structure in $[(C_6H_5CH_2)_5C_5Tl]_2$ is therefore expected to be the large repulsive forces between the $(C_6H_5CH_2)_5C_5Tl$ moieties in the linear R–Tl–Tl–R arrangement, as suggested by Budzelaar and Boersma,[5] rather than to be the Tl–Tl bond suggested by Janiak and Hoffmann.[4] Note also the very small Tl–Tl distance in Tl_2H_2 (3.28 Å) compared with $[(C_6H_5CH_2)_5C_5Tl]_2$ (3.63 Å). This suggests that other effects (e.g. steric effects) are present, which increase the Tl–Tl distance. Even the fairly short Tl–Tl internuclear distances in compounds like Tl_2SnO_3 (3.23 Å)[22] may be explained as being due to interactions of thallium with other atoms, e.g. the oxygen atom in the case of Tl_2SnO_3.[22] It is therefore unlikely that reasonably strong Tl(I)–Tl(I) bonds exist in any of the known inorganic or organometallic compounds of the element.[23] However, Tl(II)–Tl(II) bonds remain a possibility, especially in the solid state. Dronkowski and Simon[24] have recently reported the preparation of $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$, which has a remarkably short Tl–Tl distance of 2.84 Å. A qualitative analysis suggested the presence of a single Tl–Tl bond between Tl^{2+} units, which may be stabilized by interaction with the oligomeric transition-metal clusters.[24]

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Registry No. [η^5-$(C_6H_5CH_2)_5C_5Tl$], 109531-29-5; Tl, 7440-28-0.

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Contribution from the Laboratoire de Chimie
Analytique, Faculté de Pharmacie, Université de Rennes I,
2 Avenue du Professeur Léon Bernard,
35043 Rennes Cédex, France, and Laboratoire d'Electrochimie,
UA CNRS Number 439, Université de Rennes I,
Campus de Beaulieu, 35042 Rennes Cédex, France

Thermochemical and Kinetic Studies of the Electron-Transfer Catalysis of Arene Replacement by $P(OMe)_3$ Ligands in (η^5-Cyclopentadienyl)(η^6-arene)iron(II) Cations

Philippe Boudeville*,† and André Darchen‡

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In the field of organometallic chemistry, recent studies have shown that some reactions may be efficiently catalyzed by electron transfer[1,2] at electrodes or by redox chemical means. The systems most generally studied involve ligand replacement in mononuclear and polynuclear complexes. For all these reactions the key step is the labilization of intermediate paramagnetic species containing 17 or 19 electrons in the valence orbitals of one metal center.[3] A complete knowledge of the course of these catalyzed reactions requires kinetic studies in order to establish the mechanism (associative or dissociative) of the ligand substitution. These kinetic studies are generally performed by electrochemical means using a working curve[4] or simulated voltammograms,[5] but they do not take into account the interference of deactivation reactions.[6] In this paper, we report that calorimetric measurements carried out during a ligand substitution catalyzed by an electron transfer constitute the basis of a kinetic study of the reaction in homogeneous solution. In the same experiments the rate of deactivation steps may be obtained. Moreover, the example described shows, for the first time, that the electron-transfer catalysis may be used for thermochemical studies of chemical reactions that are otherwise unfeasible.

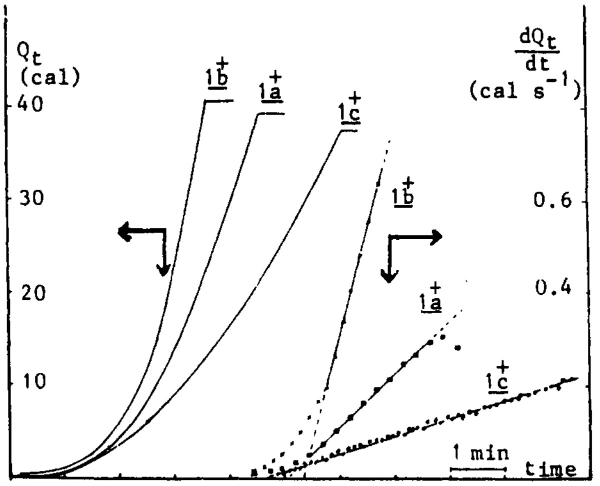

Figure 1. Thermograms of reaction 1 catalyzed by electron transfer and their derivative curves (8×10^{-4} mol of $\mathbf{1}^+(PF_6^-)$ and 4.8×10^{-3} mol of $P(OMe)_3$ in 0.1 L of CH_3CN–0.1 M $Bu_4N^+BF_4^-$).

The chemical reaction investigated by our calorimetric method is the arene ligand replacement (1) in complexes (η_5-C_5H_5)-Fe^{II}(η^6-arene) ($\mathbf{1}^+$). This ligand exchange (1) can be performed

$$\underset{\mathbf{1}^+}{(\eta^5\text{-}C_5H_5)Fe^{II}(\eta^6\text{-Ar})^+} + 3P(OMe)_3 \rightarrow \underset{\mathbf{2}^+}{(\eta^5\text{-}C_5H_5)Fe^{II}[P(OMe)_3]_3^+} + \text{Ar} \quad (1)$$

by heating,[7] but it slowly leads to low yield of $\mathbf{2}^+$. It is obvious that calorimetric studies are not possible in these experimental conditions. However, when reaction 1 is catalyzed[8a] by electron

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† Laboratoire de Chimie Analytique.

‡ Laboratoire d'Electrochimie.

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Table I. Enthalpy Changes, Rate Constants, and Deactivation Rate Constants of Reaction 1 (at 293 ± 1 K in CH_3CN–0.1 M $Bu_4N^+BF_4^-$)

substrate (Ar)	electrolysis current, mA	ΔH, kJ·mol^{-1}	$k^{\ddagger}$,^{a} s^{-1}	$k_d^{\S}$,^{b} 10^{-7} mol·l^{-1}·s^{-1}	$k^{\S}$,^{b} s^{-1}
1a$^+$ (C_6H_6)	10	−206 ± 9	1.08 ± 0.15	2.5 ± 0.6	1.4 ± 0.3
	5	−197 ± 6	0.76 ± 0.05		
1b$^+$ ($C_6H_5OCH_3$)	10	−195	2.29	1.4	2.6
	5	−207	1.95		
1c$^+$ ($C_6H_5CO_2CH_3$)	10	−187	0.33	1.1	0.5
	5	−191 ± 2	0.20		
1d$^+$ (*p*-$CH_3C_6H_4CH_3$)	20	−186	0.69	3.0	0.8
	10	−192	0.53		
	5	−176	0.34		

^{a} $k^{\ddagger}$ values are obtained from eq 8. ^{b} $k^{\S}$ and $k_d^{\S}$ values are obtained from eqs 10 and 12.

transfer at a cathode in CH_3CN/0.1 M $Bu_4N^+BF_4^-$, it rapidly affords **2**$^+$ with a quantitative yield, at room temperature. These conditions allowed calorimetric investigations that were performed in an adiabatic divided electrolysis cell working at constant current.

Experimental Section

Chemicals. Substrates $(\eta^5\text{-}C_5H_5)Fe^{II}(\eta^6\text{-arene})^+(PF_6^-)$ were prepared as previously described.[8b] Acetonitrile was twice distilled from calcium hydride and stored over molecular sieves. The supporting electrolyte *n*Bu_4NBF_4 (Fluka) was of electrochemical grade and was dried over P_2O_5 in a vacuum dessicator. $P(OMe)_3$ (Fluka), which was used as received, contained 0.5% of $OP(OMe)_3$.[9]

Instrumentation and Measurements. The calorimetric investigations were performed at 293 ± 1 K in an adiabatic divided electrolysis cell previously described.[10] Each compartment contained 100 mL of acetonitrile with 0.1 M *n*Bu_4NBF_4 as supporting electrolyte. Electrodes were 8-cm^2 platinum grids. Substrates **1**$^+(PF_6^-)$ and $P(OMe)_3$ were added in the cathodic compartment of the electrolysis cell. The solution was degassed with solvent-saturated nitrogen. After deoxygenation, electrolysis was carried out with constant current afforded by a galvanostat (PAR 363). A continuous stream of nitrogen was passed over the solution while measurements were being performed. The temperature inside each compartment was measured by using standard equipment: thermistor, voltage source, wheatstone bridge, and operational amplifier. The temperatures were recorded and stored in a computer (HP 85F) for data processing. The relationships used to extract the thermal effect of the chemical reaction (1) from the total thermal effects (including reaction heat, stirring Joule effect of the current, and heat exchanges) were established elsewhere.[11] All along the electrolysis the potential of the cathode was measured versus a reference electrode (Ag/AgCl).

Results and Discussion

The corrected thermograms of reaction 1 (Figure 1) show an induction period (without considerable temperature variation) followed by an increase of temperature that reaches a maximum at time t_m when all the substrate **1**$^+$ has reacted. The thermogram shape agrees with phenomena occurring during controlled potential electrolysis: at the beginning the current, which is the reaction course indicator, remains approximately constant, and then it rapidly decreases until the residual value is reached. During the induction period the electrons provided by the cathode are not used for the catalysis of reaction 1, but they reduce oxidizing impurities in the solution. Indeed, the induction period is larger for carelessly deoxygenated solutions, and it shortens when the electrolysis current increases.

The enthalpy change ΔH of reaction 1 is calculated from the final thermal effect (Table I). Assuming that without $P(OMe)_3$ in solution the cathodic reaction uses one electron[8b] per molecule of **1**$^+$, the electricity consumption shows that the ΔH values correspond to more than 98% conversion of **1**$^+$ through reaction 1.

Considering that the heat dissipated in the cathodic compartment of the electrolysis cell is proportional to the amount of substrate **1**$^+$ that has reacted, we can use the increasing part of the thermograms for kinetic studies. This part follows quadratic eq 2 as shown by the large linear portion of the derivative curve

$$Q(t) = at^2 + bt \qquad (2)$$

of the thermograms (Figure 1). This observation agrees with a first-order kinetic of the overall reaction 1 beyond the induction period and confirms the voltammetric behavior of **1**$^+$ with increasing $P(OMe)_3$ concentrations.[8a] We have fitted the increasing part of the thermograms and eq 2 in order to obtain a starting time usable during further kinetic investigations.

Scheme I, which details the rate-determining steps in the overall reaction 1, has been used for the rate constant evaluation ($K = i/VF$; i is the current; V is the volume of solution in the cathodic compartment; F is the Faraday constant). Whatever the constant current used we have controlled that the cathode potential always corresponds to the reduction of **1**$^+$ before time t_m and to the reduction of **2**$^+$ after t_m.

Scheme I

electrochemical initiation

$$\mathbf{1}^+ + e^- \xrightarrow{K} \mathbf{1}^{\bullet} \quad (K = i/VF) \qquad (3)$$

chain propagation

$$\mathbf{1}^{\bullet} + xCH_3CN \xrightarrow{k} \mathbf{3}^{\bullet}(\eta^5\text{-}C_5H_5)Fe^{I}(NCCH_3)_x + Ar \qquad (4)$$

$$\mathbf{3}^{\bullet} + 3P(OMe)_3 \xrightarrow{\text{fast}} \mathbf{2}^{\bullet} + xCH_3CN \qquad (5)$$

$$\mathbf{2}^{\bullet} + \mathbf{1}^+ \xrightarrow{\text{fast}} \mathbf{2}^+ + \mathbf{1}^{\bullet} \qquad (6)$$

Assuming irreversibility[12] for step 4 and steady state for both intermediates **2**$^{\bullet}$ and **3**$^{\bullet}$, the thermal effect $Q(t)$ and its derivative dQ/dt versus time are expressed by relationships 7 and 8.

$$Q(t) = [(\mathbf{1}^+)_0 - (\mathbf{1}^+)_t]V\Delta H = (0.5kKt^2 + Kt)V\Delta H \qquad (7)$$

$$dQ/dt = (kKt + K)V\Delta H \qquad (8)$$

Whatever the substrate may be, the results show a discrepancy between the rate constants k obtained for different current intensities ($k^{\ddagger}$ in Table I). This observation suggests the occurrence of deactivation reactions, which have not been taken into account up to now. In order to investigate the kinetic implications of this deactivation,[6] we carried out electrolysis with the current switched off at time t^* after the catalyzed reaction 1 has started (Figure 2). As shown by the derivative curve, the deactivation reactions slow down the heat dissipation. The results are consistent with a first order for reaction 1 and a zero order for the deactivation reactions, as shown by the good fit between the experimental curve and the simulated one (Figure 2). The drawings of simulated thermograms taking into account first- or second-order deactivation reactions do not present the linear parts observed on the experimental derivative curves before and after time t^*.

Deactivation reactions occur in the bulk of the solution and involve the intermediates of the catalytic cycle (**1**$^{\bullet}$, **2**$^{\bullet}$, or **3**$^{\bullet}$ in Scheme I). In the absence of $P(OMe)_3$, it is known that **1**$^{\bullet}$ may

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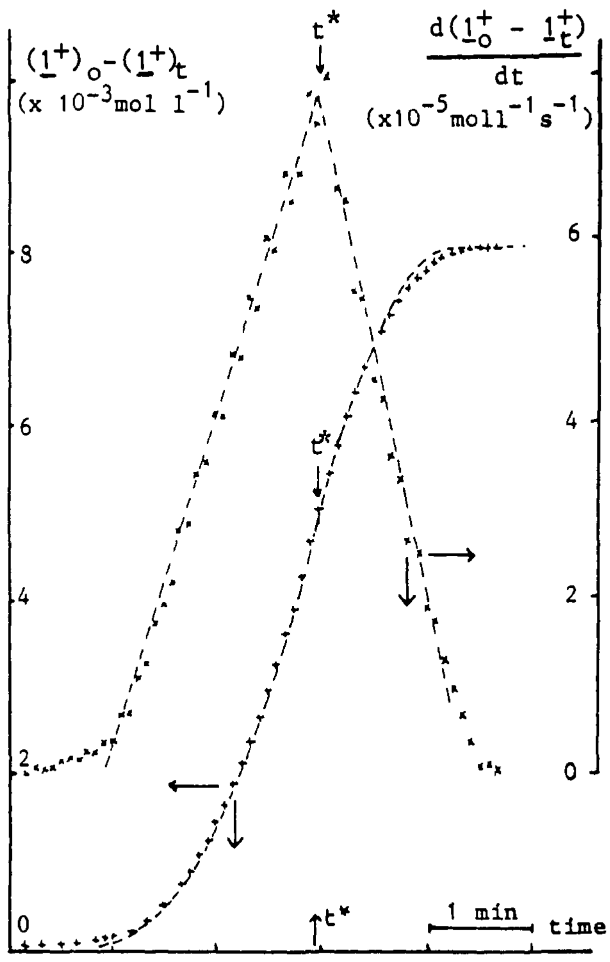

Figure 2. Experimental (+,×) and simulated (···) thermograms of reaction 1 catalyzed by electron transfer and their derivative curves with the electrolysis current switched off at time t^* (8×10^{-3} mol·L^{-1}, of $\mathbf{1a}^+(PF_6^-)$; 48×10^{-3} mol·L^{-1} of $P(OMe)_3$ in CH_3CN - 0.1 M $Bu_4N^+BF_4^-$).

react with dioxygen[13] or slowly with water.[14] The irreversible voltammetric behavior of $\mathbf{1}^+$ and $\mathbf{2}^+$ in acetonitrile shows that $\mathbf{2}^\bullet$ and $\mathbf{3}^\bullet$ decay, leading to ferrocene and unknown decomposition products.[8b] The few amounts of side products formed during the catalysis of reaction 1 do not allow us to establish the true deactivation reactions. However that may be, a zero order is uncommon and may be explained by one of the following hypotheses. (i) In reaction Scheme I, we have considered a steady state for the intermediates $\mathbf{2}^\bullet$ and $\mathbf{3}^\bullet$, so their concentrations are lower than the deactivating substrate ones (oxidizing impurities, water, etc.). If $\mathbf{2}^\bullet$ or $\mathbf{3}^\bullet$ deactivates according to a pseudo-first-order kinetic, the overall observed deactivation is equivalent to a zero order with respect $\mathbf{1}^\bullet$. (ii) Another hypothesis may be a fast reaction of $\mathbf{1}^\bullet$ with an impurity continuously introduced in the solution. This impurity should be the dioxygen present at 5 ppm in the dinitrogen used for the deoxygenation of the solution. We have already noted that dioxygen deactivated the reaction during the induction period.

Taking into account a zero order for the deactivation reactions (rate constant k_d), the thermal effect $Q(t)$ and its derivative dQ/dt versus time are expressed by the new relationships 9-12.

during the electrolysis

$$Q(t) = [0.5k(K - k_d)t^2 + (K - k_d)t]V\Delta H \tag{9}$$

$$dQ/dt = (k(K - k_d)t + K - k_d)V\Delta H \tag{10}$$

after switching off the current ($t > t^*$)

$$Q(t) = [-0.5kk_d(t - t^*)^2 + (k(K - k_d)t^* - k_d)(t - t^*) + (1^+)_0 - (1^+)_{t^*}]V\Delta H \tag{11}$$

$$dQ/dt = [-kk_d(t - t^*) + k(K - k_d)t^* - k_d]V\Delta H \tag{12}$$

Relations 10 and 12 allow access to the rate constants k and k_d from derivative curve slopes for two electrolyses carried out with different current intensities or from one experiment with the current switched off. The values of k and k_d are given in Table I ($k^\S$, $k_d^\S$).

The rate constant $k^\S$ of reaction 1, corrected for the deactivation reactions, is arene ligand dependent. The rate decreases following the sequence $\mathbf{1b}^+ > \mathbf{1a}^+ > \mathbf{1d}^+ > \mathbf{1c}^+$. This order agrees with stability of the corresponding paramagnetic species $\mathbf{1}^\bullet$ in acetonitrile without $P(OMe)_3$, as shown by voltammetric studies.[8b] Owing to uncertainties about the nature of deactivation reactions occurring during reaction 1, we cannot discuss the values of k_d.

As a concluding remark, we could emphasize that the reaction investigated in this paper shows, for the first time, that electron-transfer catalysis allows new ways for thermochemical investigations of chemical reactions.[15,16] From an experimental point of view, a chemical reaction may be easily carried out by means of chemical redox reagents, and in such conditions, the heat dissipation may be a useful indicator of the course of the reaction. The enthalpy change ΔH of reaction 1 does not seem to be influenced by the arene ligands. It is likely that the substituents of substrates $\mathbf{1}^+$ do not significantly modify the energy of the iron-arene bond. Unfortunately, because of the ionic nature of starting and final compounds ($\mathbf{1}^+$, $\mathbf{2}^+$), we have not been able to link the enthalpy change and bond energy with more accuracy.

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Contribution from the Department of Chemistry
and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405

Complete Carboxylate Removal from $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ with Me_3SiCl: Synthesis and Characterization of Polymeric $[MnCl_3(bpy)]_n$ and an Improved Synthesis of $(NEt_4)_2MnCl_5$

Spiros P. Perlepes, Allan G. Blackman, John C. Huffman,
and George Christou*

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Introduction

The red-brown air-stable Mn^{III} compounds of empirical formula $MnCl_3L$ (L = bpy, phen) have been known since 1965 when Goodwin and Sylva isolated them from the reaction of L with the purple ether extract of the black solid obtained from reduction of MnO_2 with dry HCl in CCl_4.[1] The same compounds were later obtained independently by Funk and Kreis using a similar method.[2] Earlier, Gill had obtained green $(NEt_4)_2MnCl_5$ from this ether extract by treatment with an ethanolic solution of NEt_4Cl.[3] Similarly, $(NEt_4)_2MnCl_5$ was obtained by addition of NEt_4Cl to the purple solution obtained from reaction of CH_3COCl with

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