Spectra and Photochemistry of Molecules Adsorbed on Silica Gel. IV

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Abstract: Measurements have been made of the electronic absorption spectra of a large number of organic compounds adsorbed on silica gel, in the form of a silica gel–solvent slurry, and the spectra have been compared to solution and vapor-phase measurements. Adsorption produces spectral shifts, and, generally, red shifts occur if the excited state of a molecule has an increased permanent dipole or if it is more polarizable than the ground state, and blue shifts occur if the reverse is true. The environmental influence of silica gel adsorption on photochemical reactions has been demonstrated in both primary and secondary photoprocesses.

The electronic spectroscopy of adsorbed molecules was first studied by deBoer in 1931.[1] This and other early studies by deBoer and co-workers involved the adsorption of halogens and some phenols from the gas phase onto sublimed salt films (BaF_2, CaF_2, SrF_2) *in vacuo*.[2] The effects of adsorption on the electronic spectra of the molecules studied often produced strong perturbations of absorption maxima and molar absorption coefficients.

Subsequent investigators have usually turned for adsorbents to transparent microporous silicon materials with extremely large surface areas (150–600 m^2/g), often immersing the adsorbent in an inert solvent having a refractive index very near that of the adsorbent, in order to increase transparency. The property of microporosity is necessary in order to place sufficient adsorbed material in the light path to obtain measurable absorbances.

The only recent large-scale investigation of the spectra of adsorbed organic molecules is that of Robin and Trueblood.[3] A number of aromatic compounds were studied—mainly anilines and nitro compounds. The adsorbent medium used was a silicic acid–cyclohexane slurry. This acidic medium gave rise to pronounced red shifts in the nitro compounds and blue shifts in the anilines.

In the present study, it was found convenient to merely add silica gel to a cyclohexane solution of the compound to be studied held in a standard quartz Beckman cell of path length 0.1 cm. By this elegantly simple technique quite well resolved spectra of adsorbed molecules can be taken down to about 2000 A. The spectra obtained are very reproducible as to λ_{max}, and reasonably so with respect to molar absorptivity, ϵ.

The character of the spectral changes resulting from adsorption helps to elucidate the nature of the physical adsorption process, and also something of the nature and configuration of the excited states of the compounds investigated. In general, red shifts occur on adsorption of a compound onto the polar adsorbent silica gel if the excited state of the molecule has an increased permanent dipole or if it is more polarizable than the ground state; the blue shifts occur if the reverse is true.

The observed effects of physical adsorption on electronic absorption spectra suggest a novel means of influencing the course of a photochemical reaction which may be accomplished by studying the photochemistry of molecules adsorbed on silica gel. Several examples are cited.

Results and Discussion

Electronic Spectra of Adsorbed Organic Molecules. Benzenoid Aromatic Hydrocarbons. The measurement of adsorption isotherms and calculation of adsorption entropies by Ron and co-workers[4] indicates that the adsorption of benzene on Vycor glass is a purely physical process, with the benzene exhibiting the mobile properties of a two-dimensional ideal gas. Also the vibrational bands of benzene vapor are merely broadened and shifted to lower frequencies, by 120 to 140 cm^{-1}, when the vapor is adsorbed on a silica gel plate.[5,6] This lack of change in the vibrational frequency of benzene in the adsorbed state is further evidence of purely physical interaction with the surface. Removal of the silanol (Si–OH) groups of the surface by methylation or sintering at 1000° *in vacuo* results in the band half-widths being decreased from 200 to 75 cm^{-1}. Thus the *broadening* of vibrational bands is due to an interaction with the surface hydroxyl groups. This information has been taken as support[2] for Terenin's hypothesis[7] that adsorption is due to the strongly acidic silanol sites of the surface forming hydrogen bonds with the π-electron system of benzene. Terenin bases his interpretation on the fact that benzene adsorption on porous silica gel decreases the infrared OH frequency of the surface silanol groups more than cyclohexane adsorption does.

In terms of the spectral shift, however, the methylated and sintered porous Vycor of Ron, *et al.*,[4] *gives the same shift as does the untreated adsorbent.* Thus the adsorption interaction which produces the spectral shift is not due to the type of hydrogen bonding proposed by Terenin. Rather, the silanol interaction with benzene only broadens the spectral bands.

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[1] J. H. deBoer, *Z. Physik. Chem.*, **B14**, 163 (1931).

[2] A. Terenin, *Advan. Catalysis*, **15**, 227 (1964).

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

[4] A. Ron, M. Folman, and O. Schnepp, *J. Chem. Phys.*, **36**, 2449 (1962).

[5] E. N. Pavlova, *Dokl. Akad. Nauk SSSR*, **49**, 272 (1945).

[6] M. Okuda, *Nippon Kagaku Zasshi*, **82**, 1115, 1118 (1961).

[7] A. N. Terenin, "Surface Chemical Compounds and Adsorption Phenomena," Moscow University Press, Moscow, 1957, p 206.

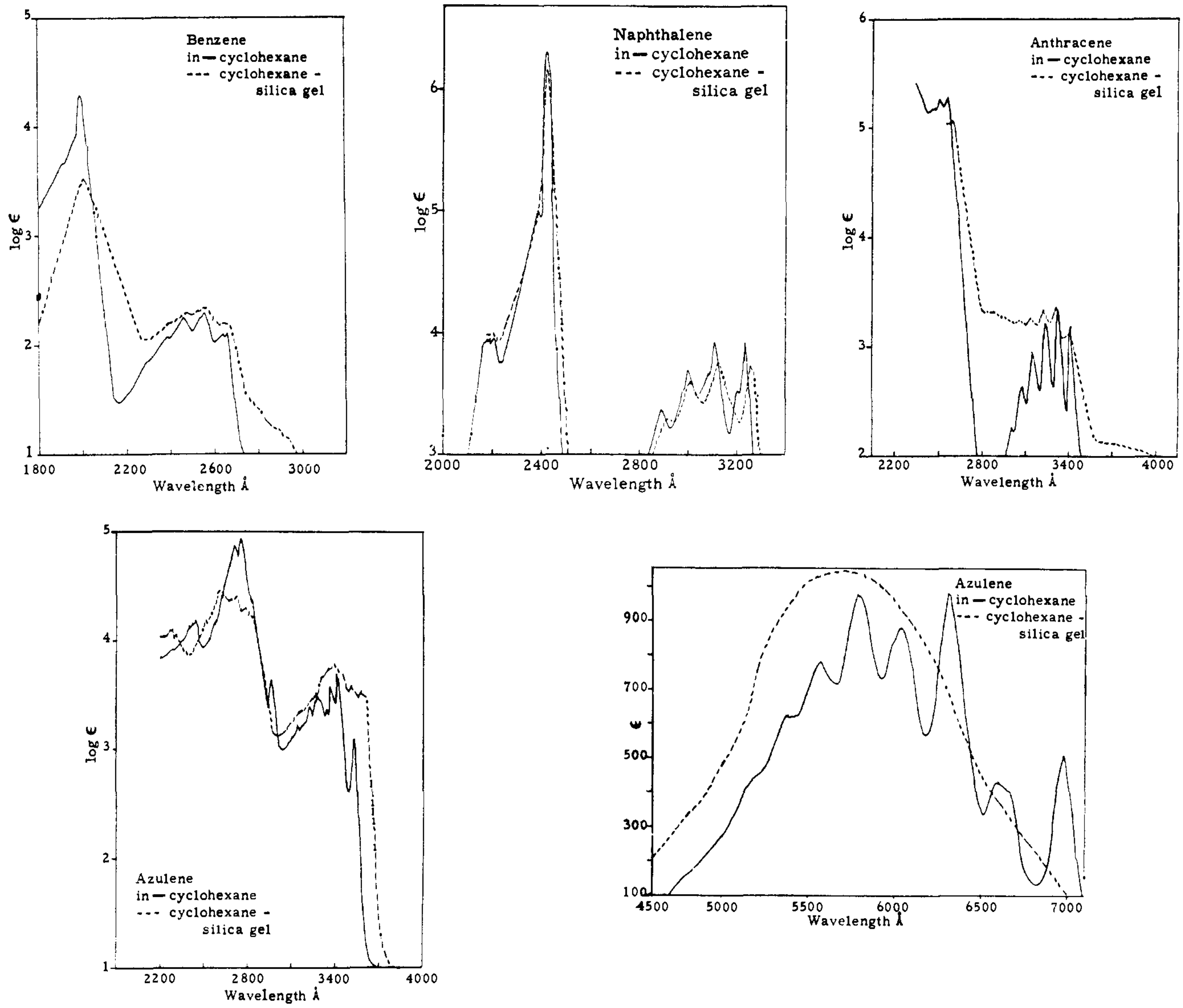

Figure 1. Spectra of aromatic hydrocarbons.

Sverdlova[8] has found that benzene dissolved in a variety of solvents shows a larger red shift (200–240 cm^{-1}) relative to the vapor than benzene adsorbed on silica gel (Table I) (hence the hypsochromic shifts observed for benzene in a silica gel–cyclohexane slurry relative to cyclohexane solutions). The interaction with these solvents is proven to be due to dispersion forces, not hydrogen bonding, and no mutual electrostatic interactions are present.[9]

We therefore propose that the adsorption process for benzene on microporous silica is also due to dispersion interactions. Hydrogen-bonding interactions are usually strong compared to dispersion forces and should therefore give larger shifts than are observed. Hydrogen bonding of any magnitude to the π electrons of benzene would be expected to change the force constants of the carbon–carbon bonds and thus change the vibrational band structure of the benzene spectrum. This change is not observed. Further, hydrogen bonding would not ordinarily be expected to give rise to a mobile type of adsorption.

Table I. Spectral Shifts of Aromatic Hydrocarbons

Compound	λ_{max}, A Cyclohexane solution	 Silica gel–cyclohexane slurry	Spectral shift, cm^{-1}
Benzene	2600	2600 (2598)[a]	0
	2547	2539 (2537)[a]	130 (blue)
	2488	2480 (2479)[a]	130 (blue)
	2430	2422 (2424)[a]	140 (blue)
Naphthalene	2844	2840	50 (blue)
	2753	2763	130 (red)
	2654	2666	170 (red)
	2580	2586	90 (red)
	2210	2203	100 (blue)
Anthracene	3754	3778	170 (red)
	3562	3590	220 (red)
	3390	3420	260 (red)
	2528	2525	50 (blue)
Azulene	5790	5700	270 (blue)
	3410	3385	120 (blue)
	2960	...	...
	2733	2612	1700 (blue)

[a] Values for benzene vapor adsorbed on a silica gel plate.[8]

Since the solvent interactions are as strong or stronger than the surface interactions, the technique of compar-

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(8) O. V. Sverdlova, *Opt. i Spektroskopiya*, 6, 349 (1959); *cf. Chem. Abstr.*, 55, 10055*d* (1961).

(9) See ref 2, p 240.

Table II. Spectral Shifts of Azulene Compared to the Vapor

Transition[a]	C_{2v} designation of transition[b]	Exptl vapor frequencies, cm^{-1}	Frequency shifts, cm^{-1}		
			Vapor to *n*-pentane	Vapor to cyclohexane	Vapor to silica gel-cyclohexane
^1L_b	$^1B_1$	14,270[d]	53 (blue)	57 (blue)	327 (blue)
^1L_a	$^1A_1$	29,760[c]	366 (red)	435 (red)	305 (red)
3000	$^1B_1$	31,464[c]	368 (red)	394 (red)	. . .
^1B_b	$^1A_1$	37,382[d]	1607 (red)	792 (red)	908 (blue)

[a] Designation of O. E. Weigang, *J. Chem. Phys.*, **33**, 892 (1960). [b] Designation of R. Pariser, *ibid.*, **25**, 1112 (1956). [c] Experimental values of E. Heilbronner and K. Wieland, *Helv. Chim. Acta*, **30**, 947 (1947). [d] Experimental values of O. E. Weigang.

Table III. Spectral Shifts of Phenol and Representative Nitrogen-Containing Compounds

Compound	λ_{max}, A		Spectral shift, cm^{-1}
	Cyclohexane solution	Silica gel-cyclohexane slurry	
Phenol	2780	2735	580 (blue)
	2700	2680	300 (blue)
	2650	2630 (shoulder)	270 (blue)
N,N-Dimethylaniline	2971	(2975)[a] 2760	30 (red)[a] 2560 (blue)
	2567	(2515)[a] 2377	780 (blue)[a] 3120 (blue)
Azobenzene	4500	4140	1920 (blue)
	3181	3260	770 (red)
Azobisisobutyronitrile	3500	3447	430 (blue)

[a] Values for N,N-dimethylaniline in ethanol.

ing spectra in cyclohexane solution to those in silica gel-cyclohexane slurry seems to be of little value for benzene. We see from Figure 1 that the vibrational bands of other benzenoid aromatic hydrocarbons are fairly well preserved on silica gel, and that the spectral shifts (Table I) are small, although not very consistent as to direction. The small shifts and the maintenance of vibrational structure in the samples studied suggest that the adsorption process for benzenoid hydrocarbons generally involves dispersion interactions. Further, a spectral shift on silica gel of the order of 250 cm^{-1} or less can be taken as an indication of an interaction due primarily to dispersion forces.

Azulene. The spectrum of azulene, a nonbenzenoid aromatic hydrocarbon, is given in Figure 1. The spectrum on silica gel is shifted to the blue compared to cyclohexane solution. An immediate indication of the difference between the adsorption of benzenoid aromatics and azulene is seen in the 1700-cm^{-1} blue shift for the band at 2733 A in cyclohexane solution.

Again, however, it is more fruitful to compare the spectrum of adsorbed azulene with that of the vapor, as in Table II. For the adsorbed molecule there are two different effects in the adsorption process. As well as the relatively weak dispersion interactions encountered in the case of benzenoid aromatics, stronger dipole-dipole interactions between surface and adsorbate are now possible. Weigang[10] has shown that dispersion interactions with azulene should produce red shifts. On the basis of calculations using the static dipoles calculated by Pariser,[11] Weigang also predicts the sign and relative magnitude of spectral shifts for static dipole interactions with azulene. His predictions include a large blue shift for the first $^1B_1$ transition (^1L_b), a large red shift for the first $^1A_1$ transition (^1L_a), and a small blue shift for the second $^1A_1$ transition (^1B_b). Although the relative magnitudes of predicted shifts do not correspond to those observed on silica gel, the dipole-dipole interactions overcome the dispersion interactions to give blue shifts where expected in the first $^1B_1(^1L_b)$ and second $^1A_1(^1B_b)$ transitions. In the first $^1A_1(^1L_a)$ transition the hydrocarbon solvents produce a larger shift than does the silica gel, so here the dipole-dipole interactions must be very nearly the same for the ground and excited states (the permanent dipoles of the ground and excited state are the same), and the interactions producing the spectral shift are due to dispersion forces.

Phenol. Robin and Trueblood have observed that phenol and anisole adsorbed on silicic acid immersed in cyclohexane exhibit relatively small (260 cm^{-1}) blue shifts compared to cyclohexane solution spectra.[3] We have found that phenol in a silica gel-cyclohexane matrix exhibits a somewhat larger blue shift relative to cyclohexane (see Figure 2 and Table III). This difference seems reasonable in light of the evidence for adsorption by hydrogen bonding and the fact that both silicic acid-cyclohexane and silica gel-cyclohexane slurries shift the spectrum to the red relative to the vapor. Abramov[12] inferred that hydrogen bonding occurred between phenol and the silica gel because the vibrational frequency of the silanol O-H group is shifted by 345 cm^{-1}, while the C-H frequency of the ring remains unchanged. Also, although the heat of adsorption on silicic acid is 2.5 kcal/mole greater for phenol than for anisole,[3] this difference is not reflected in the absorption spectra. This implies interaction with the substituent rather than the ring, for it is the π,π^* transition of the ring which remains unaffected.

The smaller red shift relative to vapor of phenol on silica gel as opposed to silicic acid (evident as a larger blue shift relative to cyclohexane) is most likely due to the greater acidity of silicic acid.

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(10) O. E. Weigang, *J. Chem. Phys.*, **33**, 892 (1960).

(11) R. Pariser, *ibid.*, **25**, 1112 (1956).

(12) V. N. Abramov, A. V. Kiselev, and V. I. Lygin, *Zh. Fiz. Khim.*, **37**, 2783 (1963); *cf. Chem. Abstr.*, **60**, 8786e (1964).

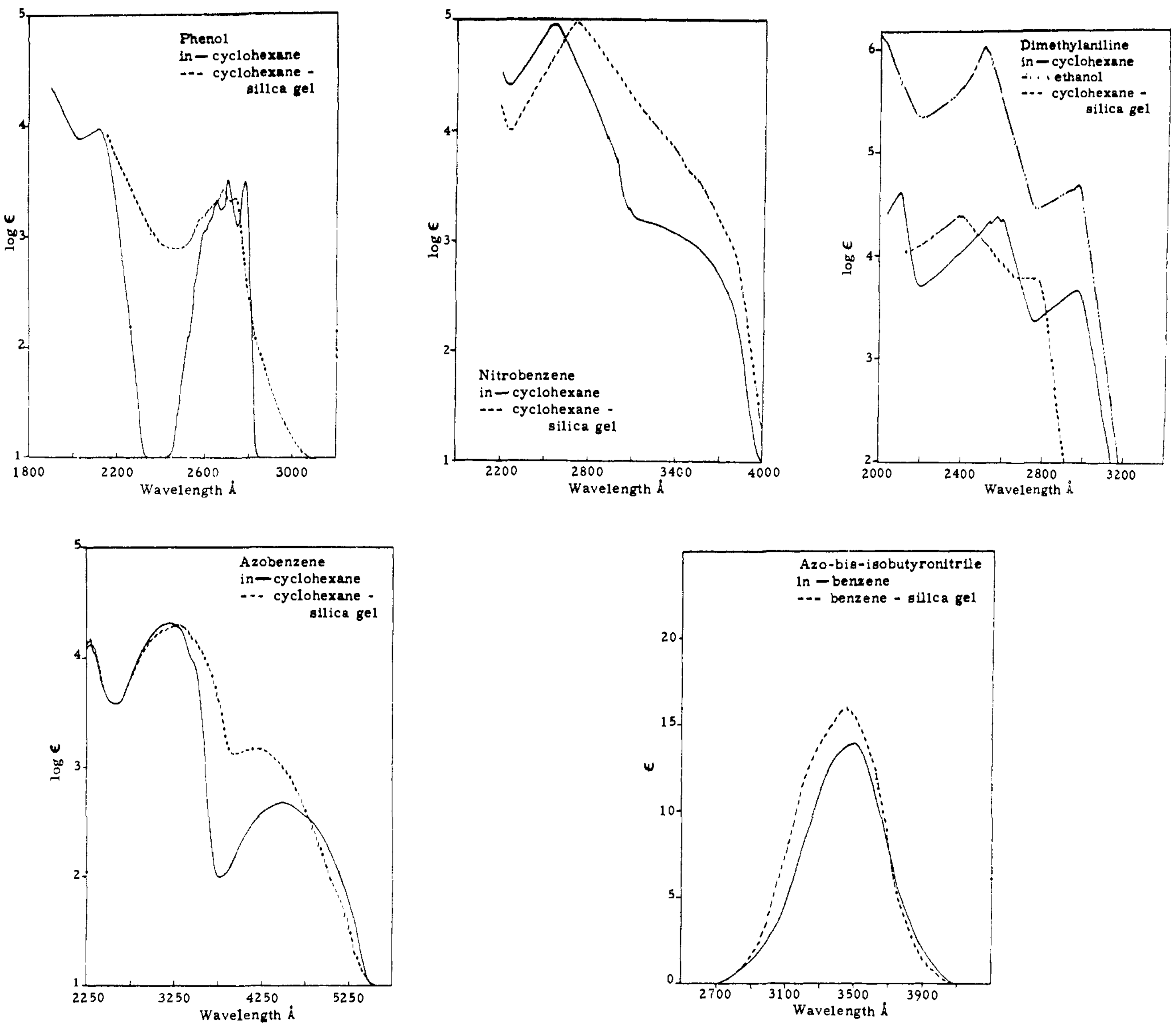

Figure 2. Spectra of phenol and some representative nitrogen-containing compounds.

N,N-Dimethylaniline. The π-π^* and π-π^{**} transitions of N,N-dimethylaniline are blue shifted by the order of 3000 cm^{-1} on adsorption on silica gel, relative to cyclohexane (Figure 2, Table III). (The π-π^{**} transition corresponds to excitation of an electron to the second lowest antibonding orbital of N,N-dimethylaniline.)

In the aniline compounds, the 2p nonbonding electrons of the nitrogen atom interact with the π electrons of the ring to shift the π-π^* transitions to longer wavelengths than benzene. N substitution by electron-donating groups such as methyl increases the electron density on nitrogen, which makes for larger interaction with the π electrons of the ring. Thus the two bands observed for aniline at 288 and 234 mμ are shifted 710 and 1750 cm^{-1} to the red in N-methylaniline and 1160 and 2895 cm^{-1} to the red in N,N-dimethylaniline.[3] Involving the 2p$_z$ electrons of N,N-dimethylaniline in a hydrogen bond with the silanol sites of the silica gel surface would decrease their interaction with the π-electron system of the ring and result in a large blue shift of the spectrum relative to the cyclohexane solution spectrum. The blue shift should be larger than for aniline since N,N-dimethylaniline is the better base and will more strongly involve the 2p$_z$ electrons in a hydrogen bond. This effect is observed. Robin and Trueblood found that silicic acid shifted the aniline absorption maxima about 1800 cm^{-1} to the blue,[3] while we have recorded a blue shift of about 3000 cm^{-1} in the absorption maxima when N,N-dimethylaniline is adsorbed on silica gel.

Further evidence for hydrogen bonding between aromatic amines and the silanol OH groups is demonstrated by the red shift (535 cm^{-1}) in the vibrational frequency of the O-H group on adsorption of aniline on the surface.[12]

Azo Compounds. In the spectra of azobenzene (Figure 2, Table III), we are dealing with n-π^* (4500 A) and π-π^* (3181 A) transitions of the azo group.[13] In general, n-π^* transitions are characterized by a blue shift of their absorption bands as solvent polarity increases.[14] This effect is usually explained by Kasha's

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(13) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 186.

(14) M. Kasha, "Light and Life," W. B. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961.

Table IV. Spectral Shifts on Nitrobenzene and Alkylpyridinium Iodides

Compound	λ_{max}, A			Spectral shifts, cm^{-1}
	Cyclohexane or chloroform solution[a]	Silica gel–solvent slurry	Ethanol solution	
Nitrobenzene	2567	2730	2590	2330 (red)
4-Carbomethoxypyridinium iodides				
1-Methyl	4200	3200	3600 (3580)[b]	7450 (blue)
1-Ethyl	4160	3250	3600 (3590)[b]	6730 (blue)
1-Isopropyl	4260	3240	3650	7390 (blue)

[a] Spectra of alkylpyridinium iodides taken in chloroform solution 6×10^{-3} *M* (0.45% ethanol) and a silica gel–chloroform slurry for solubility reasons. [b] Values of E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

postulate of hydrogen bonding to the nonbonding electrons in the ground state. This hydrogen bond lowers the energy of the ground state an amount equal to the energy of the hydrogen bond, but the excited state cannot sustain the hydrogen bond and remains at about the same energy. Thus the hydrogen bond is broken in the transition, and spectral shifts in various solvents can be taken as a measure of hydrogen-bond strengths[15] and solvent polarity.[16]

In the case of the n–π^* transition of azobenzene in a silica gel–cyclohexane matrix, however, the spectral shift cannot be wholly accounted for by hydrogen bonding since the shift is greater than for the spectrum of azobenzene in concentrated sulfuric acid, λ_{max} 430 mμ.[17]

It is also difficult to account for the blue shift by dipole–dipole interactions, since the n–π^* excited state for azo compounds should be more polar than the ground state, which would produce a red shift in the case of dipole–dipole interactions.

A possible explanation for the large observed blue shift could be that the molecule is adsorbed parallel to the surface, with the nonbonding sp^2 electrons of the azo group also parallel to the surface. This orientation should be the case for maximum adsorption interaction. Then the nonbonding electrons could be easily involved in weak bonding interactions with molecular orbitals of the surface. These interactions could not be as strong as chemisorption since the energy difference in the spectra is small compared to chemisorption energies (>9000 cm^{-1}) and azobenzene is eluted from silica gel by relatively nonpolar solvents. This type of interaction, coupled with hydrogen bonding, could explain the relatively large blue shifts obtained.

Support for this hypothesis is rendered by the spectrum of azobisisobutyronitrile (AIBN) (Figure 2, Table III), where the blue shift of the n–π^* transition is much smaller. Steric hindrance in AIBN would necessarily weaken the type of interaction postulated above, and the blue shift would be correspondingly smaller. Also, however, the nitrile groups of AIBN are strongly adsorbed on the surface (see Photochemistry section), but it is not known how this would affect the n–π^* transition. Since the azo and nitrile groups of AIBN are not conjugated, presumably the n–π^* transition of the azo group could only be perturbed by surface–azo group interactions. Further experimental investigations are needed to help elucidate the nature of the interaction of azo compounds with the surface of silica gel. These could include (1) determination of spectral shifts on silica gel in which the SiOH sites have been destroyed by methylation or sintering, (2) investigation of the infrared frequencies of the surface silanol groups as a function of adsorbed azo compounds, and (3) investigation of the infrared frequencies of the azo groups adsorbed on silica gel. The mechanism postulated would be consistent with the observation of roughly the same spectral shift on methylated or sintered silica gel, and silanol frequencies in the infrared should not be perturbed to any great extent. Correspondingly, the azo group frequencies should exhibit relatively large perturbations on adsorption onto silica gel.

Charge-Transfer Transitions. a. Nitrobenzene. In the spectrum of nitrobenzene in a silica gel–cyclohexane slurry (Figure 2, Table IV), we have an example of a large shift which is not due to hydrogen bonding. Okuda observed that in the infrared spectrum of nitrobenzene adsorbed on a silica gel plate, the NO_2 frequencies were not perturbed relative to carbon disulfide solution spectra, while the C–H vibrational frequencies showed marked shifts.[18] Abramov and co-workers showed that the silanol OH frequencies of silica gel were not shifted or perturbed at all by adsorption of nitrobenzene.[12] Taken together, these data show that there is no interaction between the silanol sites and the nitro group, as opposed to the hydrogen bonding previously proposed by Robin and Trueblood[8] on the basis of observed shifts for intramolecular hydrogen bonding.

The 2567-A band of nitrobenzene has been assigned to an intramolecular charge transfer between the benzene ring and the nitro group.[19] Obviously the excited state of the charge-transfer transition will be much more polar than the ground state.[20] Bakshiev has calculated the static dipole of the excited state to be 9 D. as compared to 4 D. for the ground state.[21] Dipole–dipole interactions with the polar adsorbent will therefore lower the energy of the excited state relative to the ground state, and thus produce the large red shift observed.

b. Alkylpyridinium Iodides. The alkylpyridinium iodides have an absorption band, the position of which is strongly solvent dependent, that has been correlated with a charge-transfer transition. The transition is

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(15) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

(16) E. M. Kosower, *ibid.*, **80**, 3253, 3261, 3267 (1958).

(17) E. Sawicki, *J. Org. Chem.*, 22, 1084 (1957); *cf. Chem. Abstr.*, **52**, 3813*c* (1958).

(18) M. Okuda, *Nippon Kagaku Zasshi*, **82**, 1121 (1961); *cf. Chem. Abstr.*, **56**, 10948*a* (1962).

(19) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **23**, 1441 (1955).

(20) N. S. Bayliss and E. G. McRai, *J. Phys. Chem.*, **58**, 1006 (1954).

(21) N. G. Bakshiev, *Opt. i Spektroskopiya*, **13**, 43, 192 (1962).

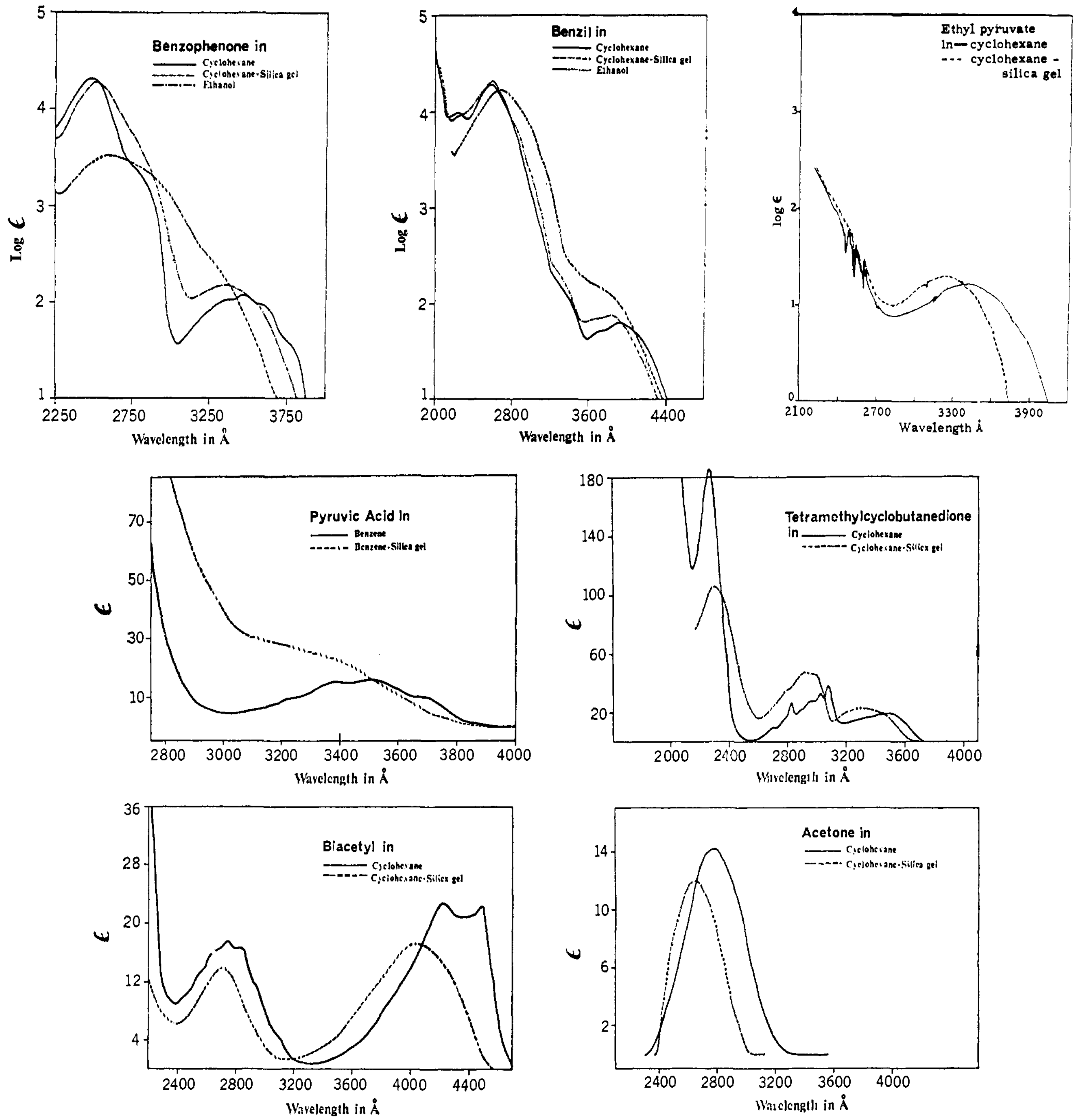
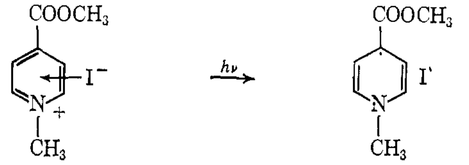


Figure 3. Spectra of ketones.

opposite to that in nitrobenzene in that the ground state is much more polar than the excited state. Kosower has calculated the dipole moment of the ground state as 13.9 D. and that of the excited state as



(1)

8.6 D.[22] Consequently dipole–dipole interactions between the ground-state molecule and the polar silica gel will be more intense than the interactions between the excited state and the adsorbent. Table IV shows that the expected large blue shift as a result of the interactions is obtained with all three salts studied. The position of the charge-transfer band in ethanol is also given for comparison. The transition energy of the 1-ethyl-4-carbomethoxypyridinium iodide in various solvents is taken by Kosower as a measure of the polarity of the solvent (Z value).[22] The λ_{max} of the charge band of 1-ethyl-4-carbomethoxypyridinium iodide on silica gel is at 3250 A, giving silica gel a Z value of 88, intermediate between that of water and methanol.

Ketones. In Figure 3 and Table V we see the spectral shifts of several ketones adsorbed on silica gel.[23] It

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(22) E. M. Kosower, *J. Am. Chem. Soc*, **80**, 3253 (1958)

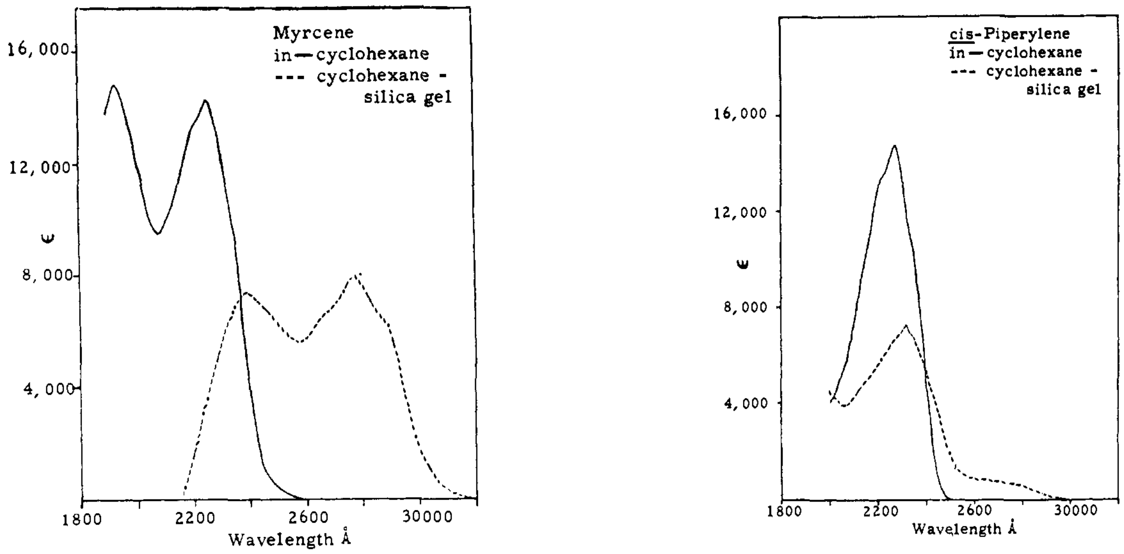


Figure 4. Spectra of myrcene and *cis*-piperylene.

is important to note that these shifts are all much more pronounced than those observed in ethanol. In general for ketones, solvent effects producing a blue shift are taken to characterize n–π^* transitions.[14,15]

Table V. Spectral Shifts of Ketones (cm^{-1})

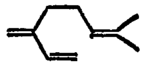
Compound	λ_{max}, A Cyclohexane solution	Ethanol solution	Silica gel–cyclohexane slurry	Spectral shift in ETOH	Spectral shift on silica gel
Acetone	2781		2656		1720 (blue)
Tetramethylcyclo-	3510	3442[a]	3300	570 (blue)	1820 (blue)
butanedione	3080	3040[a]	2915	430 (blue)	1840 (blue)
	2268		2296		520 (red)
Biacetyl	$\left.\begin{matrix}4485\\4230\end{matrix}\right\}4357$		4025		3890 (blue)
	2735		2700		480 (blue)
Pyruvic acid	3525[b]		3400[b] (shoulder)		1040 (blue)
Ethyl pyruvate	3380		3233		1360 (blue)
Benzophenone	3365	3325	...	360 (blue)	...
	2483	2512	2612	460 (red)	1960 (red)
Benzil	3911	3830	3725	520 (blue)	1280 (blue)
	2576	2600	2681	370 (red)	1530 (red)

[a] E. M. Kosower, *J. Chem. Phys.*, **38**, 2813 (1963). [b] Spectra taken in benzene and silica gel–benzene slurry for solubility reasons.

As in the case of the spectral shifts in azo compounds, hydrogen bonding cannot be used to explain the blue shift of the n–π^* bands of ketones adsorbed on silica gel simply because the shifts are so large. Rather, since the excited state is less polar than the ground state in the n–π^* transitions of ketones, dipole–dipole interactions are probably responsible for the blue shifts observed. The red shift of the π–π^* transition bands of ketones in polar solvents is believed due to the greater stabilization of the more polar excited state compared to the stabilization of the ground state.[24] Presumably the stabilization is due to dipole–dipole interactions, and this mechanism can also explain the shift on silica gel.

Again, further experiments are needed to elucidate the nature of the adsorption process for ketones. These experiments would be similar to those called for in connection with the azo compounds. If dipole–dipole interactions and not hydrogen bonding are responsible for the adsorption process for ketones, the same spectral shifts would be expected to occur on methylated or sintered silica gel, and adsorption of ketones would not be expected to greatly perturb the infrared silanol frequencies.

Myrcene. The spectrum of myrcene (I) adsorbed on silica gel is shown in Figure 4 compared to cyclohexane solution. It is seen that the spectrum is shifted from that of a conjugated diene (2250 A) to something more like that of a conjugated triene (2775 A). The shift amounts to 8400 cm^{-1}, or 24 kcal/mole. Chemisorption is not involved here, since myrcene can be eluted from silica gel with cyclohexane. About 60% of the myrcene is recovered (the polymerization which is observed can account for the discrepancy), and ultraviolet spectra show that the species that gave rise to



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(23) P. A. Leermakers and H. T. Thomas, 87, *J. Am. Chem. Soc.*, 1620 (1965).

(24) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 257.

the absorption at 2775 A is present neither in the cyclohexane washings nor on the silica gel. This means that when *physically* adsorbed on silica gel, myrcene exhibits the spectral characteristics of a conjugated triene, which necessitates overlap of the π electrons of the isolated double bond with the conjugated diene π system. The conjugated diene by itself does not exhibit this sort of behavior, as shown by the small shift in the spectrum of *cis*-piperylene in Figure 4.

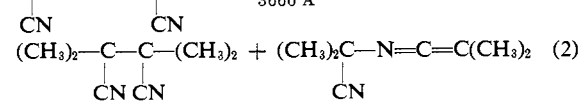
In solution, free rotation and steric hindrance prohibit the isolated double bond of myrcene from interacting with the diene moiety. Adsorption on silica gel, probably with the molecule lying flat on the surface, impresses more rigid geometrical requirements on the molecule, and if the isolated double bond is adsorbed in a configuration which allows overlap with the diene system, it will be held in that configuration.

The two bands observed for myrcene adsorbed on silica gel could then be due to two types of adsorbed configuration. That is, the band at 2775 A would be due to a configuration where overlap occurs between the diene system and the isolated double bond, and the band at 2388 A is due to a configuration where no overlap occurs but the band is merely shifted from 2250 A. Alternately, the band at 2388 A could be considered as shifted from 1930 A and there may be only one configuration upon adsorption.

Photochemical Reactions.[25] The adsorption of molecules on the surface of silica gel not only perturbs the electronic absorption spectra, and, consequently, the initial energy input for a photochemical reaction, but also provides an environment which can profoundly affect the course of secondary photochemical reactions. The environment can be considered intermediate between that of a solution, where the molecules have complete freedom of movement, and a solid glass at 77°K, where most molecules occupy their zeroth vibrational level.

The direct photolyses of azobisisobutyronitrile (AIBN) and tetramethyl-1,3-cyclobutanedione (TMCD),[25] and the photosensitization of piperylene by various donors,[26] illustrate several aspects of this environmental control.

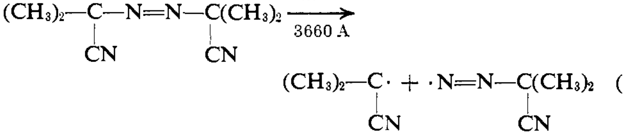
AIBN in benzene solution undergoes photodecomposition[27] with light of 3660 A to yield approximately 60% of the ketenimine dimethyl-N-(2-cyano-2-propyl)-ketenimine (eq 2), the remainder being tetramethylsuccinonitrile. The quantum yield for decomposition of AIBN was found to be 0.46. The course of the reaction can be followed by the appearance of the characteristic ketenimine absorption band at 2900 A, and the simultaneous disappearance of the n,π^* (3200–3500 A) band of the azo compound. The ketenimine is formed as an unsymmetrical coupling product between cyanopropyl radicals and valence isomeric cyanopropyl radicals ($((CH_3)_2\text{-}C{=}C{=}N\cdot)$).



$$(CH_3)_2\underset{CN}{C}-N=N-\underset{CN}{C}-(CN_3)_2 \xrightarrow[3660\ A]{h\nu} N_2 + (CH_3)_2\underset{CN}{C}-\underset{CN}{C}-(CH_3)_2 + (CH_3)_2\underset{CN}{C}-N=C=C(CH_3)_2 \quad (2)$$

On changing the medium to a silica gel–benzene matrix, the AIBN decomposes at a similar rate, but no ketenimine is formed, the sole nongaseous product being tetramethylsuccinonitrile.[24] The difference can be explained by the nature of the binding between AIBN and the silica gel surface. The cyano groups are bound to the surface's active sites; consequently, the cyanopropyl radicals produced by photolysis are not free to rearrange as in solution. Hence no unsymmetrical coupling product can be formed and carbon–carbon coupling is the exclusive reaction.

An EPA glass at 77°K creates even stricter environmental controls. Photolysis of AIBN in this medium results in negligible decomposition over a period of 12 hr, while in EPA solution at 25° almost complete decomposition occurs within 4 hr. The difference can be attributed to the "cage effect" of the medium, and the results indicate that the radicals formed on photolysis are a cyanopropyl and an azo cyanopropyl radical, (eq 3) which recombine within the cage to give AIBN, *i.e.*, nitrogen is lost in a two-step process and not in a concerted step as was considered to be the general case by early workers.[28] Although later workers[29] were undecided between a one- and two-step mechanism, recent studies on the thermal decomposition of azo compounds[30] and the esr spectra of several irradiated azo compounds[31] have favored a two-step rupture, with the second step much faster than the first. At 77°K the loss of nitrogen from the azo cyanopropyl radical becomes a much slower process so that radical–radical recombination within the matrix cage greatly predominates over the loss of nitrogen. Asycough[31] studied the esr spectra of six irradiated azo compounds at 77°K, and found that only AIBN produced stable azo radicals. The others decomposed, even at 77°K, with the evolution of nitrogen. Warming the azo cyano radical, or allowing it to stand for several days at 77°K, resulted in its decomposition. Presumably the cyano group β to the azo group confers stability to this particular radical.



$$(CH_3)_2\underset{CN}{C}-N=N-\underset{CN}{C}(CH_3)_2 \xrightarrow[3660\ A]{h\nu} (CH_3)_2\underset{CN}{C}\cdot + \cdot N=N-\underset{CN}{C}(CH_3)_2 \quad (3)$$

TMCD in benzene solution undergoes photodecomposition with light of 3660 A to yield 80% tetramethylethylene and carbon monoxide. The reaction proceeds *via* an intermediate cyclopropanone, and the quantum yield for decomposition was found to be 0.38.[32]

In a silica gel–cyclohexane matrix, and irradiating at 3130 A, the quantum yield for decomposition is reduced threefold. The difference again can be attributed to the environmental effect of the binding between

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ketone and surface. Assuming a two-step rupture for release of carbon monoxide, after the initial step the two radicals are held in close proximity on the silica gel surface and consequently acyl–alkyl bond re-formation can compete effectively with unredeemable photodecarbonylation.

Photolysis of TMCD in an EPA glass at 77°K results in negligible decomposition for the radicals formed within the solvent cage directly recombine to yield TMCD.

The photostationary state produced in piperylene (1,3-pentadiene) by sensitizing the *cis–trans* isomerization is strongly dependent upon the triplet energy of the sensitizer.[33] The silica gel–solvent matrix provides an opportunity of altering the triplet energy of the sensitizer, while that of the piperylene remains little affected. Benzophenone, 2-acetonaphthone, and biacetyl were used as photosensitizers, and the values for the *cis–trans* photostationary state produced in piperylene in benzene solution and in a silica gel–benzene matrix are consistent with electronic perturbations, as we have recently reported.[26]

Experimental Section

Materials. Silica gel was chromatography grade Fisher 28–200 mesh and was activated by heating in an oven at 200° for at least 10 hr. The solvents used in determining spectra were Fisher Certified Reagent spectranalyzed cyclohexane, Rossville Gold Shield alcohol (200 proof ethanol), and Baker Analyzed reagent spectrophotometric benzene. Samples of the alkylpyridinium iodides were kindly donated by Professor E. M. Kosower. 1-Methyl-4-carbomethoxypyridinium iodide was purified by two recrystallizations from methanol, mp 188–190°. The 1-ethyl salt was dissolved in warm methanol and precipitated by the addition of ether. Two recrystallizations gave a salt with mp 110–112°. The 1-isopropyl salt was used without further purification, mp 134–136°. All other materials were of reagent grade and were used without further purification.

Spectra. All spectra were recorded on a Cary 14 spectrophotometer. Cells were standard quartz Beckman cells with a path length of 0.1 cm. The procedure for filling the cells was as follows. The material, at known concentration in the appropriate solvent, was poured into the cell. The silica gel was added slowly to the solution in small amounts from a tiny spatula, with considerable agitation and stirring from a fine wire. All air bubbles were removed by this technique, and the slurry took on a homogeneous appearance. The net increase in volume after addition of the silica gel was 10–15%.

Photolyses. Determination of Relative Quantum Yields of AIBN Photolyzed in Benzene and Silica Gel–Benzene Matrix. The apparatus used consisted of an optical bench with light source (500-w, high-pressure mercury arc made by PEK Manufacturing Co.), collimating lens, filter (Corning 7-60 glass filter), and sample holder to permit simultaneous irradiation of four samples. The samples were in 0.1-cm quartz Beckman cells, filled as before, and the reaction was followed on the Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer by observing the disappearance of the absorption band at 3500 and 3447 A for photolysis in solution and matrix, respectively.

Product Analysis for AIBN Photolyzed in Silica Gel–Benzene Matrix. For gross product analysis 5.0 g of AIBN (Eastman Kodak White Label) was placed in a matrix consisting of 180 ml of benzene and 88 g of silica gel and irradiated until 88% of the theoretical yield of nitrogen was evolved (150 min). The product was washed off silica gel with methanol, the solvent stripped, and the crystalline mass chromatographed on alumina; 3.28 g of tetramethylsuccinonitrile (90% net yield) was obtained which melted at 166–168° after sublimation (lit.[34] 169°). Identification was based on comparison of infrared and nmr spectra with those of an authentic sample.

Determination of Relative Quantum Yields of TMCD Photolyzed in Cyclohexane and Silica Gel–Cyclohexane Matrix. The apparatus used was the same as that for the AIBN quantum yield determination, with exception of the filter system, where an aqueous solution filter containing 145 g of nickel sulfate hexahydrate and 41.5 g of cobaltous sulfate heptahydrate per liter was placed in series with a Corning 7-54 glass filter. Analysis was based on the disappearance of the bands at 3080 and 2915 A for the solution and matrix, respectively.

The rate of CO evolution on photolysis of the dione was determined by photolysis in a Pyrex 450-w Hanovia immersion reactor, measuring the gas evolved in an eudiometer. The initial rates for 1.4 g of dione were 147 ml of CO/hr in solution and 43 ml/hr in the matrix.

Photolyses in an EPA Glass. Degassed solutions of AIBN or TMCD in EPA (1.6×10^{-3} *M*) were sealed under vacuum in Pyrex vessels. These were cooled in liquid nitrogen yielding a clear glass, and suspended in liquid nitrogen held in an unsilvered dewar placed adjacent to the Hanovia immersion reactor. A jet of air playing on the dewar surface prevented frosting of the dewar wall.

Analyses were based on the disappearance of absorption bands as in the solution and silica gel photochemistry.

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