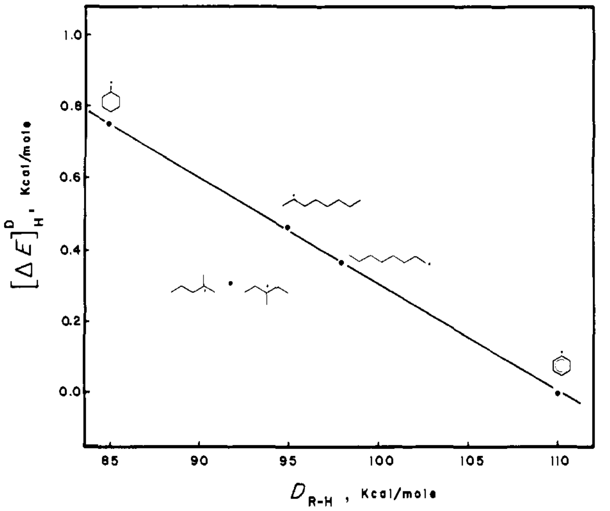

Figure 1. Plot of the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state, $[\Delta E]_H^D$, vs. the bond dissociation energy,[13] D_{R-H}, of the carbon-hydrogen bond formed as a result of the hydrogen atom transfer between R· and n-Bu_3SnH. Those values corresponding to the tertiary systems (entries 5 and 6) are plotted to show the magnitude of their deviation but are ignored in computing the best-fit line.

transition state, i.e., $[\Delta E]_H^D$, is linearly related to the bond energy, D_{R-H}, of the resulting carbon-hydrogen bond (vide infra), the best-fit equation being

$$[\Delta E]_H^D = -0.0302(D_{R-H}) + 3.329 \text{ kcal/mol}$$

This observation provides experimental justification of a fundamental tenet of kinetic isotope theory, viz., that for a linear 3-center hydrogen transfer, the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state is linearly proportional to the heat of the reaction,[8] and sustains earlier suggestions[3,9] of the likelihood of using kinetic isotope effect studies as a means of determining C-H bond energies.

Fourth, this linear correlation fails for the tertiary systems (entries 5 and 6) when, presumably because of increased steric repulsion, the activation energy, E_a, for hydrogen atom transfer is increased, resulting in a less unsymmetrical transition than would have occurred in the absence of such steric effects.

Finally, the influence of polar contributions on the nature of the transition state is revealed in entries 8-11, from which it is apparent that the difference between the difference in the zero-point energy of the reactant and the difference in the zero-point energy of the transition state increases as the electron density at the carbon radical center is enhanced. Such contributions can result in substantial differences in bond-dissociation energies: cf. $D(p\text{-}MeOC_6H_4CH_2\text{-}H)$ = 83.5 kcal/mol vs. $D(p\text{-}CF_3C_6H_4CH_2\text{-}H)$ = 88.5 kcal/mol. Thus, within an homologous series, as the transition state for H transfer becomes less symmetrical, i.e., as $[\Delta E]_H^D \rightarrow 0$, radical selectivity will be diminished. As might be expected, this behavior manifests itself in a linear free-energy relationship in the case of benzyl series ($[\Delta E]_H^D$ vs. σ), with a ρ value of -0.189 ($r = 0.996$), the magnitude of which is consistent with the intervention of a free-radical reaction. Collectively, these findings provide strong support for the frequently cited role of polar contributions in determining free-radical reactivity patterns.[14]

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(8) Westheimer, F. *Chem. Rev.* **1961**, *61*, 265.
(9) Lewis, E. S.; Butler, M. M. *Chem. Commun.* **1971**, 941.
(10) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.
(11) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.
(12) Benz, H. *Anal. Chem.* **1980**, *52*, 248.
(13) Values of D_{R-H} are those reported: Chamberlain, G. A.; Wittle, E. *Trans. Faraday Soc.* **1971**, *67*, 2077. Rodgers, A. S.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1967**, *89*, 4578.
(14) Cf.: Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 150-177. Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.

Excited-State Porphyrin-Quinone Interactions at 10-Å Separation

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To investigate the effects of distance and orientation in electron-transfer reactions[1] and to provide a model for a photosynthetic reaction center,[2] we synthesized a molecule (PQ) containing a porphyrin and a quinone held rigidly at a center-to-center distance of 10 Å.[3] The photochemical properties of PQ and its derivatives have now been characterized, using measurements of fluorescence yield and lifetime, delayed fluorescence, and flash photolysis. We report the results of these measurements, which indicate that electron transfer over a distance of 10 Å is the dominant photoreaction in the zinc porphyrin-quinone.

The photochemical properties of PQ are compared with two reference compounds where intramolecular electron-transfer reactions cannot occur. *meso*-Tetrakis[α-o-((p-anisyl)amino)phenyl]porphyrin (PA_4) has the same substituents as PQ but lacks the quinone, and reduction of PQ gives the porphyrin-hydroquinone PQH_2.

The visible absorption and fluorescence spectra of PQ and PA_4 are identical. The yield of fluorescence emission was identical for PA_4 and PQ, but the fluorescence yield in ZnPQ was only 0.4 of that of $ZnPA_4$, indicating charge transfer from the porphyrin to the quinone in ZnPQ. Further studies were carried out on the amides $ZnPQ(Ac)_4$ and $ZnPA_4(Ac)_4$, in which the aniline groups at the periphery of the porphyrin were acetylated to prevent their oxidation (Figure 1).

The fluorescence yields and lifetimes of $ZnPQ(Ac)_4$ were measured and compared with $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$. The quantum yield of fluorescence in $ZnPQ(Ac)_4$ is 0.011 (by comparison with zinc tetraphenylporphyrin, yield 0.04),[4] and is reduced by 60% in comparison with both $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$. Both of the reference compounds gave single fluorescence lifetimes of 2.2 ns, but $ZnPQ(Ac)_4$ exhibited a biphasic exponential decay of 0.5 and 1.3 ns in a 3:2 ratio (Figure 2). The lifetimes were the same at two emission wavelengths (614 and 660 nm) and two exciting wavelengths (337 and 575 nm), and were constant in the concentration range examined, 10^{-5}-10^{-6} M. The decrease in fluorescence yield and the shortened lifetimes indicate quenching, which we assign to charge transfer from the singlet state of the porphyrin to the quinone,[5] with quantum yield of 60%.

Interaction of the quinone with the porphyrin triplet state was studied by laser flash photolysis at 337 and 347 nm, where the porphyrin absorption is 55 times that of the quinone. Flash photolysis of $ZnPQH_2(Ac)_4$ and $ZnPA_4(Ac)_4$ gave transients identified as triplet states by their lifetimes ($\tau > 10^{-4}$ s), spectra,[6] and quenching by oxygen. The formation of the triplet state occurred within the response time (30 ns) of the flash photolysis instrument.[7]

The results with $ZnPQ(Ac)_4$ were quite different. In the wavelength region 390-415 nm, a new absorption was found to

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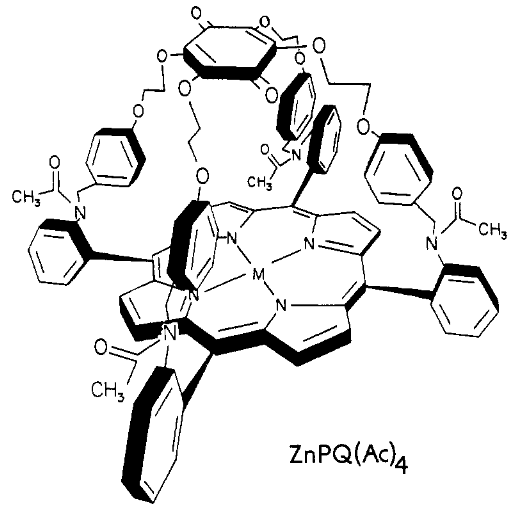
(1) Mauzerall, D.; Ballard, S. G. *Ann. Rev. Phys. Chem.* **1982**, *33*, 377-407.
(2) Clayton, R. K. In "The Photosynthetic Bacteria"; Clayton, R. K., Sistrom, W. R., Eds.; Plenum Press: New York, 1978; pp 387-396.
(3) Lindsey, J. S.; Mauzerall, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4498-4500.
(4) Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1978-1985.
(5) Livingston, R.; Ke, C. L. *J. Am. Chem. Soc.* **1950**, *72*, 909-914. Hales, B. J.; Bolton, J. R. *Ibid.* **1952**, *94*, 3314-3320. Gouterman, M.; Holton, D. *Photochem. Photobiol.* **1977**, *25*, 8591.
(6) Pekkarinen, L.; Linschitz, H. *J. Am. Chem. Soc.* **1960**, *82*, 2407-2411.
(7) Andrews, L. J.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304-2309.



ZnPQ(Ac)$_4$

Figure 1. The zinc porphyrin–quinone with the four acetylated aniline groups. The two symmetry axes of the quinone are parallel to and centered above the N–N symmetry axes of the porphyrin.

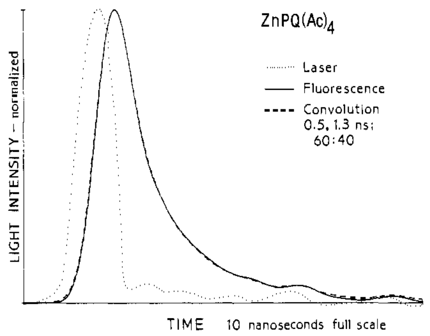


Figure 2. Fluorescence lifetime measurement of ZnPQ(Ac)$_4$ in acetonitrile at room temperature. A nitrogen laser (PRA Nitromite) was used in conjunction with a Hamamatsu Microchannel 1294 PMT, Tektronix 7912 AD digitizer, and HP 9825A computer. The laser pulse is convoluted with a chosen exponential decay to curve-fit the observed fluorescence decay.

grow in following the flash, with a rise time of 150 ns and a decay time of 1.4 μs. At other wavelengths, particularly at 470 nm where the triplet absorbs strongly, only a fast rise ($\tau < 30$ ns) and subsequent decay, again with $\tau \sim 1.4$ μs, were seen. Since this behavior occurs only with the quinone derivative, we assign this species to the P$^+$Q$^-$ charge-separated state. The porphyrin cation radical of ZnPQ(Ac)$_4$ was prepared by Fe(ClO$_4$)$_3$ oxidation in acetonitrile and its spectrum generally agreed with the observed flash transient. However, the breadth of both the porphyrin triplet and cation spectra and their apparent close similarity make it difficult to distinguish these species by their absorption.[8] Nevertheless, we may take the constant recovery time found at all wavelengths, in regions both of transient absorption and reversible bleaching, to indicate conversion of the triplet to a single intermediate with lifetime $\tau \sim 1.4$ μs, corresponding to that seen to develop at 415 nm. The rate of transient growth and absence of long-lived decay indicate that the porphyrin triplet state is the progenitor of the charge-separated state, and all of the triplets undergo electron transfer. No very short-lived flash transients were observed over the wavelength interval examined (370–650 nm), indicating that the lifetime of a possibly distinguishable singlet charge-transfer state must be less than 30 ns, as determined by the resolving time of the flash apparatus.

The short triplet lifetime was verified by measurement of delayed fluorescence. The triplet state in both ZnPQ and ZnPQ(Ac)$_4$ was quenched over 100-fold at 100 μs in comparison with that of ZnPA$_4$ and ZnPA$_4$(Ac)$_4$. Further and absolute proof of the charge-separated state was obtained by measuring the change in ionic conductivity on charge exchange with another metalloporphyrin and on protonation of the semiquinone radical anion.[9]

We estimate the quantum yield of the charge-separated state observed in the flash experiments to be about 30%, based on measurements of flash energy absorbed and cation formed. The total yield of electron transfer is much greater if the quenching of the singlet state also gives a charge-separated state. Thus the electron-transfer processes in ZnPQ(Ac)$_4$ occur in high yield. Both the singlet- and triplet-state reactions are quantitatively reversible. The rate constant of electron transfer estimated from the fluorescence lifetimes of ZnPQ(Ac)$_4$ is only 3 times less than that for electron transfer from bacteriopheophytin to ubiquinone in the bacterial reaction center. These components are separated by an estimated 9–12 Å in the reaction center.[2]

The existence of two fluorescence lifetimes in ZnPQ(Ac)$_4$ suggests that two states may be involved in the singlet charge-transfer process. An intriguing possibility is that the two states correspond to electron occupation of the two closely spaced LUMO's of the porphyrin, which differ by a 90° rotation of the porphyrin symmetry axis.[10]

We may conclude that electronic interactions in the excited state are extensive at distances much greater than the sum of the van der Waals radii of the reacting molecules. Charge-transfer processes in solution must be reconsidered with this in mind.[1,11]

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[8] The effects of ortho substitution in the porphyrin cation spectra have been noted previously. See: Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451–3459.

[9] Lindsey, J. S.; Ballard, S. G., manuscript in preparation.

[10] Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138–163.

[11] Mauzerall, D. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Part C, pp 29–52. Miller, J. R. *J. Phys. Chem.* **1975**, *79*, 1070–1078.

Heterogeneous Gas-Phase Ethylation of Methane with Ethylene over Solid Superacids. A ^{13}C Isotope Tracer Study [1]

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The acid-catalyzed alkylation of methane with the lower alkenes is known to be thermodynamically favorable (see Table I),[2] especially at lower temperatures where unfavorable entropy effects are less important. As to date the alkylation of methane with olefins has been carried out under liquid superacid-catalyzed conditions in 'closed' or pressurized flow systems.[3,4] These systems are rather complex due to the ready competing oligomerization

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[1] Electrophilic Reactions at Single Bonds. 18. For part 17, see: Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2928.

[2] Data derived from: Benson, S. W. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976. Also quoted in ref 3.

[3] Siskin, M.; Schlosberg, H.; Kocsi, W. P. in "New Strong Acid Catalyzed Alkylation and Reduction Reactions"; Albright, L. F., Goldshy, A. R., Eds.; American Chemical Society: Washington, DC, 1977; No. 55. Siskin, M. *J. Am. Chem. Soc.* **1976**, *98*, 5413.

[4] Sommer, J.; Muller, M.; Laali, K. *Nov. J. Chim.* **1982**, *1*, 3.

0002-7863/83/1505-6529$01.50/0