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Photoinduced isomerization and electron transfer in the all-*trans*-retinyl cation

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Abstract

Two-laser flash photolysis was carried out on all-*trans*-retinol in acetonitrile solution at room temperature. As reported previously, the first laser pulse causes ionic photodissociation leading to the production of the all-*trans*-retinyl cation. The second pulse, tuned to the cation absorption, causes *trans* → *cis* photoisomerization, yielding a *cis*-retinyl cation. In the presence of aromatic electron donors with $E_{ox} < +1.5$ V (vs. saturated calomel electrode), excitation of the all-*trans* cation leads to electron transfer.

Keywords: Photoinduced isomerization; Electron transfer; All-*trans*-retinyl cation

1. Introduction

Recently we reported that the cation radicals of all-*trans*-1,6-diphenyl-1,3,5-hexatriene and 1,8-diphenyl-1,3,5,7-octatetraene (^{t}DPH$^{\cdot+}$ and ^{t}DPO$^{\cdot+}$, respectively) undergo *trans* → *cis* photoisomerization in acetonitrile solution at room temperature [1]. For these studies a two-laser nanosecond flash photolysis technique was used in which a UV laser pulse photoionized the polyenes and a pulse from a second laser firing a short time after the first laser photoexcited the cation radicals. In a second study it was shown that cation radical excitation in the presence of a variety of aromatic electron donors resulted in electron transfer, presumably due to an increase in the electron affinity of the cation radical in the excited state [2].

Since the lifetimes of the excited states of neutral polyenes are usually quite short, the direct time-resolved study of isomerization and other photochemical events can be problematic. However, the corresponding polyene cation radicals are much longer lived and therefore offer a better opportunity for investigation while at the same time preserving the polyene structure. As it turns out, their long lifetimes and large extinction coefficients make the cation radicals particularly well suited to the two-laser flash photolysis technique.

We originally undertook the study of these compounds because they have structures similar to retinyl polyenes, the major chromophores in rhodopsin and related pigments. We have now extended our two-laser studies to include an investigation of all-*trans*-retinol, ^{t}RETOH, a model compound that is much closer to vision chromophores than the diphenylpolyenes. Laser photolysis of ^{t}RETOH in solution at room temperature has been shown previously to cause ionic photodissociation leading to the production of the all-*trans*-retinyl cation, ^{t}RET$^+$ [3–9]. Like the polyene cation radicals, ^{t}RET$^+$ is long lived and has a large extinction coefficient in the visible region of the spectrum and is therefore also a good candidate for two-laser studies.

We report here the photochemistry of ^{t}RET$^+$ in solution at room temperature. In addition to indirect preliminary evidence for photoisomerization of ^{t}RET$^+$, electron transfer between ^{t}RET$^+$ and a variety of aromatic electron donors was also observed.

2. Experimental details

2.1. Materials

All chemicals were obtained from Aldrich unless otherwise specified. Acetonitrile (MeCN) and cyclohexane (CH) were spectrophotometric grade and were used as received. Anisole (99%), 1,2-dimethoxybenzene (99%) and 1,2,4-trimethoxybenzene (TMB) (97%) were distilled prior to use. Biphenyl (99%) was recrystallized twice from hexane. *trans*-STILBENE (96%) was recrystallized twice from ethanol. ^{t}RETOH was purified by passing a solution through a silica

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gel column followed by recrystallization from hexane. 9,10-dicyanoanthracene (Eastman Kodak) was recrystallized from hexane.

2.2. Cyclic voltammetry

Oxidation potentials of the aromatic donors were obtained in purified acetonitrile (MeCN) with an EG&G Princeton Applied Research potentiostat using a Ag/AgCl reference electrode. The electrode was calibrated using ferrocene as an internal standard (E_{ox}(ferrocene) = +0.44 V in MeCN) [10].

2.3. Laser flash photolysis

The two-laser flash photolysis system has been described in detail elsewhere [11]. Briefly, samples were irradiated with the frequency-tripled output of a Continuum "Surelite" Nd/YAG laser (355 nm; less than 50 mJ pulse^{-1}; 6 ns). In the two-laser experiments, the transient species produced by the first pulse were excited after a short (ca. 1 μs) delay by a pulse from a Candela SLL 250 flashlamp-pumped dye laser (590 nm; less than 200 mJ pulse^{-1}; 350 ns). In the two-laser experiments, the spatial overlap of the pulses from each laser was the same for each experiment. Samples (optical density was less than 0.7) were contained in a specially constructed 7 × 7 mm^2 quartz flow cell. The solution was caused to flow from a reservoir through the cell by the action of a peristaltic pump, thus ensuring that each laser pulse irradiated a fresh volume of sample. In those experiments which were run under "nitrogen-saturated" conditions, air was removed by constantly bubbling a stream of dry nitrogen through the reservoir. "Air-saturated" experiments were run without nitrogen bubbling.

3. Results and discussion

3.1. Generation and photolysis of ^{t}RET^{+}

Fig. 1 shows the transient absorption spectrum obtained 1 μs following 355 nm pulsed laser photolysis of a 1.3×10^{-3} M solution of ^{t}RETOH in nitrogen-saturated CH (round symbols) and MeCN (square symbols) at room temperature. The spectrum in CH exhibited an oxygen-sensitive major band with λ_{max} = 380–400 nm ($\tau = 7.2 \pm 0.2$ μs) which has been previously identified as the ^{t}RETOH T–T absorption [3,4,6]. In air-saturated solution the triplet was quenched, leaving a weak residual absorption (λ_{max} = 380 nm, $\tau = 4.2 \pm 0.9$ μs) which is consistent with the presence of the retinyl radical [4].

In nitrogen-saturated MeCN an intense absorption, λ_{max} = 580 nm, was observed in addition to the weaker T–T band. This absorption, which is insensitive to oxygen and was not observed in non-polar CH, has been assigned previously to the retinyl cation, ^{t}RET^{+}, formed by ionic photodissociation. The cationic nature of the transient is further indicated by quenching of the 580 nm absorption by TMB (E_{ox} = 1.12 V vs. saturated calomel electrode (SCE)) [12] presumably by electron transfer, $k_q = (5.7 \pm 1.1) \times 10^{6}$ M^{-1} s^{-1}. Quenching was also observed with diethylamine, $k_q = (4.3 \pm 0.7) \times 10^{7}$ M^{-1} s^{-1}.

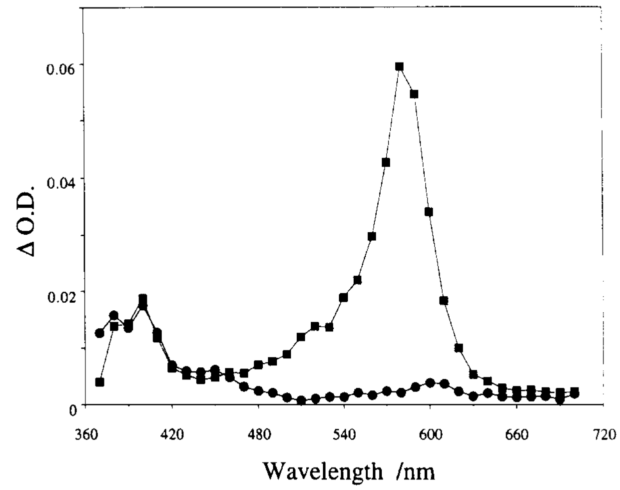


Fig. 1. Transient absorption spectra obtained 1 μs following 355 nm laser photolysis of ^{t}RETOH in nitrogen-saturated CH (●) and MeCN (■) at room temperature.

Photoexcitation of ^{t}RET^{+} in air-saturated MeCN by the pulse from a flashlamp-pumped dye laser (590 nm) resulted in bleaching, or depletion, of the 580 nm absorption band when monitored at 570 nm. (Monitoring at 580 nm was not possible owing to scattered light from the laser.) However, when the kinetic decay was monitored at 610 nm a new absorption was produced concurrently with the dye laser pulse. The decay of this new absorption was also insensitive to the presence of oxygen. Fig. 2 shows the transient absorption spectrum obtained 1.9 μs following the UV pulse and 400 ns after the dye laser pulse. For comparison, the absorption spectrum obtained 1.9 μs after the UV pulse in a one-laser experiment is also shown. Fig. 2 also shows the kinetic behavior at the two monitoring wavelengths. The depletion at 570 nm and enhanced absorption at 610 nm are clearly reflected in the red shift of the absorption and offer direct support for the existence of a second transient generated by photoexcitation of ^{t}RET^{+}.

A variety of polyene cation radicals including 1,3-cyclohexadiene [13], octatetraene and decapentaene [14,15] generated in low temperature matrices have been shown to undergo photoinduced *trans*→*cis* isomerization. In each case, production of the *cis* cation radical led to a red shift of the absorption spectrum. More recently, results from this laboratory demonstrated that photoexcitation of ^{t}DPH$^{•+}$ (produced by photoionization of ^{t}DPH) in MeCN solution with a 590 nm laser led to bleaching of the ^{t}DPH$^{•+}$ absorption at wavelengths less than 600 nm and the production of a new absorption at wavelengths greater than 600 nm, which was assigned to a *cis*-isomerized cation radical, ^{c}DPH$^{•+}$. Similar behavior was observed for ^{t}DPO [1]. Given these observa-

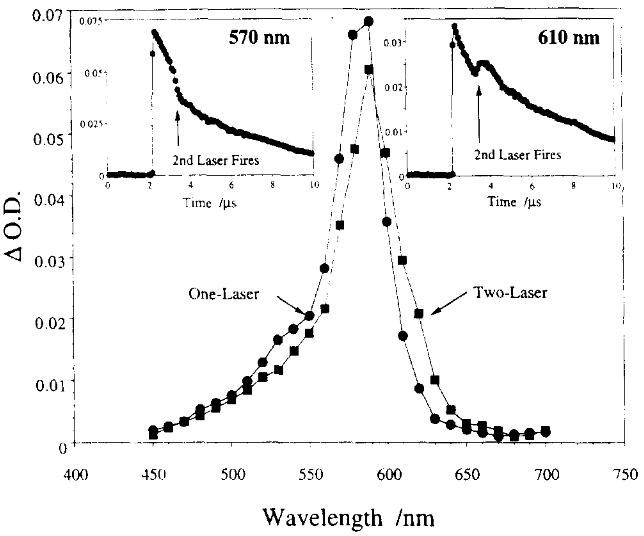


Fig. 2. Transient absorption spectra obtained following one- (355 nm; ●) and two-laser (355 + 590 nm; ■) photolysis of 'RETOH in air-saturated MeCN. In the one-laser experiment, the spectrum was obtained 1.9 µs following the 355 nm pulse. In the two-laser experiment, the spectrum was obtained 1.9 µs after the 355 nm pulse and 400 ns following the 590 nm pulse. The kinetic behaviors observed at 570 and 610 nm are also shown.

tions, we tentatively identify the new red-shifted transient as a *trans* → *cis* isomerized cation, ^{c}RET^{+}, produced by photoexcitation of 'RET^{+}. It should be pointed out that the number and positions of double bonds undergoing isomerization are not known at this point. However, the photoinduced red shift observed and the general observation that formation of *cis* isomers in polyene cation radicals leads to shifts [13–18] are strong evidence for *trans* → *cis* isomerization.

3.2. Electron transfer quenching of the 'RET^{+} excited state

Addition of 0.1 M TMB to an MeCN solution of 'RET resulted in only a slight decrease in the 'RET^{+} lifetime (as would be expected from the small quenching rate constant measured; vide supra). However, two-laser photolysis in the presence of 0.1 M TMB led to dramatically enhanced dye-laser-induced bleaching at 570 nm and bleaching rather than enhanced absorption at 610 nm. Enhanced bleaching at 570 nm indicates that, in addition to isomerization, the excited state, 'RET^{+*}, produced by the dye laser pulse is being quenched by TMB. Furthermore, since there was a lack of ^{c}RET^{+} production, this quenching must compete favorably with isomerization. (It is likely that bleaching at 610 nm occurs as a result of competitive deactivation of 'RET^{+*} rather than photolysis of ^{c}RET^{+} since most of the 590 nm dye laser pulse would be absorbed by 'RET^{+}.) Fig. 3 shows the two-laser behavior at 570 and 610 nm obtained in the presence of TMB.

Excited cations including xanthenium, thioxanthenium [7,19,20], 9-phenylxanthenyl and dibenzosuberenyl [21] are reported to be quenched by aromatic substrates at near diffusion-controlled rates. That the quenching process involved is electron transfer from the aromatic donor to the excited cation was shown by the direct detection, in some cases, of electron transfer transient products, i.e. the aromatic cation radical and the neutral radical of the corresponding cation. In other cases, notably dibenzosuberenyl, xanthenyl and 9-phenylxanthenyl, the cation fluorescence was quenched with rate constants which were correlated with the oxidation potential of the aromatic donor.

While in the case of 'RET^{+*} quenching rate constants could not be directly obtained owing to our inability to detect either the absorption or the emission of the excited state, it was possible to correlate the extent of bleaching with the oxidation potentials of a variety of electron donors. Thus, enhanced bleaching was observed in the presence of relatively high concentrations (ca. 0.1 M) of TMB, 1,2-dimethoxybenzene (E_{ox} = + 1.42 V) (oxidation potentials measured as described in Section 2) and *trans*-stilbene (+ 1.44 V) but not in the presence of anisole (+ 1.72 V) or biphenyl (+ 1.82 V). (It should be noted that none of these compounds was observed to quench ground state 'RET^{+}.) In addition to confirming electron transfer, this bleaching behavior also allows a rough estimate of the reduction potential of 'RET^{+}. The assumption that a donor is required with E_{ox} < 1.5 V and the excited state energy E_{ES} for 'RET^{+} is 47 kcal mol^{-1} (590 nm) yields E_{red} > − 0.5 V.

Direct confirmation of electron transfer could be obtained by using a quencher with a readily measured cation radical absorption. For 'DPH$^{\cdot+}$ and 'DPO$^{\cdot+}$ electron transfer from biphenyl following excitation was confirmed by detection of the biphenyl cation radical [2]. However, since it does not interact with the 'RET^{+} excited state, biphenyl is not a suitable choice of quencher. On the contrary, *trans*-stilbene does quench the excited state and has an intense cation radical absorption band, λ_{max} = 470 nm, that is well removed from the 'RETOH ground state absorption [22]. Fig. 4 shows the transient absorption spectrum for 'RETOH in the presence of 0.1 M *trans*-stilbene obtained 2.2 µs after the UV pulse and

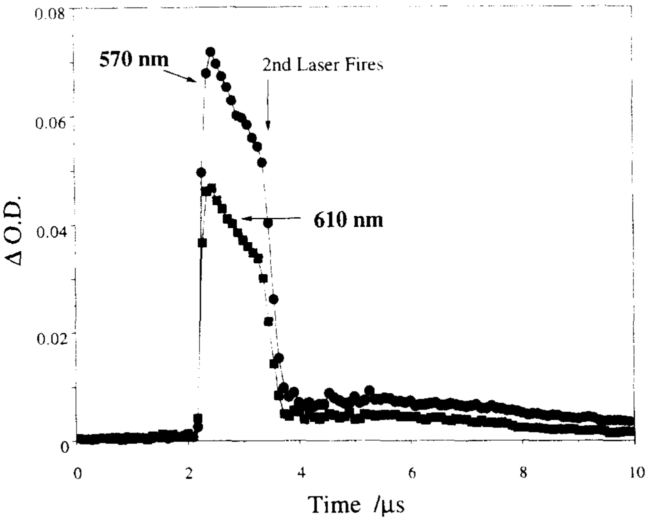


Fig. 3. Decay of transient absorption monitored at 570 nm (●) and 610 nm (■) following two-laser (355 + 590 nm) photolysis of 'RETOH in air-saturated MeCN in the presence of 0.1 M TMB.

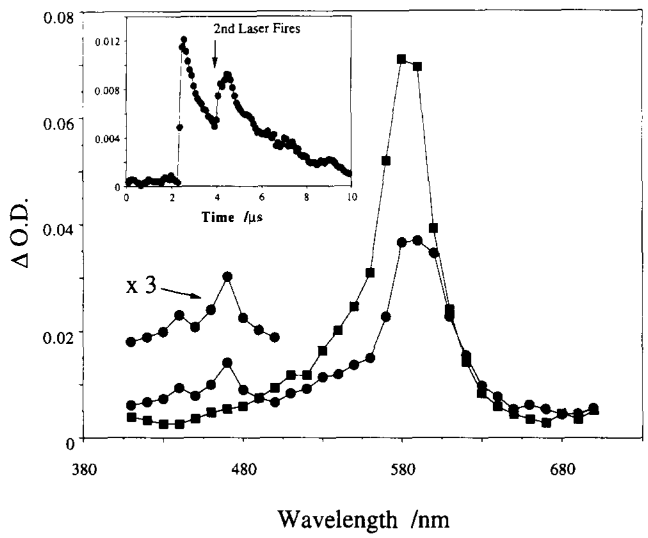


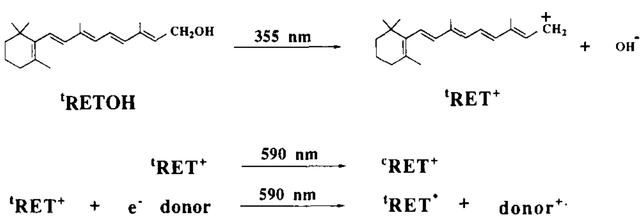
Fig. 4. Transient absorption spectrum obtained following one- (355 nm; ■) and two-laser (355 + 590 nm; ●) photolysis of ^{t}RETOH in air-saturated MeCN in the presence of 0.1 M *trans*-stilbene. Spectra were obtained 2.2 μs after the 355 nm pulse in both experiments and 400 ns following the 590 nm pulse in the two-laser experiment. The 410–500 nm region in the two-laser experiment is also shown at three times the sensitivity. The kinetic decay observed at 470 nm for the two-laser experiment is also shown.

400 ns after the dye laser pulse in a two-laser experiment. The spectrum obtained 2.2 μs after the UV pulse in a one-laser experiment with ^{t}RETOH in the presence of *trans*-stilbene is shown for comparison: Fig. 4 shows the kinetic behavior at 470 nm. While bleaching was observed at 570 and 610 nm (similar to Fig. 3), enhanced absorption was observed at 470 nm. The transient absorption spectrum clearly reveals the production of an absorption band centered at 470 nm. This band was not observed in the absence of *trans*-stilbene or when the dye laser was used as the only excitation pulse. As confirmation, the cation radical of *trans*-stilbene was generated independently by 355 nm photolysis of a nitrogen-saturated solution of *trans*-stilbene in MeCN in the presence of 9,10-dicyanoanthracene, a good electron acceptor [22]. The transient absorption spectrum obtained was in good agreement with the absorption band observed at 470 nm in the two-laser experiment described above. These results indicate that the cation radical of *trans*-stilbene is produced concurrently with ^{t}RET^{+} excitation as a result of electron transfer to ^{t}RET^{+}. The enhanced electron accepting ability of the ^{t}RET^{+} excited state compared with the ground state can be explained by an increase in the electron affinity which occurs on excitation.

4. Summary

Laser flash photolysis of a solution of ^{t}RETOH in MeCN results in ionic photodissociation producing the all-*trans*-retinyl cation, ^{t}RET^{+}, which absorbs strongly at 580 nm. Photolysis of ^{t}RET^{+} with a second laser pulse gave evidence for a second, red-shifted, transient. The absorption measured at 570 nm was bleached concurrently with the laser pulse while enhanced absorption was observed at 610 nm. Similar two-laser behavior reported previously for ^{t}DPH$^{\bullet+}$ and ^{t}DPO$^{\bullet+}$ leads to the conclusion that ^{t}RET^{+} undergoes photoinduced *trans* → *cis* isomerization.

Extensive bleaching at both 570 nm and 610 nm in the presence of a variety of electron donors indicates that the excited state ^{t}RET^{+*} undergoes electron transfer instead of isomerization (as a result of the increase in electron affinity caused by excitation). A rough estimate for the reduction potential was obtained from a qualitative comparison of the extent of bleaching for each of the donors: $E_{red} > -0.5$ V. Direct confirmation of electron transfer was obtained in a two-laser experiment using *trans*-stilbene as an electron donor. The cation radical of *trans*-stilbene was produced concurrently with the laser-induced bleaching at 570 and 610 nm. This photoinduced isomerization and electron transfer behavior is summarized in Scheme 1.



Scheme 1.

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