yields and high purity suggest that the reactions described herein will prove particularly useful in both small- and large-scale synthesis. Preliminary experiments indicate that $ClCH_2SO_2Br$[12] can be substituted for **1** in eq 1 providing added flexibility and reduced cost. Additional synthetic applications of **1** and related reagents will be described elsewhere.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the Phillips Petroleum Co. and Prof. W. Closson for generously providing us with samples of a variety of olefins used in this study.

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(12) $ClCH_2SO_2Br$ can be readily prepared in 60–70% yield by treatment of $ClCH_2SO_2Na$ (obtained by Na_2SO_3 reduction of $ClCH_2SO_2Cl$) or $ClCH_2SSCH_2Cl$ with Br_2/H_2O.

Charge-Transfer Excitation of Electron Donor–Acceptor Complexes. Direct Observation of Ion Pairs by Time-Resolved Picosecond Spectroscopy

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Received April 11, 1983

Electron donor–acceptor (EDA) complexes have been observed experimentally[3] and have been proposed as intermediates in many types of chemical reactions.[4] Among the earliest and most important examples are the 1:1 EDA complexes of various dienes and dienophiles involved in the Diels–Alder reaction.[5,6] Indeed, theoretical studies have delineated the importance of charge-transfer (CT) interactions in thermal [4 + 2] as well as [2 + 2] cycloadditions.[7] Experimental support for such formulations is found in the observation of a direct relationship between the second-order rate constant (log k) for the Diels–Alder cycloaddition and the CT transition energy ($h\nu_{CT}$) for the EDA complexes of various anthracenes with tetracyanoethylene.[8-10]

The EDA complex consisting of either 9-cyanoanthracene (CNA) or indene (IN) with tetracyanoethylene (TCNE) is ideally suited for picosecond spectroscopic studies since the CT absorption bands (Figure 1) are well separated from the absorption bands of the uncomplexed donors and TCNE. Thus we are assured that irradiation with the available 532-nm, 25-ps laser pulse (~1–2 mJ)[11] specifically populates only the CT excited state of the EDA complex.[12,13]

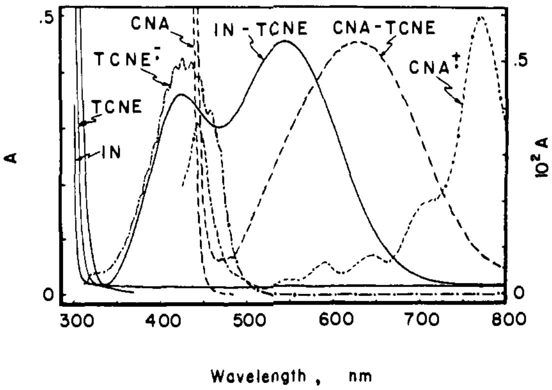

Figure 1. Electronic absorption spectra of CNA, IN, TCNE, CNA–TCNE EDA complex, IN–TCNE EDA complex, $TCNE^{-}\cdot$, and $CNA^{+}\cdot$ in CH_2Cl_2. The absorbances of IN, TCNE, and IN–TCNE were plotted relative to the left ordinate while CNA and CNA–TCNE were plotted relative to the right ordinate; concentrations of IN, CNA, and TCNE were uniformly 0.015 M. The radical ions, whose spectra are plotted in relative absorbance units, were generated electrochemically in CH_2Cl_2 containing 0.1 M TBAP at room temperature.

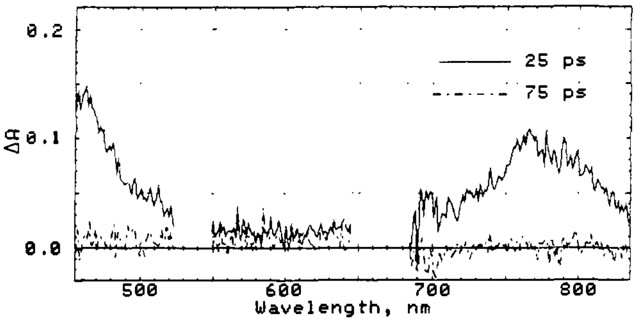

Figure 2. Difference absorption spectra measured for the CNA–TCNE (0.08 M each) EDA complex in CH_2Cl_2 at 25 and 75 ps after excitation with a 532-nm, 25-ps laser pulse.

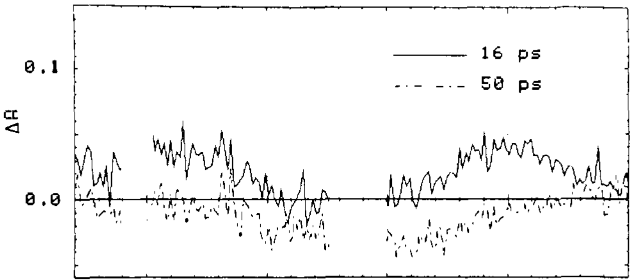

Figure 3. Difference absorption spectra measured for the IN–TCNE (0.05 M each) EDA complex in CH_2Cl_2 at 16 and 50 ps after excitation with a 532-nm, 25-ps laser pulse.

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For the CNA–TCNE EDA complex, CT excitation produced transient absorption bands near 460 and 750 nm. Both appeared within 20 ps and decayed simultaneously within ~60 ps after excitation (Figure 2). We assign the band near 750 nm to the cyanoanthracene cation (CNA$^{+}\cdot$) and that near 460 nm to a composite of the tetracyanoethylene anion (TCNE$^{-}\cdot$) and CNA$^{+}\cdot$. Such an assignment follows from the absorption spectra (Figure 1) of CNA$^{+}\cdot$ ($\epsilon_{715} \approx 7700$ M^{-1} cm^{-1})[14] and TCNE$^{-}\cdot$ ($\epsilon_{435} \approx 7100$ M^{-1} cm^{-15})[15] generated electrochemically from CNA[16] and TCNE,[17] respectively, and from consideration of a superposition of these absorptions and the negative absorption arising from depopulation of the ground-state EDA complex ($\epsilon_{615} \approx 250$ M^{-1} cm^{-1}).[18] The picosecond absorption data thus suggest the occurrence of the CT process:

$$\mathrm{CNA + TCNE} \rightleftarrows [\mathrm{CNA\,TCNE}] \overset{h\nu_{CT}}{\rightleftarrows} [\mathrm{CNA^{+}\cdot TCNE^{-}\cdot}]$$

where [CNA TCNE] is the ground-state EDA complex and [CNA$^{+}\cdot$TCNE$^{-}\cdot$] is the radical-ion pair. Such a formulation represents in this study a confirmation of Mulliken theory, in which CT band excitation of the relatively nonpolar ground state produces an ion pair. Electron transfer within the EDA complex effectively occurs with the absorption of a photon. No evidence exists from the picosecond absorption data for an excited-state intermediate of the EDA complex.

The short lifetime observed for the transient absorptions in Figure 2 indicates that the radical-ion pair is formed and resides within the ground-singlet-state manifold during its lifetime.[19] The decay time is consistent with vibrational and solvent relaxation phenomena.[20] Since the transient absorption bands return to $\Delta A = 0$ within 60 ps after excitation, the radical-ion pair must react via rapid back electron transfer to regenerate the original EDA complex.

The IN–TCNE EDA complex also was investigated. CT band excitation (Figure 1) afforded two absorption bands (Figure 3) near 460 and 600 nm, which were assigned to TCNE$^{-}\cdot$ and the indene cation (IN$^{+}\cdot$),[21] respectively, and which appeared within the time duration of the laser pulse. No transient absorptions were apparent in the region between 640 and 770 nm within 0–500 ps after excitation. As the absorption bands of TCNE$^{-}\cdot$ and IN$^{+}\cdot$ disappeared within ~60 ps, the negative absorption arising from depopulation of the ground-state EDA complex became quite apparent in the spectral region from 420 to ~650 nm.[22] We detected no product that was irreversibly formed. The original EDA complex ultimately was regenerated to its initial concentration because the difference absorption spectrum returned to $\Delta A = 0$ within 500 ps.

The rapid decay of the IN$^{+}\cdot$/TCNE$^{-}\cdot$ pair indicates that it resides in the singlet manifold, but unlike the CNA$^{+}\cdot$/TCNE$^{-}\cdot$ pair, the appearance of negative absorption is evidence for an intermediate that subsequently regenerates the original EDA complex. This species does not absorb between 420 and 770 nm and could result from a one-bond formation between IN$^{+}\cdot$ and TCNE$^{-}\cdot$ to generate a metastable biradical or zwitterion.[23] We currently are investigating the absorption spectrum at $\lambda < 420$ nm in an effort to observe and identify the intermediate spectroscopically.

Acknowledgment. J.M.M., C.A., and J.K.K. thank the National Science Foundation for financial support.

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NMR Studies of Ruthenium(II) Porphyrin π-Cation Radicals with Relevance to Horseradish Peroxidase Compound I

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Higher oxidation states of metalloporphyrins have been investigated[1] because they have structural relevances to the reaction intermediates formed in the oxidation of peroxidase and catalase by H_2O_2, compounds I and II, in the electron transfer reactions of cytochromes and in the photooxidattion of chlorophyll. As to the compound I of HRP (horseradish peroxidase), it is now described as ferryl (Fe^{IV}) porphyrin π-cation radical in which the electron spins on the iron d-orbitals and porphyrin π-orbitals are coupled to give a strongly broadened ESR spectrum[2] and, in contrast, the well-defined proton NMR spectrum[3,4] in the paramagnetically shifted region. One of the prevalent arguments on the electronic structures of compound I and related porphyrin π-cation radicals is the electron spin distribution on the porphyrin ring, especially at the meso carbon, from which the symmetry of the π-cation radical orbital (a_{1u} or a_{2u}) is readily discerned.[5] However, there have been quite limited studies on determination of spin distribution at the meso carbon in porphyrin π-cation radical.[1,5] We wish to report here the first NMR studies[6] of porphyrin π-cation radicals with $^2A_{1u}$ or $^2A_{2u}$ state and of these radicals incorporated into HRP. Resulting isotropic paramagnetic shifts for the porphyrin peripheral protons allowed us to determine

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