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The Use of Electrochemical Methods for Studying the Structure and Reactivity of Organometallic Compounds

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The different aspects of using electrochemical methods for studying the structure and reactivity of organometallic compounds as well as for investigating certain details of their reaction mechanisms such as regioselectivity, process compatibility, the role of nucleophilic assistance, and so forth are examined.
The bibliography includes 95 references.

CONTENTS

I. Introduction 864
II. Redox processes in which electron changes are localised on the metal atom 865
III. Redox processes in which electron changes are localised on the π-bond orbitals 867
IV. Redox processes in which electron changes are localised on the σ-bond orbitals 868
V. Simultaneous calculation of electrochemical oxidation and reduction potentials of organometallic compounds in order to determine their reactivity 870

I. INTRODUCTION

In recent years electrochemical methods have become more widely used not only for the purposes of analysis but also for studying the structure and reactivity of organic molecules.[1,2] Electrode reactions can be regarded as models of the fundamental stages of a large number of organic reactions, above all redox reactions.[3]

However, electrochemical methods, apart from classical polarography and cyclic voltammetry, are still not sufficiently popular among organic chemists and organometallic chemists although their relative simplicity to use in terms of equipment could be very useful for solving such theoretical and practical questions as: 1) quantification of redox properties of compounds; 2) determination of the electronic effects of substituents 3) the use of half-wave potentials ($E_{1/2}$) for oxidation and reduction in quantum chemical calculations, including those for determining the site of localisation of electron changes in the molecule during redox reactions; 4) the study of processes leading to the formation of unstable products such as radicals and radical ions; 5) studying the mechanism (kinetics, stoichiometry) of the electrochemical process as a model of the fundamental event of a chemical reaction; 6) establishing a correlation between $E_{1/2}$ for reduction of the M—R σ-bond and the properties of the carbanion R^- or radical R, such as the acidity of RH, nucleophilicity of R^-, electron affinity of R, and so on; 7) the choice of conditions for electrosynthesis of organic and organometallic compounds.

Half-wave potentials are not standard redox potentials in the strict thermodynamic sense. They also include kinetic, adsorption, solvation, and other effects. Nevertheless, they characterise sufficiently precisely the redox properties of a vast number of organic molecules in solution and are often the only available numerical indicators of these properties. Values of $E_{1/2}$, to a greater degree than many other physicochemical quantities, are sensitive to electronic effects in molecules but reflect the spatial configuration and conformation of organic molecules less precisely.

Electrochemical methods can be successfully used to study heterolytic reactions in which the key stage is transfer of an electron from donor to acceptor. Specific criteria have been developed[4] for electrochemical modelling of the fundamental event of a chemical reaction.

1. In drawing an analogy between chemical and electrochemical reactions it is necessary that the same products are obtained as a result of their taking place.
2. After the electron transfer has been defined in a chemical reaction, it is necessary to introduce products formed from electron donors or acceptors into the solutions intended for electrochemical studies and to model their action using electrochemical methods.
3. If the reversibility of the events of electron transfer for the reagents studied can be demonstrated using electrochemical methods and EPR can be used to identify radical ions that are formed in electrochemical and chemical reactions, it may be assumed that the radical ions are sufficiently stable and that the rate of reaction is determined by the slow stage of their decomposition, after which σ-radicals are formed.
4. It should be taken into account that a change in the type of medium can produce a marked change in reaction mechanism and this is clearly defined using electrochemical methods.

It is necessary to take great care when considering the possibilities of using polarography for quantitative determination of the structure and reactivity of organic molecules. It is usually recommended that irreversible waves are immediately excluded from consideration, since the subsequent reactions of radical ions also contribute to their potentials. Two-electron waves are also unsuitable because in the majority of cases transfer of two electrons is due to rapid chemical reactions in the vicinity of the electrode. Consequently, consideration can only be given to reversible one-electron waves for oxidation or reduction, but in this case the heterogeneous nature of the electrode reaction and the specific interaction of substrate with reagent that precedes the transfer of an electron, etc, should be borne in mind. Therefore $E_{1/2}$ values may only reflect a general trend in the change of properties and are relative values. In this connection Okhlobystrin[5] has criticised Pozharskii,[6] who had proposed the use of polarography "as a guiding principle in quantitative studies on reactivity." Nevertheless, even a purely qualitative approximate assessment of the properties of compounds based on electrochemical data can often be very useful.

There have recently been a number of reviews and monographs published on the electrochemistry of heteroorganic compounds such as derivatives of nontransition elements,[7,63] Group I-III elements and transition metals,[8,9] and also metal chelates.[10,11] Aspects of electrochemical synthesis have been examined in reviews.[12,13] Works

devoted to studying π-complexes of transition metals have been correlated in reviews.[14,15] The increased interest in these compounds is due to the fact that the majority of them readily undergo redox conversions that occur with a change in formal oxidation state of the metal while retaining the structure of the organometallic compound and also because the values of the half-wave potentials lie in a convenient region to study. Moreover, processes in which cleavage of C−M or M−X σ−bonds does not occur, are, as a rule, reversible, which increases the strictness of the correlations obtained.

In the present review we examine the works of those authors who do not confine themselves to measuring redox potentials of a given compound and determining the products of their electrochemical conversions but use electrochemical data to study the electronic structure of molecules and predict their chemical properties. The subject matter is arranged in accordance with the site of localisation of electron changes during chemical and electrochemical redox reactions of π- and σ-organometallic compounds, the method for determination of this being proposed in [16].

II. REDOX PROCESSES IN WHICH ELECTRON CHANGES ARE LOCALISED ON THE METAL ATOM

If the metal atom in a complex is bonded by a delocalised π-bond only to carbocyclic ligands and has an electron shell similar to the atoms of an inert gas, when redox processes occur the electron changes are localised on the metal atom. Reactions such as this have the following characteristics: 1) the electron configurations of the oxidised and reduced forms are similar and the electrode reaction is reversible; 2) potentials are virtually independent of the solvent; 3) the polarographic properties do not depend on the addition of a proton donor:

The system ferrocene−ferrocenium ion is very convenient for study, as it is firstly, reversible and, secondly, the rate of its electron exchange is high. The electrochemical behaviour of this system and also π-complexes of other metals has been examined in reviews,[14,15] so we will not go into this subject in detail. The first attempts to establish correlations between the reactivity of organic compounds and the half-wave potentials for their oxidation or reduction date back to the beginning of the 1950s, when the linear free energy principle (equations of Hammett, Taft, Yukawa−Tsuno, and others) started to be applied to polarography. Leaders of this trend were Jaffé [17] and Zuman;[18] the latter applied the Hammett equation to half-wave potentials:

$$\Delta E_{1/2} = E^{X}_{1/2} - E^{H}_{1/2} = \rho\sigma_X,$$

where $E^{x}_{1/2}$ and $E^{H}_{1/2}$ are the half-wave potentials for oxidation or reduction of a compound with a substituent X and an unsubstituted compound, ρ is the reaction constant (measured in volts), σ is the substituent constant. This relationship is valid for both irreversible and reversible electrochemical processes. In the first instance it represents the perturbation introduced by the electronic effect of substituent X to the change in free energy when going from the oxidised (reduced) to the reduced (oxidised) form of the molecule, and in the second instance it represents the perturbation introduced by the substituent to the change in free energy of activation when going from the oxidised (reduced) form to the transitional electrode complex.

It was possible to make use of this concept in order to arrange systematically the material obtained from the polarography of organic compounds and to study the nature of the electronic effect of substituents on the reaction centre (metal atom) in redox reactions.

Comparison of different σ constants of substituents and also from a number of their combinations showed that the best correlation occurs between $E^{o}_{1/2}$ and σ^{0}_{n} derived by Taft.[22] The correlation dependences obtained were successfully used to determine the σ constants of metallocenyl groups and other polyatomic groups.[14,19,27] The electronic effects in ferrocenes,[20,21,23,24,28] and in arenecyclopentadienyliron cations,[29] ruthenocenes and osmocenes[25,30] are such that σ^{0}_{n} constants correlate better with $E_{1/2}$. This indicates that there is conjugation between the aromatic ring and the substituent. However, in *bis*-arenechromium compounds it is very weak, so $E_{1/2}$ for oxidation of *bis*-arene complexes of chromium correlates better with σ_m constants.[26,31,32] The difference between complexes of chromium and other metals is probably due to differences in the nature of the metal−ligand bond,[31] although it should be stressed that in both cases an inductive mechansim for transmission of the electronic effect of substituent to metal atom is the decisive factor.

The half-wave potentials of irreversible processes also correlate with σ constants of substituents. For example, $E_{1/2}$ for the irreversible two-electron oxidation of platinum complexes

$$[P(C_2H_5)_3]_2\,Pt(X{-}C_6H_4)_2 \xrightarrow[-2e]{} [P(C_2H_5)]_2\,Pt(X{-}C_6H_4)_2]^{2+}$$

correlates well with Hammett σ constants,[34] while $E_{1/2}$ for the reduction of chelate complexes of nickel with dithiocations [sic] of general formula $Ni(S_2C_2R_2)_2$ show a linear dependence on the inductive constants of substituents.[35]

It has been shown[36–38] that standard redox potentials E^0 for different one-electron redox transfers in sandwich-type π-complexes of transition metals, such as $Cp_2M^- \rightleftharpoons Cp_2M \rightleftharpoons Cp_2M^+ \rightleftharpoons Cp_2M^{2+}$ give a linear correlation with the corresponding ionisation potentials *IP* of metals and their ions, and this correlation should be common for all metals and all possible redox changes in a series of complexes with the same ligand environment. The existence of such a correlation is due to the fact that the main contribution to the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of metallocenes is made by the atomic orbital (AO) of the metal. Therefore, the potentials for the reactions of metallocenes, including the electron-transfer stage involving the HOMO and LUMO, must be determined by the properties of the metal itself in the given oxidation stage. Although this correlation is approximate and holds for complexes with 12-17 and 19-21 electron configurations (the number of electrons in the valence shell of the metal is given), it is very useful and can be used to predict redox properties from known *IP* values of the metal, and hence also ranges of potential in which different classes of sandwich π-complexes are stable.

In one study[37] a diagram of zones of thermodynamic stability for metallocenes Cp_2M and their cations is given (Fig.1). As can be seen from the diagram, as the atomic weight of M increases the zone of stability for Cp_2M shrinks, in other words, metallocenes of 4d- and 5d-metals are oxidised more readily than their 3d-analogues. This makes it difficult to synthesize heavy metallocenes. The synthesis of doubly charged cations of type $(C_7H_7)M^{2+}$ is also very difficult as they are incompatible with most known solvents as a result of their very strong oxidising capacity ($E^0 > 3.0$ V). Thus, it is very useful to know the values of E^0 when choosing the most convenient method of synthesizing metallocenes and also to understand the nature of the active particles that are formed in reactions catalysed by metallocenes (for example, the products from the

reduction of Cp_2MCl_2, where M = V, Nb, catalyse the low-temperature reduction of carbon monoxide to hydrocarbons in the presence of added quantities of proton-donor compounds[39-41]).

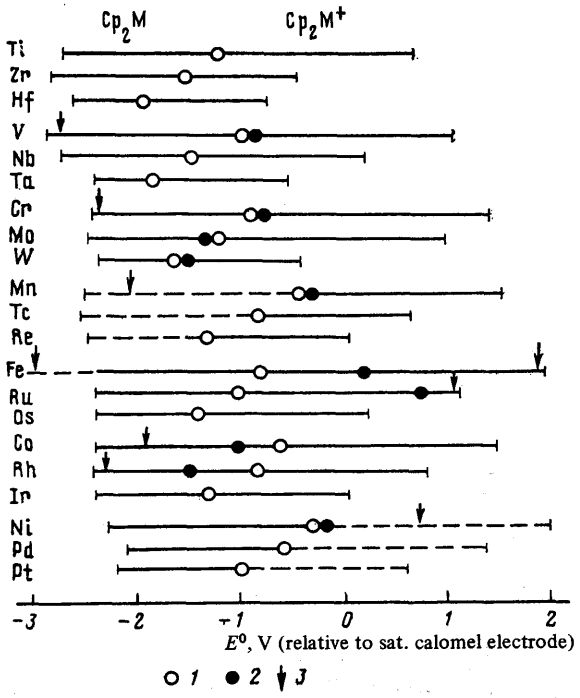


Figure 1. The zones of thermodynamic stability for Cp_2M complexes and their cations; (1) calculated values of E^0 for $Cp_2M^{0/+}$ redox pairs; (2) experimental values of E^0 for $Cp_2M^{0/+}$ redox pairs; (3) experimental values of E^0 for $Cp_2M^{0/-}$ and $Cp_2M^{2+/+}$ redox pairs; the dotted lines denote the zones of stability for Cp_2M^+ cations and Cp_2M complexes for $d^{5/6}$ and $d^{6/7}$ electron transitions for which there is a deviation from the linear dependence of E^0 on *IP*.[37]

Study of π-complexes of Fe, Co, Ni, Cr, Mo, W, Mn, Ru, Re, Au, and Cu,[37,38] has shown that the tangent of the gradient angle of the dependence of E^0 on *IP* for different types of sandwich complexes does not depend on the nature of the ligand and is equal to ~0.11:†

$$E^0 = a + 0.11 \cdot IP,$$

where a is a constant dependent only on the nature of the ligand (E_0 in V, *IP* in eV). It has been calculated for the main types of π-ligands: Cp (-2.08 V), C_6H_6 (-0.73 V), $C_7H_7^+$ (+1.52 V), etc.[37]

Studies[42-48] are devoted to linear relationships between $E_{1/2}$ and *IP*. In particular, a correlation has been found between $E_{1/2}$ for the reduction $M^{II} \rightarrow M^{I}$ and the second ionisation potential of Cp_2M metallocenes, where M = V, Cr, Co, Ni.[45] The value of $E_{1/2}$ for the process $Cp_2M^{III} \rightleftharpoons Cp_2M^{II}$ correlates with *IP* for the complexes Cp_2V, Cp_2Cr, Cp_2VCl_2, $CpNi(\eta^3\text{-}C_5H_7)$.[46] The oxidation potentials of bimetallic compounds:

$$R_3M{-}M'R_3 \xrightarrow{-e} R_3M{-}M'R_3^+ \rightarrow R_3M^{\cdot} + M'R_3^+$$
M, M'=Si, Sn, Ge

correlate with vertical *IP* values.[44]

There is also a linear relationship between the electrochemical potentials for one-electron oxidation and the vertical ionisation potentials for compounds of type R_4Pb.[48]

Thus, it may be concluded from the data examined that in a number of cases the values of $E_{1/2}$, readily measured in solution, can be used to determine ionisation potentials in the gas phase.

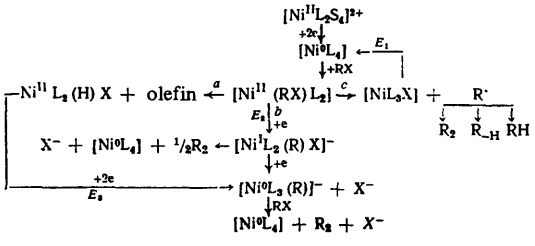
Electrochemical methods can be used to study the disproportionation reactions of unstable complexes of various metals in which the metal is in an intermediate oxidation state and also to determine their HOMO and LUMO energies and spin state.[49] For example, in a study of the two redox systems:

$$Fe^{IV}L_3^+/Fe^{III}L_3 \text{ and } Fe^{III}L_3/Fe^{II}L_3^-$$

it was shown[50] that electrochemical electron-transfer reactions which are accompanied by a change in spin state are slower than reactions in which such a change does not occur. Values of E^0 have also been determined[51] for redox changes of $MF_6^{z/z-1}$ (z = 0, -1, -2; M = Ta, W, Re, Os, Nb, Mo, Ru) and it was shown that for the same metal E^0 increases for the different transitions according to the following series: $d^2/d^3 < d^1/d^2 < d^0/d^1$. The existence of a stepwise relationship between the standard redox potentials and the d^n-configuration of the metal for high-spin and low-spin octahedral complexes has been demonstrated.[52]

Electrochemical methods can be very useful in studying reaction mechanisms. For example, the dimerisation of alkyl and aryl halides catalysed by a Ni(0) complex has been studied.[49] Electrochemical methods were used to show the possibility of regenerating the catalyst, the reaction mechanism was studied and it was established that the Ni(II) complex containing a Ni–R σ-bond that is formed by oxidative addition can decompose by different routes depending on the nature of R (see Scheme 1). Thus, if R = Ar, the complex is thermally stable and can only be broken down by further reduction (route *b*). If R = Alk, the complex is thermally unstable and immediately decomposes according to route *a* (when β-H is present) or route *c*:

Scheme 1



†The tangent of the gradient angle of the correlation dependence must theoretically be close to unity. (Thus, for example in some studies,[42-44] where the correlation between $E_{1/2}$ and *IP* is given for a number of organometallic compounds, it is equal to 0.89, 0.92, 0.98, and 0.87). The experimental value of 0.11 in the relationship obtained in these studies[37,38] is particularly interesting and needs to be explained.

Kochi et al.[48] studied alkyl transfer reactions using lead derivatives as a model and showed that Alk_4Pb reacts with $IrCl_5^{2-}$ according to the scheme:

$$R_4Pb + Ir^{IV}Cl_6^{2-} \xrightarrow{k} R_4Pb^{+} + Ir^{III}Cl_6^{3-}$$
$$R_4Pb^{+} \rightarrow R^{\cdot} + R_3Pb^{+}$$
$$R^{\cdot} + IrCl_6^{2-} \rightarrow RCl + IrCl_5^{2-} \text{ etc.}$$

The linear correlation found between $\log k$ for oxidation of $(C_2H_5)_{4-n}Pb(CH_3)_n$ with hexachloroiridate in acetonitrile and the electrochemical oxidation potentials indicates that the rate-determining stage of the overall process is formation of a radical cation. A similar type of correlation also occurred between $\log k$ in the reaction of Grignard reagents with di-tert-butyl peroxide and $E^{\circ x}_{1/2}$ values of Grignard reagents.[53]

III. REDOX PROCESSES IN WHICH ELECTRON CHANGES ARE LOCALISED ON THE π-BOND ORBITALS

Identification of the general rules governing the change in properties of arenes when coordinated with a metal atom is one of the most important aspects of the chemistry of organometallic compounds. In order to determine this it is possible to make use of an approach based on the comparison of redox properties of free arenes and those coordinated with a metal. Reduction of most complexes and the corresponding uncoordinated ligands in aprotic solvents is a reversible process, which makes it possible to study quantitatively the effect of coordination on the reactivity of π-bonded carbocyclic ligands in redox reactions. A quantitative determination is possible because: 1) these are equilibrium processes, so the difference in reactivity is not due to the nature of the transition state for coordinated and uncoordinated ligands; 2) one-electron reduction processes usually have a low activation energy and proceed rapidly, it may therefore be assumed that the difference between the reduction potentials of coordinated and uncoordinated ligands is caused only by electronic interactions and the changes in steric, solvation, and other effects are minimal; 3) the difference in potentials for reversible reduction of coordinated and uncoordinated ligands determined under the same conditions corresponds to the change in LUMO energies on coordination.

Among the large number of publications devoted to the electrochemical reactions of functional groups of a π-bonded ligand[15] it is possible to select some studies in which attempts have been made to relate the electrochemical behaviour of the compounds with their reactivity and electron properties. For example, a polarographic method was used to determine the electron affinity and σ constants for a number of metallocenyl groups,[54,55] the change in LUMO energy was calculated for acetophenone and benzoquinone when coordinated with $Cr(CO)_3$ [56] and π-$C_5H_5Rh(Ir)$[57] groups respectively. The values of $E_{1/2}$ for oxidation of nitrosyl cation complexes [π-$C_5H_5Mn(NO)LL'$], where L is a Lewis base, can serve as a measure of the π-acceptor properties of Lewis bases as ligands.[58]

The relationship between $E_{1/2}$ and the structure of complexes of Mg, Zn, Cu, Pb, Ni, Co, and V with ethylporphin and other porphyrins has been followed.[59] It was shown that introduction of a metal atom into the porphyrin molecule leads, as a rule, to $E_{1/2}$ changing to a more negative potential, while in a number of complexes of similar structure the change in reduction (oxidation) potentials depending on the nature of the metal is consistent with the change in LUMO (HOMO) energy of the complex.

Coordination affects the reactivity of arenes in different ways depending on the nature and donor-acceptor properties of substituents in the arene.[60,62] Not only the absolute magnitude of the effect can vary here but also its sign. Since the half-wave potential for oxidation of complex to radical cation ($E^{x}_{1/2}$) can serve as a measure of donor-acceptor properties of substituents

$$Arene_2Cr \underset{-e}{\rightleftharpoons} (Arene_aCr)^{+}$$

there must be a connection between the change in $E_{1/2}$ for reduction of arene due to complex-formation ($\Delta E^{ca}_{1/2}$) and $E^{x}_{1/2}$ values. Such a correlation was actually found:[60]

$$\Delta E^{ca}_{1/2} = a + \alpha E^{x}_{1/2},$$
$$a = (0.072 \pm 0.007)\,B;\ \alpha = (0.25 \pm 0.015);$$
$$r = 0.991.$$

Here $\Delta E^{ca}_{1/2}$ is the difference in half-wave potentials between a π-complex with chromium and free arene for a one-electron reversible reduction ($\Delta E^{ca}_{1/2} = E^{c}_{1/2} - E^{a}_{1/2}$).

Thus, the electrochemical cathode reduction reaction is an indicator that can be used to determine the change in free energy on going from arene to π-complex.

The electrochemical reduction of benzalacetophenone and its symmetrical chromium π-complex in DMSO has been studied,[61] and it was shown that the difference in half-wave potential for reduction of π-complex and free arene ($\Delta E^{ca}_{1/2}$) can be regarded as a measure of the effect of coordination on the ability of arene to be reduced to radical anion:

$$\Delta E^{ca}_{1/2} \approx \frac{RT}{nF} \ln \frac{k_c}{k_a}$$

where k_c and k_a are rate constants of reduction for π-complex and free arene respectively.

The dependence of the reactivity of coordinated arene on the nature of the second ligand is a unique feature of *bis*-arenechromium compounds. The high sensitivity of the cathode reaction to substituents in the second ligands is caused by the presence of the chromium atom, which transfers electron density to the ligand, and itself is positively charged.[62] Introduction of a substituent into the ligand has a strong effect on the electron density at the chromium atom and on the dative component of the metal–ligand bond, therefore for these components $\rho = 0.51$ V [62] (we should mention for comparison that $\rho = 0.33$ V [18] for the cathode reduction of substituted benzaldehydes in aqueous alkaline solution).

Thus, the electronic effects of substituents are transmitted from one ligand to another, and the chromium atom considerably intensifies the substituent effect on the second ligand, in other words, the systems in their way resemble an "amplifier" in radioelectronics. The half-wave potential for oxidation of *bis*-arenechromium ($E^{x}_{1/2}$) can be used as an indicator of the capacity of the chromium atom to transmit electron density to ligands. As was also demonstrated,[60] there is a linear correlation between $E^{x}_{1/2}$ and the change in reactivity in the cathode reaction when going from free arene to chromium π-complex ($\Delta E^{ca}_{1/2}$). The correlation equation obtained can be reduced to the general form:[62]

$$\Delta E^{ca}_{1/2} = b + \beta \sum \sigma,$$

where $b \approx 0.125$ V, $\beta = 0.13$ V. It follows from this that the first term in the equation is constant and is independent of the nature of substituent, while the second term expresses the effect of substituent

on the change in free energy when going from free arene to π-complex. The larger the electron-withdrawing effect of the substituent the greater is the decrease in absolute value of $\Delta E^{ca}_{1/2}$.

IV. REDOX PROCESSES IN WHICH ELECTRONIC CHANGES ARE LOCALISED ON THE σ-BOND ORBITALS

The reduction or oxidation of compounds with an M—M, M—C, or M—Hal σ-bond is known to be an irreversible process in most cases. In order to achieve a correlation between $E_{1/2}$ and the structural features, an essential condition is that there exists a constant electron-transfer coefficient for a series of compounds of similar structure. Experimental data indicates that when π-complexes contain localised σ-bonds, reduction in most cases affects only that bond which has the LUMO as an antibonding orbital. Capture of an electron in this orbital leads to cleavage of the σ-bond. When homo- and hetero-polymetallic compounds containing an M—M σ-bond are reduced, metal carbonyl anions $[L_nM]^-$ are usually formed, and readily undergo electrochemical oxidation.[64,65] There is a linear correlation between $E_{1/2}$ for oxidation of anion to radical and $\log k_2$, where k_2 is the rate constant for the nucleophilic substitution reaction:

$$[L_nM]^- + RHal \xrightarrow{k_2} L_nMR + Hal^-.$$

By comparing the values of k_2 for different anions it is possible to determine their relative nucleophilicity, and on the basis of the correlation obtained the relative nucleophilicity of those anions for which direct measurements of k_2 are not possible can be predicted. Using the experimental data obtained for various metal-containing anions (M = Bi, Sb, As, Ge, Sn, Pb, Fe, Ru, Co, Ni, Mn, Re, Cr, Mo, W) as a basis, the following conclusions have been made: in Groups Va, VI, and VII the nucleophilicity of the anions increases on moving down the Group, while in Groups VIII and IVa the nucleophilicity increases going up the Group.[65]

Extension of this approach showed that after measuring the oxidation and reduction potentials of two organometallic compounds it is possible to predict whether a one-electron exchange reaction will take place between them.[66] Thus, for example, for the reaction

$$m^- + S \rightarrow m^{\cdot} + S^- \qquad (1)$$

(where m^- is a metal-containing anion and S is a neutral or charged electron-acceptor molecule) a table has been compiled,[66] in which metal-containing anions arranged in order of increasing nucleophilicity (decrease in $E^{ox}_{1/2}$) are aligned vertically, while acceptor molecules, namely, different organometallic compounds which have $E^{Red}_{1/2}$ values that decrease in absolute value from left to right, are aligned horizontally. So in the top right-hand corner of the table are entered rapid reactions, while in the bottom left-hand corner are reactions which do not go at all or occur extremely slowly. And although the oxidation of anions to radicals on mercury or platinum electrodes is irreversible and $E_{1/2}$ is a kinetic rather than a thermodynamic parameter, the predictions based on these data are in good agreement with experiment (see Table.1).

Polarographic reduction of compounds of type $[\pi\text{-}C_5H_5M(CO)_3]_2$ and $\pi\text{-}C_5H_5M(CO)_3X$ (where M = Cr, Mo, W; X = Hal, CN, Ar, Alk) has been studied[67] and it has been shown that the ease of reduction of the M—M σ-bond decreases on changing from Cr to W.

Studies on the reduction of metal complexes that contain metal-halogen σ-bonds have shown[15,67] that the order of decrease in ease of reduction of this σ-bond for both one-electron and two-electron reduction is opposite to the series of increasing electronegativity of the halogens Cl > Br > I that determines the polarity of this bond. The observed order for decrease in ease of reduction of the M—Hal bond agrees with that of the change in $E_{1/2}$ values for reduction of the C—Hal bond in alkyl halides, which is accounted for by a radical mechanism for reduction. It may be concluded from this that the M—Hal bond in carbonyl complexes of transition metals has a strongly covalent character and has a tendency mainly to homolytic cleavage and not heterolytic cleavage.

Table 1. The dependence of the rate of reaction of (1) on $E^{ox}_{1/2}$ and $E^{Red}_{1/2}$ of reagents (DME, Ag/AgCl).[66]

Metal-containing anion ($E^{ox}_{1/2}$, V)	Acceptor molecules ($E^{Red}_{1/2}$, V)								
	$Cr(acac)_3$ (−2.5)	azulene (−2.3)	(bipy). $Mo(CO)_4$ (−2.2)	$Fe(acac)_3$ (−1.4)	1,3,5-trinitrobenzene (−1.3)	$Co(acac)_3$ (−1.2)	$(C_6H_6)_2Cr^+$ (−1.2)	quinone (−1.2)	$Mn(acac)_3$ (−0.8)
Ph_2Sb	*f*	—	—	—	—	—	—	*f*	—
Ph_3Ge	*f*	*s*	*s*	*f*	*f*	*f*	*f*	*f*	*f*
Ph_2Sn (−1.9)	*s*	*s*	*s*	*f*	*f*	*	*f*	*f*	*f*
$CpFe(CO)_2$, (−1.9)	*s*	*s*	*s*	*f*	*f*	*f*	*f*	*f*	*f*
PhSe (−1.6)	—	—	—	*f*	—	*s*	—	*f*	*f*
PhS (−1.4)	—	—	—	*s*	—	*s*	*s*	*s*	*f*
Ph_3Pb (−1.4)	—	—	—	*s*	*f*	*s*	*s*	*f*	*f*
$Cp_2Mo(CO)_3$ (−1.1)	—	—	—	*f*	*s*	*s*	*f*	*f*	*f*
$CpCr(CO)_3$ (−1.1)	—	—	—	—	*s*	—	—	*f*	*f*

Notation: *f*—fast; *s*—slow.

*Time for half-conversion was 4 sec.

Transition metal compounds with a metal—carbon σ-bond are reduced, as a rule, at more negative potentials than complexes with M—Hal and M—M σ-bonds, and this occurs in a single irreversible stage that involves addition of one or two electrons. The irreversibility of the waves is due to the high reactivity of the particles formed. Three possible types of transition state in the reduction of the Fe—R bond for a series of $\pi\text{-}C_5H_5(CO)_2FeR$ compounds have been examined.[74] The route that leads to polarisation of the form $(Fe^{\delta+}\cdots R^{\delta-})$ can immediately be rejected as the least favourable, and the choice between radical $(Fe^{\cdot}\cdots R^{\cdot})$ and ionic $(Fe^{\delta-}\cdots R^{\delta+})$ routes can be made by studying the effect of substituents at the *para* position of the σ-phenyl ring on reduction. A linear correlation occurs between $E^{Red}_{1/2}$ and σ^0_n (r = 0.973, ρ = 0.12 V). If the contribution of the conjugation effect is greater than that allowed by σ^0_n, then large deviations from a linear relationship occur for such substituents. This fact and also the low value of ρ suggest that in the transition state of the electrochemical reaction studied the demands of the "reaction centre" for a polar substituent effect are not large, which corresponds well with a proposed homolytic type of activation of the Fe—C bond in the electrode field.

It has been shown[68] that replacement of a CO group in $\pi\text{-}C_5H_5.Re(CO)_3$ compounds by a phosphine ligand leads to a change in reduction mechanism (one-electron rather than two-electron). The values of $E_{1/2}$ of the first reduction wave were used to determine the

effect of substituents on the transition state of the electrode reaction. The best linear correlation occurred between $E_{1/2}^{Red}$ and the sum of the inductive constants from substituents at the phosphorus atom or with the basicity of the corresponding phosphines.

The polarographic reduction of compounds of type $XM(CO)_5$ (M = Mn, Re; X = Hal, Ar, acetyl, aroyl) occurs irreversibly according to a two-electron mechanism.[69] In all cases there is homolytic activation of the bond being reduced. In contrast to other types of σ-bond, the reduction of the M–C σ-bond (aromatic ring) is virtually independent of the nature of the metal.[69] The effect of substituents in the benzene ring of aryl derivatives on $E_{1/2}^{Red}$ is also small, which suggests that there is no conjugation between the aryl group and the metal atom in both the ground and transition states. However, the $E_{1/2}^{Red}$ values of acyl substituents vary considerably with the nature of the substituent. A good linear relationship is observed between $E_{1/2}^{Red}$ and Hammett σ constants (r = 0.985); ρ = +0.288 V and is the same for both Re and Mn derivatives.

An investigation using polarography and cyclic voltammetry showed[70] that reduction of planar cobalt chelate complexes occurs in the following way (chel is polydentate chelate ligand):

$$[RCo^{III}(Chel)L] \underset{-e}{\overset{+e}{\rightleftharpoons}} [RCo^{III}(Chel)L]^- \underset{-e}{\overset{+e}{\rightleftharpoons}} [RCo(Chel)L]^{2-}.$$

The $E_{1/2}$ values of the first reduction stage for the same type of complex depend on R, in other words, the electron affinity of the organometallic chelate depends on the stability of the R^- anion, and there is a correlation between $E_{1/2}^{Red}$ and pK_a (RH). This means that the orbital into which the electron goes on reduction is the antibonding orbital of the Co–C bond. Thus, the electrode process examined can serve as a model of a reductive cleavage reaction.

It was previously shown[71] that there is a clear correlation between the nucleophilicity of Co(I) complexes in oxidative addition reactions and $E_{1/2}$ for reduction of complexes Co(II) → Co(I). Special attention should be given to the fact that redox potentials of cobalt chelates can vary over a very wide range depending on the nature of the ligand. If the electron density on the Co atom varies to the same extent, the distribution of charge on the Co–C bond must vary accordingly. A change in electron density on the Co atom and a distribution of charge on the Co–C bond can mean that there are various mechanisms for cleavage of this bond, including the extreme cases – nucleophilic and electrophilic and electrophilic reactions on the carbon atom—and the intermediate homolytic cleavage. Such an approach can possibly be used to develop the chemistry of coenzymes that belong to the vitamin B_{12} group and which contain a Co–C bond.

Polarography can be a convenient method for determining the electron affinity of various radicals.[72,73] Organomercury compounds that are reduced on an Hg cathode in two one-electron stages can be used for this purpose:

$$RHgHal + e \rightarrow RHg^{\cdot} + Hal^-,$$
$$RHg^{\cdot} + e \xrightarrow{H^+} RH + Hg.$$

Since the C-Hg bond in $RHg^{\cdot}$ is weakened, it may be assumed that when this particle is reduced the changes in electron density are localised mainly in the half-filled orbital of R$^{\cdot}$, so that there is a good linear correlation between $E_{1/2}$ for the second reduction wave and the electron affinity of radical R$^{\cdot}$. The limited number of other methods for determining this value are less accurate. Study of the dependence of $E_{1/2}$ for the second wave on the substituent in the radical showed[73] that the best correlation occurs between $E_{1/2}^{Red}$ and σ_n^0, namely, the dependence of $E_{1/2}^{Red}$ on polar effects is small, as is typical for homolytic cleavage of a bond.

Electrochemical data can be used to predict the type of decomposition of radical cations formed as intermediates. Decomposition of the form $RH^{+\cdot} \rightarrow R^{\cdot} + H^+$. The scheme for decomposition of the triethylsilane radical cation predicted[74] on the basis of this principle

$$(C_2H_5)_3SiH \underset{-e}{\rightarrow} [(C_2H_5)_3SiH]^{+\cdot} \rightarrow (C_2H_5)_3Si^+ + H^{\cdot}$$

($E_{1/2}^{ox} = 0.230$ V) is in good agreement with the experimental data.

Electrochemical methods can be successfully used to study the properties of organomagnesium compounds, in particular for determining their basicity.[75] Cathode-anode polarisation curves of solutions of RMgX and R_2Mg in THF on a hydrogen electrode probably correspond to the following process:

$$RMgX + {}^1/_2H_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} RH + MgX^+.$$

The zero current potential $E_{i=0}$ of the polarisation curve is the equilibrium value for this redox system and depends on the basicity of RMgX. The pH value [sic] of solutions of organomagnesium compounds, calculated as a function of $E_{i=0}$, is a quantitative measure of their basicity. Polarography data can be used to determine the acidity of hydrocarbons. Determination of the acidity of weak CH acids such as hydrocarbons is not possible by a direct method because of the large pK_a value for most hydrocarbons and their slow dissociation. At the same time it is possible to measure the equilibrium constants of other reactions of carbanions and compare them with the pK_a values of hydrocarbons. The first attempt to use polarography for determination of the relative stability of carbanions was undertaken by Streitwieser and Perrin,[76] who tried to relate $E_{1/2}^{Red}$ for substituted benzyl chlorides and polycyclic arylmethyl chlorides in DMF with pK_a values of the corresponding arylmethanes. Then the $E_{1/2}$ value of the second reduction wave of organomercury salts was suggested[77] as a measure of the relative acidity of CH acids. However, the use of this parameter did not prove very successful because the value of $E_{1/2}^{Red}$ for the second wave depends on the rate of dimerisation of the initially formed radicals. A correlation was found successfully in two studies,[78,79] in which it was recorded that the acidity of CH acids over a wide range of pK_a values is related to the polarographic reduction parameters for symmetrical organomercury compounds R_2Hg, which undergo a two-electron reduction to form the corresponding carbanions R^-. There was found to be a linear relationship between values of $\alpha n_\alpha E_{1/2}$ (α is the electrochemical transfer coefficient, n_α is the number of electrons in the potential-determining stage) and pK_a values:

$$\Delta(\alpha n_\alpha E_{1/2}) = \rho \Delta pK_a,$$

where ρ is an empirical coefficient that is dependent on the experimental conditions. Using this equation a scale of CH acidity covering more than 50 hydrocarbons was compiled. Later the CH

acidity of some brominated toluenes was determined by the same method.[80]

Denisovich and Gubin[81] studied three series of compounds—RHgX, R_2Hg, and σ-derivatives of π-cyclopentadienyldicarbonyliron—in order to compare the reduction parameters and pK_a (RH). All these compounds are reduced by cleavage of the carbo–metal bond to give the carbanion R^-. The correlation between $E_{1/2}$ and structure is known to be good only for reversible processes. For irreversible processes the correlation holds only if the α coefficient is strictly constant. The reason for the scatter in α values for the different series of organomercury compounds is related to the unsaturated state of the coordinated mercury atom, which leads to complex-formation between molecules of organomercury compound and solvent and with each other. Iron π-complexes are free of these problems. The α coefficient for these series is virtually constant. It is therefore more suitable to use σ-derivatives of π-cyclopentadienyldicarbonyliron in the determination of unknown pK_a (RH) values. It is true that a significant shortcoming of these compounds is that it is difficult to synthesize them. The pK_a values of ferrocene have been determined[81] as well as those of cyclopentadienyltricarbonyls of manganese and rhenium.

Up to this point we have examined studies in which electrochemical methods have been used on processes that occur with cleavage of a carbon– metal σ-bond and on the properties of the particles formed by this. However, it is also possible to use electrochemical methods to determine the tendency of compounds to form such a bond. For example, it was shown[82] that preliminary polarographic analysis can be a useful test of whether benzyl bromide containing different substituents in the ring will readily undergo a reaction with metallic mercury to give the corresponding benzylmercury bromide. The C–Br bond in benzyl bromide is known to be reduced in a single two-electron stage (see [3], p.217). Such behaviour was observed[82] for unsubstituted benzyl bromide, the three isomeric monobromo derivatives, 3,5-dibromo- and pentafluoro-benzyl bromides. However, pentabromo-, pentachloro-, 2,3,4,6-tetrabromo-, 2,4,6-tribromo-, and 2,6-dibromo-benzyl bromides give polarograms that are identical with those of the corresponding benzylmercury bromides. This suggests that these benzyl bromides are reduced via organomercury compounds that are rapidly formed by contact of the benzyl bromides with the surface of the mercury electrode. Reduction by this route in fact occurs for those benzyl bromides which give organomercury compounds after a short time in good yield when the reactions are carried out preparatively.

Electrochemical methods in combination with different spectral methods can provide valuable information on the electronic structure of σ- and π-organometallic compounds, the charge transfer mechanism in reduction or oxidation products, the distribution of spin density in molecules, and skeletal rearrangements during reduction or oxidation. Answers to these questions are important for both theoretical and preparative chemistry. For example, there are a number of studies[83–89] on the mechanism for charge transfer to the metal atom and carbonyl groups in octahedral and bipyramidal complexes of Fe, Cr, Mo, and W and in their one-electron reduction products. It was shown that in the octahedral complexes transfer of charge to and from the metal atom occurs by a σ-mechanism, namely, one involving metal–ligand σ-bonds, while in the bipyramidal complexes there is a π-mechanism for charge transfer towards the metal atom, namely, one involving metal–ligand π- or δ-bonds, and a σ-mechanism in the opposite direction. The force constants calculated from IR spectra for octahedral complexes of the form $LM(CO)_5$ (M = Cr, Mo, W; L = Py, quinoline) and their reduction products are also discussed in terms of σ- and π-bonding; the electrochemical properties and EPR spectra of 27 different bimetallic compounds were also studied.

V. SIMULTANEOUS CALCULATION OF ELECTROCHEMICAL OXIDATION AND REDUCTION POTENTIALS OF ORGANOMETALLIC COMPOUNDS IN ORDER TO DETERMINE THEIR REACTIVITY

In the studies examined in the preceding chapters, the relation between the reactivity of a compound and only one of the redox potentials–oxidation potential or reduction potential—has been investigated. In our opinion a much more fundamental relation between the electrochemical potentials and electronic structure of molecules and their reactivity can be followed if both the oxidation potentials and reduction potentials measured under the same conditions are known. Then for reversible electrochemical processes it is possible to determine the relative energies of frontier HOMO and LUMO orbitals, their change of position in relation to molecular structure, and also the magnitude of the energy gap between these orbitals, on which the stability of a molecule is dependent during thermal or photoexcitation. In the case of irreversibly oxidised or reduced systems, which includes the majority of organic compounds, similar direct correlations are less good. Nevertheless, it may transpire that even for electrochemically irreversible processes the effect of substituents in a series of related substrates on $E_{1/2}^{ox}$ and $E_{1/2}^{Red}$ will have a corresponding effect on the HOMO and LUMO energies, and then readily available electrochemical potentials can be used to predict reactivity at a semi-quantitative level.

Such an approach was used for the first time[90] when oxidation and reduction potentials on a platinum electrode under absolutely identical conditions were measured for 35 alkyl-, aryl-, and benzylmercury halides. On the basis of the derived values of the half-wave potentials for oxidation and reduction, a new classification of organomercury halides was proposed, making it possible to predict their relative reactivity in reactions with different forms of cleavage of the C–Hg bond (Fig.2, Table 2). According to this classification organomercury compounds can be divided into four types—anionogenic, cationogenic, radicalogenic, and inert (labelled as A, C, R, and I respectively in Fig.2); this reflects the relative stability of carbanions (A), carbocations (C), and radicals (R) formed. This classification is very provisional and there is no sharp boundary between groups. For example, not only secondary benzyl but also primary benzyl and alkyl organomercury compounds can undergo radical decomposition. It should however be emphasised that on moving upwards along the diagonal *ir* the relative tendency to radical decomposition will increase, since as this occurs the magnitude of "the inherent polarographic gap" of the compound (i.e, the difference $E_{1/2}^{ox} - E_{1/2}^{Red}$) will decrease.

In one study,[91] of the stability of organometallic compounds (OMC) in their synthesis and decomposition processes, the values of the OMC ionisation potentials (or oxidation potentials in solution) are used to predict the stability of the compounds and their tendency to different types of cleavage of the C–M bond. For nontransition metals that have ionisation potentials IP_M of the order of 4–8 eV, there is typically formation of those OMC for which $IP_{OMC} > IP_M$ (when $IP_R > IP_M$) with organic radicals ($IP_R \sim 8-10$ eV). In this

case as a result of the electropositive nature of the metal the contribution of the orbital of the radical to the HOMO in the organometallic compound will be greater, which corresponds to the formation of a polar M–R bond with a negative charge on R. When $IP_M \approx IP_R$ the M–R bond will be covalent, even though $IP_{OMC} > IP_M \approx IP_R$. When $IP_M > IP_R$ the negative charge of the dipole will be localised on the metal atom and the HOMO will have a primary contribution from the metal orbital.

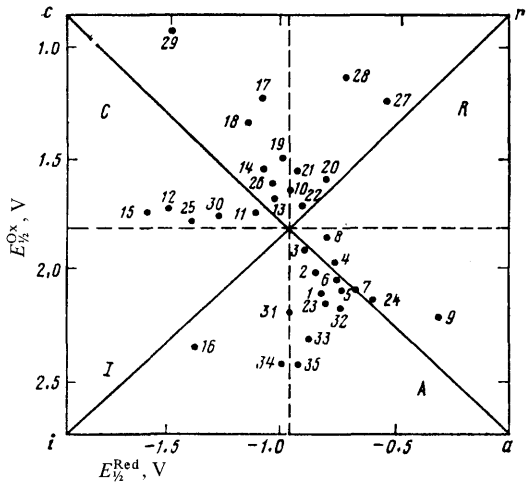


Figure 2. The classification of RHgHal compounds in accordance with their oxidation and reduction potentials measured on a Pt electrode in CH_3CN with 0.05 M Bu_4NBF_4 as supporting electrolyte at 20 °C relative to Ag/AgCl (sat. KCl), ω = 2700 revs/min.[90] Organomercury compounds of type 4-X–$C_6H_4CH(COOEt)HgHal$ (points 1–9) where X is: (1) tert-C_4H_9, (2) iso-C_3H_7, (3) C_2H_5, (4) H, (5) F, (6) Cl, (7) Br, (8) I, (9) NO_2; organomercury compounds of type AlkHgHal (points 10–16) where Alk is: (10) C_2H_5, (11) n-C_3H_7, (12) n-C_4H_9, (13) iso-C_3H_7, (14) tert-C_4H_9, (15) neo-C_5H_{11}, (16) CF_3; organomercury compounds of type Y–$C_6H_4CH_2HgHal$ (points 17–26) when Y is: (17) 4-OCH_3, (18) 4-CH_3, (19) 4-H, (20) 4-F, (21) 4-Cl, (22) 4-Br, (23) 4-CF_3, (24) 4-NO_2, (25) 3-OCH_3, (26) 3-Br; organomercury compounds of type $ArCH(CH_3)HgHal$ (points 27 and 28) where Ar is: (27) C_6H_5, (28) 8-quinoly; organomercury compounds of type 4-Z–C_6H_4HgHal (points 29–35) where Z is: (29) $N(CH_3)_2$, (30) OCH_3, (31) iso-C_3H_7, (32) CH_3, (33) H, (34) F, (35) Br.

However, calculation of only the ionisation potentials (or oxidation potentials in solution) is insufficient for an understanding of the nature of the R–M bond, since, as mentioned above, there is no one-to-one correspondence between the values for oxidation and reduction potentials. Simultaneous calculation of the tendency of OMC to both oxidation and reduction makes it possible in many cases to rule out a structure of type $R^+ - M^-$. These are probable only for compounds that are readily oxidised and are difficult to reduce, but if the compounds that are readily oxidised are comparatively easy to reduce, then a nonpolar structure R–M should be considered instead of structure $R^+ - M^-$. This is in accordance with the suggestion[90] that readily oxidised and reduced compounds must have a tendency to decompose into radicals.

Table 2. The classification of organomercury halides RHgHal on the basis of their electrochemical potentials.[90]

Area in Fig.2	RHgHal		R	Typical reactions
	oxidised	reduced		
C (cationogenic)	readily	with difficulty	ZC_6H_4, Alk, $ArCH_2$	$RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-}$ $RHg^+ \rightarrow R^- + Hg$
A (anionogenic)	with difficulty	readily	ArCH(COOEt), $4\text{-}NO_2C_6H_4CH_2$, YC_6H_4	$RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-}$ $RHgHal + N^- \rightarrow R^- + HgHalN$
R (radicalogenic)	readily	readily	ArCH (Alk)	$RHgHal \rightarrow R^\cdot + HgHal^\cdot$ $RHgHal \overset{+e}{\rightleftarrows} (RHgNal)^{\cdot-} \rightarrow R^\cdot + Hg + Hal^-$ or $RHgHal \overset{+e}{\rightleftarrows} (RHgHal)^{\cdot-} \rightarrow R^\cdot + HgHal^-$
I (inert)	with difficulty	with difficulty	CF_3, R_F	—

Notation: Z—strong electron-donor; Y—strong electron-acceptor, N—mercurophile.

The approach suggested in this work[90] is also very fruitful for studying bimolecular reactions. It has been used[92] to study symmetrization reactions of substituted ethyl α-bromomercuryphenylacetates. Since the substituent effect conforms to the Hammett equation both in symmetrization[93] and (with a poorer correlation coefficient) electrochemical reduction of ethyl α-bromomercuryphenylacetates,[33] there must automatically be a correlation between $\log k_{symm}$ and $E^{Red}_{1/2}$. However, it does not follow from this that both reactions have an identical or similar mechanism (for example, symmetrization occurs via one-electron transfer) as the Hammett equation is obeyed by hundreds of reactions with a variety of mechanisms. The conclusion[33] that the rate of symmetrization tends to increase as the tendency of RHgHal to reduction grows but is not related in any way to its tendency to oxidation, is not at all consistent with a cyclic structure for the transition state in which one of the two RHgHal molecules is a donor and the other an acceptor. Therefore, in establishing correlations between redox potentials and rates of reaction it would be necessary to seek approaches in which both $E^{Red}_{1/2}$ and $E^{ox}_{1/2}$ were taken into consideration.

An equation was obtained[92] for the symmetrization reaction, relating the rate of symmetrization to the electrochemical oxidation and reduction potentials of organomercury halides:

$$\log k = a(1/G_1 + 1/G_2) + b, \qquad (2)$$

where a and b are constants, $G_1 = E^{ox}_{1/2} - E^{Red}_{1/2}$ is the polarographic gap for the given RHgX, $G_2 = E^{ox}_{1/2}(Hg-Br) - E^{Red}_{1/2}$ is the difference between the oxidation potential of the Hg–X bond (when X = Br) and $E^{Red}_{1/2}$ (see Fig.3). It follows from this that organomercury salts that are readily oxidised and readily reduced must also readily undergo symmetrization, namely, an increase in electron-withdrawing properties of the substituents in the benzene ring must have an

accelerating effect, which was in fact observed experimentally.[93] This is due to the increased degree of nucleophilic assistance exerted by the bromine atom in the RHgBr molecule, but at the same time the ability of the R—Hg σ-bond in the other molecule to coordinate with the mercury atom of the first molecule must also increase. The second effect is stronger in all cases, namely, the decisive factor is dependence on the inherent polarographic gap. For a cross-symmetrization reaction the regioselectivity of reaction was shown[92] to be related to the electrochemical parameters of the reagents.

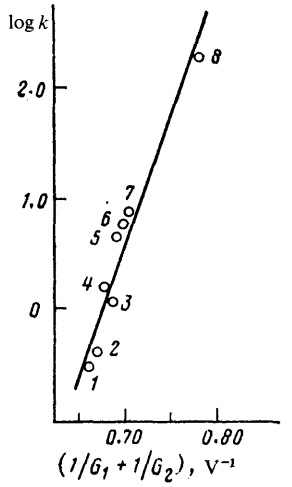
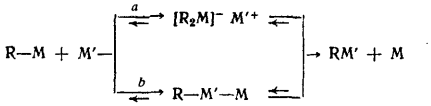


Figure 3. The dependence of the logarithm of rate constant for the symmetrization reaction of 4-X—$C_6H_4CH(COOC_2H_5)HgBr$ on the magnitude of the polarographic gap[92] where X is: (1) tert-C_4H_9, (2) iso-C_3H_7, (3) C_2H_5, (4) H, (5) F, (6) Cl, (7) Br, (8) I, (9) NO_2.

An electrochemical method has been used[94] to study the bromo- and iodo-mercuration of organomercury halides and an equation similar to (2) has been selected, only in this case $G_1 = E^{o}_{1/2}(\text{RHg.Hal}) - E^{\text{Red}}_{1/2}(\text{Hal}^-_3)$; $G_2 = E^{o}_{1/2}(\text{Hal}^-_3) - E^{\text{Red}}_{1/2}(\text{RHgHal})$. The results obtained[94] can briefly be summarised as follows: 1) if RHgX is readily oxidised and readily reduced, the reaction must proceed rapidly since both electrochemical gaps G_1 and G_2 will be narrow; 2) if RHgX is readily oxidised but is reduced with difficulty, the rate of reaction is mainly determined by gap G_1 and will be higher the narrower this gap; 3) if RHgX is readily reduced but oxidised with difficulty, the rate of reaction is mainly determined by gap G_2 and will be higher the narrower this gap; 4) if RHgX is oxidised with difficulty and reduced with difficulty, the reaction must proceed slowly as both gaps will be wide. These conclusions are valid not only for bromomercuration but also apparently for other reactions of organomercury compounds that proceed via a cyclic transition state. The important factor is the relative position on the potential scale of the oxidation and reduction levels of the second ("electrophilic") agent, the width of gaps G_1 and G_2 being dependent on this.

An attempt was made[95] to predict the reaction pathway—ionic (a) or covalent (b)—for redox transmetallation reactions:



On the basis of the redox properties of the reacting metals (metal complexes or metalloids) expressed numerically as ionisation potential (IP) and electron affinity (E)‡ it was concluded that in reactions involving two metals M and M', each of which has $IP + E < 8$ eV, ionic compounds are formed as intermediates. When $IP + E > 10$ eV, covalent bonding occurs. Metals, metalloids, and complexes that have an average total value of $IP + E$ in the region 8—10 eV can evidently react by either an ionic or covalent pathway depending on the conditions. These findings make it possible to carry out a purposeful synthesis of polynuclear compounds and to choose metals—catalysts in thermodestruction processes of organometallic compounds.

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From the material reviewed it may be concluded that electrochemical redox potentials can be used as energy characteristics of reagents in order to analyse the effect of structure on reactivity. A rational approach is to assign oxidation and reduction potentials to specific localised sites of electron change in the molecule being studied (bonds, individual atoms) during electrochemical oxidation and reduction and then to local regions of change in electron density in a nonelectrochemical reaction.

In order to establish a correlation between the rates of homogeneous reactions and electrochemical potentials it is necessary to measure both the oxidation potential and the reduction potential of both reagents. With such an approach it is possible to reveal the essential features of the reaction, which cannot be detected when a correlation with only $E^{o}_{1/2}$ or only $E^{\text{Red}}_{1/2}$ is considered; an example of this is the degree of reaction compatability on the terminal atoms of reacting molecular fragments (relative contribution of G_1 and G_2).

It cannot be concluded from the existence of a correlation between the rates of reaction and electrochemical potentials that these reactions must proceed according to a one-electron transfer mechanism (similarly for the existence of correlations with ionisation potentials or electron affinity) since both the rate of reaction and the redox potentials are related to the energies of the frontier orbitals. Interaction between the frontier orbitals does not necessarily lead to complete electron transfer and the formation of radical cation and radical anion particles.

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‡Instead of these properties the possibility of using the values of the standard redox potentials of reagents is admitted by Bochkarev and Pankratov.[95]

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