# Transient Phenomena in the Pulse Radiolysis of Retinyl Polyenes. 3. Radical Cations<sup>1,2</sup>

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Results are presented concerning transient absorption phenomena observed upon pulse radiolysis of several retinyl polyenes at submillimolar concentrations in acetone, n-hexane, and 1,2-dichloroethane under conditions favorable for radical cation formation. Oxygen insensitive, the polyene radical cations are characterized by intense absorption maxima (575-635 nm) with locations that show little or no dependence on functional groups. In acetone, they undergo decay predominantly by first-order kinetics with lifetimes 4-11 µs. The biomolecular rate constants for radical cation quenching by water, triethylamine, and bromide ion in acetone are in the ranges  $(0.8-2) \times 10^5$ ,  $(0.3-2) \times 10^8$ , and  $(3-5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

## Introduction

Thermal or photoinduced, a majority of biomolecular processes in nature involve charge transfer in one sense or another. Retinyl polyenes, well-known for their chromophoric roles in visual and photosynthetic pigments (rhodopsin and bacteriorhodopsin), have inspired research interest primarily as subjects of spectroscopic and photochemical studies.<sup>3,4</sup> In these studies, the charge-transfer properties of retinyl polyenes in ground or excited states have drawn only limited attention. This is understandable in the light of the fact that charge transfer has not been established as an important factor in the early stages of visual excitation by rhodopsin or light transduction by bacteriorhodopsin. However, from time to time, there have been suggestions<sup>5</sup> implicating visual excitation with charge-transfer interaction between the retinyl moiety and suitable donor groups in the protein (opsin). Besides relevance to vision, extended  $\pi$  systems (carotenoids) are considered<sup>6</sup> potential mediators of charge transport in bilayer lipid membranes and related multiphase systems.

We have undertaken a relatively detailed study of the spectral and kinetic behavior of radical ions and related transients produced as a result of pulse radiolysis of retinyl polyenes in solutions. The results concerning radical anions and ground-state protonation kinetics have been presented in earlier papers.<sup>2</sup> The present paper deals with spectra and kinetics associated with radical cations when observed in relatively dilute solutions ( $\leq 1$  mM). At higher concentrations (>1 mM), nanosecond transient behaviors in several cases suggest association of the radical cations with corresponding polyene ground states giving rise to dimeric species; this forms the subject matter of the following paper.<sup>7</sup> The structures of all-trans-retinyl derivatives under study are shown in Chart I.

Several years ago, Land and co-workers<sup>8a</sup> carried out a pulse radiolytic study of radical ions of all-trans-retinal and its homologoues in hexane and methanol. More recently, while the present work was in progress, Lo, Land, and Truscott<sup>8c</sup> reported on the primary intermediates, namely, triplets, radicals, and radical ions produced under pulsed irradiation (electron/laser) of retinyl acetate and retinoic acid in the same solvents. Thus, some of the results described here for retinal (1), retinyl acetate (4), and retinoic acid (5) are, to a certain extent, supplementary to the findings reported by Land and co-workers.<sup>8a,c</sup> However, a great deal of new results and understandings have been obtained in the course of the present pulse radiolysis work because it has been extended to several additional solvents (acetone and 1,2-dichloroethane) and substrates (retinyl Schiff base, retinol, and methyl retinoate). Also, kinetic data are presented regarding the reactivity of retinyl radical cations with a number of nucleophiles, namely, water, triethylamine, and bromide ion.

### **Experimental Section**

The sources or syntheses of retinyl substrates are described in previous papers.<sup>2</sup> Acetone (Fisher, spectral grade) was refluxed CHART I

Retinol, R 🔿 O 1.

- n-Butylamine Schiff Base of retinal, R 🔨 N-Bu <u>2</u>.
- 3. Retinol , R CH
- Retinyl acetate , R OCOCH<sub>3</sub> 4.
- Retinoic acid, R <u>5</u>.

Methyl retinoate R <u>6</u>.

with potassium permanganate, fractionally distilled, and then stored over molecular sieves (4A). 1,2-Dichloroethane (Eastman, spectral grade) was passed, before use, through a column of alumina. n-Hexane (Aldrich) was fractionally distilled and then passed through a column of silica gel.  $\beta$ -Carotene (Aldrich) was recrystallized twice from a 1:1 ethanol:chloroform mixture, and N, N, N', N'-tetramethylbenzidine (Aldrich) was sublimed under vacuum. Triethylamine (Eastman) was distilled after storage over KOH, and tetra-n-butylammonium bromide (Eastman) was used as received.

For pulse radiolysis, electron pulses (5 ns) from the Notre Dame 7 MeV ARCO LP-7 linear accelerator were used at dose rates of  ${\sim}23\times10^{16}\,eV/g$  per pulse. The description of the computer-controlled kinetic spectrophotometer and data collection system is available elsewhere.<sup>9a-c</sup> The change in optical density ( $\Delta OD$ ) at 300-700 nm following electron irradiation was measured as a function of time (microseconds to milliseconds) and expressed as an extinction coefficient parameter ( $\epsilon'$ ) given by the relationship  $\epsilon' = (\Delta OD \times K)/(G \times dose)$ , where K is a multiplying factor

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<sup>(1)</sup> The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No.

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appropriately chosen to obtain a value of 7600  $M^{-1}$  cm<sup>-1</sup> for  $\epsilon'$  of  $(SCN)_2$ - at 475 nm in N<sub>2</sub>O-saturated aqueous solutions in the same cell and G is the yield per 100 eV. All pulse radiolysis experiments were performed in a flow system. The absorption of monitoring light by retinyl substrates was kept to the minimum by using suitable Corning cutoff filters.

The laser flash photolysis experiments were carried out using, for excitation, 355-nm pulses (5-20 mJ, 6 ns) generated from a quanta-Ray Nd:YAG system. The kinetic spectrophotometer and data collection system are described elsewhere.<sup>9d,e</sup>

#### Results

The three principal solvents used for pulse radiolysis studies described here are 1,2-dichloroethane (DCE), acetone, and n-hexane. From the interaction of high-energy electron pulses with solvent, solvated electrons and solvent-derived radical cations (holes) are produced (eq 1) as free ions. In chlorinated hydro-

$$S + e_{fast} \rightarrow S^+ + 2e_s^-$$
 (1)

carbons,<sup>10</sup> the solvated electron does not persist because of its dissociative capture by the solvent molecules (eq 2). The sol-

$$-C - CI + e_{s} - C + CI \qquad (2)$$

vent-derived cations remain available for diffusional charge transfer to an added solute. For DCE, in particular, two kinetically distinct cationic species have been implicated, <sup>10a</sup> namely, a radical cation (assigned as CH<sub>2</sub>Cl-CH<sub>2</sub>Cl<sup>+</sup> or ClCHCH<sub>2</sub><sup>+</sup>; G = 0.68) and a carbocation (assigned as CH<sub>2</sub>Cl-CH<sub>2</sub><sup>+</sup> or A; G = 0.20).



In acetone,<sup>11</sup> the relatively long-lived species that are involved in charge or energy transfer to a solute at millimolar concentrations are acetone triplet (formed via geminate recombination in ion pairs),  $(CH_3)_2C=O^-$ , and  $(CH_3)_2C=O^+$ . The triplet and free-ion yields have been measured<sup>11a</sup> to be 1.0 and 0.75, respectively. Of particular interest in the present study is the molecular cation,  $(CH_3)_2C=O^+$ , which has been shown<sup>11b</sup> to decay with a rate constant of  $3.6 \times 10^7$  s<sup>-1</sup> in acetone containing 2% nitromethane at 303 K. The decay apparently occurs by proton transfer to solvent or a hydroxylic impurity, as shown in eq 3 and 4. In *n*-hexane,<sup>12</sup> the charge exchange with a solute is best

$$(CH_3)_2 C = O^+ + (CH_3)_2 C = O \rightarrow CH_2 COCH_3 + (CH_3)_2 COH^+ (3)$$

$$(CH_3)_2 C = O^+ + ROH \rightarrow CH_2 COCH_3 + ROH_2^+ \quad (4)$$

described in terms of solvated electron and positive hole as precursors, the former being considerably more mobile than the latter.

In order to sort out the contributions of individual radical anion and cation to transient absorption, we have frequently used  $O_2$ and  $N_2O$  as scavengers for solvated electrons and solvent/solute radical anions (in some cases) and triethylamine (TEA) as scavenger for radical cations and solvated protons. Oxygen also served as a strong quencher for triplets of solutes and solvents (e.g., acetone). Since the primary purpose of this work was to obtain information on radical cations of retinyl substrates, the pulse



Figure 1. Transient absorption spectra observed upon pulse radiolysis of (A) 0.015, (B) 0.048, and (C) 0.34 mM retinal in N<sub>2</sub>-saturated DCE (at 5, 5, and 2  $\mu$ s, respectively, following the electron pulse). Inset: plots of maximum absorbances at (a) 595 and (b) 650 nm vs. [retinal] and of observed first-order rate constants for growth at (c) 595 and (d) 650 nm vs. [retinal] (solvent: DCE).

radiolysis experiments in acetone and *n*-hexane were mostly carried out under oxygen saturation  $(10-15 \text{ mM } [O_2])$ .

Spectral and Kinetic Behavior of Radical Cations. (i) Retinal (1). The transient absorption spectra observed upon pulse radiolysis of retinal at three different concentrations in N2-saturated DCE are presented in Figure 1. At relatively low retinal concentrations (Figure 1A,B), the absorption maximum is at 650 nm. However, as the concentration is increased, a second absorption maximum at 595 nm becomes more and more prominent (Figure 1C). Although the first-order decay of transient absorption at the two maxima is very similar ( $\tau_{1/2} = 28 \ \mu s$  at [retinal] = 0.048 mM), the formation kinetics on a microsecond time scale at a given [retinal] are found to be slightly faster at the shorter wavelength maximum (595 nm). The inset of Figure 1 shows the linear plots of observed pseudo-first-order rate constants  $(k_{obsd})$  for growth at 595 and 650 nm vs. [retinal]; the difference in intercepts suggests that two distinct cationic species with varying precursor lifetimes ( $\tau = 5$  and >10  $\mu$ s) are responsible for transient absorptions at 595 and 650 nm, respectively. The bimolecular rate constants for formation are practically the same  $(7 \times 10^9 \text{ M}^{-1}$  $s^{-1}$ ) for the two wavelengths. The absorbance change ( $\Delta OD_{max}$ ) at the maximum of the formation/decay profile is also shown as a function of [retinal] in the inset of Figure 1. Evidently, at relatively high retinal concentrations (>0.2 mM) where  $\Delta OD_{max}$ at 650 nm reaches a plateau, that at 595 nm continues to increase.

On the basis of the fact that the 595-nm species is also observed in acetone (see below), hexane,<sup>7</sup> and a variety of other solvents<sup>13</sup> under conditions appropriate for radical cation formation, we identify this as the retinal radical cation. The most reasonable precursor responsible for its formation is the solvent radical cation,  $CH_2CI-CH_2CI^+$ . The continuation of increase in absorbance at 595 nm at increasing [retinal] is explainable in terms of association of the radical cation with the ground state, the dimer cation having enhanced absorption at 580–600 nm relative to the monomer. The details of arguments supporting the aggregation phenomena at relatively high concentrations of retinal and related polyenes will be presented in a subsequent paper. The assignment of the 650-nm species is not obvious, although very plausibly it may be an adduct of the solvent carbocation,  $CH_2CI-CH_2^+$ , with the polyene (eq 5).

$$R-CH=O + CH_2Cl-CH_2^+ \rightarrow R-C^+H-O-CH_2-CH_2Cl (5)$$

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Figure 2. Transient absorption spectra observed upon pulse radiolysis of retinal in acetone. The retinal concentrations, the times at which the spectra were obtained after the electron pulse, and the conditions regarding scavengers are as follows: (A) 0.46 mM, 1  $\mu$ s, N<sub>2</sub> saturated; (B) 0.46 mM, 1.4  $\mu$ s, N<sub>2</sub>O saturated; (C) 0.46 mM, 0.4  $\mu$ s, O<sub>2</sub> saturated; and (D) 0.82 mM, 1.4  $\mu$ s, N<sub>2</sub> saturated, 0.022 M TEA.

Pulse radiolytic transient phenomena observed with retinal in acetone under  $N_2$ ,  $N_2O$ , and  $O_2$  saturation as well as in the presence of TEA (0.022 M) are described by spectra A-D in Figure 2. The spectrum (Figure 2A) under deoxygenated conditions is a superimposition of contributions from three major species: triplet ( $\lambda_{max} = 445 \text{ nm}, \tau_{1/2} = 6.5 \mu s$ ), radical anion ( $\lambda_{max} = 495 \text{ nm}$ ), and radical cation ( $\lambda_{max} = 585 \text{ nm}$ ). In the presence of oxygen, the triplet and the anion disappear completely leaving behind the oxygen-insensitive radical cation (Figure 2C). Under  $N_2O$  saturation, although the contribution from the radical anion becomes substantially reduced (Figure 2B), it is not wiped out completely. The persistence of the radical anion under  $N_2O$ saturation in acetone suggests that the scavenging of electron donor precursor(s) by N<sub>2</sub>O is incomplete under this condition. A similar observation has been made by Kira et al.<sup>14</sup> using trans-stilbene as the substrate. TEA is an effective quencher (nucleophile) for retinal radical cation itself (see later) as well as for its precursor  $(CH_3)_2CO^+$  (eq 6). At the same time, it consumes acetone triplet by photoreduction (eq 7). Thus, in its presence, the transient

$$(CH_3)_2CO^+ + N \longrightarrow CH_3COCH_2 + H \longrightarrow N \longrightarrow (6)$$

$$(CH_3)_2CO^* + N - CH_2CH_3 - (CH_3)_2COH + N - CHCH_3 (7)$$

spectrum is primarily that of retinal radical anion ( $\lambda_{max} = 495$  nm,  $\tau = 11 \ \mu$ s; Figure 2D). In the presence of water (~1%) in N<sub>2</sub>-saturated acetone, retinal triplet is the only species that appears to be formed. Understandably, both (CH<sub>3</sub>)<sub>2</sub>CO<sup>+</sup> and (CH<sub>3</sub>)<sub>2</sub>CO<sup>-</sup> are efficiently quenched via proton transfer from and to water, respectively.



Figure 3. Transient absorption spectra observed upon pulse radiolysis of (A, B) 0.55 and (C, D) 0.056 mM retinal in N<sub>2</sub>O-saturated *n*-hexane. The times ( $\mu$ s) after electron pulse at which the spectra were obtained are (A) 0.4, (B) 13, (C) 2, and (D) 13.

In  $N_2O$ -saturated *n*-hexane (Figure 3), retinal radical cation shows its principal absorption maximum at 600 nm; this is in agreement with the report by Land et al.<sup>8a</sup> Two other transient processes in the spectral regions around 445 and 650 nm deserve mention (Figure 3). First, at a relatively high [retinal] (Figure 3A,B), a second absorption maximum shows up at 445 nm. That this is not cation related is established by the fact that it nearly disappears upon O<sub>2</sub> saturation. Understandably, the retinal triplet  $(\lambda_{\rm max} = 445 \text{ nm}, \tau_{1/2} \sim 6 \ \mu s)^{15}$  is partially responsible for the absorption at 445 nm; however, the persistence of the peak at a time when the triplet has decayed considerably (Figure 3B) suggest that there is also contribution from radical-type transient(s) (unidentified). Second, the decay behaviors at 630-670 nm at both low and high [retinal] indicate the formation of a species  $(\lambda_{max} = 645 \text{ nm})$  longer lived than the radical cation. This species appears to be analogous to the 650-nm species observed in DCE (vide supra) and may be carbocationic in nature.

In acetone and DCE, retinal radical cation decays primarily by first-order kinetics. The lifetimes at 0.05-0.5 mM [retinal] are typically 40-60  $\mu$ s in N<sub>2</sub>-saturated DCE and 4-7  $\mu$ s in O<sub>2</sub>saturated acetone. The lifetimes from measurement to measurement vary somewhat because of variable concentrations of nucleophilic impurities. Since the oxidation potential of retinal  $(E_p = 1.20 \text{ V})^{16}$  is higher than that of  $\beta$ -carotene  $(E_p = 0.74 \text{ V})^{16}$ and N, N, N', N'-tetramethylbenzidine (TMB;  $E_{1/2}^{\text{ox}} = 0.32 \text{ V vs.}$ SCE in 1:1 benzene:methanol mixture),<sup>17</sup> retinal radical cation is expected to be a ready acceptor of electrons from  $\beta$ -carotene and TMB. By following the decay of retinal radical cation at 585 nm as a function of quencher concentration, we measured the biomolecular rate constants for charge exchange with  $\beta$ -carotene and TMB to be  $3.3 \times 10^9$  and  $1.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, respectively (in acetone). Pulse radiolysis of retinal ( $\sim 1 \text{ mM}$ ) in the presence of 0.1 mM TMB in O<sub>2</sub>-saturated acetone shows the formation of TMB<sup>+</sup> with its characteristic absorption spectrum at 420–490 nm ( $\lambda_{max} = 475$  nm).<sup>18</sup> The relatively slow formation of the major portion of TMB<sup>+</sup> at 475 nm matches kinetically with the decay

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Figure 4. Transient absorption spectra observed upon pulse radiolysis of 0.1 mM RSB in (A, B) N<sub>2</sub>O- and (C, D) O<sub>2</sub>-saturated *n*-hexane. The times in  $\mu$ s (after laser pulse) the spectra correspond to are (A) 1 (B) 5.5, (C) 1, and (D) 14.5.

of retinal radical cation at 585 nm.

(ii) Retinal Schiff Base (RSB, 2). The transient absorption spectra observed upon pulse radiolysis of retinal Schiff base (RSB) in N<sub>2</sub>O- and O<sub>2</sub>-saturated *n*-hexane are presented in Figure 4. The major absorption maximum at 635 nm that remains unaltered in the presence of N<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>O is attributable to the radical cation. At 0.1 mM [RSB], the radical cation formation becomes complete within ~800 ns after the electron pulse and its decay takes place predominantly by first-order kinetics ( $\tau = 3 \ \mu s$ ). Over 4-5  $\mu s$  following the pulse, relatively slow formation of longer lived transients ( $\tau_{1/2} \sim 100 \ \mu s$ ) is evident from the time-resolved spectra at 380-450 nm ( $\lambda_{max} = 410$  and 430 nm under N<sub>2</sub>O and N<sub>2</sub> saturation and 415 nm under O<sub>2</sub> saturation). The short-wavelength locations of the absorption maxima rule out identification of these transients as products of proton or carbocation addition. Assignments as products of free radical addition seem more plausible.

RSB in acetone (O<sub>2</sub>-saturated) shows primarily dual transient processes (Figure 5), namely, relatively fast formation of radical cation ( $\lambda_{max} = 615$  nm) and slower protonation leading to a stronger absorption at 400–500 nm ( $\lambda_{max} = 450$  nm). The absorption spectral behavior of protonated RSB ( $\lambda_{max} = 450-460$ nm in various solvents) is well-documented in the literature.<sup>2b,19</sup> The most likely proton donor in acetone is (CH<sub>3</sub>)<sub>2</sub>COH<sup>+</sup> produced from the molecular cation (eq 3) in competition with its charge-exchange reaction with RSB. Thus, kinetic analyses of the transient absorption data are possible on the basis of eq 3, 8, and 9. Figure 6 shows maximum absorbance changes at 450

$$(CH_3)_2CO^+ + RCH = NBu \xrightarrow{\kappa_{\alpha}} (CH_3)_2CO + RCH = NBu^+ \cdot$$
(8)

$$(CH_3)_2COH^+ + RCH = NBu \xrightarrow{k_{H^+}} RCH = N^+HBu + (CH_3)_2CO (9)$$



Figure 5. Transient absorption spectra at (A) 0.4 and (B) 1.4  $\mu$ s following pulse radiolysis of 0.1 mM RSB in O<sub>2</sub>-saturated acetone and (C) at 0.13  $\mu$ s following pulse radiolysis of 0.15 mM RSB in N<sub>2</sub>-saturated acetone containing 0.097 M TEA. Insets: kinetic traces at (a) 605 and (b) 435 nm for 0.1 mM RSB in O<sub>2</sub>-saturated acetone.



**Figure 6.** Plots of maximum absorbances at (A) 450 and (B) 610 nm as functions of [RSB] in O<sub>2</sub>-saturated acetone. Insets: plots (a) of rate constant for growth of absorbance at 450 nm vs. [RSB] and (b) of  $1/\epsilon'_{max}$  at 610 nm vs. 1/[RSB].

and 610 nm (following completion of growth in each case) as functions of [RSB]. From eq 3, 8, and 9 and assuming a first-order decay of  $(CH_3)_2COH^+$  with lifetime of  $\tau'$  (representing its neutralization in the absence of RSB), we obtain the following equations for  $[RCH=NBu^+]_{max} = [RCH=N^+HBu]_{max}$ 

$$[\text{RCH}-\text{NBu}^+]_{\text{max}} = [(\text{CH}_3)_2 \text{CO}^+]_0 \frac{k_{\text{et}}\tau[\text{RSB}]}{1 + k_{\text{et}}\tau[\text{RSB}]}$$
(10)

$$[\text{RCH}=\text{N}^{+}\text{HBu}]_{\text{max}} = \frac{k_{\text{H}^{+}}\tau'[\text{RSB}]}{[(\text{CH}_{3})_{2}\text{CO}^{+}\cdot]_{0}\frac{k_{\text{H}^{+}}\tau'[\text{RSB}](1+k_{\text{H}^{+}}\tau'[\text{RSB}])}{(1+k_{\text{H}^{+}}\tau'[\text{RSB}])(1+k_{\text{H}^{+}}\tau'[\text{RSB}])}$$
(11)

where  $\tau$  is the lifetime of  $(CO_3)_2CO^+$  (in the absence of RSB) and  $[(CH_3)_2CO^+\cdot]_0$  is its initial concentration (pulse radiolytic).

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That  $[RCH=N^{+}HBu]_{max}$  as a function of [RSB] should go through a maximum (Figure 6A) is predicted by eq 11.

The plot of the observed pseudo-first-order rate constant  $(k_{obsd})$  for formation of protonated RSB at 450 nm against [RSB] is reasonably linear (see inset a of Figure 6) and gives  $1.6 \times 10^9$   $M^{-1} \, s^{-1}$  for  $k_{H^+}$  and 5.0  $\mu$ s for  $\tau'$  (so that  $k_H^+ \tau' = 8.0 \, \text{mM}^{-1}$ ). Also, the double-reciprocal plot of  $1/\epsilon_{\text{RSB}^+,\text{ max}}$  against 1/[RSB], shown in inset b of Figure 6, gives an intercept-to-slope ratio of 0.70 mM<sup>-1</sup>. Based on eq 10, this becomes an estimate  $k_{et}\tau$ . Using the lifetime data of 27.8 ns<sup>11b</sup> for  $\tau$ , we obtain a value of  $2.5 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$  for  $k_{et}$ , not unreasonable for diffusion-controlled electron transfer in acetone. Curves calculated on the basis of eq 10 and 11 and given values of  $k_{et} \tau$  and  $k_{H^+}\tau'$  are shown by dotted lines in Figure 6A,B; they appear to fit the experimental points reasonably well.

It was possible to resolve the spectrum due to RSB radical anion by pulse radiolysis in N<sub>2</sub>-saturated acetone containing excess of TEA (Figure 5C). The latter prevented the formation of RCH=NBu<sup>+</sup> and RCH=N<sup>+</sup>HBu by scavenging their precursors (CH<sub>3</sub>)<sub>2</sub>CO<sup>+</sup> and (CH<sub>3</sub>)<sub>2</sub>COH<sup>+</sup>. Furthermore, it acted as a quencher for RCH=NHBu<sup>+</sup>. The radical anion exhibits an absorption maximum at 590 nm (Figure 5C) which is considerably red-shifted compared to that in methanol (430 nm).<sup>2a</sup> The rate constant for its first-order decay is  $3.6 \times 10^6$  s<sup>-1</sup> (in the presence of 0.097 M TEA).

With RSB in DCE, the transient phenomena are dominated by intense absorption ( $\lambda_{max} = 450 \text{ nm}$ ) due to a very long-lived species ( $\tau > 2 \text{ ms}$ ) formed primarily by a slow process ( $\tau_{1/2} =$ 9.5  $\mu$ s at [RSB] = 0.06 mM). We attribute this to carbocation and proton addition to the Schiff base. Transient absorption due to radical cation appears only as a shoulder at long wavelengths (550-650 nm), but this is too weak to be satisfactorily resolved for kinetics or spectra.

(iii) Retinol (3) and Retinyl Acetate (4). The formation of retinyl carbocation,  $RCH_2^+$ , via solvent carbocation addition (eq 12)

$$RCH_2OR' + CH_2CICH_2^+ \rightarrow RCH_2O^+(R')CH_2CH_2CI \rightarrow RCH_3^+ + CH_3CI-CH_3OR' \quad (R' = H \text{ or } COCH_3) (12)$$

and from protonation<sup>2b</sup> appears to be a serious complication in the course of pulse radiolysis of retinyl acetate and retinol in DCE. This is particularly true because, as recognized by Lo et al.<sup>8c</sup> with retinyl acetate as the substrate, the absorption spectra of radical cations are almost identical with those of the carbocation (obtainable by protonation<sup>2b,20</sup> and photodissociation<sup>21</sup>). The heterogeneity of transient species ( $\lambda_{max} = 595-600 \text{ nm}$ ) formed in DCE is evidenced from dual kinetics in both formation and decay. No attempt was made for detailed kinetic analysis, although it was noted that the slow component of formation of transient absorption at 580-610 nm could not be fitted into single-exponential kinetics. The generation of retinyl carbocation in DCE is analogous to that of arylmethyl carbocations from the corresponding carbinols (presumably with CH<sub>2</sub>Cl-CH<sub>2</sub><sup>+</sup> acting as the precursor).<sup>10a</sup>

Since the pulse radiolysis of retinyl acetate in hexane has been reported in detail by Lo et al.,<sup>8c</sup> our results in this solvent will pertain to retinol only. Figure 7A shows the spectrum obtained with 0.11 mM retinol in N<sub>2</sub>O-saturated *n*-hexane. The main absorption maximum (600 nm) is assigned to the radical cation which decays with a half-life of 4.1  $\mu$ s. The shorter wavelength region (370-420 nm) shows a second transient characterized by dual maxima (375 and 410 nm) and a long decay time ( $\tau_{1/2} \sim$ 100  $\mu$ s). On the basis of spectral and kinetic similarity of the two-band spectral feature with that of the product of reaction of pulse radioltic *tert*-butoxy radical<sup>22</sup> with retinol, we conclude that



Figure 7. Transient absorption spectra at (A) 0.8 and (B) 13  $\mu$ s following pulse radiolysis of 0.11 mM retinol in N<sub>2</sub>O-saturated *n*-hexane, (C) 0.5  $\mu$ s for 0.98 mM retinol in O<sub>2</sub>-saturated acetone, (D) 0.5  $\mu$ s for 0.91 mM retinyl acetate in O<sub>2</sub>-saturated acetone, and (E) 4  $\mu$ s for 1.0 mM retinol in O<sub>2</sub>-saturated acetone containing 0.081 mM TMB. Insets: kinetic traces for decay of transient absorption (a) at 585 nm for retinol and (b) at 580 nm for retinyl acetate.

the short-wavelength absorption has a contribution from the retinyl ketyl radical, RCHOH.

Detailed studies have been carried out with both retinol and retinyl acetate as substrates in acetone under  $O_2$  saturation. In particular, we were intrigued by the possibility that the radical cations of these two retinyl derivatives might undergo fast, intramolecular or solvent-assisted transformation to the retinyl carbocation (eq 13 and 14, R' = H or COCH<sub>3</sub>). The spectra

$$RCH_2OR'^+ \rightarrow RCH_2^+ + OR'$$
(13)

$$\operatorname{RCH}_{2}\operatorname{OR}'^{+} \cdot + \operatorname{HR}'' \to \operatorname{RCH}_{2}^{+} + \cdot \operatorname{R}'' + \operatorname{R}'\operatorname{OH} \quad (14)$$

of major transients obtained by experiments on the same day using the two substrates at similar concentrations in acetone of the same stock are shown in Figure 7C,D. It is noted that the absorption maximum (585 nm) in the case of retinol (Figure 7C) is red-shifted by  $\sim 5$  nm relative to that in the case of retinyl acetate. However, the decay kinetics are almost identical in the two cases ( $\tau = 11$  $\mu$ s); see kinetic traces a and b in the inset of Figure 7.

While the above-mentioned spectral difference, though small, suggests that the transient species observed with retinol and retinyl acetate in acetone are not the same (i.e., retinyl carbocation,  $\text{RCH}_2^+$ ), other observations provide more conclusive evidence in support of their assignment as radical cations (rather than the carbocation). Since the oxidation potential of retinol ( $E_p = 0.95$  V)<sup>16</sup> is higher than that of  $\beta$ -carotene by 0.21 V, the radical cation of the former is expected to be efficiently quenched by the latter (via electron transfer). The 590-nm species from retinol and retinyl acetate is found to be quenched by  $\beta$ -carotene with bimolecular rate constants ( $k_q$ ) of 2.6 × 10<sup>9</sup> and 1.9 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (in acetone). In the case of retinyl acetate in hexane, Lo et al.<sup>8c</sup> observed similar quenching concurrent with first-order formation of  $\beta$ -carotene

<sup>(20)</sup> Blatz, P. E.; Pippert, D. L. J. Am. Chem. Soc. 1968, 90, 1296-1300.
(21) (a) Rosenfeld, T.; Alchalal, A.; Ottolenghi, M. Chem. Phys. Lett.
1973, 20, 291-297. (b) Rosenfeld, T.; Alchalal, A.; Ottolenghi, M. In "Excited States of Biological Molecules"; Birks, J. B., Ed.; Wiley: London, 1976; pp 540-554. (c) Chattopadhyay, S. K.; Bobrowski, K.; Das, P. K. Chem. Phys. Lett. 1982, 91, 143-148.

<sup>(22)</sup> Das, P. K., unpublished results.



Figure 8. (A, B) Transient absorption spectra upon 355-nm laser flash photolysis of  $\sim 0.1$  mM retinol in aerated acetone. (C, D) Same as in (A) and (B), but in the presence of 0.058 mM TMB. The spectra correspond to (A, C) 0.4 and (B, D) 5  $\mu$ s following the laser flash.

radical cation absorption at 1040 nm. TMB proved to be a better quencher for the 590-nm species ( $k_q = 8.9 \times 10^9$  and  $9.3 \times 10^9$   $M^{-1} s^{-1}$  for retinol and retinyl acetate, respectively), and with this, we observed the slow formation of TMB<sup>+</sup> at 430–475 nm. The transient spectrum observed with retinol as substrate and TMB as quencher in acetone (Figure 7E) agrees very well with that<sup>18</sup> of TMB<sup>+</sup> at 420–490 nm, suggesting that electron transfer is the major mode of quenching. An electron-transfer process with retinyl carbocation as the acceptor (eq 15) should result in con-

$$RCH_2^+ + TMB \rightarrow RCH_2 + TMB^+$$
 (15)

 $RCH_2OR'^+ + TMB \rightarrow$ RCH\_2OR' + RMB<sup>+</sup> (R' = H or COCH\_3) (16)

comitant growth of short-wavelength absorption (370-400 nm) due to RCH<sub>2</sub>. The latter, recognized<sup>8c</sup> to be the product of CH<sub>3</sub>COO<sup>-</sup> elimination from retinyl acetate radical anion, has a very high extinction coefficient ( $\epsilon_{max} \simeq 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  at 385 nm in Ar-saturated methanol). In our experiments with both retinol and retinyl acetate in the presence of TMB, although we noted nonnegligible growth phenomena at 380-390 nm, these were nowhere close to what was expected from a transient having an extinction coefficient 2.5 times greater than that of TMB<sup>+</sup> ( $\epsilon_{max} \simeq 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>18</sup>

For comparison, the retinyl carbocation (RCH<sub>2</sub><sup>+</sup>) was generated by laser flash photolysis (355 nm) of retinol in the same solvent, i.e., acetone (air saturated). The major transient (Figure 8) is retinyl carbocation, RCH<sub>2</sub><sup>+</sup>, which is produced by biphotonic photodissociation<sup>21c</sup> of retinol and bears a striking spectral resemblance ( $\lambda_{max} = 585$  nm) with retinol radical cation. It decays by mixed kinetics over a time period longer than that for the retinol radical cation (seen in pulse radiolysis). In the presence of  $\sim 1$  $\times 10^{-4}$  M  $\beta$ -carotene, the decay kinetics remain nearly unchanged. On the contrary, TMB proves to be a strong quencher ( $k_a = 1.2$  $\times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>), but the lack of slow formation of TMB<sup>+</sup>. (Figure 8B,B') concurrent with carbocation decay suggests that electron transfer (eq 15) does not occur in the course of the quenching. The observation of fast formation of a small amount of TMB+. upon laser flash photolysis of retinol in the presence of TMB (Figure 8B,B') is accounted for by partial absorption of laser photons by TMB itself causing its photoionization.<sup>18</sup> The efficient quenching of retinyl carbocation by TMB is explainable by its addition<sup>10c</sup> to the amine forming a quarternary ammonium ion (eq 17).

$$RCH_{2}^{+} + N - R' - RCH_{2} - N - R' (R'=C_{6}H_{4} - C_{6}H_{4} - N(CH_{3})_{2})$$

$$| \qquad (17)$$



Figure 9. Transient absorption spectra of radical cation of (A, B) retinoic acid and (C, D) methyl retinoate in  $(A, C) N_2O$ -saturated *n*-hexane and  $(B, D) O_2$ -saturated acetone.

TABLE I: Absorption Spectral Maxima and Decay Lifetimes of Radical Cations of Retinyl Polyenes at 22 °C

	$\lambda_{\max}^{a}$ nm			
polyene	acetone	DCE	n-hexane	$\tau_{\rm d},^b \mu { m s}$
retinal	585	595	595	4-7
retinal Schiff base	615		635	4-5
retinol	585	600	600	7-11
retinyl acetate	580	595	590 <sup>c</sup>	6-11
retinoic acid	575	585	590	6-7
methyl retinoate	575	585	590	6-10

 $a \pm 5$  nm. <sup>b</sup> These are frequently observed first-order decay lifetimes at 0.4–0.8 mM substrate concentrations in O<sub>2</sub>-saturated acetone. <sup>c</sup> Taken from ref 8c.

From the intercept of the plot of  $1/\epsilon'_{max}$  against 1/[retinol] or 1/[retinyl] acetate],  $G\epsilon_{max}$  values are estimated at  $8.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for both substrates. From the free-ion yield<sup>11a</sup> (G) of 0.75 in acetone,  $\epsilon_{max}$  is calculated to be  $1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . From a comparison of  $\Delta \text{OD's}$  at 580–585 nm due to RCH<sub>2</sub>OH<sup>+</sup> · and RCH<sub>2</sub>OCOCH<sub>3</sub><sup>+</sup> · with those due to TMB<sup>+</sup> · formed as a result of the quenching of the radical cations by TMB, the efficiency of electron transfer (eq 16) in the quenching process is estimated at 70–90%.

(iv) Retinoic Acid (5) and Methyl Retinoate (6). The absorption spectra of radical cations of retinoic acid and methyl retinoate in N<sub>2</sub>O-saturated *n*-hexane and O<sub>2</sub>-saturated acetone are presented in Figure 9. The absorption maxima of the acid and the ester in a given solvent are identical, and their decay behaviors are also very similar ( $\tau = 6-10 \ \mu$ s in acetone). This suggests that the acid radical cation remains undissociated. In deoxygenated acetone, transient absorptions due to triplets ( $\lambda_{max} = 435 \ nm$ ) and radical anions ( $\lambda_{max} \sim 550 \ nm$ ) become dominant. As with retinal and RSB, the  $\lambda_{max}$ 's of the radical anions in acetone are red-shifted compared to those in protic solvents (480–510 nm in alcohols).

The absorption maxima and decay lifetimes of radical cations of retinyl polyenes are summarized in Table I.



Figure 10. Representative plots based on eq 18 for the quenching of retinyl radical cations in acetone. Substrates: (A, B, C) retinal and (A', B', C') retinoic acid. Quenchers: (A, A') water, (B, B') TEA, and (C, C') Br<sup>-</sup>.

TABLE II: Bimolecular Rate Constants for the Quenching of Radical Cations of Retinyl Polyenes in O<sub>2</sub>-Saturated Acetone at 22  $^\circ C$ 

polyene		$k_{q}, {}^{a} M^{-1} s^{-1}$	
	H <sub>2</sub> O	TEA	Br-
retinal	$8.4 \times 10^{4}$	$1.8 \times 10^{8}$	$5.3 \times 10^{10}$
retinal Schiff base	$1.5 \times 10^{5}$	$3.9 \times 20^{7}$	$3.1 \times 10^{10}$
retinol	$1.9 \times 10^{5}$	$2.7 \times 10^{7}$	$4.1 \times 10^{10}$
retinyl acetate	$1.3 \times 10^{5}$	$3.9 \times 10^{7}$	$3.1 \times 10^{10}$
retinoic acid	$3.5 \times 10^{5}$	$1.9 \times 10^{8}$	$3.9 \times 10^{10}$
methyl retinoate	$1.6 \times 10^{5}$	$1.2 \times 10^{8}$	$3.7 \times 10^{10}$

<sup>a</sup>Ca. ±20%.

Quenching Studies with Radical Cations. The quenching behavior of the radical cations toward water, TEA, and Br<sup>-</sup> has been examined in O<sub>2</sub>-saturated acetone by following their decay at the absorption maxima in the presence of varying concentrations of the quenchers (Q). Tetra-*n*-butylammonium bromide was used to furnish Br<sup>-</sup>. The bimolecular rate constants ( $k_q$ ) for quenching were obtained from linear plots (Figure 10) based on eq 18, where

$$k_{\text{obsd}} = k_0 + k_0[Q] \tag{18}$$

 $k_{obsd}$  and  $k_0$  are the first-order rate constants for radical cation decay in the presence and absence of a given quencher. The data concerning  $k_q$  are presented in Table II.

## Discussion

Theoretical considerations<sup>8b</sup> as well as experimental data<sup>8a,b</sup> for retinal homologues show that the absorption maxima of polyene radical ions become red-shifted in a linear manner as the polyene chain length is increased. For example, on going from retinal to its immediate higher or lower homologue,<sup>13</sup> the radical cation

absorption maximum is shifted by 60-70 nm. Based on retinol or retinyl acetate as the reference polyene with five double bonds, an increase in the chain length by addition of an aldehyde or acid/ester group (in conjugation) does not seem to cause any significant change in the radical cation absorption maxima (Table I). Only with RSB do we see a small red shift of 20-25 nm (relative to retinol and retinyl acetate). This behavior suggests that the radical cation center is not extensively delocalized into the carbonyl or imino double bond. The secondary role of the functional group is also evident from the general lack of variation in radical cation decay lifetimes (Table I) among the retinyl derivatives.

The solvent effect on  $\lambda_{max}$  of radical cations is interesting. On going from the nonpolar solvent, *n*-hexane, to the relatively polar nonprotic solvent, acetone, blue shifts of 10–20 nm are noted for each of the polyene substrates (Table I). A similar hypsochromic effect, but more pronounced, has been documented<sup>8,23</sup> for  $\lambda_{max}$ of radical anions of retinal,  $\beta$ -carotene, and lycopene (in hexane vs. methanol). This is suggestive of stronger ion-dipole interaction in the ground state of radical ions relative to that in the excited state (responsible for the intense absorption band system).

The rate constants (Table II) for radical cation quenching by Br are as high as expected under diffusion control (augmented by Coulombic interaction between two oppositely charged ions). They indicate exothermic charge neutralization<sup>24</sup>a at the cation site. In comparison, TEA ( $E_p = 0.95$  V in acetonitrile vs. SCE)<sup>24b</sup> quenches the radical cations with rate constants well below the limit of diffusion control. In this case, the quenching probably involves both electron transfer and addition at the cation site (forming a quarternary ammonium ion). The fact that  $k_q$  by TEA is smaller for retinol than for retinal appears to be a manifestation of more favorable electron transfer in the case of the latter radical cation (that is,  $E_p$ , 1.2 V, is more positive for the aldehyde).<sup>16</sup> Water is apparently a weak nucleophilic quencher causing hydroxylation at the cation site. The reactions of radical cations with H<sub>2</sub>O, TEA, and Br<sup>-</sup> should result in formation of radicals with reduced chain length relative to, for example, RCH<sub>2</sub> or RCHOH. The absorption spectra of these radicals remain inaccessible under the conditions of our measurements because of their strong overlap with the ground-state absorption of retinyl substrates.

**Registry No.** 1, 116-31-4; 1<sup>+</sup>, 67529-90-2; 1<sup>-</sup>, 34504-14-8; 2, 36076-04-7; 2<sup>+</sup>, 98462-61-4; 2<sup>-</sup>, 34512-76-0; 3, 68-26-8; 3<sup>+</sup>, 98462-62-5; 4, 127-47-9; 4<sup>+</sup>, 98462-63-6; 5, 302-79-4; 5<sup>+</sup>, 98462-64-7; 6, 339-16-2; 6<sup>+</sup>, 98462-65-8; TMB, 366-29-0; TEA, 121-44-8; DCD, 107-06-2; H<sub>2</sub>O, 7732-18-5; Br<sup>-</sup>, 24959-67-9; Me<sub>2</sub>C(O), 67-64-1; CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, 110-54-3;  $\beta$ -carotine, 7235-40-7.

<sup>(23)</sup> Dawe, E. A.; Land, E. J. J. Chem. Soc., Faraday Trans. 1 1975, 71, 2162-2169.

<sup>(24) (</sup>a) Based on an estimated electron affinity of 6.6 eV for Br· in aqueous solution (Treinin, A.; Hayon, E. J. Am. Chem. Soc. 1976, 98, 3884-3891), electron transfer from Br<sup>-</sup> to retinyl radical cations would be highly endothermic (~1 eV). (b) Siegerman, H. In "Techniques of Chemistry"; Weinberg, N. L., Ed.; Wiley: New York, 1975; Vol. V, Part II.