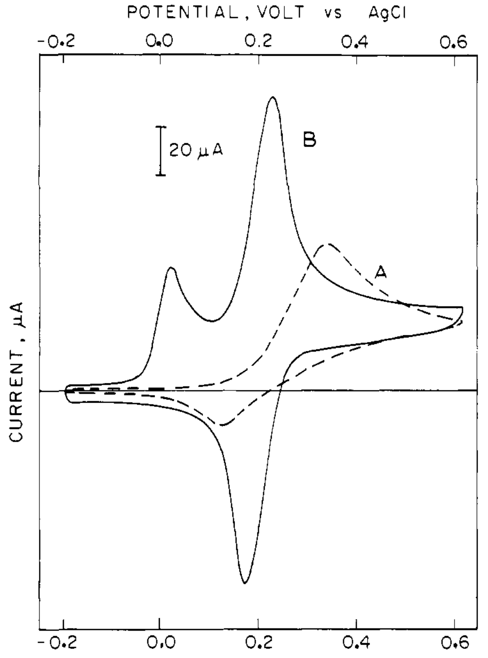

Figure 2. Cyclic voltammograms for oxidation of a mixture containing 1.0 mM catechol and 1.0 mM ascorbic acid in phosphate buffer at pH 7.0 without (---) and with (—) alumina dispersed on carbon surface: scan rate 0.1 V/s; geometric area of glassy carbon electrode, 0.071 cm^2.

The electrical charge, Q, was evaluated as a function of scan rate for differing concentrations of solution catechol to study the adsorption and to verify the catalysis. The anodic and cathodic charges (Q_a and Q_c) were plotted as a function of the inverse of the square root of the scan rate for a glassy carbon electrode with and without alumina. The "clean" electrode exhibited the usual current dependence characteristic of the electrolysis of a diffusing species with the extrapolated intercept on the charge axis at zero (background corrected).[6] On the other hand, the intercept for the alumina-dispersed electrode is nonzero. This intercept value of Q is assumed to correspond to the saturation coverage of catechol on alumina as evidenced by the common intercept for all three concentrations. In addition, the close correspondence of the slopes for Q_a and Q_c for the glassy carbon electrodes with and without alumina indicates that the diffusing catechol is indeed being electrolyzed in the potential range where the adsorbed catechol is being electrolyzed. The saturation coverage of catechol adsorbed on the surface depended on the amount of alumina dispersed. The extent of catalysis was also dependent on the amount adsorbed. At low alumina coverages, high concentrations of solution catechol, and high scan rates, the uncatalyzed wave due to electrolysis on the bare carbon becomes evident and is superimposed on the wings of the adsorbed/catalyzed wave.

An interesting bioanalytical problem is the in vivo identification and quantitation of various catechols such as dopamine and epinepherine in the presence of ascorbic acid in the neural system.[3,4] The irreversible oxidation of these substances at most electrodes produces ill-defined i–E waves without any clear separation between individual components. For example, trace A in Figure 2 is a typical i–E wave at a bare glassy carbon electrode in a solution containing 1.0 mM catechol and 1.0 mM ascorbic acid in 0.1 M phosphate buffer at pH 7.0. The irreversible ascorbic acid wave merges with the catechol wave. Trace B is the repeat of the same experiment using an α-alumina-modified glassy carbon electrode. The i–E wave for ascorbic acid with a peak potential of +0.025 V is well separated from that of catechol (E_{pa} = +0.23V). The ascorbic acid wave also is catalyzed by adsorption on alumina and appears at a potential of ca. 200 mV less than that of the uncatalyzed wave on bare carbon. We have also been able to easily distinguish three separate waves for the oxidation of a mixture containing 1,2-dihydroxybenzene, 1,4-dihydroxybenzene, and ascorbic acid at pH 7.0 at the alumina-modified electrode. The applicability of this electrode for the catalysis of other oxidizable compounds and for the quantitative analysis of mixtures is currently under study.

Although alumina itself is a nonconductor, the adsorbed species are apparently electroactive, similar to the case of catechols that have been "anchored" to graphitic surfaces via large aromatic side chains[7] or incorporated into polymeric matrices.[8,9] Electrocatalysis using immobilized redox mediators[10] such as the catechols can be understood in terms of an *ec* catalytic regeneration mechanism where the mediator acts as an effective "bridge" for electron transfer from the electrode to the isolation species.[11] In the case of alumina, it appears that any oxidative process involving the loss of a proton in the electron-transfer process can be catalyzed. Tentatively, we believe that the alumina is "base" catalyzing the oxidation. The variation in acid–base properties of alumina in effecting chromatographic separations is well-known, and correlation of these properties with their applicability to electrochemical adsorption/catalysis is in progress.[12]

Registry No. Al_2O_3, 1344-28-1; carbon, 7440-44-0; 1,4-hydroquinone, 123-31-9; ascorbic acid, 50-81-7; catechol, 120-80-9.

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[6] Differentiation of the charge due to strong adsorption from diffusing species appears valid since the nonzero intercept is the same for three different concentrations. Verification of results by chronocoulometry is in progress and will be reported separately.

[7] Jaegfeldt, H.; Johansson, G.; Kuwana, T. *J. Am. Chem. Soc.*, in press.

[8] Ueda, C.; Tse, D. C.; Kuwana, T. *Anal. Chem.* **1982**, *54*, 850–856.

[9] Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728.

[10] (a) Tse, D. C.; Kuwana, T. *Anal. Chem.* **1978**, *50*, 1315. (b) Snell, K. D.; Keenan, A. G. *Chem. Soc. Rev.* **1979**, 259. (c) Roullier, L.; Laviron, E. *J. Electroanal. Chem.* **1982**, *134*, 181–186. (d) Murray, R. W. *Philos. Trans. R. Soc. London.* **1981**, *A302*, 253–265 and reference therein.

[11] (a) Andrieux, C. P.; Blocman, C.; Duman-Bouchiat, J. M.; M'Halla, F.; Saveant, J. M.; *J. Electroanal. Chem.* **1980**, *113*, 19–40. (b) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Saveant, J. M. *J. Electroanal. Chem.* **1981**, *123*, 171–187 and references therein. (c) DiMarco, D. M.; Forshey, P. A.; Kuwana, T. *ACS Symp. Ser.*, in press.

[12] Contributions of R. J. H. Chan and D. Karweik to this work are hereby acknowledged.

Molecular Structure and Charge Transfer Excitation of Electron Donor–Acceptor Complexes. Ion Pairs from Arenes and Mercury(II)

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We report the isolation and crystal structure of an unusual electron donor–acceptor (EDA) complex, in which the irradiation of the charge-transfer (CT) absorption band induces electron transfer and ion-pair formation. Although numerous types of donor–acceptor complexes are known, the direct relationship between the structure (established by X-ray crystallography) and the CT excitation (performed in solution) has been difficult to achieve.[1,2] For this study, we chose the intermolecular interaction of aromatic compounds with mercuric complexes since new charge-transfer bands are observed immediately upon mixing.[3]

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[1] For reviews, see: (a) Kosower, E. M. *Prog. Phys. Org. Chem.* **1965**, *3*, 81. (b) Colter, A. K.; Dack, M. R. J. "Molecular Complexes"; Foster, R., Ed.; Crane, Russak: New York, 1973; Vol. 1, pp 301–362; Vol. 2, pp 1–61. (c) Andrews, L. J.; Keefer, R. M. "Molecular Complexes in Organic Chemistry"; Holden-Day: San Francisco, CA, 1964.

[2] (a) Mataga, N.; Kubota, T. "Molecular Interactions and Electronic Spectra"; Marcel Dekker: New York, 1970. (b) Mataga, N.; Ottolenghi, M. *Mol. Assoc.* **1979**, *2*, 1–78. (c) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312.

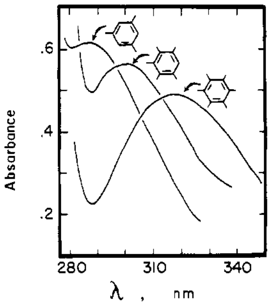

Figure 1. Charge-transfer spectra of 1:1 EDA complexes. Hexamethylbenzene (0.0025 M), pentamethylbenzene (0.0025 M), and mesitylene (0.005 M) were each mixed with equimolar amounts of $Hg(O_2CCF_3)_2$ in CH_2Cl_2 at -40 °C.

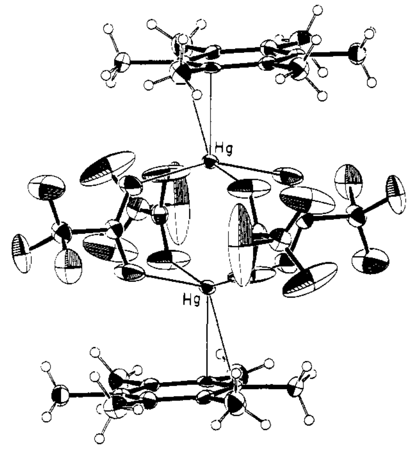

Figure 2. ORTEP drawing of the 1:1 EDA complex of hexamethylbenzene and mercuric trifluoroacetate as the dimeric species. Anisotropic thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were located by difference synthesis and portrayed at 0.5 Å^2.

In accord with theoretical expectations,[4] the absorption bands gradually shift to progressively lower energies with the decrease in the ionization potential of the aromatic donor—the trend for the EDA complexes of mercuric trifluoroacetate (HgT_2) with a series of polymethylbenzenes being hexamethylbenzene (λ_{max} 315 nm, I_D 7.85 eV), pentamethylbenzene (300 nm, 7.92 eV), 1,2,4,5-tetramethylbenzene (295 nm, 8.05 eV), and 1,3,5-trimethylbenzene (288 nm, 8.40 eV).[5]

The hexamethylbenzene (HMB) complex is unique for two reasons. First, the charge-transfer band is shown in Figure 1 to be well separated from the absorption bands of either the HMB donor or the HgT_2 acceptor. Thus we could specifically excite only the CT component of the ground state of the complex [HMB,HgT_2] by direct irradiation through narrow band-pass interference filters.[6] Second, we successfully isolated the 1:1 EDA complex of HMB and HgT_2 as pale yellow single crystals from trifluoroacetic acid under carefully controlled conditions. The isolation of the crystalline EDA complex thus enabled us to relate the molecular structure directly to the charge-transfer excitation.

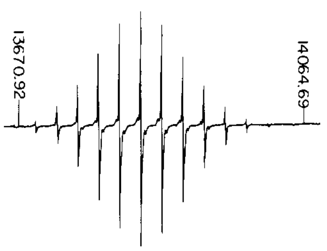

Figure 3. ESR spectrum obtained from the irradiation of the CT absorption band of the 1:1 EDA complex of HMB and HgT_2 in trifluoroacetic acid solution at 25 °C. The proton NMR field markers are in kHz.

The molecular structure shown in Figure 2 represents the first example of an arene–Hg(II) EDA complex that has been definitively characterized by X-ray crystallography.[7] The η^2 bonding of mercury to the aromatic ring consists of two unusually long Hg–C distances, 2.56 and 2.58 Å, expected for weak π interactions in such complexes.[8] Importantly, the comparison of the absorption spectrum of the crystalline complex with that measured in trifluoroacetic acid indicates the integrity of the CT transition, both in the solid state and in solution.[9] Furthermore, the ^1H and ^{13}C NMR spectra of the crystalline complex measured by magic angle spinning accords with those obtained in solution.[10]

Direct irradiation of the CT band of the 1:1 complex readily afforded an intense, well-resolved ESR spectrum of the HMB cation radical shown in Figure 3.[11] The cation-radical formed

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(3) (a) Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *Dokl. Akad. Nauk, SSSR* **1971**, *197*, 101. (b) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 648. (c) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116.

(4) See: Foster, R. "Organic Charge Transfer Complexes"; Academic Press: New York, 1969.

(5) (a) The intensity of the CT absorbances of various arene–HgT_2 complexes in CH_2Cl_2 increases with the addition of CF_3CO_2H, accompanied by a slight blue-shift of the bands.[3c] (b) For details of these changes, see: Lau, W. Ph.D Thesis, Indiana University, Bloomington, IN. (c) Note that the trends in $h\nu_{CT}$ are the same as those for the corresponding arene complexes with a variety of electrophiles and acceptors listed in ref 3c.

(6) The spectral isolation of the CT band was carried out with interference filters transmitting at 320 and 340 nm, each with half bandwidths of less than 10 nm [Melles Griot Co., F1U 023 and F1U 025, respectively].

(7) (a) The 1:1 EDA complex crystallizes in the space group $P\bar{1}$ with cell dimensions at -165 °C of $a = 12.338$ (0) Å, $b = 9.984$ (0) Å, $c = 8.900$ (0) Å, $\alpha = 70.86$ (6)°, $\beta = 107.10$ (5)°, $\gamma = 116.29$ (6)°, $D_{cald} = 2.139$ for $Z = 1$. Final residuals were $R_F = 0.045$ and $R_{wF} = 0.034$. (b) For spectroscopic evidence pertaining to arene–Hg(II) complexes based on ^1H and ^{13}C NMR shifts, see: Olah, G. A.; Yu, S. H.; Parker, D. G. *J. Org. Chem.* **1976**, *41*, 1983. Damude, L. C.; Dean, P. A. W. *J. Organomet. Chem.* **1979**, *181*, 1. (c) For the structures of the somewhat related arene–silver(I) complexes, see: Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337. Smith, H. G.; Rundle, R. E. *Ibid.* **1958**, *80*, 5075. Griffith, E. A. H.; Amma, E. L. *Ibid.* **1971**, *93*, 3167 and related papers. (d) For a summary of arene complexes, see ref 3c and Herbstein, F. H. In "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1971; Vol. 4, p 166 ff.

(8) The length of σ bonds between mercury and carbon are typically 2.1–2.2 Å. Compare: Kamenar, B.; Penavic, M. *Inorg. Chim. Acta* **1972**, *6*, 191. For some examples of π-bond lengths, see: Canty, A. J.; Chaichit, N.; Gatehouse, B. M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 786. Lampe, P. A.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 27.

(9) (a) The reflectance spectrum of crystalline [HMB HgT_2] which was ground in the form of a fine powder showed a broad CT band centered at about 330 nm on a Cary 14 spectrometer with use of a Model 1411 diffuse reflectance accessory. (b) Similarly, the spectrum of the crystalline complex in a mineral oil mull taken in a transmission mode showed the CT absorption with λ_{max} ~320 nm but with a slightly broader envelope. (c) For other examples of charge transfer in the solid state, see: Soos, Z. G.; Klein, D. J. *Mol. Assoc.* **1975**, *1*, 2.

(10) (a) Typically, the ^{13}C chemical shifts for a solution consisting of a 1:1 mixture of HMB and HgT_2 are δ 133.0 and 16.6 for the aromatic and methyl carbons, respectively, in CH_2Cl_2, and δ 140.1 and 18.0 in CF_3CO_2H. The corresponding values for the crystalline 1:1 EDA complex are δ 135.8 and 17.5. For free HMB, the values are δ 131.7 and 16.5 (or δ 134.7 and 16.8) in CH_2Cl_2 (or CF_3CO_2H), and δ 132.3 and 17.4 in the crystalline solid. Comparison of the ^{199}Hg chemical shifts in solution[5b] with those in the solid are in progress. Low-temperature magic angle spinning studies of the crystalline complex are also in progress (with C. A. Fyfe and P. A. W. Dean), since there is evidence for facile rotation of arene rings in crystalline complexes (see: Fyfe, C. A.; Harold-Smith, D.; Ripmeester, J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2269 for leading references). (b) For a similar comparison of arene–$Hg(SbF_6)_2$ complexes, see: Damude, L. C.; Dean, P. A. W.; Sefcik, M. D.; Schaefer, J. *J. Organomet. Chem.* **1982**, *226*, 105. (c) For previous evidence of a 1:1 complex of HMB and HgT_2, see Damude and Dean in ref 7b.

(11) (a) The spectrum ($a_H = 6.5$ G, $\langle g \rangle = 2.0024$) is identical with that derived by an independent procedure. See: Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 5061. (b) The ESR spectrum of an additional minor species was observed when the irradiation was carried out at -40 °C in the presence of excess HMB. Since the computer simulated spectrum is consistent with splitting from 36 equivalent protons ($a_H = 3.1$ G, $\langle g \rangle = 2.0023$), the spectrum is tentatively assigned to a 1:1 complex, e.g., [$HMB,HMB^{+\cdot}$]. Compare: Edlund, O.; Kinell, P.-O.; Lund, A.; Shimizu, A. *J. Chem. Phys.* **1967**, *46*, 3679. Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2582.

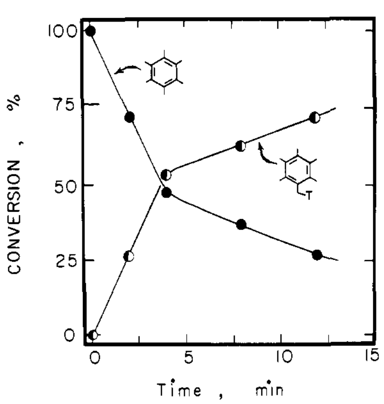
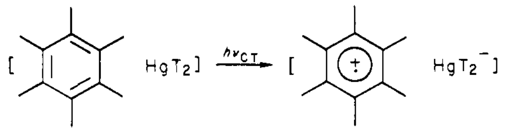


Figure 4. The quantitative conversion of hexamethylbenzene (HMB) to the benzylic ester ($Me_5C_6CH_2O_2CCF_3$) upon the irradiation of the CT band of the 1:1 EDA complex derived from 1.00 × 10^{-2} M HMB and 1.00 × 10^{-2} M $Hg(O_2CCF_3)_2$ in trifluoroacetic acid at 25 °C.

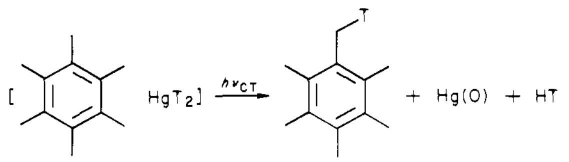
under these conditions is a transient intermediate since it disappeared rapidly upon shuttering the light. The photochemical excitation of the HMB complex to form the cation radical is a direct consequence of the Mulliken theory of charge transfer,[12,13] i.e.



(1)

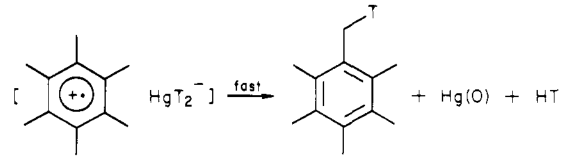
As such, we directed our attention to the chemical fate of the ion pair in eq 1.

Product isolation indicated that HMB was converted to the corresponding benzylic ester in eq 2 upon the irradiation of the



(2)

CT band of an equimolar mixture of HMB and HgT_2 in trifluoroacetic acid. The periodic, quantitative monitoring of the photochemical process in Figure 4 showed that HMB afforded the benzylic ester with the 1:1 stoichiometry in eq 2 with high quantum yields.[14] [It is important to note that no thermal reaction occurs upon heating the same mixture at 80 °C for more than 24 h.] The formation of benzylic ester in quantitative yields provides strong support that the HMB cation radical observed in Figure 3 is the prime intermediate since it has been generated previously by a variety of independent electrochemical and chemical oxidative methods, and it is known to afford the same benzylic ester in excellent yields.[15] Accordingly, the collapse of the ion pair following the CT excitation in eq 1 represents an economical route to this benzylic ester,[16] i.e.



(3)

Such a process may proceed via a prior proton loss from $HMB^{+\cdot}$ to afford a benzylic radical which is then readily oxidized to the ester in a rapid followup step.[15]

The transformation of HMB to the benzylic ester in eq 2 represents an overall two-electron oxidation, in which HgT_2 is concomitantly reduced to a globule of metallic mercury.[17] These results thus establish the connection between the molecular structure of an EDA complex, its CT excitation, and the formation of ion pairs.[18]

Acknowledgment. We thank the National Science Foundation for financial support, Dr. James S. Frye of the NSF Regional Instrumentation Facility (Colorado State University) for kindly measuring the NMR spectra of the crystalline samples with the magic angle spinning technique, and Dr. Philip A. W. Dean for helpful discussion.

Registry No. $HMBHgT_2$, 82871-36-1; $Me_5C_6CH_2O_2CCF_3$, 35843-80-2.

Supplementary Material Available: Tables of interatomic distances and angles, fractional coordinates, and isotropic thermal parameters for $[C_6Me_6Hg(O_2CCF_3)_2]_2$ (4 pages). Ordering information is given on any current masthead page.

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(12) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811; *J. Phys. Chem.* **1952**, *56*, 801. (b) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley: New York, 1969. (c) For the experimental verification of Mulliken theory, see ref 2b and Nagakura, S. "Excited States"; Lim, E. C., Ed.; Academic Press: New York, 1975; Vol. 2, p 334.

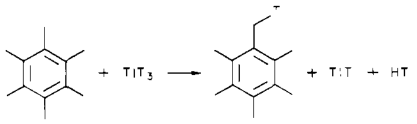
(13) Attempts to observe the mercury(I) counteranion by its expected ^{199}Hg splitting have been unsuccessful so far. From the reports of mercury(I) radicals trapped in solid matrices [see: Booth, R. J.; Starkic, H. C.; Symons, M. C. R. *J. Chem. Soc.* (*A*) **1971**, 3198. Symons, M. C. R.; Yandell, J. K. *Ibid.* 760], we surmise that such species may be unobservable under experimental conditions.

(14) Quantum yields for product (ester) formation and HMB disappearance were slightly dependent on the solvent, being 1 in CH_2Cl_2 and 2 in trifluoroacetic acid (±15%) by irradiation through either the 320- or the 340-nm filter with a 300-W xenon lamp (Eimac).

(15) (a) Svanholm, U.; Parker, V. D. *Tetrahedron Lett.* **1972**, 471. (b) Dessau, R. M.; Shih, S.; Heiba, E. I. *J. Am. Chem. Soc.* **1970**, *92*, 412. (c) Wagner, P. J.; Lam, H. M. H. *Ibid.* **1980**, *102*, 4167. (d) For useful reviews of chemical and electrochemical methods for the oxidative transformations of methylarenes to benzylic esters by successive one-electron transfer, see: Littler, J. S.; Nonhebel, D. C. *Int. Rev. Sci. Org. Chem., Ser. 2* **1975**, *10*, 211–275. Chambers, J. Q. *Ibid.* **1975**, *10*, 317–355.

(16) Although our inability to observe the ESR spectrum of mercury(I) counteranion in eq 1 precludes a proof of ion-pair collapse (as in eq 3), there is little doubt that the ester is directly derived from the $HMB^{+\cdot}$ intermediates.[15]

(17) (a) In this regard, the photochemical oxidative substitution in eq 2 is analogous to a corresponding *thermal* reaction that occurs spontaneously at room temperature when HMB and thallium(III) trifluoroacetate are mixed in trifluoroacetic acid. (K. S. Chen, unpublished results.)



Evidence for arene cation radicals as intermediates in aromatic oxidations with TlT_3 is given in ref 11a and by Taylor, E. C.; et al. *J. Am. Chem. Soc.* **1980**, *102*, 6504; **1981**, *103*, 6856. (b) For other photochemical studies of CT complexes, see the review: Davidson, R. S. *Mol. Assoc.* **1975**, *1*, 216.

(18) This study also relates the CT spectroscopy to a chemical process,[1] which we believe to be relevant to other aromatic compounds.[19] Indeed the close relationship of the absorption spectrum of the HMB complex to the spectra of the other arenes in Figure 1 suggests that analogous ion pairs are formed during the charge-transfer excitations.[20] Unfortunately the very rapid thermal reactions leading to aromatic mercuration of these arenes have not, as yet, allowed us to quantitatively interrelate them with the CT excitation.[21] We hope that the further development of instrumentation for time-resolved experiments will enable us to examine this important problem.

(19) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240.

(20) For example, the ESR spectrum of the cation radical of pentamethylbenzene can also be readily observed if the photoirradiation is carried out at temperatures below −40 °C to slow down the thermal reaction.

(21) (a) Note that the rapid rates of electrophilic mercuration of pentamethylbenzene and the other less methylated benzenes arise from the facile loss of a ring proton, in contrast to that of HMB, which would require the less favorable loss of a methyl cation. However, the CT excitations are fundamentally the same for these arenes. (b) For the interrelation of the CT excited states of arene EDA complexes and the activated complexes for electrophilic aromatic substitution, see ref 19.