

Transient Phenomena in the Pulse Radiolysis of Retinyl Polyenes. 4. Environmental Effects on Absorption Maximum of Retinal Radical Anion¹

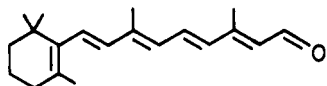
K. Bobrowski[†] and P. K. Das*

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556 (Received: June 13, 1985)

The absorption-spectral and kinetic behaviors of radical ions of *all-trans*-retinal in various solvents have been studied by spectrophotometric pulse radiolysis at room temperature. Upon going from nonpolar and polar-nonprotic solvents to polar-protic ones (alcohols), large hypsochromic shifts occur in the absorption maximum (λ_{\max}) of retinal radical anion. The anion absorption maxima in the alcohols correlate well with solvent dielectric constants. In a number of solvents, parallelism is noted between the energies corresponding to λ_{\max} 's of retinal anion and of solvated electron (the latter at 77 K and room temperature). Transient phenomena associated with the radical anion (λ_{\max} 's = 448–460 nm) and the retinyl alcohol radical (λ_{\max} = 405 nm) are observed in the course of the pulse radiolysis of retinal in several normal micelles (aqueous). The blue-shifted locations of the anion λ_{\max} 's strongly suggest a polar-protic, alcohol-like nature of the micellar region where the polyenal resides.

Introduction

The solvent effect on the absorption spectral maxima of polyene radical ions has been recognized in the early studies²⁻⁴ based on pulse radiolysis in fluid solutions. In particular, this effect is quite pronounced for the radical anion of *all-trans*-retinal (1), a bio-



All-trans Retinal

logically significant long-chain polyenal. For example, on going from hexane to alkaline methanol, the absorption maxima (λ_{\max}) of retinal radical anion is blue-shifted from 590 to 405 nm; this shift covers a major portion of the visible spectral region. The large solvent effect on λ_{\max} , combined with the high extinction coefficient of absorption (ϵ_{\max} = 7.9×10^4 M⁻¹ cm⁻¹ at 405 nm in alkaline methanol),² makes retinal radical anion an attractive probe for polarity and hydrogen-bonding nature of microenvironments.

We have carried out a pulse radiolysis study of spectra and kinetic behavior of retinal radical ions in a number of nonpolar, polar-nonprotic, and polar-protic solvents. The results are described in this paper. We have found that polar-protic solvents (alcohols) are more effective than polar-nonprotic ones in causing blue shifts in the absorption maximum of retinal radical anion and that there is a good parallelism between the absorption maxima of the latter and the solvated electron in various solvents. Furthermore, retinal has been subjected to pulse radiolysis in several micellar solutions in order to probe the nature of the interior of the micelles based on spectral and kinetic properties of retinal radical anion located in them. The present work is also of interest in shedding light on radiation-chemical charge separation leading to formation of free ions and electronically excited states (singlets/triplets) in various solvents. In the past, a variety of substrates, namely, *trans*-stilbene,⁵ aromatic hydrocarbons,⁶ and leucocyanide of malachite green dye,⁷ have been used for this purpose.

Experimental Section

The solvents were of best grades commercially available. In most cases, they were either distilled or passed through columns of alumina (or silica gel) before use. Triton X-100, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), all from Aldrich, were used as received. *All-trans*-retinal

(Sigma) was chromatographed on silica gel by using petroleum ether + 5% methyl *tert*-butyl ether as the eluent and then recrystallized from *n*-hexane.

The procedure and apparatus for pulse radiolysis experiments have been described in previous papers.^{8,9} All experiments were carried out in a flow cell (quartz, 1-cm path length) using 5-ns electron pulses from the Notre Dame 7 MeV ARCO LP-7 linear accelerator for pulsed irradiation at dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse. The retinal concentrations in the micellar solutions were in the range 0.05–0.20 mM. The micellar solutions with Triton X-100 as a component were prepared by mixing an aliquot portion of 0.05 M retinal solution in methyl *tert*-butyl ether with Triton X-100 and then dissolving the resulting mixture in water by prolonged stirring. For CTAB solutions, aliquots of a 0.05 M solution of retinal (in the ether) were slowly injected into the requisite volume of the micelle solution under constant stirring. Each of the solutions was flushed with N₂ for ~ 1 h to get rid of most of the ether.

Results

(a) *Pulse Radiolysis of Retinal in Various Solvents.* The pulse radiolytic generation and characterization of retinal radical anion and/or cation in methanol, 2-propanol, acetone, tetrahydrofuran, hexane, and 1,2-dichloroethane have been described in previous papers from this and other laboratories.^{2,8} Transient phenomena in three other alcohols, namely, ethanol, *tert*-butyl alcohol, and ethylene glycol, as well as in diethyl ether and triethylamine (TEA) are similar to those in methanol (or 2-propanol) and tetrahydrofuran; the radical anion, formed by solvated electron (e_s^-) attachment^{10,11} is the major transient species in these solvents under

(1) The work described herein was supported by the Office of Basic Energy Sciences, Department of Energy. This is Document No. NDRL-2728 from the Notre Dame Radiation Laboratory.

(2) Land, E. J.; Lafferty, J.; Sinclair, R. S.; Truscott, T. G. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 538–545.

(3) Dawe, E. A.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2162–2169.

(4) Lafferty, J.; Roach, A. C.; Sinclair, R. S.; Truscott, T. G.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 416–429.

(5) Kira, A.; Arai, S.; Imamura, M. *Int. J. Radiat. Phys. Chem.* **1973**, *5*, 127–134.

(6) Hayon, E. *J. Chem. Phys.* **1970**, *53*, 2353–2358.

(7) Borowski, K.; Dzierzkowska, G.; Grodkowski, J.; Stuglik, Z.; Zagorski, Z. P.; McLaughlin, W. L. *J. Phys. Chem.* **1985**, *89*, 4358–4366.

(8) (a) Raghavan, N. V.; Das, P. K.; Bobrowski, K. *J. Am. Chem. Soc.* **1981**, *103*, 4569–4573. (b) Bobrowski, K.; Das, P. K. *J. Am. Chem. Soc.* **1982**, *104*, 1704–1709. (c) Bobrowski, K.; Das, P. K. *J. Phys. Chem.*, in press.

(9) (a) Patterson, L. K.; Lilie, J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129–141. (b) Schuler, R. H. *Chem. Ed.*, submitted for publication.

(10) Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224–230. Arai, S.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 2190–2194. Taub, I. A.; Harter, D. A.; Sauer, Jr., M. C.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 979–965.

[†] On leave of absence (1978–81) from the Institute of Nuclear Research, Poland. Present address: Polish Academy of Sciences, Institute of Biochemistry and Biophysics, 02532 Warsaw, Poland.

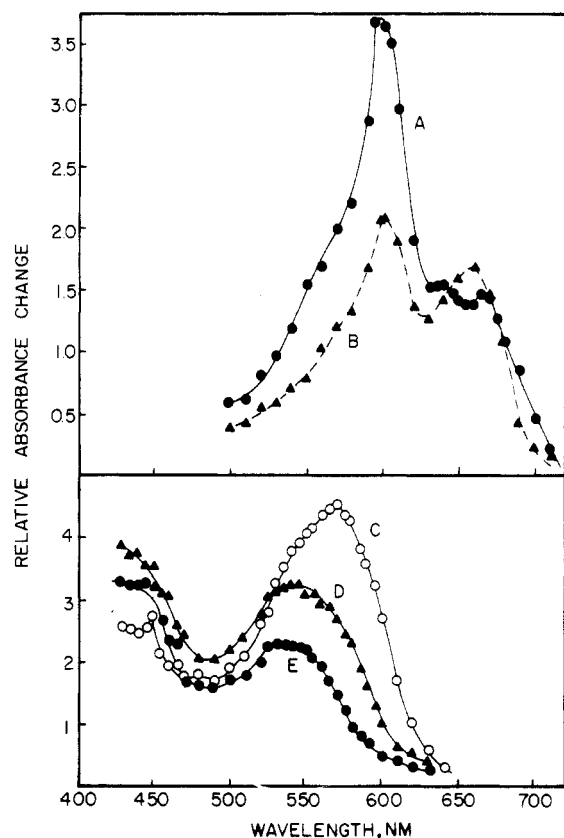


Figure 1. Transient absorption spectra observed at (A) 0.30, (B) 2.5, (C) 0.08, (D) 0.48, and (E) 1.4 μ s following pulse radiolysis of retinal in cyclohexane. (A) 0.87 mM retinal under O_2 saturation, (B) 0.087 mM retinal under O_2 saturation, and (C–E) 1.0 mM retinal under N_2 saturation in the presence of 70 mM TEA.

deaceration and its formation is suppressed in the presence of O_2 or N_2O (efficient scavengers for e_s^-).

The transient spectra associated with cationic species resulting from the pulse radiolysis of retinal in O_2 -saturated cyclohexane consist of two maxima, namely, 595 and 655 nm (Figure 1A,B). Subject to slight variations (± 10 nm) in location, the major maximum at 595 nm is commonly observed in various solvents under conditions favorable for radical cation formation. On the other hand, the minor maximum at 655 nm is prominent only in a few selected solvents, e.g., aliphatic hydrocarbons (cyclohexane, hexane,^{2,8c} etc.) and 1,2-dichloroethane.^{8c} This suggests that the two maxima probably belong to different cationic species. This is also indicated by the dependence of the relative intensity of the two maxima on retinal concentration, the longer wavelength one being relatively pronounced at lower [retinal]. Addition of the cation scavenger, TEA at 7.2 mM, wipes out the transient absorptions at both wavelengths. That neither of the two absorption maxima is due to the cation of an impurity in the solvent is established by pulse radiolysis of the blank solvent. The quenching of the decay of transient absorptions at the two wavelengths was studied with β -carotene as the quencher at varying concentrations ($(2\text{--}6) \times 10^{-5}$ M). From the plot of observed pseudo-first-order rate constants for decay of transient absorption at 595 nm vs. [β -carotene], we obtained $8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as the bimolecular rate constant for the quenching by β -carotene. The decay kinetics of transient absorption at 655 nm remained practically unchanged at the β -carotene concentrations used. These results confirm the existence of two cationic species contributing to the two maxima. On the basis of the fact that the 580–600-nm maximum is universally observed in solvents in which charge exchange with positive holes or solvent-derived cations is feasible, we attribute

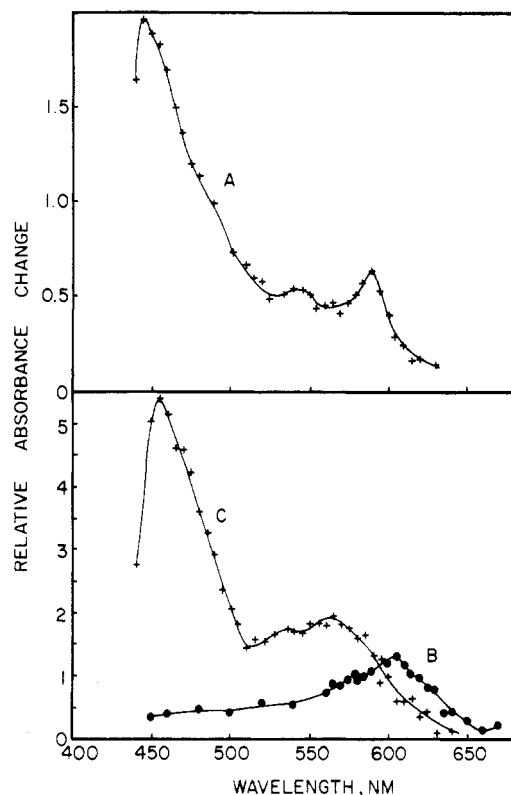
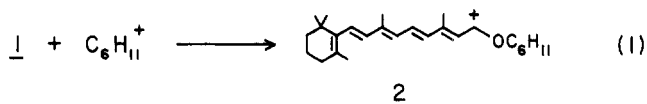
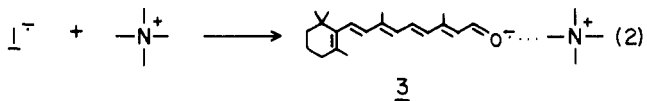


Figure 2. Transient absorption spectra at (A) 0.08, (B) 0.18, and (C) 0.09 μ s following pulse radiolysis of (A) ~ 0.5 mM retinal in N_2 -saturated dioxan, (B) 1.1 mM retinal in O_2 -saturated benzene, and (C) 1.1 mM retinal in N_2 -saturated benzene containing 70 mM TEA.

it to the retinal radical cation. A tentative assignment for the 655-nm maximum may be sought in terms of a retinylcarbenium ion (**2**) derived from the addition of solvent-derived carbocation ($C_6H_{11}^+$), see eq 1.



As expected¹² under deoxygenated conditions, pulse radiolysis of retinal in N_2 -saturated cyclohexane gives rise to additional transient absorptions due to the triplet ($\lambda_{\text{max}} = 450$ nm) and the radical anion (500–600 nm). Unlike in *n*-hexane, because of the high mobility¹³ of positive hole(s) in cyclohexane, the solute cation is formed fast and it is difficult to temporally resolve its spectrum from that of the anion. In order to isolate the retinal radical anion spectrum, pulse radiolysis was carried out in N_2 -saturated cyclohexane solutions in the presence of 70 mM TEA, the latter acting as a scavenger for positive ions (solvent-derived). The resulting time-resolved spectra are shown in Figure 1C–E. The absorption maximum at 570 nm, observed at a time close to the electron pulse, is ascribable to retinal radical anion. Interestingly, in the course of its decay, the maximum shifts progressively to shorter wavelengths (see Figure 1C–E). This is explainable by the association of the anion with tetralkylammonium cations in the given nonpolar solvent (eq 2). The latter result from the



(11) (a) Beaumont, D.; Rodgers, M. A. *J. Trans. Faraday Soc.* **1969**, *65*, 2973–2980. (b) Bockrath, B.; Dorfman, L. M. *J. Phys. Chem.* **1973**, *77*, 1002–1006. (c) Bockrath, B.; Dorfman, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 5708–5715. (d) Dorfman, L. M.; Bockrath, B. *J. Phys. Chem.* **1975**, *79*, 3040.

(12) (a) Capellos, C.; Allen, A. D. *J. Phys. Chem.* **1969**, *73*, 3264–3268; **1970**, *74*, 840–845. (b) Dainton, F. S.; Peng, C. T.; Salmon, G. A. *J. Phys. Chem.* **1968**, *72*, 3801–3807. (c) Zador, E.; Warman, J. M.; Hummel, A. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1368–1376; *J. Chem. Phys.* **1975**, *62*, 3897–3906.

(13) (a) de Haas, M. P.; Warman, J. M.; Infelta, P. P.; Hummel, A. *Chem. Phys. Lett.* **1975**, *31*, 382–386. (b) Zador, E.; Warman, J. M.; Hummel, A. *Chem. Phys. Lett.* **1973**, *23*, 363–366. (c) Trifunac, A. D.; Sauer, Jr., C. M.; Jonah, C. D. *Chem. Phys. Lett.* **1985**, *113*, 316–319.

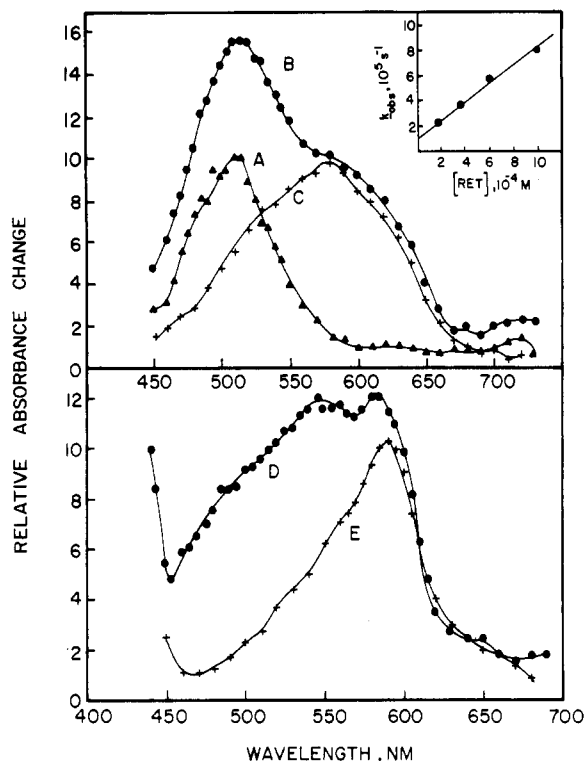


Figure 3. Transient absorption spectra observed at (A) 0.08, (B) 1.4, (C) 0.66, (D) 0.76, and (E) 1.4 μ s following pulse radiolysis of ~ 0.5 mM retinal in (A, B) N_2 -saturated acetonitrile, (C) O_2 -saturated acetonitrile, (D) N_2 -saturated benzonitrile, and (E) O_2 -saturated benzonitrile. Inset: plot of pseudo-first-order rate constant for growth of retinal cation in O_2 -saturated acetonitrile vs. retinal concentration.

scavenging of solvent positive ions by TEA. Such ion pairing causing blue shifts in absorption maxima is known¹¹ to be facile with radical anions in low-polarity solvents and has been noted¹⁴ for retinal anion itself in tetrahydrofuran containing tetraalkylammonium salts.

The transient phenomena observed upon pulse radiolysis of retinal in 1,4-dioxan (deoxygenated) are dominated by the triplet ($\lambda_{\max} = 450$ nm). In addition, the radical anion ($\lambda_{\max} = 545$ nm) and cation ($\lambda_{\max} = 595$ nm) are formed, see Figure 2A. The transient absorption due to both triplet and radical anion is suppressed upon oxygen saturation while that due to the radical cation remains unchanged in intensity. The formation of cation and triplet in 1,4-dioxan contrasts the situation with higher polarity ethers, namely, diethyl ether and tetrahydrofuran, in which the anion is the major pulse radiolytic transient, and is in agreement with the results¹⁵ of other steady-state and time-resolved radiolysis studies in this solvent. As far as the formation of triplet and two ions is concerned, pulse radiolysis of retinal in benzene¹⁶ is quite similar to that in 1,4-dioxan. In oxygenated benzene, the radical cation shows up with its maximum at 600 nm (Figure 2B); this vanishes in the presence of 0.07 M TEA under N_2 saturation while the absorptions due to triplet and radical anion appear with maxima at 465 and 570 nm, respectively (Figure 2C).

Both acetonitrile¹⁷ and benzonitrile¹⁸ are known for pulse ra-

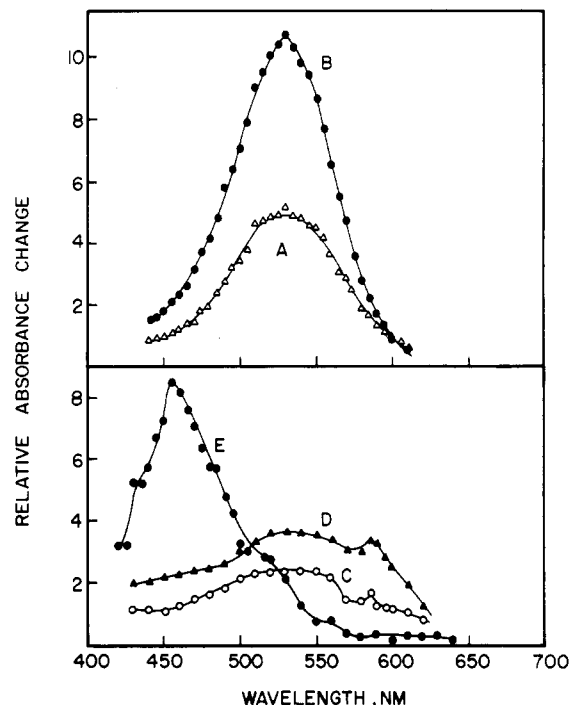


Figure 4. Transient absorption spectra observed at (A) 0.07, (B) 1.3, (C) 0.14, (D) 1.4, and (E) 13.3 μ s following pulse radiolysis of (A, B) 0.80 mM retinal in DMF (under N_2) and (C-E) ~ 0.5 mM retinal in Me_2SO (under N_2).

diolytic generation of cation as well as anion precursors. In these two solvents, both radical ions of retinal and only the radical cation are formed under N_2 and O_2 saturation, respectively. These are illustrated in Figure 3. In acetonitrile under N_2 , the absorption due to retinal radical cation ($\lambda_{\max} = 585$ nm) is less pronounced than that due to the anion ($\lambda_{\max} = 520$ nm). The formation of the former takes place with slower kinetics which remains essentially unchanged upon O_2 saturation. From the concentration dependence of the cation formation kinetics (see the inset of Figure 3), the rate constant for electron transfer from retinal to the cation precursor and the lifetime of the latter are estimated to be $7.4 \times 10^8 M^{-1} s^{-1}$ and 10 μ s, respectively (under O_2 saturation). In benzonitrile, radical anions are known to be formed only with substrates having favorable reduction potentials. For example, with *trans*-stilbene^{5,18a} and leucocyanide of malachite green,⁷ no anion (in the former case) or anion-derived radical (through loss of CN^- in the latter case) is observed upon pulse radiolysis in benzonitrile. On the other hand anions are formed^{18a} from a variety of aromatic solutes, e.g., pyrene, perylene, anthracene, and 1,2-benzanthracene. Since the reduction potential of retinal ($E_p^{\text{red}} = -1.42$ V in tetrahydrofuran, vs. SCE)¹⁹ is less negative than those of these aromatic hydrocarbons, it is not surprising that the radiation-chemical yield of retinal radical anion is reasonably high in benzonitrile.

In agreement with previous pulse radiolysis studies^{5-7,20} in *N,N*-dimethylformamide (DMF), only retinal radical anion ($\lambda_{\max} = 535$ nm) is formed as the major transient species in this solvent (in the absence of O_2), see Figure 4A,B. From the dependence of anion formation kinetics on [retinal], the rate constant for electron transfer from the anion precursor and the lifetime of the latter are estimated at $7 \times 10^9 M^{-1} s^{-1}$ and 400 ns, respectively. As criteria for the radical anion, a substantial reduction in its yield and a considerable shortening of its lifetime occur upon introduction of oxygen into the solution.

In neat dimethyl sulfoxide (Me_2SO),²¹ the solvated electron

(14) Bobrowski, K.; Das, P. K., unpublished work.

(15) (a) Baxendale, J. H.; Rodgers, M. A. J. *Trans. Faraday Soc.* **1967**, *63*, 2004-2011. (b) Baxendale, J. H.; Rodgers, M. A. J. *J. Phys. Chem.* **1968**, *72*, 3849-3855.

(16) (a) Kemp, T. J.; Roberts, J. P.; Salmon, G. A.; Thompson, G. F. J. *Phys. Chem.* **1967**, *71*, 3052-3053. (b) Kemp, T. J.; Salmon, G. A.; Thompson, G. F. J. *Phys. Chem.* **1968**, *72*, 1464-1470. (c) Bensasson, R. V.; Thomas, J. K. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 185-197.

(17) (a) Singh, A.; Gesser, H. D.; Scott, A. R. *Chem. Phys. Lett.* **1968**, *2*, 271-273. (b) Bell, I. P.; Rodgers, M. A. J.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 315-326. (c) Burrows, H. D.; Kosower, E. M. *J. Phys. Chem.* **1974**, *78*, 112-117. (d) Baptista, J. L.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 2066-2079. (e) Tran-Thi, T. H.; Koules-Pujo, A. M.; Gilles, L.; Genies, M.; Sutton, J. *Radiat. Phys. Chem.* **1980**, *15*, 209-214.

(18) (a) Kira, A.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 2094-2098. (b) Kira, A.; Arai, S.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890-4895.

(19) Park, S.-M. *J. Electrochem. Soc.* **1978**, *125*, 216-222.

(20) Hayashi, N.; Hayon, E.; Ibata, T.; Lichtin, N. N.; Matsumoto, A. J. *Phys. Chem.* **1971**, *75*, 2267-2272.

TABLE I: Absorption-Spectral and Kinetic Data for Retinal Radical Ions in Various Solvents at 295 K

solvent	dielec const ^a	λ_{\max} , nm		for retinal radical ions ^c		rate const for retinal anion decay, ^d 10 ⁵ s ⁻¹
		for e _s ^{-b}		anion	cation	
		room temp	77 K			
acetone (1) ^g	20.7			495	580	0.90
acetonitrile (2)	37.5	1450 ^e		520	585	1.2
benzene (3)	2.28			570	600	
benzonitrile (4)	25.2			550	595	
cyclohexane (5)	2.023		1641	530	595	
1,2-dichloroethane (6) ^g	10.36				595	
diethyl ether (7)	4.4		1372	545		4.1
dimethylformamide (8)	37	650		535		0.98
dimethyl sulfoxide (8)	46.6	≥1500		535	595	
1,4-dioxan (10)	2.21	>1100		545	595	
ethanol (11)	24.3	700	540	458		0.58
ethylene glycol (12)	38.0	580	514	440		
hexane (13) ^g	1.88		1650 ^f	580	(590)	
methanol (14) ^g	32.6	630	524	445		7.0
2-propanol (15) ^g	18.3	820	644	460		0.081
tert-butyl alcohol (16)	12.3		>750	475		
tetrahydrofuran (17) ^g	7.5		1200 ^f	530		0.76
triethylamine (18)	2.44		167	560		

^a Taken from ref 6 and 24. ^b Taken from ref 15b, 20, 21, 25, and 26. ^c ± 5 nm. ^d The kinetic data are for the solvents in which the anion decay follows primarily first-order kinetics. ^e Probably corresponds to the solvent anion (see ref 17b). ^f The given data are for methylcyclohexane, 3-methylhexane, and 2-methyltetrahydrofuran, respectively. ^g Data for retinal radical ions are taken from ref 2 and 8a,c.

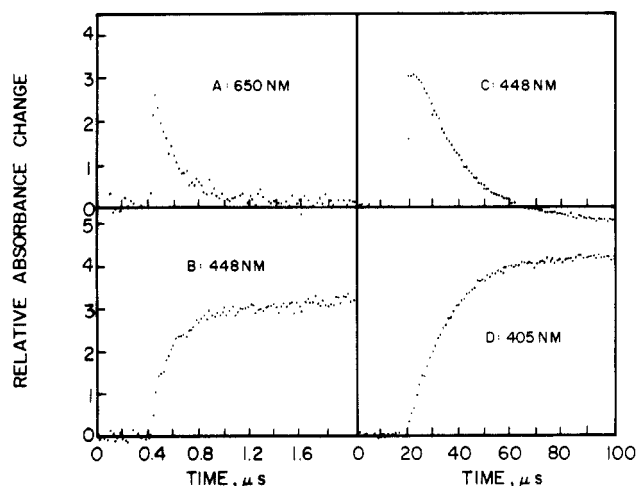


Figure 5. Representative kinetic traces at (A) 650, (B) 448, (C) 448, and (D) 405 nm, observed in the course of pulse radiolysis of 0.05 mM retinal in an aqueous solution of 18 mM CTAB (N_2 -saturated).

($\lambda_{\max} \geq 1500$ nm) seen in pulse radiolysis is very short-lived ($\tau_{1/2} = 14\text{--}15$ ns). In addition, several longer lived species with half-lives in the range $0.6 \mu\text{s}$ – 3 s have been recognized;²¹ these display transient absorptions at 260–900 nm. Among the latter, the one characterized^{21b} by λ_{\max} at 600 nm and a first half-life of $6 \mu\text{s}$ is assignable^{22a} to a species derived from Me_2SO radical cation. Both radical cations and anions have been shown^{5,6,16b,21b,22} to be formed in the course of the pulse radiolysis of various solutes (e.g., *trans*-stilbene, biphenyl, naphthalene, and anthracene) in Me_2SO . The transient absorption spectra (Figure 4C,D) within a few microseconds following the pulse radiolysis of retinal in Me_2SO under N_2 show two maxima at 535 and 595 nm, respectively. Between these, the one at the shorter wavelength becomes reduced in intensity upon O_2 saturation, suggesting that it is associated with the radical anion. The cation-related 595-nm maximum remains unaffected by O_2 . Interestingly, while the radical ions decay over a microsecond time scale, a longer lived

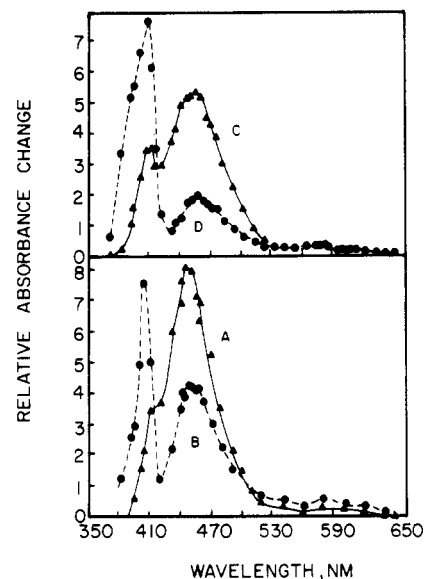


Figure 6. Transient absorption spectra observed at (A) 4.5, (B) 15.5, (C) 4.5, and (D) 15.5 μs following pulse radiolysis of 0.05 mM retinal in aqueous solutions of (A, B) 18 mM CTAB and (C, D) 40 mM Triton X-100 + 18 mM CTAB (both N_2 -saturated).

species ($\tau_{1/2} > 100 \mu\text{s}$, $\lambda_{\max} = 460$ nm) grows in with a rise time of $5 \mu\text{s}$. Although the transient spectrum (Figure 4E) is located in the region where retinal triplet is known to absorb, the triplet assignment for the 460-nm species is ruled out by its unusually long lifetime²³ as well as its persistence in the presence of oxygen. An assignment in terms of a radical-like product from the reaction (addition or hydrogen abstraction) of retinal with long-lived Me_2SO -derived radicals ($\text{CH}_3\text{SOCH}_2\cdot$, $\text{CH}_3\text{SO}\cdot$)^{21b} seems likely.

The data concerning retinal radical ion absorption maxima and anion lifetimes (in some solvents) are summarized in Table I. Table I also contains solvent dielectric constants and solvated electron absorption maxima compiled from the literature.^{6,20,21,24–26}

(21) (a) Walker, D. C.; Klassen, N. V.; Gillis, H. A. *Chem. Phys. Lett.* **1971**, *10*, 636–638. (b) Bensasson, R.; Land, E. J. *Chem. Phys. Lett.* **1972**, *15*, 195–198.

(22) (a) Koulkes-Pujo, A. M.; Gilles, L.; Lesigne, B.; Sutton, J. J. *Chem. Soc., Chem. Commun.* **1971**, 749–750. (b) Koulkes-Pujo, A. M.; Michael, B. D.; Hart, E. J. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 333–344.

(23) Retinal triplet lifetimes are usually short, $\tau_T = 9\text{--}15 \mu\text{s}$. Azerad, R.; Bensasson, R.; Cooper, M. B.; Dawe, E. A.; Land, E. J. in "Excited States of Biological Molecules"; Birks, J. B., Ed.; Wiley: New York, 1976; p 531. Bensasson, R.; Land, E. J. *Nouv. J. Chim.* **1972**, *2*, 503–507. Das, P. K.; Becker, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 6348–6353.

(24) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

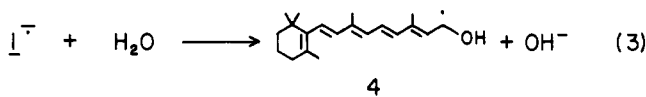
TABLE II: Absorption Maxima and Decay Kinetics of Retinal Radical Anion in Micellar Solutions at 295 K

micelle	rate const ^a (e_{aq}^-), 10^9 $M^{-1} s^{-1}$	retinal anion absorp max, ^b nm	rate const (anion decay), ^c $10^5 s^{-1}$
Triton X-100 (40 mM)	2.9	460	≥ 1.8
CTAB (18 mM)	75	448	0.61
Triton X-100 (40 mM) + CTAB (18 mM)	16	455	1.0
Triton X-100 (40 mM) + SDS (17 mM)	1.7	~ 450	<i>d</i>

^a Rate constant for reaction with e_{aq}^- ; $\pm 15\%$. ^b ± 5 nm. ^c Rate constant for anion decay; $\pm 15\%$. ^d Could not be reliably measured.

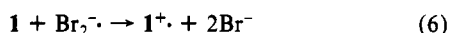
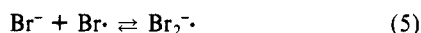
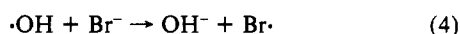
(b) *Retinal Radical Anion and Its Protonation Kinetics in Micelles.* In order to test if the solvent effect on retinal anion maxima can be utilized to explore the nature of microenvironments in multiphase systems, we have carried out some pulse radiolysis experiments using the polyenal as a substrate in normal micelles. In these experiments, the concentrations of the substrate were 0.05–0.20 mM. Since retinal is insoluble in water, it is expected to harbor in the hydrophobic domains of micellar media.

The major transient processes observed upon pulse radiolysis of retinal in various micelles consist of the formation of its radical anion ($\lambda_{max} = 448$ –460 nm) as a result of the attachment of hydrated electron (e_{aq}^-) and the subsequent protonation of the anion (eq 3) giving rise to retinyl alcohol radical ($\lambda_{max} = 405$ nm).



These phenomena in CTAB solution are illustrated by four representative kinetic traces in Figure 5. The transient absorption spectra in CTAB and CTAB + Triton X-100 micelles are presented in Figure 6. The identification of the 405-nm species as the retinyl alcohol radical (4) is supported by the generality^{2,8a} of the protonation of retinal anion in alcohols and on the observation²⁷ of a spectrally and kinetically similar species upon the reaction of pulse radiolytic *tert*-butoxy radical with retinol in a 9:1 benzene:di-*tert*-butyl peroxide mixture. The possibility that the 405-nm species could be the product of reaction (addition or hydrogen abstraction) of $\cdot OH$ or some other radical is ruled out by the fact that, upon saturation with N_2O , the transient absorptions at 370–500 nm vanish nearly completely.

A close examination of the transient spectra in Figure 6 shows the presence of a weak band system at 550–650 nm. This band system becomes slightly pronounced upon N_2O saturation (Figure 6D). The plausible candidate for the minor, long-wavelength band system is the retinal radical cation resulting from oxidation by Br_2^- (see eq 4–6). A similar observation has been made²⁸ for



the oxidation of β -carotene in the course of its pulse radiolysis in mixed micelles composed of Triton X-100 and CTAB.

Table II contains the data concerning decay and absorption maximum of retinal anion in several micellar solutions. The rate constants for the reaction of the polyenal with e_{aq}^- (monitored at 650 nm) were measured from the dependence of e_{aq}^- decay on [retinal]. These data (Table II) reflect the relative reactivity of e_{aq}^- with retinal as modified by the environments. Relative to the

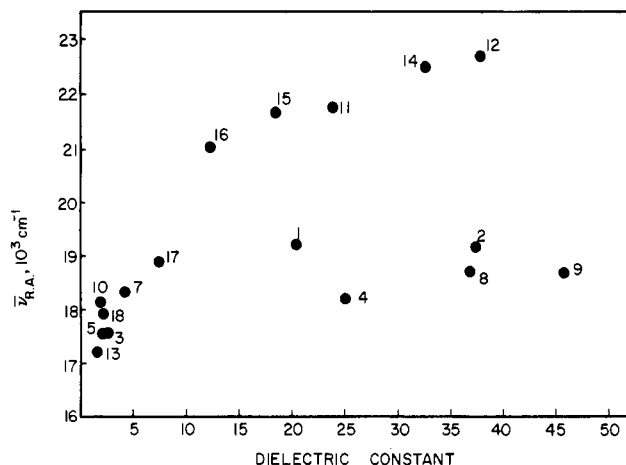


Figure 7. Plot of energy location of retinal radical anion absorption maximum vs. solvent dielectric constant. For the numbers identifying the solvents, see Table I.

nonionic micelle (Triton X-100), the cationic one (CTAB) enhances the rate of reaction with e_{aq}^- while the anionic one (SDS mixed with Triton X-100) retards it. Explainable²⁹ by favorable or unfavorable electrostatic effects from the charges carried by head groups at micellar boundaries, similar behaviors have been noted earlier for e_{aq}^- attachment to other substrates solubilized in micelles. In spite of the slow rate, at 0.20 mM [retinal] in mixed Triton X-100 + SDS micelle, the fraction of e_{aq}^- reacting with the polyenal is about 60%; yet, the transient absorptions due to the anion or the ketyl radical are relatively weak (probably due to short lifetime of the anion decaying by modes other than protonation). No attempt was made to study the behavior of the anion in pure SDS micelle.

Discussion

The results concerning the pulse radiolytic formation of retinal triplet and radical ions in various solvents are in general agreement with those obtained in earlier studies using aromatic solutes. One interesting negative observation that deserves mention in this context is that in alcohols no transient phenomenon attributable to the reaction of alkoxy radicals³⁰ with retinal is displayed. In the polar media, the alkoxy radicals are usually implicated by radical cation formation from their oxidative reaction with substrates with low oxidation potentials (e.g., *N,N,N',N'*-tetramethylphenylenediamine^{30a} and malachite green leucocyanide⁷). It appears that the oxidation potential of retinal ($E_p^{ox} = 1.20$ V in tetrahydrofuran, vs. SCE¹⁹) is not favorable for efficient electron transfer to alkoxy radicals. Other reactions,³¹ namely, abstraction of allylic and aldehydic hydrogen atoms and addition to double bonds, also are unrecognizable at ≤ 1 mM [retinal], probably because of short lifetimes of alkoxy radicals (in polar media) and/or slow rates of the reactions.

As evident from the spectral data for radical ions in Table I, the solvent effect on absorption maximum is far more pronounced for the anion than for the cation. One may argue that the spectral data for the cation in alcohols are missing and it is in the alcohols that the large blue shifts occur in anion maximum. However, the laser flash photolytic photoionization³² of retinoic acid in methanol gives its radical cation with λ_{max} at 590 nm which is identical with or close to those observed for pulse radiolytically generated retinoic

(29) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133–138.

(30) (a) Ellison, D. H.; Salmon, G. A.; Wilkinson, F. *Proc. R. Soc. London, Ser. A*, **1972**, *328*, 23–26. (b) Sargent, F. P.; Gardy, E. M. *Can. J. Chem.* **1974**, *52*, 3645–3650. (c) Sargent, F. P. *J. Phys. Chem.* **1977**, *81*, 89–90. (d) Baxendale, J. H.; Mellows, F. W. *J. Am. Chem. Soc.* **1961**, *83*, 4720–4726.

(31) Although very little is known about the transient spectra of the products of addition of radicals to retinal and of allylic hydrogen abstraction by them, the radical species from aldehydic hydrogen abstraction, identical with the product of OH^- loss from retinoic acid radical anion, has³² its absorption maximum at 420 nm in methanol.

(32) Lo, K. K. N.; Land, E. J.; Truscott, T. G. *Photochem. Photobiol.* **1982**, *36*, 139–145.

(25) Kevan, L. In "Advances in Radiation Chemistry"; Burton, M., Magee, J. L., Eds.; Wiley: New York, 1974; Vol. 4, pp 181–305.

(26) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; M.I.T. Press: Cambridge, MA, 1969.

(27) Das, P. K., unpublished results.

(28) Almgren, M.; Thomas, J. K. *Photochem. Photobiol.* **1980**, *31*, 329–335.

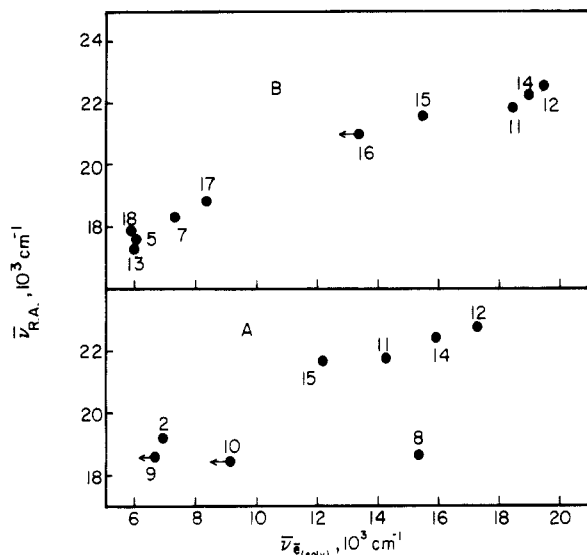


Figure 8. Plots of energy location of absorption maximum of retinal radical anion vs. that of solvated electron at (A) room temperature and (B) 77 K. For numbers identifying the solvents, see Table I. The arrows with some of the points indicate that the true energies for e_s^- absorption maxima are possibly lower in these cases.

acid cation in hexane ($\lambda_{\max} = 590$ nm),³² acetone ($\lambda_{\max} = 575$ nm),^{8c} and 1,2-dichloroethane ($\lambda_{\max} = 585$ nm). Furthermore, in micelles containing CTAB, while the λ_{\max} 's of retinal anion are significantly blue-shifted (as in alcohols, see later), those of the cation appear to be located in the same long-wavelength region (580–600 nm) as in nonprotic solvents (Table I). Figure 7 shows retinal anion maximum as a function of solvent dielectric constant. Clearly, relative to nonpolar solvents, the polar-protic ones (alcohols) cause much larger blue shifts in λ_{\max} than the polar-nonprotic ones. Within the alcohols, a systematic variation is indicated for λ_{\max} with respect to polarity (dielectric constant).

The interactions of the ground and excited states of retinal anion with solvents are expected to be similar to those of solvated electron. Figure 8 shows the plots of energies corresponding to

retinal anion maxima against those corresponding to solvated electron at room temperature and 77 K. Reasonably good correlation is suggested by either of the plots. This is reminiscent of a similar comparison³³ between absorption maxima of e_s^- and of iodide ion (charge-transfer-to-solvent band system) in ethylenediamine and concentrated aqueous electrolytes. Some specific points in this context are as follows. (i) Me_2SO , the polar-nonprotic solvent with high dielectric constant, proves to be weakly solvating for both solvated electron and retinal anion. (ii) Although the primary anionic species seen in the course of pulse radiolysis in acetonitrile at room temperature is recognized^{17b} to be the solvent anion (CH_3CN^-) rather than e_s^- , its λ_{\max} correlates very well with that of retinal anion. (iii) In contrast, the λ_{\max} (650 nm) assigned²⁰ to e_s^- in DMF at room temperature deviates significantly from the general parallelism (Figure 8A) in λ_{\max} 's of the two anionic systems.

The λ_{\max} 's of retinal anion in the aqueous micelles are all in the short-wavelength spectral region (448–460 nm, Table II). Rather unambiguously, this establishes the polar/hydrogen-bonding, alcohol-like nature of the micellar interiors where the substrate is located. In the cationic micelles, e.g., those consisting of CTAB, the ion pairing of retinal anion with cationic head groups can possibly cause blue shifts in λ_{\max} . The magnitudes of these shifts would be small³⁴ in a relatively polar environment. However, the ion-pairing interaction can explain the small progressive red shifts on going from CTAB to mixed CTAB + Triton X-100 to Triton X-100 micelles. Interestingly, the retinal anion decay rate representing its protonation is the slowest in the CTAB micelle. This is not expected if the polyenal anion is strongly ion-paired with the cationic head groups, because the protonation reactivity is usually enhanced upon cation pairing as observed with several carbanions^{11c} and aromatic radical anions.³⁵

Registry No. 2, 98921-61-0; 4, 83868-27-3; $\text{C}_6\text{H}_{11}^+$, 22499-63-4; *all-trans*-retinal, 116-31-4; retinal radical anion, 34504-14-8; retinal radical cation, 67529-90-2; cyclohexane, 110-82-7.

(33) Anbar, M.; Hart, E. J. *J. Phys. Chem.* **1965**, *69*, 1244–1247.

(34) In tetrahydrofuran, the hypsochromic shifts in λ_{\max} upon the pairing of retinal anion with tetraalkylammonium ions are typically 20–40 nm.¹⁴

(35) Bank, S.; Bockrath, B. *J. Am. Chem. Soc.* **1971**, *93*, 430–437; **1972**, *94*, 6076–6083.

Solvation Thermodynamics of Inert-Gas Molecules in Inert-Gas Liquids

A. Ben-Naim[†]

Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Received: December 18, 1985; In Final Form: May 17, 1985)

The solvation process as defined and discussed in previous articles is applied to inert-gas liquids. The thermodynamics of the solvation process are computed for the following systems: pure inert-gas liquids above the triple points, including neon, argon, krypton, and xenon; mixtures of inert-gas liquids, argon–krypton and krypton–xenon.

1. Introduction

Recently a new approach to the study of solvation thermodynamics has been suggested and developed.^{1–3} The main novelty of this approach consists of a new definition of the solvation process and the corresponding thermodynamic quantities. These quantities reflect the change that occurs in the surroundings of a given molecule when it is placed in a fluid. The fluid may be a “solvent”, in the conventional sense of this concept, or may be a liquid consisting of the same species as the “solute” molecule. Thus we

may be speaking about the solvation of “argon in xenon” as well as the solvation of “argon in argon”. The latter is essentially a new concept that broadens the range of systems studied under the term of “solvation”. Furthermore, the solvation quantities as defined in this and in previous papers, truly reflect the changes in the environment of the molecule being transferred from one phase to another.

(1) Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *80*, 4438.

(2) Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016.

(3) Ben-Naim, A. *J. Phys. Chem.* **1985**, *89*, 3791.

[†] Present address: NIH, Bldg 10, Room 4B-56, Bethesda, MD 20892.