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Rate Constants for the Solution and Electrode Electron-Transfer to Substituted Bromobenzenes in DMF

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Abstract: The rate constants k_{SET} for the solution electron-transfer between radical anions of chrysene and a series of substituted bromobenzenes have been obtained using homogeneous redox catalysis. Linear correlation of log k_{SET} versus the Hammett substituent constants has been found and used to estimate formal potentials. The heterogeneous standard rate constant, calculated from voltammetric peak potentials, is independent of the substituent in agreement with the Marcus-Hush model.

The effects of reactant structure on the rate constants for the solution[1] as well as electrode[2] electron-transfer (ET) processes have been considered in terms of the activation-driving force relationship predicted by the Marcus-Hush model. However, for irreversible proceses with the slow ET step and/or fast chemical step like bond cleavage, the formal potentials E° and ΔG° changes are not accessible by direct electrochemical techniques. In those cases the homogeneous redox catalysis with a series of catalysts used for the reduction of one reactant was proposed by Savéant's group[3-7] for the estimation of E° values and standard rate constants for the heterogeneous ET. The modification of the above method based on the Hammett equation is suggested here for a series of substituted reactants. The proposed procedure offers the estimation of E° values from measurements with only one catalyst if the formal potential for unsubstituted reactant is known.

A series of *para*- and *meta*- substituted bromobenzenes was chosen for the investigation performed in N,N-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate because the standard potential for unsubstituted bromobenzene in this solvent (E°_{PhBr} = -2.44 V vs. SCE) and the electroreduction mechanism are well established.[5] Chrysene with the standard potential $E^{\circ}_{P/Q}$ = -2.20V was chosen as the most suitable catalyst.[5] For all reactants under investigation the overall process at the mercury electrode is the same as that found[4,5] for bromobenzene: the formation of chrysene radical anion Q from chrysene P (1) is followed by the solution electron transfer (SET) to bromobenzene A (2) which is the rate-determining step:

$$P + e \rightleftarrows Q \qquad (1)$$

$$Q + A \overset{k_{SET}}{\rightleftarrows} P + B \quad (2)$$

The third step is the fast bond cleavage of a radical anion B. The observed increase in the ratio of peak currents of the catalyst in the presence and absence of the reactant i_p/i_p^d with the increase of bulk concentration of the catalyst c_P (within the range of 1 - 5 mM) confirms that the catalytic current depends solely on the forward rate constant k_{SET} for step (2). Then the values of k_{SET} can be determined by fitting the experimental current ratios, measured at different scan rates ν, to the theoretical curve[4,5] of $i_p/2\gamma i_p^d$ *vs.* $\log(RTk_{SET}c_P/F\nu)$, where $\gamma = c_A/c_P$ is the excess factor. Examples of the fitting of experimental points to theoretical curves for two reactants using different excess factors are shown in Fig. 1. The rate constants found for the reaction series under investigation are collected in Table 1; the estimated errors in $\log k_{SET}$ are not higher than ±0.1.

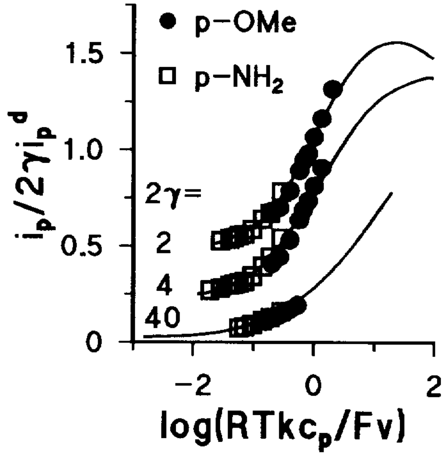

Fig. 1. Dimensionless plots for determining the rate constants k_{SET}: fitting of experimental points for *p*-bromoanisole and *p*-bromoaniline to the theoretical curves; c_p = 2mM.

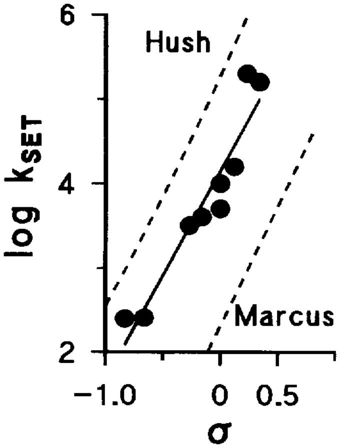

Fig. 2. Relationship between the rate constants k_{SET} and the Hammett substituent constants for a series of bromobenzenes. Theoretical curves obtained from the Marcus-Hush model are shown.

The forward rate constants k_{SET} found depend on the Hammett substituent constants σ as shown in Fig. 2; this result can be explained by a predicted relationship of E° vs. σ, similar to that established for many reversible couples.[2] The acceptable linear correlation[8] obtained (with $r = 0.952$) supports the same SET mechanism for the whole reaction series of interest. For unsubstituted PhBr and a series of catalysts giving $\log k_{SET}$ in the range of 2.5 to 5.6 the process is under the activation control, as shown by Andrieux et al.[5] on the basis of a comparison with the theoretical dependence:

$$\log k_{SET} = \log k_s^{SET} - \alpha^{SET} F\Delta E°/2.303RT \quad (3)$$

Table 1. Rate constants for the solution and the electrode electron-transfer, formal potentials and characteristics of peak currents for a series of substituted bromobenzenes in DMF at 22°C

Substituent	σ [a]	$\log k_{SET}$/ $\log(dm^3mol^{-1}s^{-1})$	$-E^o$/ V vs. SCE	$i_p\nu^{-1/2}$/ $\mu A\ V^{-1/2}s^{1/2}$	$-\log k_s^{el,ap}$/ $\log(cm\ s^{-1})$
m-F	0.34	5.2	2.27	22±2	1.7
p-Cl	0.23	5.3	2.26	25±2	2.0
m-OMe	0.12	4.2	2.39	23±2	2.3
H	0	3.7	2.44[b]	21±1	2.3
p-NHAc	0	4.0	2.41	18±2	2.4
m-NH_2	-0.16	3.6	2.46	21±2	2.1
p-OMe	-0.27	3.5	2.47	19±2	2.0
p-NH_2	-0.66	2.4	2.60	21±2	2.3
p-NMe_2	-0.83	2.4	2.60	25±3	1.9

[a] Hammett substituent constant extracted from Ref. 9.

[b] Literature value from Ref. 5.

where k_s^{SET} is the standard rate constant, i.e., for $\Delta G^o=0$, $\alpha^{SET} \approx 0.5$ is the transfer coefficient for SET process and $\Delta E^o = E^o_{P/Q}-E^o_{PhBr}$ is the difference in formal potentials of a catalyst and a reactant. For $\log k_{SET}$ below 2.0 the slope was two times greater,[5] indicating the "counter diffusion" control, when the backward electron-transfer step (2) has reached the diffusion limit. The last zone has not been observed for the series under investigation, as supported by the results shown in Fig. 2. Thus, eqn.(3) can be used to estimate the E^o values for substituted reactants, assuming the same intercept[10] as found[5] for bromobenzene $\log k_s^{SET} = 5.8$. The formal potentials obtained are collected in Table 1; their errors do not exceed ±0.02 V. Theoretical curves shown in Fig. 2 were calculated from the ΔE^o values found using eqn.(3) with the quadratic term, the values of $\log k_s^{SET}$ for PhBr predicted from the Marcus and Hush models[5] and the reorganization energy λ_o estimated from the catalyst and reactants radii on the basis of the empirical equation proposed by Savéant.[11]

Voltammetric curves at different scan rates were also recorded in the absence of chrysene. The practically constant value of $i_p\ \nu^{-1/2}$ (Table 1) indicates the two-electron process for all reactants with a variation in diffusion coefficients and reactants radii being negligibly small. The value of $\partial E_p/\partial \log\nu$ = -63 mV (log unit)$^{-1}$ found for unsubstituted PhBr is close to that reported in the literature[5] and higher values were obtained for substituted reactants, up to -98 mV (log unit)$^{-1}$ for *p*-bromoacetanilide. These high values indicate that the electrode reaction is under kinetic control of the first ET step and thus the electrochemical transfer coefficients α^{el} can be calculated. The apparent standard rate constants for heterogeneous ET, $k_s^{el,ap}$, were calculated from the dependence of the peak potential on the scan rate[5] using the diffusion coefficient for unsubstituted chloro- and bromobenzene[3,5] $D = 9x10^{-6}$ cm^2s^{-1}. The values of $\log k_s^{el,ap}$ are given in Table 1; their accuracy is of the order of ±0.2.[12] It is evident that the standard rate constant is independent of the substituent nature in agreement with the Marcus-Hush model of ET processes.

In conclusion, it was shown that for the rate constants of ET processes the Hammett equation describes only the thermodynamic part of the activation barrier.

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10. According to the Marcus-Hush model the intrinsic activation barriers, corresponding to standard rate constants, depend on a function of the reactants radii,[1] but this effect is small giving a change in $\log k_s$ not more than 0.2 for the reactants under investigation, as calculated for the radii estimated from the molar mass and the density.

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