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the intensity of the incoming (I_0) and transmitted (I) photons. Photocurrent (I_1) in a solution (~0.005 M) of $Re_2(CO)_{10}$ in dry 2,2,4-trimethylpentane was recorded with a Keithley current amplifier. For the measurements, 100–300 V were applied to the electrodes. Further details of the set-up and related considerations will be published elsewhere. Re L_{III} absorption spectra have been obtained with both transmission and conductivity techniques. Typical single-scan spectra (~5 min) are shown in Figure 1.

Figure 1a shows the L_{III} edge transmission absorption spectrum of a $Re_2(CO)_{10}$ solution. The Re L_{III} edge exhibits a sharp resonance (peak A). This, a common feature for the $L_{II,III}$ edge of transition metal compounds with unoccupied d states,[13] can be attributed to a $2p_{3/2} \rightarrow 5d$ transition. Peak B, ~20 eV above peak A, is tentatively assigned to higher energy unoccupied states of s and d character while peaks C and D can be regarded as EXAFS oscillations. It is interesting to note that although $Re_2(CO)_{10}$ is an 18-electron molecule, the fact that there exists such an intense resonance indicates the presence of partially unoccupied molecular orbitals containing Re 5d character. The primary concern of this paper, however, is the question of whether or not the conductivity measurement technique is feasible. The answer is given in Figure 1b, which plots the ratio conductivity (I_1)/photon monitor (I_0). It is very gratifying that not only the edge jump but also the accompanying structures are observed. The noise in the present measurements is attributed to the presence of considerable leakage currents. We expect that improved cells and counting techniques will alow a much better signal-to-noise ratio.

To interpret the results we return to eq 1 and note that for $\mu t \ll 1$

$$I_1/I_0 \simeq K(E)\mu t \qquad (2)$$

while for a very thick sample all of the X-rays are absorbed and

$$I_1/I_0 \simeq K(E) \qquad (3)$$

The present case is intermediate and I_1/I_0 is not directly proportional to μt. However, as expected the amplitude of peak A in the conductivity measurements is reduced relative to the edge since as the absorption increases the ratio I_1/I_0 is less sensitive to changes in μt.

Although the exact quantitative details of the I_1/I_0 spectrum cannot be revealed at present, the fact that all the absorption features are reproduced is a good indication that this technique may offer us an opportunity to study the decay of the core hole in ions (or molecule) upon deep core excitation and ionization in solution. As discussed above three processes are definitely important in conductivity measurement: first, the creation of the core hole (this is the only important process in transmission measurements) and then the decay of the core hole followed by secondary ionization of the solvent molecules by fluorescence X-ray (8561 eV for Re L_{III} edge) and L_3 MM Auger electrons. What follows are radiochemical processes in which the energetic electrons become equilibrated with the environment and when slowing down create a lot of secondary electrons, some of which finally escape the Coulombic potential of the ions to avoid ion-pair formation and recombination and are collected at the electrodes. In the case of dilute solutions the solvent molecule should play a main role because they provide most of the secondary electrons and ions that we can count as current. In essence, they serve as counting molecules analogous to gas molecules used in an ionization chamber. The fluorescence yield[12] of the Re L_{III} edge decay has been documented to be 0.2. This means that the Auger yield is 0.8 and is the dominant source for secondary ionization.

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Registry No. $Re_2(CO)_{10}$, 14285-68-8; 2,2,4-trimethylpentane, 540-84-1.

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Triplet Excitation Transfer to Carotenoids from Biradical Intermediates in Norrish Type II Photoreactions of *o*-Alkyl-Substituted Aromatic Carbonyl Compounds[1]

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Biradicals (II) produced as a result of intramolecular hydrogen abstraction (Norrish type II photoreaction) in the triplet state of *o*-alkyl-substituted aromatic carbonyl compounds (I) are describable[2-6] as the triplets of the corresponding photoenols (III) (Scheme I). While, in some cases, the biradicals are observed[3] directly by their transient absorption, a more convenient method[7] of probing these intermediates has been based on electron transfer from the ketyl site to an acceptor, notably, paraquat (1,1′-dimethyl-4,4′-bipyridinium) dication. Except for the finding[3,6] that these biradicals are oxygen quenchable, to our best knowledge, their triplet nature has not been explicitly established. In this communication we demonstrate that the biradicals (II) derived from *o*-alkyl-substituted aromatic carbonyl compounds interact with long-chain carotenoids producing the triplets of the latter. This behavior not only permits estimation of the triplet energies (E_T) of the biradicals that apparently act as donors but also provides a convenient method of probing these transient species and their triplet precursors in situations not accessible to the paraquat technique.

When a photoenolizable substrate such as *o*-methylacetophenone (OMA), *o*-methylbenzaldehyde (OMB), or 2,4,6-trimethylbenzaldehyde (TMB), each at 0.04–0.06 M, is flash photolyzed in solutions containing β-carotene at $(1-5) \times 10^{-4}$ M with nitrogen laser pulses (337.1 nm, 2–3 mJ/pulse, ~8 ns), intense transient absorptions at 500–550 nm growing on a nanosecond time scale are observed. Figure 1A shows an experimental trace obtained with OMA as the substrate in toluene. The transient absorption spectrum matches completely with that of β-carotene triplet observed with benzophenone or *p*-methoxyacetophenone as the triplet donor under similar conditions. The growth of transient absorption (Figure 1A) follows first-order kinetics, and the corresponding rate constants (k_{obsd}) show a linear dependence on β-carotene concentrations. Figure 1B shows the plots of k_{obsd} vs. [β-carotene] for OMA and TMB. The slopes of the plots, representing the bimolecular rate constants for triplet energy transfer to β-carotene, are practically the same (4.1×10^9 M^{-1} s^{-1}) for the two substrates (in toluene). On the other hand the intercepts are quite different for the two systems, giving lifetimes

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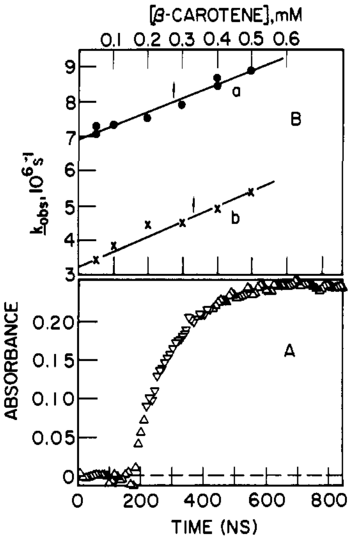
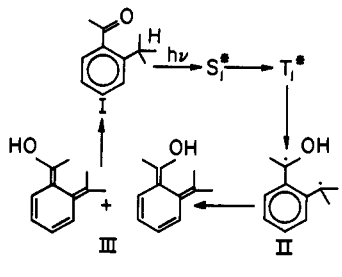


Figure 1. (A) Experimental trace for growth of transient absorbance (at 525 nm) upon 337.1-nm laser flash photolysis of a deaerated solution of 0.05 M *o*-methylacetophenone and 3.0×10^{-4} M β-carotene in toluene. (B) Plots of the observed, first-order rate constant for the growth of β-carotene triplet absorbance vs. β-carotene concentration, with *o*-methylacetophenone, (a) and 2,4,6-trimethylbenzaldehyde (b) as the substrates in toluene.

Scheme I



of 145 and 310 ns for the triplet energy donors derived from OMA and TMB, respectively.

The only possible way in which the relatively slow formation of β-carotene triplet can be explained is the energy transfer from the biradicals II formed via intramolecular hydrogen abstraction in the carbonyl triplets. Note that the lifetime of 145 ns for the triplet precursor in the case of OMA is comparable to that reported[3] for the corresponding biradical enol, 130 ns in cyclohexane. The carbonyl triplets themselves are too short-lived[7] to be identifiable as the donors. More importantly, addition of carbonyl triplet quenchers (short-lived) such as 2,5-dimethyl-2,4-hexadiene and styrene, each up to 0.3–0.4 M, does not make any difference in the observed rate constant for the growth of β-carotene triplet absorption (at a particular [β-carotene]). However, the yield of the carotenoid triplet, measured in terms of plateau absorbance, gradually decreases as the diene or styrene concentration is increased. This proves conclusively that the precursor for the carotene triplet is a product derived from the triplets of carbonyl compounds. The possibility that the observed carotene-related transient could be a reduction product formed by hydrogen or electron transfer from the ketyl sites of biradicals is ruled out by experiments in which *p*-methoxyacetophenone, an electron-rich ketone, is flash photolyzed in the presence of β-carotene and excess of triethylamine; the intense T–T absorption of β-carotene observed in the absence of triethylamine is nearly totally suppressed when the latter is added in sufficiently large concentration to quench the *p*-methoxyacetophenone triplet and thereby generate the (*p*-methoxyphenyl)hydroxymethyl radical.

Using styrene as a carbonyl triplet quencher over a wide range of concentrations (≤35 mM), we have obtained Stern–Volmer plots for the quenching of β-carotene triplet yields (at constant [β-carotene]) with OMA and TMB as substrates. With TMB, the plot is linear with a slope ($k_q^T\tau^T$) of 5.0 M^{-1}, giving a lifetime of 0.6 ns for the TMB triplet (on the basis of $k_q^T = 8.0 \times 10^9$ M^{-1} s^{-1}, measured from benzophenone triplet quenching by styrene). On the other hand, the plot in the case of OMA is bent sublinearly, suggesting the involvement of more than one carbonyl triplets as precursors of biradicals. Analysis[8] of the data in terms of contributions from syn (short-lived) and anti (long-lived) forms of OMA triplets, as proposed by Wagner,[2] gives the corresponding $k_q^T\tau^T$-values as 1.1 and 74 M^{-1}, respectively, with the former contributing to the extent of 75%. Thus, the lifetimes of the two triplets are 0.14 and 9.3 ns, respectively (in toluene). A comparison of the data concerning biradical and carbonyl triplet lifetimes obtained in toluene by the present method to those for the same systems measured in wet acetonitrile by paraquat reduction[7] shows that both biradical and triplet lifetimes in toluene are substantially shorter. Pronounced solvent effect on biradical lifetimes has been documented in previous studies.[3,9]

A few other carotenoids, namely, β-apo-8′-carotenal (a polyenal with 10 double bonds including C=O) and lycopene, are found to accept triplet energy from the biradical derived from TMB, in the same fashion as β-carotene does. The triplet energy of β-carotene has been estimated[10] within the limits of 21 and 25 kcal/mol. Since the rate constant for energy transfer to β-carotene is almost that of diffusion, the biradicals (triplet states of photoenols) must have triplet energies as high as the carotene. In view of this, the results of semiempirical calculations[3] that put the triplet photoenol of OMA ~10 kcal/mol above the ground state become subject to reevaluation.

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Registry No. OMA, 577-16-2; OMB, 529-20-4; TMB, 487-68-3; β-carotene, 7235-40-7; β-apo-8′-carotenal, 1107-26-2; lycopene, 502-65-8.

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(8) The data were fit into an equation of the form

$$\Delta OD_0^T/\Delta OD^T = 1/\sum_{i=1,2}\alpha_i(1 + k_{q,i}^T\tau_i^T[Q]), \qquad \sum_{i=1,2}\alpha_i = 1$$

where ΔOD^T represents the plateau absorbance of β-carotene triplet at a styrene concentration [Q], ΔOD_0^T represents the same in the absence of styrene, and α_i's are fractional contributions of the two triplets.

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Quintet Ground State of a Non-Kekulé Tetraradical, 3,6-Dimethyleneanthracenediyl-1,7-dioxy

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As a test[1] of theoretical predictions[2h–m] of the total electronic spin of molecules, we have synthesized 3,6-dimethyleneanthracenediyl-1,7-dioxy (**1**), a new type of π-conjugated non-Kekulé system with four unpaired electrons. This species may

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