5.15 (each 1 H, d, J = 16 Hz, 6-H_2), 7.50–8.30 (5 H, m, 5 Ar H); mass spectrum, m/e 380 (M^+). Anal. Calcd for $C_{21}H_{20}N_2O_5 \cdot 0.5H_2O$: C, 64.77; H, 5.44; N, 7.19. Found: C, 64.74; H, 5.30; N, 7.08.

3-(Acetoxymethyl)-12b,2-(epoxyetheno)-1,2,3,12b-tetrahydro-14-(methoxycarbonyl)-13-methyl-6*H*-indolizino[1,2-*b*]quinolin-4-one (31). A solution of the above methyl ester (**30b**, 100 mg, 0.265 mmol) and Ac_2O (0.5 mL) in pyridine (0.5 mL) was stirred for 2 h at 50 °C. The reaction mixture was poured into aqueous $NaHCO_3$ and then extracted with benzene. After the extract was dried over Na_2SO_4, evaporation of the solvent gave a crystalline mass, which was recrystallized from MeOH to afford the acetate **31b**: 104 mg (93.6%); colorless needles; mp 200–202.5 °C; IR ($CHCl_3$) 1725, 1700, 1655, 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (3 H, s, Ac), 2.20 (3 H, s, 13-Me), 3.70 (3 H, s, OMe), 4.51 (2 H, d, J = 6 Hz, CH_2OAc), 4.73 and 5.20 (each 1 H, each d, J = 16 Hz, 6-H_2), 7.56–8.33 (5 H, m, 5 Ar H); mass spectrum, m/e 422 (M^+). Anal. Calcd for $C_{23}H_{22}N_2O_6 \cdot 0.75H_2O$: C, 63.37; H, 5.43; N, 6.43. Found: C, 63.72; H, 5.23; N, 6.41.

The epimer **30a** (100 mg) was converted, by the same procedure, to the corresponding acetate **31b**: 102 mg (93.0%); mp 194–195 °C; IR ($CHCl_3$) 1725, 1700, 1660, 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.05 (3 H, s, Ac), 2.18 (3 H, s, 13-Me), 3.70 (3 H, s, OMe), 4.73 and 5.20 (each 1 H, each d, J = 16 Hz, 6-H_2), 7.45–8.30 (5 H, m, 5 Ar H); mass spectrum, m/e 422 (M^+). Anal. Calcd for $C_{23}H_{22}N_2O_6 \cdot 0.75H_2O$: C, 63.37; H, 5.43; N, 6.43. Found: C, 63.12; H, 5.13; N, 6.32.

3-(Acetoxymethyl)-1,2,3,12b-tetrahydro-2-[1-(methoxycarbonyl)-2,2-(ethylenedithio)propyl]-6*H*-indolizino[1,2-*b*]quinolin-4-one (33). To a solution of the acetate **31b** (100 mg, 0.238 mmol) in CF_3CO_2H (3 mL) was added ethanedithiol (0.5 mL), and the mixture was refluxed for 2 h. After evaporation of the reagents, the residue was chromatographed on silica gel. Elution with benzene–Me_2CO (26:1 v/v) afforded the thioketal **33**: 70 mg (57.7%); syrup; IR ($CHCl_3$) 1725, 1650 cm^{-1}; NMR ($CDCl_3$) δ 4.90 (2 H, s, 6-H_2), 6.27 (1 H, d, J = 4.5 Hz, 1-H); mass spectrum, m/e 498 (M^+).

3-(Acetoxymethyl)-2-[1-(methoxycarbonyl)propyl]-6*H*-indolizino[1,2-*b*]quinolin-4-one (34). A mixture of the thioketal **33** (65 mg, 0.127 mmol) and W-2 Raney Ni (1.3 g) in EtOH (10 mL) was refluxed for 2 h. After filtration, the filtrate was evaporated, and the residue was chromatographed on silica gel. Elution with benzene–Me_2CO (19:1 v/v) afforded a syrup (30 mg), which was dissolved in benzene (5 mL). After addition of DDQ (46 mg, 0.2 mmol), the mixture was refluxed for 10 min and then poured into aqueous $NaHCO_3$. Extraction with benzene, followed by washing with H_2O, drying over Na_2SO_4, the evaporation of the solvent, gave a residue, which was chromatographed on silica gel. Elution with $CHCl_3$ afforded a powder, which was recrystallized from $CHCl_3$–*n*-hexane to give 34: 14 mg (31.3% from **33**); mp 176–179.5 °C (lit.[13] mp 171–178 °C); UV and NMR spectra were identical with reported ones.[13]

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Silica Gel Mediated Photoisomerization of Retinal Isomers and Comparisons with Other Forms of Environmental Perturbation

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The electronic spectra and photoreactivity of slurries of retinal isomers, prepared by adsorbing the isomers onto wet silica gel and suspending the support in cyclohexane, have been investigated. Adsorption of 9-*cis*-, 11-*cis*-, 13-*cis*-, and *all-trans*-retinal is accompanied by an ~3000-cm^{-1} red shift of their lowest energy absorption band maxima relative to their band positions in homogeneous cyclohexane solution. Irradiation of the slurries at 514.5 nm, a wavelength inefficiently absorbed in the absence of silica gel, leads to reasonably efficient photoisomerization of each of these isomers. Prolonged photolysis yields a mixture of the four isomers that is photostationary with respect to relative concentrations and richest in 11-*cis*-retinal, which constitutes ~35% of this mixture. Although small quantities of other isomers are present, the photostationary composition of the heterogeneous photolysate can be predicted with reasonable accuracy from the relative absorptivities and primary photoprocesses of the four principal isomers comprising the photolysate. Comparisons with primary photoprocesses reported for retinal isomers in polar and nonpolar solvents reveal that adsorption onto silica gel can result in novel patterns of photoisomerization. Complementary comparisons are made with the electronic spectra and photoreactivity of adducts formed in hydrocarbon solution from retinal isomers and a lanthanide β-diketonate complex. The excited-state properties of these various retinal-based systems highlight the importance of environment in controlling photoreactivity. Steric and electronic factors that may contribute to the observed features of silica gel mediated photoisomerization are discussed in this context.

The perturbation of electronic structure and excited-state reactivity through changes in environment is well established for molecular species. Although solvent and temperature have traditionally been used to elicit these effects,[1] recent studies have demonstrated that adduct formation and adsorption onto silica gel can also profoundly influence the excited-state properties of a substrate. Examples of systems for which adduct-mediated photochemistry has been reported include the Lewis acid/Lewis base combinations of BF_3/3,4,6,6-tetramethyl-2,4-cyclohexadienone,[2] $EtAlCl_2$/α,β-unsaturated

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Table I. Spectral Properties of Retinal Isomers in Different Environments[a]

retinal isomer	medium[b]	λ_{max},[c] nm	$10^{-4}\epsilon$,[d] M^{-1} cm^{-1}	$10^{-3}\Delta E$,[e] cm^{-1}	retinal isomer	medium[b]	λ_{max},[c] nm	$10^{-4}\epsilon$,[d] M^{-1} cm^{-1}	$10^{-3}\Delta E$,[e] cm^{-1}
all-trans	isooctane	369	4.9	3.5	11-cis	isooctane	363	2.7	3.9
	adduct	424	5.4			adduct	423	3.9	
	cyclohexane	368	5.0	2.8		cyclohexane	364	2.7	3.1
	silica gel	410	4.8			silica gel	410	2.4	
9-cis	isooctane	361	3.9	3.7	13-cis	isooctane	363	4.0	3.9
	adduct	417	4.3			adduct	422	4.1	
	cyclohexane	365	3.9	2.5		cyclohexane	360	4.0	2.9
	silica gel	402	4.0			silica gel	402	3.6	

[a] Electronic spectral features of retinal isomers in several environments, obtained by using N_2-saturated solvents at 295 K. [b] The first entry for each isomer, taken from ref 4, refers to data acquired in isooctane solution. Entries for adduct refer to isooctane solutions to which $Eu(fod)_3$ was added until spectral changes ceased, as described in ref 4. Entries labeled cyclohexane correspond to spectral features in that solvent, and entries labeled silica gel represent data obtained for cyclohexane slurries of retinal adsorbed onto silica gel ($(\sim 2\text{-}4) \times 10^{-6}$ mol retinal/g of silica gel), prepared as described in the Experimental Section. [c] Wavelength of maximum absorption for the lowest energy absorption band. [d] Extinction coefficient at λ_{max}. [e] Spectral shift of the lowest energy absorption band. For the adduct, the shift is relative to the λ_{max} value in isooctane solution; for the silica gel environment, it is relative to the λ_{max} value found in cyclohexane solution.

esters,[3] $Eu(fod)_3$/retinal isomers,[4] and $Eu(fod)_3/(\eta^6$-acetophenone)$Cr(CO)_3$,[5] where fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate. For several of these systems, selective excitation of the adduct was possible, owing to a significant spectral shift in the Lewis base's absorption spectrum upon adduct formation.

Electronic spectral shifts for a wide variety of organic substrates have been observed following their adsorption onto silica gel, yet only in a few cases has the photochemistry of the adsorbed species been examined.[6-8] Only in one case, to our knowledge, that involving the aforementioned 2,4-cyclohexadienone derivative, has a direct comparison of the effects of solvent, adduct formation, and silica gel on photochemistry been made. Exploration of photochemistry in the heterogeneous system has perhaps been hindered by complexity arising from such features as multiple-binding-site environments and possibilities for intergranular and intragranular motion.[7]

While investigating the $Eu(fod)_3$/retinal adduct system, we became aware that shifts in the *all-trans*-retinal spectrum induced by $Eu(fod)_3$ were similar to those produced by adsorption onto silica gel[9] and by phenol at 77 K in 3-methylpentane.[10] These similarities prompted us to investigate the photochemistry of retinal isomers adsorbed onto wet silica gel. Retinal, of course, has a rich photochemistry based on isomerization, a reaction whose significance is highlighted by the crucial role that the 11-cis and all-trans isomers play in the vision process.[11] *All-trans*-retinal is a particularly attractive candidate for study, since the dependence of its isomerization photoproducts on solvent polarity and adduct formation is indicative of a strong sensitivity to environment; the 11-cis isomer, for example, is not found when *all-trans*-retinal is photolyzed in a nonpolar solvent such as isooctane but appears when $Eu(fod)_3$ is added to such a solution or when the photolysis is conducted in a polar solvent such as ethanol or acetonitrile.[4,12-14]

We report in this study that, like $Eu(fod)_3$/retinal adducts, silica gel can mediate the isomerization of certain retinal isomers by using relatively low-energy photons. We show that a mixture of isomers is produced under these conditions that is photostationary with respect to relative concentrations and richest in the 11-cis isomer. Moreover, we demonstrate that the photostationary composition can be predicted with reasonable accuracy from the relative absorptivities and primary photoprocesses of each isomer present in significant quantities in the heterogeneous photolysate. In many cases the primary photoprocesses observed for silica gel mediated photoisomerization differ markedly from those reported for homogeneous solutions of the isomers, and steric and electronic features that might contribute to these differences are discussed.

Results and Discussion

Our studies have focused on four retinal isomers—all-trans, 9-cis, 11-cis, and 13-cis. In sections below we describe the electronic spectra and photochemistry of these isomers when adsorbed onto wet silica gel to form a slurry in cyclohexane. The silica gel is characterized by its supplier as having a surface area of ~ 300 m^2/g, a surface density of ~ 5 SiOH groups/nm^2, and a pore volume of 1.6 mL/g (average pore radius of ~ 100 Å).

Electronic Spectra. Exposure of yellow cyclohexane solutions of retinal isomers to wet silica gel resulted in slurries that appeared orange to the eye. The similar refractive indices of the silica gel and cyclohexane permit electronic spectra of slurries to be recorded with minimal interference from scattering.[6] Spectra so obtained indicate that the observed color change is accompanied by a substantial red shift in the lowest energy absorption band maximum for all four retinal isomers, Figure 1 and Table I; the spectral change observed for the all-trans isomer accords well with a previous report.[9] At the concentrations employed ($\sim 3 \times 10^{-6}$ mol of retinal/g of silica gel), essentially all of the retinal was adsorbed, as indicated by the absence of retinal absorption bands in electronic spectra of the supernatant liquid.

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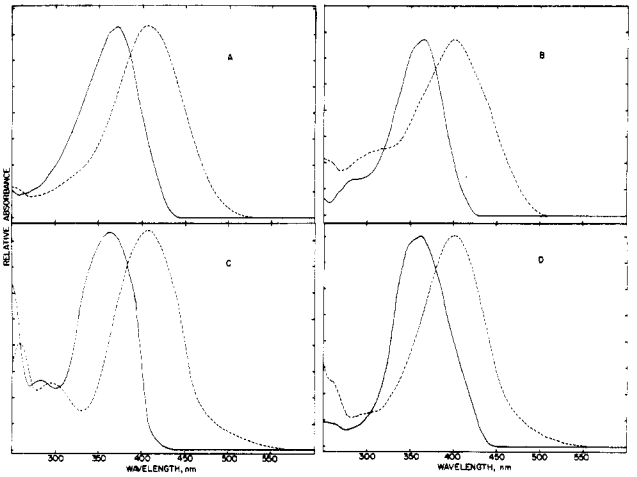

Figure 1. Absorption spectra of retinal isomers. Panels A, B, C, and D correspond to the all-trans, 9-cis, 11-cis, and 13-cis isomers, respectively. Solid curves are spectra of ~0.4–0.9 mM cyclohexane solutions of retinal. Dashed curves are spectra of retinal isomers adsorbed onto silica gel ((~4–8) × 10^{-7} mol of retinal/g of silica gel), which was subsequently suspended in cyclohexane to form a slurry. For each isomer, the quantity of retinal adsorbed was adjusted to give an absorbance comparable to that shown in the corresponding solid curve; this quantity was generally within 5–10% of the amount of retinal used for the solution spectrum. A 0.10-cm path-length cell was employed for all spectra.

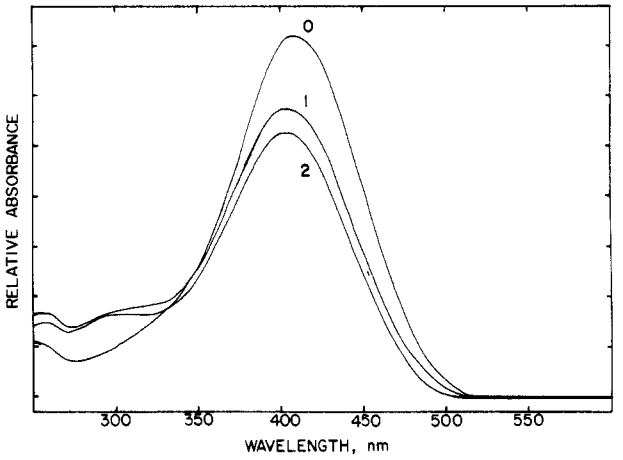

Figure 2. Absorption spectral changes accompanying the 514.5-nm photolysis of a cyclohexane slurry of *all-trans*-retinal adsorbed onto silica gel (6.5 × 10^{-7} mol of retinal/g of silica gel; 0.10-cm path-length cell). Curve 0 is the initial spectrum, and curves 1 and 2 are spectra after total photolysis times of 1 and 10 min. The entire solution (~1.5-cm^2 cell window area) was irradiated with ~80 mW of power.

The enormous spectral shifts of ~3000 cm^{-1} accompanying adsorption of retinal isomers onto silica gel are comparable to shifts observed with $Eu(fod)_3$[4] and phenol (77 K)[10] in hydrocarbon solutions and prompt us to speculate on the sites and forces involved in these interactions. In the case of $Eu(fod)_3$, NMR data obtained with related lanthanide β-diketonate complexes indicated that adduct formation occurred between the lanthanide center and the retinal carbonyl oxygen atom through the latter's lone pairs of electrons.[15] For phenol, hydrogen bonding through the carbonyl oxygen atom was proposed as the interaction responsible for the spectral shift.[10] A similar interaction utilizing the silanol groups of silica gel could be present in the heterogeneous system, but siloxane groups as well as the water present could be involved too. We found that adsorption of retinal isomers did not occur after dehydroxylation of the silica gel with $(CH_3)_2SiCl_2$ but did occur after dehydration (110 °C at 10^{-5} torr for ≥3 h), suggesting that the silanol groups serve as the primary binding sites. A need for surface protons for binding *all-trans*-retinal to silica gel was also inferred from experiments in which silica, deprotonated by NH_3 and then reactivated by heating, did not bind the isomer.[9] As might be predicted from these observations, no substantial spectral shift was observed for silica gel slurries of retinal in ethanol where binding to the support presumably must compete with the favorable solvation interactions offered by a hydrogen-bonding solvent. Although these observations collectively implicate binding between the silanol and aldehyde functionalities, the retinal polyene chain may also contribute to adsorption and to the observed spectral shift, effects that have been observed with silica gel for a variety of olefinic species.[6]

With regard to the forces operating in the silica gel/retinal system, adsorption has generally been described in terms of hydrogen bonding, electrostatic interactions, and dispersion forces.[7] While all of these forces could be involved in producing the observed spectral shift, the $Eu(fod)_3$ data and studies of rhodopsin suggest that electrostatic interactions might be particularly important. In the latter case, the large spectral red shift that occurs when retinal is combined with opsin to form rhodopsin has been described by a "point charge" model.[16] For retinal, polarization from electrostatic interactions could certainly be expected to red shift the intense π,π* band by analogy to solvent polarity effects.[17] That the spectral shifts induced by $Eu(fod)_3$ and silica gel greatly exceed those resulting from changes in solvent polarity[18] may be due to the more localized interaction present in the adduct and heterogeneous systems. Another factor that could contribute to the spectral perturbation is conformational change induced in retinal by complexation. The absorptivity of the 11-cis isomer is believed to be particularly sensitive to environment in this regard.[18] Although a large absorptivity increase does accompany complexation of this isomer with $Eu(fod)_3$, Table I shows that adsorption of 11-*cis*-retinal onto silica gel results in only a modest decrease in its absorptivity. In fact, Table I reveals that all of the isomers exhibited only minor changes in absorptivity (≤10%) for the lowest energy absorption band when adsorbed onto silica gel.

Photochemistry. The spectral shifts depicted in Figure 1 indicate that the adsorption of retinal isomers onto silica gel permits the exploration of photochemistry with efficient absorption of relatively low-energy photons. We employed 514.5-nm excitation in our photolyses. At this wavelength, a 2-mM cyclohexane solution (1.0-cm path-length cell) of *all-trans*-retinal was optically dilute and showed a negligible change in its absorption spectrum when photolyzed for 1 h with 80 mW of incident power. In contrast, a cyclohexane slurry of silica gel containing the same quantity of retinal was optically dense and, when photolyzed under identical conditions, yielded immediate spectral changes. Figure 2 reveals that a substantial decline in absorbance is readily apparent after only 1 min

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Table II. Photostationary Composition of Retinal Isomers Adsorbed onto Silica Gel[a]

retinal isomer	% obsd in mixture[b]	% calcd in mixture[c]
all-trans	29	29
9-cis	22	26
11-cis	36	35
13-cis	12_5[d]	10

[a] Composition of the photolysate prepared by prolonged 514.5-nm excitation of *all-trans*-, 9-*cis*-, 11-*cis*-, or 13-*cis*-retinal adsorbed onto silica gel in a cyclohexane slurry. [b] Percentage of each of the four indicated isomers in the photolysate, as determined by HPLC. The summation of these percentages to 100 assumes the absence of other isomers. As described in the text, evidence that other isomers are present in small quantities was obtained. [c] Percentage of each of the four indicated isomers in the photolysate calculated from relative absorptivities (footnote 23) and primary photoprocesses (Table III; Figure 3), as described in footnote 24. The assumption is made that these are the only isomers contributing to the photostationary composition. [d] Probably includes a small contribution from 9,13-*cis,cis*-retinal, which has a similar retention time under our experimental conditions.

of 514.5-nm excitation. This is consistent with the occurrence of photoisomerization, based on the absorptivities of Table I.

Analysis of the photolysate was accomplished by using ^{1}H NMR spectroscopy and high-pressure liquid chromatography (HPLC); methylene chloride, used to desorb retinal, was subsequently removed under vacuum, and the residue was redissolved in $CDCl_3$ or isooctane for characterization by ^{1}H NMR spectroscopy or HPLC, respectively. Photolysates prepared by prolonged irradiation of adsorbed *all-trans*-retinal exhibited four prominent doublets in the NMR aldehyde region and four principal peaks in the HPLC trace. These features correspond to the all-trans, 9-cis, 11-cis, and 13-cis isomers of retinal, as demonstrated by agreement with literature data[19] and authentic samples. The photodependence of the product isomers was established in dark control experiments in which each of the isomers, adsorbed onto silica gel for times comparable to those used in the photolyses, was recovered from silica gel with negligible isomerization. Roughly 85% of the retinal was recovered in these experiments with at least part of the loss attributable to retention of the isomers by the silica gel (vide infra).

Quantitative HPLC analysis of the heterogeneous photolysate permitted us to determine that the four retinal isomers establish a photostationary composition with respect to relative concentrations upon prolonged photolysis. Our evidence consists of (1) an invariant set of relative concentrations when the photolysate is examined after successive long-term excitation periods and (2) observation of the same relative concentrations independent of which of the four isomers is initially present. The photostationary composition, presented in Table II, is richest in the 11-cis isomer, which accounts for about a third of this mixture. Together, the four isomers represent a recovery after ~1 h of photolysis of ~85% of the retinal initially present. We find that the quantity of the retinal recovered decreases with increasing irradiation times, declining, for example, to ~75% after 2 h. This trend may not reflect decomposition so much as a progressive inability to desorb the retinal: after exhaustive desorption attempts using CH_2Cl_2, a slurry of the now pale orange silica gel in cyclohexane gave an electronic spectrum consistent with the presence of a mixture of retinal isomers. Similar difficulties in desorbing retinal with increasing time were seen in dark control experiments. A possible explanation for this behavior is the slow migration of retinal into sites from which its extrication is particularly difficult. Pores in the silica gel might, for example, provide such an environment.

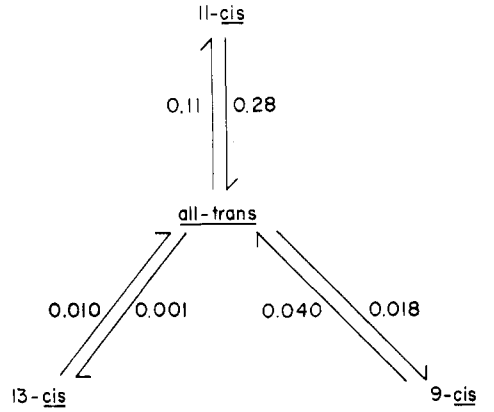

Figure 3. Primary photoprocesses of retinal isomers adsorbed onto silica gel and photolyzed as a cyclohexane slurry with 514.5-nm excitation. Arrows point toward the principal primary photoproduct(s) of the starting isomer, and numbers alongside of the arrows are the appearance quantum yields, ϕ_a, for the photoproduct. As described in the text, these isomers represent the principal species found in photolysates, but small quantities of other isomers are present as well.

Although the four isomers of Table II dominate the photolysate, HPLC reveals the presence of several other species as well. Specifically, we see peaks that we believe correspond to the 7-cis and 11,13-cis,cis isomers of retinal on the basis of retention times;[4,12] while only a minor product here, the 11,13-cis,cis isomer was a major product in adduct-mediated photolyses.[4] We also believe that some 9,13-*cis,cis*-retinal is present and contributes to the HPLC band of 13-*cis*-retinal: the retention times are similar,[20] and a species having this retention time appears to be a primary photoproduct of 9-*cis*-retinal (vide infra). Supporting the presence of other retinal isomers are changes in the HPLC trace accompanying successive injections of a photolysate after irradiation has ceased: modest increases in the 9-*cis*- and 13-*cis*-retinal bands are apparent, behavior consistent with the dark thermal isomerization that has been observed for the cis,cis isomers.[21,22] While our lack of authentic samples precludes a definitive determination of the identity and quantity of these other isomers, we emphasize that they do represent only a minor portion of the photolysate on the basis of the quantity of identifiable retinal isomers recovered.

The availability of the principal isomers contributing to the photostationary composition in pure form makes the composition amenable to prediction from a knowledge of isomeric absorptivities and primary photoprocesses. We determined relative absorptivities at 514.5 nm by adsorbing identical quantities of the four isomers separately onto silica gel and recording their absorbances at this wavelength;[23] Beer's Law was verified for *all-trans*-retinal over

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(22) A sample of 9,13-*cis,cis*-retinal was isolated by HPLC from the photolysate of a cyclohexane solution of 9-*cis*-retinal irradiated with an 8-W General Electric blacklight (output from ~330 to 380 nm).[20] HPLC revealed that in isooctane/2% diethyl ether, the 9,13-cis,cis isomer thermally isomerized to the 9-cis and 13-cis isomers.

Table III. Primary Photoprocesses of Retinal Isomers in Different Environments[a]

retinal isomer	medium[b]	λ_{ex},[c] nm	ϕ_d[d]	ϕ_a[e] for photoproducts: all-trans	9-cis	11-cis	13-cis	ref
all-trans	3-methylpentane	350	0.12		0.015		0.105	31
	methanol	350	0.006		0.0006	0.0018	0.0036	32
	silica gel	514.5	0.13		0.018	0.11	0.001	
9-cis	3-methylpentane	350	0.18	0.12				20
	methanol	350	0.04	0.03				20
	silica gel	514.5	0.040	0.040		f	f	
11-cis	3-methylpentane	350	0.25	0.25				33
	methanol	350	0.04	0.04				20
	silica gel	514.5	0.28	0.28	f		f	
13-cis	3-methylpentane	350	0.32	0.32				31
	methanol	350	0.05	0.05				20
	silica gel	514.5	0.010	0.010	f	f		

[a] Quantum yields and primary photoproducts of retinal isomers in different environments. [b] Environment in which experiments were conducted. Data for homogeneous solutions (3-methylpentane or methanol solvents) were obtained from the literature, as noted in the table. Silica gel refers to data from this study in which isomers were adsorbed onto that support. Conditions under which the data were acquired are detailed in the Experimental Section. [c] Excitation wavelength. [d] Quantum yield for the disappearance of the starting retinal isomer at the indicated wavelength; ϕ_d values for this study, determined by HPLC, are uncorrected for reflective losses and have estimated error bars of ±10%. [e] Quantum yields for the appearance of photoproducts from photolysis of the indicated starting retinal isomer whose disappearance is represented by ϕ_d (cf. footnote d). Only ϕ_a values for four isomers are given, although in several cases isomers other than those shown (e.g., 7-*cis*-, 9,13-*cis*,*cis*-retinal) are reported to be primary photoproducts in the homogeneous solution systems (see Table III references). As described in the text, HPLC indicates that isomers besides those listed may also be primary photoproducts in silica gel mediated photoisomerization. Quantum yields obtained in this study are uncorrected for reflective losses and have estimated error bars of ±10%. [f] We found no evidence by HPLC that the three monocis isomers were primary photoproducts of one another. The quantum yields for their interconversion can be obtained indirectly by multiplying the quantum yield for conversion of the starting cis isomer to *all-trans*-retinal by the quantum yield for conversion of *all-trans*-retinal to the final cis isomer (two-photon processes).

the concentration range of (~0.1–3) × 10^{-6} mol/g of silica gel.

Primary photoproducts and appearance and disappearance quantum yields (ϕ_a and ϕ_d, respectively) were determined for each isomer in short-term irradiation experiments, the photolysates of which were analyzed by HPLC. Quantum yields were determined several times for each isomer by using at least five irradiation periods, and in all cases the data were extrapolated back to zero conversion at zero time; retinal recovery in these experiments was ~90–95%. Table III summarizes our results and Figure 3 shows the relevant isomeric interconversions pictorially. Although ϕ_d for each isomer is roughly equivalent to the ϕ_a value of its photoproduct (or to the sum of ϕ_a values in the case of the all-trans isomer), the ϕ_d values in some cases do slightly exceed the ϕ_a values, consistent with the formation of small quantities of other isomers whose presence is observed in the photostationary composition. In modeling this system, we have assumed the absence of these isomers, since their fractional contribution to the photolysate appears to be small. With this assumption and equations corresponding to the steady-state concentrations of retinal isomers,[24] the photostationary-state composition was calculated and is given in Table II. Agreement between the calculated and observed compositions is seen to be quite good.

Besides summarizing the primary photoprocesses observed in silica gel mediated photoisomerization, Table III provides analogous information previously reported for homogeneous solutions of retinal in a polar and nonpolar solvent. Comparisons of the tabulated values demonstrate that silica gel yields novel photoisomerization patterns. For example, the ϕ_d value for *all-trans*-retinal resembles that found in a nonpolar solvent, yet the photoproducts include the 11-cis isomer, which is characteristic of a polar solvent. Despite that similarity, however, the absolute and relative ϕ_a values differ greatly from those of the polar solvent. The other isomers also afford interesting comparisons: photoreactivity of the 9-cis and 13-cis isomers on silica gel more closely resembles their properties in the polar solvent, whereas adsorbed 11-*cis*-retinal mimics photoreactivity in the nonpolar solvent.

Although a detailed discussion of the origin of these effects is premature at this time, some of the steric and electronic effects that may be influencing the course of photoisomerization are worth discussing. We will focus on *all-trans*-retinal, since it exhibits the greatest diversity of photoproducts and has been the isomer most intensively studied. For this isomer, the presence of 11-*cis*-retinal in its photolysate has been shown to be dependent on solvent polarity; the 11-cis isomer is absent when the photolysis is conducted in hydrocarbon solvents but present with use of a variety of polar solvents.[12–14] A model that has been proposed for this behavior is "state-switching", wherein, in polar solvents, the $^1\pi,\pi^*$ excited state crosses below the $^1n,\pi^*$ excited state (reversing the order found in nonpolar solvents) and leads to a greater diversity of photoproducts;[10,25–27] sensitization studies have demonstrated that

(23) Absorptivities at 514.5 nm relative to *all-trans*-retinal are 13-cis:11-cis:9-cis:all-trans = 0.28:0.32:0.50:1.00; the absolute absorptivity for the adsorbed all-trans isomer is ~9.9 × 10^2 M^{-1} cm^{-1} at 514.5 nm. Measurements were made at a concentration of ~3 × 10^{-6} mol of retinal/g of silica gel by using a 0.10-cm path-length cell.

(24) The assumption described corresponds to an equation in which the sum of the concentrations of the four retinal isomers (9-cis, 11-cis, 13-cis, and all-trans) is the total retinal concentration, C_0. A steady-state equation can be written for each of the three cis isomers and is of the form of eq 1,

$$\frac{[\text{cis}]}{[\text{all-trans}]} = \frac{\epsilon_{all\text{-}trans}\phi_{\text{all-trans}\rightarrow\text{cis}}}{\epsilon_{\text{cis}}\phi_{\text{cis}\rightarrow\text{all-trans}}} \quad (1)$$

where ϵ is the relative absorptivity[23] of the subscripted isomer and $\phi_{a\rightarrow b}$ corresponds to the quantum yield for conversion of isomer a to isomer b (Table III or Figure 3). Substitution of the appropriate values into these four equations yields the photostationary composition given in Table II.

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singlet excited states are responsible for the isomerization of the all-trans isomer.[20,28] A similar excited-state reordering mechanism for adduct and silica gel mediated isomerization is consistent with the dramatic red shift of the π,π^* band.

Given the polar environments introduced by adduct formation and silica gel adsorption, the presence of 11-*cis*-retinal in photolysates of *all-trans*-retinal prepared in those environments is not surprising. Differences between the methanol and silica gel environments for the all-trans isomer, Table III, are substantial, however, and may reflect steric effects. The inhomogeneity of the silica gel surface due, e.g., to local variations in silanol density,[7] provides a wide variety of binding sites that can potentially influence both the local density of adsorbed retinal and its coordination geometry. What we observe could thus be a weighted average of primary photoprocesses of retinal in various environments. The different binding sites could influence excited-state reactivity by, for example, restricting certain kinds of molecular motion and by perturbing the efficiency of excited-state deactivation. Similar considerations would, of course, apply to the other isomers of Table III, and, additionally, triplet excited states may be important. Studies designed to provide a better understanding of these effects and of silica gel mediated photochemistry in general are in progress.

Experimental Section

Materials. *All-trans*-retinal was obtained from Eastman and used as received. The 9-*cis*-, 11-*cis*-, and 13-*cis*-retinal isomers were generous gifts of Hoffmann-LaRoche. Isooctane and cyclohexane were Aldrich spectrophotometric grade; methylene chloride and deuteriochloroform were obtained from Fisher and Stohler, respectively. The isooctane and cyclohexane were dried over 4-Å molecular sieves and N_2 purged. Large-pore silica gel (Alfa; 70 μm), 2,6-di-*tert*-butyl-4-methylphenol (Aldrich) and dimethyldichlorosilane (Petrarch) were used as received.

Optical Measurements. Electronic spectra were recorded on a Cary 17D spectrophotometer. All solutions were prepared in a N_2-filled glovebag. Spectra of 0.3–2 mM retinal solutions in cyclohexane were obtained in quartz cells with a 0.10-cm optical path and a 1.8-mL volume. A slurry consisting of 1.8 mL of the retinal solution and 1 g of silica gel was prepared to obtain spectra of retinal adsorbed onto silica gel; the solvent was evaporated under a stream of N_2. Thus treated, the silica gel was poured into a 0.10-cm path-length quartz cell (nearly filling it), shaken for several minutes, and combined with cyclohexane to again form a slurry. A cell filled with the same quantity of untreated silica gel in cyclohexane was employed as a reference. Spectra were obtained in a similar manner for silica gel that had been dehydrated[29] by heating at 110 °C for at least 3 h under vacuum (10^{-5} torr) and dehydroxylated[30] by exposure to $(CH_3)_2SiCl_2$ vapor for 14 h.

Photolyses. The 514.5-nm line of a Coherent Radiation CR-12 Ar ion laser was the irradiation source in all photolyses. Photolyses were conducted on slurries consisting of 3 mL of cyclohexane and 5 mg of retinal adsorbed onto 0.5 g of silica gel. The slurries were optically dense at 514.5 nm in the 1.0-cm path length cell in which they were photolyzed. In the absence of silica gel, an identical cyclohexane solution of retinal was optically dilute and was also photolyzed. Irradiation was carried out by passing the 2–3-mm diameter laser beam sequentially through an Oriel 5302 interference filter to eliminate laser plasma background and a 10X beam expander; the expanded beam roughly filled the window of the photolysis cell. Laser power, measured with a Scientech 362 power meter, was maintained at 80 mW during all experiments. The slurries were mechanically agitated at 5-min intervals during photolysis. Electronic spectra of the supernatant liquid showed no evidence of retinal, indicating that the molecule is completely adsorbed onto the silica gel. After irradiation, the retinal was desorbed with CH_2Cl_2. The solvent was then removed under reduced pressure (~10 torr), and the residue was redissolved in $CDCl_3$ for ^1H NMR analysis or in isooctane for HPLC analysis.

Proton NMR spectra were obtained at 270 MHz on a Bruker WH-270 spectrometer. Spectra were analyzed by comparison with spectra of authentic samples and literature data. HPLC analyses were performed on a Waters Model 6000A analytical liquid chromatograph equipped with a Model 440 Dual Channel UV detector and a 30 × 0.4-cm diameter μ-Porasil column. The retinal isomers were eluted with 2% diethyl ether in isooctane and detected simultaneously at 254 and 365 nm. Isomers were identified by comparison with authentic samples, reported retention times, and the ^1H NMR data. A standard, 2,6-di-*tert*-butyl-4-methylphenol (BHT), was used to determine the total quantity of retinal isomers present; a known quantity of the standard was added to the isooctane/ether solution of the photolysate just prior to injection into the HPLC instrument. Peak areas in HPLC traces were integrated by the instrument's data module and corrected for the different isomeric absorptivities at the wavelengths used for detection.

Determination of Quantum Yields and Primary Photoproducts. Techniques for obtaining the quantum yields for photoprocesses of molecules in the adsorbed state have been described.[8] Our experimental conditions provided the high transparency (minimal light scattering because of the match in cyclohexane and silica gel refractive indices) needed for these measurements. For determination of quantum yields and primary photoproducts, five 5-mg samples of retinal were photolyzed as previously described for short intervals of time (15, 30, 45, 60, and 90 s) corresponding to maximum conversions of the starting isomers of 5% (9-*cis*- and 13-*cis*-retinal) or 10% (*all-trans*- and 11-*cis*-retinal). The photolysate mixtures were then analyzed by HPLC, as described above. Primary photoproducts were identified as such by the linear extrapolation of their concentrations to 0 at zero time. These experiments were repeated at least twice for each of the four isomers investigated. Quantum yields are uncorrected for reflective losses and have estimated errors of ±10%.

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Registry No. *all-trans*-Retinal, 116-31-4; 9-*cis*-retinal, 514-85-2; 11-*cis*-retinal, 564-87-4; 13-*cis*-retinal, 472-86-6.

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