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The Origin of Leaving-Group Effects in Radical Reactions Triggered by Solvated Electron Reduction

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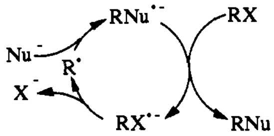
Abstract: Reactions between solvated electrons and substrates yielding fast-cleaving anion radicals or giving rise to concerted bond cleavage occur during the mixing of the two reactants. They are described by a model allowing the quantitative prediction of product distribution in which the initial and successive chemical steps take place in a thin reaction layer located within the diffusion layer where the two reactants mix. The essential cause of the observed leaving-group effects resides in the decrease of the amount of electrons in the reaction layer as the initiating reaction becomes faster and faster. In the case of $S_{RN}1$ substitutions, an additional factor is the parallel acceleration of the electron transfer between the substituted anion radical and the substrate.

Reduction of organic molecules by solvated electrons in liquid ammonia[1] has received a particularly interesting application in $S_{RN}1$ nucleophilic aromatic substitution reactions.[2,3] The chain reaction sketched in Scheme I is triggered by the reduction of the substrate, RX, by solvated electrons diffusing out of pieces of an alkali metal introduced in a solution of RX in liquid ammonia or by mixing of a solution of solvated electrons with an RX solution.

Such $S_{RN}1$ reactions may also be induced photochemically[2,3] as well as by direct or indirect[4a] electrochemical means.[4] Concerning the latter mode of induction, the factors that govern the competition with the side reactions and the dependence of selectivity and reactivity upon the structure of the substrate, including the nature of the leaving group, are reasonably well understood. This was made possible by the precise control one can exert on the electrode potential and the convenience of determining the overall kinetics and their variations through the current flowing through the electrode surface. Much less is known about the exact association of the various successive or competing steps when the reaction is induced photochemically[2,3,5] or by solvated electrons.[2,3,6]

In the latter case, striking leaving-group effects on product distribution have been observed.[2,3,6] A typical example is the reaction of acetone enolate with a series of substituted benzenes bearing as leaving groups I, Br, $^+N(CH_3)_3$, SPh, Cl, F, and OPh.[6a] As recalled in Scheme II, three main products are observed, the aryl ketone, the hydrogenolysis product, RH, and the aryl alcohol deriving from the reduction of the ketone. It was observed that the relative amount of hydrogenolysis product and of aryl alcohol increases from I to OPh in the above series. This observation looks very puzzling at first sight since it seems that the $S_{RN}1$ mechanism would imply that product selection takes place at the level of the aryl radical, where the leaving group has already left and should therefore be independent from its nature.[7] In fact, within the chain propagation loop (Scheme I), the structure of the substrate, RX, and therefore the nature of the leaving group may interfere in two of the three steps, the dissociation of the $RX^{\bullet-}$ anion radical and the electron-transfer reduction of RX by the $RNu^{\bullet-}$ anion radical. It has been shown, on semiquantitative grounds, that, under homogeneous conditions, the speed at which the propagation loop rotates, which depends upon X through the two reactions above, governs the competition with the termination steps and may therefore influence the distribution of products[8] (under current concentration conditions, in poor H-atom donor solvents such as liquid NH_3, the termination steps involve the electron-transfer reduction of the $R^\bullet$ radical by all electron donors present.[4b,c,9]).

Scheme I



However, the reductions by solvated electrons, introduced either by means of pieces of alkali metal or as solutions in liquid ammonia, are not homogeneous processes. As previously hypothesized[6] and demonstrated in the following discussion, these reactions occur during mixing. As will be shown, the initial reduction and the successive or competing reactions it triggers all take place in a thin reaction layer inside the diffusion layer within which the solvated electrons and the substrate diffuse toward one another. This is the starting idea of the quantitative model developed in the following sections, allowing the description of the kinetics and product distributions in solvated electron reactions with particular attention to $S_{RN}1$ reactions and to other related radical reactions.

Results and Discussion

Basic Features and Implications of the Model. Mixing of the solvated electrons and RX molecules and their reaction may be

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[1] Smith, H. *Chemistry in Anhydrous Liquid Ammonia, Part II, Organic Reactions in Liquid Ammonia*; Interscience: New York, 1963.

[2] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

[3] Rossi, R. A.; Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph Series 178; American Chemical Society: Washington, DC, 1983.

[4] (a) That is, by molecular outer-sphere electron donors reversibly generated at the electrode surface.[4c] (b) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (d) Pinson, J.; Savéant, J.-M. Electrochemical Induction of SRN1 Nucleophilic Substitution. In *Electroorganic Synthesis. Festschrift for Manuel M. Baizer*; Little, R. D., Weinberg, N. L., Eds.; 1991; pp 29–44. (e) Savéant, J.-M. Submitted for publication.

[5] (a) Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690. (b) Fox, M. A.; Yonnathan, J., Fryxell, *J. Org. Chem.* **1983**, *48*, 3109.

[6] (a) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2852. (b) Tremelling, M. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7375.

[7] (a) The existence of leaving-group effects is taken as the leading argument against the $S_{RN}1$ mechanism in a recent reconsideration which proposes its replacement by an $S_{RN}2$ mechanism in which the bond-breaking and bond-forming step of the $S_{RN}1$ mechanism would be concerted instead of stepwise.[7b] (b) Denney, D. B.; Denney, D. Z. *Tetrahedron* **1991**, *47*, 6577.

[8] Amatore, C.; Pinson, J.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

[9] (a) It has been shown recently that at high substrate concentrations dimerization of the aryl radicals may compete significantly with their reduction.[9b] (b) Ettayeb, R.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1992**, *114*, 10991.

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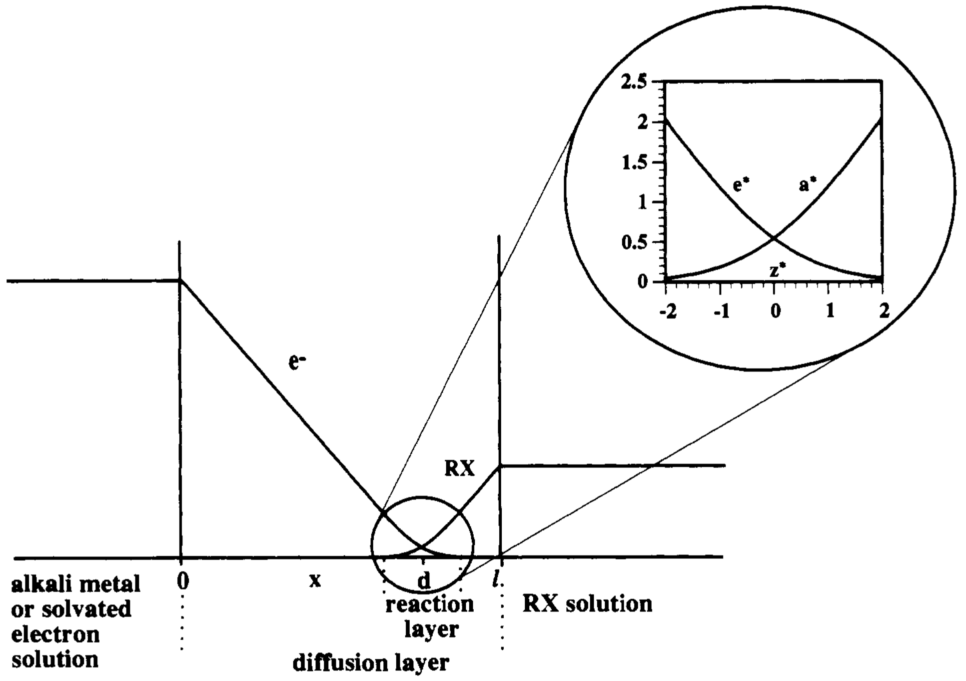
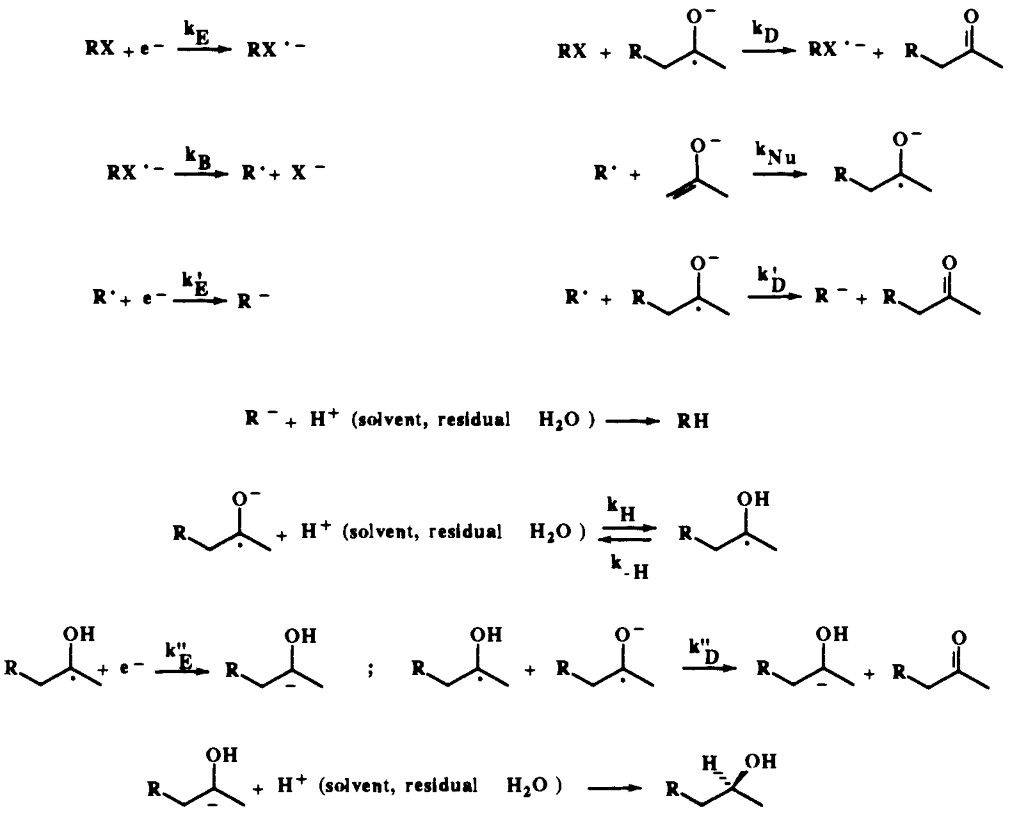


Figure 1. Concentration profiles for the reaction RX + e^- → product. For the definitions of a^*, e^*, and z^*, see text.

Scheme II



represented approximately as sketched in Figure 1. They each diffuse out of a zone where their concentration is maintained constant by natural or forced (agitated solutions) convection. In the case where a piece of metal is used as a source of electrons, their concentration is constant at the surface of the metal. Since solvated electrons are potent reducing agents (standard potential: $E^\circ = -2.69$ V vs 0.1 M Ag^+/Ag at -40 °C[10]), they react rapidly with the incoming RX molecules. It follows that solvated electrons and RX molecules may coexist only within a thin region of space, the "reaction layer", in which their respective concentrations are small compared to their bulk concentrations. The reaction induces the e^- and RX concentrations to vary with space within a diffusion layer as represented in Figure 1, in which, with the exception of the thin reaction layer, their profiles are linear. The thickness, *l*, of the diffusion layer is, with no agitation or with moderate agitation such as that obtained with the usual magnetic stirrers, on the order of 10^{-2} cm.[11]

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[10] Teherani, T.; Itaya, K.; Bard, A. J. *Nouv. J. Chim.* **1978**, *2*, 481.

[11] (a) Andrieux, C. P.; Savéant, J.-M. Electrochemical Reactions. In *Investigations of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305–390. (b) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *J. Electroanal. Chem.*, in press. (c) Andrieux, C. P.; Savéant, J.-M. Catalysis at Redox Polymer Electrodes. In *Molecular Design of Electrode Surfaces, Techniques of Chemistry*; Murray, R. W., Ed.; Wiley: New York, 1992; Vol. XXII, Chapter V, pp 207–270.

The diffusion coefficient of current organic molecules in liquid ammonia at −40 °C, the most commonly used temperature for the kind of experiments we are discussing, is on the order of 3×10^{-5} cm^2 s^{-1},[12] as is that of solvated electrons.[10] The duration of the travel of the RX molecules as well as of the solvated electrons across such a diffusion layer is thus on the order of seconds. In view of their high reducing power, the reaction of solvated electrons with the RX molecules takes place in a much shorter time range. In other words, such reactions occur during mixing of the two reactants.

The kinetics of the overall process involving the initial reduction step and all the reactions it may trigger may thus be described by steady-state linear diffusion differential equations (second Fick's law) implemented by homogeneous kinetic terms, as in electrochemical reactions involving homogeneous reactions associated with the electrode electron transfer.[11a] In the present case, however, the reactions do not take place in a reaction layer adjacent to a solid surface as in electrochemistry but rather within a reaction layer located inside the diffusion layer, the exact location of which is a function of the reaction mechanism and of the reactant concentrations. In this sense, the situation more closely resembles that of catalytic reactions inside redox polymer coatings on electrode surfaces.[11c]

The concept of "pure kinetic conditions" developed for the above systems[11a,c] is also useful for the reactions under discussion. It applies to fast reactions, as is the case here, i.e., to reaction layers that are thin vis-à-vis the diffusion layer. As rigorously elaborated elsewhere,[12] the distances and reactant concentrations involved in the physical description of the system may then be normalized in the following manner:

$$z^* = \frac{x-d}{l}\lambda_E^{1/3} \qquad c^* = \frac{C}{C_E^\circ}\lambda_E^{1/3}$$

with

$$\lambda_E = \frac{k_E C_E^\circ l^2}{D}$$

where the symbols have the following meaning. D is the diffusion coefficient, assumed to be approximately the same for the solvated electrons, the substrate, and the products. C is the space-dependent concentration of the considered reactant, solvated electron, or substrate, and C_E° is the concentration of solvated electrons just outside the piece of alkali metal (where it is on the order of 10 M[13]). x is the distance from the surface of the metal, l the thickness of the diffusion layer, and d the distance from the metal at which is located the center of the reaction layer. k_E is the bimolecular rate constant of the reaction of solvated electrons with the RX molecules. Thus, whereas the solvated electron and RX concentrations are very small inside the reaction layer, the products $e^* = ([e^-]/C_E^\circ)\lambda_E^{1/3}$ and $a^* = ([RX]/C_E^\circ)\lambda_E^{1/3}$ are on the order of unity.[12] Similarly the size of the reaction layer is such that z^* is on the order of unity.

For example, with the simplest reaction scheme,

$$RX + e^- \xrightarrow{k_E} \text{product}$$

the concentration profiles of the solvated electrons and of the substrate are as represented in the insert in Figure 1. It is seen that the amount of solvated electrons present in the reaction layer decreases as the rate constant of the initial electron attachment reaction increases. For example, at the center of the reaction layer, the solvated electron concentration, $(C_E)_0$, is given by the following equation:[12]

$$(C_E)_0 = 0.545\frac{(C_E^\circ)^{2/3}}{k_E^{1/3}}\frac{D^{1/3}}{l^{2/3}}$$

Since, in most cases, the side products result from the reduction of the intermediates by the solvated electron competing with the target reaction, the root of the leaving-group effects resides in the fact that the concentration of solvated electrons in the reaction layer decreases when the rate constant of the initial reduction step increases in a way that is defined by the above equation.

Radical Cyclization Reactions. The radical cyclization reaction sketched in Scheme III[14] is an interesting example of a reaction that occurs under the heterogeneous conditions described in the preceding section and exhibits a significant leaving-group effect.

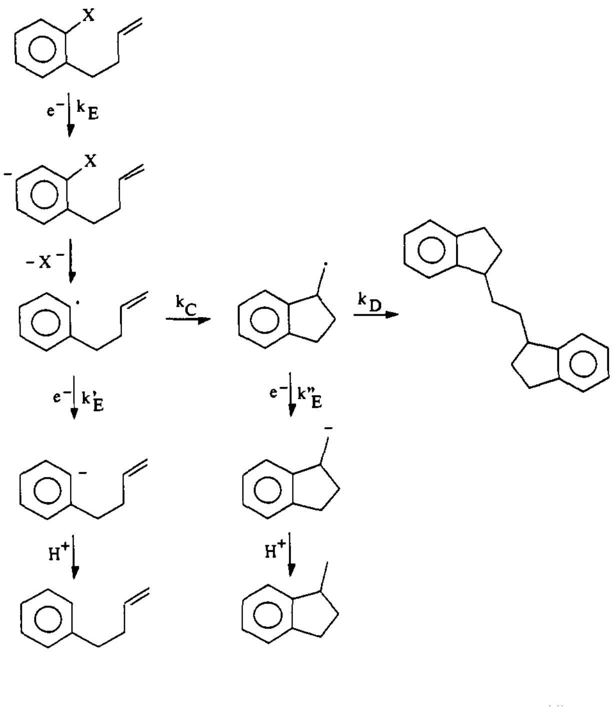
Three products are formed, the hydrogenolysis product, the reduced cyclized product, and the cyclized radical dimer, in yields that are recalled in Table I.[15] Since the anion radicals in the series undergo fast cleavage, the distribution of products is, as shown rigorously elsewhere,[12] a function of two competition parameters, σ and ρ, defined as

$$\sigma = \frac{k_C k_E^{1/3}}{k'_E}\frac{l^{2/3}}{(C_E^\circ)^{2/3}D^{1/3}}$$

$$\rho = \frac{(k''_E)^2}{k_D k_E}$$

(The rate constants are those defined in Scheme III). The yield of the hydrogenolysis product and the overall yield of the cyclized product depend solely on the parameter σ (the variation is shown in Figure 2). σ indeed contains the ratio of the rate constants of cyclization of the radical and of its reduction by the solvated electrons. The remaining set of parameters in σ represents, under the form of $(C_E^\circ)^{2/3}D^{1/3}/(k_E^{1/3}l^{2/3})$, the concentration of the solvated electrons in the reaction layer. The relative amount of the cyclized radicals that are reduced or that dimerize depends on the two parameters σ and ρ as depicted in Figure 3. Indeed, the competition between the reduction and the dimerization pathway is a function of both the concentration of solvated electrons in the reaction layer and the result of the preceding competition between reduction and cyclization of the open-chain radical.

Scheme III



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[12] Andrieux, C. P.; Savéant, J.-M. *J. Phys. Chem.*, in press.

[13] (a) Lepoutre, G.; Debacker, M.; Demortier, A. *J. Chem. Phys.* **1974**, *71*, 113. (b) Sienko, M. J. In *Solutions Métal-Ammoniac. Propriétés Physico-Chimiques*; Lepoutre, G., Sienko, M. J., Eds.; Benjamin: New York, 1964; pp 24–40.

[14] Meijs, G. F.; Bunnett, J. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 4899.

[15] The sums of the yields given in ref 14 are somewhat lower than 1. The yields reported in Table I have been renormalized so that their sum is equal to 1.

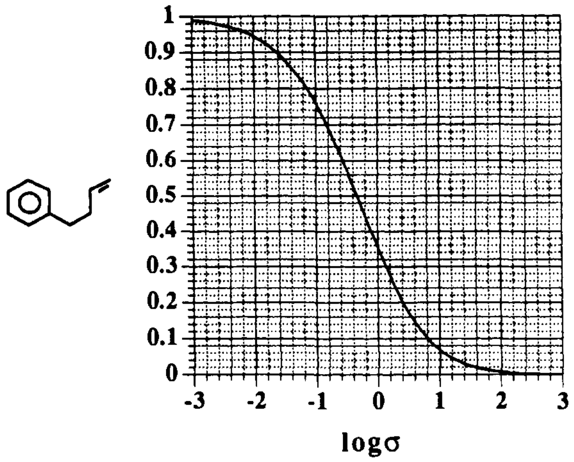
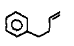
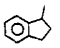
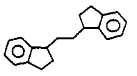
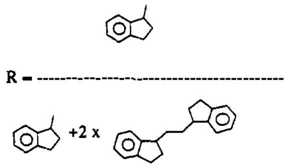


Figure 2. Predicted variation of the yield of hydrogenolysis product with the competition parameter σ.

Table I. Product Distribution, Competition Parameters, and Reduction Rate Constant for the Reaction in Scheme III[a]

X	I	Br	Cl	F
 [b]	0.09	0.10	0.18	0.40
 [b]	0.70 (0.70)	0.72 (0.74)	0.79 (0.80)	0.60 (0.60)
2 x  [b]	0.21 (0.21)	0.18 (0.16)	0.03 (0.02)	0.00 (0.00)
	0.77	0.80	0.96	1.00
σ	7.1	6.3	3.2	0.8
k_E (M^{-1} s^{-1})	2.1 10^{10}	1.5 10^{10}	1.9 10^{9}	3.0 10^{7}
ρ	1.4	2.0	15.8	1000

[a] From the data in ref 14. The figures between parentheses are the yields predicted from the application of the model (see text).

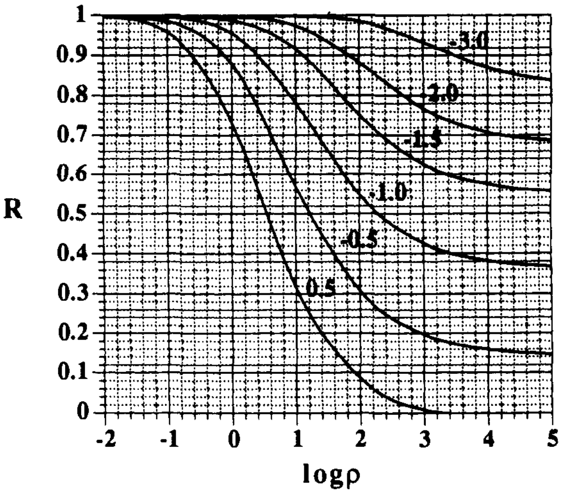


Figure 3. Predicted variation of the relative amount of reduced cyclized radical with the competition parameters ρ and σ. The number on each curve is the value of log σ.

The rate constants of the reduction of the open-chain and cyclized radicals, k'_E and k''_E, are most probably close to, or at, the diffusion limit (3×10^{10} M^{-1} s^{-1}) since they are reduced at much less negative potentials[4e,16] than the standard potential of the solvated electrons. The cyclization rate constant, k_C, has been previously estimated to be 10^8 s^{-1}.[14,17] We note that the distribution of products is closely the same for the iodo and bromo derivatives, meaning that k_E should be close to the diffusion limit in accord with the reduction potentials of iodo- and bromobenzene being much more positive than the standard potential of solvated electrons.[18] In the determination of the $l^{2/3}/((C_E°)^{2/3}D^{1/3})$ factor in the parameter σ, rather large uncertainties affect the a priori estimation of all three quantities, particularly $C_E°$.[19] It is thus preferable to use the experimental values of the RH yield for the iodo and bromo derivatives to obtain an estimate of this factor. This leads to $l^{2/3}/((C_E°)^{2/3}D^{1/3}) = 0.77$[19] (where l is in cm, D in cm^2 s^{-1}, and $C_E°$ in M l^{-1}) and to $k_E = 2.1 \times 10^{10}$ and 1.5×10^{10} M^{-1} s^{-1} for the iodo and bromo derivatives, respectively, values indeed very close to the diffusion limit (3×10^{11} M^{-1} s^{-1}). The yields of hydrogenolysis product obtained with the other halogens allow the estimation of σ in each case and, using the value of $l^{2/3}/((C_E°)^{2/3}D^{1/3})$ just computed, that of k_E (Table I).

The values of k_E thus found decrease from I to Br, Cl, and F, as expected from the values of their reduction potentials[18] (the value for the bromo derivative is close to the diffusion limit, as expected from the above discussion). We thus see that the leaving-group effect on the relative amount of reduction and cyclization of the open-chain aryl radical is satisfactorily explained by the variation of the rate of reduction of the starting halide by solvated electrons in the framework of our model.

From the values of k_E thus estimated, one obtains the values of ρ for each compound that are reported in Table I. It is then possible to predict, knowing ρ and σ in each case, what the yields of the reduced cyclized product and the cyclized radical dimer should be according to the model (figures between parentheses in Table I). We see (Table I) that there is excellent agreement between the values thus predicted and the experimental values.

The model thus allows one to explain satisfactorily the leaving-group effect not only on the relative amount of reduction and cyclization of the open-chain radical but also on the relative importance of the reduction and dimerization of the cyclized radical.

It is also interesting to examine whether the product distribution obtained in the reduction of 6-bromo-1-hexene by solvated electrons under similar conditions may be rationalized in the same way (Scheme IV). With this aliphatic halide, reduction consists of a concerted electron-transfer bond-breaking reaction,

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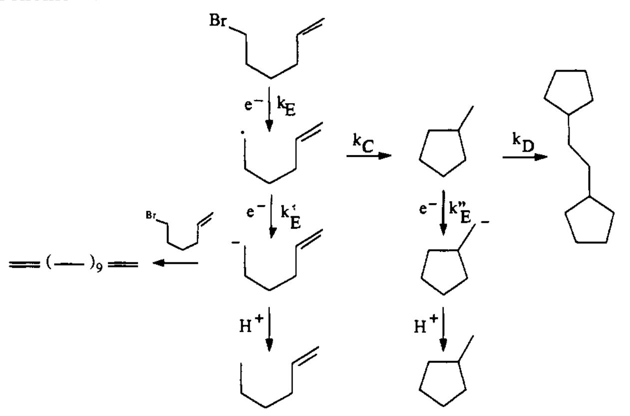
(16) (a) Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764. (b) Sim, B. A.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 754. (c) Griller, D.; Martino, Simoes, J. A.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7832. (d) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635. (e) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 1620. (f) Occhialini, D.; Kristensen, J.-S.; Daasberg, K.; Lund, H. *Acta Chem. Scand.* **1992**, *46*, 474.

(17) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

(18) (a) The cyclic voltammetric peak potentials at 0.2 V s^{-1} at the various substituted benzenes in liquid NH_3 at −38 °C are (in V vs 0.01 M Ag^+/Ag)[8] −1.85[18b], −2.00[18b], −2.24, −2.30, −2.34, and −2.40 for I, Br, $^+N(CH_3)_3$, SPh, Cl, and F, respectively. PhOPh is more difficult to reduce since it does not exhibit a reduction wave prior to the solvated electron generation current rise. (b) These potentials have been measured at a glassy carbon electrode.[18c] They are substantially more negative than the values reported earlier[8] that were derived from anomalous waves at a gold electrode. They also fall in line with the values found in DMF at room temperature, where the potential scale vs SCE is 0.44 V more negative than that in liquid NH_3 at −38 °C referred to 0.01 M Ag^+/Ag.[18c] (c) Thiébault, A. Personal communication.

(19) (a) The molar fractions of saturated solvated electrons obtained from the dissolution of potassium metal in liquid NH_3 at the temperature of interest is 0.16,[13b] i.e., a concentration of about 7.5 M. Taking $l = 10^{-2}$ cm and $D = 3 \times 10^{-5}$ cm^2 s^{-1}, $l^{2/3}/(C_E°)^{2/3}D^{1/3}) = 0.2$, indicating that $C_E°$ is thus most probably overestimated. The application we make of Fick's law assumes the ideality of the solvated electron solution. This assumption is correct within the reaction layer and a substantial portion of the diffusion layer at its left-hand side but certainly not all the way to the surface of the potassium metal. There, activity effects are expected to be important,[13a] amounting to a strong formal decrease of $C_E°$.

Scheme IV



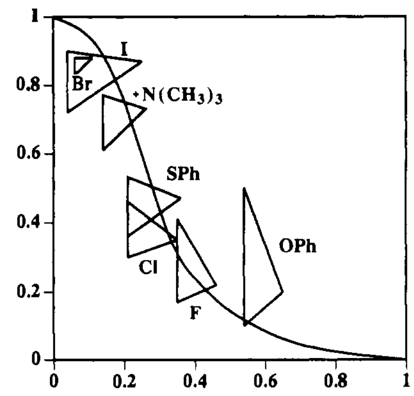


Figure 4. Correlated variations of the yield in benzene and of the ratio $R = [\mathrm{PhCH_2COCH_3}]/[\mathrm{PhCH_2COCH_3} + \mathrm{PhCH_2CHOHCH_3}]$ with the leaving group in the reaction of the corresponding substituted benzenes with acetone enolate ions in the presence of potassium metal (from the data in ref 6a[23a]). The solid line represents the predictions of the model for the following values of the parameters: $\alpha = \beta = \epsilon = 1$, $3 \log \sigma + \log \rho = 0.7$ (see text).

as with all aliphatic halides.[4c,20] The carbanion resulting from the reduction of the open-chain radical is partly protonated and partly reacts with the starting bromide, yielding the open-chain dimer, as observed in the electrochemical reduction of other alkyl halides.[21] The total yield of reduced open-chain product is thus 98.4%, whereas the yield of reduced cyclized radical is 1.2%, and no cyclized radical dimer was detected. These results lead to a value of $\sigma = 1.5 \times 10^{-3}$ from which the reduction rate constant of the starting bromide is found to be 8×10^9 $\mathrm{M^{-1}\ s^{-1}}$, a quite reasonable value in view of the reduction potentials of alkyl bromides.[22] The parameter ρ is thus equal to 3.6, and it is then predicted from the model that no dimer of the cyclized radical should be found, in keeping with the experimental data.

We may thus conclude that the experimental results found in the reduction of 6-bromo-1-hexenyl by solvated electrons in liquid $\mathrm{NH_3}$ are perfectly consistent with the model and with its application to the series of aromatic halides discussed previously.

$\mathrm{S_{RN}1}$ Aromatic Nucleophilic Substitutions. The most striking example of leaving-group effects in $\mathrm{S_{RN}1}$ aromatic substitution reactions triggered by solvated electrons is provided by a series of experiments where substituted benzenes were reacted with potassium metal in liquid $\mathrm{NH_3}$ at −33 °C in the presence of acetone enolate ions as the nucleophilic.[6a] Three products were obtained: benzene, benzyl methyl ketone, and the corresponding alcohol (Scheme I). The variations of the product distribution with the leaving group[6a] are summarized in Figure 4. In spite of rather large uncertainties in the yields of the three products,[23] there is a clear correlated decrease of the PhH yield and of the $[\mathrm{PhCH_2COCH_3}]/[\mathrm{PhCH_2COCH_3} + \mathrm{PhCH_2CHOHCH_3}]$ ratio in the order

$$\mathrm{I} \approx \mathrm{Br} > {}^{+}\mathrm{N(CH_3)_3} > \mathrm{SPh} \gtrsim \mathrm{Cl} > \mathrm{F} > \mathrm{OPh}$$

We propose to interpret these observations in the framework of the reaction mechanism depicted in Scheme I, where the reaction is initiated by the reduction of the substrate, RX, into its anion radical, which then rapidly cleaves, yielding the $\mathrm{R}^{\bullet}$ radical, which reacts with the nucleophile, thus giving the anion radical of the substituted product. The latter intermediate reacts with the substrate, thus closing the $\mathrm{S_{RN}1}$ propagation loop. A first series of termination steps, leading to benzene, consists of the reduction of the phenyl radical by the solvated electrons and anion radicals of the substituted product. In view of the rapidity of the cleavage of the substrate anion radical, we neglect the reduction of the phenyl radical by this species. A second series of termination steps is related to the reduction of the anion radical of the substituted product, i.e., the ketone anion radical into the corresponding alcohol. We propose that this reduction occurs according to the protonation–electron-transfer mechanism indicated in Scheme I, i.e., according to the classical "ECE" mechanism shown to be followed in the electrochemical reduction of many carbonyl compounds.[24] In this framework, we assume that the protonation of the anion radical acts as a preequilibrium vis-à-vis the reduction of the resulting neutral radical by the solvated electrons or by other anion radical molecules (ketone anion radicals are indeed not very strong bases[24]). Under these conditions, the overall rate constants for the reduction of the anion radical by a solvated electron and another anion radical molecule designated in the following by k''_{E} and k_D are related to the rate constants shown in Scheme II by

$$k''_{\mathrm{E}} = (k_{\mathrm{H}}/k_{-\mathrm{H}})k''_{\mathrm{e}}, \quad k''_{D} = (k_{\mathrm{H}}/k_{-\mathrm{H}})k''_{\mathrm{d}}$$

For the same reasons as discussed above, we neglect the possible reduction of the substituted product anion radical by the substrate anion radical. The following discussion is not, in fact, critically dependent upon the exact nature of the sequence of steps that allows the conversion of the substituted product anion radical to the alcohol. It suffices that the overall process be first order toward the substituted product anion radicals and the solvated electrons in the first case and second order toward the anion radicals in the second case.

Generally speaking, the product distribution for the reaction scheme thus defined is a function of the following dimensionless competition parameters:[12]

$$\sigma = \frac{k_{\mathrm{Nu}}[\mathrm{Nu^-}]k_{\mathrm{E}}{}^{1/3}}{k'_{\mathrm{E}}} \frac{l^{2/3}}{(C_{\mathrm{E}}{}^{\circ})^{2/3}D^{1/3}}, \quad \rho = \frac{k''_{\mathrm{E}}}{k_{\mathrm{E}}}$$

$$\alpha = \frac{k_{\mathrm{E}}}{k_{\mathrm{D}}}, \quad \beta = \frac{k'_{\mathrm{E}}}{k'_{\mathrm{D}}}, \quad \epsilon = \frac{k''_{\mathrm{E}}}{k''_{\mathrm{D}}}$$

(or any other combination of them leading to five independent parameters). Since the phenyl radicals are very easy to reduce ($E^{\circ} \approx -0.5$ V vs 0.01 M $\mathrm{Ag^+/Ag}$ in liquid $\mathrm{NH_3}$ at −40 °C[4e]), k'_{E} and k'_{D} are expected to be equal to the diffusion limit, and therefore

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[23] (a) The material balances were in general poorer than in the above radical cyclization experiments. The triangles representing the experimental data in Figure 4 were obtained for each leaving group by attributing the difference between 1 and the observed material balance, successively to each of the three products. (b) The data for PhSePh[6a] were excluded from the discussion because the corresponding experiments were carried out in the presence of THF from which H-atoms may be abstracted by phenyl radicals[4c,d] to yield benzene.

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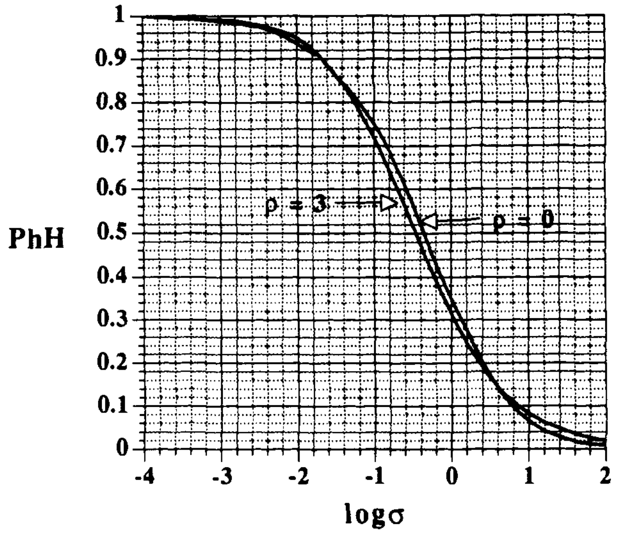

Figure 5. Predicted variations of the PhH yield with the competition parameters σ and ρ ($\alpha = \beta = \epsilon = 1$).

$\beta = 1$. In cyclic voltammetry, nonconjugated ketones do not exhibit a reduction wave prior to the current rise corresponding to the generation of the solvated electrons in liquid NH_3 with a potassium salt as supporting electrolyte, whereas they show a wave close to the discharge of the supporting electrolyte (tetraalkylammonium salts) in DMF at room temperature.[25] It is thus reasonable to assume that solvated electrons and the present ketone anion radicals have a comparable reducing power. We therefore assume that $\alpha = 1$ and $\epsilon = 1$.

Under these conditions, the predicted variations of the yield of PhH and of the ratio R with the parameters σ and ρ are as shown in Figures 5 and 6, respectively. As expected intuitively, the PhH yield is essentially a function of the parameter σ with little influence of ρ. The ratio R is mainly a function of the parameter ρ, although σ exerts also a significant influence especially when it becomes small, i.e., when substitution is less and less efficient vis-à-vis reduction of the phenyl radical.

Eliminating k_E between the two equations that define σ and ρ, we have found that the best fit of the experimental data displayed in Figure 4 is obtained for

$$3 \log \sigma + \log \rho = \log k''_E \left\{ \frac{l^{2/3}}{(C_E^\circ)^{2/3} D^{1/3}} \frac{k_{Nu}[Nu^-]}{k'_E} \right\}^3 = 0.7$$

Taking for, $l^{2/3}/((C_E^\circ)^{2/3}D^{1/3})$ the same value as that determined in the preceding section, 0.77 $M^{-2/3}\ s^{1/3}$, and for k_{Nu}, a value $1.3 \times 10^8\ M^{-1}\ s^{-1}$, i.e., slightly smaller than the value previously determined for pinacolone enolate ions,[26] we find that $k''_E = 6 \times 10^9\ M^{-1}\ s^{-1}$. A value of σ and ρ corresponds to each value of [PhH] and R. These values of σ and ρ are related by the above equation along the theoretical curve in Figure 4 (full line). The average values of σ and ρ corresponding to each compound may thus be derived from the midpoints of the segments of the theoretical curve that intersect the experimental triangles. From there, the following series of k_E values is obtained.

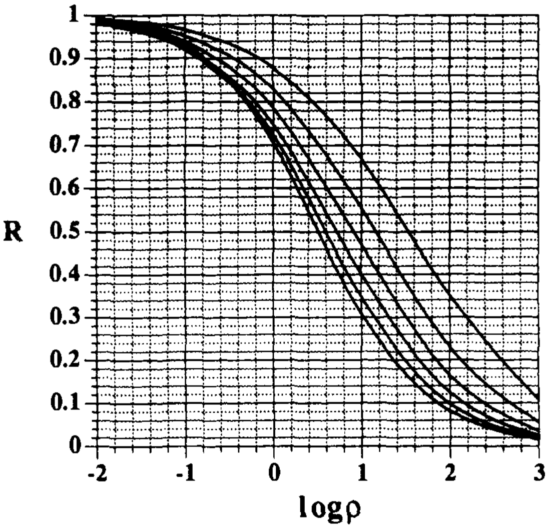

Figure 6. Predicted variations of the ratio $R = [PhCH_2COCH_3]/([PhCH_2COCH_3] + [PhCH_2CHOHCH_3])$ with the competition parameters σ and ρ. From bottom to top, $\log \sigma = -1.7, -1.0, -0.5, 0.0, 0.7$.

X	k_E ($M^{-1}\ s^{-1}$)
I	2×10^{10}
Br	4×10^{10}
$^+N(CH_3)_3$	5×10^9
SPh	1×10^9
Cl	7×10^8
F	7×10^7
OPh	4×10^7

The latter again fall in the same order as the cyclic voltammetric peak potentials of these substituted benzenes.[19,27]

We again see that, in spite of some uncertainties in the experimental data and several approximations in the definition of the reaction mechanism, there is satisfactory agreement between the predictions of the model and the observed leaving-group effects.

Conclusions

Reactions between solvated electrons and organic substrates giving rise to fast-cleaving anion radicals or to concerted bond cleavage occur during mixing of the two reactants. These reactions may be described by a model in which the initial and further chemical steps take place in a thin reaction layer located inside the steady-state diffusion layer within which the two reactants mix. Under these conditions, the essential cause of the leaving-group effects observed in radical reactions, such as $S_{RN}1$ substitution and radical cyclization reactions, is the decrease of the amount of solvated electrons present in the reaction layer as the initial step becomes faster and faster. Subsequent reduction of the radical intermediate by solvated electrons is thus minimized at the expense of the chemical steps leading to the target product. In the case of $S_{RN}1$ substitution, an additional cause of the observed leaving-group effects is the parallel variation of the rate of reaction of the substituted anion radical with the substrate, an essential step of the chain propagation loop. Quantitative application of the model leads to satisfactory agreement with the available product distribution data.

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(27) In view of the relatively large uncertainties in the determination of the product yields and the approximation contained in the kinetic analysis, the agreement between these series of rate constants and those extracted from the radical cyclization studies may be considered as satisfactory.