

# The Nucleophilicity of Superoxide towards Different Alkyl Halides Estimated from Kinetic Measurements

Kim Daasbjerg and Henning Lund

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

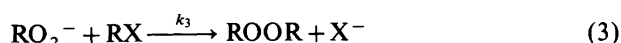
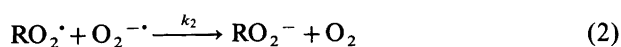
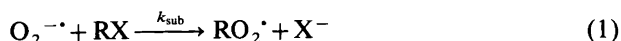
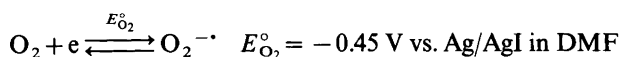
Daasbjerg, K. and Lund, H., 1993. The Nucleophilicity of Superoxide towards Different Alkyl Halides Estimated from Kinetic Measurements. – Acta Chem. Scand. 47: 597–604.

Values of the rate constant  $k_{\text{sub}}$  are measured for the substitution reaction between superoxide  $\text{O}_2^{\cdot-}$  and the alkyl halides butyl chloride, 2-butyl chloride, benzyl chloride, ethyl bromide, butyl bromide, 2-butyl bromide, neopentyl bromide, benzyl bromide, (1-bromo-2,2-dimethylpropyl)benzene and 1-iodoadamantane. These rate constants are compared with the expected rate constant  $k_{\text{ET}}$  for the electron transfer reaction between the same alkyl halides and an aromatic anion radical  $\text{A}^{\cdot-}$  with the same standard oxidation potential as  $\text{O}_2^{\cdot-}$ . The  $k_{\text{sub}}/k_{\text{ET}}$  ratios show that the mechanism of the substitution reaction may shift from  $\text{S}_{\text{N}}2$ -like to ET-like on changes in the steric hindrance and the acceptor ability of the alkyl halide. The influence on  $k_{\text{sub}}/k_{\text{ET}}$  of the difference in self-exchange reorganization energy  $\lambda(0)$  between  $\text{O}_2^{\cdot-}/\text{O}_2$  and  $\text{A}^{\cdot-}/\text{A}$  is discussed.

The role of superoxide ( $\text{O}_2^{\cdot-}$ ) as a strong nucleophile in substitution reactions has been the subject of much research during the last two decades.<sup>1</sup> Both kinetic and stereochemical results have indicated that  $\text{O}_2^{\cdot-}$  is a very potent nucleophile, although no exact measure of its nucleophilicity has been developed. For an investigation of its nucleophilicity it is an advantage that it is rather stable, especially in aprotic solvents, and easily accessible either chemically from, e.g.,  $\text{KO}_2$  or electrochemically from dioxygen. Furthermore the standard oxidation potential of  $\text{O}_2^{\cdot-}$  is known in many solvents.

In this paper we report on the rate constants for the substitution reactions between electrochemically generated  $\text{O}_2^{\cdot-}$  and different alkyl halides in *N,N*-dimethylformamide (DMF). These rate constants are compared with those expected for an electron transfer (ET) to the alkyl halides from an outer-sphere electron donor with the same standard oxidation potential as  $\text{O}_2^{\cdot-}$  in order to describe the ET-character of the substitution reactions.

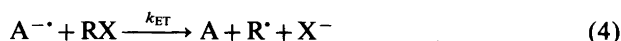
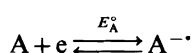
The reaction scheme for the reaction between electro-generated  $\text{O}_2^{\cdot-}$  and alkyl halides  $\text{RX}$  in aprotic solvents has already been investigated and can be described in the following way.<sup>1a, b</sup>



With secondary and tertiary alkyl halides competing elimination reactions occur leading to olefins. For long

reaction times, with an excess of superoxide, alcohols may be formed from the degradation of dialkyl peroxide or directly from  $\text{ROO}^-$ .<sup>1c, d</sup> Reaction (2) is near the diffusion-controlled limit and reaction (3) is normally considered to be faster than (1).

The reaction scheme for the reaction between electro-generated anion radicals ( $\text{A}^{\cdot-}$ ) and alkyl halides has previously been thoroughly investigated.<sup>2</sup>



The products  $\text{AR}^-$  and  $\text{R}^-$  will either be protonated or react with the alkyl halide in a nucleophilic substitution. Dimerization and H-atom disproportionation of the alkyl radicals and H-atom abstraction from the solvent can be assumed to be negligible. The aromatic and heteroaromatic anion radicals with the unpaired electron delocalized over a large  $\pi$ -electron system are normally considered to be outer-sphere electron donors. In the following this will be assumed, although recent calculations and experiments suggest that their reactions with simple alkyl halides might involve some inner-sphere character.<sup>3</sup> By comparing the rate constant  $k_{\text{sub}}$  for the reaction between  $\text{O}_2^{\cdot-}$  and a given alkyl halide with the rate constant  $k_{\text{ET}}$  for the electron transfer reaction between the alkyl halide and an aromatic anion radical with the same self-exchange reorganization energy and standard oxidation potential as  $\text{O}_2^{\cdot-}$ , the degree of

electron transfer in the substitution reaction may be judged. The stabilization energy in the transition state  $\Delta\Delta G^\ddagger$  is related to the  $k_{\text{sub}}/k_{\text{ET}}$  ratio by eqn. (7).<sup>4c</sup>

$$\Delta\Delta G^\ddagger \approx 2.3 RT \log(k_{\text{sub}}/k_{\text{ET}}) \quad (7)$$

When  $k_{\text{sub}}/k_{\text{ET}}$  is close to 1 ( $\Delta\Delta G^\ddagger \approx 0$ ), the rate determining step is assumed to be the transfer of an electron. This has been found for some anions and dianions with sterically hindered alkyl halides.<sup>4</sup> When the steric hindrance of the system is less pronounced  $k_{\text{sub}}/k_{\text{ET}}$  increases indicating that the transition states are stabilized due to bond formation. In this way we have been able to show that a nucleophile, like the enolate ion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine, can be involved in a continuous spectrum of substitution reactions with transition states involving stabilization energies from very little in the case of a sterically hindered alkyl halide such as 1-bromoadamantane ( $k_{\text{sub}}/k_{\text{ET}} = 0.2$ ) to near 6 kcal mol<sup>-1</sup> in the case of butyl chloride ( $k_{\text{sub}}/k_{\text{ET}} = 11600$ ). However, compared with a classical S<sub>N</sub>2-reaction such as the Finkelstein reaction (e.g., I<sup>-</sup> + ethyl bromide) with an estimated  $k_{\text{sub}}/k_{\text{ET}}$  ratio of  $4 \times 10^{20}$  corresponding to 29 kcal mol<sup>-1</sup> in stabilization energy,<sup>4c</sup> the reactions investigated are all positioned at the S<sub>ET</sub> end of an S<sub>ET</sub>-S<sub>N</sub>2 diagram. Thus it would be interesting to find some substitution reactions involving stronger nucleophiles in the grey area between S<sub>ET</sub> and the classical S<sub>N</sub>2 covering the range of  $k_{\text{sub}}/k_{\text{ET}}$  from 11000 and upwards.

The  $k_{\text{sub}}/k_{\text{ET}}$  ratio is, however, also influenced by differences in the self-exchange reorganization energy  $\lambda(0)$  between the O<sub>2</sub><sup>-•</sup>/O<sub>2</sub> and the A<sup>-•</sup>/A couple. The reorganization energy for the self-exchange reaction of aromatic anion radicals has been measured by means of EPR spectroscopy<sup>5</sup> in DMF to be approximately 10 kcal mol<sup>-1</sup>. Unfortunately the same has not been possible for O<sub>2</sub><sup>-•</sup> in the liquid phase, since solutions of superoxide only give EPR signals near the freezing point of the solvent and under these conditions negligible electron exchange occurs between O<sub>2</sub> and O<sub>2</sub><sup>-•</sup> on the EPR timescale.<sup>6</sup> In principle  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}}$  may be evaluated from the Marcus or Hush relation between the self-exchange rate constant in homogeneous solution and the electrochemical standard rate constant  $k^\circ$ , which is known,<sup>1e</sup> but since the agreement between experiment and theory has been shown to be rather poor,<sup>7</sup> the reliability is poor. Indirect determinations of  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}}$  using the Marcus cross-relation have given values<sup>8</sup> varying from 22 kcal mol<sup>-1</sup> to 103 kcal mol<sup>-1</sup>. The large range is probably caused by the fact that the high solvation energy of O<sub>2</sub><sup>-•</sup> is affected by the other reactant in the transition state. Recently a direct determination of the self-exchange rate constant by <sup>18</sup>O/<sup>16</sup>O isotope marking gave  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}} = 45$  kcal mol<sup>-1</sup> in water.<sup>9</sup> The contribution from the inner reorganization energy  $\lambda_1$  to  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}}$  can theoretically be estimated from a classical treatment<sup>5a</sup> to be 15 kcal mol<sup>-1</sup> resulting in an outer reorganization

energy  $\lambda_o$  equal to 30 kcal mol<sup>-1</sup>. According to the Marcus model for spherical molecules this corresponds to an effective radius of 3.1 Å. With the use of this value,  $\lambda_o$  can be calculated to be 25 kcal mol<sup>-1</sup> in DMF giving a total  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}}$  of ca. 40 kcal mol<sup>-1</sup> in this solvent.

The effect on the  $k_{\text{sub}}/k_{\text{ET}}$  ratio of the difference between the reorganization energies for O<sub>2</sub><sup>-•</sup>/O<sub>2</sub> and A<sup>-•</sup>/A can be estimated, if Marcus theory<sup>10</sup> is assumed to be valid for the dissociative electron transfer process. The activation energy  $\Delta G^\ddagger$  is then given by eqn. (8).

$$\Delta G^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{\Delta G^\circ}{\lambda} \right)^2 \quad (8)$$

The driving force  $\Delta G^\circ = -F(E_{\text{RX/R}\cdot\text{X}^-}^\circ - E_{\text{D}}^\circ)$  is the difference in standard potential between the donor and acceptor multiplied by the Faraday constant  $F$ . The standard potential for RX/R·X<sup>-</sup> depends upon the structure and the nature of the halide, but in general it is estimated<sup>11</sup> to be ca. -0.8 V vs. Ag/AgI. The parameter  $\lambda$ , which is the reorganization energy for the whole ET reaction, can be estimated as the average value of the self-exchange reorganization energies of the donor and acceptor,<sup>12</sup> e.g., for reaction (1)  $\lambda_1 = 1/2[\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}} + \lambda(0)_{\text{RX/R}\cdot\text{X}^-}]$ . The value of  $\lambda(0)_{\text{RX/R}\cdot\text{X}^-}$  is not known exactly, but it is high ( $\approx 100$  kcal mol<sup>-1</sup>) owing to the profound changes in the length of the R-X bond during the formation of the transition state. The reorganization energy for reaction (1),  $\lambda_1$ , is thus 70 kcal mol<sup>-1</sup>, if  $\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}}$  and  $\lambda(0)_{\text{RX/R}\cdot\text{X}^-}$  are assumed to be 40 kcal mol<sup>-1</sup> and 100 kcal mol<sup>-1</sup>, respectively, and  $\lambda_4 = 55$  kcal mol<sup>-1</sup>.

With the use of eqn. (8) the minimum value of  $k_{\text{sub}}/k_{\text{ET}}$  can be evaluated from expression (7) rewritten as eqn. (9).

$$k_{\text{sub}}/k_{\text{ET}} = \exp\left(\frac{\Delta G_4^\ddagger - \Delta G_1^\ddagger}{RT}\right) \quad (9)$$

$$\begin{aligned} & (k_{\text{sub}}/k_{\text{ET}})_{\text{min}} \\ &= \exp\left(\frac{1/2\lambda(0)_{\text{A/A}^{\cdot-}} - 1/2\lambda(0)_{\text{O}_2/\text{O}_2^{\cdot-}} + (\Delta G^\circ)^2(1/\lambda_4 - 1/\lambda_1)}{4RT}\right) \\ &= 2.0 \times 10^{-3} \end{aligned} \quad (10)$$

An exact knowledge of  $\lambda(0)_{\text{RX/R}\cdot\text{X}^-}$  and  $E_{\text{RX/R}\cdot\text{X}^-}^\circ$  is not important, since the contribution from the term  $(\Delta G^\circ)^2(1/\lambda_4 - 1/\lambda_1)$  is small. The same result is obtained if the theory for the dissociative electron transfer process, proposed by Savéant,<sup>11</sup> is applied. At this point, however, it must be emphasized that it is questionable whether either of the two theories are completely adequate for the description of this kind of reaction.<sup>3b</sup> The calculated  $(k_{\text{sub}}/k_{\text{ET}})_{\text{min}}$  value should, in any case, be considered only to be indicative of the magnitude of a correction factor for the experimental  $k_{\text{sub}}/k_{\text{ET}}$  ratios.

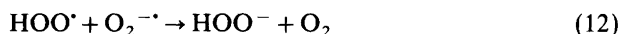
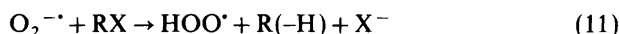
## Results and discussion

Values of the rate constant  $k_{ET}$  measured for a number of ET-reactions between aromatic/heteroaromatic anion radicals and butyl chloride, 2-butyl chloride, benzyl chloride, ethyl bromide, butyl bromide, 2-butyl bromide, neopentyl bromide, benzyl bromide, (1-bromo-2,2-dimethylpropyl)benzene and 1-iodoadamantane are given in Table 1. The measurements were determined by means of cyclic voltammetry<sup>13</sup> or a potentiostatic method<sup>14</sup> using a rotating disk electrode. In Fig. 1 is shown an example of a plot of  $\log k_{ET}$  vs.  $E_A^\circ$  for (1-bromo-2,2-dimethylpropyl)benzene. According to the Marcus theory this plot should be parabolic but recent experimental results rather indicate a linear relationship.<sup>3b</sup> The experimental data presented here did not indicate any decisive curvature in the potential range investigated and we thus decided to extrapolate the expected  $k_{ET}$  for an ET-donor with the same standard oxidation potential as  $O_2^{\cdot -}$  ( $-0.45$  vs. Ag/AgI) from a line determined by linear least-squares analysis. The correlation coefficients are included in Table 1. Small variations in  $\lambda(0)$  among the aromatic anion radicals appear in the plots as discontinuities, but since the plots consist of several points there will be some averaging in the determination of the relevant  $k_{ET}$ . According to eqn. (10) a change in  $\lambda(0)$  of, e.g.,  $2 \text{ kcal mol}^{-1}$  will change the rate constant by a factor of 1.5.

Values of the rate constant  $k_{sub}$  were measured for the substitution reaction between  $O_2^{\cdot -}$  and the 10 alkyl halides by two methods. The rate constants for the slower reactions ( $k_{sub} < 10 \text{ M}^{-1} \text{ s}^{-1}$ ) were determined by the potentiostatic method<sup>14</sup> and for the faster reactions by

double potential step chronoamperometry (DPSC). In Fig. 2 is shown the theoretical curve of the dependence of the current ratio  $-i(2\tau)/i(\tau)$  on  $\log(k_{sub} C_{RX}^\circ \tau)$ , where  $C_{RX}^\circ$  is the bulk concentration of RX and  $\tau$  is the step time. The curve is calculated by simulation of reaction scheme (1)–(4) assuming pseudo-first-order conditions ( $C_{RX}^\circ \gg C_{O_2}^\circ$ ). In Fig. 2 is also shown the best fit to the working curve for the reaction between  $O_2^{\cdot -}$  and 2-butyl bromide giving a value of  $300 \text{ M}^{-1} \text{ s}^{-1}$  at 298 K for the rate constant. This result is in good agreement with the value ( $320 \text{ M}^{-1} \text{ s}^{-1}$ ) extrapolated from an Arrhenius plot consisting of six rate constants measured with the potentiostatic method in the temperature range from  $-50^\circ \text{C}$  to  $-20^\circ \text{C}$ . The rate constant measured for butyl bromide ( $k_{sub} = 950 \text{ M}^{-1} \text{ s}^{-1}$ ) is also in agreement with the corresponding one determined from rotating ring-disk electrode measurements ( $k_{sub} = 960 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>1f</sup>

In the cases of the secondary substrates the measured rate constants need to be corrected for the influence of elimination reactions.



Reaction (11), together with reaction (1), is the rate-determining step, since (12), like (2), is near the diffusion-controlled limit.<sup>1g</sup> The preparative reduction of  $O_2$  in the presence of 2-butyl bromide or 2-butyl chloride gave butene in a yield of 42% and 15%, respectively. The yield determination was performed indirectly by reacting the butene gas produced with  $Br_2$  at low temperature and then by determining the yield of 1,2-dibromobutane and

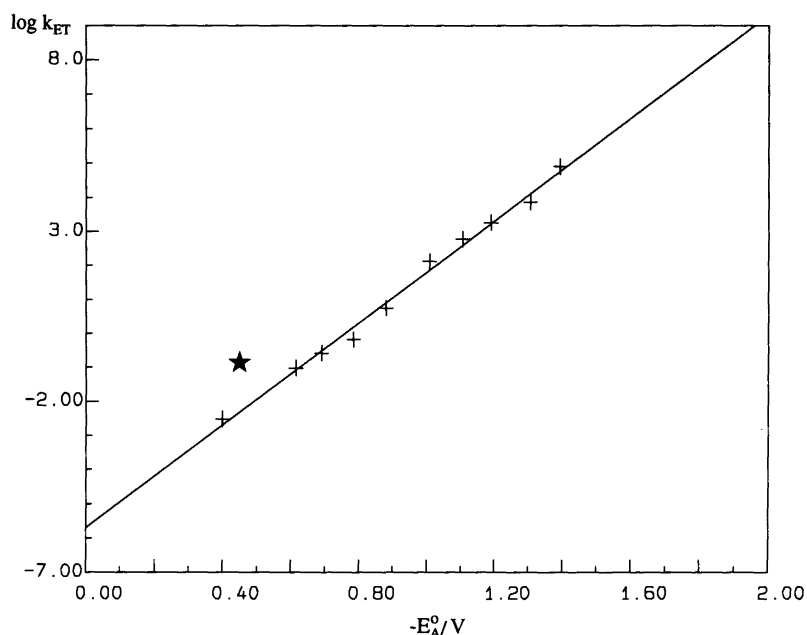


Fig. 1. Plot of  $\log k_{ET}$  vs.  $E_A^\circ$  for the electron transfer reaction between some electrochemically generated anion radicals and (1-bromo-2,2-dimethylpropyl)benzene in 0.1 M TBABF<sub>4</sub>/DMF at 25°C (+). Also shown is the rate constant  $k_{sub}$  for the substitution reaction between  $O_2^{\cdot -}$  and the same alkyl halide (\*).

Table 1. Rate constants for the reaction between different kinds of alkyl halide RX and anion radicals in 0.1 M TBABF<sub>4</sub>/DMF at 25 °C. Also included is the correlation coefficients R<sup>2</sup> for the linear log k<sub>ET</sub> vs. -E<sub>A</sub><sup>o</sup> plots.

RX	Donor	-E <sub>A</sub> <sup>o</sup> /V <sup>a</sup>	k <sub>ET</sub> /M <sup>-1</sup> s <sup>-1</sup>	R <sup>2</sup>
Butyl chloride	1-Methoxynaphthalene	2.137	5800	0.996
	Naphthalene	2.057	1800	
	<i>p</i> -Tolunitrile	1.937	390	
	Benzonitrile	1.830	78	
	Isoquinoline	1.731	16	
	Pyrene	1.618	0.68	
	Anthracene	1.490	0.20	
	9,10-Diphenylanthracene	1.394	0.023	
Ethyl bromide	Chrysene <sup>b</sup>	1.782	81000	0.995
	Isoquinoline <sup>b</sup>	1.731	38000	
	Pyrene <sup>b</sup>	1.618	3300	
	Anthracene <sup>b</sup>	1.490	830	
	Benzophenone <sup>b</sup>	1.307	40	
	Perylene	1.213	4.7	
	<i>p</i> -Dicyanobenzene	1.085	0.39	
	<i>p</i> -Diacetylbenzene	1.007	0.085	
Butyl bromide	Chrysene <sup>b</sup>	1.782	90000	0.979
	Pyrene <sup>b</sup>	1.618	2450	
	Anthracene <sup>b</sup>	1.490	970	
	Benzophenone <sup>b</sup>	1.307	92	
	Perylene	1.213	7.5	
	<i>p</i> -Dicyanobenzene	1.085	0.4	
	<i>p</i> -Diacetylbenzene	1.007	0.078	
2-Butyl chloride	1-Methoxynaphthalene	2.137	17000	0.989
	Naphthalene	2.057	4900	
	<i>p</i> -Tolunitrile	1.937	1400	
	Benzonitrile	1.830	270	
	Isoquinoline	1.731	35	
	Quinoline	1.675	20	
	Pyrene	1.618	2.3	
	Anthracene	1.490	0.55	
	9,10-Diphenylanthracene	1.394	0.083	
2-Butyl bromide	Chrysene <sup>b</sup>	1.782	207000	0.998
	Isoquinoline <sup>b</sup>	1.731	119000	
	Pyrene <sup>b</sup>	1.618	11500	
	Anthracene <sup>b</sup>	1.490	2400	
	9,10-Diphenylanthracene <sup>b</sup>	1.394	540	
	Benzophenone <sup>b</sup>	1.307	92	
	Perylene <sup>b</sup>	1.213	16	
	<i>p</i> -Dicyanobenzene	1.085	2.2	
	<i>p</i> -Diacetylbenzene	1.007	0.34	
	Azobenzene	0.879	0.063	
Neopentyl bromide	Chrysene <sup>b</sup>	1.782	3440	0.993
	Pyrene <sup>b</sup>	1.618	120	
	Anthracene <sup>b</sup>	1.490	14	
	9,10-Diphenylanthracene	1.394	2.5	
	Benzophenone	1.307	0.22	
	Fluoranthene	1.288	0.38	
	Perylene	1.213	0.12	
	<i>p</i> -Dicyanobenzene	1.085	0.01	
Benzyl chloride	Pyrene	1.618	255000	0.993
	Anthracene	1.490	50000	
	9,10-Diphenylanthracene	1.394	15400	
	Benzophenone	1.307	2400	
	Perylene	1.213	600	
	Tetracene	1.105	140	
	<i>p</i> -Diacetylbenzene	1.007	25	
	Azobenzene	0.879	2.3	
	<i>p</i> -Nitroanisole	0.784	0.43	
	Phenazine	0.690	0.052	
	1-Nitronaphthalene	0.600	0.039	
	<i>o</i> -Nitroacetophenone	0.500	0.015	
	<i>p</i> -Nitroacetophenone	0.400	0.0039	

(Continued)

Table 1. Continued.

RX	Donor	$-E_A^0/V^a$	$k_{ET}/M^{-1} s^{-1}$	$R^2$
Benzyl bromide	<i>p</i> -Diacetylbenzene	1.007	9500	0.994
	Azobenzene	0.879	2000	
	<i>p</i> -Nitroanisole	0.784	300	
	2-Nitrobiphenyl	0.747	130	
	Phenazine	0.690	62	
	1-Nitronaphthalene	0.600	14	
	<i>o</i> -Nitroacetophenone	0.500	7.3	
	<i>p</i> -Nitroacetophenone	0.400	1.5	
	Benzantraquinone	0.272	0.18	
	Naphthoquinone	0.175	0.034	
(1-Bromo-2,2-dimethylpropyl)benzene	9,10-Diphenylanthracene	1.394	79000	0.992
	Benzophenone	1.307	7200	
	Quinoxaline	1.189	1800	
	Tetracene	1.105	590	
	<i>p</i> -Diacetylbenzene	1.007	130	
	Azobenzene	0.879	5.5	
	<i>p</i> -Nitroanisole	0.784	0.65	
	Phenazine	0.690	0.26	
	<i>p</i> -Methoxycarbonylazobenzene	0.615	0.095	
	Anthraquinone	0.400	0.003	
1-Iodoadamantane	Anthracene	1.490	76000	0.964
	9,10-Diphenylanthracene	1.394	26000	
	Fluoranthene	1.288	6250	
	Perylene	1.213	2450	
	Quinoxaline	1.189	2600	
	Acenaphthylene	1.190	360	
	<i>p</i> -Dicyanobenzene	1.085	160	
	1-Cyanoisoquinoline	1.035	23	
	<i>p</i> -Diacetylbenzene	1.007	8	
	Azobenzene	0.879	0.10	
	<i>p</i> -Nitroanisole	0.784	0.02	
	Phenazine	0.690	0.003	

<sup>a</sup> Vs. Ag/AgI, 0.1 M I<sup>-</sup>. <sup>b</sup> Taken from Ref. 4 (a).

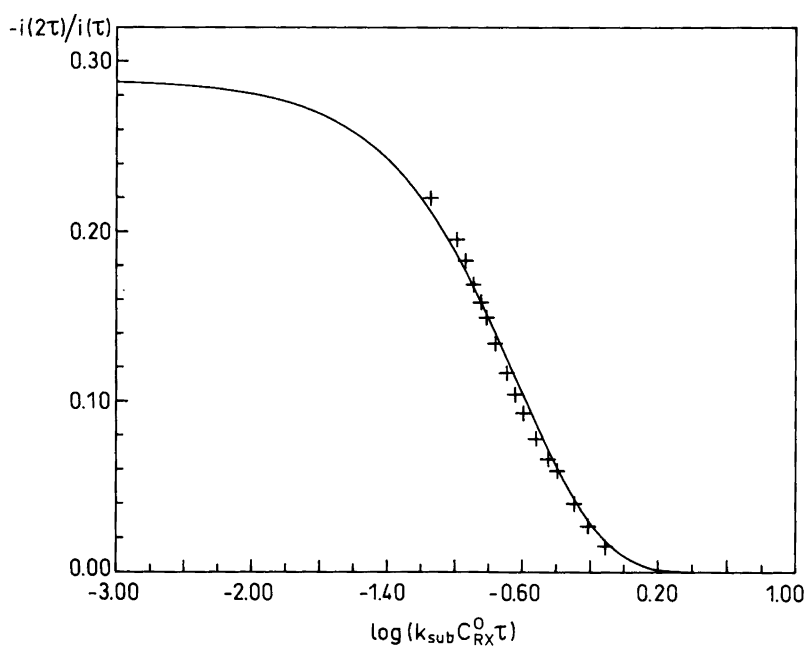


Fig. 2. The solid curve shows the dependence of the current ratio  $-i(2\tau)/i(\tau)$  on  $\log(k_{\text{sub}} C_{\text{RX}}^0 \tau)$ . The crosses are the experimental points for the reaction between  $O_2^{\cdot -}$  and 2-butyl bromide in 0.1 M TBABF<sub>4</sub>/DMF at 25 °C.

2,3-dibromobutane by gas chromatography (GC). This procedure seems to give correct results, since an experiment with 2-octyl bromide gave a yield of elimination products near 40%, which could be determined directly by GC. The results are also in reasonable accordance with other results obtained in DMSO with  $\text{KO}_2$  and 2-butyl bromide (31% elimination).<sup>1c</sup> Besides butene, the main product was, as expected, di-2-butyl peroxide accompanied by a minor amount of 2-butanol, which probably originates from the degradation of the dialkyl peroxide by  $\text{O}_2^-$ . The influence of the latter reaction in the determination of the rate constant  $k_{\text{sub}}$  was ignored, since the kinetic measurements were taken in the presence of a high excess of RX. From the preparative results, e.g., 42% elimination for 2-butyl bromide,  $k_{\text{sub}}$  was calculated as 58% of the rate constant for the reaction between  $\text{O}_2^-$  and 2-butyl bromide. The uncertainty of  $k_{\text{sub}}$  is thus slightly higher for the secondary halides than for the primary ones. In preparative experiments with superoxide and butyl bromide the yield of dibutyl peroxide was 70% in agreement with other results.<sup>1b</sup> No elimination product could be detected and only small amounts of butanol were found.

In Table 2 are given all the measured  $k_{\text{sub}}$  values corrected for the influence of the elimination reactions in the cases of the two secondary alkyl halides. The reaction with 1-iodoadamantane was too slow for the rate constant to be determined and the upper limit was governed by the stability of  $\text{O}_2^-$  ( $t_{1/2} \approx 6$  h). The uncertainty in the determination of  $k_{\text{sub}}$  is, in most cases, 10%, but for the fast reaction with benzyl bromide it might be higher. Also, included in Table 2 are the extrapolated  $k_{\text{ET}}$  values.

The calculated  $k_{\text{sub}}/k_{\text{ET}}$  ratios shown in column 4 of Table 2 are in the range  $<0.6$ – $1.7 \times 10^9$ . Possibly these values should be multiplied by a factor of ca. 500 in order to take into account the differences in self-exchange reorganization energies between  $\text{O}_2^-/\text{O}_2$  and the

**Table 2.** Ratio of the rate constants,  $k_{\text{sub}}$ , for the reaction between  $\text{O}_2^-$  and some alkyl halides and the rate constant,  $k_{\text{ET}}$ , for electron transfer between an anion radical with the same  $E_A^\circ$  as  $\text{O}_2$  and the alkyl halide in 0.1 M TBABF<sub>4</sub>/DMF at 25 °C.

RX	$k_{\text{sub}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{ET}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{sub}}/k_{\text{ET}}$
Butyl chloride	6.6 <sup>a</sup>	$3.8 \times 10^{-9}$	$1.7 \times 10^9$
Ethyl bromide	1350 <sup>b</sup>	$6.8 \times 10^{-6}$	$2.0 \times 10^8$
Butyl bromide	950 <sup>b</sup>	$1.0 \times 10^{-5}$	$9.5 \times 10^7$
2-Butyl chloride	1.0 <sup>a, c</sup>	$1.6 \times 10^{-8}$	$6.3 \times 10^7$
2-Butyl bromide	174 <sup>b, c</sup>	$4.2 \times 10^{-5}$	$4.1 \times 10^6$
Neopentyl bromide	0.045 <sup>a</sup>	$7.6 \times 10^{-8}$	$5.9 \times 10^5$
Benzyl chloride	440 <sup>b</sup>	$4.0 \times 10^{-3}$	$1.1 \times 10^5$
Benzyl bromide	14000 <sup>b</sup>	2.3	$6.1 \times 10^3$
(1-Bromo-2,2-dimethylpropyl)benzene	0.11 <sup>a</sup>	$5.1 \times 10^{-3}$	22
1-Iodoadamantane	$<10^{-5}$ <sup>a</sup>	$1.8 \times 10^{-5}$	$<0.6$

<sup>a</sup> Measured by the potentiostatic method. <sup>b</sup> Measured by DPSC. <sup>c</sup> Corrected for the elimination reaction.

ET-donors. If so, the corresponding stabilization energies of the transition state  $\Delta\Delta G^\ddagger$  range from below 4 kcal mol<sup>-1</sup> to 17 kcal mol<sup>-1</sup>. These values are somewhat higher than the corresponding ones with the enolate ion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine (0–6 kcal mol<sup>-1</sup>), indicating the much stronger nucleophilicity of  $\text{O}_2^-$ , but still smaller than the  $\Delta\Delta G^\ddagger$  value for the Finkelstein reaction. Superoxide can thus be involved in substitution reactions covering the range from S<sub>N</sub>2-like reactions to reactions with a high ET character. Previously we have been able to show that reactions with  $k_{\text{sub}}/k_{\text{ET}}$  ratios higher than 10 will proceed by pure inversion.<sup>4c, g, i</sup> Even though some of the substitution reactions investigated in this report display low stabilization of the transition state, the stereochemistry is still expected to be like that of the classical S<sub>N</sub>2-reaction, which is supported by results in literature.<sup>1h, i</sup>

The  $k_{\text{sub}}/k_{\text{ET}}$  ratios of the alkyl halides depend upon their steric hindrance and acceptor ability. The ratios decrease with increased steric hindrance in the order ethyl bromide, butyl bromide, 2-butyl bromide, neopentyl bromide and 1-iodoadamantane; in the last mentioned halide S<sub>N</sub>2 reaction is totally excluded. For a given alkyl group  $k_{\text{sub}}/k_{\text{ET}}$  decreases when the acceptor ability is increased on going from chloride to bromide; the effect is somewhat greater than observed for the enolate ion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine as the nucleophile.<sup>4j</sup> The acceptor effect is especially pronounced when comparing alkyl halides and benzyl halides. The larger differences in  $k_{\text{sub}}/k_{\text{ET}}$  ratios between, e.g., ethyl bromide and benzyl bromide or neopentyl bromide and (1-bromo-2,2-dimethylpropyl)benzene may be attributed mainly to the much higher electron affinity of the benzylic compounds, since the steric hindrance within each of these two pairs is rather similar.

In summary it can be concluded that the alkyl halides react with superoxide leading to elimination and substitution. The  $k_{\text{sub}}/k_{\text{ET}}$  values show that the transition states range from S<sub>N</sub>2-like to ET-like indicating a continuous shift from the latter to the former. The shift is strongly promoted by steric hindrance and acceptor abilities.

## Experimental

**Materials.** The electron donors were the same as used previously. Butyl chloride, 2-butyl chloride, benzyl chloride, ethyl bromide, butyl bromide, 2-butyl bromide, neopentyl bromide and benzyl bromide were obtained commercially and distilled before use. (1-Bromo-2,2-dimethylpropyl)benzene,<sup>15</sup> 1-iodoadamantane,<sup>16</sup> dibutyl peroxide and di-2-butyl peroxide<sup>17</sup> were prepared according to the references given. The crude product of (1-bromo-2,2-dimethylpropyl)benzene was purified by flash chromatography through a silica gel column with petrol ether as the eluent. 1,2-Dibromobutane, 2,3-dibromobutane, 1-octene and 2-octene were obtained commercially. The supporting electrolyte, Bu<sub>4</sub>NBF<sub>4</sub>, and the solvent *N,N*-dimethylformamide (DMF) were purified by standard procedures.

The yields were determined by GC using naphthalene or 1-bromoadamantane as internal standards.

**Instrumentation.** Instrumentation and data-treatment procedures have been described in detail elsewhere.<sup>13</sup> The RDE system (Metrohm 628-10, gold electrodes with  $\varnothing = 3$  mm) was obtained commercially. The working electrode in the CV and DPSC measurements was a gold electrode ( $\varnothing = 1$  mm or 0.5 mm) and the reference electrode a silver wire in 0.1 M TBABF<sub>4</sub>/DMF. GC was performed with a Hewlett-Packard 5890 gas chromatograph with a DB-23 column: injector temperature 115 °C; 50 °C for 5 min to 150 °C at 8 °C min<sup>-1</sup>.

**Procedure.** The rate constants  $k_{ET}$  were measured by cyclic voltammetry (CV)<sup>13</sup> for the faster reactions or by a potentiostatic method<sup>14</sup> using a rotating disk electrode when  $k_{ET} < 10$  M<sup>-1</sup> s<sup>-1</sup>. The procedure for measuring small  $k_{sub}$  values was almost the same as for the anion radicals. Superoxide was produced electrochemically at a platinum net in an oxygen-saturated solution. Before the alkyl halide was added in high excess (>20) and the decay of the anodic current of O<sub>2</sub><sup>•-</sup> was followed, the excess of oxygen was removed with argon. Argon was kept over the surface throughout the whole decay.

For faster reactions  $k_{sub}$  was determined by DPSC rather than CV to eliminate the problems due to the quasi-reversible nature of the reduction step of dioxygen to superoxide. In the treatment described here, the following assumptions have been made: Firstly the rate-determining step in the reaction scheme [(1)–(3)] is the substitution reaction between O<sub>2</sub><sup>•-</sup> and RX [reaction (1)]; reaction (2) is much faster and the steady-state approximation can be applied to ROO<sup>•</sup>. Secondly it is assumed that reaction (1) occurs under pseudo-first-order conditions thus making reaction (3) unimportant. Thirdly the diffusion coefficient  $D$  of O<sub>2</sub> is three times as high as that of O<sub>2</sub><sup>•-</sup>, which is the known ratio in DMSO.<sup>15</sup>

Calling  $a$  and  $b$  the concentrations of O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> normalized towards the bulk concentration of O<sub>2</sub> we can describe the reaction scheme mathematically by the following differential equations and boundary conditions.

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial y^2} + \lambda b$$

$$\frac{\partial b}{\partial \theta} = 1/3 \frac{\partial^2 b}{\partial y^2} - 2\lambda b$$

$$0 < \theta \leq 1: a_{y=0} = 0$$

$$1 < \theta \leq 2: b_{y=0} = 0$$

$$\left(\frac{\partial a}{\partial y}\right)_{y=0} = -1/3 \left(\frac{\partial b}{\partial y}\right)_{y=0}$$

$\theta = t/\tau$  and  $y = x/(\tau D)^{1/2}$  are dimensionless time and space variables, respectively ( $t$  = time,  $\tau$  = steptime and  $x$  = distance from the electrode surface). The parameter  $\lambda = k_{sub} C_{RX}^0 \tau$  is the dimensionless expression for the rate

constant  $k_{sub}$ , where  $C_{RX}^0$  is the bulk concentration of RX. The DPSC experiments were simulated with the assumption that the reduction of O<sub>2</sub> is diffusion-controlled during the first step ( $a_{y=0} = 0$ ) and that the oxidation of O<sub>2</sub><sup>•-</sup> is diffusion-controlled during the second potential step ( $b_{y=0} = 0$ ). This is the case when the potential is stepped 300 mV more negative and 300 mV more positive than  $E_{O_2}^0$ , respectively. The knowledge of the exact ratio of the diffusion coefficients between O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> is not important. Simulations show that even an assumption with equal diffusion coefficients only change the working curve slightly.

In the DPSC experiment dried oxygen or a mixture of nitrogen/oxygen was used to saturate 10 ml of 0.1 M TBABF<sub>4</sub>/DMF solution giving a maximum oxygen concentration of 4.8 mM.<sup>1k</sup> The approximate concentration of O<sub>2</sub> could be estimated from the peak height in a linear sweep voltammogram. The excess of alkyl halide was normally at least 20, except in the case of benzyl bromide, where an excess of 10 was used in order to lower the reaction rate. The steptimes used were in the range 1–100 ms.

The preparative experiments were performed in an H-cell with a mercury pool as the cathode. The cathodic solution with the alkyl halide was saturated with dry oxygen, which was kept over the surface during the whole experiment. Superoxide was generated electrochemically from the reduction of dioxygen and the number of moles produced was measured by coulometry. The alkyl halide was always in excess. After reduction the solution was analyzed by GC and yields of dialkyl peroxide and alcohol determined using naphthalene as an internal standard. In the reactions with 2-butyl bromide and 2-butyl chloride, 1-butene and 2-butene gas developed. In order to capture these gases the continuous flow of oxygen over the cathodic solution was led into a flask containing bromine in 1,1,2-trichlorotrifluoroethane at –25 °C. The reaction between Br<sub>2</sub> and butene is known to be fast and effective.<sup>18</sup> The flow of oxygen was continued for additional 2 h after the reduction. The yield of produced dibromobutane was found by GC using 1-bromoadamantane as an internal standard. A single experiment with butyl bromide was performed with a platinum plate as the cathode, but this did not have any influence on the product distribution.

**Acknowledgments.** Statens Naturvidenskabelige Forskningsråd is thanked for financial support.

## References

- (a) Sawyer, D. T. and Gibian, M. J. *Tetrahedron* 35 (1979) 1471; (b) Dietz, R., Forno, A. E. J., Larcombe, B. E. and Peover, M. E. *J. Chem. Soc. B* (1970) 816; (c) Chern, C.-I., DiCosimo, R., De Jesus, R. and San Filippo, J., Jr. *J. Am. Chem. Soc.* 100 (1978) 7317; (d) Magno, F., Bontempelli, G. and Andruzzi Sedeà, M. M. *J. Electroanal. Chem.* 97 (1979) 85; (e) Chiericato, G., Jr., Rodrigues, S. and Da Silva, L. A. *Electrochim. Acta* 36 (1991) 2113; (f) Calderwood, T. S. and Sawyer, D. T. *J. Am. Chem. Soc.* 106 (1984) 7185; (g)

- Andrieux, C. P., Hapiot, P. and Savéant, J.-M. *J. Am. Chem. Soc.* 109 (1987) 3768; (h) San Filippo, J., Jr., Chern, C.-I. and Valentine, J. S. *J. Org. Chem.* 40 (1975) 1678; (i) Johnson, R. A. and Nidy, E. G. *J. Org. Chem.* 40 (1975) 1680; (j) Sawyer, D. T. and Roberts, J. L., Jr. *J. Electroanal. Chem.* 12 (1966) 90; (k) Sawyer, D. T., Chiericato, G., Jr., Angelis, C. T., Nanni, E. J., Jr. and Tsuchiya, T. *Anal. Chem.* 54 (1982) 1720; (l) Sawyer, D. T. and Valentine, J. S. *Acc. Chem. Res.* 14 (1981) 393; (m) Merritt, M. V. and Johnson, R. A. *J. Am. Chem. Soc.* 99 (1977) 3713; (n) Danen, W. C. and Warner, R. J. *Tetrahedron Lett.* (1977) 989; (o) Magno, F., Seeber, R. and Valcher, S. *J. Electroanal. Chem.* 83 (1977) 131; (p) Frimer, A. and Rosenthal, I. *Tetrahedron Lett.* (1976) 2809; (q) Hamon, J.-R. and Astruc, D. *J. Am. Chem. Soc.* 105 (1983) 5951; (r) Carelli, I., Curulli, A. and Inesi, A. *J. Chem. Res. (S)* (1989) 338.
2. Simonet, J., Michel, M.-A. and Lund, H. *Acta Chem. Scand., Ser. B* 29 (1975) 489; Lund, H. and Simonet, J. *J. Electroanal. Chem.* 65 (1975) 205.
  3. (a) Ebersson, L. and Shaik, S. S. *J. Am. Chem. Soc.* 112 (1990) 4484; (b) Daasbjerg, K., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 45 (1991) 424.
  4. (a) Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B* 40 (1986) 470; (b) *ibid.*, *Ser. B* 41 (1987) 93; (c) *ibid.*, *Ser. B* 42 (1988) 269; (d) *ibid.* 45 (1991) 655; (e) Daasbjerg, K., Pedersen, S. U. and Lund, H. *ibid.* 43 (1989) 876; (f) Müllen, K., Alexander, J., Klabunde, K.-U., Klärner, F.-G., Lund, H. and Lund, T. *Chem. Ber.* 125 (1992) 505; (g) Daasbjerg, K., Lund, T. and Lund, H. *Tetrahedron Lett.* 30 (1989) 493; (h) Daasbjerg, K., Hansen, J. N. and Lund, H. *Acta Chem. Scand.* 44 (1990) 711; (i) Lund, T. *Tetrahedron Lett.* 32 (1991) 1595; (j) Jørgensen, L. V. and Lund, H. *Acta Chem. Scand., Ser. B* 3435.
  5. (a) Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer Verlag, New York 1987; (b) Larsen, H., Pedersen, S. U., Pedersen, J. A. and Lund, H. *J. Electroanal. Chem.* 331 (1992) 971.
  6. Bagchi, R. N., Bond, A. M., Scholz, F. and Stösser, R. *J. Am. Chem. Soc.* 111 (1989) 8270.
  7. Kojima, H. and Bard, A. J. *J. Am. Chem. Soc.* 97 (1975) 6317.
  8. McDowell, M. S., Espenson, J. H. and Bakač, A. *Inorg. Chem.* 23 (1984) 2232.
  9. Lind, J., Shen, X., Merényi, G. and Jonsson, B. Ö. *J. Am. Chem. Soc.* 111 (1989) 7654.
  10. Marcus, R. A. *J. Chem. Phys.* 24 (1956) 966; *ibid.* 26 (1957) 867, 872.
  11. Savéant, J.-M. *J. Am. Chem. Soc.* 109 (1987) 6788.
  12. Marcus, R. A. *J. Phys. Chem.* 67 (1963) 853.
  13. Pedersen, S. U. and Svensmark, B. *Acta Chem. Scand., Ser. A* 40 (1986) 607.
  14. Pedersen, S. U. and Daasbjerg, K. *Acta Chem. Scand.* 43 (1989) 301.
  15. Conant, J. B. and Blatt, A. H. *J. Am. Chem. Soc.* 50 (1928) 551.
  16. Schleyer, P. v. R. and Nicholas, R. D. *J. Am. Chem. Soc.* 83 (1961) 2700.
  17. Welch, F., Williams, H. R. and Mosher, H. S. *J. Am. Chem. Soc.* 77 (1955) 551.
  18. Olah, G. A., Hockswender, T. R., Jr. *J. Am. Chem. Soc.* 96 (1974) 3574.

Received August 27, 1992.