

Estimation of Reduction and Standard Potentials of Some Allyl and Substituted Alkyl Radicals

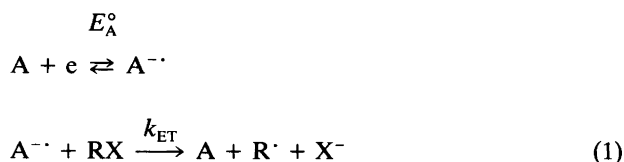
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Anion radicals of aromatic compounds react with alkyl halides by dissociative electron transfer; the radicals thus formed may either couple with the anion radicals or may be reduced by the anion radicals. The competition between the coupling and the reduction may be used to determine the reduction potential and standard potential of the radicals. In this report the results concerning the redox properties of allyl radicals and different kinds of alkyl radical, such as methyl, ethyl and propyl, very sterically hindered alkyl radicals and 2-methoxy-substituted cycloalkyl radicals, are presented. The standard potentials of the allyl radicals are between -1.39 and -1.72 V vs. SCE. For most of the alkyl radicals the interval is from -1.63 to -1.81 V. However, the potential of the methyl radical is, quite unexpectedly, found by this method to be approximately 400 mV more positive than the potential of a primary alkyl radical and even more positive than that of the benzyl radical.

The reaction between an electrogenerated aromatic or heteroaromatic anion radical and an alkyl halide can be described by the following general scheme,¹ eqns. (1)–(3).



The anion radicals react with the radical R^{\cdot} formed in the dissociative electron transfer either with coupling [eqn. (2)] or by reduction [eqn. (3)]. The products AR^- and R^- will either be protonated or react with the alkyl halide in a nucleophilic substitution.

The rate-determining step in this mechanism is the electron transfer (ET) from the aromatic anion radical to the alkyl halide [eqn. (1)], since R^{\cdot} , except for some alkyl iodides, is more easily reduced than RX (and thus $k_3 \gg k_{ET}$) and the coupling between the anion radical and R^{\cdot} (k_2) occurs with a rate constant close to the diffusion limit.² The first ET reaction [eqn. (1)] which generates the alkyl radical and the halide ion is generally regarded as being dissociative, i.e. the ET step and the C–X bond cleavage are concerted.³ Attempts^{1c} to describe this reaction within

the frames of the Marcus theory⁴ or other theories³ with a quadratic correlation between the logarithm of the rate constant (k_{ET}) and the driving force have been made, but recent experimental results^{5,6} indicate, rather, a linear relationship.

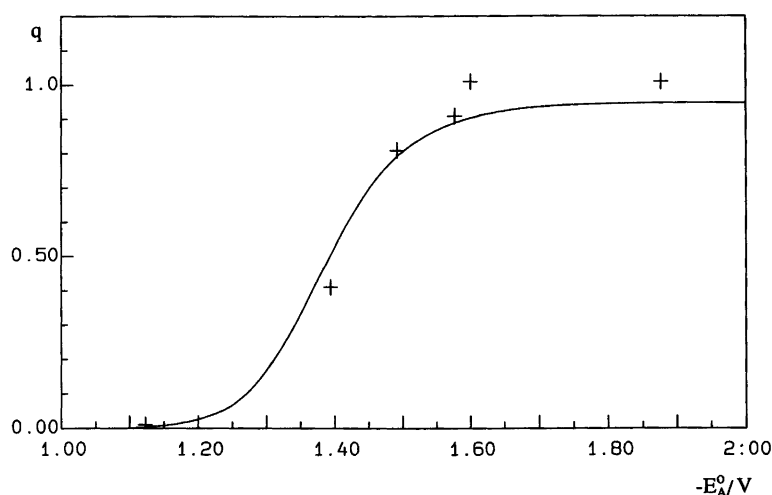
The competition between reactions (2) and (3) can be expressed by the dimensionless parameter q defined by eqn. (4). If the anion radical couples with R^{\cdot} ($k_2 \gg k_3$)

$$q = k_3(k_2 + k_3)^{-1} \quad (4)$$

q is equal to 0; if R^{\cdot} is reduced by the anion radical ($k_3 \gg k_2$) q is equal to 1. From previous investigations^{7,8} it has been shown that the competition between these two pathways depends on the difference between the standard potential of the mediator and the reduction potential of the radical R^{\cdot} . When q is equal to 0.5 ($k_2 = k_3$) the corresponding standard potential of the anion radical can be considered as the reduction potential of R^{\cdot} ($E_{1/2}^q$). In practice $E_{1/2}^q$ can be determined by interpolation among points in a plot of q versus the standard potentials of different mediators (Fig. 1) to the standard potential of an imaginary mediator, which will cause $q = 0.5$. In this way it has been possible to determine reduction potentials of not only long-lived radicals such as benzyl radicals, but also short-lived radicals such as alkyl radicals. The competition parameter can be determined in different ways, e.g., by preparative reduction and isolation of the products, by coulometry, and by linear-sweep voltammetry.

The reaction shown in eqn. (3) between an aromatic anion radical and an alkyl radical can be considered to be

Fig. 1. q -Values of 3-chloro-1-propyne vs. the redox potential E_A° (vs. SCE) of some aromatic anion radicals. The curve is calculated from eqn. (8) using $k_2k_d^{-1} = 0.05$ and $\lambda = 15$ kcal mol $^{-1}$.



an outer-sphere ET reaction, i.e. the bonding stabilization of the transition state is very small (<1 kcal mol $^{-1}$). According to the Marcus theory⁴ the rate constant k_3 can be expressed as eqn. (5). k_d is the diffusion-controlled rate

$$k_3 = \frac{k_d}{1 + A \exp[\lambda/4(1 + \Delta G^\circ/\lambda)^2/RT]} \quad (5)$$

$$\Delta G^\circ = -F(E_R^\circ - E_A^\circ) \quad (6)$$

$$\lambda = 1/2[\lambda_{A^{\cdot-}}(0) + \lambda_{R^{\cdot}}(0)] \quad (7)$$

constant ($\approx 10^{10}$ M $^{-1}$ s $^{-1}$), A is the preexponential parameter (taken to be 0.2), λ the reorganization energy and ΔG° the driving force. The driving force can be expressed by the difference in standard potential between the aromatic anion radical (E_A°) and the radical (E_R°) multiplied with Faraday's constant F [eqn. (6)]. According to the Marcus cross-relation the reorganization energy λ can be expressed as the average value of the self-exchange reorganization energy of the electron donor $\lambda_{A^{\cdot-}}(0)$ and electron acceptor $\lambda_{R^{\cdot}}(0)$ [eqn. (7)].⁹ The reorganization energy for the self-exchange reaction of aromatic anion radicals has been measured by means of EPR spectroscopy in N,N -dimethylformamide (DMF) to approximately 10 kcal mol $^{-1}$.¹⁰ Determination of the total reorganization energy of reaction (3) will thus make it possible to find the self-exchange reorganization energy for the R'/R $^-$ couple.

Substitution of eqn. (5) into the expression for the competition parameter q gives eqn. (8) as the complete expression for q . From eqn. (8) it is found, that the maximum value of q (q_{\max}) is given by eqn. (9); in eqn. (8) K is given by eqn. (9').

$$q = \left\{ \frac{k_2}{k_d} \left[1 + A \exp(K) \right] + 1 \right\}^{-1}, \quad (8)$$

$$q_{\max} = \frac{1}{k_2k_d^{-1}(1 + A) + 1} \quad (9)$$

$$K = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ}{\lambda} \right)^2 / RT. \quad (9')$$

A diagram of q vs. ΔG° gives an S-shaped curve; the reorganization energy λ determines its width and the ratio $k_2k_d^{-1}$ its height. By comparing the experimental curves with simulated ones it should thus be possible to determine these two parameters.

It is possible to estimate $k_2k_d^{-1}$ from literature data. Recently published results² of measurements of k_2 for the reaction between aromatic anion radicals and radical clocks show a variation of k_2 from 0.5×10^9 M $^{-1}$ s $^{-1}$ for the reaction between benzophenone anion radical and 6-bromo-1-hexene to 3.5×10^9 M $^{-1}$ s $^{-1}$ for the reaction between quinoxaline and 6-bromo-5,5-dimethyl-1-hexene. As a first approximation, k_2 will be assumed equal to 10^9 M $^{-1}$ s $^{-1}$. The diffusion-controlled rate constant, k_d , is taken to be 1×10^{10} M $^{-1}$ s $^{-1}$. The ratio $k_2k_d^{-1}$ would thus be expected to be close to 0.1, which would lead to $q_{\max} = 0.89$. However, experimentally we observe q_{\max} near 1.0 in certain cases. We believe that this is caused by the fact that k_d is somewhat larger than 10^{10} M $^{-1}$ s $^{-1}$ owing to the small size of alkyl radicals. However, in the following we have chosen to use a ratio of $k_2k_d^{-1}$ equal to 0.10 so the calculated potentials are consistent with the previously published potentials.^{7,8} Small variations from this ratio will be indicated as discontinuities in the plot of q vs. E_A° , but since $E_{1/2}^q$ is determined from reactions with a number of different aromatic anion radicals small variations in $k_2k_d^{-1}$ are unimportant, as there will thus be some averaging in the determination of $E_{1/2}^q$.

With the knowledge of λ and $k_2k_d^{-1}$ it is possible from eqn. (8) to extract the standard potential of the radical. At $q = 0.5$ where $k_2 = k_3$ and $E_A^\circ = E_{1/2}^q$, the following expression for E_R° results [eqn. (10)], where H_{corr} is given by eqn. (10').

$$E_R^\circ = E_{1/2}^q + H_{\text{corr}} \quad (10)$$

$$H_{\text{corr}} = \frac{\lambda}{F} \left\{ 1 - \sqrt{\frac{4RT}{\lambda}} \ln \left[\frac{1}{A} \left(\frac{k_d}{k_2} - 1 \right) \right] \right\} \quad (10')$$

Table 1. Competition parameter (q) for some allyl and alkyl halides (RX) in DMF/0.1 M TBABF₄, measured by LSV and preparative reductions.

RX	Mediator	$-E_{1/2}^0/V^a$	q	RX	Mediator	$-E_{1/2}^0/V^a$	q	
Allyl chloride	<i>p</i> -Diacetylbenzene	1.407	0.0 ^b	1-Bromo-1-chloro-adamantane	Anthracene	1.890	0.0 ^b	
	Tetracene	1.505	0.4		Isoquinoline	2.131	0.2	
	Acenaphthylene	1.590	0.6		3-Methylisoquinoline	2.154	0.2	
	Perylene	1.613	0.8		Methyl benzoate	2.183	0.3	
	Fluoranthene	1.688	0.9		Benzonitrile	2.230	0.4	
	Anthracene	1.890	1.0		<i>m</i> -Toluonitrile	2.264	0.4	
	1,2-Benzanthracene	1.922	1.0		<i>o</i> -Toluonitrile	2.277	0.5	
3-Chloro-2-methyl-1-propene	<i>p</i> -Diacetylbenzene	1.407	0.0 ^b		<i>p</i> -Toluonitrile	2.337	0.8	
	Tetracene	1.505	0.4		Phenanthrene	2.388	0.9	
	Acenaphthylene	1.590	0.6		Naphthalene	2.457	0.9	
	Perylene	1.613	0.8		Biphenyl	2.519	1.0	
	Fluoranthene	1.688	0.9		1-Methoxynaphthalene	2.537	1.0	
	Anthracene	1.890	1.0		<i>trans</i> -1-Bromo-2-methoxycyclohexane	Quinoxaline	1.589	0.0 ^c
	1,2-Benzanthracene	1.922	1.0			Anthracene	1.890	0.3
3-Chloro-1-propyne	3-Chloroazobenzene	1.135	0.0 ^b	1,2-Benzanthracene		1.922	0.4	
	<i>p</i> -Diacetylbenzene	1.407	0.4	Pyrene		2.018	0.5	
	Tetracene	1.505	0.8	Quinoline		2.075	0.5	
	Acenaphthylene	1.590	0.9	3-Methylisoquinoline		2.154	0.7	
	Perylene	1.613	1.0	Methyl benzoate		2.183	0.8	
	Anthracene	1.890	1.0	<i>cis</i> -1-Bromo-2-methoxycyclohexane	Quinoxaline	1.589	0.0 ^c	
4-Chloro-2-pentene	Acenaphthylene	1.590	0.0 ^b		Anthracene	1.890	0.3	
	Perylene	1.613	0.0 ^b		1,2-Benzanthracene	1.922	0.4	
	Fluoranthene	1.688	0.0 ^b		Pyrene	2.018	0.5	
	9,10-Diphenylanthracene	1.794	0.4		Quinoline	2.075	0.5	
	Anthracene	1.890	0.4		3-Methylisoquinoline	2.154	0.7	
	1,2-Benzanthracene	1.922	0.5		Methyl benzoate	2.183	0.8	
	Pyrene	2.018	0.7	<i>trans</i> -1-Bromo-2-methoxycyclopentane	Quinoxaline	1.589	0.0 ^c	
2,7-Di- <i>t</i> -butylpyrene	2.074	1.0	Anthracene		1.890	0.3		
3-Chloro-1-butene	Acenaphthylene	1.590	0.1		1,2-Benzanthracene	1.922	0.5	
	Fluoranthene	1.688	0.3		Pyrene	2.018	0.6	
	9,10-Diphenylanthracene	1.794	0.9		Quinoline	2.075	0.6	
	9-Phenylanthracene	1.830	0.9		3-Methylisoquinoline	2.154	0.8	
	Anthracene	1.890	0.9		Methyl benzoate	2.183	0.8	
<i>exo</i> -Norbornyl chloride	Anthracene	1.890	0.0 ^c	Methyl iodide ^d	<i>p</i> -Diacetylbenzene	1.407	0.0 ^c	
	Pyrene	2.018	0.0 ^b		Fluoranthene	1.688	0.3	
	Benzonitrile	2.230	0.4		<i>p</i> -Methylbenzophenone	1.736	0.4	
	<i>o</i> -Toluonitrile	2.277	0.5		<i>p</i> -Methoxybenzophenone	1.771	0.4	
	<i>p</i> -Toluonitrile	2.337	0.7		9-Phenylanthracene	1.830	0.6	
	Phenanthrene	2.388	0.8		Anthracene	1.890	0.6	
	Naphthalene	2.457	0.8		Pyrene	2.018	0.7	
	Biphenyl	2.519	0.9		3-Methoxypyrene	2.081	0.8	
	1-Methoxynaphthalene	2.537	0.9		Ethyl bromide	Anthracene	1.890	0.0 ^c
	Isobornyl chloride	Anthracene	1.890			0.0 ^c	Pyrene	2.018
Pyrene		2.018	0.0 ^b	1-Methoxypyrene		2.081	0.2	
Benzonitrile		2.230	0.4	<i>trans</i> -Stilbene		2.136	0.2	
<i>o</i> -Toluonitrile		2.277	0.4	Methyl benzoate		2.183	0.3	
<i>p</i> -Toluonitrile		2.337	0.7	2-Phenylpyridine		2.286	0.5	
Phenanthrene		2.388	0.8	<i>p</i> -Toluonitrile		2.337	0.6	
Naphthalene		2.457	0.8	Naphthalene	2.457	0.8		
Bornyl chloride	Biphenyl	2.519	0.9	<i>n</i> -Propyl bromide	Anthracene	1.890	0.0 ^c	
	1-Methoxynaphthalene	2.537	0.9		Pyrene	2.018	0.1	
	Boryl chloride	Anthracene	1.890		0.0 ^c	3-Methoxypyrene	2.081	0.2
		Pyrene	2.018		0.0 ^b	Methyl benzoate	2.183	0.3
		Benzonitrile	2.230		0.4	<i>m</i> -Toluonitrile	2.264	0.5
		<i>o</i> -Toluonitrile	2.277		0.4	<i>p</i> -Toluonitrile	2.337	0.7
		<i>p</i> -Toluonitrile	2.337		0.7	Triphenylene	2.388	0.8
		Phenanthrene	2.388	0.8				
		Naphthalene	2.457	0.8				
		Biphenyl	2.519	0.9				
		1-Methoxynaphthalene	2.537	0.9				

^aVs. SCE. ^bFrom coulometric experiments. ^cFrom coulometric experiments and isolation of coupling products. ^dMeasurements were performed in acetonitrile/0.1 M TBABF₄.

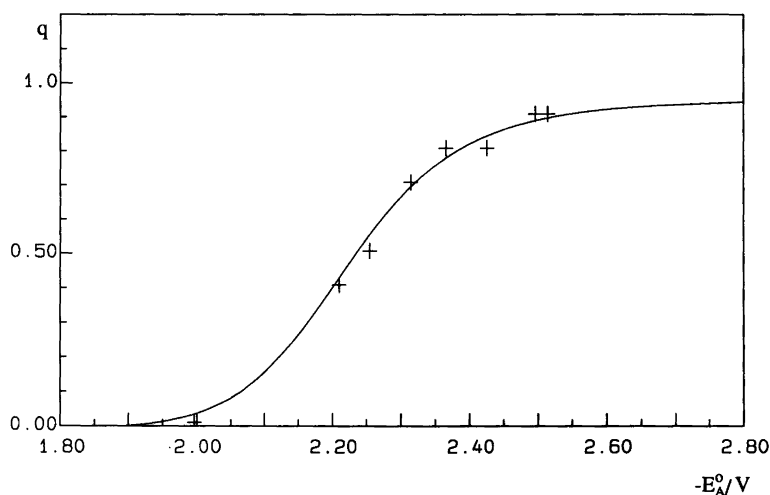


Fig. 2. q -Values of *exo*-norbornyl chloride vs. the redox potential E_A^0 (vs. SCE) of some aromatic anion radicals. The curve is calculated from eqn. (8) using $k_2k_d^{-1} = 0.05$ and $\lambda = 30 \text{ kcal mol}^{-1}$.

In this report the following substrates have been investigated as examples of allyl radicals, sterically hindered and 2-methoxy-substituted alkyl radicals: allyl chloride (1), 3-chloro-2-methyl-1-propene (2), 3-chloro-1-propyne (3), 4-chloro-2-pentene (4), 3-chloro-1-butene (5), *exo*-norbornyl chloride (6), isobornyl chloride (7), bornyl chloride (8), 1-adamantyl chloride and bromide (9), *trans*-1-bromo-2-methoxycyclohexane (10), *cis*-1-bromo-2-methoxycyclohexane (11), *trans*-1-bromo-2-methoxycyclopentane (12), methyl iodide (13), ethyl bromide (14), propyl bromide (15).

Results and discussion

The experimental q -values obtained for the reaction between electrogenerated anion radicals and alkyl halides are presented in Table 1. In some cases the measurements of q over the whole range from 0 to 1 could be performed by

LSV only by varying the halide in the substrate RX. In this way a sufficiently high rate constant ($>10 \text{ M}^{-1} \text{ s}^{-1}$) of the first electron transfer to RX [eqn. (1)] could always be achieved, thus making possible the measurement of the competition between reactions (2) and (3) by LSV. Theoretically the nature of the leaving group should not have any influence on the determination of q and this has been confirmed experimentally in several cases. As shown in Table 1, in the case of the 1-adamantyl radical, there is agreement between the points which were measured with 1-bromoadamantane (from $q = 0.0$ to 0.8) and 1-chloroadamantane (from $q = 0.8$ to 1.0). The point corresponding to $q = 0.8$ was obtained with both substrates.

In general the potential interval between q equal to 0.0 and 1.0 is about 300 mV for the allyl radicals and for the 3-propynyl radical and 500–600 mV for the alkyl radicals. In Figs. 1 and 2 two examples of plots of q vs. E_A^0 for 3-chloro-1-propyne and *exo*-norbornyl chloride are shown

Table 2. Reduction potentials $E_{1/2}^q$, standard potentials E_R^0 , and self-exchange reorganization energies $\lambda_R(0)$ for allyl and alkyl radicals.

RX	$-E_{1/2}^q/V^a$	$-E_R^0/V^a$	$\lambda_R(0)/\text{kcal mol}^{-1}$
1 Allyl chloride	1.54	1.39	20
2 3-Chloro-2-methyl-1-propene	1.54	1.39	20
3 3-Chloro-1-propyne	1.40	1.25	20
4 4-Chloro-2-pentene	1.87	1.72	20
5 3-Chloro-1-butene	1.70	1.55	20
6 <i>exo</i> -Norbornyl chloride	2.26	1.67	50
7 Isobornyl chloride	2.26	1.67	50
8 Bornyl chloride	2.26	1.67	50
9 1-Bromo/chloro-adamantane	2.24	1.81	40
10 <i>trans</i> -1-Bromo-2-methoxycyclohexane	1.98	1.39	50
11 <i>cis</i> -1-Bromo-2-methoxycyclohexane	1.98	1.39	50
12 <i>trans</i> -1-Bromo-2-methoxycyclopentane	1.96	1.37	50
13 Methyl iodide	1.78	1.19	50
14 Ethyl bromide	2.23	1.64	50
15 Propyl bromide	2.22	1.63	50

^aVs. SCE.

and in both cases they clearly exhibit S-shaped curvature. The solid lines in the two figures are the best fit of simulated curves to the experimental results. The simulations in these two cases were done using $k_2k_d^{-1} = 0.05$ and λ equal to 15 kcal mol⁻¹ (Fig. 1) and 30 kcal mol⁻¹ (Fig. 2), respectively. Since the reorganization energy λ can be expressed as the average of the self-exchange reorganization energy of the electron donor $\lambda_{A^{\cdot-}}(0) = 10$ kcal mol⁻¹ and electron acceptor $\lambda_R(0)$ [eqn. (7)], we can evaluate the self-exchange reorganization energy of the radicals. These values are presented in Table 2. The data are not good enough to allow a determination of reliable $\lambda_R(0)$ values for the different alkyl radicals so an average value is used for all the unconjugated alkyl radicals (50 kcal mol⁻¹), with the exception of the adamantyl radical (40 kcal mol⁻¹), and for all the allyl radicals (20 kcal mol⁻¹).

Knowledge of the value of the reorganization energy and $k_2k_d^{-1}$ also allows the calculation of the potential correction H_{corr} [eqn. (10)] necessary to transform the reduction potential of the radical $E_{1/2}^q$ into the corresponding standard potential E_R° .

The potential correction is equal to 150 and 590 mV for allylic and unconjugated aliphatic radicals, respectively, when the average values for λ (15 and 30 kcal mol⁻¹) are used. For the 1-adamantyl radical the correction is equal to 430 mV. In all the cases the calculations were made assuming $k_2k_d^{-1} = 0.10$. The uncertainty in the measurement of $E_{1/2}^q$ is estimated to be ± 50 mV, while the calculation of the standard potential E_R° involves a number of assumptions and an uncertainty in the determination of λ , which enlarges the interval of accuracy to ± 150 mV. In Table 2 the reduction and standard potentials of all the radicals investigated are presented. If more reliable values for the different parameters, especially for λ , become available the standard potentials may be calculated with less uncertainty from the data in Table 1.

The reduction potentials of the allyl radicals are, in general, only a little more negative than those previously found for the benzyl radicals but substantially more positive than those of the alkyl radicals. This is in accordance with the ability of the allyl and especially benzyl systems to delocalize charge, in contrast with the alkyl systems. Also, the values of the self-exchange reorganization energy $\lambda_{A^{\cdot-}}(0)$ (20 kcal mol⁻¹) for allyl radicals are closer to $\lambda_R(0)$ for the benzyl radicals (10 kcal mol⁻¹), than to $\lambda_R(0)$ for the alkyl radicals (50 kcal mol⁻¹). According to the physical model underlying the Marcus treatment of ET reactions (the dielectric continuum model), the solvent reorganization energy λ_0 , which depends only on the charge and the radii of the molecules, will be expected to be of the same magnitude for the three different kinds of system. Thus the differences in λ values can be attributed mainly to differences in the inner-reorganization energy λ_i . Recent *ab initio* calculations¹¹ have shown that the change in bond angles and lengths, on going from the flat benzyl radical to the almost flat and delocalized benzyl anion, is very small, leading to a small inner-reorganization energy, whereas,

for alkyl radicals, a considerable reorganization of the structure is needed in order to form pyramidal and localized alkyl anions. Owing to the possibility of delocalization, the allyl system will presumably behave in almost the same way as the benzyl system, which may explain the higher but comparable λ value of the former relative to the latter.

The coupling between allyl radicals and anion radicals is assumed to have a rate similar to that of alkyl radicals. This is based on the fact that when the method was applied to the determination of the redox potential of benzyl radicals the $E_{1/2}^q$ values were close (within 50 mV) to those measured by phase-sensitive voltammetry of photochemically generated benzyl radicals.¹² This suggests that the coupling between benzyl radicals and anion radicals occurs at a rate similar to that of alkyl radicals, and, as allyl radicals in other respects have properties between those of alkyl and benzyl radicals, a rate of coupling between allyl radicals and anion radicals of 10⁹ M⁻¹ s⁻¹ is assumed.

The presence of alkyl substituents at the ends of the allyl system influences the value of the reduction and standard potential of the radical. The presence of one methyl group (compound 5) shifts the reduction potential to a more negative value (160 mV). Introduction of a second methyl group (compound 4) makes the reduction potential even more negative (330 mV). It is noteworthy that the introduction of a methyl group at the end of the allyl system shifts the reduction potential more than introduction of a methyl group in a primary or secondary alkyl radical. On the other hand, a methyl group at the central carbon atom (compound 2) does not affect the redox properties at all. This behaviour can easily be explained if one takes into account the fact that the coefficient of the non-bonding molecular orbital of the allyl system is negligible at the central carbon atom. The effect of substituents in the central position is thus negligible, whereas it is large and of the same magnitude in the terminal positions.

The regioselectivity of the coupling between radical ions and allyl radicals was not investigated. It might be mentioned that in the reduction of benzaldehyde in DMF in the presence of different allyl halides¹³ the major isomer of the coupled products was that in which the allyl radical attacked the carbonyl carbon through the less-substituted carbon atom of the allyl system.

The reduction potential of the 3-propynyl radical (compound 3) is more positive (140 mV) than that measured for the allyl radical. This result is in reasonable agreement with the finding that the anion, formed by the reduction of the 3-propynyl radical, is more stabilized than the allyl anion; the propenyl anion is, at least in the gas phase, considered to have an allenic rather than an acetylenic structure.¹⁴

For the aliphatic radicals 6–8, but not 9, the $\lambda_R(0)$ values (50 kcal mol⁻¹) and standard potentials are similar to those found for the previously investigated alkyl radicals. Alkyl substituents and high steric hindrance seem, in most cases, to have a negligible effect on these parameters. However, in the case of 9 the self-exchange reorganization energy of the adamantyl radical is found to be smaller than 50 kcal

mol⁻¹. The estimated $\lambda_{\text{R}}(0)$ is 40 kcal mol⁻¹. A reasonable explanation for this different value of $\lambda_{\text{R}}(0)$ is that the 1-adamantyl radical, being pyramidal,¹⁵ does not need a large inner-reorganization energy to be reduced to the corresponding anion. On going from the adamantyl radical to the adamantyl anion, the difference in bond lengths and angles is not as big as, for example, in the propyl system. A consequence of the smaller λ value is that the correction term H_{corr} for transferring the reduction potential into the standard potential is smaller for the adamantyl radical than for the other alkyl radicals. Thus although the reduction potential of the tertiary adamantyl radical is more positive than that of, for example, the secondary bornyl radical, the opposite order is found for the standard potentials.

The standard and reduction potentials of the bornyl radical and the very similar norbornyl radical are the same. The three methyl groups in the bornyl radical thus do not have any detectable effect on these parameters.

In the substrates **10** to **12**, the introduction of a methoxy group in the β -position makes the reduction potential of the radical more positive (about 300 mV) in comparison with the corresponding unsubstituted cycloalkyl radical. This can easily be explained by the stabilizing inductive effect of the methoxy group on the formation of the carbanion. However, the more positive reduction potential could also be attributed to a concerted reduction of the radical and elimination of the methoxy group, which would lead to olefinic compounds. In order to confirm the existence of an anionic intermediate, a preparative electrolysis of **10** was carried out in *N,N*-dimethylformamide in the presence of a mediator (*p*-toluonitrile) in the $q = 0.9$ region. Methoxycyclohexane and the elimination product cyclohexene, detected by means of GC-MS, were formed in nearly equal amounts. Direct reductions of **10** were also performed in *N,N*-dimethylformamide and acetonitrile in the presence of phenol as a proton donor. Also in these cases, the same products were detected as in the mediated electrolysis. These results indicate that the carbanions of **10–12** have a certain lifetime, which excludes the concerted reduction-elimination reaction. Possibly the alkene is generated from the substrate in an elimination catalyzed by the electro-generated base.

In the investigation of the bornyl radical and the 2-methoxycyclohexyl radical the results are independent of whether bornyl chloride/isobornyl chloride or *cis*-1-bromo-2-methoxycyclohexane/*trans*-1-bromo-2-methoxycyclohexane are used as the substrates, since in both cases the same radical is generated.

The methyl radical represents an exception to the general behaviour of the alkyl radicals. Its reduction and standard potentials were found to be much more positive in comparison with, e.g., ethyl and propyl radicals. The value obtained for the standard potential is even more positive than that of the benzyl radical. However, the self-exchange reorganization energy $\lambda_{\text{R}}(0)$ was found to be equal to the $\lambda_{\text{R}}(0)$ of other alkyl radicals (50 kcal mol⁻¹). In order to exclude the possibility that the more positive potential ob-

tained for the methyl radical was caused by a direct nucleophilic substitution between anion radicals and methyl iodide, a number of experiments were performed at low temperature (-40°C) with methyl bromide. Even though a slightly higher uncertainty is expected owing to the difficulty of controlling the concentration of the gaseous methyl bromide, the results obtained for methyl iodide and methyl bromide agree to within the uncertainty of the method. Furthermore, some LSV measurements were made with other kinds of iodide, e.g., *trans*-1-iodo-2-methoxycyclohexane, and also, in this case, the same q -values as for the other methoxycycloalkyl halides were obtained. It thus seems that although the ET between aromatic anion radicals and methyl iodide has a certain (and probably more than the larger primary alkyl halides) inner-sphere component¹⁶ this does not result in a direct displacement of the iodide by the electron donor, but in the formation of the methyl radical.

Standard potentials of radicals R^{\cdot} can be estimated by using thermodynamic cycles. This method was introduced by Ebersson¹⁷ and in recent years has been used, among others, by Pearson.¹⁸ Pearson gives an expression for the ionization potential I' of R^{-} in aqueous solution, eqn. (11),

$$I' = I - \Delta G_{\text{R}^{-}}^{\circ} + \Delta G_{\text{R}^{\cdot}}^{\circ} \quad (11)$$

where $-\Delta G_{\text{R}^{-}}^{\circ} = E_{\text{pa}} - 267 - \Delta G_{\text{RH}}^{\circ} - 1.36 \text{ p}K_{\text{a}}$ and $\Delta G_{\text{R}^{\cdot}}^{\circ} \approx \Delta G_{\text{RH}}^{\circ}$; I is the ionization potential of R^{-} in the gas phase and $\Delta G_{\text{R}^{-}}^{\circ}$ and $\Delta G_{\text{R}^{\cdot}}^{\circ}$ the free energies of hydration for R^{-} and R^{\cdot} , respectively. E_{pa} is the proton affinity of R^{-} and $\text{p}K_{\text{a}}$ is the value for the acid RH in water. The approximation $\Delta G_{\text{R}^{\cdot}}^{\circ} \approx \Delta G_{\text{RH}}^{\circ}$ is valid as long as the R-H bond considered is not very polar.

The proton affinity, which is defined as the enthalpy change associated with the reaction $\text{RH}(\text{g}) \rightarrow \text{R}^{-}(\text{g}) + \text{H}^{+}(\text{g})$, can be expressed in terms of the enthalpy of formation of the species involved [eqn. (12)]. The enthalpy of

$$\begin{aligned} E_{\text{pa}} &= -\Delta H_{\text{f}}[\text{RH}(\text{g})] + \Delta H_{\text{f}}[\text{R}^{-}(\text{g})] + \Delta H_{\text{f}}[\text{H}^{+}(\text{g})] \\ &\approx -\Delta H_{\text{f}}[\text{RH}(\text{g})] + \Delta H_{\text{f}}[\text{R}^{\cdot}(\text{g})] - I + \Delta H_{\text{f}}[\text{H}^{+}(\text{g})] \quad (12) \end{aligned}$$

formation of H^{+} in the gas phase at 25°C is 365.7 kcal mol⁻¹¹⁹ and $\Delta H_{\text{f}}[\text{R}^{-}(\text{g})]$ can be calculated from the ionization potential I and $\Delta H_{\text{f}}[\text{R}^{\cdot}(\text{g})]$ assuming that the integrated heat capacities of the ion and the radical are identical. Substitution of eqn. (12) into eqn. (11) gives the following expressions for I' and the standard potential $E_{\text{R}^{\cdot}}^{\circ}$ at 25°C of the radical (vs. SCE).

$$\begin{aligned} I' &= -\Delta H_{\text{f}}[\text{RH}(\text{g})] + \Delta H_{\text{f}}[\text{R}^{\cdot}(\text{g})] \\ &\quad - 1.36 \text{ p}K_{\text{a}} + 98.7 \text{ kcal mol}^{-1} \quad (13) \end{aligned}$$

$$\begin{aligned} E_{\text{R}^{\cdot}}^{\circ} &= -\Delta H_{\text{f}}[\text{RH}(\text{g})] + \Delta H_{\text{f}}[\text{R}^{\cdot}(\text{g})] \\ &\quad - 1.36 \text{ p}K_{\text{a}} - 10.6 \text{ kcal mol}^{-1} \quad (14) \end{aligned}$$

Table 3. Calculated (in aqueous solution) and experimental standard potentials (in DMF) of alkyl radicals R[•] vs. SCE.

R [•]	pK _a	-E _{R[•]} ^o (calc)/V	-E _{R[•]} ^o (exp)/V
Methyl	48	0.99	1.19
Ethyl	50	1.41	1.64
Propyl	50	1.35	1.63
2-Propyl	51	1.60	1.72 ^a
s-Butyl	51	1.61	1.72 ^a

^aFrom Ref. 8.

The transformation of I' into $E_{R^{\bullet}}^{\circ}$ is effected using a value of 4.5 V as the absolute potential of the hydrogen electrode.¹⁸ Values of $\Delta H_f^{\circ}[\text{RH}(\text{g})]$ and $\Delta H_f^{\circ}[\text{R}^{\bullet}(\text{g})]$ have been measured for a large number of compounds.²⁰ pK_a values have been published for several of the compounds we investigated, but since the very weak acids, such as methane and ethane, have been estimated only in aqueous solution²¹ the standard potential was calculated in this solvent. However, the difference in the solvation energies of the organic anions are not appreciably solvent dependent, and the difference in pK_a between two RH compounds in water and another solvent will be approximately independent of the solvent as long as the acids being compared are of the same charge type and are very similar in structure. Thus the relative difference between the standard potentials in water and DMF would be expected to be the same for very similar compounds. In Table 3 standard potentials of a selected number of aliphatic radicals thus calculated are compared with the experimental values.

Although the calculated potentials are, in general, a little more positive than the experimental results, the agreement is satisfactory, considering that the pK_a-values for the alkanes are estimated from kinetic acidities of the compounds. The trend in the two sets of results are clearly the same and the potentials may be divided into three distinct groups. The methyl radical has a substantially more positive standard potential than the two other groups with the primary alkyl radicals having potentials more positive than the secondary alkyl radicals.

Experimental

Materials. The mediators were the same as used previously.^{7,8} Allyl chloride, 3-chloropropyne, 1-bromo-adamantane, 1-chloroadamantane, methyl iodide, ethyl and propyl bromide were obtained commercially and distilled or recrystallized before use. 3-Chloro-2-methyl-1-propene and 4-chloro-2-pentene were prepared from the reaction of the corresponding alcohol with an excess of gaseous hydrogen chloride in anhydrous diethyl ether and were distilled before use. 3-Chloro-1-butene was also prepared from the corresponding alcohol.²² *trans*-1-Bromo-

2-methoxycyclohexane,²³ *cis*-1-bromo-2-methoxycyclohexane²⁴ and *trans*-1-bromo-2-methoxycyclopentane²³ were prepared according to the references given. *exo*-Norbonyl chloride,²⁵ bornyl chloride²⁶ and isobornyl chloride²⁷ were synthesized according to the references given using gaseous hydrogen chloride instead of hydrogen bromide. The supporting electrolyte, Bu₄NBF₄, and the solvents, *N,N*-dimethylformamide and acetonitrile, were purified by standard procedures.

Equipment. Instrumentation and data-handling procedures have been described previously.²⁸ The cells and the electrodes were of conventional type.

Procedures. Estimation of the competition parameter q by LSV was performed by the method given by Pedersen.²⁸ All the LSV experiments were carried out in DMF, except for the measurements with methyl iodide which were performed in acetonitrile owing to better reproducibility of the results. A reaction between methyl iodide and DMF, akin to the reaction between dimethyl sulfate and DMF,²⁹ might be responsible for the poorer reproducibility in this solvent. The LSV measurements with methyl iodide and ethyl and propyl bromide were performed at low temperature (-20 to -30 °C) in order to decrease the high rate constant of the first electron transfer (k_{ET}). All other experiments were carried out at room temperature. For the slower reactions ($k_{\text{ET}} < 10 \text{ M}^{-1} \text{ s}^{-1}$) the LSV method was not applicable and instead coulometry was used in the determination of q . In cases where the consumption of electrons in the reaction between the electrogenerated anion radical and the halide was 2 ± 0.3 the reaction was considered to be a pure coupling reaction ($q = 0$). The preparative reductions were carried out as already described⁷ and in the cases where $q = 0$, characterization of the products was performed in order to confirm the formation of coupling products. The reaction mixture was usually purified by chromatography on silica gel, and coupling compounds separated and characterized by means of NMR and mass spectra. In some cases, the electrolyzed solution was analyzed only by means of GC-MS.

The following coupling compounds from the reaction between anthracene anion radical and ethyl and propyl bromide were isolated: 9-ethyl-9,10-dihydroanthracene, ¹H NMR (CDCl₃): δ 0.85 (t, 3 H, $J = 8$ Hz), 1.55–1.75 (m, 2 H), 3.75 (t, 1 H, $J = 7$ Hz), 3.85 (d, 1 H, $J = 18$ Hz), 4.10 (d, 1 H, $J = 18$ Hz), 7.1–7.3 (m, 8 H). MS [IP 70 eV, m/z , (%)]: 208 (17), 179 (98), 152 (74), 89 (37), 76 (28), 62 (27), 51 (23), 40 (100); 9-propyl-9,10-dihydroanthracene, ¹H NMR (CDCl₃): δ 0.8–1.0 (m, 3 H), 1.2–1.8 (m, 4 H), 3.75–3.95 (m, 2 H), 4.10 (d, 1 H, $J = 18$ Hz), 7.1–7.4 (m, 8 H). MS [IP 70 eV, m/z , (%)]: 222 (4), 179 (92), 152 (7), 115 (10), 89 (12), 75 (8), 63 (19), 41 (100). The isolated coupling compound for the reaction between *p*-diacetylbenzene and methyl iodide was 4-(1-hydroxy-1-methyl-ethyl)acetophenone, ¹H NMR (CDCl₃): δ 1.55 (s, 6 H), 2.58 (s, 3 H), 7.55 (d, 2 H, $J = 8$ Hz), 7.90 (d, 2 H,

$J = 8$ Hz); MS [IP 70 eV, m/z , (%): 178 (5), 163 (100), 121 (11), 105 (5), 91 (7), 77 (9), 43 (66).

Coupling products from the following reductions were detected by GC-MS. *p*-Diacetylbenzene and 1: MS [IP 70 eV, m/z , (%): 203 (15), 202 (90), 187 (72), 159 (48), 147 (100), 121 (52), 119 (98), 104 (98), 91 (97), 77 (98). *p*-Diacetylbenzene and 2: MS [IP 70 eV, m/z , (%): 216 (13), 201 (10), 147 (100), 119 (57), 104 (45), 91 (78), 76 (57). 3-Chloroazobenzene and 3: MS [IP 70 eV, m/z , (%): 257 (15), 255 (50), 221 (30), 172 (25), 135 (20), 110 (20), 77 (50), 63 (18), 51 (50), 40 (100). Acenaphthylene and 4: MS [IP 70 eV, m/z , (%): 222 (8), 153 (100), 152 (98), 126 (10), 69 (31), 53 (15). Acenaphthylene and 5: MS [IP 70 eV, m/z , (%): 208 (5), 152 (100), 151 (50), 62 (10), 55 (98).

The compounds obtained from the coupling of anion radicals and *exo*-norbornyl bromide, isobornyl bromide, bornyl bromide, *trans*-1-bromo-2-methoxycyclohexane, *cis*-1-bromo-2-methoxycyclohexane and *trans*-1-bromo-2-methoxycyclopentane have been described previously.^{30,31}

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References

- (a) Simonet, J., Michel, M.-A. and Lund, H. *Acta Chem. Scand., Ser. B* 29 (1975) 489; (b) Lund, H. and Simonet, J. *J. Electroanal. Chem.* 65 (1975) 205; (c) Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B* 40 (1986) 470.
- Pedersen, S. U. and Lund, T. *Acta Chem. Scand.* 45 (1991) 397.
- Savéant, J.-M. *Bull. Soc. Chim. Fr.* (1988) 225; Savéant, J.-M. *J. Am. Chem. Soc.* 109 (1987) 6788.
- Marcus, R. A. *J. Chem. Phys.* 24 (1956) 966; *J. Chem. Phys.* 26 (1957) 867, 872.
- Grimshaw, J., Langan, J. R. and Salmon, G. A. *J. Chem. Soc., Chem. Commun.* (1988) 1115.
- Daasbjerg, K., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 45 (1991) 424.
- Fuhendorff, R., Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 43 (1989) 803.
- Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 44 (1990) 715.
- Marcus, R. A. *J. Phys. Chem.* 67 (1963) 853.
- Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer Verlag, New York 1987.
- Mikkelsen, K. V., Pedersen, S. U., Swanstrøm, P. and Lund, H. *J. Phys. Chem.* 95 (1991) 8892.
- Wayner, D. D. M., McPhee, D. J. and Griller, D. *J. Am. Chem. Soc.* 110 (1988) 132; Sim, B. A., Griller, D. and Wayner, D. D. M. *J. Am. Chem. Soc.* 111 (1989) 754.
- Tokuda, M., Satoh, S. and Suginome, H. *J. Org. Chem.* 54 (1989) 5608.
- Oakes, J. M. and Ellison, G. B. *J. Am. Chem. Soc.* 105 (1983) 2969.
- Krusic, P. J., Rettig, T. A. and Schleyer, P. v. R. *J. Am. Chem. Soc.* 94 (1972) 995.
- Ebersson, L. and Shaik, S. S. *J. Am. Chem. Soc.* 112 (1990) 4484.
- Ebersson, L. *Acta Chem. Scand.* 17 (1963) 2004.
- Pearson, R. G. *J. Am. Chem. Soc.* 108 (1986) 6109.
- Lias, S. G., Liebman, J. F. and Levin, R. D. *J. Phys. Chem. Ref. Data* 13 (1984) 695.
- Baghal-Vayjooee, M. H., Colussi, A. J. and Benson, S. W. *J. Am. Chem. Soc.* 100 (1978) 3214; *Int. J. Chem. Kinet.* 11 (1979) 147; Golden, D. M. and Benson, S. W. *Chem. Rev.* 69 (1969) 125; Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M. and Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh 1953.
- March, J. *Advanced Organic Chemistry*, Wiley, New York 1985, p. 222.
- Magid, R. M., Fruchey, O. S., Johnson, W. L. and Allen, T. G. *J. Org. Chem.* 44 (1979) 359.
- Grady, G. L. and Chokshi, S. K. *Synthesis* (1972) 483.
- Müller, E., Heischkeil, R. and Bauer, M. *Justus Liebigs Ann. Chem.* 677 (1964) 55.
- Roberts, J. D., Trumbull, E. R., Bennet, W. and Armstrong, R. *J. Am. Chem. Soc.* 72 (1950) 3116.
- Wallach, O. *Justus Liebigs Ann. Chem.* 239 (1887) 1.
- Semmler, F. W. *Ber. Deutch. Chem. Ges.* 33 (1900) 3420.
- Pedersen, S. U. *Acta Chem. Scand., Ser. A* 41 (1987) 391.
- LeMenn, J. C., Sarrazin, J. and Tallec, A. *Electrochim. Acta* 36 (1991) 819.
- Daasbjerg, K., Hansen, J. N. and Lund, H. *Acta Chem. Scand.* 44 (1990) 711.
- Lund, T. *Tetrahedron Lett.* 32 (1991) 1595.

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