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The Nature of Electron Transfer from Metal Surfaces to the Carbon–Halogen Bond[1]

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Abstract: Electrochemical reduction of a number of organic halides at a glassy carbon electrode are reported. The results have been interpreted as showing that the electron transfer and cleavage of the carbon–halogen bond for the substrates studied is concerted.

Introduction

In the course of numerous investigations on the stereochemistry and mechanism of organometallic compound formation effected by electron-transfer reactions from metal surfaces, the use of cyclopropyl systems as probes has been the subject of several reviews and articles.[2] The advantage of the cyclopropyl system in this type of investigation resides in the fact that, in contrast to other saturated hydrocarbons, once the carbanion or organometallic reagent is formed it is capable of maintaining its optical activity and configuration,[3] whereas the cyclopropyl radical is a σ radical which has been shown to reach its inversion equilibrium, with a rate constant on the order of $10^{11}\ \mathrm{s}^{-1}$, before reacting with the solvent[4] or being trapped by a second electron transfer.[5] On the basis of these observations, (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**) and (*S*)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (**3**) were selected as probes to establish the surface nature of Grignard reagent formation[6] and other metal surfaces such as alkali metals[7] as well as mercury.[8] The aliphatic cyclopropyl system (*S*)-(+)-1-bromo-1-methylspiro[*2.5*]octane (**4**) was devised[9] mainly to remove the criticism[12] related to the presence of the phenyl moiety in **1** and **3** when these probes were used to establish the surface nature of Grignard reagent formation.[3,4,6] (*S*)-(+)-**5**, which would give rise to a planar π delocalized radical,[11] has also been included in our studies. All the mechanistic conclusions reported from the use of the above probes were based on stereochemical analyses, radical trapping experiments, and product distributions observed during the organometallic compound formation. For example, in all the cases studied, retention of optical activity was observed in the organometallic species formed, and this was taken as evidence, *inter alia*, for the surface nature of the reaction.

However, the questions of interest that still remain are the following: Is bond breaking a concerted or stepwise process when electrons are transferred from metal surfaces to the carbon–halogen bond? Are radical anions formed as intermediates? Do the π^* orbitals of the aromatic moiety in **1**, **3**, and **5** compete with the σ^* orbital of the carbon–halogen bond during the electron-transfer process from the surface, thus causing these systems to be atypical?[12]

The most conclusive studies devised to ascertain whether electron transfer and bond breaking are concerted or stepwise have been conducted by Savéant and co-workers,[13] who examined the electrochemical reductive cleavage of the carbon–halogen bond at inert electrodes, using a variety of aromatic and aliphatic halides. In order to determine whether or not an anion radical is formed as an intermediate in the probes that we have used during our investigation of the Grignard reagent formation, we investigated the reductive cleavage of the carbon–halogen bond in these systems by cyclic voltammetry as suggested in the work of Savéant.[13] This technique provides a convenient means for generation and detection of anion radicals and also provides a means for deciding whether they are intermediates or transition states.

Results and Discussion

In the present study, experiments were first carried out on the following substrates: 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**), 1-fluoro-1-methyl-2,2-diphenylcyclopropane (**2**), 1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (**3**), 1-bromo-1-methylspiro[2.5]octane (**4**), and methyl 2-bromodibenzobicyclo[2.2.2]octadiene-2-carboxylate (**5**). Cyclic voltammetry of those substrates was performed at a glassy carbon electrode (diameter = 3 mm) which, in contrast to the mercury electrode or other reactive electrodes, is believed to be sufficiently inert toward chemical reactions with radical intermediates formed during the reduction process.[14,15] Acetonitrile was used as solvent and tetrabutylammonium fluoroborate (0.1 M) as supporting electrolyte.

Table I and Figure 1 show the most relevant information concerning the electrochemical reduction of the substrates **1**–**5** at a scan rate of 0.1 V. With one exception, that of 1-fluoro-1-methyl-2,2-diphenycyclopropane (**2**), which exhibited no reduction before concomitant reduction of either the solvent or the supporting electrolyte, a single irreversible cathodic wave was observed in all cases. The values of the transfer coefficients were derived from the cyclic voltammetric peak widths, assuming that

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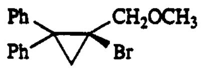
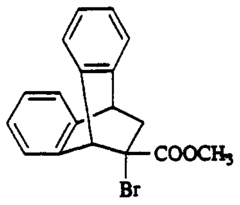
Chart I


(S)-(+)-1

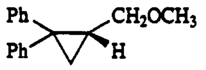

(S)-(+)-2


(S)-(+)-3


(S)-(+)-5


(R)-(-)-6


(S)-(+)-4


(R)-(-)-7

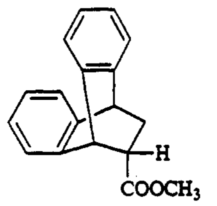
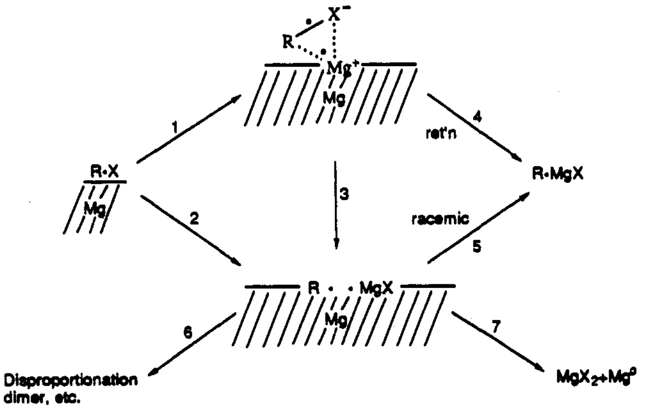

(S)-(+)-8

Table I. Cyclic Voltammetric Peak Potentials[a] and Transfer Coefficientα[c] Determined for the Substrates 1, 3, 4 and 5[c]

compd	no. of characteristic waves	$-E_p$ (V vs SCE)	$-E_{p/2}$ (V vs SCE)	$E_{p/2} - E_p$ (mv)	α
1	1 irreversible	2.65	2.49	160	0.3
3	1 irreversible	2.61	2.43	175	0.27
4	1 irreversible	2.85	2.66	180	0.25
5	1 irreversible	1.61	1.46	150	0.32

[a] Measured at glassy carbon, in acetonitrile + 0.1 M n-Bu$_4$BF$_4$ at 25 °C, scan rate 0.1 V s^{-1}. [b] The average values of α were determined from the cyclic voltammetric peak widths assuming the Butler–Volmer kinetics applies $\alpha = 1.85(RT/F)/(E_{p/2} - E_p)$.[14a,b] [c] No reduction was observed for compounds 2, 6–8 at a potential less negative than the concomitant reduction of either the solvent or the supporting electrolyte (–2.9 V.).

Scheme I. Mechanism for Grignard Reagent Formation



Butler–Volmer kinetics applies: $\alpha = 1.85(RT/F)/(E_{p/2}-E_p)$.[14a,b] Of interest is that the values of the transfer coefficient, which were shown to be independent of the scan rate,[14b,16] were small for all the substrates (between 0.25 and 0.32). Similar observations have been reported by Savéant *et al.* in their studies on the electrochemical reduction of simple aliphatic halides[14a] (n-, *sec*-, and *tert*-butyl halides) at a glassy carbon electrode. Cyclic voltammetry of the butyl halides showed one or two irreversible waves according to the relative reducibility of the alkyl halide RX and of the radical R$^\bullet$. All transfer coefficients reported were smaller than 0.5 (between 0.2 and 0.32). The fact that the transfer coefficient is small was taken as further evidence that the reduction pathway does not involve the RX$^{\bullet-}$ anion radical as an intermediate. Our observations from the electrochemical reduction of 1, 3, 4, and 5 at the glassy carbon electrode are in agreement with this. The cyclic voltammetry shape, the peak width $E_{p/2} - E_p = (180 - 150)$ mV, and the value of $\alpha = 0.25$–0.32 at different scan rates[16] showed without question that electron transfer and decomposition of the anion radical for these substrates is concerted.

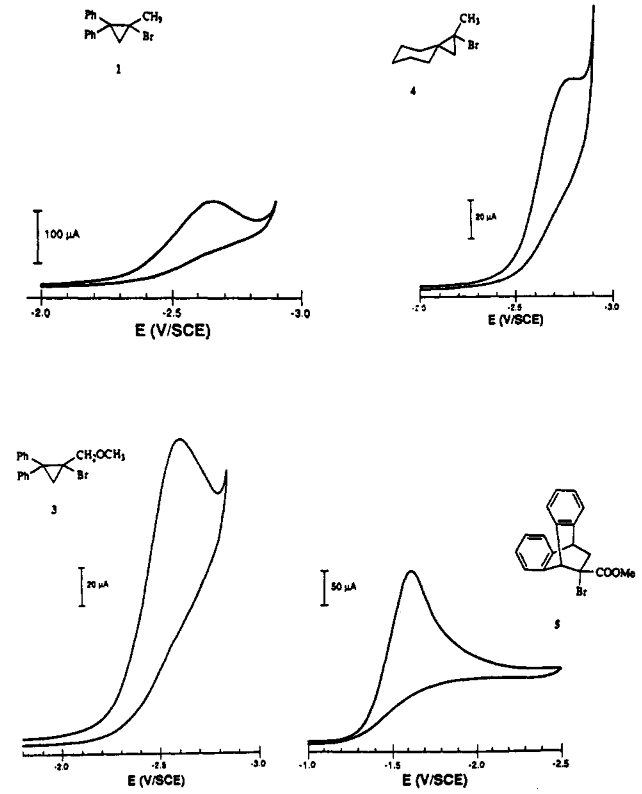


Figure 1. Cyclic voltammetry of the substrates 1, 2, 3, 4, and 5 (5 mM) on a glassy carbon electrode in acetonitrile + 0.1 M n-Bu$_4$BF$_4$ at 25 °C, scan rate 0.1 V s^{-1}. Vertical scale in μA; horizontal scale in V vs SCE.

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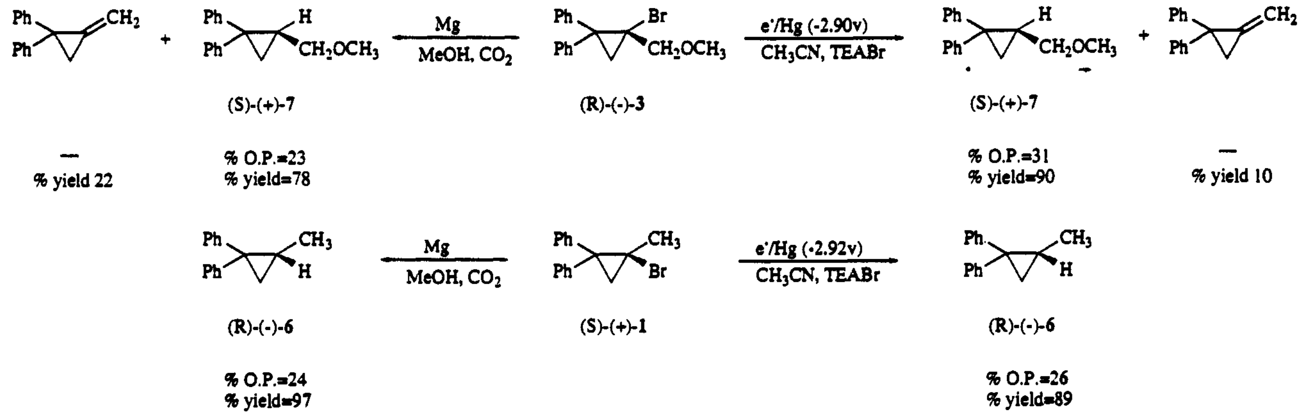
(16) The variation of the scan rate from 0.002 to 1 V did not induce an important change of the values of the coefficient transfer for the compound 1, 3, 4, and 5.

Scheme II



$$RX + e^- \rightarrow R^\bullet + X^-$$

If a radical anion were formed as an intermediate, it would lead to a transfer coefficient closer to or larger than 0.5[14d] since the standard potential of $RX/RX^{\bullet-}$ must be much more negative than that of $RX/R^\bullet + X^-$, as in the case of aromatic halides[14d] and ring-substituted nitrobenzyl halides, where a stepwise mechanism involving the intermediacy of anion radical was shown to take place.

$$RX + e^- \rightleftarrows RX^{\bullet-}$$

$$RX^{\bullet-} \rightarrow R^\bullet + X^-$$

It is also of interest to note that the ease of reduction as shown by the peak potential of the wave is in the order 5 > 3 ≥ 1 > 4 ≫ 2. In order to make sure that the waves observed were not due to the electron transfer to the aromatic moieties, cyclic voltammetry experiments were carried out on the derivatives 1-methyl-2,2-diphenylcyclopropane (**6**), 1-(methoxymethyl)-2,2-diphenylcyclopropane (**7**), and methyl dibenzobicyclo[2.2.2]-octadiene-2-carboxylate (**8**) under the same conditions. As expected, no wave appears before discharge of the supporting electrolyte cation. This confirms that the dissociation of the carbon–halogen bond in **1**, **3**, **4**, and **5** takes place before any reduction of the aromatic moiety.

The reaction of organic halides with metal surfaces falls into the category of electrochemical reactions at an electrode surface provided that the ionization potential of the metal surface is sufficiently low. Thus, the electrochemical results support the mechanism proposed for organometallic reagent formation effected by electron transfer from metal surfaces to the alkyl halide substrate,[17] as, for example, in Grignard reagent formation (Scheme I). We have also presented further evidence that in the proposed mechanism the first electron transfer from the metal surface to the σ^* antibonding orbital of the carbon–halogen bond is either insertive, leading to a tight radical anion–radical cation pair as a transition state and insertion of the metal to give the organometallic reagent with retention of configuration (pathways 1 and 4), or purely dissociative, producing a radical pair adsorbed on the surface (pathway 2). A 180° rotation of $R^\bullet$ followed by combination with $^\bullet MgX$ gives rise to racemic product (pathway 5). The amount of retention of configuration is halogen dependent and increases in the order I < Br < Cl. This is in agreement with the conclusion that the amount of radical pair formed (pathway 2) can be determined by the strength of the carbon–halogen bond. Thus, there is a competition between inner-sphere (pathways 1 and 4) and outer-sphere (pathways 2 and 5) electron transfer,[14f,g] and the ratio of pathways 2,5:1,4 is halogen dependent and is greater for I > Br > Cl. Since transition states and not intermediates are involved in the rate-determining electron-transfer step, pathway 3 only obtains when the halogen substrate yields an intermediate upon electron transfer. The halogen dependency of the ratio is also supported by Savéant's finding that the ease of the concerted electron-transfer bond breaking (outer-sphere, pathway 2) falls in the order iodides > bromides > chlorides.[14a]

Stereochemical observations (Scheme II) also support the analogy between electrochemical reactions[18] and organometallic reagent formation of organic halides at metal surfaces.[17] Reduction of (*R*)-(−)-**3** yields (*S*)-(+)-**7** with overall retention of configuration and an optical purity of 31% at a mercury electrode[8a] and reduction in methanol on a magnesium surface[19] where the optical purity is 23%. A similar result is obtained in the reduction of (*S*)-(+)-**1**, leading to the formation of (*R*)-(−)-**6** with overall retained configuration and optical purities of 26[8a] and 24%,[11] respectively. Finally, it is of interest to note that even at an unreactive electrode such as glassy carbon, the retention observed is high, 47% retention of optical activity with overall retention of configuration.[8] This indicates that a very fast second electron transfer leading to the configurationally stable carbanion occurs at the surface.

Experimental Section

Cyclic Voltammetry. Cyclic voltammetry experiments were performed at 25 °C using EG&G Princeton Applies Research Model 362 apparatus. The working electrode was a glassy carbon disc of 3-mm diameter, and the counter electrode was a platinum wire which was polished by using diamond paste and rinsed with ethanol before each use. The reference electrode was double junction Ag/AgCl.

Reagents. The acetonitrile used in all electrochemical experiments was purchased from Fisher, HPLC–GC/MS Grade. The tetrabutylammonium fluoroborate used as supporting electrolyte (Aldrich) was carefully dried under vacuum. 1-Halo-1-methyl-2,2-diphenylcyclopropane (X = Br, **1**; X = F, **2**)[3], 1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane (**3**),[8] 1-bromo-1-methylspiro[2.5]octane (**4**),[9] and methyl 2-bromodibenzobicyclo[2.2.2]octadiene-2-carboxylate (**5**)[11] as well as their derivatives 1-methyl-2,2-diphenylcyclopropane (**6**),[3] 1-(methoxymethyl)-2,2-diphenylcyclopropane (**7**),[8] and methyl dibenzobicyclo[2.2.2]octadiene-2-carboxylate (**8**)[11] were prepared according the procedures previously described. All the electrochemical experiments were performed under an argon atmosphere.

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