ADVANCES IN

Physical Organic Chemistry

VOLUME 26

Advances in Physical Organic Chemistry

Volume 26

Edited by

D. BETHELL

The Robert Robinson Laboratories
Department of Chemistry
University of Liverpool
P.O. Box 147
Liverpool L69 3BX

ACADEMIC PRESS
Harcourt Brace Jovanovich, Publishers

London San Diego New York
Boston Sydney Tokyo Toronto

ACADEMIC PRESS LIMITED
24/28 Oval Road
London NW1 7DX

United States Edition published by
ACADEMIC PRESS INC.
San Diego, CA 92101

British Library Cataloguing in Publication Data

Advances in physical organic chemistry
  Vol. 26
  1. Physical organic chemistry
  547.1'3'05

ISBN 0-12-033526-3
ISSN 0065-3160

FILMSET BY BATH TYPESETTING LTD, BATH, UK
AND PRINTED IN GREAT BRITAIN BY T. J. PRESS, PADSTOW, CORNWALL

Advances in
Physical Organic Chemistry

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Preface

This series of volumes, established by Victor Gold in 1963, aims to bring before a wide readership among the chemical community substantial, authoritative and considered reviews of areas of chemistry in which quantitative methods are used in the study of the structures of organic compounds and their relation to physical and chemical properties.

Physical organic chemistry is to be viewed as a particular approach to scientific enquiry rather than a further intellectual specialization. Thus organic compounds are taken to include organometallic compounds, and relevant aspects of physical, theoretical, inorganic and biological chemistry are incorporated in reviews where appropriate. Contributors are encouraged to provide sufficient introductory material to permit non-specialists to appreciate fully current problems and the most recent advances.

The series has been extremely fortunate in the quality of the contributors, who have allowed the editors to persuade them to devote much time and effort in order to expound their specialist interests for the benefit of a wider audience. The Editor would welcome feedback from readers. This might merely take the form of criticism. It might also contain suggestions of developing areas of chemistry that merit a forward-looking exposition or of the need for a new appraisal of better established topics that have escaped the notice of the Editor and his distinguished Advisory Board.

D. BETHELL

Contributors to Volume 26

John Emsley Department of Chemistry, King's College London, Strand, London, WC2R 2LS, UK

Frank Hibbert Department of Chemistry, King's College London, Strand, London, WC2R 2LS, UK

Hiizu Iwamura Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-Ku, Tokyo 113, Japan

Hans-Gert Korth Institut für Organische Chemie der Universität Gesamthochschule Essen, Postfach 103764, D-4300 Essen 1, FRG

Jean-Michel Savéant Laboratoire d'Electrochimie Moleculaire, Université Paris 7, 2 Place Jussieu, 75251 Paris Cedex 05, France

Reiner Sustmann Institut für Organische Chemie der Universität Gesamthochschule Essen, Postfach 103764, D-4300 Essen 1, FRG

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Single Electron Transfer and Nucleophilic Substitution

JEAN-MICHEL SAVÉANT

Laboratoire d'Electrochimie Moléculaire, Université de Paris 7,
2 Place Jussieu, 75251 Paris Cedex 05, France

ADVANCES IN PHYSICAL ORGANIC CHEMISTRY
VOLUME 26 ISBN 0-12-033526-3

1 Introduction

The possible role of single electron transfer in organic reactions, as opposed to the classical notion of electron-pair transfer, has attracted continuous and active attention during the past twenty-five years. An important step in this connection, experimentally exemplifying such reaction pathways, has been the discovery of nucleophilic substitution reactions proceeding via anion radical intermediates and taking place at benzylic carbon centres (Kornblum *et al.*, 1966; Russell and Danen, 1966) or at aromatic carbon centres (Kim and Bunnett, 1970). The term "$S_{RN}1$" used to designate these reactions (Kim and Bunnett, 1970; Bunnett, 1978) underlines that, while belonging to the general class of nucleophilic (N) substitution (S) reactions, they involve radical intermediates (R), the first of which in the reaction sequence, i.e. the anion radical of the substrate, undergoes a monomolecular cleavage of the nucleofugic group (1). On the other hand, the continuous development of organic electrochemistry, particularly in its mechanistic and kinetic aspects (Andrieux and Savéant, 1986a; Baizer and Lund, 1983; Savéant, 1986, 1988), has been another source of interest and information for reactions triggered by single electron transfer.

The $S_{RN}1$ mechanism is now reasonably well understood (Bunnett, 1978; Kornblum, 1971, 1975; Rossi and Rossi, 1983; Russell, 1970; Savéant, 1980a). In the case of $S_{RN}1$ aromatic nucleophilic substitution, the electrochemical approach to the problem has allowed a detailed and quantitative description of the various steps of the substitution process and of the side-reactions (Savéant, 1980a, 1986, 1988). As discussed in more detail in the following, the reaction proceeds by a chain mechanism in which the electron supplied during the (chemical, electrochemical, photochemical) initiation process plays, *stricto sensu*, the role of a catalyst. The species that reacts with the nucleophile is not the substrate but the aryl radical deriving from its anion radical by cleavage of the nucleofugic group. Single electron transfer is thus involved in the generation of the key intermediate of the reaction, viz., the aryl radical. It is also involved in the reoxidation of the anion radical of the product which closes up the propagation loop. One of the most important side-reactions (termination step), namely the reduction of the aryl radical, also proceeds by means of single electron transfer from the various reducing species present in the reaction medium (initiator, anion radical of the substrate and of the product).

The $S_{RN}1$ reaction thus appears as a reaction in which single electron transfer plays a pre-eminent role but is by no means a single elementary step. A different problem is that of the possible involvement of single electron transfer in reactions that are not catalysed by electron injection (or removal). A typical example of such processes is another substitution reaction, namely,

$$\mathrm{RX} + \mathrm{D}^- \rightleftharpoons \mathrm{RX}\cdot^- + \mathrm{D}\cdot \tag{1}$$

$$\mathrm{RX}\cdot^- \longrightarrow \mathrm{R}\cdot + \mathrm{X}^- \tag{2}$$

$$\mathrm{R}\cdot + \mathrm{D}\cdot \longrightarrow \mathrm{RD} \tag{3}$$

the S_N2 reaction. The question which then arises is whether or not these reactions, that are classically viewed as proceeding via electron-pair transfer, in fact involve single electron transfer. The latter would then be associated with bond breaking and bond formation. The problem thus amounts to distinguishing between processes in which electron transfer, bond breaking and bond formation are stepwise [as in (1)–(3) where X^- = nucleofugic group, D^- = single electron donor or nucleophile] and processes where they are concerted. Although the outer sphere/inner sphere terminology was coined originally for electron-transfer reactions involving coordination complexes (Espenson, 1986; Taube, 1970), it can be used profitably for organic processes of the type under discussion after some extension of the definitions (Lexa *et al.*, 1988). In outer sphere electron-transfer reactions, either no bond is cleaved or formed within the time scale of the experiment, or in the opposite case, bond breaking and bond formation take place in separated steps, distinct from the electron-transfer step. Conversely, if all three steps are concerted one will deal with an inner sphere electron transfer. In this context, an S_N2 reaction may be considered as being formally equivalent to an inner sphere electron-transfer reaction, or even close to being truly equivalent in many instances, as discussed in the following. An intermediate situation exists, however, in between the two extreme cases of outer sphere and inner sphere electron transfers, just defined. The reduction of alkyl halides by inert electrodes or by aromatic anion radicals in solution offers an example of such a situation. Electron transfer is dissociative there in the sense that the carbon–halogen bond is cleaved in concert with electron transfer. On the other hand, the electron donor, while transferring one electron, is not the object of any bond formation or cleavage. The reaction has thus an outer sphere character from the point of view of the electron donor and an inner sphere character from the point of view of the electron acceptor. Such a reaction may be termed an outer sphere dissociative electron transfer. The outer sphere/inner sphere terminology may also be used to characterize the way in which the reactants react rather than to characterize the overall reaction. In the preceding case, the alkyl halide behaves as an inner sphere electron acceptor whereas the inert electrode or the aromatic anion radical behaves as an outer sphere electron donor.

Alkyl and aryl halides are among the most commonly investigated substrates in S_N2 and $S_{RN}1$ reactions. They will thus serve as the main experimental examples in the general discussion presented in the first part of this chapter, which aims to answer the following questions. How does a frangible substrate react with outer sphere electron-transfer donors? Do electron transfer and bond breaking then occur concertedly or in a stepwise manner? What kind of activation *vs* driving force relationships are applicable in each case? The second part will be devoted to the $S_{RN}1$ reaction and the third to the S_N2 reaction. In all cases, some emphasis will be laid on electrochemical approaches. This is not only a matter of personal inclination but also because it offers some distinct advantages over strictly chemical approaches. One is that, rather obviously, electrochemical methods may be of help for gathering thermodynamic information, such as standard potentials, required for the analysis of reactivity patterns in reactions where electron transfer is involved. On the other hand, electrochemical generation of homogeneous electron donors (nucleophiles) belonging to a reversible redox couple has several advantages. One is that the species thus generated need not be very stable. It suffices that its reaction with the desired substrate be faster than all the reactions that cause its disappearance in the reaction medium. The standard potential characterizing thermodynamic properties of the electron donor can be easily measured by current electrochemical techniques such as cyclic voltammetry. The same techniques can be used conveniently for determining, upon addition of the substrate, the kinetics and mechanism of its reaction with the electrogenerated homogeneous electron donor (nucleophile). Much faster reactions can thus be characterized than with conventional chemical techniques. On the other hand, as far as outer sphere electron donors are concerned, it is of interest to examine whether or not the same activation–driving force relationships are applicable to heterogeneous (inert electrodes) and homogeneous outer sphere electron donors as is, for example, predicted by Marcus–Hush theory in the particular case of purely outer sphere electron transfer (Hush, 1958, 1961; Marcus, 1956, 1963, 1964, 1965, 1977, 1982; Marcus and Sutin, 1985; Waisman *et al.*, 1977).

2 Single electron transfer and bond breaking

A substitution reaction involves the breaking of one bond and the formation of another one. We discuss in this section reactions in which electron transfer is associated with the breaking of a bond but in which either no bond formation occurs or, if it does, takes place in a further separated step. For such processes, a series of fundamental questions arise. Are electron transfer and bond breaking concerted or stepwise? Can experimental data concerning elementary steps (in the first case the dissociative electron transfer, in the second the electron transfer and the bond breaking steps) be organized under the form of activation versus driving force relationships (rate constant versus equilibrium constant or synonymously "Brønsted plots", "Marcus plots" and, for electrochemical reactions, "Tafel plots")? If so, what models are available to analyse these plots in terms of shape and reorganization barriers?

In the case of stepwise electron-transfer bond-breaking processes, the kinetics of the electron transfer can be analysed according to the Marcus–Hush theory of outer sphere electron transfer. This is a first reason why we will start by recalling the bases and main outcomes of this theory. It will also serve as a starting point for attempting to analyse inner sphere processes. Alkyl and aryl halides will serve as the main experimental examples because they are common reactants in substitution reactions and because, at the same time, a large body of rate data, both electrochemical and chemical, are available. A few additional experimental examples will also be discussed.

MODELLING OF OUTER SPHERE ELECTRON TRANSFER

The Marcus–Hush theory of outer sphere electron transfer (Hush, 1958, 1961; Marcus, 1956, 1963, 1964, 1965, 1977, 1982; Marcus and Sutin, 1985) is based on the Born–Oppenheimer approximation and thus relates the activation barriers to the nuclear reorganization that accompanies electron transfer. In its currently most often used version, it deals with adiabatic processes: at the intersection between potential energy surfaces of the reactants and products (Fig. 1), the resonance energy between the reactant and product states (crossing avoidance) is sufficient for the probability for the system to cross the barrier to be unity. Note, however, that, in current applications, this energy is, at the same time, considered small enough so as not to affect significantly the height of the barrier.

The nuclear reorganization energy is assumed to be the sum of two independent terms, one representing the solvent reorganization (external reorganization, outer sphere reorganization) and the other, the internal (inner sphere) reorganization, i.e. the changes in bond lengths and angles in the reactants occurring upon electron transfer. Both terms are evaluated within a harmonic approximation. This appears quite natural for the internal reorganization term, provided the transition state is not too far from the reactant and product equilibrium states in term of bond distances and angles (otherwise the stretching of the bond might fall in the anharmonic region). Insofar as the various vibrational modes involved in the internal

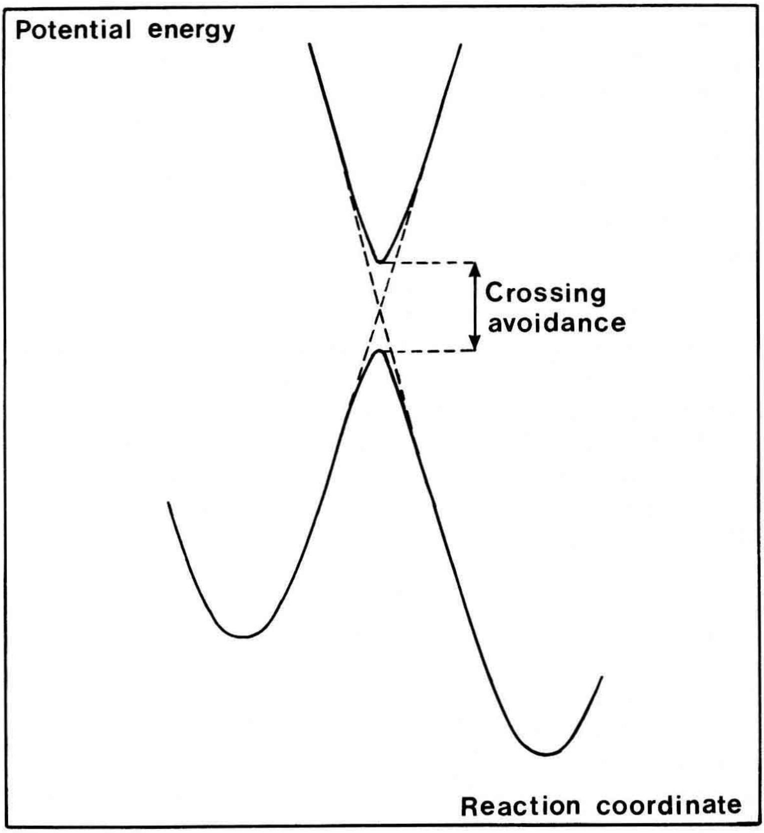

Fig. 1 Potential energy surfaces in adiabatic outer sphere electron transfer.

$$G_{i,R} = \tfrac{1}{2}\sum f_R(y - y_R)^2 \tag{4}$$

$$G_{i,P} = \tfrac{1}{2}\sum f_P(y - y_P)^2 \tag{5}$$

reorganization can be considered as independent of each other, their contributions are additive. So also are the internal reorganization terms of the two reactants in the case of a homogeneous cross-exchange electron-transfer reaction. Thus, the dependence of the free energy of the reactant and product systems upon the variations of the vibration coordinates can be expressed as in (4) for the reactant system and in (5) for the product system. Here, y designates the various vibration coordinates involved in the electron transfer process, y_R and y_P are their values for the reactant and product, respectively, and f_R and f_P are the corresponding force constants in the reactants and products. The summations are extended to all vibration coordinates involved and to the two reactants and products in the homogeneous case.

The contribution of solvent fluctuational reorganization to the free energy of the reactant and product systems can also be expressed in a quadratic manner. In the framework of the Born model of solvation, a fictitious electric charge, x, borne by the reactant or product is taken as the reaction coordinate (in the homogeneous case, the increase of the fictitious charge borne by one reactant occurs at the expense of that borne by the other reactant and the same applies to the products). The contribution of solvent reorganization to the free energy of the reactant and product systems can thus be expressed (Marcus, 1965, 1977) as in (6a) and (6b), where x_R and x_P are the charges borne by the reactant and product at their equilibrium state.

$$G_{O,R} = \tfrac{1}{2}\lambda_0(x - x_R)^2 \tag{6a}$$

$$G_{O,P} = \tfrac{1}{2}\lambda_0(x - x_P)^2 \tag{6b}$$

$$\lambda_0^{\text{hom}} = e_0^2\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_S}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{a_1 + a_2}\right) \tag{7}$$

In the homogeneous case, λ_0 is given by (7), where e_0 is the electron charge, D_{op} and D_S the optical and static dielectric constants of the solvent respectively, and a_1 and a_2 are equivalent hard sphere radii of the two reactants (and products). For the electrochemical case, there are two versions for the expression of λ_0. In Marcus's treatment (Marcus, 1965) the reaction site is assumed to be located at a distance from the electrode equal to its radius, a, and the effect of image forces in the electrode is taken into account (8). In Hush's treatment (Hush, 1961) the reaction site is assumed to be located farther from the electrode surface and the effect of image forces is neglected (9).

$$\lambda_0^{\text{het}} = e_0^2\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_S}\right)\frac{1}{4a} \tag{8}$$

$$\lambda_0^{\text{het}} = e_0^2\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_S}\right)\frac{1}{2a} \tag{9}$$

In total, the free energy surfaces for the reactant and product systems are (as shown in Fig. 1, but in terms of free energy rather than energy, and with more than one reaction coordinate, namely, the fictitious charge representing solvent reorganization and all the bond lengths and bond angles of the reactants that vary significantly upon electron transfer) given by (10) and (11). G_R^0 and G_P^0 are the standard free energies of the reactants and products

$$G_R = G_R^0 + w_R + \tfrac{1}{2}\lambda_0(x - x_R)^2 + \tfrac{1}{2}\sum f_R(y - y_R)^2 \qquad (10)$$

$$G_P = G_P^0 + w_P + \tfrac{1}{2}\lambda_0(x - x_P)^2 + \tfrac{1}{2}\sum f_P(y - y_P)^2 \qquad (11)$$

respectively when they are at infinite distance one from each other in the homogeneous case, or of the reactant and product when they are at infinite distance from the electrode surface in the electrochemical case. The term w_R is the work required to bring the reactants from infinity to the reacting distance, i.e. to form the "precursor complex" whereas w_P is the work required to form the "successor complex" from infinity to the reacting distance. In the electrochemical case, it is often assumed that the reaction site is located at the external boundary of the compact double layer, i.e. in the outer Helmholtz plane (Delahay, 1965). The introduction of the w_R and w_P terms in the above equations then amounts to performing the "Frumkin correction" of the double layer effect on the kinetics of the electrochemical electron-transfer reaction (Delahay, 1965). Minimizing then the free energy of the pathways going from the reactant to the product systems leads to the expressions (12) and (13) for the activation barriers, in terms of free energy,

$$\Delta G_+^{\ddagger} = w_R + \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^0 - w_R + w_P}{4\Delta G_0^{\ddagger}}\right)^2 \qquad (12)$$

$$\Delta G_-^{\ddagger} = w_P + \Delta G_0^{\ddagger}\left(1 - \frac{\Delta G^0 - w_R + w_P}{4\Delta G_0^{\ddagger}}\right)^2 \qquad (13)$$

for the forward and backward reactions. Here, $\Delta G^0 = G_R^0 - G_P^0$ is the standard free energy of the reaction (the opposite of the driving force in terms of free energy) and $\Delta G_0^{\ddagger}$ the standard free energy of activation, i.e. the free energy of activation of the forward and backward reactions at zero driving force, in other words, the intrinsic barrier. $\Delta G_0^{\ddagger}$ is related to the internal and external reorganization factors by (14) where λ_0 is given by (7)–

$$\Delta G_0^{\ddagger} = \frac{\lambda_0 + \lambda_i}{4} \qquad (14)$$