

The solution was dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatography of the crude residue on silica gel (230-400 mesh, 10% ethyl acetate in hexane) afforded 14.7 mg (57%) of the desired ketone **53** as a white solid: mp 131-133 °C; IR λ_{\max} (CHCl₃) 5.75 μm ; ¹H NMR (CDCl₃) δ 0.11 (s, 6), 0.93 (s, 9), 1.17-1.73 (m, 1), 2.07-2.43 (m, 1), 2.51 (s, 3), 3.14 (d, $J = 18$ Hz, 1), 3.17 (m, 1), 3.43 (s, 3), 3.66 (d, $J = 18$ Hz, 1), 4.03 (m, 1), 4.33 (s, 2), 5.34 (br d, $J = 10.5$ Hz, 1), 5.91 (s, 2), 6.26 (br d, $J = 10.5$ Hz, 1), 6.91 (s, 1), 7.09 (s, 1). Mass spectrum, m/e calcd for C₂₄H₃₅NO₅Si: 445.2285 (P). Found: 445.2256.

Further elution with 30% ethyl acetate in hexane gave 9.5 mg (33%) of the acetate of **52** as a side product: IR λ_{\max} (CHCl₃) 5.72 μm ; ¹H NMR (CDCl₃) δ 0.14 (s, 6), 0.94 (s, 9), 1.4-1.7 (m, 1), 1.71 (s, 3), 2.0-2.6 (m, 2), 2.43 (s, 3), 3.11 (m, 1), 3.35 (s, 3), 3.60 (m, 1), 3.88 (m, 1), 4.65 (s, 2), 5.14 (t, $J = 7$ Hz, 1), 5.75-6.05 (m, 2), 5.91 (s, 2), 6.86 (s, 1), 7.00 (s, 1); mass spectrum, m/e 489 (P).

dl-Tazettine (4). The ketone **53** (14.0 mg, 0.0314 mmol) was dissolved in 2 mL of dry tetrahydrofuran. A solution of tetra-*n*-butylammonium fluoride (85 μL , 0.5 M, 0.0425 mmol) was added, and the mixture was allowed to stir at room temperature for 20 min. The solvent was evaporated in vacuo, and the residue that remained was chromatographed on silica gel (230-400 mesh, 3% methanol in chloroform) to afford 10.1 mg (97%) of *dl*-tazettine (**4**): mp 175-176 °C (acetone); IR λ_{\max} (CHCl₃) 2.97, 3.00 μm ; ¹H NMR (CDCl₃, 600 MHz) δ 1.63 (ddd, $J = 2.2, 10.1, 13.1$ Hz, 1), 2.23 (ddd, $J = 4.8, 5.2, 13.5$ Hz, 1), 2.40 (s, 3), 2.68 (d, $J = 10.5$ Hz, 1), 2.87 (m, 1), 3.31 (d, $J = 10.5$ Hz, 1), 3.47 (s, 3), 4.13 (br dd, $J = 5.2, 10.1$ Hz, 1), 4.64 (d, $J = 14.4$ Hz, 1), 4.96 (d, $J = 14.4$ Hz, 1), 5.61 (br d, $J = 10.1$ Hz, 1), 5.90 (s, 2), 6.14 (br dd, $J = 10.1$ Hz, 1), 6.50 (s, 1), 6.85 (s, 1). Mass spectrum, m/e calcd for C₁₈H₂₁NO₅: 331.1420. Found: 331.1408.

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Registry No. (\pm)-**1**, 83379-58-2; (\pm)-**4**, 28405-99-4; (\pm)-**5**, 74120-60-8; (*E*)-**8**, 54125-02-9; (\pm)-**11**, 74120-50-6; **12**, 4676-39-5; (\pm)-**13**, 83379-59-3; (\pm)-**14**, 83379-60-6; **15**, 77627-83-9; (\pm)-**16**, 83379-61-7; **17**, 83379-64-0; **18**, 83379-62-8; (\pm)-**19**, 83379-63-9; **22**, 74120-41-5; **23**, 83379-54-8; **23** silyl enol ether, 83379-56-0; **24**, 83379-55-9; (*E*)-**26**, 74120-46-0; (*Z*)-**26**, 74120-47-1; (\pm)-**37** (isomer 1), 74120-48-2; (\pm)-**37** (isomer 2), 74120-49-3; (\pm)-**38** α , 74120-59-5; (\pm)-**38** β , 74120-51-7; (\pm)-**42**, 74120-57-3; (\pm)-**43**, 74120-58-4; (\pm)-**44**, 74120-52-8; (\pm)-**45**, 74120-54-0; (\pm)-**46**, 74120-53-9; (\pm)-**49**, 74165-12-1; (\pm)-**51**, 74165-11-0; (\pm)-**52**, 74120-55-1; (\pm)-**52** acetate, 83379-57-1; (\pm)-**53**, 74120-56-2; thiophenol, 108-98-5; *N,N*-dimethylformamide dimethyl acetal, 4637-24-5; methylamine, 74-89-5; trimethyl orthoformate, 149-73-5.

Supplementary Material Available: Experimental procedures for the preparation of model compounds **13**, **15**, **16**, **17**, **18**, **19**, and **20** and infrared and NMR (600 MHz) spectra of authentic and synthetic tazettine (7 pages). Ordering information is given on any current masthead page.

Transition-State Barrier for Electrophilic Reactions. Solvation of Charge-Transfer Ion Pairs as the Unifying Factor in Alkene Addition and Aromatic Substitution with Bromine

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Abstract: Alkenes and arenes are known to form 1:1 electron donor-acceptor complexes with molecular bromine. The disappearance of the charge-transfer (CT) absorption bands for these alkene and aromatic complexes coincides with the kinetics of electrophilic addition and electrophilic aromatic substitution, respectively. The rate constants ($\log k_B$) for both classes of electrophilic brominations follow linear but separate correlations with the CT transition energies ($h\nu_{CT}$). However, a single free energy relationship in eq 29 obtains for both alkene addition and aromatic substitution when the solvation energies of alkene and aromatic cations are specifically included. Solvation energies (ΔG^{\ddagger}) for these transient cations are evaluated from the gas-phase ionization potentials of the alkene and aromatic donors together with their rates of oxidation in solution by a prescribed series of outer-sphere iron(III) oxidants. The theoretical basis of eq 29 is shown to derive directly from Mulliken theory, in which the CT transition $h\nu_{CT}$ relates to the vertical excitation of the donor-acceptor complex to the ion-pair state, i.e., $[\text{DBr}_2] \rightarrow [\text{D}^+\text{Br}_2^-]^*$, where D represents the alkene and aromatic donors. Inclusion of the solvation term ΔG^{\ddagger} with $h\nu_{CT}$ corresponds to the formation of the solvated ion pair $[\text{D}^+\text{Br}_2^-]_s$. The single, remarkable correlation in Figure 8 indicates that the activation process is equivalent to the formation of solvated ion pairs in both classes of electrophilic brominations. The CT formulation thus unifies the activation processes for electrophilic additions to alkenes and electrophilic aromatic substitution into a single concept readily amenable to physical interpretation. Its significance to the more conventional linear free energy relationships based on the Taft σ^* and Brown σ^+ correlations for alkenes and arenes, respectively, is delineated.

The definition of an *electrophilic reaction* forms an important mechanistic basis of organic chemistry, especially as it refers to olefin additions and aromatic substitutions.^{1,2} In particular,

molecular bromine has served as an ideal electrophile for mechanistic studies owing to its facile reactions with both olefins and aromatic compounds.^{3,4} Since these reactions occur at measurable

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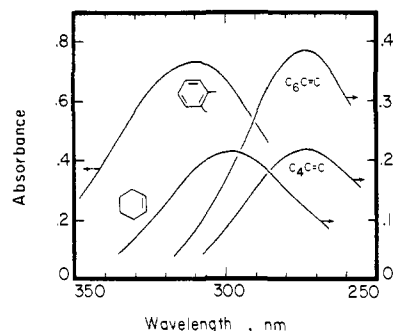
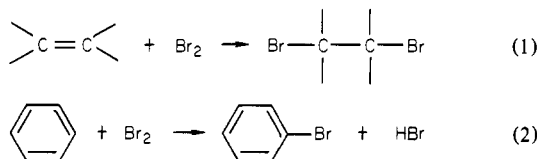


Figure 1. Typical charge-transfer spectra of the EDA complexes of alkene and aromatic donors with bromine in carbon tetrachloride solution.

rates in a wide variety of solvents, extensive kinetic studies have been carried out on electrophilic brominations; i.e.,^{5,6}



The relative rates of various electrophilic additions and substitutions have been successfully correlated with the donor properties of substituted alkenes and arenes such as those based on the Taft σ^* constants^{5,7} and the Brown σ^+ constants,^{6,8} respectively. Indeed these linear free energy relationships provide considerable understanding of the influence of molecular structure on electrophilic reactivity. As successful as these empirical correlations have been for alkenes and arenes *separately* however, no general mechanistic formulation has been brought forth to unify the concepts of electrophilic reactivity.⁹ Thus no quantitative insight has been deduced to relate alkene donors and arene donors with features of commonality sufficient to explain their significant differences in reactivity toward various electrophiles. Furthermore, no quantitative accounting of solvent effects in electrophilic addition and substitution is extant.

In order to develop a unified view of electrophilic processes, our principal goal here is to generate a direct, quantitative rela-

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Table I. Charge-Transfer Spectral Data of Bromine Complexes with Alkenes and Arenes

no.	alkene	$h\nu_{CT}$, ^a eV
1	H ₂ C=CH ₂	5.14
2	H ₂ C=CHMe	4.64
3	H ₂ C=CHEt	4.61
4	<i>n</i> -PrCH=CH ₂	4.56 (4.61)
5	H ₂ C=CMe ₂	4.3 ^b
6	H ₂ C=CMe(Et)	4.2 ^b
7	(<i>Z</i>)-MeCH=CHMe	4.25
8	(<i>E</i>)-MeCH=CHEt	4.24
9	(<i>E</i>)-MeCH=CH(<i>t</i> -Bu)	4.04
10	<i>t</i> -BuCH=CH ₂	4.51
11	Me ₂ C=CMe(Et)	3.6 ^b
12	Me ₂ C=CMe ₂	3.61 (3.61)
13	Me ₂ C=CMe(<i>n</i> -Pr)	3.5 ^b
14	Me ₂ C=CMe(<i>n</i> -Bu)	3.5 ^b
15	cyclohexene	4.16 (4.21)
no.	arene	$h\nu_{CT}$, ^c eV
16	C ₆ H ₆	4.32 (4.49)
17	MeC ₆ H ₅	4.15 (4.30)
18	EtC ₆ H ₅	4.15 (4.30)
19	<i>i</i> -PrC ₆ H ₅	4.13 (4.29)
20	MeOC ₆ H ₅	3.73
21	<i>o</i> -Me ₂ C ₆ H ₄	4.00 (4.17)
22	<i>m</i> -Me ₂ C ₆ H ₄	3.97
23	<i>p</i> -Me ₂ C ₆ H ₄	4.13 (4.27)
24	1,3,5-Me ₃ C ₆ H ₃	3.79
25	Me ₆ C ₆	3.36

^a Values in parentheses in carbon tetrachloride, others in Freon-113 (from ref 15). ^b Evaluated from the correlation between $h\nu_{CT}$ and I_D in Figure 2. ^c Values in parentheses in trifluoroacetic acid, others in carbon tetrachloride.

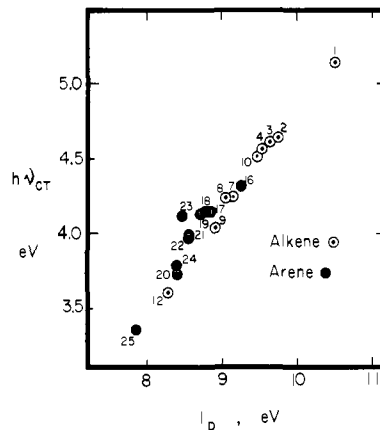


Figure 2. Relationship between the charge-transfer transition energies ($h\nu_{CT}$) of bromine complexes and the ionization potentials of alkene (○) and arenes (●) identified by the numbers in Table I.

tionship between the rates of electrophilic addition to alkenes and electrophilic substitution of arenes with bromine, including solvent effects. We approach this mechanistic problem from our earlier studies of charge-transfer (CT) interactions, in which we showed how the formation of the ion pair [D^+A^-] can be used as a quantitative model of the activation process between electron donors (D) and acceptors (A).¹⁰ Such a formulation allows the evaluation of the donor properties of alkenes and arenes in their reaction with bromine as the common electrophile or acceptor.¹¹ In particular, the donor properties for ion-pair formation can be obtained in the absence of solvation from the well-known charge-transfer spectra of electron donor-acceptor complexes of

(10) For the basis of the CT formulation for organometallic and other donors, see: (a) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 2246, 2254. (b) Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 571 and references therein.

(11) The direct relationship between *electrophiles* and *electron acceptors* in their interaction with arenes has been recently emphasized. See the discussion in ref 16.

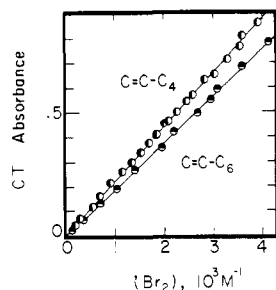


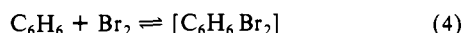
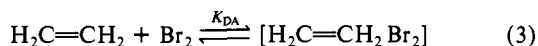
Figure 3. Direct relationship between the decay of the CT absorbance and the decrease in bromine concentration during the reaction of 0.13 M 1-hexene with 3.9×10^{-3} M Br_2 (○) and 0.10 M 1-octene with 4.1×10^{-3} M Br_2 (●) in carbon tetrachloride at 25 °C.

alkenes and arenes with bromine.^{12,13} The solvent effect is determined separately from a knowledge of the free energy change in the solvation of alkene and arene cations resulting from electron transfer in solution relative to that in the gas phase.¹⁴

Results and Discussion

In this study, the direct comparison of the electrophilic reactivity of alkenes and arenes proceeds initially from their donor properties evaluated from the charge-transfer transitions in the electron donor-acceptor or EDA complexes with bromine under standard conditions. The rates of bromine addition to alkenes and bromine substitution in arenes were then determined from the decay of the respective CT absorption bands. Finally, the contribution from solvation was determined as the energy difference between electron transfer from alkenes and arenes in the gas phase and in solution as measured by their ionization potentials and rates of chemical oxidations, respectively.

Charge-Transfer Transitions in Bromine Complexes with Alkene and Aromatic Donors. Dependence on Their Ionization Potentials. A wide variety of alkenes and arenes form electron donor-acceptor (EDA) complexes with molecular bromine.^{15,16} The existence of the EDA complexes is readily ascertained from the appearance of new absorption bands in the UV-vis region immediately upon mixing the alkene or arene with bromine in carbon tetrachloride solutions. Some representative examples are presented in Figure 1. The new absorption bands are due to 1:1 complexes of bromine and alkene or arene; e.g.,



The charge-transfer spectral data for various alkenes and arenes are listed in Table I. Since the formation constants K_{DA} for these bromine complexes are uniformly small,¹⁷ they are best considered as weak.

Figure 2 illustrates the direct relationship between the transition energy ($h\nu_{\text{CT}}$) and the donor property of the arenes and alkenes as measured by their ionization potential (I_{D}).¹⁸ The rather smooth correlation in Figure 2 thus emphasizes that there is no

(12) (a) Banthorpe, D. V. *Chem. Rev.* **1970**, *70*, 295. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev.* **1981**, *50*, 151. (c) Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Russ. Chem. Rev.* **1973**, *42*, 697. (d) Poleshchuk, O. Kh.; Maksyutin, Yu. K. *Russ. Chem. Rev.* **1976**, *45*, 1077.

(13) Andrews, L. J.; Keefer, R. M. "Molecular Complexes in Organic Chemistry"; Holden-Day, Inc.: San Francisco, 1964.

(14) See: Peover, M. E. *Electroanal. Chem.* **1967**, *2*, 1.

(15) Dubois, J. E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *23A*, 2279.

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(17) For example, $K_{\text{DA}} = 0.31 \text{ M}^{-1}$ at 30 °C for cyclohexene and Br_2 in hexane solution (Sergeev, G. B.; Chen, T. *Teor. Eksp. Khim.* **1967**, *3*, 240). The enthalpy and entropy of formation ($\Delta H = -0.4 \text{ kcal mol}^{-1}$; $\Delta S = -16 \text{ eu}$) are characteristic of weak intermolecular complexes. See: Tamres, M.; Strong, R. L. "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 5.

(18) Hereinafter, all energy terms are uniformly expressed in units of electron volts (eV). Although error bars are not included in the figures, the correlations and trends are to be considered significant to two digits.

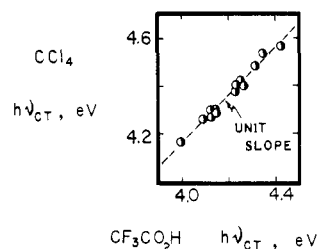


Figure 4. Constancy of the solvent-induced blue shift of the CT absorption band $h\nu_{\text{CT}}$ in trifluoroacetic acid relative to carbon tetrachloride. Note the line is arbitrarily drawn with a slope of 1.¹⁶

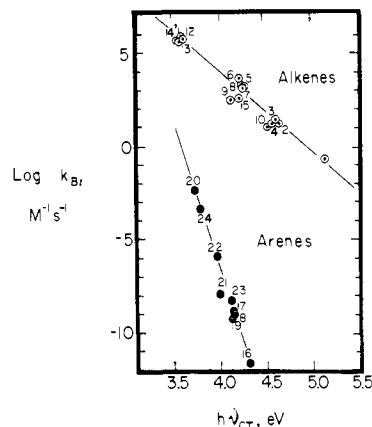
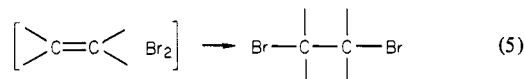


Figure 5. Correlation of the rates ($\log k_{\text{Br}}$) of electrophilic bromination in glacial acetic acid at 25 °C with the CT transition energies ($h\nu_{\text{CT}}$) of the bromine complexes of alkenes (○) and arenes (●) identified by the numbers in Tables I and II.

marked distinction between arenes and alkenes insofar as the CT transition is concerned at a given value of the ionization potential of the donor.

Rates of Electrophilic Bromination of Alkenes and Arenes. The charge-transfer absorption bands of the alkene-bromine complexes listed in Table I are transient. Indeed, the decay of the CT absorbance coincides with the addition of bromine to the double bond; i.e.,

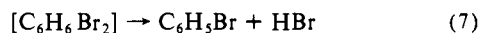


Thus the rates of bromination of alkenes could be measured in carbon tetrachloride solution simply by monitoring the disappearance of the CT bands listed in Table I spectrophotometrically. As shown in Figure 3, the CT absorbance A is proportional to the bromine concentration when the olefin is present in excess; i.e.,

$$A/A_0 = [\text{Br}_2]/[\text{Br}_2]_0 \quad (6)$$

where the subscripts zero refer to the initial states. The rates of electrophilic bromination were followed by measuring the decrease in the bromine absorption at $\lambda_{\text{max}} 415 \text{ nm}$ ($\epsilon 205.9 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁹ The diminution of the two different absorption bands occurs in exactly the same manner over the entire course of the reaction.

The decay of the CT band of the benzene-bromine complex also coincides with the electrophilic aromatic substitution in trifluoroacetic acid according to eq 7. It is noteworthy that the



absorption maximum λ_{CT} in trifluoroacetic acid is blue-shifted relative to that observed in carbon tetrachloride (see Table I). However, the magnitude of the blue shift is constant irrespective of the aromatic donor, as shown by the correlation of the data in Figure 4¹⁶ to the line arbitrarily drawn with a slope of 1.

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Table II. Second-Order Rate Constants for the Electrophilic Bromination of Arenes and Alkenes^a

no.	alkene	log k_{Br} , ^b M ⁻¹ s ⁻¹
1	H ₂ C=CH ₂	-0.66
2	H ₂ C=CHMe	1.25
3	H ₂ C=CHEt	1.46
4	<i>n</i> -PrCH=CH ₂	1.22 (-4.38)
5	H ₂ C=CMe ₂	3.18
6	H ₂ C=CMe(Et)	3.52
7	(<i>Z</i>)-MeCH=CHMe	3.09 ^c
8	(<i>E</i>)-MeCH=CHEt	3.25 ^c
9	(<i>E</i>)-MeCH-CH(<i>t</i> -Bu)	2.48 ^c (-1.25)
10	<i>t</i> -BuCH=CH ₂	1.01 ^c (-4.77)
11	Me ₂ C=CMe(Et)	5.92 ^d
12	Me ₂ C=CMe ₂	5.76 ^d (0.52)
13	Me ₂ C=CMe(<i>n</i> -Pr)	5.58 ^d
14	Me ₂ C=CMe(<i>n</i> -Bu)	5.62 ^d
15	cyclohexene	2.53 ^d (-1.96)

no.	arene	log k_{Br} , ^e M ⁻¹ s ⁻¹
16	C ₆ H ₆	-11.63 (-6.11)
17	MeC ₆ H ₅	-8.85 (-2.66)
18	EtC ₆ H ₅	-8.97 (-2.51)
19	<i>i</i> -PrC ₆ H ₅	-9.22 (-2.57)
20	MeOC ₆ H ₅	-2.37
21	<i>o</i> -Me ₂ C ₆ H ₄	-7.90 (-1.40)
22	<i>m</i> -Me ₂ C ₆ H ₄	-5.89 (0.57)
23	<i>p</i> -Me ₂ C ₆ H ₄	-8.23 (-1.77)
24	1,3,5-Me ₃ C ₆ H ₃	-3.35 (2.20)

^a From kinetic data obtained directly in glacial acetic acid at 25 °C unless stated otherwise. ^b From ref 21. Values in parentheses in CCl₄. ^c From ref 22. ^d See ref 23. ^e From ref 24. Values in parentheses in trifluoroacetic acid from ref 29.

The direct comparison of the reactivity of alkenes and arenes toward bromine requires a common medium, since it is well-known that there is a large solvent effect on the rates of both of these electrophilic reactions. Carbon tetrachloride and trifluoroacetic acid are not suitable for this comparison owing to rates of electrophilic bromination, which are either too fast (alkenes) or too slow (arenes) to measure reliably. However, acetic acid is a particularly useful compromise since both reactions occur at easily measured rates in this solvent. The rates of electrophilic brominations can be expressed by the second-order kinetics in eq 8,²⁰

$$-d[Br_2]/dt = k_{Br}[Br_2][D] \quad (8)$$

where D represents the alkene and arene donors. The second-order rate constants k_{Br} in acetic acid as reported in the literature are collected in Table II for convenience.²¹⁻²⁴

Correlation of the Charge-Transfer Transition with the Rate of Electrophilic Bromination of Alkenes and Arenes. In Figure 5 we find a direct relationship between the reactivity of alkenes and arenes in electrophilic brominations (log k_{Br}) and the charge-transfer transition energies ($h\nu_{CT}$) of their EDA complexes. Indeed the experimental plot shows two linear but separate correlations—the one for arenes is described by the relationship

$$\log k_{Br} = -16h\nu_{CT} + 55 \quad (9)$$

and that for alkenes is given by

$$\log k_{Br} = -4.1h\nu_{CT} + 20 \quad (10)$$

(20) (a) At higher bromine concentrations, a third-order term (second order in Br₂) must be included in eq 8 (see ref 21 and 24). (b) For a discussion of the second- and third-order rate constants as they apply to the CT mechanism, see: Fukuzumi, S.; Kochi, J. K. *Int. J. Chem. Kinet.*, in press.

(21) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673; see also ref 29 and 64.

(22) Ruasse, M. F.; Dubois, J. E.; Argile, A. *J. Org. Chem.* **1979**, *44*, 1173.

(23) Evaluated from the relationship $\log k_{Br}(\text{HOAc}) = 1.18 \log k_{Br}(\text{MeOH}) - 2.23$ from ref 21 with the data from: Dubois, J. E.; Mouvier, G. *Tetrahedron Lett.* **1963**, 1325. Bienvenue-Goët, E.; Dubois, J. E. *J. Org. Chem.* **1975**, *40*, 221. Dubois, J. E.; Alcais, P.; Barbier, G. *J. Electroanal. Chem.* **1964**, *8*, 359, and ref 7a in methanol.

(24) (a) Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1957**, *79*, 1421. (b) Stock, L. M.; Brown, H. C. *Ibid.* **1960**, *82*, 1942. (c) Keefer, R. M.; Ottenberg, A.; Andrews, L. J. *Ibid.* **1956**, *78*, 255.

Table III. Kinetic Data for the Oxidation of Alkenes by Iron(III) Complexes^a

no.	alkene	I_D , eV	log k_{Fe} for FeL ₃ ³⁺ , ^c M ⁻¹ s ⁻¹			
			5-NO ₂	5-Cl	H	4,7-Ph ₂
1	2,3-dimethyl-2-heptene	8.15	2.78	1.30	-0.81	-1.66
2	2,3-dimethyl-2-hexene	8.19	2.76	1.54	-0.76	
3	2,3-dimethyl-2-pentene	8.21	3.08	1.52	-0.79	
4	2,3-dimethyl-2-butene	8.27	3.00	1.20	-0.58	
5	3-ethyl-3-hexene	8.48	-0.80	-1.74	-3.40	
6	2-methyl-2-butene	8.68	-0.89	-2.39	-3.80	
7	cycloheptene	8.81		-3.49	-4.85	
8	cyclohexene	8.95	-3.36	-5.04	-5.89	
9	4,4-dimethyl-2-pentene	8.92			-4.76	
10	1-octene	9.43	-4.89		<-7	
11	1-pentene	9.52	-5.85			

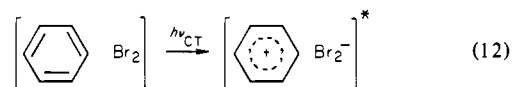
^a At 25 °C in acetonitrile solution. ^b From ref 38. ^c For FeL₃³⁺: 5-NO₂ = Fe(5-NO₂phen)₃³⁺; 5-Cl = Fe(5-Clphen)₃³⁺; H = Fe(phen)₃³⁺; 4,7-Ph₂ = Fe(4,7-Ph₂phen)₃³⁺.

The expression for the arenes in eq 9 merits special attention, since the slope of the correlation is remarkably close to unity when the rate constant (log k_{Br}) and CT transition ($h\nu_{CT}$) are expressed in the same energy units. (For a 1:1 relationship, the more exact relationship is $\log k_{Br} = 16.9h\nu_{CT} + \text{constant}$.²⁵) In other words, the reactivity of the arene in electrophilic bromination, as represented by the activation free energy $\Delta G^\ddagger = -RT \ln(k_{Br}/Z)$, corresponds directly to the charge-transfer transition energy in the arene-bromine complex; i.e.,

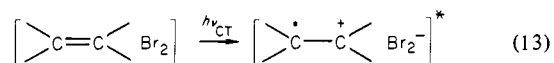
$$\Delta G^\ddagger = h\nu_{CT} + \text{constant} \quad (11)$$

However, the same does not apply to alkene bromination, as shown by the different correlation in eq 10. Indeed the inapplicability of eq 11 to alkenes is reflected in the huge difference in reactivity between alkenes and arenes when they are evaluated at the same donor ability. For example, ethylene, which represents the least reactive alkene, is still more than 50 times as reactive as anisole, the most reactive arene in Table I, even after discounting the substantial difference of 32 kcal mol⁻¹ in their CT donor abilities. Clearly the CT transition energy $h\nu_{CT}$ does not provide the sufficient means by itself to bridge the gap in electrophilic reactivity between alkenes and arenes.

In order to understand the reactivity difference between alkenes and arenes, let us consider the mechanistic significance of the important relationship in eq 11, realizing that it rests on the physical description of the charge-transfer excitation. According to Mulliken theory for weak EDA complexes of the π type described in eq 3 and 4, the absorption maximum $h\nu_{CT}$ corresponds to an electronic transition from the neutral ground state to the polar excited state,^{26,27}



and



(25) The relationship between ΔG^\ddagger and k_{Br} is given by the expression $\Delta G^\ddagger = -RT \ln(k_{Br}/Z)$, where Z is the frequency factor taken as 10¹¹ M⁻¹ s⁻¹. The slope of 16.9 is obtained as $(23.04 \times 10^3)/2.3RT = 16.9$. (1 eV = 23.04 kcal mol⁻¹, $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$.)

(26) The nature of the CT excited state of the π -type EDA complexes has been experimentally verified to be the polar ion pair by applying spectroscopic methods with pulsed laser excitation in accord with the Mulliken theory. See: Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 31 and references cited therein. Nagakura, S. "Excited States"; Lim, E. C., Ed.; Academic Press: New York, 1975; Vol. 2, p 334. For a current review, see: Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312.

(27) (a) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. (b) Foster, R. "Organic Charge Transfer Complexes"; Academic Press: New York, 1969.

The asterisk identifies an excited ion pair derived by electron transfer from the alkene or aromatic donor to bromine as the common acceptor within the EDA complex. The charge-transfer transition energy $h\nu_{CT}$, which is a measure of the donor ability of the alkene or arene (see Figure 2), thus represents the energetics of ion-pair formation.²⁸ As such, the striking correlation of eq 11 suggested to us that the energetics of ion-pair formation could also be related to the activation energy for aromatic substitution;²⁹ i.e., $\Delta G^* = -RT \ln(k_B/Z)$. It should be noted, however, that the photochemical excitation in eq 12 and 13 represents a vertical (Franck-Condon) transition. As such, the conversion of the alkene-bromine and arene-bromine EDA complexes to their respective CT excited ion pairs occurs with minimal changes in solvation.^{27,30} Thus the relative donor properties of alkenes and

(28) According to Mulliken and others,²⁷ $h\nu_{CT}$ corresponds to the electronic excitation from the ground state Ψ_N of the complex to the excited singlet state Ψ_E as described in eq a and b, respectively, where $\Psi(DA)$ and $\Psi_i(D^+A^-)$

$$\Psi_N = a\Psi(DA) + \sum_i b_i \Psi_i(D^+A^-) + \sum_j c_j \Psi_j(D^*A) + \sum_k d_k \Psi_k(DA^*) \quad (a)$$

$$\Psi_E = a^* \Psi(DA) + \sum_i b_i^* \Psi_i(D^+A^-) + \sum_j c_j^* \Psi_j(D^*A) + \sum_k d_k^* \Psi_k(DA^*) \quad (b)$$

represent the wave functions for the no-bond structure and the i th zero-order electron-transfer singlet state, respectively. $\Psi_i(D^+A^-)$ and $\Psi_k(DA^*)$ are the wave functions of the zero-order singlet states corresponding to the j th and k th local excitation within the electron donor and acceptor, respectively. For the weak EDA complexes of the type between bromine and alkenes¹⁵ or arenes,¹⁶ in which the overlap integrals between the donor and acceptor orbitals are small, the transition energy can be expressed to first order as

$$h\nu_{CT} = I_D^i - E_A^m + \omega \quad (c)$$

In eq c, $h\nu_{CT}$ corresponds to the transition energy from $\Psi(DA)$ to $\Psi_i(D^+A^-)$, I_D^i is the i th ionization potential of the donor, E_A^m is the m th electron affinity of the acceptor, and ω is the interaction energy between the donor and acceptor moieties in the $\Psi_i(D^+A^-)$ state. [For weak complexes of the type described here, the nondiagonal terms in the secular eq derived from eq a and b is neglected, Ψ_E is given as $\Psi_i(D^+A^-)$, $\Psi_j(D^*A)$, or $\Psi_k(DA^*)$ and the transition energy from $\Psi(DA)$ to $\Psi_i(D^+A^-)$ is given in eq c. Thus any significant deviation from eq c owing to the interaction between $\Psi(DA)$, $\Psi_i(D^+A^-)$, $\Psi_j(D^*A)$, and $\Psi_k(DA^*)$ in eq a and b is unlikely for weak complexes. For the nature of Ψ_N in molecular complexes, see: Morokuma, K. *Acc. Chem. Res.* 1977, 10, 294.]

The charge-transfer absorption bands in Table I correspond to the first or lowest CT band in eq c, since there are no additional discrete bands at lower energies other than those ascribed to λ_{max} . Accordingly, for our purposes here, the observed CT band corresponds to

$$h\nu_{CT} = I_D - E_A + \omega \quad (d)$$

where $h\nu_{CT} \propto 1/\lambda_{max}$, I_D is the first vertical ionization potential of the alkene or arene, and E_A is the first vertical electron affinity of the acceptor, i.e., bromine. The relationship in eq d predicts a linear correlation between $h\nu_{CT}$ and I_D with a unit slope (compare Figure 2), provided the interaction energy ω remains invariant in a series of EDA complexes involving a family of structurally related donors. Such a correlation is tantamount to a constant steric effect, since ω reflects the mean separation between the donor and acceptor moieties in the EDA complex. [For a discussion of steric effects in arene complexes, see: Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* 1981, 85, 648; and for steric effects in halogen complexes, see: Fukuzumi, S.; Kochi, J. K. *Ibid.* 1980, 84, 608, 617.] Thus for weak complexes, Mulliken theory predicts an excited ion-pair state in which the mean separation is the same as that in the EDA complex itself. For the experimental verification of CT ion pairs, see ref 26.

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

(30) (a) Kosower, E. M. *Prog. Phys. Org. Chem.* 1965, 3, 81. (b) Davis, K. M. C. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1975; Vol. 1, Chapter 3. (c) The relaxation from the Franck-Condon excited state to the equilibrium fluorescent state is associated with an extraordinarily large Stokes shift of 34 kcal mol⁻¹ for the tetracyanobenzene-toluene EDA complex in toluene. These experiments were verified (using a pulsed nitrogen laser excitation) as a time-dependent (1-100 ns) red shift of the fluorescence of the excited TCNB-toluene EDA complex, which directly reflects the solvent reorientation. (Egawa, K.; Nakashima, N.; Mataga, N.; Yamanaka, C. *Chem. Phys. Lett.* 1971, 8, 108; *Bull. Chem. Soc. Jpn.* 1971, 44, 3287.) It is noteworthy that the Stokes shift for the fluorescence of the toluene-TCNB complex is about the same as the solvation energy of aromatic cation (38 kcal mol⁻¹).²⁹ When the solvation of the TCNB anion and the difference of the solvent are taken into account, the solvation in the equilibrium fluorescent state may be approximated by the sum of the solvation of each cation and anion. Thus, the Stokes shift in the fluorescence of the excited EDA complexes could provide further insight into the solvent effects in the electrophilic aromatic substitutions on the absolute scale.

Table IV. Kinetic Data for the Oxidation of Aromatic Compounds with Iron(III) Complexes^a

no.	aromatic compd	I_D^b , eV	$\log k_{Fe}$ for FeL_3^{3+} , $^c M^{-1} s^{-1}$				
			5-NO ₂	5-Cl	H	4,7-Ph ₂	bpy ^d
12	1,4-(MeO) ₂ C ₆ H ₄	7.96	2.19	0.72	-1.80	-2.82	-1.80
13	1,3-(MeO) ₂ C ₆ H ₄	8.14	1.86		-4.04		
14	1,4-MeO(Me)C ₆ H ₄	8.18	-0.37	-2.00	-3.72	-4.54	
15	1,3-MeO(Me)C ₆ H ₄	8.28	-2.40	-3.89	-5.46		-5.34
16	MeOC ₆ H ₅	8.39	-4.36		-7.70		
17	1,3,5-Me ₃ C ₆ H ₃	8.40	-4.47		-8.22		
18	1,2,4,5-Me ₄ C ₆ H ₂	8.05	-1.06	-2.48	-4.09	-5.42	-4.69
19	1,2,3,4-Me ₄ C ₆ H ₂		-0.37		-4.24		
20	RC ₆ H ₅ ^e	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>

^a At 25 °C in acetonitrile solution. ^b From ref 39. ^c For the iron(III) complex, see footnote c in Table III. ^d bpy = tris(α,α' -bipyridine)iron(III). ^e Alkylbenzenes. ^f Too slow to measure reliably.

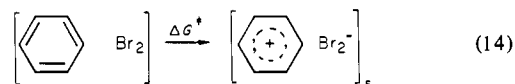
Table V. Standard Reduction Potentials of Iron(III) Complexes^a

FeL ₃ (ClO ₄) ₃ , L	E°_{red} , V vs. SCE ^b	i_c/i_a^c	Δ , ^d mV
1,10-phenanthroline	0.98	1.00	68
5-chloro-1,10-phenanthroline	1.08	1.01	67
5-nitro-1,10-phenanthroline	1.18	1.02	72
4,7-diphenyl-1,10-phenanthroline	0.91	1.01	65
2,2'-bipyridine	0.97	1.02	70

^a By cyclic voltammetry at 25 °C in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate. ^b Corrected from data in ref 35h to SCE. ^c Ratio of the peak currents for the cathodic (i_c) and anodic (i_a) waves. ^d Separation of anodic and cathodic peaks at 50 mV s⁻¹ scan rate.

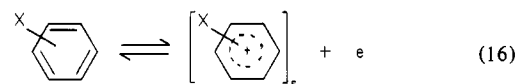
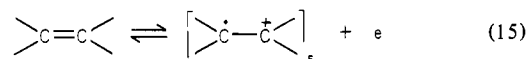
arenes measured from the CT transitions represent essentially those in the gas phase.³¹

By contrast, the thermal activation of electrophilic brominations in solution is an adiabatic process in which the formation of the polar ion pair in eq 14 must be accompanied by large changes



in solvation, as indicated by the subscript s.³² Therefore any comparison of the reactivity of arenes and alkenes in electrophilic brominations according to this model must specifically address the question of solvation.

Let us focus our attention on only the solvation change associated with the donor moiety, since the bromine acceptor is common to both systems. Indeed, for the solution process, we need consider only that energy change for the oxidation of the alkene and arene moiety, as given by the standard oxidation potentials E°_{ox} , i.e.;



where the subscript s refers to the solvated cationic species.³³

(31) This is particularly applicable to structurally related donors in which the differences in solvation of the ground-state EDA complexes are minor. See discussion in ref 30b.

(32) For the treatment of solvation in adiabatic electron-transfer processes, see: Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966.

(33) In practice, the standard oxidation potentials of most alkene and arenes cannot be experimentally determined owing to their irreversible anodic oxidation.²⁹ The latter arises from the transient character of these alkene and arene cations; see comments in ref 48c. For E° of irreversible outer-sphere electron transfer, see ref 34.

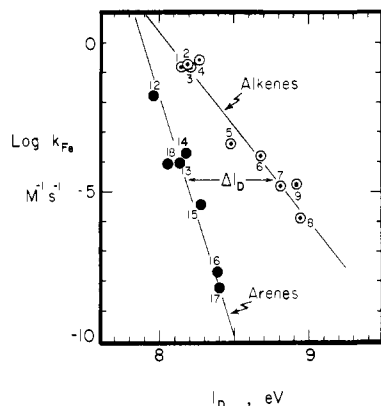
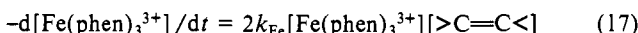


Figure 6. Rates of oxidation of alkene and aromatic donors by $\text{Fe}(\text{phen})_3^{3+}$ as a function of their ionization potentials. Numbers refer to alkenes (○) in Table III and arenes (●) in Table IV. For the significance of ΔI_D , see eq 21 and 28.

Accordingly, we next examined the chemical oxidation of the same alkene and arene donors in solution, in order to show how it can be used to evaluate the solvation energies of transient cations.

Donor Properties of Alkenes and Arenes from Their Oxidation in Solution. The Evaluation of Solvation Energies of Transient Cations. (A) Structural Effects of Donors in Their Oxidation by $\text{Fe}(\text{phen})_3^{3+}$. Tris(phenanthroline)iron(III) ($\text{Fe}(\text{phen})_3^{3+}$) is known to effect one-electron oxidation of a variety of inorganic, organometallic, and organic compounds only by an outer-sphere process.^{35,36} Owing to its rather positive oxidation potential ($E^\circ = 0.98$ V vs. SCE), we find that it is also capable of oxidizing alkenes and arenes. The stoichiometric requirement of iron(III) in the oxidation of alkenes and arenes was determined in acetonitrile solution by the spectral titration of the reduced iron(II). Two equivalents of the iron(II) complex were required for each mole of alkene or arene, as described separately in the Experimental Section.³⁷

The rates of oxidation by iron(III) were measured spectrophotometrically at 25 °C by following either the appearance of the iron(II) bands (e.g., $\text{Fe}(\text{phen})_3^{2+}$, $\lambda_{\text{max}} 507$ nm, $\epsilon 1.31 \times 10^4$) or the disappearance of iron(III) ($\text{Fe}(\text{phen})_3^{3+}$, $\lambda_{\text{max}} 592$, $\epsilon 5.79 \times 10^2$).^{35h} The rate of alkene oxidation obeyed second-order kinetics in acetonitrile solution, being first order in each reactant; i.e.,



as described in the Experimental Section. The second-order rate constants k_{Fe} for the oxidation of a series of alkenes with $\text{Fe}(\text{phen})_3^{3+}$ are listed in Table III, together with the values of the vertical ionization potentials of the alkene donors.³⁸

(34) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 4186.

(35) For inorganic systems, see: (a) Dulz, G.; Sutin, N. *Inorg. Chem.* **1963**, *2*, 917. (b) Diebler, H.; Sutin, N. *J. Phys. Chem.* **1964**, *68*, 174. (c) Hicks, K. W.; Sutter, J. R. *Ibid.* **1971**, *75*, 1107. (d) Wilkins, R. G.; Yelin, R. E. *Inorg. Chem.* **1968**, *7*, 2667. (e) Campion, R. J.; Purdie, N.; Sutin, N. *Ibid.* **1964**, *3*, 1091. (f) Gordon, B. M.; Williams, L. L.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 2061. For organic systems, see: (g) Ng, F. T. T.; Henry, P. M. *Ibid.* **1976**, *98*, 3606; *Can. J. Chem.* **1977**, *55*, 2900. (h) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(36) For the importance of outer-sphere mechanisms in electron transfer, see: Wong, C. L.; Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928. Klingler, R. J.; Kochi, J. K. *Ibid.* **1981**, *103*, 5839.

(37) For the stoichiometric requirement of 2 equiv of $\text{Fe}(\text{phen})_3^{3+}$ for each mole of donor in these and related oxidations, see ref 35h. We hope to report the products of alkene oxidation by $\text{Fe}(\text{phen})_3^{3+}$ later. For the products derived from the oxidation of alkenes by various 1-equiv oxidants, see the review by: Henry, P. M.; Lange, G. L. In "Chemistry of Double-Bonded Functional Groups"; Patai, S., Ed.; Wiley: New York, 1977; Suppl. A, Part 2, Chapter 11.

(38) (a) Masclat, P.; Grosjean, D.; Mouvrier, G.; Dubois, J. E. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225. (b) Remane, H.; Graefe, J.; Herzschuh, R. *Z. Chem.* **1972**, *12*, 194. (c) Demeo, D. A.; El-Sayed, M. A. *J. Chem. Phys.* **1970**, *52*, 2622. (d) Kobayashi, T.; Yokota, K.; Nagakura, S. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *3*, 449.

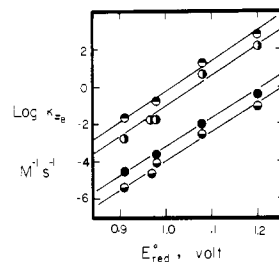
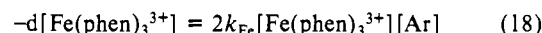


Figure 7. Effect of the reduction potentials E°_{red} of the iron(III) complexes FeL_3^{3+} on the rates of donor oxidation: (○) 2,3-dimethyl-2-heptene, (●) *p*-dimethoxybenzene, (●) *p*-methoxytoluene, (●) durene.

Aromatic compounds, particularly the substituted benzenes Ar in Table IV, are also oxidized by the tris(1,10-phenanthroline)-iron(III) complex, $\text{Fe}(\text{phen})_3^{3+}$. Furthermore, the oxidation of the substituted benzenes obeyed the same second-order kinetics and exhibited the same stoichiometric requirement for $\text{Fe}(\text{phen})_3^{3+}$ as those found in the oxidation of alkenes⁴⁰ (eq 18). The values of the second-order rate constants ($\log k_{\text{Fe}}$) are collected in Table IV.⁴¹



(B) Effect of the Iron(III,II) Reduction Potential on the Oxidation of a Donor. Let us now examine the effect of changing the iron(III) oxidant on the rate of oxidation of a particular donor. The accessibility of a variety of substituted 1,10-phenanthroline ligands L allows the systematic variation in the standard reduction potential E°_{red} in the corresponding iron(III) complexes FeL_3^{3+} listed in Table V. The kinetics and stoichiometry of alkene and aromatic oxidation with these iron(III) complexes were found to be the same as those established for $\text{Fe}(\text{phen})_3^{3+}$. The second-order rate constants ($\log k_{\text{Fe}}$) are also included in Tables III and IV for these iron(III) complexes.

(C) Linear Free Energy Relationship (LFER) for the Oxidation of Alkene and Arene Donors. For the oxidation of various alkene and aromatic donors by the iron(III) oxidant $\text{Fe}(\text{phen})_3^{3+}$, the second-order rate constant ($\log k_{\text{Fe}}$) is a linear function of the ionization potential of the alkene and aromatic donor. However, Figure 6 shows the existence of two different correlations—that for the alkenes is given by eq 19, and the linear correlation for the aromatic donors is described by eq 20.⁴² The discrepancy

$$\text{alkenes} \quad \log k_{\text{Fe}} = -6.3I_D + \text{constant} \quad (19)$$

$$\text{arenes} \quad \log k_{\text{Fe}} = -17I_D + \text{constant} \quad (20)$$

ΔI_D between alkene and aromatic donors can be evaluated from the combination of eq 19 and 20 as

$$\Delta I_D = 0.1 \log k_{\text{Fe}} - 0.15 \quad (21)$$

For the oxidation of a particular alkene or aromatic donor by various iron(III) oxidants FeL_3^{3+} , the second-order rate constant ($\log k_{\text{Fe}}$) is a linear function of the standard iron(III) potential E°_{red} as shown in Figure 7. It is especially noteworthy that the slopes of the correlations in Figure 7 are the same for the alkene and aromatic donors. For each donor, the relationship between the oxidation rate constant and the iron(III) reduction potential is

$$\log k_{\text{Fe}} = 17E^\circ_{\text{red}} + \text{constant} \quad (22)$$

(39) (a) Reference 16 and references cited therein. (b) Watanabe, K.; Nakayama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369. (c) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2563.

(40) For typical products of 1-equiv oxidation of aromatic compounds, see the reviews by: (a) Littler, J. S.; Nonhebel, D. C. *Int. Rev. Sci., Org. Chem. Ser. Two* **1975**, *10*, 212. (b) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidation of Organic Compounds"; Academic Press: New York, 1981. (c) Beletskaya, I. P.; Makhon'kov, D. I. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 1007.

(41) Note that the rates of oxidation of only the more electron-rich aromatic compounds are included, since the others were too slow to measure reliably.

(42) The constants in eq 19 and 20 are 51 and 134, respectively.

Table VI. Solvation Energies of Transient Alkene Cations^a

no.	alkene	I_D^b eV	solvation energy, ^c eV		
			MeCN ^d	HOAc ^e	TCE ^e
1	H ₂ C=CH ₂	10.52	1.69 ^f	1.45	0.98
2	H ₂ C=CHMe	9.74	1.21 ^f	1.04	0.70
3	H ₂ C=CHEt	9.63	1.13 ^f	0.97	0.66
4	<i>n</i> -PrCH=CH ₂	9.52	1.07 ^f	0.92	0.62
5	H ₂ C=CMe ₂	9.24	0.89 ^f	0.77	0.52
6	H ₂ C=CMe(Et)	9.15	0.84 ^f	0.72	0.49
7	(<i>Z</i>)-MeCH=CHMe	9.12	0.82 ^f	0.71	0.48
8	(<i>E</i>)-MeCH=CHMe	9.04	0.77 ^f	0.66	0.45
9	(<i>E</i>)-MeCH=CH(<i>t</i> -Bu)	8.91	0.73	0.48	0.42
10	<i>t</i> -BuCH=CH ₂	9.45	1.03 ^f	0.89	0.60
11	Me ₂ C=CMe(<i>E</i> t)	8.21	0.27	0.23	0.16
12	Me ₂ C=CMe ₂	8.27	0.34	0.29	0.20
13	Me ₂ C=CMe(<i>n</i> -Pr)	8.19	0.25	0.22	0.15
14	Me ₂ C=CMe(<i>n</i> -Bu)	8.15	0.20	0.17	0.12
15	cyclohexene	8.95	0.68	0.58	0.39

^a Evaluated according to eq 27. ^b From ref 38. ^c As ΔG_r^s .

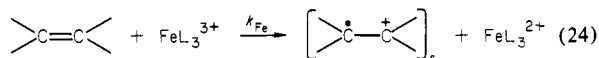
^d Evaluated from ΔI_D in Figure 6 and eq 28. ^e Evaluated from eq 46 in the Experimental Section. ^f See ref 48d.

This experimental observation expressed by eq 22 is actually equivalent to the linear free energy relationship in eq 23,⁴³ where

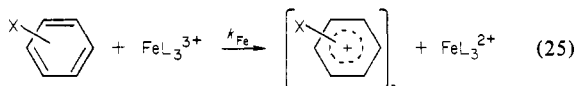
$$\Delta G^* = \Delta G + \text{constant} \quad (23)$$

ΔG^* represents the activation free energy (i.e., $-RT \ln(k_{Fe}/Z)$) and ΔG is the free energy change (i.e., $\mathcal{F}(E^{\circ}_{ox} - E^{\circ}_{red})$) for these alkene and aromatic oxidations.⁴⁴

The 1:1 correspondence between ΔG^* and ΔG in eq 23 pertains to a highly endergonic electron-transfer process.⁴⁶ This coupled with the observed second-order kinetics indicates that an alkene cation is initially formed in the oxidation by FeL_3^{3+} via a rate-limiting electron transfer; i.e.,



Aromatic oxidations by the iron(III) complexes proceed in a similar manner shown below. As such, the second equivalent of



the iron(III) complex required by the stoichiometry is then involved in a rapid, followup oxidation of the transient alkene and aromatic cations formed in eq 24 and 25, respectively.⁴⁷

(D) Evaluation of the Solvation Energies of Transient Alkene and Aromatic Cations. The free energy change (ΔG) for the oxidation of a donor in solution includes the solvation term ΔG^s for the donor cation D^+ . Accordingly, the relationship between the free energy change for oxidation in solution and that in the gas phase is given by⁴⁸

$$\Delta G = I_D + \Delta G^s \quad (26)$$

(43) The slope of 17 in eq 22 is equivalent to the slope of 1 in eq 23, as described in ref 25.

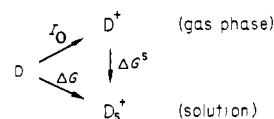
(44) Note that E°_{ox} is constant for each series in Figure 7. \mathcal{F} is the Faraday constant. For a highly endergonic reaction, the constant in eq 23 may be neglected, i.e., $\Delta G^* \approx \Delta G$.⁴⁵

(45) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.

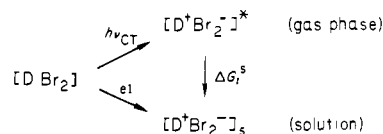
(46) This follows from the general form of the free energy relationship applicable to the endergonic region, see: Agmon, N. *Int. J. Chem. Kinet.* **1981**, *13*, 333. See also ref 34.

(47) For the products from the further oxidation of alkene and aromatic cations, see ref 37 and 40.

Scheme I. For Cations



Scheme II. For Ion Pairs



The solvation energies of the *transient* alkene and aromatic cations formed in eq 24 and 25, respectively, cannot be determined by this direct method owing to their kinetic instability.³³ However, solvation energies can be evaluated from the free energy relationship for electron transfer, such as that established experimentally in eq 22. In order to utilize this relationship, we relate the solvation energies of all the cations to that of a reference donor. It follows from a combination of eq 23 and 26 that

$$\Delta G^s - \Delta G^s_0 = \Delta G^* - \Delta G^*_0 - (I_D - I_{D_0}) \quad (27)$$

where the subscript zero refers to the reference. We now arbitrarily choose the aromatic cations as the reference, since their solvation energies are rather invariant at 2.0 eV for a series of aromatic compounds in acetonitrile.²⁹ Thus the solvation energy of an alkene cation can be evaluated relative to that of an aromatic cation under isokinetic conditions, i.e., the rate at which the oxidation of an alkene is the same as that of an arene, $\Delta G^*(>C=C<) = \Delta G^*(Ar)$. The latter is readily identified in Figure 6 to be ΔI_D , representing the difference in ionization potential of a given alkene and that of an aromatic donor. It thus follows from eq 27 that the relative solvation energy ΔG^s_r of the alkene cation is

$$\Delta G^s - \Delta G^s_0 = \Delta G^s_r = -\Delta I_D \quad (28)$$

The values of ΔG^s_r obtained in this manner from the data in Figure 6 are listed in Table VI for the various alkenes employed in this study. The relative solvation energies in acetic acid can be obtained from those evaluated in acetonitrile by using the Born model,⁴⁹ as separately described in detail in the Experimental Section. These are also listed in Table VI, together with the relative solvation energies of alkene cations in the aprotic tetrachloroethane (TCE) medium.

There is a trend in Table VI for the solvation energies of transient alkene cations to vary with the substituents on the double bond. In general, the magnitude of the solvation energy is seen to decrease as the number of methyl substituents increases, ap-

(48) (a) The solvation of the neutral species is neglected in comparison with that of the donor cation (Lofti, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2137. Abraham, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085) in eq 26. (b) It is also assumed that the vertical and adiabatic cations have essentially the same structure. However, see: Bellville, D. J.; Bauld, N. L. *Ibid.* **1982**, *104*, 294. (c) This relationship has been proved for polynuclear aromatic compounds, for which $\Delta G = \mathcal{F}E^{\circ}_{ox} + \text{constant}$ can be measured electrochemically. (See ref 14 and: Case, B. In "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Wiley: New York, 1971; p 125. Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1965**, *25*, 321.) Since the accurate ionization potentials were not available for all the compounds when the values of ΔG^s were first evaluated above, we recalculated ΔG^s by using the recent data for the ionization potentials of these compounds. (Herndon, W. C. *J. Am. Chem. Soc.* **1976**, *98*, 887.) The results are: anthracene, 40.1 kcal mol⁻¹; phenanthrene, 38.0 kcal mol⁻¹; crysene, 37.3 kcal mol⁻¹; pyrene, 36.6 kcal mol⁻¹; triphenylene, 38.2 kcal mol⁻¹; tetracene, 36.6 kcal mol⁻¹. The average value is 37.8 ± 1.3 kcal mol⁻¹ in acetonitrile. (d) Solvation energy was evaluated from the expression $\Delta G^s_r = \Delta I_D = 0.63I_D(\text{alkene}) - 4.90$, which was obtained from eq 19 and 20,⁴² for the alkenes not included in Figure 6.

(49) (a) Latimer, W. M.; Pitzer, K. S.; Slansky, C. M. *J. Chem. Phys.* **1939**, *7*, 108. (b) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513. (c) Coetzee, J. F.; Campion, J. J. *Ibid.* **1967**, *89*, 2513. (d) Tanaka, M. *Inorg. Chem.* **1976**, *15*, 2325. (e) Bockris, J. O'M.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum: New York, 1970; Vol. 1, p 56 ff.

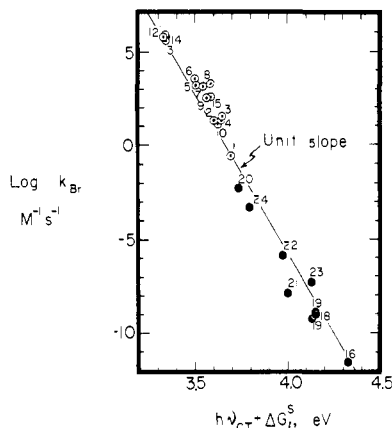


Figure 8. Unified LFER of the electrophilic bromination of alkenes (○) and arenes (●) identified in Tables II and III with the charge-transfer transition energies $h\nu_{CT}$ and cation solvation ΔG_s^{\ddagger} . Compare with Figure 5. Note the line is arbitrarily drawn with a slope of 1 to emphasize the fit of the data to eq 29 and 30, as described in the text.

proaching that of the aromatic cations. Thus the solvation energies of these transient cations do reflect the degree of charge delocalization.⁵⁰

Unified View of the Transition States for Electrophilic Bromination of Alkenes and Arenes. The Evaluation of Solvated Ion Pairs from Charge-Transfer and Oxidation Data. The foregoing evaluation of the solvation energies of transient cations allows the donor abilities of alkenes and arenes D in solution to be determined from the gas-phase data. A knowledge of solvation energies is thus sufficient to evaluate donor cations in solution from those in the gas phase, as graphically illustrated in Scheme I.

Let us now make an analogous connection between the ion pairs generated photochemically by CT excitation ($h\nu_{CT}$) and those formed thermally by an adiabatic electron transfer (et) in solution, as presented in the thermochemical cycle in Scheme II.⁵¹ Indeed, the extent to which the formation of the solvated ion pair in Scheme II is equivalent to the activation barrier ΔG^{\ddagger} for electrophilic bromination is then given by eq 29.⁵² (Note the contribution from the solvation of the common bromine moiety is included in the constant term in eq 29.)

$$\Delta G^{\ddagger} = h\nu_{CT} + \Delta G_s^{\ddagger} + \text{constant} \quad (29)$$

The experimental fit of the rate data for electrophilic bromination to eq 29 is shown in Figure 8, which is a remarkable transformation of the two separate correlations for alkenes and arenes in Figure 5.⁵³ In other words, bromine addition to alkenes

(50) For the structural effects on some typical cation solvations, see: Arnett, E. M.; Pienta, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 3329. Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *Ibid.* **1978**, *100*, 1240 for leading references.

(51) (a) The implication in Scheme II is for the structural effects on the free energy of solvation of the D^+ moiety in the vertical ion pair to parallel those in the free energy of formation of the same moiety in the adiabatic ion pair, as evaluated by eq 26 for the free cation. Similarly, the changes in the mean separation, the entropy, etc., in the vertical ion pair are also considered to parallel those in the adiabatic ion pair. (A less restrictive formulation would suggest that changes in one be proportional to those in the other.) The differences in the absolute energy changes for these and other effects are thus included in the constant term in eq 29. (b) This analysis implies that the irradiation of the CT band at low temperatures would also afford the ion pair. (See Fukuzumi et al. [Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961] for such an experimental observation in the CT excitation of analogous EDA complexes.)

(52) (a) Since the formation constants K_{DA} of these EDA complexes are small,¹⁷ the free energy of formation (ΔG_{DA}) of the precursor complex can be ignored in comparison with the activation barrier for the electrophilic process. (b) The constant term also includes the solvation energy of aromatic cations, etc. (c) For questions regarding the solvation of transition states in relation to that of stable molecular analogues, see: Ritchie, C. D. *Pure Appl. Chem.* **1979**, *52*, 153. Ritchie, C. D.; VanVerth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491 for leading references.

(53) Note the use of the solvation energies from Table VI for the fit to eq 29 implies that the mean separations (r_{DA}) in the ion pairs are related in Scheme II.

and bromine substitution of arenes are included in a single correlation, despite their distinctive stoichiometries and widely divergent rates. We interpret such an unprecedented interrelationship to signify that related transition states are involved in these otherwise disparate processes.

The fit of the experimental data in Figure 8 to the line arbitrarily drawn with a slope of 1 emphasizes the 1:1 correspondence between the kinetic barrier ($-RT \ln(k_{Br}/Z)$) for electrophilic bromination and the energetics of ion-pair formation in solution.¹⁸ Although the precise structure of the transition state is presently unknowable in detail, the correlation provided by eq 29 indicates that the solvated ion pair is certainly a feasible model of the transition state for both alkene addition and aromatic substitution.⁵⁴ Indeed, it provides the common means to unify the very large differences in the reactivity of alkenes and arenes toward bromine in a quantitative way.

Significance of the CT Formulation to Other Linear Free Energy Relationships. Unity of Brown σ^+ and Taft σ^* Constants. The charge-transfer formulation in Scheme II for electrophilic bromination leads to the conception of the transition state as the solvated ion pair. In the general form, eq 29 can be quantitatively expressed as the single linear free energy relationship in eq 30

$$\log k = -\frac{1}{2.3RT}(h\nu_{CT} + \Delta G_s^{\ddagger}) + \text{constant} \quad (30)$$

applicable to both alkenes and arenes.⁵⁵ As such, we now show how this formulation unifies the two separate linear free energy relationships that have been previously developed independently for electrophilic additions to alkenes and for electrophilic aromatic substitutions. In particular, the rates of electrophilic aromatic substitution are well correlated by the Brown σ^+ aromatic substituent constants, viz.,^{6,8}

$$\text{arenes} \quad \log(k/k_0) = \rho\sigma^+ \quad (31)$$

Likewise, the rates of electrophilic additions to alkenes follow a similar free energy relationship based on the Taft σ^* aliphatic substituent constants, viz.,^{7,56}

$$\text{alkenes} \quad \log(k/k_0) = \rho^*\sigma^* \quad (32)$$

Since the sensitivity factors ρ and ρ^* in eq 31 and 32, respectively, have been subjected to various physical interpretations, our primary task is to relate ρ and ρ^* to the CT formulation in which the parameters bear definitive physical significance.

We begin by noting that in Figure 2 the CT transition energy $h\nu_{CT}$ is linearly related to the ionization potentials of alkene and aromatic donors by a single correlation, viz.,

$$h\nu_{CT} = 0.7I_D + \text{constant} \quad (33)$$

Likewise, the solvation term ΔG_s^{\ddagger} for alkenes in Table VI is rather linear with the ionization potential, i.e.,

$$\text{alkene} \quad \Delta G_s^{\ddagger} = -\alpha I_D + \text{constant} \quad (34)$$

where α is the solvent-dependent slope of the relationship (e.g., $\alpha = 0.6$ for acetic acid). As mentioned earlier, the value of ΔG_s^{\ddagger} for the aromatic donors is constant irrespective of the solvent, i.e.,

$$\text{arene} \quad \Delta G_s^{\ddagger} = \text{constant} \quad (35)$$

(54) In this formulation, we do not intend to convey the notion that the configurational structure of the transition state and that of the CT excited ion pair are necessarily the same but only that the energy change in the formation of one serves as a viable model for that of the other. In more rigorous terms, eq 29 states alkenes and arenes are subjected to the same perturbations in electrophilic brominations as in the CT transition in the EDA complexes when changes in solvation are taken into account. It must be emphasized that the CT formulation does not require the proof that an EDA complex is (or is not) an intermediate in electrophilic brominations. For a discussion of this point, see footnotes 19 and 20 in: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141. The strongest kinetic evidence for the direct involvement of the EDA complex is the observation of a negative temperature coefficient. See: Sergeev, G. B.; Pokolok, T. V.; Ch'eng, T. *Kinet. Katal.* **1969**, *10*, 36.

(55) The rate constant k_{Br} is rewritten as k for generality.

(56) Substituent constant represented here as σ^* is actually the sum $\sum \sigma^*$ in ref. 7. The values of ρ^* in Table VII are from Modro, Schmid, and Yates,²¹ who excluded *trans*-di-*tert*-butylethylene in their correlation.

Table VII. Comparison of the Experimental and Calculated Values of ρ and ρ^* for Electrophilic Brominations in Several Solvents

donor	solvent	ρ or ρ^*	
		exptl	calcd
arenes	HOAc	-12.1 ^a	-11
arenes	CF ₃ CO ₂ H	-12.3 ^b	-11
alkenes	CH ₃ CO ₂ H	-2.8 ^c	-2.4
alkenes	Cl ₂ CHCHCl ₂	-4.1 ^c	-5.1

^a From ref 6b. ^b See ref 59. ^c See ref 56.

Linear relationships have been well established for the substituent constants σ^* and σ^+ as a function of the ionization potential of the alkene and aromatic donors, respectively.^{57,58}

$$\text{alkenes} \quad \sigma^* = 1.1I_D + \text{constant} \quad (36)$$

$$\text{arenes} \quad \sigma^+ = 1.1I_D + \text{constant} \quad (37)$$

The combinations of eq 33-37 with the charge-transfer eq 30 afford alternative forms of the free energy relationship, viz.,

$$\text{alkenes} \quad \log(k/k_0) = -15(0.7 - \alpha)\sigma^* \quad (38)$$

$$\text{arenes} \quad \log(k/k_0) = -11\sigma^+ \quad (39)$$

The comparison of these expressions with the original linear free energy relationships in eq 31 and 32 leads to the important result that the sensitivity factors in electrophilic brominations are given by

$$\text{alkenes} \quad \rho^* = -15(0.7 - \alpha) \quad (40)$$

$$\text{arenes} \quad \rho = -11 \quad (41)$$

According to eq 41, the relative reactivity of arenes in electrophilic substitution is solvent independent. The data available in the extant literature for glacial acetic acid and trifluoroacetic acid support this conclusion. Indeed, the experimental values of ρ accord favorably with that predicted in eq 41, as shown by the comparisons in Table VII. Furthermore, the solvent dependency of the electrophilic bromination of alkenes as predicted by eq 40 accords with the experimental results in media as different as glacial acetic acid and tetrachloroethane. The calculated values of ρ and ρ^* in Table VII show reasonable agreement with the experimental values.⁵⁹ The agreement is especially noteworthy considering that the absolute magnitude of ρ and ρ^* , otherwise unpredictable, can be independently evaluated for both aromatic substitution and alkene addition by bromine in different solvents.⁶⁰ Since alkenes and arenes show common relationships between $h\nu_{CT}$ and I_D (eq 33) as well as between σ^* or σ^+ and I_D (eq 36 or 37), the principal difference in their reactivities to electrophilic bromination can be attributed to differences in the solvation of alkene and aromatic cations (compare eq 34 and 35 or see eq 28).

Summary and Conclusions

It is generally recognized that alkenes are significantly more reactive than arenes in a variety of electrophilic processes. Although experimental data that allow direct quantitative comparisons between alkene and arene reactivity are scarce, there are clear indications of the problem. For example, the electrophilic

chlorination of benzene ($I_D = 9.23$ eV) in acetic acid proceeds slowly with a second-order rate constant of $1.54 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, whereas the chlorination of 1-butene, which is a weaker donor ($I_D = 9.63$ eV), proceeds at much faster rates even in nonpolar solvents.⁶¹ The electrophilic mercuration of benzene with Hg(OAc)₂ proceeds with a second-order rate constant of $7.5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ in acetic acid,⁶³ but 1-pentene ($I_D = 9.52$ eV) reacts with Hg(OAc)₂ at rates that are $>2 \times 10^7$ times faster than benzene in methanol.⁶⁴ Such reactivity differences and solvent effects are difficult to assess quantitatively by the conventional mechanisms of electrophilic processes.²

The charge-transfer formulation, which we have outlined in Scheme II and expressed by eq 30, provides a direct and general method for evaluating the activation barriers of electrophilic brominations. The CT transition energy ($h\nu_{CT}$) represents the energetics of ion-pair formation and serves as a model for the activation process when changes in solvation are explicitly taken into account. Thus the single correlation of the remarkable free energy relationship in Figure 8 underscores the conceptual unity of the activation process for both electrophilic addition to alkenes and electrophilic substitution of arenes. Moreover, the charge-transfer formulation of the activation process employs physical concepts amenable to direct molecular interpretation. Indeed, the notion of the solvation of ion pairs offers a general solution to solvent effects in electrophilic reactions.⁵⁰ The question of whether the adiabatic ion pairs are actually intermediates along the reaction coordinate of electrophilic brominations is of course not directly addressed in this study. However, the further development of instrumentation for time-resolved experiments will enable us to examine this important problem.

We emphasize that the charge-transfer formulation, in a more general context, relates to the electron-rich nucleophiles (such as alkenes and arenes as electron donors) and the electron-poor electrophiles (such as bromine as electron acceptors) as they were broadly envisioned by Mulliken in his pioneering approach to intermolecular interactions. We hope the availability of additional kinetic and product data in various solvents will provide further, critical tests of the generality of the CT formulation as it applies to reaction mechanisms.

Experiment Section

Materials. Bromine (Fisher Scientific Co., reagent grade containing less than 0.05% chlorine and 0.001% iodine) was refluxed over solid potassium bromide and redistilled from phosphorus pentoxide prior to use. Fresh standard solutions of bromine were carefully prepared by vacuum transfer into a dry, glass-stoppered bottle in which the solvent was introduced in the dark. The alkenes used in this study were commercially available and were redistilled from sodium prior to use. Since the rates of alkene oxidation were sensitive to diene impurities, particular care was exercised in the purification of the less reactive ones. Thus 1-pentene, 1-hexene, 1-octene, cyclohexene, and cycloheptene were further treated with maleic anhydride for a few hours to remove the dienes and redistilled from sodium. The aromatic compounds were described previously.²⁹

2,2'-Bipyridine and 1,10-phenanthroline (monohydrate) were obtained from Baker Chemical Co. and Fisher Scientific Co., respectively. All the substituted 1,10-phenanthroline ligands were obtained from G. F. Smith Chemical Co. The iron(II) complexes were prepared by adding 3 equiv of the appropriate ligand to an aqueous solution of ferrous sulfate. The perchlorate and hexafluorophosphate salts of the iron(II) complexes were precipitated with sodium perchlorate and ammonium hexafluorophosphate, respectively.^{35b} The iron(III) complexes of 2,2'-bipyridine and 1,10-phenanthroline were prepared by chlorine oxidation of an acidic aqueous solution of the sulfate salt of the corresponding iron(II) complexes. After complete oxidation, ammonium hexafluorophosphate was added, and the resultant blue precipitate was filtered. The iron(III)

(57) For the relationship between σ^* and I_D in eq 36, see ref 38a.

(58) For the relationship between σ^+ and I_D , see: (a) Gibson, H. W. *Can. J. Chem.* **1973**, *51*, 3065. (b) Thompson, M.; Hewitt, P. A.; Wooliscroft, D. S. In "Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy"; Briggs, D., Ed.; Clowes: London, 1978; Chapter 10, p 344. (c) In eq 37, σ^+_{para} values were used since they include contributions from both the resonance and inductive effects. For disubstituted benzenes, the summation of σ^+_{para} values, i.e., $\sum \sigma^+_{para}$, were used. The slope of the correlation is 0.893.²⁹

(59) For aromatic substitutions by bromine in trifluoroacetic acid, the ρ value is determined from the relation of $\log k(\text{AcOH}) = 0.986 \log k(\text{CF}_3\text{CO}_2\text{H}) - 0.62$ ($r = 0.984$)²⁹ and the ρ value in acetic acid.

(60) The agreement between the calculated and the experimental ρ values has been shown previously for various electrophiles, i.e., Hg(O₂CCF₃)₂, Br₂, and Cl₂, in aromatic substitutions.²⁹

(61) (a) Brown, H. C.; Stock, L. M. *J. Am. Chem. Soc.* **1957**, *79*, 5175. (b) Although the rate constant for the chlorination of 1-butene is not reported, the rate constant is roughly estimated to be $k > 2.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, on the basis of the fact that the reaction is complete ($100 \pm 10\%$) within 4-6 min at 264 K, with 1-butene as the solvent with 0.1 M chlorine in excess.⁶² [$2.8 \times 10^{-2} = -\ln(10/100 \times 6 \times 60 \times 0.1)$]

(62) Poutsma, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 4285.

(63) Brown, H. C.; McGary, C. W., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 2310.

(64) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783.

Table VIII. Stoichiometric Oxidation of Alkenes and Arenes by Iron(III) Complexes^a

alkene or arene	iron(III) oxidant FeL ₃ ³⁺ , ^b equiv mol ⁻¹		
	5-Cl	5-NO ₂	H
2,3-dimethyl-2-butene	2.0	2.0	1.8
2,3-dimethyl-2-hexene	2.0	2.0	
2,3-dimethyl-2-heptene	2.0	2.0	
1,4-(MeO) ₂ C ₆ H ₄		2.0	2.1
1,3-(MeO) ₂ C ₆ H ₄		2.0	2.4 ^c
1,4-MeO(Me)C ₆ H ₄	2.0	1.9	
1,2,4,5-Me ₄ C ₆ H ₂			2.1 ^c
1,2,3,4-Me ₄ C ₆ H ₂			2.0 ^c

^a In acetonitrile at 25 °C, unless indicated otherwise. ^b Numbers refer to equivalents of iron(II) product per mole of alkene or aromatic donor. 5-Cl = Fe(5-Clphen)₃³⁺, 5-NO₂ = Fe(5-O₂-Nphen)₃³⁺, H = Fe(phen)₃³⁺. ^c In trifluoroacetic acid.

complexes of substituted 1,10-phenanthrolines were prepared by oxidation of the corresponding iron(II) complexes in concentrated sulfuric acid with ceric ammonium sulfate. The perchlorate salts of the iron(III) complexes were precipitated by the careful addition of 0.1 M perchloric acid to the resultant blue solution. Acetonitrile used as a solvent for oxidation reactions was reagent-grade material obtained commercially, which was further purified by initially stirring it with calcium hydride overnight. After filtration, the acetonitrile was treated with potassium permanganate and redistilled from phosphorus pentoxide under a nitrogen atmosphere.

Spectral Measurements. Bromine has an absorption at λ_{max} 415 nm with ε_{max} 205.9 M⁻¹ cm⁻¹ in carbon tetrachloride but does not show significant absorbance in the region between 270 and 330 nm. Thus the charge-transfer absorption spectra of the alkene-bromine and the arene-bromine complexes in Table I could be conveniently measured by the procedure described previously.^{29,64}

The stoichiometric requirements of iron(III) in the oxidations of the alkenes and arenes in Tables III and IV, respectively, were measured by the spectral titration method. After the oxidation reaction was complete, the absorption spectrum of the reduced iron(II) species was found to be the same as that of authentic iron(II) complexes prepared independently (vide supra). The spectroscopic data for the iron(II) and the iron(III) complexes were described previously.^{35b} Since the rates of oxidation of many of the alkenes and arenes listed in Tables III and IV were too slow, only the most reactive compounds were chosen for the determination of the stoichiometry. The stoichiometries of some of the less reactive arenes were also determined in trifluoroacetic acid, since the oxidation rates in this solvent were fast enough to allow completion in several hours. The stoichiometries for the iron(III) oxidation of the alkenes and arenes by several iron(III) complexes are listed in Table VIII.

Evaluation of the Donor Properties of Alkenes and Arenes from Their Oxidation in Solution. The donor properties of alkenes and arenes are evaluated in the gas phase by values of their ionization potentials (I_D). In solution, the most direct measure of the donor properties is given by the standard oxidation potential (E°), which unfortunately is not experimentally accessible for most alkenes and arenes owing to irreversibility.³³ However, in an earlier study we showed that the outer-sphere oxidation can be used to evaluate E° for irreversible systems.⁶⁵ Accordingly, we next measured the rates of oxidation of these various alkene and arene donors with a series of tris(phenanthroline)iron(III) oxidants that are known to be outer-sphere reagents.³⁵

Kinetic Measurements. The rates of oxidation of the alkene and arene donors by the various iron(III) complexes were followed spectrophotometrically at 25 °C in acetonitrile solutions either by the appearance of the iron(II) bands or by the disappearance of the iron(III) bands. A stock solution of the iron(III) complex was freshly prepared in acetonitrile under argon. The reactions were carried out in a Schlenk tube equipped with a small side arm fused to a square quartz cuvette. A 3.0-mL aliquot of the stock iron(III) solution was introduced with a glass pipette, and an appropriate amount of the donor (typically 1–100 μL) was transferred into the side arm under argon. The cuvette was placed in the compartment of a Cary 14 spectrophotometer thermostated at 25 °C. After thermal equilibration for approximately 5 min, the two solutions were mixed by shaking the Schlenk cell vigorously for a few seconds. The spectrum was recorded immediately.

For less reactive donors such as cyclohexene, mesitylene, and 2-methyl-2-butene, the reactions were carried out in the presence of a large

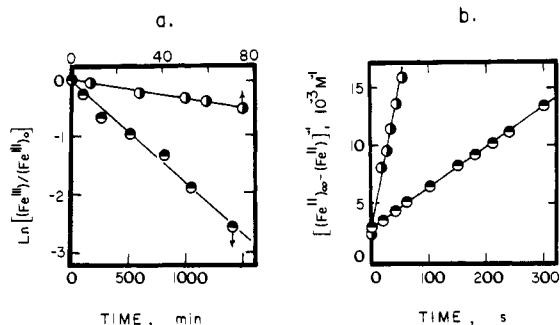


Figure 9. Typical second-order kinetics obtained in the iron(III) oxidation of alkenes and arenes in acetonitrile solution at 25 °C. (a) Under pseudo-first-order conditions according to eq 42, 2.8 × 10⁻³ M Fe(5-Clphen)₃(ClO₄)₃ with 1.4 × 10⁻² M donor: (●) 2-methyl-2-butene; (○) cycloheptene. (b) Under second-order conditions according to eq 43: (●) 3.4 × 10⁻⁴ M Fe(5-Clphen)₃(ClO₄)₃ with 1.7 × 10⁻⁴ M 2,3-dimethyl-2-hexene; (○) 4.3 × 10⁻⁴ M Fe(5-NO₂)₃(ClO₄)₃ with 2.15 × 10⁻⁴ M *p*-dimethoxybenzene.

excess of the donor. The rate of the disappearance of iron(III) is given by eq 42, as shown in Figure 9a. For the more reactive donors such as

$$\ln ([Fe^{III}] / [Fe^{III}]_0) = -2k_{Fe}[D]_0 t \quad (42)$$

the tetrasubstituted ethylenes and the dimethoxybenzenes, the reactions were carried out with equimolar amounts of iron(III) and donor. Under these second-order conditions, i.e., [Fe^{III}] = 2[D], the rate is given by eq 43. The results are shown in Figure 9b

$$([Fe^{II}]_{\infty} - [Fe^{II}])^{-1} = k_{Fe} t + [Fe^{II}]_{\infty}^{-1} \quad (43)$$

Evaluation of the Solvation Energies of Transient Donor Cations. The change in the solvation energies for alkene and arene donors attendant upon electron-transfer oxidation is given by eq 26 as the difference between the ionization potential in the gas phase and the oxidation in solution. Since the lifetime of the alkene and arene cation is very short, the free energy change (Δ*G*) was obtained by a kinetic technique utilizing the outer-sphere oxidations in acetonitrile, as described earlier.⁶⁶ The relative solvation energy (Δ*G*_r) for the alkene and aromatic donors in acetonitrile was obtained from Figure 6 and eq 28. The values of Δ*G*_r in other solvents were then evaluated relative to those in acetonitrile with the aid of the modified Born expression,^{49,66}

$$\Delta G_r^s = -\beta \left[1 - \frac{1}{\epsilon} \right] \Delta f(r_+) \quad (44)$$

The constant β is given as *Ne*²/2, Δ*f*(*r*₊) is function of the radius of the cation in solution,⁶⁷ and ε is the dielectric constant.

Accordingly, we define Δ*G*₀ as the solvation energy of the cation in acetonitrile with a dielectric constant of 37.5.⁶⁸ From eq 44, the solvation energy in this reference solvent is

$$\Delta G_0^s = -0.97\beta \Delta f(r_+) \quad (45)$$

The combination of eq 44 and 45 gives the solvation energy in a solvent of dielectric constant ε in terms of that in acetonitrile as

$$\Delta G_r^s = 1.03 \left(1 - \frac{1}{\epsilon} \right) \Delta G_0^s \quad (46)$$

The values of the solvation energies in the other solvents listed in Table VI were computed from eq 46 by using the measured value of Δ*G*₀ in acetonitrile and known values of the dielectric constants.⁶⁸

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Registry No. H₂C=CH₂, 74-85-1; H₂C=CHMe, 115-07-1; H₂C=CHEt, 106-98-9; *n*-PrCH=CH₂, 109-67-1; H₂C=CMe₂, 115-11-7; H₂C=CMe(Et), 563-46-2; C₆H₆, 71-43-2; MeC₆H₅, 108-88-3; EtC₆H₅, 100-41-4; *i*-PrC₆H₅, 98-82-8; MeOC₆H₅, 100-66-3; *o*-Me₂C₆H₄, 95-47-6; *m*-Me₂C₆H₄, 108-38-3; *p*-Me₂C₆H₄, 106-42-3; 1,3,5-Me₃C₆H₃, 108-67-8; 1,4-(MeO)₂C₆H₄, 150-78-7; 1,3-(MeO)₂C₆H₄, 151-10-0; 1,4-MeO-

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(67) The parameter Δ*f*(*r*₊) is given as (*r*₊ + *r*₊')⁻¹ where *r*₊ and *r*₊' correspond to the crystal radius of the cation and the correction factor applied to solution, respectively. In the present case, Δ*f*(*r*₊) is cancelled out in eq 46.

(68) The dielectric constants ε are given by: Koppel, I. A.; Palm, V. A. "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, Y., Ed.; Plenum Press: London, 1972, Chapter 5.

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(Me)₆C₆H₄, 104-93-8; 1,3-MeO(Me)₆C₆H₄, 100-84-5; 1,2,4,5-Me₄C₆H₂, 95-93-2; 1,2,3,4-Me₄C₆H₂, 488-23-3; Fe(5-NO₂phen)₃³⁺, 22327-24-8; Fe(5-Clphen)₃³⁺, 22327-23-7; Fe(phen)₃³⁺, 13479-49-7; Fe(4,7-Ph₂phen)₃³⁺, 53204-05-0; Fe(2,2'-bpy)₃³⁺, 18661-69-3; H₂C=CH₂·Br₂, 16489-63-7; H₂C=CHMe·Br₂, 15506-62-4; H₂C=CHEt·Br₂, 16489-65-9; *n*-PrCH=CH₂·Br₂, 16489-66-0; H₂C=CMe₂·Br₂, 6742-50-3; H₂C=CMe(Et)·Br₂, 83561-88-0; (Z)-MeCH=CHMe·Br₂, 16489-68-2; (E)-MeCH=CHMe·Br₂, 83561-87-9; (E)-MeCH=CH(t-Bu)·Br₂, 77836-23-8; *t*-BuCH=CH₂·Br₂, 77836-22-7; Me₂C=CMe(Et)·Br₂, 52766-91-3; Me₂C=CMe₂·Br₂, 16489-45-5; Me₂C=CMe(*n*-Pr)·Br₂,

52766-93-5; Me₂C=CMe(*n*-Bu)·Br₂, 52766-95-7; C₆H₆·Br₂, 6142-76-3; MeC₆H₅·Br₂, 16734-75-1; EtC₆H₅·Br₂, 78716-30-0; *i*-PrC₆H₅·Br₂, 78716-47-9; MeOC₆H₅·Br₂, 78716-58-2; *o*-Me₂C₆H₄·Br₂, 16840-57-6; *m*-Me₂C₆H₄·Br₂, 78716-66-2; *p*-Me₂C₆H₄·Br₂, 78716-71-9; 1,3,5-Me₃C₆H₃·Br₂, 78717-12-1; Me₆C₆·Br₂, 78717-25-6; cyclohexene·Br₂, 16489-73-9; 2,3-dimethyl-2-heptene, 3074-64-4; 2,3-dimethyl-2-hexene, 7145-20-2; 2,3-dimethyl-2-pentene, 10574-37-5; 2,3-dimethyl-2-butene, 563-79-1; 3-ethyl-3-hexene, 16789-51-8; 2-methyl-2-butene, 513-35-9; cycloheptene, 628-92-2; cyclohexene, 110-83-8; 4,4-dimethyl-2-pentene, 26232-98-4; 1-octene, 111-66-0.

Syntheses of Polycyclic Ring Systems Based on the New Generation of *o*-Quinodimethanes

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Abstract: A mild and efficient generation of *o*-quinodimethane intermediates, in which fluoride anion is simply added to [*o*-[α -(trimethylsilyl)alkyl]benzyl]trimethylammonium halides at room temperature, and their inter- and intramolecular Diels–Alder reactions leading to polycycles are described in detail. The starting [*o*-[α -(trimethylsilyl)alkyl]benzyl]trimethylammonium halides are readily prepared via alkylation of the silicon-stabilized benzyl carbanion of [*o*-((trimethylsilyl)methyl)benzyl]-dimethylamine. Of interest is that the 1,4 elimination of a diastereoisomeric mixture of [α -[*o*-[α -(trimethylsilyl)alkyl]-phenyl]alkyl]trimethylammonium halides generates (*E,E*)- α,α' -dialkyl-*o*-quinodimethanes selectively. But the 1,4 elimination of [4-(trimethylsilyl)-1,2,3,4-tetrahydronaphth-1-yl]trimethylammonium halide proceeds as well, producing (*Z,Z*)- α,α' -disubstituted-*o*-quinodimethane, i.e., 2,3-dihydronaphthalene. Moreover, [2-(trimethylsilyl)-3-picol-3-yl]trimethylammonium bromide is treated with fluoride anion to generate a pyridine analogue of *o*-quinodimethane, of which inter- and intramolecular cycloadditions produce N-containing polycycles. Finally, on the basis of the new generation of *o*-quinodimethane intermediates, stereoselective synthesis of steroidal structures such as estrone methyl ether, 4-methoxyestra-1,3,5(10)-trien-17-one, and 6 β -methyl-estra-1,3,5(10)-trien-17-one is achieved.

The intramolecular Diels–Alder reaction has been widely used as a key step in the stereocontrolled construction of complex frameworks. *o*-Quinodimethane as an enophile in the Diels–Alder reaction is very reactive, because of the restoration of aromaticity on the cycloaddition, and has been utilized for the synthesis of polycyclic ring systems that are otherwise difficult to prepare. Especially the successful applications of the *o*-quinodimethane intermediate for the syntheses of steroid and alkaloid structures having an aromatic A ring have profoundly aroused the interest of synthetic organic chemists.

Since the existence of this elusive *o*-quinodimethane species was first recognized by Cava^{1a} in 1957, a variety of methodologies for the generation of *o*-quinodimethanes have been developed.^{1–3} Those methodologies may be differentiated by their applicabilities to the syntheses of steroidal structures, e.g., estrone, that require an efficient generation of appropriately α -substituted-*o*-quinodimethanes, of which precursors are prepared via a regiocontrolled carbon–carbon bond formation. The intramolecular Diels–Alder reaction with *o*-quinodimethanes generated by thermal electrocyclic ring-opening of benzocyclobutene precursors has so far found wide applications in construction of various complex molecules including steroids⁴ and alkaloids.⁵ Elegant preparations of ap-

propriately substituted benzocyclobutenes by cobalt-catalyzed cotrimerization of acetylene derivatives⁶ have made the benzocyclobutene methodology more attractive. But the generation of *o*-quinodimethanes by the ring-opening of benzocyclobutenes as well as cheletropic desulfurization from 1,3-dihydrobenzo[*c*]thiophene-2,2-dioxides⁷ needs relatively higher temperature, around 200 °C, although it is not a serious drawback.

In the previous communications,⁸ we described a mild and efficient generation of *o*-quinodimethane intermediates, in which fluoride anion is simply mixed with [*o*-[α -(trimethylsilyl)alkyl]benzyl]trimethylammonium halides at ambient temperature and its application to the estrone synthesis. Herein, we give full details of polycycle synthesis on the basis of our methodology of *o*-quinodimethane generation.

Results and Discussions

Preparations of Precursors for Generation of *o*-Quinodimethane Intermediates. The new method for the generation of *o*-quino-

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