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Homogeneous Mediator Reduction of Arylalkylphosphates

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The enthalpy and entropy of activation in the homogeneous electrochemical reduction of phosphoric acid esters $[(PhO)_{3-n}(BuO)_nPO$, $n = 0–2]$ are assumed to reflect transition state stabilization of the electron transfer step due to partial bonding between substrate and mediator.

Electron transfer (ET) is the key step in various reactions of organic compounds. Thermodynamic and kinetic data for this step are of great importance in order to understand more profoundly its peculiarities, the role of chemical substrate structure and nature of the medium in the elementary process.[1] The subsequent steps, including fission of chemical bonds initiated by electron transfer are also of interest. This study deals with homogeneous electron transfer from electrochemically

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Table 1 Characteristics of triorganylphosphate (BX) reduction by radical anions $A^{\cdot -}$.

BX ($-E_{1/2}$/V)	A	$-E^{A}_{1/2}$/V	$\Delta H^{\ddagger}$/kJ mol^{-1}	ln $k^{25°C}_{eff}$/ dm^{3}mol^{-1}s^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1}K^{-1} [a]
$(PhO)_3PO$ (2.24)	$C_6H_{13}OC_6H_{14}C(O)-C_6H_4C_7H_{15}$	1.780	39±3	3.21	−62
	N,*N*-Diethylpyridine-3-carboxylic acid	1.825	25±6	3.20	−13
	Triphenylphosphine oxide	1.960	48±5	6.85	−2
	Naphthalene	1.975	44±2	7.20	−12
	1-Methylnaphthalene	2.020	48±5	7.39	3
$(PhO)_2P(O)OBu$ (2.34)	Benzonitrile	1.810	16±6	5.95	−116
	Triphenylphosphine oxide	1.960	41±11	5.16	−39
	Naphthalene	1.975	50±5	5.08	−10
	1-Methylnaphthalene	2.020	57±13	5.60	18
	2,6-Dimethylnaphthalene	2.110	49±6	7.85	10
$PhOP(O)(OBu)_2$ (2.37)	Benzonitrile	1.810	21±3	4.60	−111
	Phenanthrene	1.910	20±5	4.98	−111
	Naphthalene	1.975	40±4	7.04	−27
	1-Methylnaphthalene	2.020	31±5	7.01	−57
	Benzyl diphenyl	2.110	47±5	8.52	9

[a] An increase in $-\Delta S^{\ddagger}$, and therefore degree of bonding in the phosphates in ET-processes, is observed if $\Delta E_{1/2} \sim \geqslant 0.35$ V.

$$A + e \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{\bullet -}$$

$$A^{\bullet -} + BX \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BX^{\bullet -} + A$$

$$BX^{\bullet -} \xrightarrow{k_3} B^{\bullet} + X^{-}$$

$$A^{\bullet -} + B^{\bullet} \xrightarrow{k_4} A + B^{-}$$

Scheme 1

generated radical anions to arylalkylphosphates and with correlations of their thermodynamic and kinetic characteristics. Radical anions are commonly considered to be outer-sphere electron transfer agents. However, it is possible that deviations from this behaviour are probable and the nature of the mediator can determine the direction of subsequent chemical reactions.[2] Generally speaking, the transition state structure and its bonding must be taken into account.

The present investigation aims to elucidate the effect of the medium on the ratio of each separate stage and on the activation parameters.

The reduction of triorganylphosphates (BX) by electrochemically generated radical anions ($A^{\cdot -}$) is accompanied by O–Ar bond fission,[3] Scheme 1.

The limiting current increase of mediator reduction resulting from substrate addition permits the calculation of an effective rate constant for the regeneration of A and an analysis of its concentration (C_A) and temperature dependences. The results are shown in Table 1.

The activation enthalpy and, especially, activation entropy of the process are connected with the transition state structure of the electron transfer step. Outer-sphere single electron transfer involves considerable activation enthalpy (≈ 50 kJ mol^{-1}) and activation entropy near zero,[4] but the inner-sphere mechanism (S_N2), in contrast, has a small enthalpy of activation $\Delta H^{\ddagger}$ (≈ 20–33 kJ mol^{-1}) and a negative value of $\Delta S^{\ddagger}$ (≈ -80 J K^{-1} mol^{-1}). The degree of bonding between reagents in the transition state is an important factor, as also is the degree of bond breaking. A high degree of bonding results in a decrease of transition state energy in the S_N2 mechanism, in comparison with the ET-mechanism.

The same tendency in changes of activation parameter in triorganylphosphate reductions by radical anion mediators is evident from analysis of the data in Table 1. The main feature is the variation of $\Delta S^{\ddagger}$ from a high negative value for the reaction with maximum value of $\Delta E^{A-BX}_{1/2}$ to nearly zero (within the limits of experimental error) for electron transfer reagents with small $\Delta E^{A-BX}_{1/2}$ values. The electron transfer resembles an outer-sphere process in the latter case and the $\Delta H^{\ddagger}$ value does not change for each substrate in reactions with structurally similar mediators. This value is significantly lower for those mediators containing heteroatoms characterized by greater charge localization (benzonitrile, *N*,*N*-diethylpyridine-3-carboxylic acid) with one exception. The transition state stabilization is probably caused by partial bond formation, together with partial bond fission, leading to a reduced $\Delta H^{\ddagger}$ value. However, this bonding results in a more geometrically ordered transition state and leads consequently to a negative activation entropy.

Orbital control of the reaction must occur for unpaired electron transfer according to the Pearson symmetry rules.[1] In the cases under investigation electron shifts occur from the aromatic π^*-orbital of $A^{\cdot -}$ to the vacant antibonding π^*-orbital of the phosphate aromatic ring and, partially, to the p_π-d_π bond of the phosphoryl group: the electron is distributed equally between substrate and mediator orbitals. When an elementary process is finished, electron density is concentrated completely on the substrate orbital. The orbital interactions can lower the real $\Delta G^{\ddagger}$ value in the transition state.[5] A negative activation entropy is probably also connected with differences in electron state symmetry of the parent (π) and the products (σ).

The most negative $\Delta S^{\ddagger}$ value is peculiar to the process with the maximum $\Delta E^{A-BX}_{1/2}$ value, which must testify to the greatest regularity in transition state. It is supposed that $\Delta H^{\ddagger}$ grows with increase of $\Delta E^{A-BX}_{1/2}$. However, an increase in bonding in the transition state leads to a decrease in the real $\Delta H^{\ddagger}$ value, and hence no change is seen throughout the mediator series.

The stabilization effect of the transition state, when observed, is insignificant for the substrates under discussion (a similar phenomenon was observed in Bu^{n}Br reduction by anthracene radical anions at low temperature, *i.e.* it is not pure outer-sphere transfer).

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