Electron Transfer from Aromatic Hydrocarbons and Their π-Complexes with Metals. Comparison of the Standard Oxidation Potentials and Vertical Ionization Potentials

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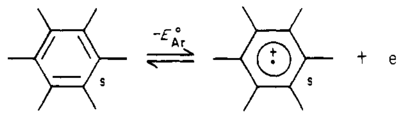
Abstract: The energetics of electron transfer from an extensive series of alkyl-substituted benzenes are measured both in solution and in the gas phase. The standard oxidation potentials $E_{\mathrm{Ar}}°$ stem from the reversible cyclic voltammograms (CV) in trifluoroacetic acid using the recently developed microvoltammetric electrodes. These values show an excellent correlation with the vertical ionization potentials I_{p} of the same aromatic hydrocarbons in the gas phase. Thermochemical analysis indicates that the slope of less than unity for the correlation arises mainly from solvation differences, particularly in the highly substituted polyalkylbenzenes. The values of $E_{\mathrm{Ar}}°$ also correlate extremely well with the anodic peak potentials E_{p} of the irreversible cyclic voltammograms, which can be readily measured in acetonitrile at a standard sweep rate. A slope of unity for the linear correlation is discussed in terms of the maximum error in the CV peak shift ($E_{\mathrm{p}} - E°$) resulting from the electrochemical kinetics of the EC mechanism for arene oxidation. The correlation of $E_{\mathrm{Ar}}°$ and E_{p} affords a prediction of the standard oxidation potential of benzene, which otherwise could not be measured directly. The same series of alkylbenzenes form stable π-complexes with chromium tricarbonyl that show reversible electrochemical behavior. The standard oxidation potentials $E_{\mathrm{ArCr}}°$ of the complexes also correlate very well with $E_{\mathrm{Ar}}°$ of the free arene. The diminished slope of the correlation arises from the nonbonding character of the HOMO. The predicted value of $E_{\mathrm{Ar}}°$ for benzene from this relationship is in reasonable agreement with that obtained from the irreversible peak potentials.

Aromatic hydrocarbons as a class of organic compounds participate in the widest variety of reaction types and mechanisms—encompassing the range of heterolytic (electrophilic, nucleophilic) and homolytic (free radical) substitutions, additions, and eliminations.[1] Although less established among organic chemists, electron transfer to and from aromatic hydrocarbons to form such reactive intermediates as arene anion radicals and cation radicals, respectively, does play a nonetheless important part in various reductive and oxidative processes.[2,3] The quantitative evaluation of the feasibility of electron transfer in such situations depends crucially on the knowledge of the standard redox potentials $E°$ of both reactants.[4,5] Thus the assessment of electron transfer in the reactions of aromatic compounds ArH with electrophiles and oxidants requires values of the standard oxidation potentials $E_{\mathrm{Ar}}°$ for



(1)

where the subscript s refers to the solvated species. (Since most organic reactions are carried out in nonaqueous media, s usually refers to solvents such as acetonitrile, trifluoroacetic acid, etc.)

Electrochemical methods offer the most direct access to oxidation potentials, and among the readily available techniques, cyclic voltammetry (CV) is the simplest and the most convenient to use, particularly in organic solvents. When the electron transfer in eq 1 is reversible, the cyclic voltammogram consists of anodic and cathodic waves with current maxima of equal magnitudes at potentials $E_{\mathrm{p}}^{\mathrm{a}}$ and $E_{\mathrm{p}}^{\mathrm{c}}$, respectively, and $E_{\mathrm{Ar}}° \cong (E_{\mathrm{p}}^{\mathrm{a}} + E_{\mathrm{p}}^{\mathrm{c}})/2$.[6,7] Unfortunately with the exception of highly condensed polycyclic and very electron-rich systems, the cyclic voltammograms of most aromatic compounds exhibit irreversible behavior at sweep rates <100 V s^{-1}.[8] This is shown by the absence of the cathodic component on the return potential sweep, largely owing to competition from fast follow-up reactions of the metastable arene cation radicals. With standard CV instrumentation, thermodynamic data cannot be obtained therefore if the arene cation radical has a lifetime less than ~100 μs.[9] As a result, the $E°$ values of the common benzene derivatives are absent in the extant literature.[4,7,10]

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(1) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981.

(2) (a) Beletskaya, I. P.; Makhon'kov, D. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 1007. (b) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, II-197. Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

(3) Sheldon, R. A.; Kochi, J. K. "Metal Catalyzed Oxidation of Organic Compounds"; Academic Press: New York, 1981.

(4) See: Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(5) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966; *Ibid.* **1965**, *43*, 679; *J. Phys. Chem.* **1968**, *72*, 891 and ref 2a.

(6) (a) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods. Fundamentals and Applications"; Wiley: New York, 1980. (b) In cyclic voltammetry, the measured value of $E° = (E_{\mathrm{p}}^{\mathrm{a}} + E_{\mathrm{p}}^{\mathrm{c}})/2$ obtained from an electrochemically reversible wave is related to the standard oxidation potential $E°'$ by the relationship $E° = E°' + (RT/\mathcal{F})\ln\{(\gamma_{\mathrm{o}}/\gamma_{\mathrm{r}})(D_{\mathrm{r}}/D_{\mathrm{o}})^{1/2}\}$, where γ_{o}, γ_{r}, D_{o}, and D_{r} are respectively the activity coefficients and diffusion coefficients of the oxidized and reduced species.[6] Since the latter appear as ratios, the term in brackets is usually close to unity. Thus equating $E°$ to $E°'$ can lead to an error of only a few millivolts, which is less than the experimental uncertainty in the determinations of $E_{\mathrm{p}}^{\mathrm{a}}$ and $E_{\mathrm{p}}^{\mathrm{c}}$. When the CV wave is not electrochemically reversible (i.e., $i_{\mathrm{p}}^{\mathrm{a}}/i_{\mathrm{p}}^{\mathrm{c}} > 1$ or $\Delta E_{\mathrm{p}} > 60$ mV), the error will also be small provided the transfer coefficient $\alpha \sim 0.5$ and/or $\Delta E_{\mathrm{p}} < 100$ mV. Furthermore, when both the anodic and cathodic waves are visible as in this study, the standard oxidation potential must lie within the interval $(E_{\mathrm{p}}^{\mathrm{c}} + 30\ \mathrm{mV}) \leqslant E°' \leqslant (E_{\mathrm{p}}^{\mathrm{a}} - 30\ \mathrm{mV})$. See: Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(7) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. Note that in this paper the $E°$ was measured only for polycyclic aromatics with more than two rings.

(8) Meites, L.; Zuman, P. "CRC Handbook Series in Organic Electrochemistry"; CRC Press: Cleveland, 1975, Vol. I, II. Meites, L.; Zuman, P.; Rupp, E. B. *Ibid.* Vol. III–V.

(9) (a) In cyclic voltammetry, the observation of a reversible CV wave at a given scan rate v requires that the half-life $t_{1/2}$ of the electrogenerated intermediate is $t_{1/2} \gtrsim 10^{-2}v^{-1}$, where $t_{1/2}$ is in s and v in V s^{-1}. (Nadjo, L.; Savêant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113.) Taking 100 V s^{-1} as the maximum value of v normally available with standard electrochemical equipment leads to $t_{1/2} > 0.1$ ms. (b) However, the use of redox catalysis can overcome the built-in limitations of transient electrochemical techniques (see, for example: Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savêant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431).

(10) For some exceptions, see ref 74 in: Eberson, L.; Jönsson, L.; Wistrand, L.-G. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 520. Reference 11.

(11) Neikam, W. C.; Dimeler, G. R.; Desmond, M. M. *J. Electrochem. Soc.* **1964**, *111*, 1190.

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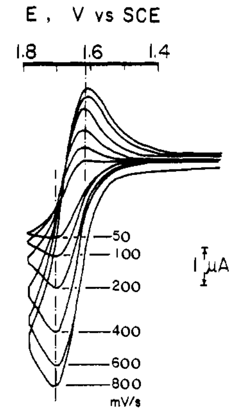


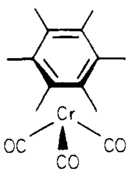
Figure 1. Reversible cyclic voltammogram of 1.0×10^{-3} M hexaethylbenzene at a scan rate varying from 50 to 800 mV s^{-1} in acetonitrile containing 0.1 M TEAP at 25 °C.

The recent development of microvoltammetric electrodes, by Wightman and co-workers in these laboratories,[12] has allowed cyclic voltammograms to be recorded at sweep rates exceeding 10 000 V s^{-1}. Voltammograms can be obtained with minimal distortion of the CV wave arising from uncompensated ohmic drop and capacitive effects, both of which are particularly limiting in nonaqueous solvents of use for organic compounds. More relevant to our interest here is the utility of microvoltammetric electrodes to facilitate voltammetric measurements on the microsecond time scale required to intercept the transient radical cations of the benzene derivatives.

We wish to report the measurement of the standard oxidation potentials of an extensive series of alkyl- and polyalkylbenzenes with the microvoltammetric technique. Concurrently we have measured the vertical ionization potentials I_P of the same series of aromatic hydrocarbons from their He(I) photoelectron spectra.[13] Since the ionization potentials are measured for the gas-phase process, i.e.,

$$\mathrm{ArH} \xrightarrow{I_P} \mathrm{ArH}^{+\cdot} + e \qquad (2)$$

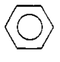
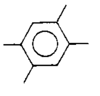
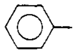
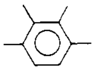
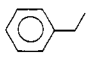
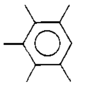
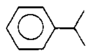
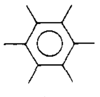
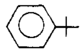
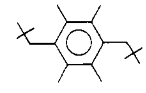
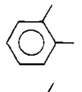
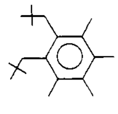
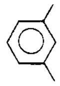
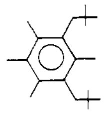
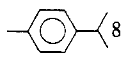
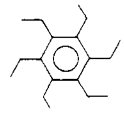
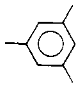
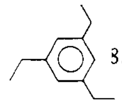
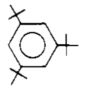
a direct comparison with the $E°$ values allows solvation effects to be assessed.[7,14] The availability of the standard oxidation potentials also allowed us to examine the correlation with (i) the anodic peak potentials of aromatic hydrocarbons obtained under irreversible CV conditions and (ii) the oxidation potentials of aromatic hydrocarbons when they are π-complexed to metal centers, e.g.,



Results

I. Cyclic Voltammetry of Aromatic Hydrocarbons in Acetonitrile. The cyclic voltammogram of hexaethylbenzene in acetonitrile (containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte) is reversible[15] at a platinum electrode, as shown in Figure 1 for scan rates varying from 0.05 to 0.8 V s^{-1}. (The CV waves corresponded to a one-electron process as in eq 1, on the basis of the calibration with ferrocene.) However, the cyclic voltammetric behavior of hexaethylbenzene is unusual, since other aromatic hydrocarbons including even the closely related hexamethylbenzene under the same conditions showed no cathodic wave on the return scan at rates as high as 10 V s^{-1}. Interestingly, the anodic peak potentials $E_p{}^a$ (measured at a constant sweep rate of 0.1 V s^{-1}) of the irreversible CV waves do vary systematically with the corresponding ionization potentials for the various aromatic hydrocarbons listed in Table I.

Table I. Structural Variations of the Anodic Peak Potentials in the Irreversible Cyclic Voltammograms of Aromatic Hydrocarbons in Acetonitrile,[a] Comparison with the Vertical Ionization Potentials in the Gas Phase

no.	arene	I_P, eV	$E_p{}^a$, V vs. NHE[b]	no.	arene	I_P, eV	$E_p{}^a$, V vs. NHE[b]
0		9.23	2.86	19		8.05	2.03
1		8.82	2.49	20		8.14	2.00
2		8.77	2.51	22		7.92	1.95
4		8.71	2.56	23		7.85	1.82
5		8.65	2.45	24		7.71	1.80
7		8.56	2.40	25		7.66	1.71
8		8.56	2.35	26		7.72	1.79
9		8.29	2.33	27		7.71	1.95
12		8.42	2.26				
15		8.32	2.24				
18		8.19	2.20				

[a] Containing 0.1 M tetramethylammonium perchlorate at 25 °C and at a constant sweep rate of 100 mV s^{-1}. [b] Peak potentials measured in V vs. SCE and converted to V vs. NHE by the relationship: $E(\mathrm{NHE}) = E(\mathrm{SCE}) + 0.24$ V.

II. Cyclic Voltammetry of Aromatic Hydrocarbons in Trifluoroacetic Acid. Arene cation radicals are known to be significantly more persistent in acidic media such as sulfuric and trifluoroacetic acids.[15b,16] Indeed the cyclic voltammogram of hexamethylbenzene showed signs of reversibility at scan rates of 10 V s^{-1} at a platinum electrode in trifluoroacetic acid containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP).[17] Penta-

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(12) (a) For a background review, see: Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1125A. (b) Howell, J. O.; Wightman, R. M., unpublished results.

(13) (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules", Halstead Press: New York, 1981. (b) Klasinc, L.; Kovač, B.; Gusten, H. *Pure Appl. Chem.* **1983**, *55*, 289.

(14) See: Peover, M. E. *Electroanal. Chem.* **1967**, *2*, 1. Case, B. In "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Wiley: New York, 1971; p 25. Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1965**, *25*, 231.

(15) (a) Parker, V. D. *J. Electroanal. Chem.* **1969**, *21*, App 1-3. (b) Fritz, H. P.; Artes, R. O. *Electrochim. Acta* **1981**, *26*, 417.

(16) See: Kaiser, E. T., Kevan, L., Eds. "Radical Ions"; Wiley: New York, 1968. Hammerich, O.; Moe, N. S.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1972**, 156. Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

(17) The solvent actually consisted of trifluoroacetic acid with 5-7 vol % trifluoroacetic anhydride, but it is hereafter referred to simply as trifluoroacetic acid. The CV experiments were less reproducible in the absence of trifluoroacetic anhydride, presumably arising from the presence of variable amounts of adventitious water.

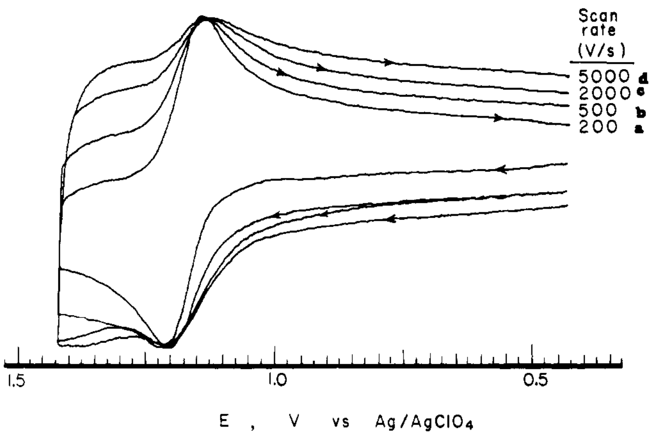

Figure 2. Cyclic voltammograms of 1 × 10^{-3} M hexaethylbenzene in trifluoroacetic acid containing 0.5 M TBAP at a gold microelectrode at sweep rates of (a) 200, (b) 500, (c) 2000, and (d) 5000 V s^{-1}. Note the cyclic voltammograms are normalized in amplitude to the sweep rate.

Table II. Cyclic Voltammetry of Hexaethylbenzene with Gold Microelectrodes in Trifluoroacetic Acid[a]

v, V s^{-1}	E_p^a	E_p^c	ΔE_p	$E_{Ar}°$
200	1.867	1.796	71	1.831
300	1.868	1.798	70	1.833
500	1.870	1.800	70	1.834
1000	1.870	1.797	73	1.833
2000	1.867	1.797	70	1.832
3000	1.872	1.792	80	1.832
5000	1.876	1.793	83	1.834

[a] Containing 7 vol % trifluoroacetic anhydride and 0.1 M tetra-*n*-butylammonium perchlorate. See also ref 17. Peak potential measured in V vs. Ag/Ag/ClO$_4$ at 25 °C and converted to V vs. NHE by the relationship $E(\mathrm{NHE}) = E(\mathrm{Ag/AgClO_4}) + 0.66$ V.

methylbenzene and durene exhibited similar reversibility under these conditions,[15b] but mesitylene required a scan rate of 20 V s^{-1} before the cathodic wave could be observed on the return potential sweep. However, at these high scan rates, problems associated with uncompensated ohmic drop and capacitive effects in the trifluoroacetic acid solvent became severe. We thus resorted to a microelectrode consisting of a 13-μm gold disc embedded in glass for the microvoltammetric studies.[12] The cyclic voltammograms of hexaethylbenzene in trifluoroacetic acid under these conditions is shown in Figure 2a–d at sweep rates progressively increasing from 200 to 5000 V s^{-1}. Even over this extensive span of scan rates, the charging current represented less than 25% of the total peak current, and the CV peaks were broadened only slightly. More relevant to our interest here, the values of the peak separation $\Delta E_p = E_p^a - E_p^c$ and the oxidation potential $E_{Ar}°$ both remained strikingly invariant over more than two decades in the sweep rates v, as listed in Table II.

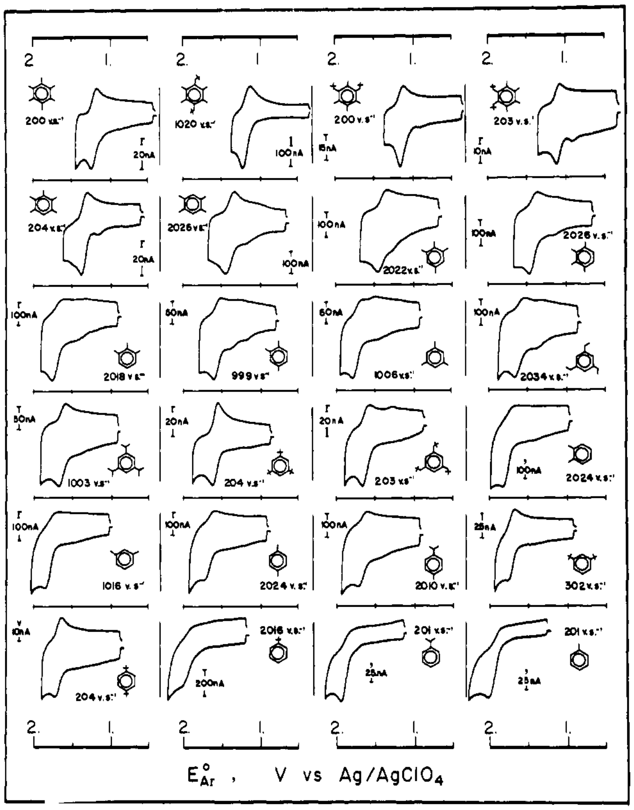

Figure 3. Typical cyclic voltammograms of various polyalkylbenzenes (~10^{-3} M) in trifluoroacetic acid at a gold microelectrode. The numbers refer to sweep rates in volts per second. (For the presence of the minor peaks prior to the anodic wave of ArH in some cyclic voltammograms, see the Experimental Section.)

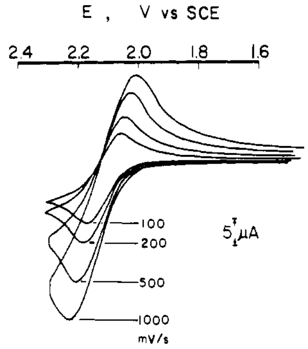

Figure 4. Cyclic voltammograms at various sweep rates of 5 × 10^{-3} M *p*-di-*tert*-butylbenzene at a conventional platinum electrode (ϕ = 1 mm) in trifluoroacetic acid containing 5 vol % trifluoroacetic anhydride and 0.1 M TBAP.

Some representative cyclic voltammograms obtained with the gold microelectrodes are presented in Figure 3 for the various polyalkylbenzenes listed in Table III. Examination of these cyclic voltammograms, a seriatim, reveals several interesting trends. First, the values of $E_{Ar}°$ progressively decrease with increasing numbers of alkyl substituents—the difference between hexamethylbenzene and toluene being more than 700 mV. Alkyl groups are not strongly differentiated insofar as their effect on $E_{Ar}°$ is concerned. Thus the fully alkylated benzenes such as hexaethylbenzene, the three isomeric dineopentyltetramethylbenzenes, and hexamethylbenzene all have values of $E_{Ar}°$ that are invariant to within ±50 mV. The same is essentially true for the series of 1,3,5-trisubstituted benzenes with methyl, ethyl, isopropyl, *tert*-butyl, and neopentyl groups. Second, the chemical reversibility of the cyclic voltammograms (as indicated by the ratio of the cathodic and anodic peak currents i_p^c/i_p^a at a given scan rate),[18] generally parallels the magnitude of $E_{Ar}°$, being the most reversible for the highly alkylated benzenes. However, the nature of the substituents plays a dominant role in determining such a reversibility. Let us consider the related series of 1,3,5-trialkylbenzenes. For mesitylene, the cathodic peak on the return potential scan is only observable at sweep rates >20 V s^{-1}. The same is also true for the cyclic voltammograms of 1,3,5-triethyl-, 1,3,5-triisopropyl-, and 1,3,5-trineopentylbenzenes, which all show reversibility only at v > 20 V s^{-1} in trifluoroacetic acid. By contrast, the cyclic voltammogram of 1,3,5-tri-*tert*-butylbenzene is reversible at scan rates as low as 0.05 V s^{-1}, and furthermore

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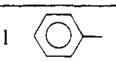
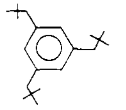
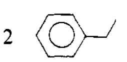
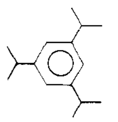
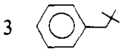
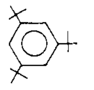
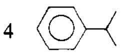
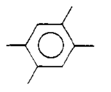
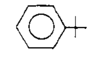
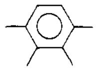
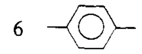
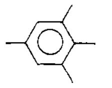
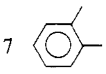
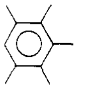
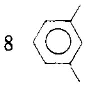
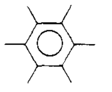
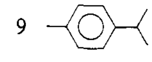
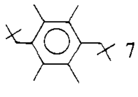
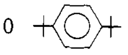
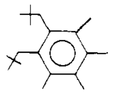
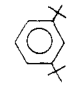
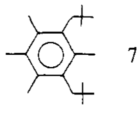
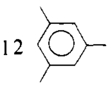
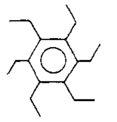
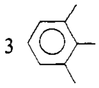
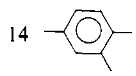
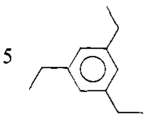
[18] Note the cyclic voltammograms in Figure 3 are not recorded at the same sweep rates.

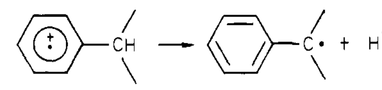
[19] Compare with $E°$ values most commonly used in the literature (2.61 V vs. NHE for toluene, 2.03 V for durene and 1.85 V for hexamethylbenzene). See, e.g., ref 4 and: Eberson, L.; Jonsson, L.; Wistrand, L.-G. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 520.

Table III. Standard Oxidation Potentials of Alkylbenzenes in Trifluoroacetic Acid[a]

no.	ArH	I_p, eV	$E_{Ar}°$, V vs. NHE[b]	no.	ArH	I_p, eV	$E_{Ar}°$, V vs. NHE[b]
1		8.82	2.64[19]	16		8.17	2.27
2		8.77	2.51	17		8.24	2.23
3		8.60	2.51	18		8.19	2.25
4		8.71	2.53	19		8.05	2.07[19]
		8.65	2.56	20		8.14	2.06
6		8.44	2.30	21		8.07	2.07
7		8.56	2.37	22		7.92	1.99
8		8.56	2.38	23		7.85	1.86[19]
9		8.29	2.29	24		7.71	1.84
10		8.28	2.27	25		7.66	1.75
11		8.43	2.37	26		7.72	1.82
12		8.42	2.35	27		7.71	1.83
13		8.42	2.23				
14		8.27	2.13				
15		8.32	2.23				

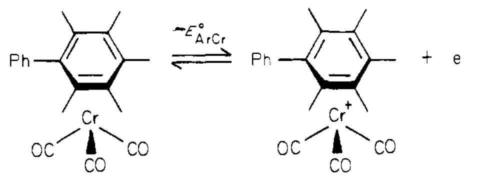
[a] Containing 7 vol % trifluoroacetic anhydride and 0.1 M tetra-*n*-butylammonium perchlorate at 25 °C. [b] Potentials measured in V vs. Ag/AgClO$_4$ obtained at scan rates between 200 and 10 000 V s^{-1} at a gold microelectrode and converted to V vs. NHE by the relationship E(NHE) = E(Ag/AgClO$_4$) + 0.66 V.

it is reversible even in acetonitrile at 0.2 V s^{-1}. The CV reversibility of alkylbenzenes is unique to the *tert*-butyl substituent since di-*tert*-butylbenzene (both meta and para isomers) affords well-characterized cathodic waves at $v < 0.1$ V s^{-1} in trifluoroacetic acid (Figure 4), where none of the other dialkylbenzenes show any signs of reversible CV behavior. It is also noteworthy that a reversible cyclic voltammogram of *tert*-butylbenzene can actually be observed at sweep rates less than 10 V s^{-1} in trifluoroacetic acid. We associate the unique CV behavior of the *tert*-butylbenzenes to the absence of α-protons, the loss of which is known to lead to the shortening of the lifetime of many arene cation radicals,[15,20] i.e.,

 (3)

Such an explanation is also consistent with the remarkable persistence of the hexaethylbenzene cation radical in Figure 1. Loss of the α-protons in this cation–radical is slow owing to the unfavorable conformation of the C–H$_\alpha$ bonds, which stems from steric crowding of the ethyl substituents.[15,21] Proton loss is also an important factor in favoring the reversible CV behavior of aromatic hydrocarbons in trifluoroacetic acid relative to that in acetonitrile (which is a significantly stronger base and nucleophile).[22]

III. Cyclic Voltammetry of Aromatic Hydrocarbons π-Complexed to Chromium Tricarbonyl. Aromatic hydrocarbons form π-complexes with chromium tricarbonyl which are known to be susceptible to oxidation, typically decomposing in solution upon exposure to air.[23] The oxidative electrochemistry of arenetricarbonylchromium(0) (ArH)Cr(CO)$_3$ proceeds by one-electron processes.[24] Indeed Rieke and co-workers[25] have recently demonstrated that the cyclic voltammograms of the biphenyl complex η^6-(C$_6$H$_5$)$_2$Cr(CO)$_3$ is reversible in trifluoroacetic acid, i.e.,

 (4)

The cation radical was so persistent under these conditions that the current ratio i_p^c/i_p^a was unity even at scan rates as low as 0.02 V s^{-1}. Of interest to our studies is the observation of a reversible cyclic voltammogram of the benzene complex (C$_6$H$_6$)Cr(CO)$_3$ with $E° = 0.79$ V. This oxidation potential is certainly more than a volt less positive than that of the uncomplexed benzene ligand.[26]

The availability of a wide variety of arene complexes of chromium tricarbonyl[27] offers the opportunity to examine their oxidation potentials in the light of $E_{Ar}°$ for the free arene ligands reported in Table III. In accord with Rieke's studies, we find the cyclic voltammograms of the various arene complexes η^6-(ArH)Cr(CO)$_3$ listed in Table IV to be consistently reversible at scan rates as low as 0.05 V s^{-1}. In each case, the proton NMR studies showed that the arene complex was stable in this medium

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(20) See: Bewick, A.; Mellor, J. M.; Pons, B. S. *Electrochim. Acta* **1980**, *25*, 931.

(21) (a) See: Onopchenko, A.; Schulz, J. G. D.; Seekircher, R. *J. Org. Chem.* **1972**, *37*, 1414 and ref 26, p 123f. (b) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

(22) Arene cation radicals also react readily with nucleophiles to afford nuclear substitution products. See: Eberson, L.; Nyberg, K. *Acc. Chem. Res.* **1973**, *6*, 106. Kochi, J. K.; Tang, R. T.; Bernath, T. *J. Am. Chem. Soc.* **1973**, *95*, 7114.

(23) See, e.g.: Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

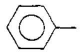
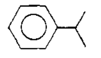
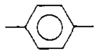
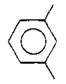
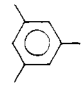
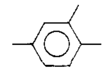
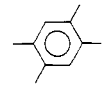
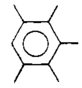
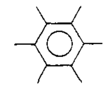
(24) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768. Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

(25) Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* **1983**, *22*, 987.

(26) Estimated to be 2.9 V vs. NHE in this study (vide infra). Note that a value of 3.03 V vs. NHE is reported in ref 4; this value was, however, estimated from an irreversible CV wave in ref 7 and is incorrectly reported as a measured $E°$ in ref 4 and: Eberson, L. *Acta. Chem. Scand., Ser. B* **1978**, *B32*, 237.

(27) (a) Nicholls, B.; Whiting, M. C. *Proc. Chem. Soc.* (*London*) **1958**, 152; (b) *J. Chem. Soc.* **1959**, 551. (c) Jackson, W. R.; Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1960**, 469. (d) Van Meurs, F.; Van der Toorn, J. M.; Van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 341. (e) Razuvaev, G. A.; Kuzvetsov, V. A.; Egorochkin, A. N.; Klimov, A. A.; Artemov, A. N.; Sirotkin, N. I. *J. Organomet. Chem.* **1977**, *128*, 213. (f) Price, J. T.; Sorensen, T. S. *Can. J. Chem.* **1968**, *46*, 515. See also: Sneeden, R. P. E. "Organochromium Compounds"; Academic Press: New York, 1975; p 19ff. Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 48. Atwood, J. D. *J. Organomet. Chem.* **1980**, *196*, 79.

Table IV. Standard Oxidation Potentials of Aromatic Hydrocarbons π-Complexed to Chromium Tricarbonyl[a]

no.	$(ArH)Cr(CO)_3$ ArH	$E_p{}^a$	$E_p{}^c$	$E_{ArCr}{}^\circ$
0		1.11	1.06	1.08_5
1'		1.10	1.02	1.06_0
4'		1.09	1.02	1.05_5
6'		1.06	0.99	1.02_0
8'		1.06	1.00	1.03_0
12'		1.04	0.98	1.01_0
14'		1.03	0.95	0.99_0
19'		0.99	0.92	0.95_5
22'		0.98	0.91	0.94_5
23'		0.98	0.89	0.93_5

[a] In trifluoroacetic acid containing 0.1 M tetra-*n*-butylammonium perchlorate at 25 °C. Potentials refer to V vs. NHE; these values are obtained according to the relationship $E(\mathrm{NHE}) = E(\mathrm{SCE}) + 0.24$ V, from the experimental potentials V vs. SCE.

(see Experimental Section). Even the most electron-rich arene hexamethylbenzene showed no signs of complications arising from either protonation or protonolysis by the acidic solvent.

Discussion

The separate measurements of electron transfer have provided in Tables I–III the reversible $E_{Ar}{}^\circ$ and the irreversible E_p in solution and the vertical I_p in the gas phase of a common series of aromatic hydrocarbons. Such results also relate to the determination of $E_{ArCr}{}^\circ$ (Table IV) for the corresponding arenes that are π-complexed to chromium tricarbonyl. The availability of these energetics encourages us now to examine the interrelationship among the various measures for effecting electron detachment.

I. Relationship between $E_{Ar}{}^\circ$ and I_p of Aromatic Hydrocarbons. The correlation of the standard oxidation potentials $E_{Ar}{}^\circ$ of the aromatic hydrocarbons in trifluoroacetic acid with the ionization potentials I_p in the gas phase is shown in Figure 5. The line in the graph describes the relationship

$$E_{Ar}{}^\circ = 0.71 I_p - 3.68 \tag{5}$$

where $E_{Ar}{}^\circ$ is given in volts vs. the $Ag/AgClO_4$ standard electrode, and I_p is given in electron volts. The correlation coefficient of 0.975 is sufficiently high (especially since it includes 27 compounds) to ensure the validity of a linear correlation between $E_{Ar}{}^\circ$ and I_p to a confidence level of >99.9%. However, a slope of considerably less than unity indicates that the energetics of the gas-phase ionization are not completely mirrored in the solution oxidation. In particular, the contribution from solvation is implicit in the values of $E_{Ar}{}^\circ$ whereas it is not in the values of I_p. Furthermore values of the vertical I_p do not include the reorganization energy of the arene cation radical, which is known to undergo a Jahn–Teller distortion.[28,29]

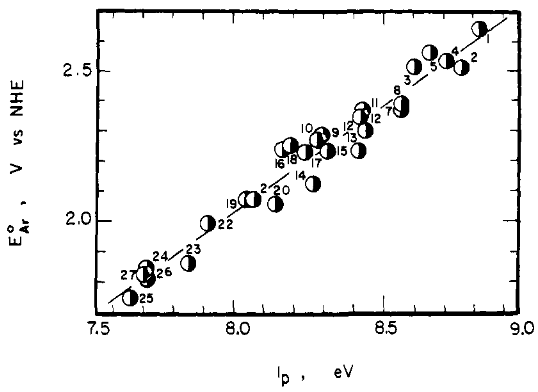


Figure 5. Correlation of the standard oxidation potentials $E_{Ar}{}^\circ$ (volts vs. $Ag/AgClO_4$) of various alkylbenzenes with the vertical ionization potentials I_p. Numbers refer to aromatic hydrocarbons identified in Table III.

The difference in free energy ($\Delta G_s{}^\circ$) associated with solvation changes may be expressed as

$$\Delta G_s{}^\circ = [(G_{Ar^+}{}^\circ)_s - (G_{Ar}{}^\circ)_s] - [(G_{Ar^+}{}^\circ)_g - (G_{Ar}{}^\circ)_g] \tag{6}$$

where the subscripts g and s refer to the gas phase and solvation states. Correspondingly, the standard oxidation potential is

$$E_{Ar}{}^\circ = (1/\mathcal{F})\{\Delta G_s{}^\circ + [(G_{Ar^+}{}^\circ)_g - (G_{Ar}{}^\circ)_g]\} + C \tag{7}$$

where $\mathcal{F}$ is the faraday constant and C is a constant determined by the particular working electrode and reference electrode. Under the same circumstances, the vertical ionization potential is

$$I_p = (1/\mathcal{F})\{(G_{Ar^{+\bullet}}{}^\circ)_g - (G_{Ar}{}^\circ)_g\} \tag{8}$$

where $(G_{Ar^{+\bullet}}{}^\circ)_g$ is the free energy of formation of the arene cation radical in the unrelaxed state in which it has the same nuclear coordinates as those in the neutral arene. The combination of eq 7 and 8 yields

$$E_{Ar}{}^\circ = I_p + [(\Delta G_r{}^\circ + \Delta G_s{}^\circ)/\mathcal{F}] + C \tag{9}$$

where $\Delta G_r{}^\circ$, the reorganization energy of $ArH^{+\bullet}$, represents the difference $(G_{Ar^+}{}^\circ)_g - (G_{Ar^{+\bullet}}{}^\circ)_g$. Comparison of eq 9 with the experimental relationship in eq 5 indicates that $(\Delta G_r{}^\circ + \Delta G_s{}^\circ)$ cannot be considered as a constant term for the series of arenes under consideration. Instead it varies with I_p of $E_{Ar}{}^\circ$, as given by the combination of eq 5 and 9, i.e.,

$$\Delta G_r{}^\circ + \Delta G_s{}^\circ = -0.29\mathcal{F} I_p + C' \tag{10}$$

where $C' = 4.1 + C$. Such a relationship implies that $(\Delta G_r{}^\circ + \Delta G_s{}^\circ)$ decreases by about 7 kcal mol^{-1} in covering the gamut of aromatic hydrocarbons from hexaethylbenzene to toluene at the extremes.[30] Interestingly this trend also parallels the structural changes of increasing size of the arene moiety resulting from polyalkyl substitution. Since size is an important factor in solvation energies,[31] the deviation of the slope in Figure 5 from unity may well represent variations of mainly $\Delta G_s{}^\circ$.[32]

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[28] Nakajima, T.; Toyota, A.; Kataoka, M. *J. Am. Chem. Soc.* **1982**, *104*, 5610.

[29] Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 320.

[30] The effect is largely due to contributions from the arene cation radicals since solvation energies of the neutral species are small. See: Lofti, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2137. Abraham, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085.

[31] For example, consider the evaluation of solvation energies using the Born model: (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 56ff.

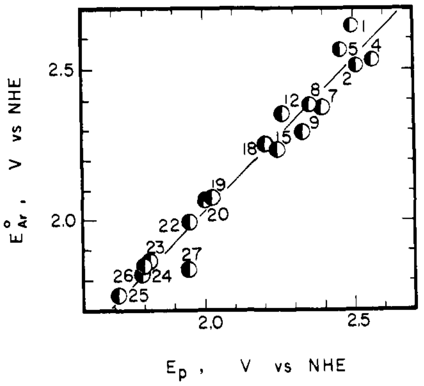

Figure 6. The correlation of the standard oxidation potentials $E_{Ar}°$ of various alkylbenzenes in trifluoroacetic acid with the irreversible CV peak potentials E_p at v = 100 mV s^{-1} in acetonitrile. Numbers refer to the aromatic hydrocarbons identified in Tables I and III.

II. Relationship between $E_{Ar}°$ and E_p of Aromatic Hydrocarbons. The correlation of the standard oxidation potentials $E_{Ar}°$ of the aromatic hydrocarbons in trifluoroacetic acid with the anodic peak potentials E_p obtained from the irreversible cyclic voltammograms in acetonitrile is shown in Figure 6. The line in the graph describes the relationship (correlation coefficient = 0.978 for 18 compounds)

$$E_{Ar}^\circ = 1.01E_p - 0.001 \qquad (11)$$

where both potentials are expressed in volts vs. NHE.[33] The existence of such a correlation with a slope close to unity is rather surprising since $E_{Ar}°$ is a purely thermodynamic measurement,[34] whereas E_p includes kinetic terms. Accordingly, let us examine how such a correlation could derive from the well-established EC mechanism for the electrochemical oxidation of aromatic hydrocarbons, which can be summarized as[35]

Scheme I

$$\mathrm{ArH} \rightleftharpoons \mathrm{ArH}^{+\cdot} + \mathrm{e} \qquad (12)$$

$$\mathrm{ArH}^{+\cdot} \xrightarrow{k} \text{....., etc.} \qquad (13)$$

It follows from the mechanism in Scheme I that the CV wave of the aromatic hydrocarbon will be generally controlled by (i) the kinetics of the electron-transfer step in eq 12 and/or (ii) the kinetics of the follow-up reaction(s) in eq 13.[36,37] There are several indications that the anodic CV waves of aromatic hydrocarbons are indeed controlled by the rates of the follow-up reactions. First, the peak-to-peak separations ΔE_p are rather small (see Experimental Section), and as illustrated in Figure 1, ΔE_p for hexaethylbenzene does not vary with the scan rate.[38] Second, we have measured the sweep-rate dependence of the peak potential $\partial E_p/\partial \log v \cong 30$ mV for both hexamethylbenzene and mesitylene at $v < 1$ V s^{-1} in acetonitrile. Similar values of $\partial E_p/\partial \log v$ have been obtained by Parker,[40] and they support the reversible electron-transfer process[41] for aromatic hydrocarbons of the type examined in this study. In other words, we conclude that the chemically irreversible CV waves observed for the aromatic hydrocarbons in acetonitrile at 0.1 V s^{-1} reflect the kinetics of the follow-up reaction in eq 13. Therefore, electron transfer in eq 12 can be considered as a rapid, reversible preequilibrium. Under these conditions, Nadjo and Savéant[37] predict the peak potential E_p to be related to the oxidation potential $E_{Ar}°$ and the rate constant k of the follow-up reaction according to the expression

$$E_p = E_{Ar}^\circ - 0.030 \log [kRT/(\mathcal{F}v)] + C \qquad (14)$$

where C is a constant the magnitude of which depends on the exact follow-up steps in eq 13 and is close to 60 mV.[42] Let us now compare the potentials for a pair of aromatic hydrocarbons ArH$_1$ and ArH$_2$. At a given sweep rate, it follows from eq 14 that

$$E_{p_1} - E_{p_2} = (E_{Ar_1}^\circ - E_{Ar_2}^\circ) - 0.030\log [k_1/k_2] \qquad (15)$$

Equation 15 indicates that the variation in the irreversible peak potential does not formally parallel that of the standard oxidation potential, but it includes an additional term of kinetic origin. Fortunately, the magnitude of the bracketed kinetic term in eq 15 can be estimated. For example, we have found the scan rates needed to restore the reversibility of the cyclic voltammograms in trifluoroacetic acid are in the range 10–500 V s^{-1} for the various hexaalkylbenzenes extending to the dialkylbenzenes (compare Figure 3).[43] Thus the variation of the follow-up rate constant does not generally exceed a factor of 50 over this series of aromatic hydrocarbons. It follows from eq 15 that the kinetic contribution to E_p does not vary by more than (30 mV × log 50) $\cong$ 50 mV among these aromatic hydrocarbons. Since the magnitude of k is principally related to the specific structure of the aromatic hydrocarbon (see eq 3),[44] it is not systematically dependent on the value of $E_{Ar}°$. Accordingly the kinetic term can be considered as merely corrective, and it will appear only as a scattering factor in the direct relationship between $E_{Ar}°$ and E_p. Therefore eq 15 can be simplified to

$$E_{p_1} - E_{p_2} = (E_{Ar_1}^\circ - E_{Ar_2}^\circ) \pm 50 \text{ mV} \qquad (16)$$

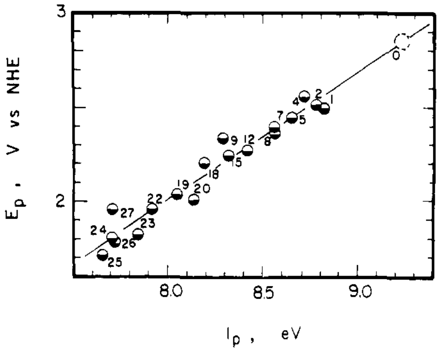

Figure 7. Correlation of the irreversible CV peak potentials E_p of various alkylbenzenes in acetonitrile and the vertical ionization potentials I_p. Numbers to the aromatic hydrocarbons identified in Table I.

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(32) (a) Indeed a careful scrutiny of the points in Figure 5 reveals that if the polyalkylatedbenzenes (no. 15–27) are considered as a single group, the resulting slope is ~1. The same is true if the mono- and dialkylbenzenes (no. 1–8) are considered as another single group. Thus among the more or less sterically related aromatic hydrocarbons, the correlation of $E°$ and I_p has a slope reasonably close to unity. (b) The reorganization energy for benzene is estimated to be only ~3 kcal mol^{-1} (see: Salem, L. "The Molecular Orbital Theory in Conjugated Systems"; W. A. Benjamin: New York, 1966; p 467–85). Thus $\Delta G_r°$ is unlikely to be a large factor in affecting the slope.

(33) Although $E_{Ar}°$ and E_p were evaluated in this study at a gold and a platinum electrode, respectively, essentially the same expression would be valid for other combinations.

(34) $E_{Ar}°$ as used here does contain a small contribution from diffusion and activity coefficients $\neq 1$.[6]

(35) Bewick, A.; Edwards, G. J.; Mellor, J. M.; Pons, B. S. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1952. See also ref 19 and 40.

(36) For a summary of the electrochemical kinetics, see ref 6.

(37) Nadjo, L.; Savéant, J.-M., cited in ref 9.

(38) (a) We posit that if the electron transfer is not rate determining at the high scan rates of 200–5000 V s^{-1}, it is unlikely to be rate limiting at the much slower scan rate of 0.1 V s^{-1} used in the determination of E_p in Table I. (b) Furthermore the solvent effect is not a factor since the intrinsic rates of electron transfer in trifluoroacetic acid should be comparable to those in acetonitrile. According to Marcus theory,[5] the outer-sphere (solvent) reorganization energy is related to the static dielectric constant D and the refractive index η, which are both comparable for these solvents: $D(CF_3CO_2H)$ 39.5, $D(CH_3CN)$ 37.5, $\eta(CF_3CO_2H)$ 1.2850, $\eta(CH_3CN)$ 1.3441.[39]

(39) Dean, J. A., Ed. "Lange's Handbook of Chemistry", 12th ed.; McGraw-Hill: New York, 1979.

(40) Baumberger, R. S.; Parker, V. D. *Acta Chem. Scand.* **1980**, *B34*, 537.

(41) For such a criterion of electron-transfer reversibility, see: Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(42) Amatore, C.; Savéant, J.-M. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *85*, 27.

(43) For a description of the sweep-rate dependence of the CV shapes in Figure 3, see the discussion in the Experimental Section.

(44) For example, some aromatic hydrocarbons such as the hexaalkyl and *tert*-butyl derivatives exhibit chemically reversible CV waves even in the more basic acetonitrile solution.

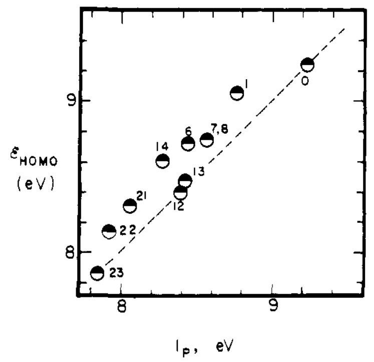

Figure 8. Relationship between the vertical ionization potentials of various methyl-substituted benzenes with the energy of the highest occupied molecular orbital calculated by the Hückel model for π-systems. The compounds are identified by the numbers in Table III. Note the dashed line is arbitrarily drawn between the points for benzene and hexamethylbenzene.

which accords with the linear correlation observed in Figure 6 with a slope of unity.[45]

The correlation of $E_{Ar}°$ with E_p in Figure 6 can be of practical value since it allows the oxidation potentials of other aromatic hydrocarbons to be estimated. For example, the cyclic voltammetry of benzene could not be examined in trifluoroacetic acid owing to the large background current at the positive potentials required. However, the peak potential of benzene at $E_p = 2.62$ V vs. SCE measured in acetonitrile together with eq 11 yields an estimate of $E_{C_6H_6}° = 2.9$ V vs. NHE.

III. Relationship of E_p and I_p of Aromatic Hydrocarbons. The combination of the empirical relationships in eq 5 and 11 leads to the correlation of the irreversible E_p with the vertical I_p as[46]

$$E_p = 0.68 I_p - 3.43 \qquad (17)$$

where E_p is expressed in volts vs. NHE and I_p in electron volts. It is noteworthy that benzene is well correlated with the other aromatic hydrocarbons in the experimental plot shown in Figure 7. This correlation is strinkingly akin to those previously noted by Miller, Dimeler, and others for polarographic oxidation potentials of a much wider variety of organic compounds.[47] Indeed such extensive correlations are all the more remarkable if one considers the assumptions regarding the variations in (i) the free energy contribution $\Delta G_s°$ from solvation in eq 9, (ii) the reorganization energy $\Delta G_r°$ of the organic cation radicals in eq 10, and (iii) the kinetic contributions as described in eq 14. Thus such changes are either small or constant, and/or there is a fortuitous cancellation of effects in these series.

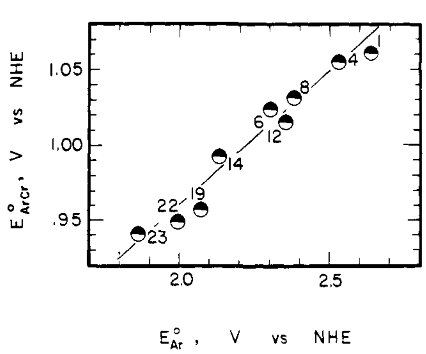

Figure 9. Correlation of the oxidation potentials $E_{Ar}°$ of various aromatic hydrocarbons with $E_{ArCr}°$ of the corresponding arenes π-complexed to chromium tricarbonyl. Numbers refer to arenes identified in Tables III and IV.

The successful correlations in Figures 5, 6, and 7 emphasize the utility of a series of alkyl- and polyalkylbenzenes to interrelate electron detachment processes in solution to that in the gas phase. At a more fundamental level, electron detachment generally from such a structurally related series of compounds as measured by the vertical ionization potential relates systematically to the energies of the highest occupied molecular orbital (HOMO) calculated by various semiempirical and ab initio molecular orbital methods.[48] [According to the Koopmans' Theorem, the negative orbital energies are set equal to the vertical ionization potential or the band maximum of the photoelectron spectrum (i.e. $\mathcal{E}(i) = I_p(i)$, where $\mathcal{E}(i)$ in this situation is that of the HOMO and $I_p(i)$ is the lowest energy band in the PE spectrum.] The "methyl effect", which results from successively replacing the hydrogen atoms on a hydrocarbon with methyl groups, is a particularly stringent test of a theoretical method to predict orbital energies since the limitations of the Koopmans' Theorem will be minimized in a comparison involving small perturbations (i.e., $\Delta I_p = \Delta\mathcal{E}$ among methylarenes). As such, the availability of the values for the vertical ionization potentials in Table III provides us with an opportunity to examine HOMO energies calculated from the Hückel model for various methyl-substituted benzenes.[48] The results illustrated in Figure 8 show the general trend; but clearly more extensive methods are needed to describe the methyl effect.

IV. Oxidation Potentials of Aromatic Hydrocarbons π-Complexed to Chromium Tricarbonyl. Relationship to $E_{Ar}°$ of Aromatic Hydrocarbons. The standard oxidation potentials $E_{ArCr}°$ of the series of arenechromium(0) complexes $(ArH)Cr(CO)_3$ in Table IV are plotted against $E_{Ar}°$ of the corresponding aromatic hydrocarbons in Figure 9. The line in the graph describes the relationship

$$E_{ArCr}° = 0.18 E_{Ar}° + 0.60 \qquad (18)$$

where both potentials refer to volts vs. NHE.[49] It is noteworthy that the correlation in Figure 9 predicts the oxidation potential of benzene to be 2.7 V vs. NHE,[26,50] which compares with the value of $E_{Ar}° = 2.9$ obtained independently by the use of eq 11.

The small slope of 0.18 for the correlation of $E_{Ar}°$ and $E_{ArCr}°$ indicates that electron detachment from $(ArH)Cr(CO)_3$ is not strongly influenced by the donor properties of the arene ligand. This is consistent with the He(I) photoelectron spectrum of (benzene)tricarbonylchromium(0), which shows the presence of only a single band (I_p 7.42 eV) in the region where the Cr 3d ionizations are expected.[51] A simple molecular orbital construction of (benzene)tricarbonylchromium assigns the HOMO to an a_1 orbital that is almost totally metal d_{z^2} in character.[52] The

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(45) (a) For error limits in the CV peak position ($E_p - E°$), see ref 6b. (b) The slope of unity for the correlation indicates that the contribution of the kinetics of the follow-up reaction on the peak potential is constant to within the experimental scatter (±0.05 V) of the plot. Such a condition could also apply in other systems consisting of a series of related compounds, such as the various aromatic hydrocarbons examined in this study. However, it should not be generally expected for systems comprised of widely divergent structures.[11,47] Thus for an irreversible CV wave, the theoretical analysis of electrochemical kinetics[37] indicates that the boundary limit of the standard oxidation potential is

$$(E_p - 0.18 \text{ V}) < E° < (E_p - 0.29 \text{ V})$$

at a typical scan rate of 1 V s^{-1}.[54] (As expected for an EC mechanism of the type presented in Scheme I, the intrinsic constant k_s for electron transfer in eq 12 and the rate constant k of the follow-up reaction in eq 13 are critical factors in setting this boundary limit.)

(46) Equation 17 obtains from the correlation of the experimental data in Table I ($r = 0.971$). The actual combination of eq 5 and 11 leads to $E_p = 0.704 I_p - 3.627$. (Note that the slight difference results from the fact that the three correlations include different arenes. For example, benzene pertains to the E_p vs. I_p correlation but not to the two others.)

(47) (a) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (b) See ref 11. (c) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. The slopes of the linear correlations of the polarographic $E_{1/2}$ and I_p are 0.89, 0.83, and 0.68 in (a), (b), and (c), respectively.

(48) Heilbronner, E.; Maier, J. P. In "Electron Spectroscopy"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: New York, 1977; Vol. 1, p 205ff.

(49) The correlation coefficient is 0.978.

(50) For an earlier cyclic voltammetric study of benzene, see: Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3994. See also ref 7 and 26. For a recent determination of the reduction potential of benzene, see: Mortensen, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 84.

(51) Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

e orbital (corresponding to the overlap of the chromium $d_{x^2-y^2}/d_{xy}$ degenerate set with the π^*-orbital of the aromatic ligand) lies very close. In this connection, it is interesting to note that the energies of the a_1 orbital for $(ArH)Cr(CO)_3$ correlate with the HOMO energies of the corresponding free arene with a slope (0.12) close to the slope observed in Figure 8 for ArH = benzene, toluene, *m*-xylene, and mesitylene.[53] An all-electron ab initio SCF molecular orbital calculation of $(C_6H_6)Cr(CO)_3$ also predicts the highest filled molecular orbitals to be e and a_1 with large metal character.[51] Population analysis indicates the e molecular orbital to have about 50% ligand character and thus provide a major contribution to the chromium–benzene bonds.

Since $E_{ArCr}°$ is more than a volt smaller than $E_{Ar}°$, the cyclic voltammetry of a wide variety of arene π-complexes can be readily examined. Such measurements, coupled with the linear correlation according to eq 18, allow the values of the standard oxidation potentials $E_{Ar}°$ to be determined for aromatic compounds such as benzene, which are not otherwise measurable by the direct method. We hope to examine other π-complexes in which the HOMO is more strongly influenced by the arene ligand, since this novel type of correlation should be applicable to a wide variety of other π-arene systems.

Experimental Section

Materials. The aromatic hydrocarbons used in this study were reagent-grade, commercial samples that were purified by either redistillation or recrystallization and then analyzed by gas chromatography, ^1H NMR spectroscopy, and GC-MS. The sources were as follows: benzene (Mallinckrodt, Analar); toluene (Matheson, Coleman and Bell, reagent grade); ethylbenzene, cumene, *p*-cymene, *p*-di-*tert*-butylbenzene, hemimellitene (repurified via the sulfonic acid derivative), pseudocumene, 1,3,5-tri-*tert*-butylbenzene, durene, prehnitene, pentamethylbenzene, hexamethylbenzene (Aldrich); neopentylbenzene (Frinton Labs); *tert*-butylbenzene, hexaethylbenzene (Eastman Kodak); *p*-, *m*-, and *o*-xylene (Fisher Scientific); *m*-di-*tert*-butylbenzene, 1,3,5-triisopropylbenzene, isodurene (Wiley Chemicals); mesitylene (J. T. Baker, reagent grade); 1,3,5-triethylbenzene (Chemical Services). 1,3,5-Tri-neopentylbenzene was donated to us by Professor S.-K. Chung (Texas A&M). Samples of 1,4-, 1,3-, and 1,2-dineopentyltetramethylbenzene were gifts from Professor M. S. Newman (Ohio State). Hexamethylbenzene-d_{18} (Merck) was given to us by A. E. Nader (Du Pont).

The π-complexes of the aromatic hydrocarbons with chromium tricarbonyl $(ArH)Cr(CO)_3$ were prepared by refluxing of a solution of hexacarbonylchromium with the corresponding aromatic hydrocarbon in appropriate solvents under a nitrogen atmosphere.[21,23,27] The reaction mixtures were filtered and concentrated in vacuo. The (arene)tricarbonylchromium(0) complexes were then recrystallized. In particular, the tricarbonylchromium complexes of benzene, toluene, cumene, *m*- and *p*-xylene, mesitylene, and pseudocumene were prepared from the neat hydrocarbon, as described in ref 27a,b. The π-complexes from durene and penta- and hexamethylbenzene were prepared according to the procedure described in ref 27c with the exception that dioxane replaced diglyme. Hexamethylbenzene complex was prepared according to Mislow et al.[21]

Trifluoroacetic acid was a generous gift from Halocarbon Corp., and it was redistilled prior to use. Trifluoroacetic anhydride was made from trifluoroacetic acid by distillation over P_2O_5. Acetonitrile (HPLC grade) from Fisher Scientific was further purified by distillation from CaH_2 through a 15-plate Oldershaw column followed by stirring overnight with $KMnO_4$ and Na_2CO_3 (5 g of each per L). The mixture was filtered, distilled under reduced pressure, and finally fractionated from P_2O_5 under an argon atmosphere and stored under argon in a Schlenk flask. Tetraethylammonium perchlorate (TEAP, G. F. Smith Chemical Co.) was further dried in vacuo. Tetra-*n*-butylammonium perchlorate (TBAP, G. F. Smith Co.) was recrystallized from a mixture of ethyl acetate and isooctane and dried in vacuo for 2 days prior to use.

Cyclic Voltammetry. The electrochemical experiments with the aromatic hydrocarbons were always performed in an air-tight cell under an argon atmosphere. The experiments in acetonitrile were carried out with standard electrochemical instrumentation consisting of a Princeton Applied Research (PAR Model 173) potentiostat equipped with a current-to-voltage converter (PAR Model 176) for suitable ohmic drop compensation and a high-impedance voltage amplifier (PAR Model 178). The working electrode consisted of a 1-mm diameter platinum disc embedded in a cobalt glass seal. The counter electrode was a grid of platinum mesh with a 1-cm² surface area. The reference electrode was a saturated calomel electrode, which was separated from the acetonitrile solution containing 0.1 M tetramethylammonium perchlorate by a fritted glass bridge filled with a solution of the same composition. The system was calibrated relative to the ferrocene standard.[55] All cyclic voltammograms in acetonitrile were recorded with solutions containing millimolar concentrations of aromatic hydrocarbons.

The microvoltammetric studies were carried out at a working electrode consisting of a 13-μm diameter gold disc imbedded in glass. The counter electrode was a platinum spiral of ~3-cm external diameter. The reference electrode was $Ag/AgClO_4$ (0.01 M) in acetonitrile 0.5 M TBAP, which was separated from the trifluoroacetic acid solution containing 7 vol % trifluoroacetic acid and 0.5 M TBAP by a cracked-glass tip capillary and a bridge filled with the same solution. The potentiostat (of local design) was constructed with an RC time constant of 0.18 μs at the lowest setting of the gain and employed 357 operational amplifiers (National Semiconductor) in the current-to-voltage conversion section.[13] To minimize stray capacitance, no switches were used, and the magnitude of the current gain was adjusted by replacing the feedback resistor. The lead from the working electrode to the current transducer was ca. 4 cm, and all experiments were conducted in a faraday cage grounded to earth. Potential wave forms were generated with a Wavetek (Model 143) function generator. Voltammograms were digitalized with a Gould-Biomation (Model 8100) transient recorder that had a minimum acquisition time of 10 ns with an 8-bit resolution. The output was sent to a computer for subsequent display and analysis. The electrode characteristics as well as the resistance and capacitance measurements of the electrochemical cell containing resistive solutions are described elsewhere.[12]

The cyclic voltammetric behavior of the aromatic hydrocarbons can be roughly separated into two categories.

(i) The dialkyl- and polyalkylbenzenes afforded cyclic voltammograms in which the current maximum of the cathodic wave on the return potential sweep was clearly defined as illustrated in Figure 3. Although the peak separations ΔE_p were consistently larger than 60 mV,[6] the absolute magnitudes could not be taken as prima facie evidence of slow electron transfer. In order to evaluate the peak-to-peak separation ΔE_p, we employed anthracene as a calibrant since electron transfer for it is known to be fast.[56] Thus for calibration purposes, anthracene was added to the analyte (after the CV measurement of the aromatic hydrocarbon was completed) and ΔE_p measured for it under the same experimental conditions. Some typical values of ΔE_p in millivolts for aromatic compounds (with that of anthracene in parenthesis) are toluene 155 (210), ethylbenzene 165 (110), neopentylbenzene 150 (76), cumene 130 (89), *tert*-butylbenzene 111 (99), *p*-xylene 112 (86), *m*-xylene 102 (65), *p*-di-*tert*-butylbenzene 75 (69), pseudocumene 100 (51), 1,3,5-triethylbenzene 102 (53), 1,3,5-tri-*tert*-butylbenzene 73 (68), pseudodurene 95 (96), hexamethylbenzene 60 (84), *p*-dineopentyltetramethylbenzene 59 (77), and hexaethylbenzene 70 (55). The values of $\Delta E_p > 60$ mV (and variable from run to run) for anthracene are symptomatic of a problem that most likely reflects an artifact arising from some modification of the surface state of the electrode[57] in this medium. We judge from the parallel values of ΔE_p above that electron-transfer rates from the aromatic hydrocarbons examined in this study are not strongly differentiated from that of anthracene. Most importantly, the values of the standard oxidation potentials measured as $(E_p^a + E_p^c)/2$ were highly reproducible both for the anthracene calibrant as well as for the aromatic hydrocarbons. Furthermore, the measurement was independent of the sweep rate to within a few millivolts (cf. Figure 2). At the highest scan rates (e.g. $v > 2000$ V s^{-1}), the variation of the peak current with the arene concentration $i_p/C°$ indicated that the ohmic drop was not totally eliminated. For this reason we did not attempt a direct evaluation of the

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(52) (a) For a review of the bonding in arene–metal complexes, see: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Albright, T. A.; Hofmann, P.; Hoffman, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (c) The nonbonding character of the HOMO in $(C_6H_6)Cr(CO)_3$ is also shown by the interesting structures of the electron donor–acceptor complexes with π-acceptors such as 1,3,5-trinitrobenzene in which the charge-transfer interaction does not occur with the arene ligand but the $(OC)_3Cr$ face (Kobayashi, H.; Kobayashi, K.; Kaizu, Y. *Inorg. Chem.* **1981**, *20*, 4135).

(53) The corresponding slope of the a_1 orbital is expectedly small (0.05), the nonzero slope arising from partial overlap of the chromium d_{z^2} orbital with the lowest energy π-orbital of benzene (Albright, T. A., private communication).

(54) Deduced from Nadjo and Savêant,[37] using limiting values of $10^{-3} < k_s < 10$ cm s^{-1}, $k < 10^{12}$ s^{-1}, $\alpha \cong 0.5$, $D \cong 10^{-5}$ cm^2 s^{-1}, $0.050 < v < 100$ V s^{-1}.

(55) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(56) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

(57) Amatore, C.; Savêant, J.-M.; Tessier, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *146*, 37; **1983**, *147*, 39.

kinetic parameters (i.e., k_s and α) for the heterogeneous electron-transfer process but hope to examine this phenomenon more completely at a later time. The standard oxidation potential of anthracene in the microvoltammetric cell was $E_{An}° = 0.928$ V vs. Ag/AgClO$_4$. The measurement using a saturated calomel electrode under the same conditions was $E_{An}° = 1.350$ V vs. SCE.

(ii) The monoalkylbenzenes afforded cyclic voltammograms in which the current maximum of the cathodic wave on the reverse potential scan was not clearly defined, particularly at the lowest sweep rates ($v \sim$ 200–500 V s^{-1}). At higher sweep rates, the cathodic maximum could be discerned, but there were complications arising from the merging of the faradaic anodic current with the capacitive and the background current of the solvent at the high positive potentials required for these aromatic hydrocarbons (see Table III). (Note the cyclic voltammograms of the monoalkylbenzenes and dialkylbenzenes presented in Figure 3 were recorded at moderate sweep rates (vide infra) and do not represent optimum examples in which the cathodic peak current was clearly delineated. At the higher sweep rates required to observe the cathodic peak, the anodic peak was less well defined owing to the complications described above. The examples shown thus represent a compromise of the two opposing factors.) The analysis of the shapes of the CV waves, such as those presented for the monoalkylbenzenes in Figure 3, by computer simulation clearly indicate an EC process in which electron transfer is reversible but somewhat displaced by the follow-up step.[58] (Note the rather sharp leveling of the wave on the reverse scan, particularly in the cyclic voltammograms of *o*-xylene, cumene, and toluene in Figure 3. This symptomatic wave shape is also quite apparent in the computations by Nicholson and Shain,[41] as shown in their Figure 11 by interpolation of the return wave in the range $10 > k_f/a > 0.1$.) Accordingly the values of $E_{Ar}°$ presented in Table III were obtained by comparison with the computer-simulated cyclic voltammograms established from the EC mechanism (vide infra) and showing the same CV shape. We believe the values of $E_{Ar}°$ reported in Table III to be valid to within 10–20 mV, but they are less accurate than those reported for the di- and polyalkyl analogues (±5 mV).

Examination of some of the cyclic voltammograms in Figure 3 shows the presence of one or more minor peaks prior to the anodic wave associated with the aromatic hydrocarbon. The peaks were not reproducible and were also sometimes observed in the absence of added aromatic compound. Accordingly we attributed these spurious peaks to adventitious impurities and ignored them in the treatment of the data.

The cyclic voltammetry of the arenechromium tricarbonyls were carried out at 0 °C in trifluoroacetic acid containing 0.2 M TBAP,[59] which was connected to the SCE reference electrode via a bridge consisting of 0.2 M TBAP in methylene chloride. The potentials in Table IV were measured relative to SCE under conditions in which $E°$ for ferrocene was 0.447 V and for anthracene was 1.312 V. The $E°$ were obtained by taking the average of $(E_p^c + E_p^a)/2$ at sweep rates of 100, 200, and 500 mV s^{-1}. Since the cyclic voltammograms of all the arenechromium tricarbonyls were reversible even at scan rates as low as 50 mV s^{-1}, the addition of trifluoroacetic anhydride to the medium was unnecessary. Indeed the deliberate addition of small amounts of water had no noticeable effect on the cyclic voltammograms. The stability of $(C_6H_5CH_3)Cr(CO)_3$ in trifluoroacetic acid was examined by measuring the ^{1}H NMR spectrum over the course of several hours. Within this span, no perceptible change was observed in the singlet methyl resonance at δ 1.60 relative to that of free toluene at δ 1.69 with an external Me$_4$Si reference.

Photoelectron Spectra. The photoelectron spectra were recorded on a Vacuum Generators UV-G3 spectrometer by using the He(I) excitation (fwhm of ~35 meV and ~15 meV for fine structure determination).[60] For the crystalline aromatic hydrocarbons, the samples were introduced through a heated inlet system, and the spectra were calibrated by the addition of argon–nitrogen and/or xenon. Since we were primarily interested in the lowest energy bands, we also employed methyl iodide as a calibrant (I_{P_1} 9.55, I_{P_2} 10.16 eV). The accuracy of the quoted vertical ionization potentials is generally ±0.02 eV. Unfortunately, the spectral resolution was insufficient to distinguish hexamethylbenzene from hexamethylbenzene-d_{18} and chlorobenzene from chlorobenzene-d_5.

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Registry No. 1, 108-88-3; **2**, 100-41-4; **3**, 1007-26-7; **4**, 98-82-8; **5**, 98-06-6; **6**, 106-42-3; **7**, 95-47-6; **8**, 108-38-3; **9**, 99-87-6; **10**, 1012-72-2; **11**, 1014-60-4; **12**, 108-67-8; **13**, 526-73-8; **14**, 95-63-6; **15**, 102-25-0; **16**, 21411-39-2; **17**, 717-74-8; **18**, 1460-02-2; **19**, 95-93-2; **20**, 488-23-3; **21**, 527-53-7; **22**, 700-12-9; **23**, 87-85-4; **27**, 604-88-6; **28**, 71-43-2; $(MeC_6H_5)Cr(CO)_3$, 12083-24-8; $(i\text{-}PrC_6H_5)Cr(CO)_3$, 12203-34-8; $(1,4\text{-}Me_2C_6H_4)Cr(CO)_3$, 12129-27-0; $(1,3\text{-}Me_2C_6H_4)Cr(CO)_3$, 12129-28-1; $(1,3,5\text{-}Me_3C_6H_3)Cr(CO)_3$, 12129-67-8; $(1,2,4\text{-}Me_3C_6H_3)Cr(CO)_3$, 32913-41-0; $(1,2,4,5\text{-}Me_4C_6H_2)Cr(CO)_3$, 33435-44-8; $(Me_5C_6H)Cr(CO)_3$, 32913-08-9; $(C_6Me_6)Cr(CO)_3$, 12088-11-8; $(C_6H_6)Cr(CO)_3$, 12082-08-5; 1,4-bis(2,2-dimethylpropyl)-2,3,5,6-tetramethylbenzene, 33770-83-1; 1,2-bis(2,2-dimethylpropyl)-3,4,5,6-tetramethylbenzene, 6668-20-8; 1,3-bis(2,2-dimethylpropyl)-2,4,5,6-tetramethylbenzene, 33781-73-6.

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(58) Amatore, C.; Savéant, J.-M., unpublished results.

(59) Compare with ref 25.

(60) Klasinc, L.; Kovač, B.; Ruščić, B. *Kem. Ind.* **1974**, *23*, 569.