Organometallic Electrochemistry. XIII. One-Electron-Transfer Processes from Metalloid Anions and Radical Anions

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Abstract: The one-electron-transfer processes from metal and metalloid anions to various transition metal complexes and organometallic species have been studied. In addition the homo- and heteroexchange processes between organometallic radical anions and organometallic species have been examined, both as to rate and position of equilibrium.

In the previous two papers[1] in this series, a well-developed series of related radical anions derived from acetylene–metal complexes and bridged dimetallic species was outlined. Earlier articles in this series presented methods for the electrochemical preparation of metal and metalloid anions derived from main-group and transition metals. Coordination chemistry and organometallic chemistry have much in common, and it is unfortunate that the philosophy and nomenclature of one area does not more readily transfer to the other discipline. It is the purpose of this paper to present sufficient data to confirm that the redox concept that is the basis for analysis of one-electron-transfer processes between coordination complexes

$$\mathrm{ML}_m{}^{x+} + \mathrm{M'L}_m{}^{y+} = \mathrm{ML}_m{}^{(x-1)+} + \mathrm{M'L}_m{}^{(y+1)+}$$

has 1:1 correspondence with one-electron-transfer processes that occur between radical anions derived from organometallic complexes and singlet, ground-state organometallic compounds. In addition it will be demonstrated that the one-electron-transfer processes from carbanions or incipient carbanions into π^* aromatic orbitals is a small portion of the vast field encompassed by one-electron-transfer processes from metal and metalloid anions into a variety of acceptor orbitals.

Results and Discussion

One-Electron Transfer from Metal and Metalloid Anions. Table I presents the results of a study which explored the extent of interaction between metal and metalloid anions and neutral or charged acceptor molecules

$$\begin{tikzcd}\mathrm{m}:^- + \mathrm{S} \arrow[r] & \mathrm{m}\cdot \arrow[d] & + \mathrm{S}\cdot^- \\ & \mathrm{m{-}m} & \end{tikzcd}$$

The table presents nine anions, ranging in nucleophilicity over nine powers of ten,[2] reacting with ten acceptor molecules, ranging from typical coordination compounds to negatively substituted π systems. Immediately below each reactant is its oxidation potential (anions) or reduction potential (substrate) measured polarographically *vs.* a 10^{-3} *M* $\mathrm{AgClO_4|Ag}$ electrode in dimethoxyethane using tetrabutylammonium perchlorate as a supporting electrolyte.

The pioneering work of Russell[3] showed very clearly that carbanions are capable of donating one electron into an acceptor.

$$\mathrm{R}:^- + \mathrm{S} \longrightarrow \mathrm{R}\cdot + \mathrm{S}\cdot^-$$

Although his work was mainly concerned with the ability of *in situ* generated carbanions to one-electron transfer, the first paper in his series suggested that the heavier core atoms (*e.g.*, Si, Ge, Sn instead of C) might be prone to exhibit this characteristic. Previous publications in the present series indicated that in a long series of metal and metalloid anions derived from main group and transition group metals, the nucleophilic character of the anions paralleled their oxidation potentials. This relationship has been expressed by Edwards in the form of one of the many linear free-energy relationships known in chemistry.[4] Edwards suggested that the linear correlation was a likely one because the process of oxidation, measured by $E_{1/2}$, involved electron donation to the electrode, while nucleophilic attack involved electron donation to the substrate. It appears that one-electron-transfer processes might also parallel oxidation potentials of the anion.

Table I presents one-electron-interchange results noted in 60 experiments. Although the oxidations of the anions to radicals at a metal electrode (Hg or Pt) are electrochemically irreversible processes and are therefore kinetic rather than thermodynamic parameters, one could hope that there would be a rather good correlation between the oxidation potentials of the anions combined with the reduction potentials of the substrate and the answer to the question of whether one-electron exchange does or does not occur. Also of interest would be the rate at which such a process occurs. Unfortunately, in the present study, the majority of reactions were either too fast to measure (complete in 5 sec at millimolar solutions at room temperature) or were too slow to measure (less than 5% reaction in several hours). However, one can at least classify the exchange as too fast (TF) or too slow (TS) to measure. The pattern is as might be expected with a complete dominance of fast reactions in the upper right-hand corner, regressing along a diagonal line to the lower left corner where very slow reactions occur.

The bold line running from top left to bottom right in the table indicates the expected division between reac-

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[1] R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Am. Chem. Soc.*, **90**, 2001 (1968); R. E. Dessy and R. L. Pohl, *ibid.*, **90**, 1995 (1968).

[2] R. E. Dessy, R. L. Pohl, and R. B. King, *ibid.*, **88**, 5121 (1966).

[3] G. A. Russell, E. G. Jansen, and T. Strom, *ibid.*, **86**, 1807 (1964).

[4] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 251–254, discussion of Edwards equation.

Table I. m:$^-$ + S $\longrightarrow$ m· + S^{-a}

Anion ($-E^{ox}$)	Acceptor molecule ($-E^{red}$) Cr(acac)$_3$ (−2.5)	Azulene (−2.3)	(bipy)Mo(CO)$_4$ (−2.2)	Fe(acac)$_3$ (−1.4)	Trinitrobenzene (−1.3)	Co(acac)$_3$ (−1.2)	(C$_6$H$_6$)$_2$Cr$^+$ (−1.2)	Quinone (−1.2)	Mn(acac)$_3$ (−0.8)	TCE (−0.5)
Ph$_2$Sb	TF							TF		
Ph$_3$Ge	TF	TS	TS	TF	TF	TF	TF	TF		
Ph$_3$Sn (−1.9)	TS	TS	TS	TF	TF	$t_{1/2}$ = 4 sec	TF	TF	TF	TF
CpFe(CO)$_2$ (−1.9)	TS	TS	TS	TF	TF	TF	TF	TF	TF	TF
PhSe (−1.6)				TS		TS		TF	TF	TF
PhS (−1.4)				TS		TS	TS	TF	TF	TF
Ph$_3$Pb (−1.4)				TS	TF	TS	TS	TF	TF	TF
CpMo(CO)$_3$ (−1.1)				TF	TS	TS	TF	TF	TF	
CpCr(CO)$_3$ (−1.1)					TS			TF	TF	TF

^{a} TF = too fast to measure; TS = too slow to observe; all potentials *vs.* 10^{-3} *M* AgClO$_4$|Ag reference; all concentrations millimolar.

tions which should go to completion and those that should not occur, based on electrochemically reversible couple potentials.

It does not appear possible at this time to discuss at great length the fine details of Table I. It seems sufficient merely to point out that there is a limited correlation between the oxidation potential of the anion and the reduction potential of the acceptor and the ability to one-electron transfer. One electron-transfer ability and nucleophilicity seem to be related. The reaction appears to be a general one, involving quite different anion sources and extremely varied substrates.

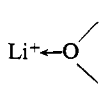
It would appear that the reaction is one that must be kept in mind in synthesis, as has been pointed out in the reaction of triphenylstannyl anion with triphenylsilyl chloride. One-electron transfer here gives triphenylstannyl radical, which couples to hexaphenylditin, and triphenylsilyl radical, which abstracts to give triphenylsilane.

Gegenion Effects. One interesting piece of information came to light in pursuit of the effect of counterion on the nucleophilicity and one-electron-transfer potentialities of the anions under study. With tetrabutylammonium perchlorate as supporting electrolyte, the counterion for the metal and metalloid anions is, perforce, the Bu$_4$N$^+$ ion. Kinetic experiments performed with lithium perchlorate as supporting electrolyte under conditions identical with those employing the tetrabutylammonium perchlorate salt (involving cells outside a controlled-atmosphere enclosure) gave relative rates one to three times slower. However, it appeared that there was a slow decomposition of the anion independent of the addition of substrate. Deliberate addition of water to a (π-C$_5$H$_5$)Fe(CO)$_2$:$^-$, gegenion solution involving Bu$_4$N$^+$ did not alter the lifetime of the anion or alter observed rate processes, but with the Li$^+$ gegenion a rapid decomposition of the anion ensued. Kinetic experiments performed in a Dry Lab–Dry Train with H$_2$O–O$_2$ concentrations below 1 ppm gave the results shown in Table II. The nucleophilicities of the anions are not altered by change in counterion. The effect of the Li$^+$ counterion is perhaps to potentiate the acidity of the water by its solvation

Table II. m:$^-$, gegenion + RX $\xrightarrow{\text{glyme}}$ m–R + X^{-a}

Anion	RX	$k_2^{Li^+}/k_2^{Bu_4N^+}$
(π-C$_5$H$_5$)Mo(CO)$_3$:$^-$	CH$_3$I	1.6
(π-C$_5$H$_5$)W(CO)$_3$:$^-$	CH$_3$I	0.8
(OC)$_5$Mn:$^-$	CH$_3$I	1.5
(π-C$_5$H$_5$)Fe(CO)$_2$:$^-$	(CH$_3$)$_2$CHBr	1.0

^{a} Conditions were anion concentration 2 × 10^{-3} *M*, substrate concentration 2 × 10^{-2} *M*, 0.1 *M* supporting electrolyte, temperatures corrected to 25°.



It is to be noted that the rates are independent of gegenion. The elegant work of Hogen-Esch and Smid[5] with carbanion systems indicate that, in ion-pair reactions, there is a large degree of difference in the observed reactivity of systems involving lithium gegenion, as compared to Bu$_4$N$^+$. This is apparently due to the fact that ether solvents favor solvent-separated ion pairs with Li counterion, but intimate ion pairing when a quaternary counterion is involved.

One is perhaps observing in the present study a consequence of the fact that, although ether donors are not good coordinators toward carbanionic sites, they certainly could be donors toward metal and metalloid anions where charge density is not as highly localized and low-lying empty orbitals are available. Such coordination would level counterion effects.

One-Electron-Transfer Reactions between Organometallic Species. Electron-transfer reactions have been extensively investigated, both theoretically and experi-

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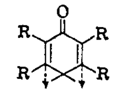
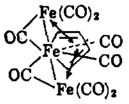
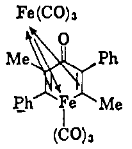
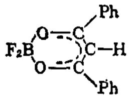
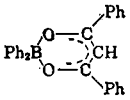
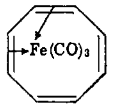
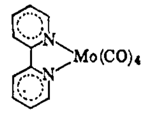
(5) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).

Table III. $A\cdot^- + B \underset{K}{\rightleftharpoons} B\cdot^- + A$; $A\cdot^- + A \xrightarrow[k]{} A + A\cdot^-$

	B						
$A\cdot^-$ ($-E_{1/2}$)	 $R = C_6H_4Cl$						
$Fe_2(CO)_7(Cl\text{-}C_6H_4C)_4$ (1.2)	$k < 10^7$	$K = 0.3$	NT	NT	NT	NT	NT
$Fe_3(CO)_8\text{-}(C_6H_5C)_4$ (1.3)	$K = 30$	$k \leq 10^7$	$K = 0.1$	NT	NT	NT	NT
$Fe_2(CO)_7\text{-}(PhC_2Me)_2$ (1.5)	CT	$K = 1$	$k < 10^7$	SOME T	NT	NT	NT
$F_2B\text{-}(PhCO)_2CH$ (1.6)	CT	CT	CT	$k \approx 10^7$	...	NT	NT
$Ph_2B\text{-}(PhCO)_2CH$ (1.7)	CT	CT	CT	...	$k \approx 10^7$	NT	NT
COT–Fe-$(CO)_3$ (2.0)	CT	CT	CT	CT	CT	...	NT
(bipy)Mo-$(CO)_4$ (2.2)	CT	CT	CT	CT	CT	...	$k = 1.8 \times 10^9$

mentally, in the area of coordination compounds and aromatic organic systems, but very little work has been done in the organometallic area, the ferrocene and chromocene systems being typical examples.

Table III presents the findings of this study on a series of homo- and heteroexchange reactions

$$A\cdot^- + A \underset{k}{\rightleftharpoons} A + A\cdot^- \text{ homoexchange}$$

$$A\cdot^- + B \overset{K}{\rightleftharpoons} B\cdot^- + A \text{ heteroexchange}$$

Of interest in homoexchange is the specific reaction rate constant, k. Normally exchange reactions of this type are so rapid that with heteroexchange processes it is the equilibrium constant, K, which is of interest. The latter would be of value since it would permit a comparison of observed equilibrium constants and those calculated from the couple potentials of the systems involved. A good correlation would tighten the increasing bond between organometallic chemistry and coordination chemistry, where the concept has been widely applied.

Homoexchange. The diagonal element in Table III represents the homoexchange rates measured by esr line-broadening techniques. The bipyridylmolybdenum tetracarbonyl system exchanges electrons at a rate near the diffusion limit, 1.8×10^9 M^{-1} sec^{-1}. The boron–diphenylpropanedione chelates exchange at a rate about 100-fold slower. The three iron-containing systems exchange very slowly indeed, no broadening in signal being observed at radical concentrations of 4×10^{-3} M and saturated solutions of neutral substrate. It would be interesting to propose a sequence of exchange rates which paralleled reduction potential. Indeed rates of electron transfer in hetero systems often do parallel the difference in couple potential. However, the previous paper in this series has pointed out that there is a structural reorganization upon reduction of these iron species, and the radical anion does not have the same structure as its parent. Electron transfer therefore would require structural reorganization; it is likely that this barrier is the source of the slow exchange rate.

Heteroexchange. If the complete application of couple potential theory is applicable to the systems of Table III which involve heteroexchange, then rough calculations from polarographic reduction potentials indicate that, except for a few cases in the upper left corner, the difference in reduction potentials for any given pair exceeds 0.2 v, predicting equilibrium constants larger than 10^3 or smaller than 10^{-3}. Thus the table should divide itself into two sections, all systems lying to the right of the diagonal showing no exchange, and all those lying to the left showing complete exchange. This expectation is realized.

In the upper left corner the closeness in couple potentials (ignoring structural reorganization) permits calculation of finite equilibrium constants, and experimentally rough values for K may be determined and are presented in the table. For the two commutation sets (tie lines indicated in Table III), two things are apparent: (1) the calculated and experimental values are close, but not in good agreement; and (2) the product of the K values determined experimentally for each member of a commutation set should be unity. In both cases this is not true. It is suggested that structural reorganization is responsible for these anomalies. Indeed it appears that care should be taken in extrapolating ground-state molecular orbital calculations to the radical anion's chemistry. The addition of an electron to a system can alter the bond angles and bond lengths that make up the skeleton and may alter the basic skeletal framework.

Conclusions

The previous papers in this series have stressed the similarity between (1) the fate of metal and metalloid radicals and organic radicals, and (2) the free-energy relationships governing nucleophilicity of metal and metalloid anions and inorganic anions. The present paper focuses on the applicability of the oxidation–reduction potential concepts so valuable in coordination chemistry to a host of new organometallic radical species. The consistency is not only useful, but beautiful.

Experimental Section

The basic equipment has been previously described.

All solutions (dimethoxyethane, 0.1 *M* tetrabutylammonium perchlorate) for kinetic studies were 2–4 × 10^{-3} *M* in both anion and substrate. All the anions except Ph_2Sb^- and $CpCr(CO_3)_3^-$ (Table I) were generated by exhaustive controlled-potential electrolysis of the homodimetallic compounds. $CpCr(CO)_3^-$ was generated by reduction of the m–Hg–m compound and Ph_2Sb^- was obtained through the two-electron reduction of $(C_6H_5)_2SbOAc$. All anion precursors and substrates were obtained from commercial sources or prepared by standard literature methods. All compounds were purified by standard techniques of sublimation or recrystallization before use.

Kinetic measurements were made by monitoring the disappearance of the oxidative polarographic wave of the anion utilizing either a rotating platinum electrode (rpe) (600 rpm, Sargent synchronous motor) or a dropping mercury electrode (dme). In some cases, the growth of the esr signal of the product radical anion was also monitored with time.

The present study employed an H cell, having a capacity of 25 ml in each arm. The arms were separated by a medium frit, 25 mm in diameter. One arm was inletted by a standard taper joint, allowing filling with supporting electrolyte and addition of mercury, which served as the counter electrode (3-cm diameter pool). The other compartment (cathode) was inletted by three standard taper joints, allowing entrance of a micro-test electrode, reference electrode, and degassing tube. A Pt wire was pinch-sealed through the base, allowing contact to be made with another mercury pool (3-cm diameter) which could be used for exhaustive controlled-potential electrolysis work. A stopcock at the bottom provided for rapid draining and cleaning.

In a typical run, the parent homodimetallic compound was dissolved in supporting electrolyte at millimolar concentrations. This solution was added to the cathode compartment and degassed. A dropping mercury electrode could be immersed in this solution and a polarographic record made, using a Metrohm polarograph equipped with a Sargent IR compensator. Choosing a voltage well up on the diffusion plateau, controlled-potential electrolysis was effected, using the large pool electrode in the cathode compartment. The potentiostat was a pair of Kepco CK-60–0.5 power supplies in a master–slave configuration, the master unit modified for potentiostatic control and high input impedance. A Heath voltage reference source was used to off-set the summing point, thus setting the controlled potential.[6]

After electrolysis, the indicator electrode, either the rpe or dme, was immersed into the sample. In order to prevent destruction of the anions by atmospheric water or oxygen, a mercury-sealed bearing was used for the rpe and a tight-fitting serum cap with a small hole equal to the diameter of the dme with a slight positive argon pressure for the dme. Using the rpe, well-defined limiting oxidative currents for each anion were observed, and, by setting $E_{test} - E_{ref}$ well up on the limiting current plateau, a continual readout of current proportional to the concentration of anion could be obtained. Using the dme, however, large oxidative maxima whose heights were not directly proportional to anion concentration were observed. These maxima do not, however, prevent one from observing if the reaction is very fast or very slow.

For kinetic experiments utilizing a rpe, the limiting current was set on full-scale travel on the *Y* axis of a Mosley 2D-2 X–*Y* recorder. The desired substrate was injected rapidly through a serum-capped port and simultaneously the time base on the *X* axis of the recorder was activated. A plot of anion concentration *vs.* time could be obtained provided the half-life of the reaction was greater than 2 sec and less than about 30 min. The lower limit is set by mixing time and recorder response, and the upper limit is set for electrode instability, due to the accumulation of solid products on the surface of the rpe. Unfortunately, the rates of all reactions studied by this method were outside these limits except for the reaction of $(C_6H_5)_3Sn:^-$ + $Co(acac)_3$. If the dme was used, the procedure described above was also employed except that the readout device was a Metrohm Polaricord polarograph in conjunction with a Sargent IR compensator. $E_{test} - E_{ref}$ was set on the oxidative wave of the anion and the chart drive of the polarogram activated and substrate injected simultaneously. Reaction rates with half-lives between approximately 5 sec and 3 hr could be observed. The upper limit is set by the fear that anion decomposition or side reactions might become important for longer reaction times. The rates of all reactions studied by this method fall outside these limits.

The third method used to observe reaction rates was the monitoring of the growth of the esr signal of the product radical anions with time. In this study, the method was used to check results obtained from the techniques described above. The anion and substrate were mixed as described above and then transferred to a 3-mm i.d. quartz esr cell *via* and through an appropriate arrangement of three Delmar O-ring valves, the normal Viton seal being replaced by Teflon and the barrel rings by low-temperature silicon rings. Evacuation of the esr cell and leads to the electrolysis cell, followed by isolation from the vacuum pump, allowed rapid transfer of the reaction mixtures. The esr cell was attached to the electrolytic cell by an O-ringed (Viton) ball and socket joint. Less than 1 min elapsed between sample injection and obtaining an esr signal. A Varian E-3 esr spectrometer was used.

The reaction products were identified by comparing their polarographic half-wave potential and esr spectra with those of authentic electrochemically generated species.

Exchange rates were measured by the line-broadening method. Samples were prepared with different ratios of radical anion to neutral material in a Dry Lab–Dry Train inert atmosphere enclosure. The spectra were recorded on a Varian E-3 spectrometer and concentrations determined by use of an electronic double integrator driven by the normal *Y*-axis signal. The integrator output was put back into the vertical recorded input.

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[6] These circuits were constructed with the aid of Paul Birman, Kepco Inc., New York, N. Y.