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Triplet State Photophysical Properties and Intersystem Crossing Quantum Efficiencies of Homologues of Retinals in Various Solvents

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Abstract: Employing the techniques of pulse radiolysis and nitrogen laser flash photolysis, several photophysical properties of the lowest triplet states of a series of polyenals related to retinals as homologues have been studied in various polar and nonpolar solvents. The series includes two polyenals not heretofore studied, an all-trans 17-carbon homologue (shorter than retinal by one double bond) and an all-trans 24-carbon homologue (longer than retinal by two double bonds). The former polyenal has high quantum efficiencies of occupation of the lowest triplet (ϕ_{T_1}) in both polar and nonpolar solvents and the latter polyenal has very low ϕ_{T_1} values in any solvent. The results are discussed in relation to the state order as a function of chain length along the series in general and as a function of the nature of the solvent in the case of certain specific members.

Introduction

Because of their importance as chromophores in rhodopsin, bacteriorhodopsin, and related pigments, the retinyl polyenes have been extensively studied regarding their intersystem crossing efficiencies and triplet state photophysical properties.[1-13] The quantum efficiencies of the lowest triplet occupation (ϕ_{T_1}) are relatively high (0.4-0.7) for retinals[2-7] at room temperature in nonpolar solvents and an excitation wavelength dependence of ϕ_{T_1} is observed[6,8,9] for these systems. On the other hand, the retinols, retinyl Schiff bases, and protonated retinyl Schiff bases are found to have relatively very low ϕ_{T_1} values.[4,10-12] This, and the fact that the intersystem crossing efficiencies of retinals are considerably decreased in polar/hydrogen-bonding solvents[4,9] as well as in the presence of a hydrogen-bonding agent (phenol),[13] has been attributed to state orders where the relative disposition of a low-lying $^1(n,\pi^*)$ state plays a significant role.[1,4,9,13]

The state ordering of retinals has long been of great interest and controversy. Three closely located states (^1B_u, $^1(n,\pi^*)$, and ^1A_g) are generally recognized to be the low-lying singlet excited states involved in the photodynamics of retinals.[14-16] Recently we have reported in detail on the absorption and emission spectral properties of a large number of polyenals and polyenones related to retinals as homologues and analogues.[17] A complementary study[18] has been performed on the triplet state properties of some of these carbonyl-containing polyenes in hexane by the methods of pulse radiolysis and laser flash spectroscopy. The present work is meant to provide a broader understanding of the photophysical dynamics of these polyene systems and includes two members not heretofore studied regarding their triplet state photophysical properties. These two members are the 17-carbon homologue with chain length shorter than that of retinal by one double bond (henceforth called C_{17} aldehyde) and the 24-carbon homologue with chain length longer than that of retinal by two double bonds (henceforth called C_{24} aldehyde). As far as intersystem

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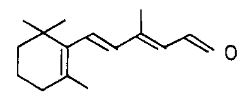
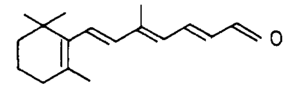
crossing efficiency is concerned, we have found that both C_{17} and C_{24} aldehyde occupy key positions in the homologous series, the former having the highest ϕ_{T_1} (among all the members), and the latter marking the transitional phase in the series where there is a large decrease in ϕ_{T_1} (relative to the shorter homologues).

In addition to the foregoing molecules, we have studied the effects of various solvents (nonpolar, polar, and hydrogen bonding) on the triplet state photophysical properties of two longer and two shorter homologues of retinal. In conjunction with other spectroscopic and photophysical data available[17] on these systems, the results are discussed in relation to possible state orders and intersystem crossing mechanisms involving the low-lying $^{1,3}(n,\pi^*)$ and $^{1,3}(\pi,\pi^*)$ states.

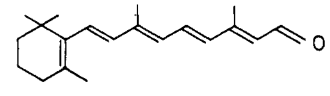
The structures of the polyenals under examination are shown in Figure 1.



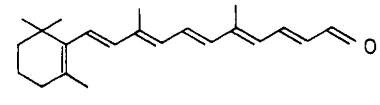
1. All-trans C_{15} aldehyde



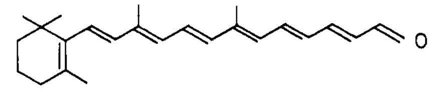
2. All-trans C_{17} aldehyde



3. All-trans retinal



4. All-trans C_{22} aldehyde



5. All-trans C_{24} aldehyde

Figure 1. Structures of the polyenals (all shown as 6-s-cis).

Experimental Section

The methods of synthesis and/or purification of the compounds are described in the previous papers.[17] Purification was accomplished using high-pressure liquid chromatography (LC) on a μ-Porasil column (Waters Associates) employing petroleum ether + 2-6% tetrahydrofuran (freshly distilled) as the mobile phase and/or by multiple recrystallization from petroleum ether. C_{24} aldehyde was found to contain an impurity even after repeated crystallization and this was apparently responsible for its triplet decay profile being marked by an initial fast growth component in the laser photolysis. This difficulty was resolved by using samples purified by LC less than 2 h before the photolysis experiments and kept under vacuum at -40 °C until the preparation of the solutions. Anthracene and biphenyl used as donors and standards were of zone-refined grade (Ultrex, J. T. Baker Chemical Co.). The solvents were of spectral grade from various commercial sources. No special procedure was used to ensure exhaustive drying of the hydrocarbon solvents. The presence of a trace of moisture, which has been shown to have a drastic effect on the fluorescence behavior of retinals[15] and related polyenals[17] at 77 K, was considered unimportant in the present studies at room temperature, because only a very insignificant ($\ll 1\%$) fraction of the polyenal molecules would be hydrogen bonded to the water under these conditions.

The pulse radiolysis and flash photolysis work was carried out at the Center for Fast Kinetics Research (CFKR) at the University of Texas, Austin. The pulse radiolysis experiments were carried out with ~4 MeV electron pulses (pulse width 30-100 ns) using a High Voltage Engineering Corp. CN Van de Graaff generator as the electron source. For flash photolysis experiments, 337-nm laser pulses (9 ns fwhm, 2-3 mJ) from a nitrogen gas laser (constructed "in-house") were used in the single-shot mode. The kinetic absorption spectrometer was a conventional one consisting of a continuously operating 450-W xenon arc lamp (monitoring source), two electromechanical shutters, quartz lenses, target cell, a Bausch and Lomb high-intensity monochromator, and a photomultiplier tube (Hamamatsu R928). Detector output waveforms were processed by a Biomation 8100 digitizer and computer combination (PDP 11T34). A Versatec 1200 A printer/plotter provided permanent records of data and kinetic fits.

For most of the experiments the solutions were deaerated by bubbling with nitrogen and transferred, under anaerobic conditions, into a 30-mL glass syringe which then was connected to a flow-through quartz target cell (~0.4-mL capacity). The syringe was mounted vertically and driven downward by a motor (controlled locally or remotely) to replenish the solution in the cell. For some of the photolysis experiments where the samples were not photochemically labile, the solution was placed in a quartz cell and deaerated as well as stirred continuously by bubbling N_2 gas through the solution above the photolyzed region. Exposure of the samples to the room light was kept to a minimum during preparation of the solutions, degassing, and photolysis/radiolysis.

The polyenal triplet states (lowest) were populated either by direct laser excitation followed by intersystem crossing (in the case of the systems having high ϕ_{T_1}'s, e.g., C_{17} aldehyde) or by energy transfer from a suitable donor triplet (biphenyl, anthracene, or C_{17} aldehyde) which was excited either by laser flash or by energy transfer from solvent triplets which were generated by pulse radiolysis (benzene or cyclohexane). Time-resolved triplet-triplet absorption spectra were thus obtained by monitoring at various wavelengths in the spectral region of interest. Triplet-triplet extinction coefficients were obtained by one of the following four methods. The first was singlet depletion[5,18] monitored near the $S_0 \rightarrow S_n$ absorption maximum of the polyenal (in the case of the systems with relatively high ϕ_{T_1}) following laser excitation. The assumption was made that the triplet-triplet absorption was negligible at the wavelength where the singlet depletion was monitored. In view of the possibility that the triplet-triplet absorption might be nonnegligible in the region of ground-state singlet absorption (as has been found by a recent flash-photolytic study on *all-trans*-retinal[7]), ϵ_{T-T} values obtained by this method were considered as the lower limits for the actual ϵ_{T-T} values. The second was triplet-triplet energy transfer[19,20] between a donor triplet (biphenyl) excited by pulse radiolysis and an acceptor (polyenal). In the present work this method was used in the case of the polyenals C_{17}-C_{24} in benzene and cyclohexane. The third was triplet-triplet energy transfer as above, except that the donor, having its $S_0 \rightarrow S_n$ absorption maximum near 337 nm and a high ϕ_{T_1} value, was excited by laser excitation. The acceptor was characterized by little $S_0 \rightarrow S_n$ absorption at 337 nm and a low ϕ_{T_1}. The triplet-triplet spectra of the donor and the acceptor were separated such that one could be monitored exclusive of the other. This method was successfully applied with C_{17} aldehyde and C_{24} aldehyde as a donor-acceptor pair. The fourth was equating the areas under the triplet-triplet absorption spectra (replotted against wavenumber) in various solvents. In the cases where the complete triplet-triplet absorption spectum was not available on the higher energy side of the absorption maximum, the complete spectra were constructed on the assumption that they were symmetrical about the maximum. This method was based on the assumption that the oscillator strength of the triplet-triplet transition involved was independent of solvent.[20,21] Thus, if the extinction coefficient in one of the solvents was known, the extinction coefficients in the other solvents could be obtained.

The details of the procedures for obtaining triplet-triplet extinction coefficients by these methods and the various corrections needed in each method are given elsewhere.[5,18]

The quantum yields of occupation of the lowest triplet state were determined by the comparative method[5,23] where an anthracene solution in cyclohexane ($\phi_{T_1} = 0.71$, ϵ_{T-T} 6.47×10^4 at 422.5 nm)[23] was used as the standard (actinometer). The solutions of the standard and the polyenal were of such concentrations that they had nearly equal optical density at 337 nm. The details of the method are given elsewhere.[23]

Table I. Triplet State Photophysical Properties of Polyenals in Various Solvents

all-trans polyenal	solvent	triplet-triplet absorption: band max, nm^a	triplet-triplet absorption: extinction coeff $M^{-1}\,cm^{-1} \times 10^{-4}$, at band max^{b,c}	triplet state decay constant, $\mu s^{-1\,d}$	$\phi_{T_1}{}^b$
C_{15}	hexane	385^e	3.85^e	10^e	0.42^e
	methanol	400	(3.4)	5.3	$\sim 0.45^j$
C_{17}	cyclohexane	410	6.3	0.16	0.66
	benzene	430	6.3 (7.1)	0.11	0.72
	acetonitrile	440	5.1 (6.1)	0.094	0.51
	methanol	440	5.1 (5.7)	0.092	0.41
C_{20} (retinal)	hexane	445^f	7.8^f	0.11^f	$0.4\text{–}0.7^g$
	benzene	460	6.7 (6.2)	0.11	0.58
	acetonitrile	470	5.9 (6.7)	0.083	0.16
	methanol	460^f	$(3.38)^f$	0.062^h	$0.08^{f,h}\text{-}0.12^f$
C_{22}	cyclohexane	470	12.1	0.14	0.54^i
	benzene	490	(11.9)	0.12	$\sim 0.038^j$
	acetonitrile	490	(11.2)	0.084	$\sim 0.095^j$
	methanol	475	(14.9)	0.097	$\sim 0.033^j$
C_{24}	cyclohexane	500	20.1^k	0.14	0.018
	methanol	510	13.6	0.12	≤ 0.01

[a] ±5 nm. [b] ±15%. [c] The figures in parentheses are the extinction coefficients obtained by assuming oscillator strength of triplet–triplet absorption band to be independent of solvents (method IV, see the text). [d] ±10%. [e] From ref 18. [f] From ref 5 and 9. [g] From ref 2–7, some in cyclohexane. [h] From ref 4. [i] This figure is slightly higher than the ϕ_{T_1} value (0.41) reported earlier[18] for C_{22} aldehyde in *n*-hexane with 265-nm laser excitation. The difference in the two values may be indicative of a slight excitation wavelength dependence on ϕ_{T_1} of this system. [j] These ϕ_{T_1} values are estimated using ϵ_{T-T} values obtained by method IV (see the text) and may have errors as high as ±30%. [k] Average from methods I–III.

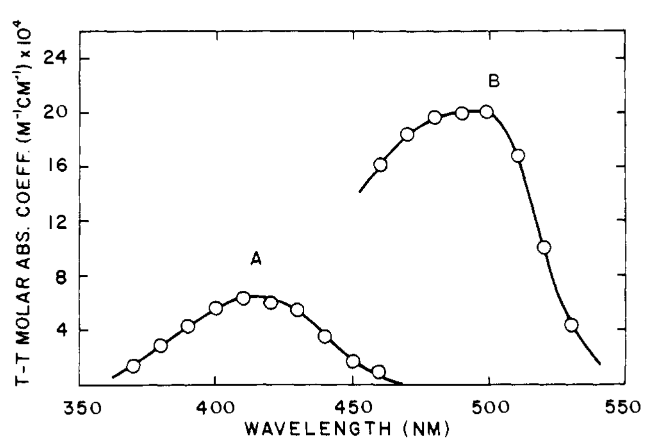


Figure 2. Triplet–triplet absorption spectra of C_{17} aldehyde (A) and C_{24} aldehyde (B) in cyclohexane at room temperature.

Results

A. Triplet–Triplet Spectra and Extinction Coefficients. The triplet–triplet absorption spectra of C_{17} aldehyde and C_{24} aldehyde in cyclohexane are shown in Figure 2. Data regarding the absorption maxima of the polyenal series in various solvents are given in Table I. It has been noted that the energy of the triplet–triplet maximum (ΔE_T) is linearly related to the singlet–singlet maximum energy (ΔE_S) in the case of many polyene systems,[18,24,25] including polyenals and carotenoids. As shown in the plot of ΔE_T vs. ΔE_S in Figure 3, the data for C_{17} and C_{24} aldehyde fit quite well into a linear relationship for the polyenals. Based on the relationship

$$\Delta E_T = k \Delta E_s + k'$$

we obtained $k = 0.68$ and $k' = 4100\ cm^{-1}$. Also it is noted that the solvent effect on $T_1 \rightarrow T_n$ absorption maxima takes place in the same direction as that on the $S_0 \rightarrow S_n$ absorption maxima, that is, there is a red shift on going from nonpolar to polar solvents (Table I).

The $T_1 \rightarrow T_n$ extinction coefficients of C_{17} and C_{24} aldehyde also fit the trend that, in ascending the polyenal series, the extinction coefficients are progressively increased (in a manner similar to that for $S_0 \rightarrow S_n$ transitions). However, the $T_1 \rightarrow T_n$ extinction coefficient of C_{24} aldehyde appears to be higher than expected from the trend. In general, a decrease in the extinction coefficient at the maximum (Table I) is observed on going from cyclohexane (or hexane) to benzene and polar solvents (acetonitrile, methanol). This is a reflection of the fact that there is a relative broadening of the spectra in the latter solvents. Such an effect has also been observed for the isomeric retinals[9] and aromatic systems.[20]

B. Triplet Lifetimes. The decay rate constants for the lowest triplet states of the polyenals, C_{15}–C_{24}, in various solvents are given in Table I. In a particular solvent, no significant change in the rate constants is observed as the polyene chain length is increased from C_{17} to C_{24}. This is contradictory to the trend observed for carotene-like polyenes where an increase in the triplet decay rate constant with an increase in the polyene chain length has been noted.[24,26] For a particular polyenal, a decrease in the rate constant is noticed on going from nonpolar solvents (hexane or cyclohexane) to polar solvents (acetonitrile or methanol).

C. Quantum Efficiency of the Lowest Triplet Occupation (ϕ_{T_1}). C_{17} aldehyde undergoes intersystem crossing very efficiently in all the solvents used in the present study (Table I). Singlet depletion studies in the region of $S_0 \rightarrow S_n$ absorption maximum show practically no permanent change in optical density in any of the solvents, indicating that photochemistry of this system is negligible under the conditions of our experiments.

C_{24} aldehyde has very low ϕ_{T_1} values in cyclohexane and methanol. When compared with shorter polyenals (C_{15}–C_{22}) which have relatively high ϕ_{T_1} values in hydrocarbon solvents, and longer polyenals [β-apo-8′-carotenal (C_{30}) and torularhodinaldehyde (C_{40})] which have very low ϕ_{T_1} values (<0.01),[18] C_{24} aldehyde appears to be the polyenal of shortest chain length where there is not the proper state order required for efficient intersystem crossing. More concerning this aspect will be presented in the Discussion section.

Like the retinals, C_{22} aldehyde has a high ϕ_{T_1} in cyclohexane. On changing the solvent from nonpolar to polar or H bonding, ϕ_{T_1} of C_{22} aldehyde is drastically reduced, Table I.

Similar behavior is also observed for retinals; however, it is interesting to note that, unlike retinal, C_{22} aldehyde has a low ϕ_{T_1} in benzene, Table I. We have also observed that in benzene or polar solvents C_{22} aldehyde undergoes photochemistry (and/or photoisomerization) to a small extent as indicated by nonnegligible permanent bleaching in the spectral region of $S_0 \rightarrow S_n$ absorption maximum. Because of lack of knowledge about the photoproduct(s), we could not estimate the quantum yield of photochemistry (and/or photoisomerization). A similar behavior was also observed for *all-trans*-retinal in acetonitrile.

There is little change in ϕ_{T_1} of C_{15} aldehyde on going from hexane to methanol. In both polar (methanol) and nonpolar (cyclohexane) solvents, laser excitation of C_{15} aldehyde also results in photochemistry/photoisomerization.

Discussion

We shall take the quantum efficiency of occupation of the lowest triplet state as a measure of the crossover yield from the singlet manifold to the triplet manifold.

A. State Order and Chain Length of Polyenal. A survey of the ϕ_{T_1} data in Table I shows that the polyenals, C_{15}–C_{22}, have high intersystem crossing efficiencies in hydrocarbon solvents. The related polyene systems, e.g., diphenyl polyenes,[27] polyene alcohols[28] including retinols,[11,12] retinyl Schiff bases, and protonated Schiff bases,[3,4] and retinoic acid ester,[29] have comparatively very low quantum yields of intersystem crossing. This fact combined with the fact that all these latter polyene systems fluoresce strongly or moderately strongly at 77 K (and in some cases at room temperature) can be attributed to a large extent to the state order whereby the lowest excited singlet state *as well as* the triplet state(s) lying closest below it are predominantly of (π,π^*) character. The low intersystem crossing efficiencies would then be a result of small spin-orbital coupling between states of the same orbital origin. $^{1,3}(n,\pi^*)$ state(s) are present in some of the foregoing molecules; however, they are located at sufficiently high energies that they are not populated and therefore not important in determining the photodynamics of the molecules. On the other hand, for C_{15} and C_{17} aldehydes and retinals, there is evidence from absorption and emission spectral studies[15,17] that a state of predominantly $^1(n,\pi^*)$ character is the lowest excited singlet state (except under certain solvent conditions). The high ϕ_{T_1} values for these systems then may be attributed to the contribution of processes of the type $^1(n,\pi^*) \rightsquigarrow {}^3(\pi,\pi^*)$ to the intersystem crossing. The lack of intersystem crossing in C_{24} aldehydes and longer polyenals is then explainable in terms of both of the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states being located above the lowest $^1(\pi,\pi^*)$ state. Under these conditions, the intersystem crossing involves a $^1(\pi,\pi^*)$ and a $^3(\pi,\pi^*)$ state and is orbitally forbidden.

C_{22} aldehyde presents an interesting situation in this model. Emission spectral studies[17] on this polyenal indicate that at room temperature a $^1(\pi,\pi^*)$ state (relatively forbidden, and hence probably of dominantly A_g^* character) is the lowest excited singlet state. In the present model, the high intersystem crossing efficiency must be the consequence of a crossing process involving a lowest $^1(\pi,\pi^*)$ state and a closely lower lying $^3(n,\pi^*)$ state.

Using the quantum yield of intersystem crossing as a relative measure of intersystem crossing rate constant (k_{isc}) in these polyenals is subject to some question. For comparison between two polyenal systems, one should use the absolute values of k_{isc} as the basis. Unfortunately, except for C_{22} aldehyde in 3-methylpentane (measured radiative lifetime, $\tau_F = 0.8$ ns)[17] no lifetime data are available for the lowest singlet state of the polyenals at room temperature. Using $\phi_{isc} = \phi_{T_1} \sim 0.5$, $\phi_F \sim 0.01$,[17] and $\tau_F = 0.8$ ns[17] for C_{22} aldehyde in hydrocarbon solvents, we obtain $\sim 10^7$ s^{-1} for the intrinsic fluorescence radiative rate constant (k_r) and $\sim 5 \times 10^8$ s^{-1} for each of k_{isc} and ($k_{ic} + k_{pc}$) where k_{ic} and k_{pc} are the rate constants for internal conversion and photochemistry (including photoisomerization, pi), respectively, from the singlet manifold. Since the fluorescence quantum yields of all the polyenals at room temperature are in the range 10^{-2}–10^{-4} (or less), any change in k_r because of a change in the nature of the fluorescing state on going from one polyenal to the next should not significantly affect the ϕ_{isc} value. Therefore, any abrupt change in the ϕ_{isc} (or ϕ_{T_1}) value, as we observe on going from C_{22} aldehyde (in cyclohexane) to C_{24} aldehyde (in cyclohexane), must be related to change(s) in one or more of the nonradiative rate constants. Of the nonradiative rate constants, k_{pc} is negligibly small and noncompeting for the all-trans polyenal systems, C_{17} to C_{24} in hydrocarbon solvents. However, k_{ic} could change from one polyenal to another because of a change in the number of vibrational modes/Franck-Condon factors and because of a decrease or increase in the extent of interaction among the closely lying singlet states resulting in a potential barrier for the radiationless process.[30,31] However, as shown by the behavior of k_{ic} of related polyenes, the polyene alcohols,[28,32] and diphenyl polyenes,[30,31,33] and the lack of dependence of triplet state decay constants on the chain length in the case of the polyenals under examination, the above-mentioned factors are not expected to cause an abrupt change in k_{ic} on going from one polyenal to the next. Thus, the ~30-fold decrease in ϕ_{T_1} on going from C_{22} aldehyde to C_{24} aldehyde in cyclohexane is to be explained primarily as a result of a pronounced decrease in k_{isc} in the latter compound. The most plausible explanation for the decrease in k_{isc} in C_{24} aldehyde is the lack of involvement of $^{1,3}(n,\pi^*)$ states in the intersystem crossing process in this molecule.

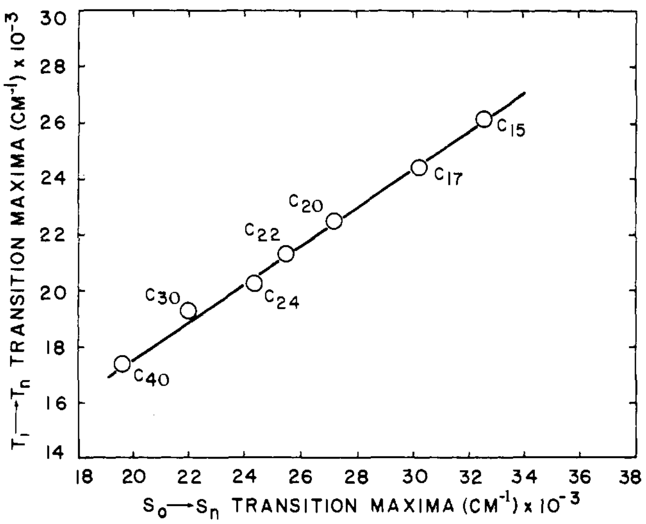
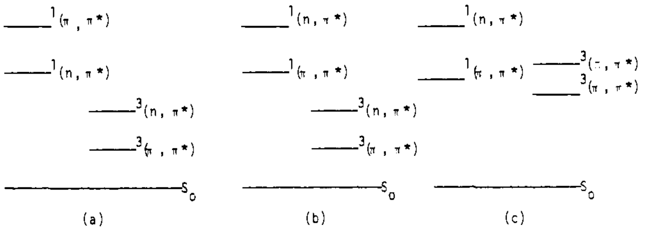


Figure 3. Plot of triplet-triplet absorption maxima (ΔE_T) against ground-state (singlet-singlet) absorption maxima (ΔE_S) for polyenals of varying chain length in hydrocarbon solvents.

It is to be noted that the values of k_{isc} and k_{ic} for C_{22} aldehyde in hydrocarbon solvents estimated above on the basis of measured fluorescence lifetime and quantum yield of lowest triplet occupation are similar in order of magnitude to the rates of nonradiative photophysical processes observed for other polyene systems, e.g., diphenyl polyenes[33] and polyene alcohols.[28,32] However, these values ($\sim 5 \times 10^8$ s^{-1}) are smaller by one to two orders of magnitude than the rates of photophysical processes (34 ps for buildup of triplet and 20 ps for decay of lowest excited singlet) reported[34] for *all-trans*-retinal in *n*-hexane. In view of the facts that $\phi_{T_1} \approx 0.5$ and $\phi_F \approx 0.0$ for *all-trans*-retinal in *n*-hexane at room temperature, k_{ic} also should be of the same magnitude as k_{isc} for this polyenal. It is difficult to see why the rate processes should abruptly increase on going from C_{22} aldehyde to *all-trans*-retinal. It is quite possible that the transients observed in the picosecond studies[34] of *all-trans*-retinal and those monitored in our fluorescence lifetime and quantum yield measurements of C_{22} aldehyde are different regarding equilibration of the initially excited states of various conformers among themselves and with the solvent.

B. State Order and Effect of Solvents. Since the relative location of the $^{1,3}(n,\pi^*)$ states appears to be crucial in the intersystem crossing processes of the polyenals, we have studied the effect of solvents (polar and nonpolar) on ϕ_{T_1} of these systems. The intersystem crossing efficiencies of C_{15} aldehyde and C_{17} aldehyde are relatively insensitive regarding the nature of solvents. While the ϕ_{T_1} of C_{15} aldehyde remains practically unchanged on going from *n*-hexane to methanol, that of C_{17} aldehyde is somewhat decreased on going from benzene and cyclohexane to acetonitrile and methanol. The solvent effect is much more pronounced in the case of retinal and C_{22} aldehyde. For retinal, ϕ_{T_1} remains practically unchanged on going from cyclohexane to benzene and is decreased by a factor of ~4–6[4,9] on going to H-bonding solvents (~threefold to acetonitrile). For C_{22} aldehyde, the solvent effect is more drastic as shown by the 5–18-fold decrease of ϕ_{T_1} on changing solvent from cyclohexane to benzene, acetonitrile, and methanol. It should be noted that the room-temperature fluorescence quantum yield (ϕ_F) of C_{22} aldehyde is also decreased significantly on changing solvents from nonpolar (3-methylpentane) to polar ones (acetonitrile or methanol).[17]

Taking, as before, the large change in ϕ_{T_1} to be the result of a change occurring primarily in k_{isc}, vide infra, we can rationalize the sensitivity of ϕ_{T_1} of retinal and C_{22} aldehyde toward the nature of solvents in terms of solvent-induced state order changes involving the location of the $^{1,3}(n,\pi^*)$ states relative to the lowest $^1(\pi,\pi^*)$ state. Three possible situations regarding relative state order concerning the $C_{15}C_{24}$ polyenals are shown below.



Situation (a) is applicable to C_{15} and C_{17} aldehyde (in all solvents) and retinals (in hydrocarbon solvents and benzene). Situation (b) is applicable to C_{22} aldehyde (in hydrocarbon solvents). Situation (c) is applicable to retinals in polar/hydrogen bonding solvents, C_{22} aldehyde (in benzene and polar/hydrogen bonding solvents), and C_{24} aldehyde (all solvents).

The state orders proposed here in some cases are necessarily somewhat tentative. The change in intersystem crossing efficiencies observed on going from one solvent to another in some cases need not necessarily be caused by solvent-induced state order reversals (as proposed here), but could be the result of solvent-induced changes in vibronic interactions among the close-lying singlet states affecting both radiative and nonradiative rate processes. The concomitant decreases of ϕ_F and ϕ_{T_1} of C_{22}-aldehyde on going from hydrocarbon solvents to polar/H-bonding solvents (at room temperature)[17] are difficult to explain in terms of a change in k_{isc} only. It is possible that k_{ic} as well as k_{pc} changes with solvents. Although we have observed a slight enhancement of photochemistry/photoisomerization of C_{22} aldehyde on going from cyclohexane to benzene and polar solvents, we have not made a quantitative evaluation of ϕ_{pc} or ϕ_{pi} occurring from the singlet manifold. However, studies[31,32] of solvent effect on fluorescence lifetimes of diphenyl polyenes have shown that k_{ic} of polyenes could be strongly solvent dependent. Thus, k_{ic} of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) decreases by a factor of 6 on going from *n*-hexane to ethanol at room temperature. The concomitant decrease of ϕ_F and ϕ_{T_1} of C_{22} aldehyde on going from a nonpolar (hydrocarbon) to a polar solvent can be explained in terms of a decrease in k_{ic} alone. Interestingly, for *all-trans*-retinal, changing the solvent from a nonpolar (*n*-hexane) to a polar (methanol) one results in a notable decrease of ϕ_{T_1} but also an enormous increase (40-fold)[7] in ϕ_F at room temperature. A similar enhancement of the ϕ_F of *all-trans*-retinal at room temperature has been observed in trifluoroethanol.[35] In this polyenal a decrease in k_{isc} alone on going from a nonpolar to a polar solvent can explain both the increase in ϕ_F and the decrease in ϕ_{T_1}. It is clear that detailed studies concerning the lifetimes and quantum yields of all the photodynamical processes occurring in various polyene systems (containing low-lying $\pi^* \leftarrow n$ transitions) and the effects of solvents and temperature upon these processes are necessary before a complete and quantitative analysis can be made.

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Mechanisms of Acid-Catalyzed Aliphatic Ketone Rearrangements and Relationships between Ketone Structure and Oxygen Function Rearrangement. Tracer Studies on 3-Methyl-2-butanone-*1*-^{14}C, 3-Methyl-2-butanone-*2*-^{14}C, 3,3-Dimethyl-2-butanone-*2*-^{14}C, and 2,4-Dimethyl-3-pentanone-*3*-^{13}C[1]

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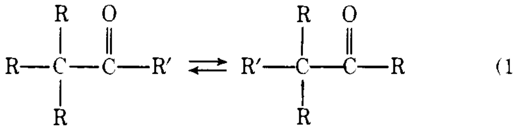
Abstract: Systematic carbon-14 and carbon-13 tracer studies and other evidence have shown that α-disubstituted ketones undergo acid-catalyzed rearrangements to isomeric ketones via a series of alkyl and oxygen function shifts in ketone conjugate acids and tertiary carbenium ions derived from them. Rearrangements via alkyl shifts only are faster than oxygen function rearrangements. Thus, the major product from the rearrangement of 2,2,4-trimethyl-3-pentanone-*3*-^{13}C (**10a**) is 3,3,4-trimethyl-2-pentanone-*2*-^{13}C (**11a**), but smaller amounts of oxygen function rearrangement product 3,3,4-trimethyl-2-pentanone-*3*-^{13}C (**11b**) are also formed; slow oxygen function rearrangement accompanies more rapid methyl scrambling in 3,3-dimethyl-2-butanone-*1*-^{14}C (**5c**) and -*2*-^{14}C (**5a**). For α-monosubstituted ketones acid-catalyzed alkyl group interchange takes place but no oxygen function rearrangement is observed, demonstrating that the reaction path involves tertiary carbenium ions and aldehyde conjugate acids, but not secondary carbenium ions. Thus, alkyl-group interchanges but no oxygen-function rearrangements were observed in the rearrangements of 3-methyl-2-butanone-*1*-^{14}C (**2c**) and -*2*-^{14}C (**2a**); the conversion of 2,4-dimethyl-3-pentanone-*3*-^{14}C (**8a**) to 3,4-dimethyl-2-pentanone-*2*-^{14}C (**9a**) takes place without the formation of 2,4-dimethyl-3-pentanone-*3*-^{14}C (**9b**). α-Unsubstituted ketones, which undergo acid-catalyzed rearrangements only with great difficulty, appear to do so with complete oxygen function rearrangement. Concerted epoxide conjugate acid formation and decomposition are suggested as the mechanism for these reactions. Two different catalyst systems, homogeneous reaction in concentrated sulfuric acid and heterogeneous reaction by passage of the ketone vapor over solid supported phosphoric acid, do not exhibit any qualitative differences in their abilities to promote the ketone rearrangements or the oxygen function rearrangements. Generalized mechanisms for the three different types of substrates are given.

Introduction

A substantial number of acid-catalyzed rearrangements of aldehydes and ketones to isomeric carbonyl compounds are reported in the literature, and the scope and mechanisms of the reactions were reviewed by Fry[3] in 1971 and Collins and Eastham[4] in 1966. Generally, these reactions involve interchange of a group attached directly to the carbonyl carbon on one side with a group attached to the α carbon on the other side, eq 1.

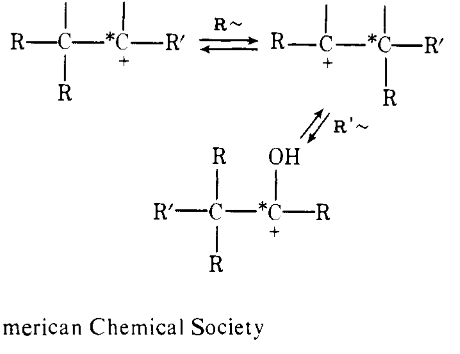


$$\mathrm{R{-}\underset{R}{\overset{R}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R'} \rightleftarrows \mathrm{R'{-}\underset{R}{\overset{R}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R} \quad (1)$$

R and R' = H, alkyl, or aryl

The simplest mechanistic path for these reactions, mechanism Ia, eq 2, involves conventional 1,2-hydrogen and/or alkyl shifts in the ketone conjugate acids or aldehyde conjugate acids and carbenium ions derived from them[5,6] (for comparisons to later mechanisms these formulations assume the use of car-

mechanism Ia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