Table I. Selected Bond Lengths (pm) and Angles (deg) in **1**

bond length		angle	
C_2–I	275.4 (3)	C_2–I–$C_{1'}$	178.9 (2)
$C_{1'}$–I	215.9 (3)	imid–phen	1.2
C_2–N_1	136.0 (4)	N_1–C_2–N_3	104.1 (3)
C_2–N_3	136.6 (4)	C_5–N_1–C_2	111.0 (3)
C_4–C_5	132.9 (5)	C_4–N_3–C_2	110.6 (3)
N_1–C_5	138.6 (4)	N_1–C_5–C_4	107.3 (3)
N_3–C_4	139.2 (4)	N_3–C_4–C_5	107.0 (3)
N_1–$C_{1\text{-Ad}}$	149.0 (4)	C_2–N_1–$C_{1\text{-Ad}}$	124.3 (2)
N_3–$C_{1\text{-Ad}'}$	148.7 (4)	C_2–N_3–$C_{1\text{-Ad}'}$	124.9 (2)
$C_{1'}$–$C_{2'}$	137.4 (5)	$C_{2'}$–$C_{1'}$–$C_{6'}$	116.4 (3)
$C_{1'}$–$C_{6'}$	138.8 (5)	$C_{1'}$–$C_{6'}$–$C_{5'}$	122.0 (3)
$C_{2'}$–F	134.3 (4)	$C_{1'}$–$C_{2'}$–F	119.9 (3)
$C_{6'}$–F	133.7 (4)	$C_{1'}$–$C_{6'}$–F	120.0 (3)
$H_{\text{eq-Ad-6}}$–$F_{2'}$	312.1	C–H–F	171.5
$H_{\text{eq-Ad}'\text{-6}}$–$F_{6'}$	393.4	C–H–F	173.8

distortions in hypervalent (linear 3-center, 4-electron) bonds has been noted.[6-9] Given the vastly different substituents on the carbon centers, the asymmetry in **2** is not surprising. An interesting feature of the solid-state structure of **2** is the near planarity of the imidazole and phenyl rings (interplane angle = 1.2°). This arrangement places the ortho fluorines of the phenyl ring proximal to the pseudo-equatorial protons at C_6 of the adamantyl units. Dipole interactions may play a role in determining this orientation.

Whereas electrophilic carbenes typically form ylides with halogen centers which result in halonium methylides ($RX^{+}{-}^{-}CR'_2$) with a characteristically small C–X–C angle,[10-12] the structure of **2** demonstrates formation (from a nucleophilic carbene) of a "reverse ylide" in which the formal charge assignments at halogen and carbon are reversed ($RX^{-}{-}^{+}CR'_2$).[13] The resulting linear geometry is best described as carbenium λ^3-halanide (10–X–2). The linear 10–I–2 arrangement in **2** is also related to the transition state (or intermediate) for metal halogen exchange reactions.[14-17]

Acknowledgment. The excellent technical assistance of W. Marshall made the crystal structure of **2** possible.

Supplementary Material Available: A complete description of the X-ray crystallographic determination on **2** and 1,3-di-1-adamantyl-2-iodoimidazolium triiodide, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, bond angles, and structure factors (14 pages). Ordering information is given on any current masthead page.

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(5) Crystal data for 1,3-di-1-adamantyl-2-iodoimidazolium triiodide at 203 K with Mo Kα radiation: $a = 1164.4$ (7) pm, $b = 1117.9$ (7) pm, $c = 1996.0$ (10) pm, $\beta = 99.20$ (1)°, monoclinic, $P2_1/c$, $Z = 4$, 2429 unique reflections with $I > 3\sigma(I)$. The final R factors were $R = 0.037$ and $R_w = 0.037$. The largest residual electron density in the final difference Fourier map was 0.74 e/Å^3. Further details of the crystal structure are available in the supplementary material.

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Photoinduced Charge Transfer between Fullerenes (C_{60} and C_{70}) and Semiconductor ZnO Colloids

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We report here the first photoinduced charge transfer between a semiconductor (ZnO) cluster and a carbon cluster. The reduced clusters of C_{60} and C_{70} exhibit absorption characteristics that are quite different from the photogenerated triplet excited states. Transient absorption studies which describe the formation of C_{60}^- and C_{70}^- in optically excited ZnO suspensions are presented here.

It has been shown that C_{60} and C_{70} clusters can be reduced electrochemically up to five successive electron reductions.[1-4] The first reduction occurs at a potential of −0.44 V vs SCE. Efforts have been made recently to characterize the absorption spectra of reduced products by steady-state spectroelectrochemical[3] and γ-radiolysis[5] experiments. Ultraviolet photoelectron spectra of mass-selected negative carbon clusters are also reported by Yang et al.[6] Characterization of the triplet excited state has recently been made by transient absorption measurements.[7,8] Arbogast et al.[7] have reported that both the C_{60} and C_{70} are photochemically stable and do not interact with singlet oxygen. The photoelectrochemical behavior of C_{60} films has also been reported recently.[9] The photochemical reduction of these clusters has not therefore been achieved.[17]

ZnO colloidal suspensions were prepared by the method of Spanhel and Anderson[10] in which a zinc complex was hydrolyzed with stoichiometric addition of LiOH in ethanol. The pH of the colloidal ZnO suspension was around 8, which is close to the point of zero charge. The size of these particles as measured from the onset of absorption[11] was 20–25 Å in diameter. Samples of C_{60} and C_{70} were the generous gift of Dr. Ying Wang of Du Pont Co. The separation of C_{60} and C_{70} was carried out chromatographically on an alumina column with hexane–toluene (95:5) as an eluant. The absorption spectra of these samples matched well with the spectra reported in the literature.[12] Laser flash photolysis experiments were performed with 308-nm laser pulses (pulse width 10 ns, ~10 mJ/pulse) from a Lambda Physik excimer laser system. All the experiments were performed at 296 K.

The transient absorption spectra recorded following the 308-nm laser pulse excitation of ZnO colloids and C_{60} (or C_{70}) clusters in 50/50 (v/v %) benzene–ethanol are shown in Figure 1, A and B. Although the ground-state absorption at 308 nm is dominated

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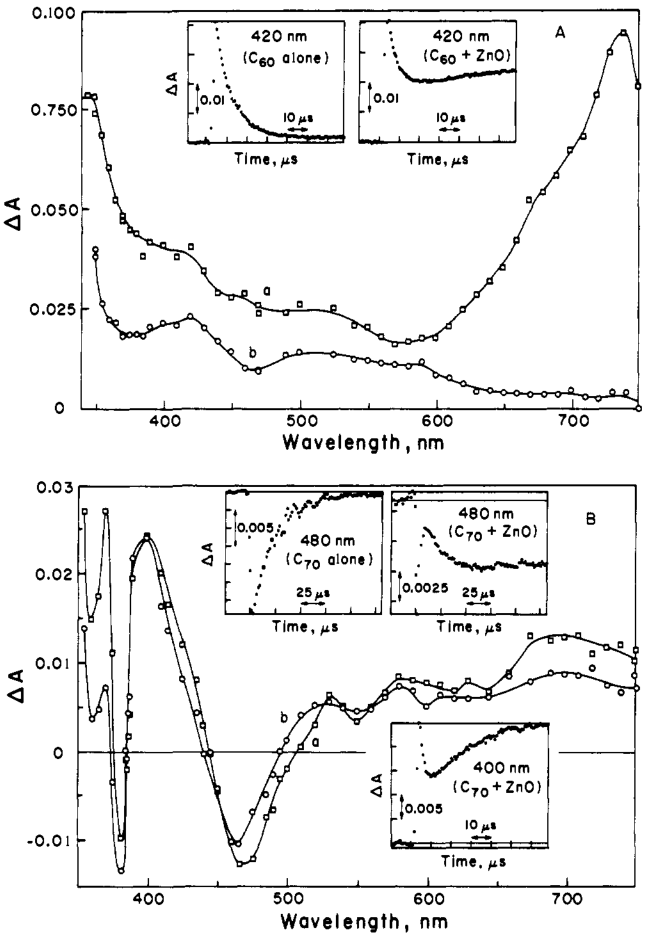

Figure 1. Time-resolved difference absorption spectra recorded following 308-nm laser pulse excitation of a 5 mM ZnO colloidal suspension containing (A) C_{60} and (B) C_{70} in 50/50 (v/v %) benzene–ethanol. The concentration of fullerenes was kept around 30 μM. The spectra were recorded at (a, □) 1 μs and (b, ○) 65 μs after the laser pulse excitation. Examples of absorption–time profiles recorded in the presence and absence of ZnO colloids are shown as inserts. The solutions were partially deaerated with Ar. Shorter lifetime of the triplet excited state facilitated resolution of the spectral features of the two transients.

by ZnO colloids, a small fraction of C_{60} (and C_{70}) also absorbs the excitation light.[13] Hence the spectrum recorded immediately after the laser pulse excitation corresponds to the triplet excited state of the carbon cluster. However, the spectra recorded at longer times (65 μs) considerably differ from the T–T absorption spectra. The absorption–decay profiles shown in the inserts clearly show the presence of a long-lived transient which survives after the initial decay of the triplet excited state. The formation of these long-lived transients was independent of the triplet decay. The slower growth in the transient absorption, which is seen only in the presence of ZnO colloids (see inserts in Figure 1, A and B), is attributed to the reduction of C_{60} and C_{70} clusters at the ZnO surface.

It has previously been shown that semiconductor colloids such as ZnO have strong reducing properties. The interfacial reduction in many such colloidal semiconductor systems proceeds via one-electron reduction.[14] In the present experiments, ultrabandgap excitation of ZnO colloids with 308-nm laser pulse results in the charge separation followed by trapping of charge carriers (reaction 1). These conduction band and trapped electrons further reduce the fullerenes (reaction 2).[15]

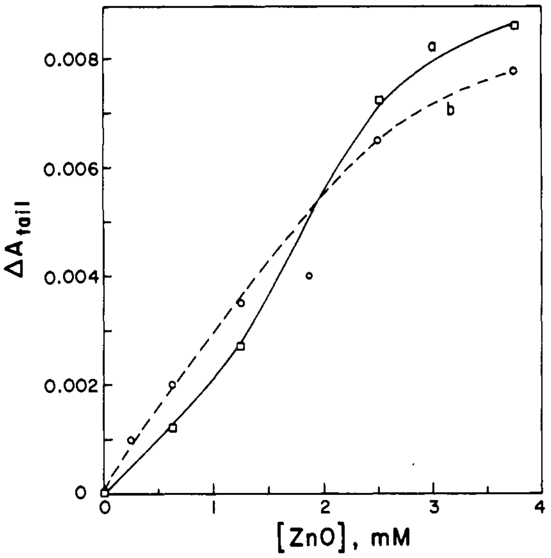

Figure 2. The dependence of yield of photochemical reduction on the concentration of ZnO colloids. (a) 60 μM C_{60} and (b) 30 μM C_{70} in 50/50 (v/v %) benzene–ethanol containing varying amounts of ZnO colloids. The difference absorbance values at 420 and 400 nm at 125 μs after the laser pulse excitation were recorded to measure the yields of C_{60}^- and C_{70}^-.

$$\mathrm{ZnO} \xrightarrow{h\nu} \mathrm{ZnO}\ (e_{CB}^- + h_{VB}^+) \rightarrow \mathrm{ZnO}\ (e_t^- + h_t^+) \qquad (1)$$

$$\mathrm{ZnO}\ (e_{CB}^- \text{ or } e_t^-) + C_{60}\ (\text{or } C_{70}) \rightarrow \mathrm{ZnO} + C_{60}^-\ (\text{or } C_{70}^-) \qquad (2)$$

Although fullerenes can be reduced up to five successive electron reductions, the primary step of charge transfer from excited ZnO into C_{60} (or C_{70}) is expected to involve only one-electron reduction. This is expected on the basis of energetics of the conduction band ($E_{CB} \approx -0.5$ V vs SCE at pH 8) and the reduction potential of C_{60} for one-electron reduction ($E^\circ = -0.36$ V vs SCE). Since further reductions of C_{60} can be carried out only at more negative potentials (<−0.83 V vs SCE),[3] multiple reduction of C_{60} is not thermodynamically feasible in the ZnO system.

A photoinduced charge transfer between two clusters is not unusual. It has been shown by us and others[16] that one can initiate a charge transfer between two semiconductor clusters (e.g., CdS and TiO_2) by exciting one of the two clusters. In the present study we have achieved electron transfer between an optically excited ZnO cluster and a carbon cluster to produce C_{60}^- and C_{70}^-.

Spectroelectrochemical studies have indicated the absorption spectrum of C_{60}^- to be featureless in the visible region,[3] but present studies indicate the presence of broad absorption bands at 400 and 525 nm. Also, C_{60}^- does not exhibit any significant absorption in the region of 700 nm where triplet C_{60} has a strong absorption band. However, a strong absorption in the far-IR has been reported recently.[5]

C_{70}^- has absorption maxima at 400, 520, 580, and 700 nm. The isosbestic points arising as a result of conversion of C_{70} to C_{70}^- were observed at 385, 440, and 495 nm. These spectral features were distinctly different than the spectral characteristics of the triplet excited state. (Note the difference in the crossover points for spectra a and b in Figure 1B at $\Delta A = 0$.) Such a difference in isosbestic point allows one to distinguish the two photochemical transients (viz., triplet excited state and anion) and selectively

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[13] The absorbances of ZnO colloidal suspension ($A_{308} > 1.0$) at the excitation wavelength was at least an order of magnitude higher than the absorbance of C_{60} and C_{70} solution ($A_{308} \sim 0.1$). The absorbance values quoted here refer to a 1-cm pathlength. The difference in transient absorbance was measured within the solution thickness of 2 mm from the place of excitation.

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probe their kinetic behavior. For example, the formation of C_{70}^- can easily be monitored at 505 nm which is an isosbestic point for the absorption of ground and triplet excited states of C_{70}. In the absence of ZnO colloids, the formation of long-lived transients was negligibly small.

Further support for a ZnO-initiated reduction of carbon cluster was gathered by varying the concentration of the ZnO colloid. The long-lived transient absorbance (Δt = 125 μs) at 420 (C_{60}^-) and 400 (C_{70}^-) nm was taken as a measure of the efficiency of charge transfer. The transient absorbance at these wavelengths increased sharply as the concentration of ZnO was varied (Figure 2). But at higher ZnO concentrations, it reached a saturation since the charge transfer at the ZnO surface was limited by the availability of carbon cluster. Steady-state photolysis of these carbon clusters in ZnO suspension also indicates changes in the absorption spectra of C_{60} and C_{70}. These spectral changes are different compared to the transient absorption spectra of C_{60}^- and C_{70}^- which were recorded immediately following the laser pulse excitation. This indicates the accumulation of fullerene-derived products during the steady-state photolysis. Further details of the charge transfer interaction between semiconductor and carbon clusters and the analysis of steady-state photolysis products are currently being studied.

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Unidentate versus Bidentate Coordination of Nitrate Ligands: Relevance to Carbonic Anhydrase Activity

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Carbonic anhydrase is a zinc-containing enzyme whose essential function is to catalyze the reversible hydration of carbon dioxide to bicarbonate.[1] Structural studies on the enzyme have identified that the zinc center is coordinated to three histidine imidazole groups and a water molecule, $[(His)_3Zn-OH_2]^{2+}$ (His = histidine).[2] The catalytic mechanism of carbonic anhydrase activity has been the subject of both intense experimental[1] and theoretical investigations,[3] and these studies have led to the proposal that a zinc bicarbonate complex $[(His)_3Zn-OCO_2H]^+$ may be a key intermediate. However, structural details of the proposed bicarbonate intermediate are not known, and theoretical treatments have explored the possibilities of both unidentate[3] and bidentate[3d,e] coordination modes. We are currently investigating model systems that are both *structural* and *chemical* mimics of the active site of carbonic anhydrase in order to provide support for the proposed mechanism of carbonic anhydrase activity, and have recently described the use of a tris(pyrazolyl)hydroborato ligand in the synthesis and structural characterization of the first monomeric 4-coordinate zinc hydroxide complex, $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}$ZnOH (3-Bu^t-5-Mepz = 3-Bu^t-5-MeC$_3$N$_2$H).[4] Here we describe structural studies on a series of nitrate complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}M(NO_3)$ (M = Co, Ni, Cu, Zn; 3-Bu^{t}pz = 3-Bu^{t}C$_3$N$_2$H$_2$)[5] which, in view of the isoelectronic relationship between bicarbonate and nitrate, are designed to provide insight as to the nature of the proposed bicarbonate intermediate of the carbonic anhydrase catalytic cycle.

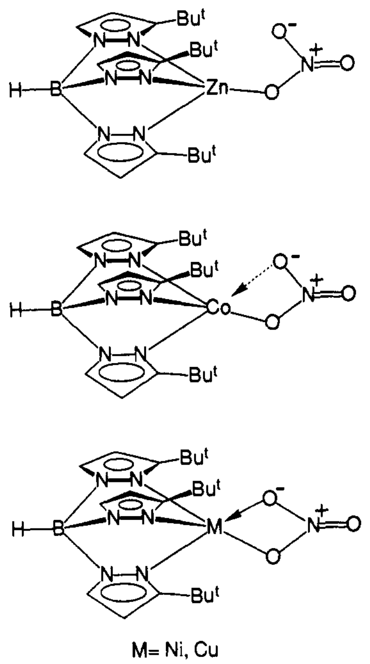

Figure 1. Molecular structures of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}M(NO_3)$ (M = Zn, Co, Ni, Cu).

Important information concerned with the structure and activity of carbonic anhydrase has been obtained by investigating metal-substituted enzymes[1,6] and also mutants.[7] Studies on metal-substituted enzymes have shown that cobalt(II) substitution reduces the activity to ca. 50% that of the zinc enzyme, whereas the corresponding Ni(II) and Cu(II) derivatives are effectively inactive.[8] The coordination mode of the bicarbonate ligand in the proposed intermediates $[(His)_3M(OCO_2H)]^+$ (M = Co, Ni, Cu, Zn) may be expected to have a profound effect upon the activity of each derivative. In order to provide evidence for the coordination mode of the bicarbonate ligand in these intermediates, we have determined the X-ray structure of a series of nitrate complexes. Since the nitrate ligand is isoelectronic with bi-

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