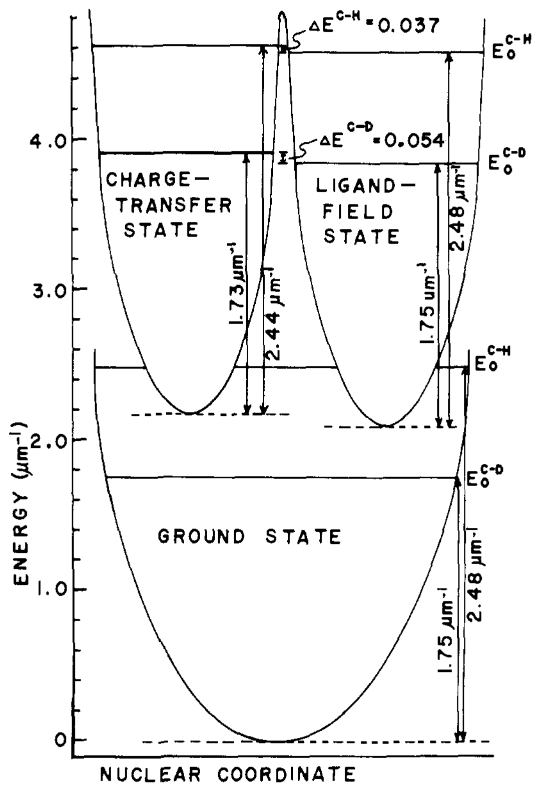

Figure 3. Interpretation of the deuterium effect on the energy gap between charge-transfer and ligand-field states. Symbols in the diagram are defined as follows: $E_0{}^{C-H}$, contribution of C-H vibrational modes to the zero-point energy; $E_0{}^{C-D}$, contribution of C-D vibrational modes to the zero-point energy; ΔE^{C-H}, difference in energy of zeroth vibrational levels of the charge-transfer and ligand-field states for the perprotonated complex; ΔE^{C-D}, difference in energy of zeroth vibrational levels of the charge-transfer and ligand-field states for the perdeuterated complex.

tions of C-H or C-D stretching modes to the zero-point energy need be considered to interpret the observed deuterium effect. Furthermore, we use the assumption (substantiated, for other cases, both experimentally[6] and theoretically[7]) that the C-H or C-D stretching motions are not coupled to each other. Thus, the vibrational contribution to the energy from the C-H or C-D bonds is roughly that of 16 independent oscillators. Using a vibrational frequency of 0.310 μm^{-1} for a C-H stretching mode and 0.219 μm^{-1} for a C-D stretching mode in the ground- and ligand-field states, the contribution of 16 C-H stretches to the zero-point energy is estimated to be 2.48 μm^{-1} while that of 16 C-D stretches is estimated to be 1.75 μm^{-1}. If the C-H stretching frequency decreases to 0.305 μm^{-1} in the charge-transfer state, then the C-D frequency should decrease to 0.216 μm^{-1}; the contributions of these modes to the zero-point energies would be 2.44 and 1.73 μm^{-1}, respectively. This would lead to an increase of 0.02 μm^{-1} in ΔE on deuteration, compared with the observed increase of 0.017 μm^{-1} (see Figure 3). Thus, a decrease of 1% in the C-H stretching frequency in the charge-transfer state is sufficient to account for the observed deuterium effect. This calculation suggests that the 0-0 band of the charge-transfer emission should lie at ~0.02 μm^{-1} higher for the deuterated species than for the protonated species compared with the difference of 0.01 ± 0.05 μm^{-1} which we observe in DMF at 77 K under high resolution.

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References and Notes

(1) R. J. Watts, T. P. White, and B. G. Griffith, *J. Am. Chem. Soc.*, **97**, 6914 (1975).
(2) R. J. Watts and D. Missimer, *J. Am. Chem. Soc.*, **100**, 5350 (1978).
(3) R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 3184 (1971).
(4) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).
(5) G. D. Hager and G. A. Crosby, *J. Am. Chem. Soc.*, **97**, 7031 (1975).
(6) See, for example, R. L. Swafford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.*, **65**, 179 (1976).
(7) W. Siebrand, *J. Chem. Phys.*, **46**, 330 (1967); **47**, 2411 (1967). C. Guttman and S. A. Rice, *ibid.*, **61**, 651 (1974). B. R. Henry and W. Siebrand, *ibid.*, **49**, 5369 (1968). B. R. Henry, *J. Phys. Chem.*, **80**, 2160 (1976). R. Wallace, *Chem. Phys.*, **11**, 189 (1975). M. L. Elert, P. R. Stannard, and W. M. Gelbart, *J. Chem. Phys.*, **67**, 5395 (1977).

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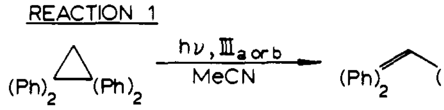
Radical Ions in Photochemistry. 9. Reactions of the 1,1,2,2-Tetraphenylcyclopropane Radical Cation[1]

Sir:

The photosensitized (electron transfer) reactions of cyclopropanes are particularly interesting because of the unusual intermediates, 1,3 radical ions, that are involved. The direct irradiation of 1,1,2,2-tetraphenylcyclopropane (I) leads to ring fragmentation to give 1,1-diphenylethylene and products derived from diphenylcarbene.[2] In contrast, we find that the sensitized (electron transfer) irradiation of I, using 1-cyanonaphthalene (IIIa) or 1,4-dicyanonaphthalene (IIIb) as electron-accepting sensitizers, gives good yields of the ring-cleaved product, 1,1,3,3-tetraphenylpropene[3] (II) (reaction 1). The



I II

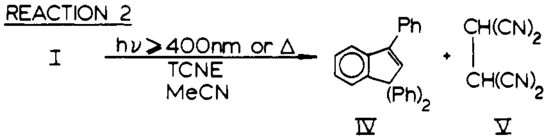
irradiations were carried out in argon-purged acetonitrile solutions under conditions such that only the sensitizer (IIIa or IIIb) absorbed light. In the time required to complete the conversion of I, little if any of the sensitizer was consumed.

This reaction can be discussed in terms of electron transfer from I to the excited sensitizer. The free-energy (ΔG) change for such a process, leading to the formation of a radical-ion pair, can be calculated from the Weller equation.[4] Reliable values were available in the literature[5] for all of the required quantities except for the oxidation potential of I; this we have determined.

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06[E(\text{D}/\text{D}^+) - E(\text{A}/\text{A}^-) - (e_0{}^2/\epsilon\alpha)] - \Delta E_{0\text{-}0}$$

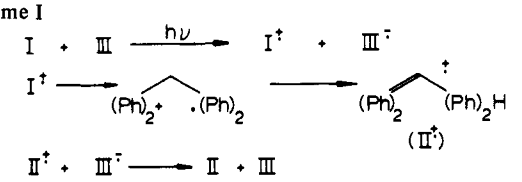
Analysis of the oxidative process (irreversible) of I by cyclic voltametry gives $E_{\text{ox}}^{1/2} = 1.22$ V (Ag/AgNO_3 (0.1 M) in acetonitrile). Since the oxidative process was irreversible, the potential derived from the voltamagram does not have thermodynamic significance. Even though it has been demonstrated that meaningful correlations can be obtained using such data,[6,7b] the value was obtained by another method. There is a known relationship between the maximum in the absorption spectra of the charge-transfer complex between tetracyanoethylene (TCNE) and various donors and the $E_{\text{ox}}^{1/2}$ of the donor.[7] The cyclopropane I forms a charge-transfer complex with TCNE which exhibits an absorption maximum at 404 nm and a shoulder at 510 nm (methylene chloride solution). The position of the maximum (540 ± 10 nm) giving rise to the long wavelength shoulder is that expected from a donor having $E_{\text{ox}}^{1/2} = 1.28 \pm 0.04$ V, in good agreement with the value obtained by cyclic voltametry. Substitution of the appropriate values into the Weller equation leads to the conclusion that the electron-transfer process involving the first excited singlets of both IIIa and IIIb as acceptors and I as donor should be favorable ($\Delta G = -8.87$ and -21.09 kcal mol^{-1}, respectively).

It seemed likely that irradiation, or thermal activation of the charge-transfer complex between I and TCNE in polar solvents, would also give products from the radical ions. We found that irradiation of the charge-transfer transition of the complex between I and TCNE in acetonitrile solution results in the formation of 1,3,3-triphenylindene[3] (IV) and dihydrotetracyanoethylene[3] (V) in essentially quantitative yield (reaction 2). These same products were also obtained upon heating solutions of I and TCNE. The rate of this thermal reaction is remarkably dependent upon solvent polarity; reaction was complete after 24 h at 125 °C when acetonitrile was the solvent, but required several days at this temperature when benzene was used.

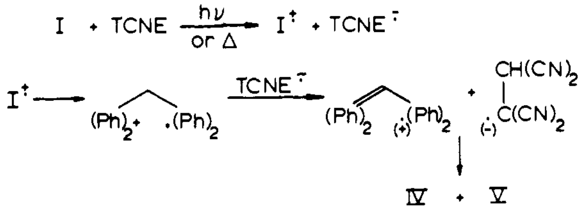


A possible mechanism for reaction 1 is shown in Scheme I. Irradiation of the sensitizer leads to the formation of the radical cation of I and the sensitizer radical anion. Cleavage of the radical cation of I, followed by proton (or hydrogen atom) migration, will give the radical cation of 1,1,3,3-tetraphenylpropene. Back electron transfer from the sensitizer radical anion completes the sequence. Although reaction 2 presumably also involves the radical cation of I, the fate of this intermediate is different from that in reaction 1. This difference may be the result of a reluctance of the TCNE radical anion to back-transfer an electron to the ring-opened radical cation. It is possible that proton or hydrogen atom transfer to the TCNE radical anion from the intermediate ring-opened radical cation leads to the propenyl radical or carbonium ion, either of which could cyclize to eventually give the indene IV (Scheme II). The mechanistic possibilities are being investigated.

Scheme I



Scheme II



Some control experiments should be mentioned. The possibility that triplet-triplet energy transfer from IIIa ($E_T = 57.4$ kcal mol^{-1}) or IIIb ($E_T = 55.5$ kcal mol^{-1}) causes reaction 1 was ruled out by showing that I is essentially stable to irradiation using 4-methoxyacetophenone ($E_T = 71.7$ kcal mol^{-1}) or 2-acetylnaphthalene ($E_T = 59.3$ kcal mol^{-1}) as photosensitizers. Heating an acetonitrile solution of II and TCNE under conditions identical with those causing reaction 2 led to no reaction. Thus, the radical cation of II is not involved in the conversion of I to IV. The propene II does, however, give the indene IV and dihydro-TCNE at much higher temperatures (~180-190 °C). The acid-catalyzed rearrangement product of I,[8] 1,1,3-triphenylindan is likewise stable to TCNE under the conditions of reaction 2.

Martini and Kampmeier have reported the reaction of 1,1-diphenylcyclopropane (VI) with TCNE in benzene at 125 °C.[9] Product formation (1,1,2,2-tetracyano-3,3-diphenylcyclopentane and 1,1,2,2-tetracyano-5,5-diphenyl-4-pentene) was rationalized in terms of the addition of TCNE to VI with ring cleavage, to give the most stable 1,5 dipole, followed by closure or proton transfer. Our results point to the importance of considering electron transfer from VI to TCNE preceding the addition and ring opening. We found no evidence for the formation of an adduct between I and TCNE.

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References and Notes

[1] Contribution No. 193 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

[2] H. Kristinsson, K. N. Mehrotra, and G. W. Griffin, *Chem. Ind.* (*London*), 1562 (1966).

[3] Positively identified by comparison of spectra (IR, NMR) with those of an authentic sample.

[4] A. Weller, *Nobel Symp. n5, Fast React. Primary Processes Chem. Kinet.*, 413 (1967).

[5] $E^{1/2}_{\mathrm{red\,IIIa}} = 2.33$ V, $E^{1/2}_{\mathrm{red\,IIIb}} = 1.67$ V, $E_{\mathrm{S(IIIa)}} = 89.4$ kcal mol^{-1}, $E_{\mathrm{S(IIIb)}} = 86.4$ kcal mol^{-1}, coulombic attraction term = 1.3 kcal mol^{-1}: D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, **98**, 5931 (1976).

[6] D. A. Labranca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972).

[7] (a) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, 1969, Chapter 3 and references cited therein. (b) $E^{1/2}_{\mathrm{ox}} = 0.095\Delta E_{\mathrm{CT}} - 0.455$ V D. R. Arnold and P. C. Wong, *Can. J. Chem.*, in press.

[8] W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).

[9] Th. Martini and J. A. Kampmeier, *Angew. Chem., Int. Ed. Engl.*, **9**, 236 (1970).

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Deuterium Nuclear Magnetic Resonance Measurements of Glycoproteins Which Have Been Specifically Deuterated Either at Selected Carbohydrate or at Lysine Residues: Determination of Motional Correlation Times

Sir:

There is currently much interest[1] in the properties and biological functions of the carbohydrate residues of glycoproteins, including those of isolated substances (such as mucin and serum glycoproteins) as well as of intact cell-surface glycoconjugates. This interest has recently prompted us,[2] and others,[3] to develop methods for attaching stable nitroxide free radicals (spin labels[4]) to selected carbohydrates and amino acid residues of a number of glycoproteins. Concerned with the possibility[5] that such studies might be compromised by the substantial steric bulk of the spin label itself, we have evaluated alternative spectroscopic probes which do not suffer from that same limitation. In the present communication we demonstrate, for the first time in the glycoprotein area, that the combination of highly selective deuteration and ^{2}H NMR studies[6] using a pulse Fourier transform instrument operating at 61.4 MHz (B_0 9.4 T) can lead to potentially valuable motional information.

Deuterium labeling at C-7 of the sialic acid residues[7] of glycoproteins was easily achieved[8] (Scheme I) by using limited

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