In other words, the partial molar free energy of the solvent components is the same, whether the solute be treated as a formal species or as a solvated species; and the formal partial molar free energy of the solute is equal to that of the unsolvated portion of the solute.

Using equations 45–51, expressions relating the formal *standard* partial molar free energy of the solute to that of actual molecular species can be obtained. Two alternative expressions are shown in equations 52 and 53, where ϕ_{ij}^0 denotes the limiting value of ϕ_{ij} as n_3 approaches zero at constant n_1, n_2.

$$F_3^0 = F_{00}^{0\prime} + RT \ln \phi_{00}^0 \tag{52}$$

$$F_3^0 = \sum_i \sum_j \phi_{ij}^0 F_{ij}^{0\prime} + RT \sum_i \sum_j \phi_{ij}^0 \ln \phi_{ij}^0 - h^0\bar{F}_1 - d^0\bar{F}_2 \tag{53}$$

It is seen that the formal *standard* chemical potential, F_3^0, is *not* simply equal to that of the unsolvated monomer, in contrast to F_3; nor is F_3^0 simply the average of the standard chemical potentials of the various solvates, as has so often been assumed in the previous literature.

Differentiation of equation 53 and simplification of the result (subtract equation 48 from the differential of 47) finally leads to

$$\sum_i \sum_j \phi_{ij}^0 \frac{dF_{ij}^{0\prime}}{dZ_1} = \frac{dF_3^0}{dZ_1} + h^0RT \frac{d \ln a_1}{dZ_.} + d^0RT \frac{d \ln a_2}{dZ_1} \tag{54}$$

In other words, the average value of $dF^{0\prime}/dZ_1$ for *all* solvates (weighted in proportion to ϕ_{ij}^0) is equal to the experimental, formal quantity, dF_3^0/dZ_1, plus two terms—one proportional to h^0 and one to d^0—which allow for the changing activities of the solvent components and are evaluated for $m_3 = 0$. All terms involving $d\phi_{ij}^0/dZ_1$, dh^0/dZ_1, or dd^0/dZ_1 have cancelled out.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions with Professor Bruno Linder.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Chronopotentiometric Studies on the Oxidation of Ferrocene, Ruthenocene, Osmocene and Some of their Derivatives[1]

BY THEODORE KUWANA,[2] DONALD E. BUBLITZ AND GEORGE HOH

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Oxidation–reduction potentials obtained by chronopotentiometric methods at a platinum electrode in an acetonitrile solution indicate electron withdrawing substituents decrease the ease of oxidation, while electron donating substituents increase the ease of oxidation with respect to the parent metallocenes. This is in accord with the results normally expected from inductive effects. The $E_{1/4}$ values of ferrocene and its derivatives have been correlated with the substituent constants of the Ingold–Taft equation. Ruthenocene has been observed to undergo a one step, two-electron oxidation while osmocene undergoes a two step, one electron each, oxidation. Ferrocene shows only a one electron transfer. The reversibilities of the electrode reactions are evaluated.

Introduction

It has been observed[3] that the reactivity of the metal cyclopentadienyl compounds toward electrophilic substitution decreases with corresponding decrease of the apparent electron density of the molecules. Thus, the compounds containing a metal atom which withdraws electrons from the ring more in comparison to the iron compounds should be less reactive toward electrophilic substitution than ferrocene. These effects are exhibited also in a similar manner by ring substituents. Thus, carboxyl or acyl substituents decrease the reactivity of the substituted rings towards electrophilic substitution, while alkyl substituents enhance the reactivity. Moreover, these effects are, in part, transmitted through the metal atom to the second ring.

The oxidation–reduction chemistry of the metallocenes should closely parallel the above observed effects for electrophilic substitutions. That is, the more easily oxidized compounds should be those which are more reactive toward electrophilic substitutions and consequently, appear to have a greater electron density around the metal atom and rings. Metallocenes of the group VIII elements, iron, ruthenium and osmium, show trends in electrophilic substitution reactions, which indicate a lower electron density around the rings for the lower elements of this group.[4] Thus osmocene and ruthenocene are expected to have a greater stability toward oxidation than ferrocene.

Page and Wilkinson[5] have reported the polarography of ferrocene, ruthenocene and cobaltocene at the dropping mercury electrode (DME) in 90% ethanol solution containing $NaClO_4$ and $HClO_4$ as supporting electrolytes. The polarographic half-wave potentials, $E_{1/2}$, for ferrocene and ruthenocene were reported as + 0.31 and + 0.26 v. *vs.* saturated calomel electrode (SCE), respectively. Reynolds and Wilkinson[6] have published recently the $E_{1/2}$ value for the more easily air oxidized 1,1′-dimethylferrocene as + 0.38 v. *vs.* SCE.

The theoretical and experimental considerations of chronopotentiometry have been well developed by Delahay and Berzins,[7] Delahay,[8] Gierst and Juliard[9] and Reilley, *et al.*[10]

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[1] Preliminary report of this work by T. Kuwana, D. E. Bublitz and G. Hoh, *Chem. and Ind.* (*London*), 635 (1959). Material in this paper has been presented before Division of Analytical Chemistry, 136th meeting American Chemical Society, Sept. 1959 at Atlantic City, N. J.

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[3] K. L. Rinehart, Jr., Abstract of Papers presented at 135th meeting of the American Chemical Society, Boston, Massachusetts, April, 1959, p. 29-O.

[4] M. D. Rausch, E. O. Fischer and H. Grubert, *Chem. and Ind.* (*London*), 756 (1958).

[5] J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952).

[6] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.*, **9**, 86 (1959).

[7] P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

[8] P. Delahay, "New Instrumental Methods of Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

[9] L. Gierst and A. Juliard, *J. Phys. Chem.*, **57**, 701 (1953).

[10] C. N. Reilley, G. W. Everett and R. H. Johns, *Anal. Chem.*, **27**, 483 (1955).

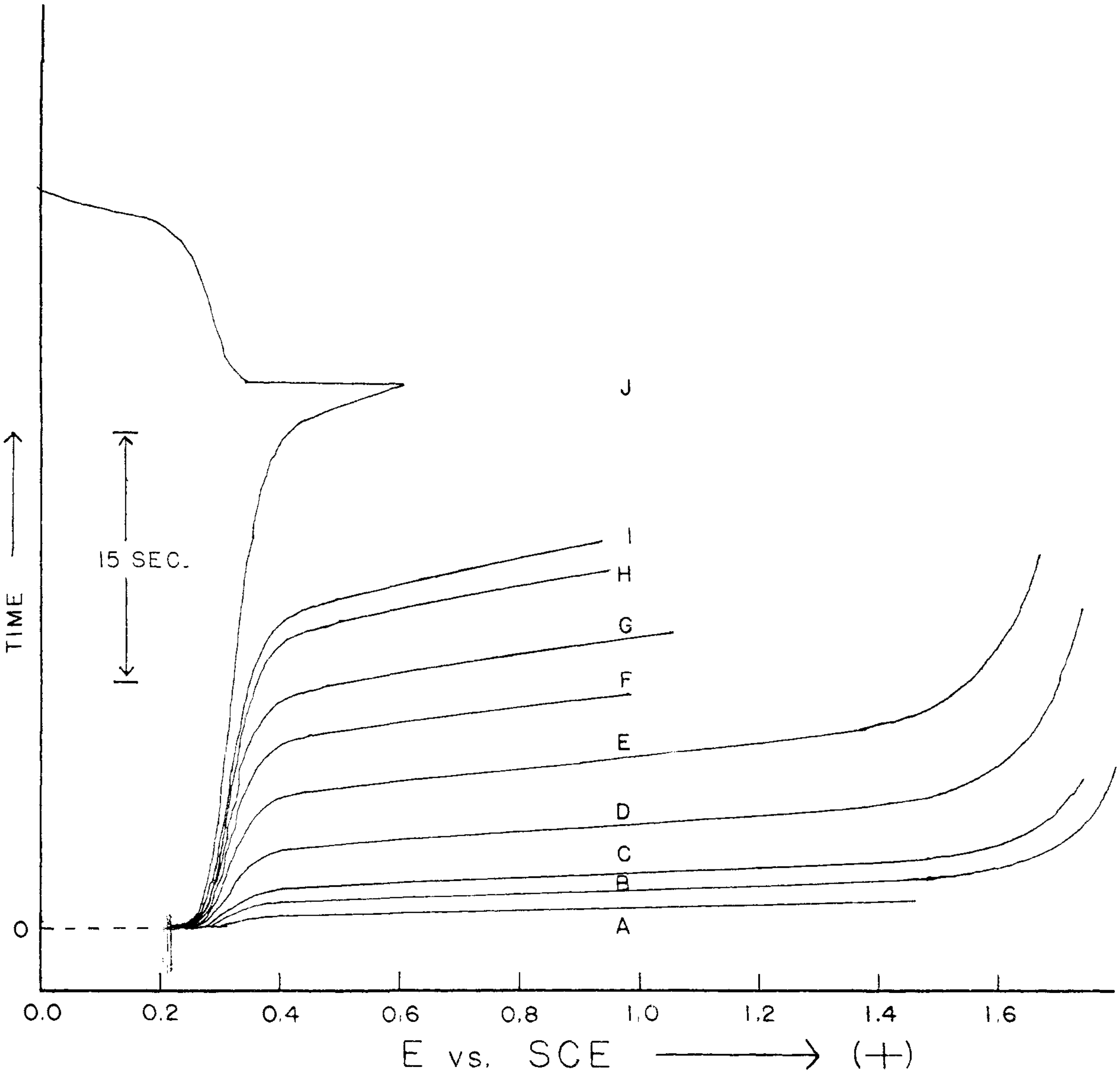

Fig. 1.—*E-t* curves for 8.09×10^{-4} *M* methylferrocenylcarbinol in 0.2 *M* $LiClO_4$-acetonitrile. A–J obtained at current densities of 313, 220, 180, 125, 93.6, 81.3, 73.7, 65.5, 63.5, and 51.2 μamp. cm.$^{-2}$, respectively.

Results and Discussion

Experiments Using DME and Ethanol Medium.—Preliminary polarographic experiments were made at the DME in the ethanol medium. A wave which merged with the background wave for the oxidation of mercury itself was observed for the ferrocene oxidation. However, no defined wave or limiting current for ferrocene was evident because of the wave merger.

Experiments with chronopotentiometric oxidations of ferrocene and ruthenocene in ethanol medium at a quiet mercury pool electrode gave waves whose initial potentials were highly current dependent. The waves eventually merged with the background wave for the dissolution of mercury. Oxidations at the bright platinum foil electrode improved the definition of the ferrocene wave, but the re-oxidation run on the same electrode without pre-treatment gave a much shorter transition time, τ, which indicated some electrode fouling. All further work was done at the platinum electrode in acetonitrile containing 0.2 *M* $LiClO_4$ as supporting electrolyte.

Chronopotentiometric Oxidation.—The chronopotentiograms for all the compounds were very well defined. Figure 1 shows a series of typical chronopotentiograms for the oxidation of methylferrocenylcarbinol at several current densities.

The transition time, τ, is given by

$$\tau^{1/2} = \frac{nFD^{1/2}C\pi^{1/2}}{2i_0} \qquad (1)$$

where n is the number of electrons transferred per molecule, D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, C is the bulk concentration of the electroactive species in moles per cc., F is the Faraday, i_0 is the current density in amp cm.$^{-2}$ and π has its usual significance. This equation defines the transition time in all cases where the electrode reaction involves only electron-transfer, regardless of the degree of reaction reversibility. The so-called "chronopotentiometric constant", $i_0\tau^{1/2}/C$, should remain constant over a wide range of current densities in such cases. Also, when the electrode reaction is reversible, the potential at one-quarter of the transition time, $E_{1/4}$, is independent of both current density and concentration.[7]

For example, methylferrocenylcarbinol gave average values for $E_{1/4}$ and $i_0\tau^{1/2}/C$ over a current density of 51 to 313 μamp./cm.² of +0.298 ± 0.002 v. *vs.* SCE, and 342 ± 7 amp. cm. sec.$^{1/2}$ mole^{-1}, respectively. Both values show excellent reproducibility and are, within experimental error, independent of current density.

Oxidation of Ferrocene, Ruthenocene and Osmocene.—Typical chronopotentiograms for the oxidation of ferrocene, ruthenocene and osmocene are shown in Fig. 2. The data for ferrocene, ruthenocene and osmocene are summarized in Table I. All values of potential will be given following the European or analytical sign convention of reduction potentials. The reduction potential of + 0.307 v. *vs.* SCE for ferrocene is in good agreement with the value of + 0.31 v. *vs.* SCE reported by Page and Wilkinson[5] for the oxidation process

$$(C_5H_5)_2Fe = (C_5H_5)_2Fe^+ + e^- \qquad (2)$$

The $E_{0.22}$ of +0.300 v. *vs.* SCE found for the reduction of the ferricinium ion by the method of current reversal immediately after the transition time for oxidation[8] indicates a nearly reversible electrode reaction. The ratio of the reverse transition time, τ_R, should be 1:3 for a reversible electrode reaction assuming similar diffusion coefficients for the oxidized and reduced states. The observed ratio is 1:3.3. The reciprocal slope of the log $\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$ *vs.* electrode potential, E, is 0.057 in good agreement with the theoretical value of 0.059 for a reversible electrode reaction involving one electron per molecule.

TABLE I

A. Ferrocene, Ruthenocene and Osmocene[a]

	$E_{1/4}$ v. *vs.* SCE)	$E_{0.22}$ (v. *vs.* SCE)	$i_0\tau^{1/2}/C$ (amp. cm. sec.$^{1/2}$ mole^{-1})	$D \times 10^5$ (cm.² sec.$^{-1}$)
Ferrocene	+0.307 ± 0.002	+0.300	417 ± 5	2.4
Ruthenocene	+ .693 ± .003	+ .315	807 ± 10	2.2
Osmocene	+ .633 ± .005	+ .03	403 ± 18	2.2
	+1.50 ± .01		755 ± 8[b]	2.0
B. Derivatives of Ruthenocene and Osmocene				
Ruthenocene substituent				
$-CHOHC_6H_5$	+0.755 ± 0.004	+0.18	577 ± 7	
$-COC_6H_5$	+ .907 ± .008	+ .45	666 ± 27[c]	
1,1'-$(COC_6H_5)_2$	+1.089 ± .018	+ .49	670 ± 59[c]	
Osmocene substituent				
$-COC_6H_5$	+0.866 ± 0.010	+0.0	505 ± 50[c]	

[a] All values average of 4 or more runs each at a different current density. [b] Value is $i_0(\tau_1 + \tau_2)^{1/2}/C$. [c] These values increase with lower current densities.

The $E_{1/4}$'s of + 0.69 and + 0.63 v *vs.* SCE for ruthenocene and osmocene, respectively, indicate that the electrons are held more tightly than in ferrocene. These values should be regarded as "comparison" potentials since the potential–time curves for both compounds show irreversible characteristics.

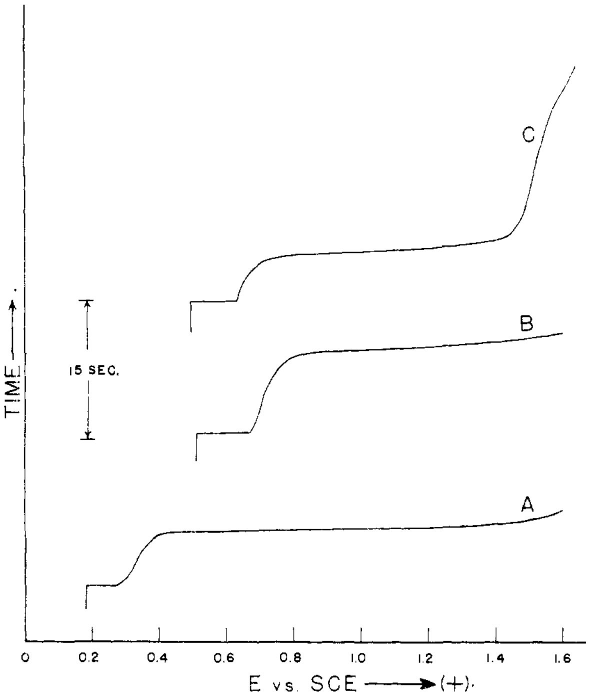

Fig. 2.—Chronopotentiograms of metallocenes in 0.2 M $LiClO_4$–acetonitrile: A, 3.25 × 10^{-3} M ferrocene, i_0 = 550 μamp. cm.$^{-2}$; B, 8.18 × 10^{-4} M ruthenocene, i_0 = 222 μamp. cm.$^{-2}$; C, 1.86 × 10^{-3} M osmocene, i_0 = 358 μamp. cm.$^{-2}$.

The more interesting feature of the data is the value of the "chronopotentiometric constant," $i_0\tau^{1/2}/C$, between the three metal cyclopentadienyl compounds. This value, which is a constant except when a rate-determining chemical reaction precedes the electron-transfer reaction or when there is catalytic regeneration of the electroactive species,[8] depends upon the number of electrons transferred per molecule and the value of the diffusion coefficient. If the structures[11] of the three metal cyclopentadienyl compounds are similar, the diffusion coefficients for the three should differ only by the differences in the molecular weights. This effect is expected to be small.

The $i_0\tau^{1/2}/C$ value for ruthenocene is approximately twice that found for ferrocene or osmocene. This strongly suggests a two-electron oxidation for ruthenocene. Therefore, the diffusion coefficients calculated using equation 1 assuming for ferrocene (n = 1), ruthenocene (n = 2) and osmocene (n = 1) are 2.4 × 10^{-5}, 2.2 × 10^{-5} and 2.2 × 10^{-5} cm.² sec.$^{-1}$, respectively.

Further evidence supporting the two-electron oxidation for ruthenocene was obtained from coulometric oxidation of known amounts of the compound by the current-step method. For ruthenocene the upper potential limit of + 0.90 v. *vs.* SCE was used. Twenty-five ml. of a 7.68 × 10^{-4} M solution of ruthenocene in the background acetonitrile solution was oxidized by the current-step method. The extrapolated value of 36.2 microequivalents as shown in Fig. 3 was obtained in

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[11] M. D. Rausch, E. O. Fischer and H. Grubert, THIS JOURNAL, **82**, 76 (1960).

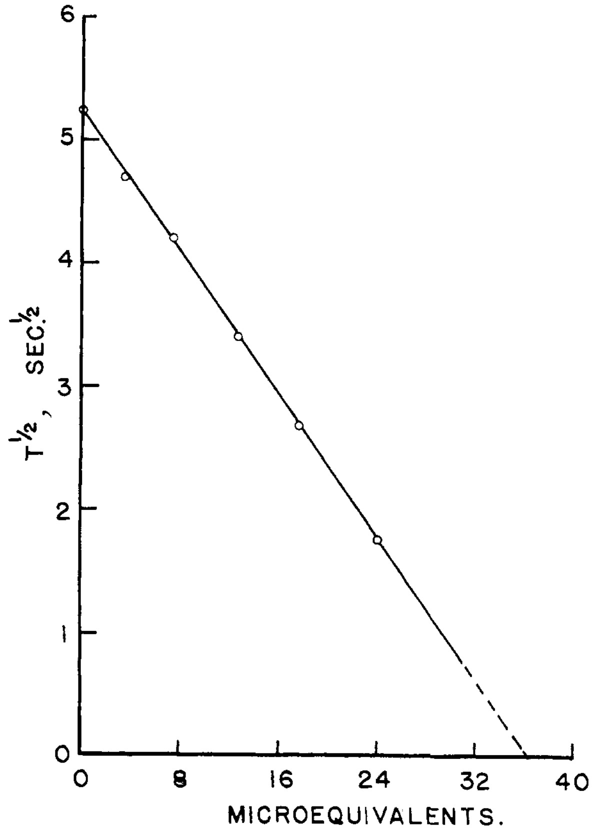

Fig. 3.—Current-step oxidation of ruthenocene, theoretical 38.3 μeq. based on $n = 2$.

comparison to the known value of 38.3 microequivalents assuming $n = 2$. There is little doubt that the over-all electrode reaction for the compound involves two electrons per molecule. The ruthenocene dipositive ion is straw colored in the acetonitrile medium. It slowly decomposes to a darker brown color over a period of *ca.* 10 hr.

For osmocene two well-defined waves were obtained at + 0.635 and + 1.50 v. *vs.* SCE. The ratio of the transition time of the first to second wave is 1:3 which is the ratio theoretically predicted for consecutive stepwise electrode reactions involving one electron each. The values of the chronopotentiometric constant for both waves of osmocene support the two step, one electron each, over-all electrode reaction. The oxidation-reduction properties of ferrocene, ruthenocene and osmocene emphasize the important role of the metal atom in determining the characteristics of the compounds.

Derivatives of Ferrocene, Ruthenocene and Osmocene.—Column 1 of Table II lists $E_{1/4}$ values for ferrocene and its derivatives in the order of increasing potentials. These compounds undergo nearly reversible electrode reactions as is evident from the approximately equal values of the $E_{1/4}$'s and $E_{0.22}$'s. The reciprocal slopes of the log $\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$ *vs.* E plot for all these compounds are in close agreement with the theoretical value of 0.059 for a reversible one-electron electrode reaction.

The simplicity of the over-all electrode reaction, coupled with its reversible nature, makes these compounds an "ideal" system for electrochemical studies, particularly in the acetonitrile medium. The stability of ferrocene and methylferrocenylcarbinol in acetonitrile make them attractive compounds to be used as "standards" for electrochemical studies at the platinum electrode. Both compounds may be chromatographed to a high degree of purity.

As discussed earlier, the relative ease of oxidation should depend on the electron-donating or withdrawing character of the substituent. The $E_{1/4}$ values listed in Table II show the expected order of potential for oxidation of derivatives compared to the parent compound. Thus, the $E_{1/4}$ of ethylferrocene is 0.062 volt lower than that of ferrocene, due to the electron-donating character of the ethyl group. Addition of a second ethyl group, as in 1,1'-diethylferrocene, lowers $E_{1/4}$ by 0.113 volt, nearly twice the amount found between ethylferrocene and ferrocene. The same additive effect, in the direction of more positive potentials due to the electron-withdrawing nature of the acetyl group, is exhibited by the acetylferrocenes.

Although the $E_{1/4}$ values of the ruthenocene and osmocene derivatives are evaluated from irreversible electrode reactions, the same generalization regarding the effect of the substituents to the potential required for their oxidation is true. The approximately same additive effect is observed for the electron-withdrawing group, benzoyl, in the benzoylruthenocenes. The values of $E_{1/4}$, $E_{0.22}$ and $i_0\tau^{1/2}/C$ for the derivatives of ruthenocene and osmocene are listed in Table I, B.

In general, the effects of ring substituents on the metal cyclopentadienyl compounds parallel those observed for benzene.[3] If this is the case, there should be a close correlation existing between the substituent constant, σ^*, of the Ingold–Taft equation[12] and the $E_{1/4}$ values of ferrocene and its derivatives. This is assuming, of course, that these $E_{1/4}$ values are related to the standard potential, and consequently, to the free energy. The σ^* depends only upon the net polar effect of the substituent relative to the standard of comparison, CH_3-($\sigma^* = 0$).

Unlike benzene, the net polar effect of a substituent may be studied directly without the necessity of introducing an additional group. Furthermore, the addition of a second group on the unsubstituted ring seems to exert its effect independent of the initial substituent. Thus, 1,1'-dimethylferrocene would be expected to oxidize at a lower positive potential than the monomethyl derivative due to the electron-donating character of CH_3. This would not be predicted if $\sigma^* = 0$ for CH_3. In order to include the effect of disubstitution, two values of the substituent constant were calculated for each compound and compared. These are: (1) A total σ^* for each compound was calculated by weighting all the substituent groups in the compound including H (relative to $\sigma^*_{CH_3} = 0$). For example, 1,1'-diethylferrocene has a (total σ^*) value of 3.72 calculated by taking the algebraic

(12) Robert W. Taft, Jr., "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

TABLE II

FERROCENE AND ITS DERIVATIVES

Compound	$E_{1/4}$ (v. *vs.* SCE)	$E_{0.22}$ (v. *vs.* SCE)	$i_0\tau^{1/2}/C$ (amp. cm. sec.$^{1/2}$ mole^{-1})	Slope E *vs.* $\log \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}}$	$\tau_R : \tau$
Ferrocene substituents					
1,1'-$(CH_2CH_3)_2$	+0.194 ± 0.001	+0.186	367 ± 3	0.056	1:3.0
$-CH_2CH_3$	+ .245 ± .003	+ .235	370 ± 6	.067	1:3.0
$-CHOHCH_3$	+ .298 ± .003	+ .304	342 ± 6	.056	1:3.2
-H	+ .307 ± .002	+ .300	417 ± 5	.057	1:3.1
$-CHOHC_6H_5$	+ .318 ± .003	+ .315	335 ± 11	.057	1:3.8
$-CH{=}CH_2$	+ .325 ± .002	+ .319	378 ± 10	.059	1:3.5
-COOH	+ .550 ± .002	+ .57[a] + .35	282 ± 5	.065	1:2.8
$-COC_6H_5$	+ .571 ± .004	+ .568	342 ± 20[b]	.056	1:4.7
$-COCH_3$	+ .573 ± .004	+ .570	400 ± 24[b]	.062	1:8
1,1'-$(COCH_3)_2$	+ .796 ± .004	+ .805	322 ± 25[b]	.064	1:17

[a] Two waves found for reduction of oxidized product. [b] These values increase with lower current densities.

sum of $8\sigma^*_H$ ($\sigma^*_H = 0.490$) and $2\sigma_{C_2H_5}$ ($\sigma^*_{C_2H_5} = -0.100$). These values of (total σ^*) are plotted *vs.* $E_{1/4}$ in Fig. 4 (closed circles). (2) The σ^* values tabulated by Robert W. Taft, Jr.,[12] were recalculated relative to comparison value of H ($\sigma^* = 0$). These values are plotted *vs.* $E_{1/4}$ in Fig. 4 (open circles).

Compounds containing substituent groups which exert only polar effects show nearly a linear relationship with $E_{1/4}$ values in both plots. The deviation from this linearity by acetyl- and diacetylferrocene is believed to be due to resonance contributions of the substituents to the $E_{1/4}$ values, which shift them more than expected from purely polar effects predicted from the σ^* alone.

Ruthenocene, osmocene and their derivatives (those listed in Table I, B) exhibit potential–time curves similar to those observed by Delahay and Mattax[13] for irreversible electrode reactions. The electrode potential, under these conditions, depends upon the rate of the electron transfer reaction. Considering the structure and chemistry of these compounds, it is highly unlikely that the electrode reaction will be complicated by more than one rate-controlling step. The logarithm of the formal rate constant, $k_{b,h}$, for these compounds evaluated from the potential–time curves following the convention and method of Delahay and Mattax[13] is in the range of − 15 to − 20 ($E_{t=0}$ *vs.* SCE).

Additional evidence regarding the reversibility of the electrode reactions was shown by Walker, Adams and Juliard[14] who observed typical peak-type waves for ferrocene, 1,1'-diethylferrocene and phenylferrocenylcarbinol at the platinum electrode in the acetonitrile medium using alternating current voltammetry. No such waves were found for osmocene or ruthenocene. Only a reversible electron transfer step gives a large wave in alternating current voltammetry.

Addition of Pyridine.—Addition of *ca.* 0.02 *M* pyridine to ferrocene or its derivatives does not affect the character of the *E–t* curves, except in the case of ferrocenylcarboxylic acid. The $E_{1/4}$ value for this latter compound is lowered from + 0.550 to + 0.430 v. *vs.* SCE. The lower $E_{1/4}$ for the oxidation in the presence of pyridine may be explained on the basis of the acid (I) undergoing a chemical reaction

$$\underset{\text{I}}{(C_5H_5)\text{-}Fe\text{-}(C_5H_4)\text{-}COOH} + C_5H_5N\colon =$$

$$\underset{\text{II}}{(C_5H_5)\text{-}Fe\text{-}(C_5H_4)\text{-}COO^-} + C_5H_5N^+\text{-}H \quad (5)$$

and, the dissociated acid (II) undergoes the electrode reaction. This explanation is reasonable considering the effect that a ten-fold greater concentration of base must have on the acid–base equilibrium. The value of $i_0\tau^{1/2}/C$ remains essentially unchanged in the presence of pyridine (290 ± 13).

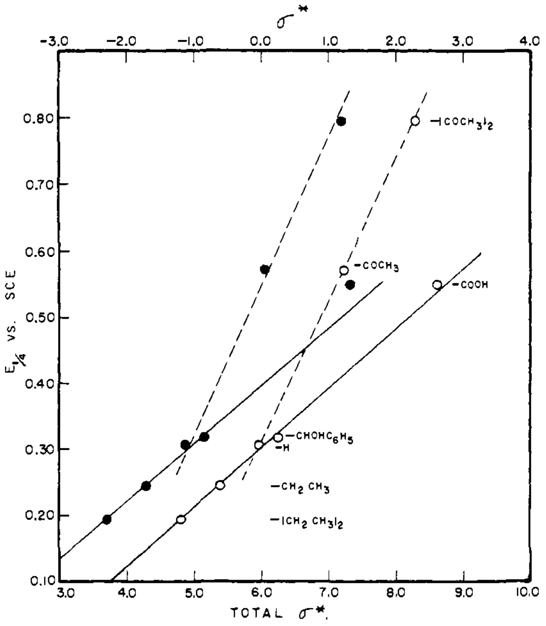

Fig. 4.—$E_{1/4}$ values of ferrocene and its derivatives plotted *vs.* substituent constant of the Ingold–Taft equation. Total σ^* *vs.* $E_{1/4}$ (closed circles); σ^* *vs.* $E_{1/4}$ based on σ^*_H = O (open circles).

$i_0\tau^{1/2}/C$ Values.—The $i_0\tau^{1/2}/C$ values remain constant over a wide range of current densities for all

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[13] P. Delahay and C. C. Mattax, THIS JOURNAL, **76**, 874 (1954).

[14] Data of D. E. Walker, R. N. Adams and A. L. Julliard presented before the Division of Analytical Chemistry, 136th meeting of the American Chemical Society, Atlantic City, September, 1959.

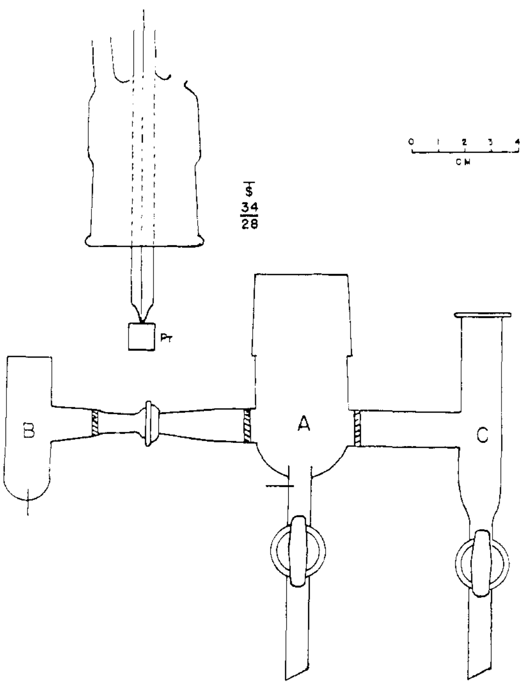

Fig. 5.—Diagram of the cell.

the compounds with the exception of the acetyl and benzoyl derivatives. For these derivatives the $i_0\tau^{1/2}/C$ values show variation with current density which are typical of electrode reactions that are preceded by a rate-determining chemical reaction. Such behavior is unexplainable in light of the present data.

Diffusion Coefficients.—The diffusion coefficients, calculated from equation 1, are tabulated in Table III. These diffusion coefficients are not corrected for ionic strength, double layer effects, *etc.*, and must be regarded as practical values that are valid for this particular system. They are nevertheless valuable for comparison purposes. The decreasing order of the diffusion coefficients is in accord with the increasing size and polar effect of the substituent.

TABLE III

CALCULATED DIFFUSION COEFFICIENTS FOR FERROCENE AND ITS DERIVATIVES

Ferrocene substituent[a]	$D \times 10^5$ (cm.^{2} sec.$^{-1}$)
-H	2.4
$-CH{=}CH_2$	2.0
$-CH_2CH_3$	1.9
$1,1'-(CH_2CH_3)_2$	1.8
$-CHOHCH_3$	1.6
$-CHOHC_6H_5$	1.5
-COOH	1.1

[a] The diffusion coefficients for the acetyl and benzoyl substituents were not calculated because of the variation in the $i_0\tau^{1/2}/C$ values.

Summary.—The novel structure and the "ideal" electrochemical behavior of the ferrocene compounds offer an interesting system for further study. There seems to be no evidence for any marked steric effects to the electrode reaction from either the mono or disubstituted compounds. At least, the changes in the redox potentials could be attributed completely to the inductive effects of the substituents. This may be in part explained by the rotation of the rings about the central axis of the molecule which makes possible a close approach to the electrode. It would be extremely interesting to study polysubstituted or bridged ferrocene systems. Irreversibility of the electrode reaction can be presently attributed to the oxidation–reduction properties of the metal atom.

If the rule of additivity for disubstituted derivatives is valid, the predicted value of $E_{\tau/4}$ for a compound such as 1-ethyl-1′-benzoylferrocene would be *ca.* 0.51 v. *vs.* SCE. If the experimental values coincide with the predicted values for several compounds, it would become evident that the effects are truly polar in nature and transmitted throughout the entire molecule. This method may eventually prove to be a convenient and simple means for evaluating σ^* values.

Experimental

The chronopotentiometric equipment and circuit[10] were conventional in all respects. The cell is shown in Fig. 5. The central compartment, A, contains a volume of 25 ml. of the solution under study. The side arms, B and C, are filled with 0.2 *M* $LiClO_4$ in acetonitrile. A probe-type saturated calomel reference electrode is inserted into side arm C. Side arm B contains a large platinum electrode which serves as a shielded electrode. The compartments are separated by medium porosity sintered discs.

A bright platinum foil, the working electrode, is permanently attached to a platinum wire which is sealed in a small glass tube. The wire enclosed in the tubing leads to the top of the cell where connection is made to the current source. The electrode area of 2.03 cm.^{2} was evaluated through oxidation of 0.00100 *M* ferrocyanide in aqueous 0.10 *M* KCl using the diffusion coefficient value[15] of 0.65×10^{-5} cm^2. sec.$^{-1}$. Although electrode fouling was not evident at the platinum electrode in acetonitrile, to insure a consistent, reproducible electrode surface for each run, the electrode was dipped in a dichromate-sulfuric acid solution for *ca.* 15 seconds, washed well with distilled water and then dried with a soft cleansing tissue and a stream of nitrogen.

The potentials reported are not corrected for any junction potentials which may appear between the SCE and the nonaqueous solution.

Eastman practical grade acetonitrile (b.p. 80.5°) was distilled twice from P_2O_5. G. F. Smith Co. anhydrous grade $LiClO_4$ was used without further purification.

Preparation of Compounds.—All the compounds used in this study were prepared by methods reported in the literature, with the exceptions of phenylruthenocenylcarbinol (m.p. 105.6–106.2° corr.) and phenylosmocenylcarbinol (m.p. 113.5– 114.0° corr.).[16]

Ferrocenylcarboxylic acid was purified by recrystallization. All other compounds were purified chromatographically using Alcoa F-20 alumina of activity grade III.[17] The chromatograms were developed using Skelly "B" or mixtures of Skelly "B" and ether, depending on the polarity of the compounds. Acetyl and diacetylferrocene were protected from light while on the column.

Procedure.—Approximately 10–20 mg. of the compounds were delivered to dry 50 ml. volumetric flasks and accurately weighed. The flasks were filled to volume with stock 0.2 *M* $LiClO_4$ in acetonitrile. About 25 ml. of the solution was delivered to the cell, the electrode inserted and the solution allowed to quiet for *ca.* 30 seconds prior to switching on the constant current for the chronopotentiogram.

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(15) M. V. Stackelberg, M. Pilgrim and V. Toome, *Z. Elektrochem.*, **57**, 342 (1953).

(16) The preparation and analysis of these compounds will be reported in a forthcoming publication by D. E. Bublitz, W. E. McEwen and J. Kleinberg.

(17) G. Hesse, I. Daniel and G. Wohlleben, *Angew. Chem.*, **64**, 103 (1952).

The current-step method used for coulometrically oxidizing ruthenocene is: Constant current is applied to a rotating platinum electrode (600 r.p.m.) and a shielded electrode. The potential of the rotating electrode is monitored *versus* a reference SCE. When the potential attains a predetermined limit, the constant current is lowered. In this manner the potential is maintained always below a given value. This upper potential limit is selected from the chronopotentiogram run on the system. The number of equivalents of electricity consumed may be easily calculated from the current and time. At different intervals of time, the coulometric oxidation is stopped, the solution allowed to quiet and a chronopotentiogram obtained at the usual platinum electrode used for chronopotentiometric work. The $\tau^{1/2}$ is proportional to the concentration of the electroactive species remaining in the solution. Therefore, a plot of $\tau^{1/2}$ *vs.* number of equivalents from the coulometric oxidation should be a linear relationship if there are no complications to the electrode reaction. Extrapolation of the above plot to where $\tau^{1/2} = 0$ should intersect the axis at a point which corresponds to the number of equivalents of electroactive species which was originally present in the solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Radiolysis of Liquid Neopentane[1]

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The products of radiolysis of liquid neopentane by Co^{60} gammas in the range −196 to 50° include, among compounds determinable by gas chromatography, ethane, ethylene, propane, propylene, isobutane, isobutylene, isopentane, neohexane, branched octanes, nonanes, dineopentyl and possibly acetylene. Hydrogen and methane are also found. The major products other than CH_4, C_2H_6, $i\text{-}C_4H_{10}$ and neohexane show minimum G values around −78°. The values of $G(CH_4)$ are higher than those previously reported by Hamashima, Reddy and Burton. Failure of carbon–hydrogen balance is attributed not merely to inaccuracies of analysis but also to possible formation of products higher than decanes. In some experiments, with iodine as solute, the C_8, C_9 and C_{10} products are completely absent, and H_2 and CH_4 are reduced in yield. The other products, C_6 and below, including ethane, are unaffected. Two conclusions regarding the mechanism of radiolysis are that (1) both free-radical and excited molecule reactions appear to be involved, and (2) a significant fraction of the CH_4 may be formed by primary rearrangement decomposition, such as suggested also by the results of Dewhurst on neohexane, who reports that CH_4 production is not completely eliminated by I_2 addition. Ion-molecule reactions may also participate.

Introduction

As background for current studies of the radiolysis of mixtures including neopentane it has been desirable to make a further study of its radiation chemistry over the temperature range −196 to 50°. Values of $G(H)_2$, $G(CH_4)$ and $G(C_2H_6)$ were obtained throughout the entire range and full analyses of the products were made for irradiations at −196, −78 and +30°. The results for $G(CH_4)$ are significantly higher than those previously reported from this laboratory.[3]

Experimental

Materials.—Neopentane (2,2-dimethylpropane), Phillips Research Grade, 99.87 and, more recently, 99.94 mole % pure, was used without purification for most of the temperature-dependence work. For full product analyses, only highly purified material was employed; this same work established that the material used as received was adequate for experiments in which only gaseous products were determined.

Sample Purification and Preparation.—In our earlier work, samples were cooled in the irradiation cells (6 ml. Pyrex ampoules) and degassed while frozen at −78°. Five freezing, evacuating and thawing cycles insured thorough degassing of the samples. Latterly, the following purification was adopted and employed before the degassing cycles.

The neopentane flowed very slowly through a two-foot-long tube packed with coconut charcoal on which bromine was absorbed.[4] The gas then passed through a similar length of pure charcoal and finally through a long phosphorus pentoxide drying tube. About 4 hr. were required to obtain 6 ml. of liquid. This process completely removed previously detected traces of propylene, isobutylene and pentene.

Irradiations.—Irradiation in an underground Co^{60} source was at a rate of about 7×10^{17} ev. ml.$^{-1}$ min.$^{-1}$, as established with the Fricke dosimeter employing an electron density correction of 0.60 for neopentane. Irradiation times varied from 30 to 120 minutes, although 60 minutes was the usual time. For runs from which all the products were examined irradiation times were 120 minutes. The low and high-temperature irradiations were performed in a Dewar flask containing coolant or hot water to give the desired temperature. In some cases, the irradiation had to be interrupted in order to maintain the required temperature.

Analyses.—Hydrogen, methane, ethylene and ethane were extracted by degassing techniques conventional in this Laboratory and were determined with a Consolidated 21-103A mass spectrometer. A Perkin-Elmer 154B Vapor Fractometer was used for the full-product analyses. Products in the range C_2 to C_4 were separated by use of two 2-meter tetraisobutylene (Dx) columns in series at room temperature, C_5 and C_6 products by a 2-meter di-2-ethylhexylsebacate (Bx) column at room temperature and higher products on the Bx column at about 80°.

Preparation of Dineopentyl.—Because the highly branched dimeric products expected were not, on the whole, readily

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(2) To whom requests for reprints should be addressed.

(3) M. Hamashima, M. P. Reddy and M. Burton, *J. Phys. Chem.*, **62**, 246 (1958).

(4) N. H. Ray, *Analyst*, **80**, 853 (1955).