible for surface binding of aromatic chromophores are evidently not sufficiently influential to compete with spatial orientations which are stabilized by excimer interactions. As a result there is no quenching of 1,3-diphenylpropane excimer fluorescence observed with adsorbant media.

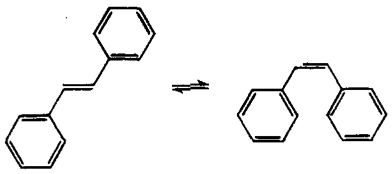
Mixed Excimers. Up to this point the excimer systems discussed have only involved excited singlet dimer interactions of like molecules in solution. However, excimer formation is certainly not restricted to liquid states and has been well studied in organic crystals.[32,33,37,41] Also one need not assume that excimer interactions occur only among like molecules. Since Birks and Christophorou first postulated the existence of "mixed excimers,"[42] a wide variety of heteropolar complexes have been successfully investigated.[43] One such system that we have chosen to study, pyrene with N,N-dimethylaniline, has been observed to produce a strong excimer fluorescence band (440 mμ) in nonpolar solvents.[44,45] The excited state of this complex can be considered essentially an electron donor–acceptor system[44] with charge resonance interactions serving as the primary contribution to intermolecular binding.[45] However, there is no indication of any *ground-state* association in this system, characteristic of charge-transfer complexes, and thus the reaction scheme for excited-state formation and decomposition is quite similar to that observed in "normal" excimer states. The charge-transfer occurs between N,N-dimethylaniline (B) and the excited aromatic hydrocarbon, pyrene (A*).



When the spectroscopic behavior of this system is examined in a silica gel–cyclohexane matrix, there is a complete quenching of the long-wavelength emission. The logical conclusion is that the polar dimethylaniline is preferentially bound by the matrix, leaving only normal fluorescence from pyrene remaining in the supernatant solution (which apparently does not choose to interact with adsorbed dimethylaniline).

C. Effects of Silica Gel–Solvent Matrices on Isomerization.

Unsensitized *cis–trans* Photoisomerization of Stilbene. Discussions of stilbene isomerization resulting from light absorbed directly by substrate have been numerous and extensive.[46–51] The net photoreaction, rotation about the stilbene central double bond, proceeds until a characteristic photostationary equilibrium is established.



Among the proposed photochemical mechanisms for this process, concensus seems limited to the following generalization: the first excited singlet state reached by light absorption is not directly responsible for isomerization but the interconversion of *cis* and *trans* excited states proceeds through an activated process involving a lower excited-state intermediate. Evidence that this is an intermediate of triplet multiplicity has been advanced by a number of investigators.[46–48] Stegemeyer[47] has postulated that singlet excited states of both the *cis* and *trans* isomers undergo very efficient intersystem crossing, leaving the activated process as an interconversion of *cis* and *trans* triplets. On the other hand, Schulte-Frohlinde[46] has suggested that activation occurs during conversion of the excited singlet state to a "planar" triplet or to some more stable intermediate structure having a nonplanar geometry common to both isomers. Dyck and McClure,[48] however, have concluded that in either case there should be considerable potential barriers to rotation about the central bond and thus the existence of two possible activated transitions is implied. Studies extended to photosensitized stilbene isomerizations[51–54] again strongly indicate the existence of a common triplet state intermediate. This metastable form is envisioned as lying just below the individual *cis* and *trans* triplet energy levels but retaining a predominantly transoid character. Such an intermediate is possibly just the minimum of a common potential curve to the individual isomeric triplet states[55] and analogous to that obtained from energy transfer utilizing low-energy sensitizers.[51] Isomeric conversion could even possibly occur in the vibrationally excited ground states formed by intersystem crossing from the metastable intermediate.[51] (See Figure 2 for a schematic representation of the possible transitions involved.) Nonetheless there is still neither sufficiently accurate nor complete evidence available to demonstrate conclusively any one hypothesis.

Recently[56] the quantum yield for *trans* → *cis* isomerization $(\Phi_{t\rightarrow c})$ has been shown to exhibit a very sub-

---

(40) H. Hirayama, *J. Chem. Phys.*, 42, 3163 (1965).

(41) B. Stevens and T. Dickinson, *Spectrochim. Acta*, **19**, 1865 (1963).

(42) J. B. Birks and L. G. Christophorou, *Nature*, **196**, 33 (1962).

(43) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, 47, 2557 (1967).

(44) N. Mataga, T. Okada, and K. Ezumi, *Mol. Phys.*, 10, 203 (1966).

(45) N. Mataga, T. Okada, and H. Oohari, *Bull. Chem. Soc. Jap.*, **39**, 2563 (1966).

(46) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962); *Ann.*, **612**, 138 (1958).

(47) H. Stegemeyer, *J. Phys. Chem.*, **66**, 2555 (1962).

(48) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(49) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

(50) S. Malkin and E. Fischer, *ibid.*, **68**, 1153 (1964).

(51) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(52) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4983 (1962).

(53) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2515 (1963).

(54) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2516 (1963).

(55) P. Borrel and H. H. Greenwood, *Proc. Roy. Soc.* (London), **A298**, 453 (1967).

(56) D. Gegiou, K. A. Muszkat, E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

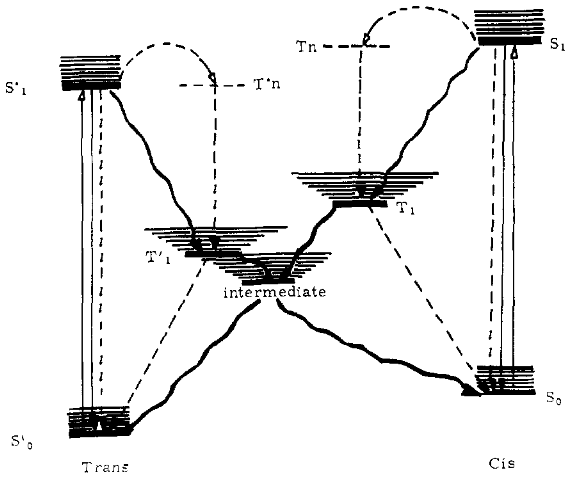


Figure 2. Schematic representation of possible energy levels and reaction pathways for *cis*- and *trans*-stilbene (adopted from that of Fischer[56]). Wavy arrows represent possible "activated" pathways.

stantial viscosity dependence. Such behavior complements strongly a number of previous investigations involving temperature and solvent polarity effects.[46–50] This phenomenon, a negligible one for *cis* → *trans* interconversion, has been ascribed by Fischer[56] to an increase in molecular volume occurring somewhere along the *trans* → *cis* photoconversion pathway and subsequent to intersystem crossing. According to Fischer's explanation, there are two possible viscosity-dependent processes involved in the isomerization: conversion of the planar *trans* triplet to some twisted intermediate, or the decay of such an intermediate to the *cis* isomeric ground state.

In the present study, highly polar environments induced by silica gel–solvent matrices have been utilized as a further probe of these excited-state conformations. The first investigations from these laboratories concerning surface adsorption effects on *cis–trans* photostationary states involved the sensitized isomerization of piperylene.[57] In these experiments, however, the silica gel matrix effects modified triplet excitation energy of the sensitizer and were only indirectly involved with the piperylene acceptor system.[58,59] As a result it became only a logical extension then to investigate the direct effect of surface phenomena on unsensitized *cis–trans* photoconversion.

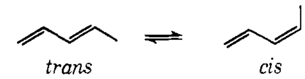


Figure 3 is a summary of the significant alterations observed in both the photostationary state and quantum yield for adsorbed stilbene photoisomerization. In line with the previous discussion, the data here do not preclude the possibility of more than one activated process along the photoconversion pathway. Presumably the adsorption effects act to increase the potential barrier for stereoisomeric rotation about the stilbene double bond. If this process occurs prior to intersystem crossing,[48] the adsorption effects could act to increase stabilization of the polar or polarizable (relative to *cis*) *trans* excited singlet state.[60] This would

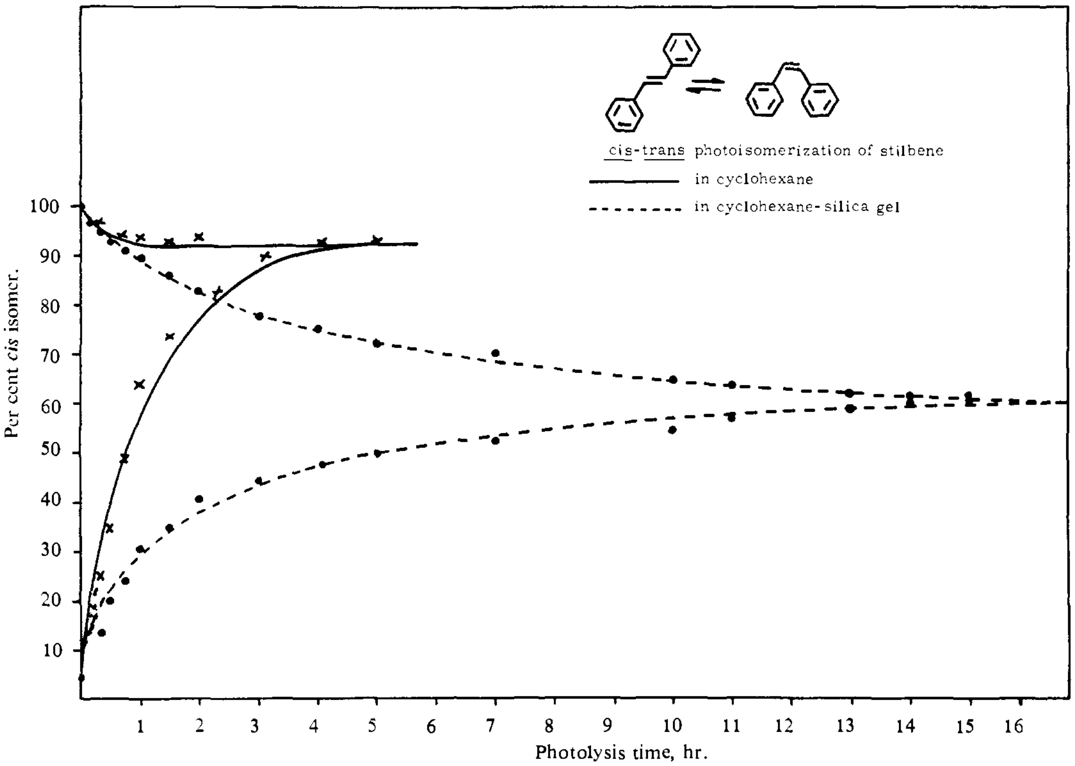


Figure 3.

---

[57] L. D. Weis, B. W. Bowen, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **88**, 3176 (1966).

[58] It is of interest to note here that recent work[59] using phosphorescence data as a direct measurement for the triplet energies of adsorbed molecules have confirmed precisely the triplet energy of adsorbed biacetyl as predicted from piperylene photostationary states in these experiments.

[59] D. Eaton, private communication.

cause a decrease both of decay efficiency to triplet and of $\Phi_{t \to c}$. On the other hand, if this process is not competitive with intersystem crossing, the adsorption effects will only serve to insulate further the triplet (already significantly closer in energy to the *trans* conformer) from attaining a cisoid orientation. Again the results would decrease $\Phi_{t \to c}$. Either of these effects could conceivably be present since individually they both account reasonably well for the large shift observed in photostationary-state composition (a shift from 93% *cis* isomer in solution to 60% *cis* isomer bound in the matrix).

An argument completely analogous to Fischer's concerning viscosity effects would include the possibility that absorption effects act on the simple conversion process of planar *trans* triplet to metastable intermediate. However, it seems unlikely that hindrance of such a process (rather analogous to internal conversion) could alone produce results of the magnitude observed in our experiment.

It should be noted that the time required for establishment of the photostationary equilibrium has been significantly increased (by a factor of approximately 3). This apparently indicates that values of $\Phi_{t \to c}$ and $\Phi_{c \to t}$, aside from being varied relative to each other, have both been decreased in an absolute sense from their values in solution. Again there is the implication of at least some adsorption effects, competitive with triplet formation, capable of stabilizing the first excited singlet states of both isomers.

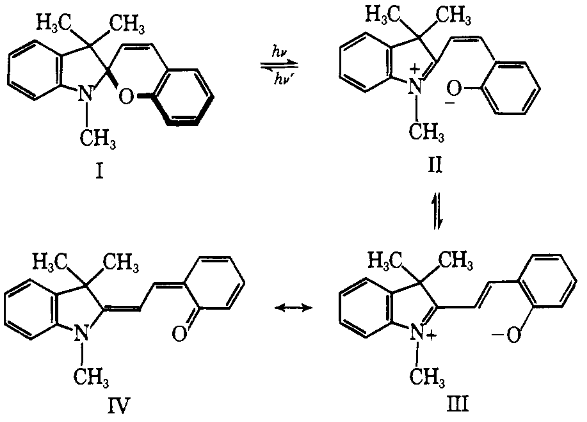
Normally, observed variations in photostationary states produced by direct irradiation would simply be attributable to a wavelength-dependent change in relative absorption of the two isomers; however, the results noted in these experiments are only effects of matrix-binding forces. Spectroscopic analysis shows virtually identical values of molar absorptivities for each isomer when compared in solvent and bound on silica in the irradiating wavelength region (3130 Å).

Additional data certainly are still needed before any definitive reaction mechanism can be constructed for this really rather complex photoisomerization. However, if these present studies can be extended to include future investigations of silica gel–solvent matrix effects upon photosensitized stilbene isomerization and upon each reaction pathway selectively, a clearer concept of the photochemical mechanisms involved may emerge.

D. Photochromic Transformations of Spiropyrans. Reversible, photoinduced, color modifications of molecules in solution (photochromism) were first described by Hirshberg for dianthronylidene derivatives[61] and thermochromic indolinospiropyrans.[62] The mechanism and kinetics of spiropyran photochromism as well as effects of temperature, viscosity, and reversing radiation have all been studied extensively by Hirshberg, Fischer, and others.[61–72]

The transformation mechanism currently proposed to explain the behavior of irradiated spiropyran involves the type of photoequilibrium scheme diagrammed in Chart I. The spiro carbon of the normally colorless molecule (structure I) requires a perpendicular orientation of the two conjugated ring systems. This effectively isolates the π electrons of each system and restricts light absorption to incident ultraviolet radiation. For such a structure to undergo a photoisomeric conversion, the following events must occur: (1) a delocalization of two σ electrons (after excitation) which results in a heterolytic cleavage of the spiro carbon pyran-oxygen bond; and (2) the establishment of a *trans* coplanar molecular configuration, *i.e.*, a simultaneous organization of the methine chain and rotation of the individual ring system planes. Conjugation then becomes extended throughout the entire molecule and results in absorption of significantly lower energy electromagnetic radiation. Electronic excitation initially produces an energetically unstable spiropyran intermediate (structure II) which in turn rapidly equilibrates to establish a more stable series of resonating stereoisomers. The colored modifications are reasoned to be conformations of dimethinmerocyanine (actually a hybrid form of structures III and IV) by analogy to the isomeric structures proposed for merocyanine dyes.[73–76] A number of recent studies[67] have begun to decipher the hierarchy of structural stabilities established among these resonance species, but it is evident that any elucidation of the thermal and photostationary equilibria must also involve consideration of solvent polarity, temperature, viscosity, and substituent effects.[62–72]

Chart I



Nmr studies (carried out in cooperation with Dr. Philip Rose of Eastman Kodak) involving "colored" spiropyran (1,3,3-trimethylindolino-6′-nitrobenzospiropyran) precipitated from nonpolar solution show positioning and splitting of the methyl and olefinic

---

(60) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 178.

(61) Y. Hirshberg, *C. R. Acad. Sci., Paris*, **231**, 903 (1950).

(62) E. Fischer and Y. Hirshberg, *J. Chem. Soc.*, 4522 (1952).

(63) Y. Hirshberg and E. Fischer, *ibid.*, 629 (1953).

(64) Y. Hirshberg, E. H. Frei, and E. Fischer, *ibid.*, 2184 (1953).

(65) O. Chaudé and P. Rumpf, *C. R. Acad. Sci., Paris*, **236**, 697 (1953).

(66) Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 3129 (1954).

(67) Y. Hirshberg and E. Fischer, *ibid.*, 3129 (1954).

(68) Y. Hirshberg, *J. Amer. Chem. Soc.*, **78**, 2304 (1956).

(69) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Chem. Soc.* 156 (1961).

(70) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2465 (1962).

(71) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *ibid.*, **66**, 2470 (1962).

(72) E. Berman, R. E. Fox, and F. D. Thomson, *J. Amer. Chem. Soc.*, **81**, 5605 (1959).

(73) L. G. S. Brooker, *et al.*, *J. Amer. Chem. Soc.*, **87**, 2443 (1965).

(74) C. F. Koelsch, *J. Org. Chem.*, **16**, 1362 (1951).

(75) J. Arnaud, C. Wippler, and F. Beaure D'Augeres, *J. Chim. Phys.*, **64**, 1165 (1967).

(76) O. Chaude and P. Rumpf, *C. R. Acad. Sci., Paris*, **233**, 405 (1951).

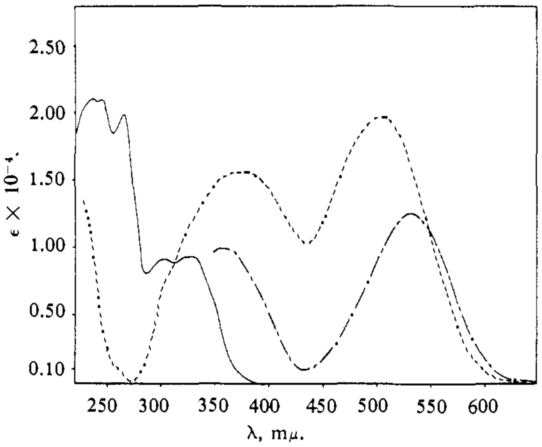


Figure 4. Absorption spectra of 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran: ——, in cyclohexane; —·—·—, in methanol (after irradiation); - - - - - - -, in cyclohexane–silica gel. (Values for ε are obviously only approximate for methanol and matrix.)

protons identical with those in spectra obtained from the spiropyran hydrochloride salt (protonated III). This would seem to indicate that resonance structure III (and its appropriate stereoisomers) plays a major role among the colored spiran modifications. In previous nmr studies on model compounds,[77] the mesomeric structure IV had been considered dominant.

Esr experiments were originally thought to have indicated an involvement of stable photochromic biradicals[78] in the photoconversion process, but more recent investigations seem to have discounted the possibility of any participating ground-state radical mechanism.[79]

Information concerning specific electronic transitions and excited states involved in these photochromic processes has recently begun to emerge from a more sophistocated application of experimental photochemical techniques. Flash photolysis,[80] phosphorescence emission,[80–83] and photosensitization analyses[84–87] all now apparently indicate at least some participation by excited triplet states in this photoreaction scheme. Unfortunately the scarcity of complete, precise data involving lifetimes and energy levels has prevented the establishment of a clear mechanistic picture. On one hand Becker and coworkers[77,87] postulate from nmr, emission, and photosensitization studies of model compounds (chromenes, pyrans, indolines) that the spiropyran *indoline* moiety does not participate significantly in the photochromic process, and that the C–O bond dissociation perhaps occurs only from upper vibrational levels of the pyran excited state. Balny and Douzou,[82,83] on the other hand, propose that the initial light absorption results in energy transfer from the π,π^* excited state of indoline to the 2-benzopyran n,π^* triplet which, depending upon substituent effects, may be further stabilized by solvent interactions. Actually the absorption spectra of the spiropyran is a good summation of the individual pyran and indoline absorptions. Most likely both chromophores (*i.e.*, the molecule as a whole) are intimately involved in the spiro carbon cleavage process.[86]

For dyes in general[88–91] and merocyanines in particular,[73,92–100] spectroscopic studies of solvent effects have been thoroughly investigated. Observed wavelength shifts have been correlated with the dependence of solute–solvent interactions on dielectric constants, refractive indices, and intermolecular hydrogen bonding. Similar considerations are also probably valid for colored spiropyran modifications with special reference to alterations incurred in the thermal equilibria established among the stereoisomeric forms. More specifically several workers have shown both increasing solvent polarity and hydrogen ion concentration shift spiropyran equilibria toward the colored conformations.[66,69,72,101,102]

In general most photochromic materials of various types behave in the manner discussed above; *i.e.*, the colorless form is converted by ultraviolet irradiation to a metastable colored form. A well-known exception to this general behavior is the 15,16-dimethyldihydropyrene system (colored) which may be transformed to the isomeric colorless metacyclophane by visible radiation, the latter isomer reverting in the dark to the more stable dihydropyrene.[103]

In a preliminary communication from these laboratories[104] concerning effects of physical adsorption on photochromic tautomerizations, this same "reverse photochromism" was reported in the spiropyran series when the medium was cyclohexane–silica gel matrix. That is, in this matrix the "open" or colored tautomer of 1,3,3-trimethylindolino-6′-nitrobenzospiropyran (6′-nitro derivative of structure III) is the stable form and, upon irradiation with wavelengths greater than 3500 Å, becomes rapidly photobleached to the colorless isomer (6′-nitro form of structure I). The latter will again revert in the dark to the intensely colored form, although continuous illumination with ultraviolet light (for short enough periods of time to prevent irreversible destruction of both isomers, *vide infra*) leads to wavelength-dependent photostationary mixtures of the two

---

(77) J. Kolc and R. S. Becker, *J. Phys. Chem.*, **71**, 4045 (1967).

(78) C. A. Heller, D. A. Fine, and R. A. Henry, *ibid.*, **65**, 1908 (1961).

(79) E. Berman, *ibid.*, **66**, 2275 (1962).

(80) M. Mossé and J. Métras, *J. Chim. Phys.*, **64**, 691 (1967).

(81) R. S. Becker and J. K. Roy, *J. Phys. Chem.*, **69**, 1435 (1965).

(82) C. Balny and P. Douzou, *C. R. Acad. Sci., Paris*, **262**, 1235 (1965).

(83) C. Balny, R. Santus, and P. Douzou, *ibid.*, **262**, 1311 (1966).

(84) J. Bercovici and E. Fischer, *J. Amer. Chem. Soc.*, **86**, 5687 (1964).

(85) G. I. Lashkov, V. L. Ermalaev, and A. V. Shablya, *Opt. Spectrosk.*, **21**, 546 (1966).

(86) C. Moreau and J. Calvert, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract No. S-98.

(87) R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, **88**, 5931 (1966).

(88) E. B. Knott, *J. Chem. Soc.*, 3038 (1951).

(89) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(90) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(91) A. L. LeRosen and C. E. Reid, *J. Chem. Phys.*, **20**, 232 (1953).

(92) L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, **63**, 3214 (1941).

(93) L. G. S. Brooker, *et al.*, *ibid.*, **73**, 5332 (1951).

(94) L. G. S. Brooker, G. H. Keyes, and D. W. Helseltine, *ibid.*, **73**, 5350 (1951).

(95) L. G. S. Brooker and W. T. Simpson, *Ann. Rev. Phys. Chem.*, **2**, 121 (1951).

(96) J. R. Platt, *J. Chem. Phys.*, **25**, 80 (1956).

(97) E. G. McRae, *Spectrochim. Acta*, **12**, 192 (1957).

(98) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(99) J. R. Platt, *J. Chem. Phys.*, **34**, 862 (1961).

(100) E. D. Bergman, A. Weizman, and E. Fischer, *J. Amer. Chem. Soc.*, **72**, 5009 (1950).

(101) H. P. Vollmer, G. Kruse, and C. Schiele, *Z. Naturforsch.*, **21**, 1001 (1966).

(102) P. Douzou, *C. R. Acad. Sci., Paris*, **256**, 1769 (1963).

(103) V. Boekelheide, *et al.*, *J. Amer. Chem. Soc.*, **89**, 1695, 1704, 1709 (1967), and references therein.

(104) T. R. Evans, A. F. Toth, and P. A. Leermakers, *ibid.*, **89**, 5060 (1967).

Table IV. Photochromic Behaviors of Spiropyrans

Compound	Reverse photochromism on SiO_2 matrix	Stabilized colored form on SiO_2 matrix
6′-Nitroindolinobenzospiropyran	Yes	Yes
Indolinobenzospiropyran	Yes	Yes
6-Chloro-6′-nitroindolinobenzospiropyran	Yes	Yes
Indolino-β-naphthospiropyran	No	Yes
7′-Nitroindolino-β-naphthospiropyran	Yes	Yes
6′-Nitro-8′-methoxyindolinobenzospiropyran	No	Yes
3′-Methyl-6′-nitrobenzoxazolindobenzospiropyran	No	Yes
3′-Ethyl-6′-nitrobenzothiazolindobenzospiropyran	No	Yes
Di-β-naphthospiropyran	No	Yes
1-Phenyl-2-methyl-7-methoxy-7-nitro-β-naphthospiropyran	No	Yes

structures. Figure 4 clearly shows this alteration of normal photochromic behavior as a function of environmental influences.

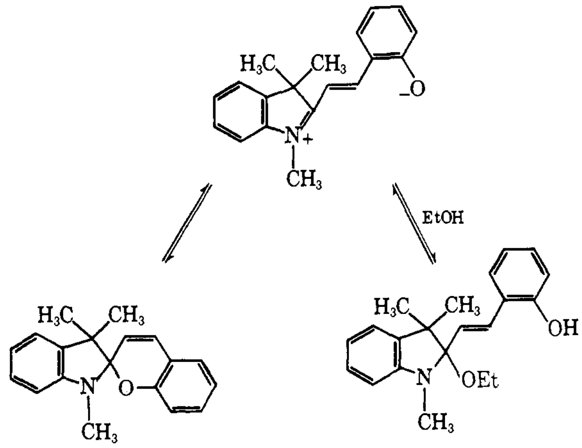
These observations are in accord with a simple mechanistic view based upon the solvent polarity effects mentioned previously. In solution, even with polar solvents, the most stable tautomer of the indolinobenzospiropyran (structure I) may be photochemically converted to relatively unstable stereoisomeric forms of structure III. However, on highly polar, partially hydrated silica gel, the polar effects are of such magnitude as to establish the "open," polar conformation (structure III) stable relative to structure I, and subject to a "reverse photochromism" of similar quantum yield. The "driving force" of either photoisomerization is maintained simply by the relative extinctions of the two isomers at the exciting wavelength.

Balny and Douzou have studied a closely related system,[105, 106] 1,3,3-trimethylindolino-6′-nitro-8′-methoxybenzospiropyran adsorbed on silicic acid, and are essentially in agreement with this discussion.

Table IV presents a series of spiropyran compounds utilized in the present investigation to expand the previously discussed adsorption studies. In each instance the colored tautomers were established as the stable isomeric species when adsorbed on silica gel surfaces. However, reverse photochromism (accompanying irradiation by visible light) was observed only in the few cases indicated. This "selectivity" is most probably a direct function of the structural characteristics intrinsic to each individual molecule. Substituent effects on ring closure rates for a representative number of 1,3,3-trimethylindolinobenzospiropyran derivatives (structure I) have been shown to produce rate variations of as much as four orders of magnitude.[72] Thus it would seem that structures of those adsorbed species which do *not* demonstrate a complete reversal of normal photochromic behavior are either too stable at ambient temperature in the open (colored) form in the matrix, or are geometrically constrained, so as to prevent ring closure.

It is observed, however, that prolonged continuous irradiation of any of the adsorbed spiropyran compounds with ultraviolet light will produce a gradual and irreversible destruction of the colored conformations. Such a process is apparently related to fatigue and oxygen quenching phenonoma which produce identical irreversible effects during prolonged photochromic activation cycles.

Shifts in tautomer stabilities due to physical adsorption influences still seem most plausibly explained as a simple polar effect on equilibria states. However, a second contributing factor could possibly be a type of equilibrium established with the hydrated SiO_2 surface itself, analogous to that already described in the literature for ethanol solvent.[107]



Spectroscopic studies coupled with paralleling nmr analyses over a wide range of low temperatures would seem to be a quite logical extension of these investigations for they would probably permit a closer examination of excited structural intermediates only transient at higher temperatures.

Experimental Section

Materials. All of the **spiropyran** compounds were most generously donated by Dr. R. Bertelson with the exception of 1,3,3-trimethylindolinobenzospiropyran and its 6′-nitro derivative which are available commercially through Eastman Organic Chemicals. The **vinyl polymers** of **naphthalene** and **pyridine** were graciously provided by Eastman Kodak Research Laboratories. **Polyvinylbiphenyl** was newly synthesized specifically for these studies. Solvents were GC-Spectrophotometric Quality, Baker Analyzed Reagents. Fisher Chromatographic Quality silica gel (mesh size, 28–600) and **silicic acid** were the exclusive adsorbants employed. All other chemicals were standard, commercially available materials.

Spectra. All absorption spectra were recorded on either a Cary 14 recording spectrophotometer or a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Emission spectra were taken with an Aminco-Bowman spectrophotofluorometer. In all cases the solvents used in determining spectra were cyclohexane and methylcyclohexane. The cells were standard quartz Beckman cells of path length 0.1 cm. In order to obtain the spectra of adsorbed

---

(105) C. Balny and P. Douzou, *C. R. Acad. Sci., Paris*, **264**, 477 (1967).

(106) C. Balny, D. Djaparidze, and P. Douzou, *ibid.*, **265**. 1148 (1967).

(107) J. C. Metras, M. Mosse, and C. Wippler, *J. Chim. Phys.*, **62**, 659 (1965).

molecules, silica gel was added in small increments to a solution of known concentration in the cell. The cells were then agitated and stirred with a fine wire until all air bubbles were absent and reproducible ϵ's were obtained. The net increase in volume subsequent to silica gel addition was never more than 10–15%.

Irradiation. For the stilbene photoisomerization, a 450-W Pyrex Hanovia immersion reactor was used. Between the water jacket and the sample tubes was placed a filter solution which allowed transmission only of a narrow wavelength band about 3130 Å. (The filter solution consisted of 72.5 g of $NiSO_4 \cdot 6H_2O$ and 20.75 g of $CoSO_4 \cdot 7H_2O$ in 250 ml of distilled water.) To ensure uniform irradiation of many samples, a merry-go-round apparatus continuously carried the sample tubes around the lamp for the entire reaction time. All samples were contained in evacuated quartz tubes.

The studies involving photoisomerization and photochromic transformations employed an apparatus consisting of an optical bench with light source (a 500-W high-pressure mercury arc made by PEK Manufacturing Co.), collimating lens, filter, and sample holder to permit simultaneous irradiation of a number of samples. The reactants were contained in 0.1-cm quartz Beckman cells. Depending upon the desired irradiating wavelength, the following Corning filters were used (transmitted light, in Ångstrom units, is given in parentheses: 7-60 ($5000 > \lambda > 3000$), 7-50 ($4000 > \lambda > 2000$), 7-39 ($4000 > \lambda > 3000$), 0-52 ($\lambda > 3500$). The mercury arc lamp was run at a current of 8 A.

The silica gel surface area was determined with methanol according to the method of Hoffmann, McConnell, *et al.*[14] **Silica gel surface capacities** for individual molecules were determined by adsorbing a decreasing series of concentrated solutions on a known quantity of silica gel and spectrophotometrically monitoring the disappearance of a characteristic absorbance in the supernatant liquid. By plotting ϵ *vs.* moles of adsorbate per gram of silica gel, a curve results which extrapolates to the monomolecular surface concentration. **Spectra utilizing silicic acid solvent matrices** were taken in the same manner as described above for silica gel. **Excimer fluorescence quenching** was observed by taking the emission spectra of an adsorbate determined to be completely adsorbed on silica gel in a solvent–silica matrix.

Stilbene photostationary states were determined by vapor phase chromatographic analysis. Solutions of both *cis*- and *trans*-stilbene, either in solution or determined to be completely adsorbed on silica gel, were irradiated *in vacuo* for varying time intervals. Then the stilbene sample was eluted from the matrix surface (using a mixture of 90% chloroform and 10% methanol) and injected into the vpc. An Aerograph dual column gas chromatograph was used with a 7-ft silicone SF-96 column. Separation of the *cis* and *trans* isomers was obtained with retention times of about 15 and 20 min, respectively. The relative amounts of each isomer were determined by cutting out the recorder peaks and weighing them.

Photochromic transformations for a number of spiropyrans were investigated both by nuclear magnetic resonance spectrometry and absorbance spectroscopy. Quite well-resolved nmr spectra of the closed spiropyran isomer were obtained using a Varian A-60A analytical spectrometer and either dimethyl sulfoxide or chloroform as a solvent. However, the insolubility of the precipitated open form necessitated using a different spectrometer at Eastman Kodak Research Laboratories with a computer averaged transient (C.A.T.) attachment. Studies of photochromic behavior of adsorbed species again utilized the ultraviolet and visible spectrophotometric techniques already described above.

Acknowledments. The authors are indebted to A. F. Toth and D. R. Van Alstine for technical assistance; to Dr. Philip Rose of Eastman Kodak for the C.A.T. nmr spectra of the spiropyrans; to Dr. A. A. Lamola for reading the section on stilbenes prior to publication: and to the National Institutes of Health (Grant GM 13592) and the American Chemical Society Petroleum Research Fund for financial support.

Stereochemical Selectivities in the Electrocyclic Valence Isomerizations of Cyclobutenones and 2,4-Cyclohexadienones[1]

John E. Baldwin[2] and Mildred C. McDaniel[3]

Contribution from the Department of Chemistry and Chemical Engineering. University of Illinois, Urbana, Illinois 61801.

Received May 3. 1968

Abstract: Three 4-monosubstituted 3-phenylcyclobutenones are converted in the presence of methanol by way of the valence isomeric α-styryl ketenes to methyl 3-phenylbut-3-enoates. The reactions are highly stereoselective, giving one of the two possible geometric isomers photochemically, the other thermally. Photolysis of three 6-acetoxy-6-methyl-2,4-cyclohexadienones in the presence of methanol gives methyl 6-acetoxy-3,5-heptadienoates stereoselectively. The factors which may be controlling influences on the stereochemistry of such valence isomerizations, which fall beyond the compass of applicability of the Hoffmann–Woodward approach to related electrocyclic reactions, are discussed.

Valence isomerizations[4] of many cyclobutenes and cyclohexadienes are now known to be highly stereoselective. The experimental results have been impressively correlated and persuasively rationalized through the proposals of Hoffmann and Woodward based on the principle of the conservation of orbital symmetry.[5]

Thermally, *cis*-3,4-substituted cyclobutenes (**1**) and *cis,trans*-1,4-substituted butadienes (**2**) are interconverted in a concerted fashion; *trans*-3,4-substituted cyclobutenes (**5**) and *trans,trans*- or *cis,cis*-1,4-substituted butadienes (**3** or **4**) may equilibrate. Photolytically, the stereochemical modes of these reactions are reversed.[6–12]

---

(1) Supported in part by U. S. Public Health Service Research Grant No. GM-14381.

(2) Alfred P. Sloan Foundation Fellow. Address inquiries to the Department of Chemistry, University of Oregon, Eugene, Ore. 97403.

(3) National Institute of General Medical Sciences Predoctoral Fellow, 1966–1967.

(4) S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 696.

(5) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(6) E. Vogel, *Angew. Chem.*, **66**, 640 (1954); *Ann.*, **615**, 14 (1958).

(7) R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959).

(8) R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965).

(9) R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965).