

# Indirect Electrochemical Reduction of Some Peroxide Derivatives

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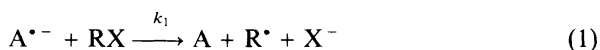
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Indirect reduction of derivatives of *tert*-butyl hydroperoxide by means of aromatic radical anions in DMF results in the formation of *tert*-butoxy radicals, which abstract a hydrogen atom from DMF. The *N,N*-dimethylaminocarbonyl radical may couple with the radical anion or be reduced by it; from this competition the reduction potential of the *N,N*-dimethylaminocarbonyl radical is estimated to be  $-1.62$  V (SCE).

Electrochemical reduction of organic compounds consists in most cases of an addition of electrons to an unsaturated center, but in some instances a  $\sigma$ -bond is reductively cleaved. Such a reduction of  $\sigma$ -bonds is generally connected with a high internal and solvent reorganisation energy  $\lambda$  for the electron transfer which leads to drawn-out voltammetric curves, and indirect electrolysis may thus be advantageous. Such indirect reductive cleavage of  $\sigma$ -bonds has mostly been studied in alkyl halides.

Electron transfer from electron donors, such as radical anions of aromatic and heteroaromatic compounds, to benzyl and alkyl halides has previously been investigated and the following scheme was suggested.<sup>1,2</sup>



The competition between the coupling of the radical anion with the radical [eqn. (2)] and the reduction of the radical by the radical anion [eqn. (3)] has been used to determine the reduction potential of some benzyl, allyl and alkyl radicals and to estimate the standard potential of these radicals.<sup>3–5</sup>

The oxygen–oxygen  $\sigma$ -bond in peroxide derivatives is electrochemically reducible.<sup>6–9</sup> Polarographic waves are typically drawn out indicating a slow electron transfer; the electrode reaction in protic solvents is a reductive cleavage of the oxygen–oxygen bond. In aprotic media

the peroxide bond may be reduced by both heterogeneous and homogeneous electron transfer (ET). It has been suggested that the reduction of di-*tert*-butyl peroxide involves a nonadiabatic dissociative electron transfer.<sup>10</sup> An ET from some donors to diacyl peroxides has been measured<sup>11</sup> and the results interpreted on the basis of the Marcus equation, which suggested a  $\lambda$  value of about  $40 \text{ kcal mol}^{-1}$ .<sup>12</sup> The homogeneous ET from some electron donors gives rise to a catalytic wave whereas this is not the case with other electron donors. This suggested that a competition similar to that between reactions (2) and (3) was operative and that this competition might be used to determine the reduction potential of the alkoxy radical in a way similar to that used for the alkyl and benzyl radicals. This communication is concerned with that problem.

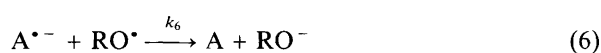
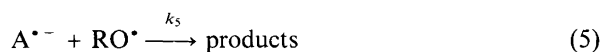
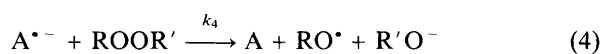
## Results and discussion

Di-*tert*-butyl peroxide (**1**) and *tert*-butyl peracetate (**2**) were chosen as peroxide derivatives to avoid complications with hydrogen abstraction by  $RO^\bullet$  from a hydrogen  $\alpha$  to the carbon substituted with oxygen. Cyclic voltammetry (CV) of **1** in nominally dry *N,N*-dimethylformamide (DMF) containing tetrabutylammonium tetrafluoroborate gave an irreversible, drawn-out cathodic peak; the peak potential depended both on the scan rate  $v$  and the electrode material. At  $v = 1 \text{ V s}^{-1}$  the peak potential was about  $-2.6$  V (SCE) at a freshly polished glassy carbon or gold disc electrode ( $-2.50$  V vs. SCE at a glassy carbon electrode at  $0.2 \text{ V s}^{-1}$ ),<sup>10</sup> whereas no peak could be seen before the background at a platinum electrode. CV of **2** also gave a drawn-out, irreversible cathodic reduction with a broad peak ( $v = 1 \text{ V s}^{-1}$ ) at about  $-1.65$  V

(SCE) at a glassy carbon electrode, at  $-1.7$  V at a gold electrode and at  $-1.95$  V at a platinum electrode. The shape of the voltammetric curves clearly points to a slow heterogeneous electron transfer.

Electrochemical reduction of suitable aromatic compounds in DMF in the presence of **1** or **2** showed a catalytic reduction of the peroxide derivatives. Linear sweep voltammetry (LSV) was used to determine the rate of electron transfer from the radical anions to the substrates.<sup>13</sup> The results are given in Table 1 and the connection between the driving force and the logarithm of the rate constants is depicted in Fig. 1. The rate constants agree well with those recently published.<sup>10</sup>

The indirect reduction of the peroxides by the radical anions is suggested to follow the scheme, where SH is a constituent (solvent or supporting electrolyte) of the medium.



In the treatment used to determine the reduction potentials of alkyl radicals the competition was between the coupling reaction of the radical anion with the radical [eqn. (2)] and the reduction of the radical by the radical anion [eqn. (3)]. For the peroxides the radical  $S^\bullet$  might be involved, and a parameter  $q = (k_6 + k_9)/(k_5 + k_6 + k_8 + k_9)$  in which the ratio between the sum of the rate constants of the reduction of radicals ( $RO^\bullet$  and  $S^\bullet$ ) and the sum of the rate constants of all the reactions

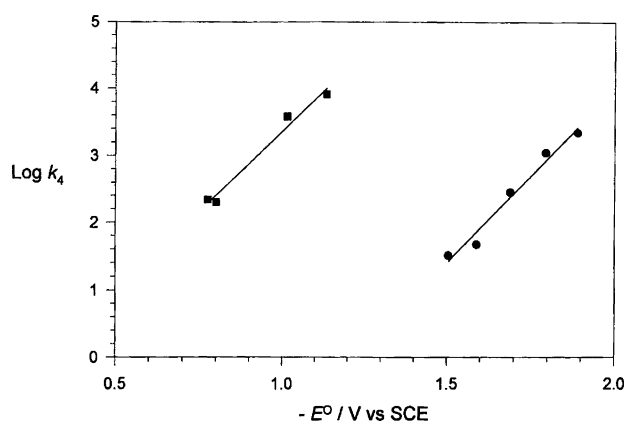


Fig. 1. Plot of the dependence of the rate constant of the electron transfer from aromatic radical anions to **1** (●) and **2** (■) on the standard potential of the mediators.

should be plotted against the standard potentials of the radical anions. The result is shown in Fig. 2; an S-shaped curve is obtained, and the potential  $E_{1/2}^q$  at which the rate of coupling is equal to the rate of reduction ( $q = 0.5$ ) is  $-1.62$  V (SCE). The question is then, what significance does this potential  $E_{1/2}^q$  have?

In the scheme the electron transfer from the radical anion to the peroxide [eqn. (4)] is the rate-determining step. However, if the competition between coupling and reduction is used to determine the reduction potential of alkoxy radicals in a way similar to the competition between reactions (2) and (3) used to determine the reduction potentials of alkyl radicals, the rate and nature of these reactions should be ascertained and possible side reactions considered.

The *tert*-butoxy radical is known to abstract hydrogen atoms from suitable donors [eqn. (7)] and to cleave to a methyl radical and acetone [eqn. (10)].



The cleavage of the *tert*-butoxyl radical is, compared with hydrogen abstraction from DMF, a relatively slow reaction<sup>14</sup> which is supported by the absence of acetone

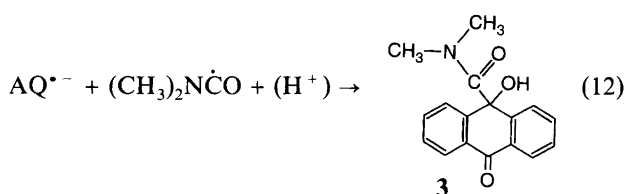
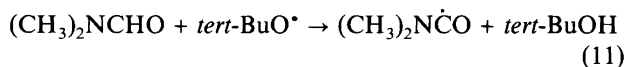
Table 1. Rate constants ( $\text{M}^{-1} \text{s}^{-1}$ ) and  $q$  values for reactions between a series of radical anions and di-*tert*-butyl peroxide (**1**) and *tert*-butyl peracetate (**2**).

Mediator	Substrate	$E_A^\circ / \text{V}^a$	$k_4 / \text{M}^{-1} \text{s}^{-1}$	$q$
Anthracene	<b>1</b>	$-1.89_0$	$2.2 \times 10^3$	0.90
9,10-Diphenylanthracene	<b>1</b>	$-1.79_5$	$1.1 \times 10^3$	0.80
Fluoranthene	<b>1</b>	$-1.69_5$	$2.8 \times 10^2$	0.60
Acenaphthylene	<b>1</b>	$-1.59_0$	$4.7 \times 10^1$	0.40
Tetracene	<b>1</b>	$-1.50_5$	$3.2 \times 10^1$	0.30
3-Chloroazobenzene	<b>2</b>	$-1.13_5$	$8.2 \times 10^3$	0.00
4-Methoxycarbonylazobenzene	<b>2</b>	$-1.01_5$	$3.8 \times 10^3$	0.00
Anthraquinone	<b>2</b>	$-0.80_0$	$2.0 \times 10^2$	$-0.10$
9,10-Dicyanoanthracene	<b>2</b>	$-0.77_5$	$2.2 \times 10^2$	0.10

<sup>a</sup>V vs. SCE.

among the products from the preparative indirect reductions; formation of methyl radicals should also have been detected through isolation of methylated derivatives of the electron donor. The rate constant for the hydrogen abstraction from DMF by *tert*-butoxy radical is not known; the rate constant for the hydrogen abstraction from several solvents by the *tert*-butoxy radical is about  $10^5$ – $10^7$   $\text{M}^{-1} \text{s}^{-1}$ .<sup>15</sup> This means that hydrogen abstraction [eqn. (7)] could be a competing reaction to the coupling [eqn. (5)] and the electron transfer [eqn. (6)]. If reaction (7) is serious competition to (5) and/or (6) then it will not be possible to have any reactions in which  $q$  is 0, unless coupling between the radical anion and the radical from the hydrogen atom donor takes place.

From the reduction of anthraquinone (AQ) in DMF in presence of *tert*-butyl peracetate 10-dimethylcarbamoyl-10-hydroxy-9(10*H*)-anthracenone (**3**) was isolated in fair yield (60% based on the electron consumption, 80% of the isolated product). The identity of the product was ascertained from the <sup>1</sup>H NMR spectrum and by an X-ray structure determination.<sup>16</sup> If the *tert*-butoxy radical functions mainly as a hydrogen atom abstractor other hydrogen atom abstractors should work similarly; the phenyl radical is a good hydrogen abstractor, and **3** is also formed on indirect reduction of iodobenzene in DMF using AQ as mediator. The compound is assumed to be formed according to eqns. (11) and (12).



Attempts to isolate coupling products from the reaction between the *tert*-butoxy radical and the electron donor using the normal work-up did not result in any *tert*-butoxylated products. This might however, be caused by an elimination of 2-methylpropene from an initially formed coupling product catalysed by the *tert*-butoxy anion, which in DMF is a very strong base. The resulting hydroxydihydroaromatic compound could then revert to the starting compound by elimination of water; alternatively *tert*-butyl alcohol could be eliminated from the coupling product.

The finding that reaction (8) is a product-forming reaction path (and probably the most important one) raises the question, which reaction is responsible for the catalytic reaction ( $q \sim 1$ ) in which the mediator is regenerated? Is it reaction (6) or (9) (or both)? From the electron consumption in preparative reduction of aryl halides the reduction potential of the radical obtained from DMF on hydrogen abstraction has been estimated to be  $-1.85$  V

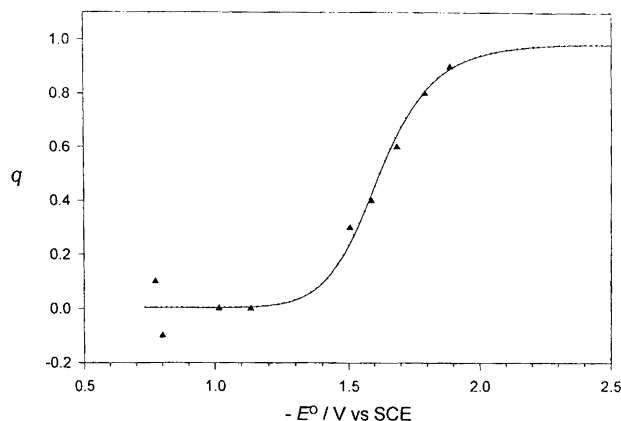


Fig. 2. Plot of the dependence of the competition parameter  $q$  on the standard potential of the mediators; the curve is simulated using  $\lambda = 40$   $\text{kcal mol}^{-1}$ .<sup>4</sup>

vs. SCE,<sup>17</sup> which is not too different from the values of reduction potentials obtained for acyl radicals.<sup>18</sup> The  $E_{1/2}^q$  value found in this investigation is about 0.2 V more positive than the potential suggested for the DMF-derived radical; however, a potential difference might be caused by the fact that the value  $-1.85$  V is obtained in a direct reduction (heterogeneous electron transfer) whereas the  $E_{1/2}^q$  is the result of a competition between a coupling and a homogeneous electron transfer. The value of  $E_{\text{tert-BuO}^\bullet/\text{tert-BuO}^-}^\circ$  has been calculated by a thermochemical cycle to be  $-0.23$  V vs. SCE in DMF.<sup>10</sup> By use of radical clocks  $k_2$  has been measured<sup>19</sup> to be about  $10^9$   $\text{M}^{-1} \text{s}^{-1}$  and the rate constant  $k_5$  for the coupling between  $\text{A}^{\bullet-}$  and the butoxy radical is probably near this value. If the reorganisation energy  $\lambda$  for the ET from the reduced mediator to the butoxy radical is assumed to be 30  $\text{kcal mol}^{-1}$  as for alkyl radicals<sup>4</sup> then  $k_6$  is faster than  $k_5$  for mediators more negative than  $-0.35$  V (SCE).

The reduction potential of anthraquinone ( $-0.8$  V vs. SCE) indicates that  $k_6$  should be fast, close to the diffusion-controlled rate constant  $10^{10}$   $\text{M}^{-1} \text{s}^{-1}$ . If reaction [11 (= 7)] is able to outrun the reduction of the butoxy radical [eqn. (6)], then the rate constant of reaction (11) must be relatively high, even though the concentration of the hydrogen donor DMF is much higher than that of anthraquinone. The rate constant for the hydrogen abstraction from DMF by *tert*-butoxy radical  $k_{11}$  is not known, but the rate constant for the hydrogen abstraction from cyclohexene by the *tert*-butoxy radical is  $5.7 \times 10^6$   $\text{M}^{-1} \text{s}^{-1}$  and from tetrahydrofuran (THF)  $8.3 \times 10^6$   $\text{M}^{-1} \text{s}^{-1}$ .<sup>15</sup> In order to ascertain that reactions (11) and (12) are fast, a good hydrogen donor, cyclohexene, was added to the catholyte. Even on addition of 25% cyclohexene **3** was still the major product, but some new products were found suggesting that the rate of hydrogen abstraction from DMF be of the same order of magnitude as the rate of hydrogen abstraction from cyclohexene. Measurements of  $q$  values with 10% of THF in the catholyte using **1** and the mediators acenaphthyl-

ene and fluoranthene gave  $q = 0.4$  and  $0.5$ , respectively, which suggests that  $k_{11}$  is about  $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . If  $k_{11}$  were slower, the  $q$  value should have been lower because the THF radical cannot be reduced by mediators with these reduction potentials,<sup>5</sup> and the electron consumption would have been lower. Measurements of  $q$  by the rotating disk electrode method<sup>20</sup> where the concentration of the electron donors is higher (10 mM) gave  $q$  values which were about 0.3 higher than those measured by LSV. This fits into the scheme where the main competition is between reactions (6) and (7); higher concentrations of anion radicals make reaction (6) faster compared with reaction (7). The picture is complicated by the fact that the exact concentration of the anion radicals at the point where the *tert*-butoxy radicals are formed in the preparative reductions is unknown as it depends on  $k_4$  and the stirring in the cell.

The conclusion is that with the low mediator concentration ( $\sim 2$  mM) usually employed in the determination of potentials of radicals reaction (7) will dominate over reaction (5) and (6), and that the  $q$  value is controlled by the competition between reactions [8 (= 12)] and (9) and the  $E_{1/2}^q$  value is thus a measure of the reduction potential of the *N,N*-dimethylaminocarbonyl radical. The uncertainty in the estimation of the  $\lambda$  value makes an estimation of the standard potential of the radical very uncertain; it is probably 0.5 to 0.7 V more positive than the  $E_{1/2}^q$  value. At higher mediator concentration ( $> 10$  mM), competition with (5) and (6) makes the picture more complicated.

The preferred abstraction of a hydrogen atom by the *tert*-butoxy radical suggests that it might be possible to add a hydrogen atom donor to the catholyte and get a coupling between the anion radical and the radical derived from the hydrogen atom donor. Attempts to use hydrogen donors such as cyclohexene which was supposed to be able to compete with DMF as a hydrogen atom donor were not successful; a fair yield of **3** was obtained, so a weaker hydrogen-atom-donating solvent than DMF should be used for such reactions.

## Experimental

**Materials.** The aromatic mediators were the same as used previously.<sup>3-5</sup> Di-*tert*-butyl peroxide was obtained commercially and *tert*-butyl peracetate was made according to literature.<sup>21</sup> The supporting electrolyte,  $\text{Bu}_4\text{NBF}_4$ , and the solvent, *N,N*-dimethylformamide (DMF), were purified by standard procedures. The electrolyte solution was dried through a column of activated alumina just before each experiment.

**Equipment.** The instrumentation, cells and electrodes have been described previously.<sup>3-5,20</sup>

**Procedure.** The procedure for the measurement of  $k_4$  and the competition parameter  $q$  by LSV is described in detail

elsewhere.<sup>13</sup> The potentials of the aromatic mediators were measured with ferrocene or anthraquinone as an internal standard,  $E_{\text{Fer}}^\circ = +0.485$  V and  $E_{\text{AQ}}^\circ = -0.80_0$  V vs. SCE. All measurements were done at  $25^\circ\text{C}$  with a gold disk electrode ( $r = 1$  mm) except for 3-chloroazobenzene, where a platinum disk was used to avoid interference by direct reduction of the peroxide. The concentration of the mediators were 2 mM except for tetracene, where it was only 1 mM. The procedure for the measurement of  $q$  by the rotating disk electrode method is described in detail elsewhere.<sup>20</sup> Here the concentration was 10 mM. As an example, a preparative reduction of anthraquinone in the presence of **2** is described.

Anthraquinone (0.21 g) was reduced in 40 ml deaerated DMF–0.1 M  $\text{Bu}_4\text{NBF}_4$  in an H-cell at room temperature at a platinum net working electrode at  $-0.9$  (V vs. SCE). Prior to the experiment, the catholyte had been dried through a column of freshly activated alumina and after the deaeration the stability of the radical anions was examined before the addition of 0.5 ml of **2**. The charge consumed was 175 C ( $n = 1.8$ ) after typically 20 h of electrolysis (average of four experiments). A sample was investigated by GC–MS showing *tert*-butyl alcohol, acetic acid (if dilute acid had been added) and anthraquinone. To the catholyte were added 30 ml of diethyl ether and 40 ml of water. The water phase was extracted several (3–9) times with 30 ml of diethyl ether, the diethyl ether was washed with water to remove the DMF, dried and the ether evaporated *in vacuo*. The product (0.18 g) was investigated by  $^1\text{H}$  NMR spectroscopy which showed 10% of anthraquinone, 80% of 10-dimethylcarbamoyl-10-hydroxy-9(10*H*)-anthracenone (**3**) and 10% other aromatic products (probably isomers of **3**). **3** was isolated by means of fractional crystallization from a diethyl ether–petroleum ether mixture. **3** decomposes to anthraquinone on injection into the GC column. M.p.  $177\text{--}78^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.33 (dd, 2 H,  $J$  7.7 and 1.4 Hz), 7.68 (ddd, 2 H,  $J$  7.6, 7.4 and 1.5 Hz), 7.55 (ddd, 2 H,  $J$  7.7, 7.4 and 1.3 Hz), 7.42 (dd, 2 H,  $J$  7.7 and 1.4 Hz), 6.67 (s, 1 H), 3.04 (br s, 3 H), 2.20 (br s, 3 H). The last two peaks are temperature dependent due to a slow rotation around the nitrogen carbonyl carbon bond, the values given were measured at  $22^\circ\text{C}$ . At  $48^\circ\text{C}$  only one peak at  $\delta$  2.7 appeared. MS (direct inlet,  $m/z$ ): 281 (16), 265 (6), 210 (18), 209 (100), 208 (15), 180 (16), 164 (7), 163 (11), 153 (11), 152 (35), 151 (10), 72 (78). IR (KBr,  $\text{cm}^{-1}$ ) 3400 (br, w), 3261 (m), 2900–3100 (w), 1653 (s), 1600 (m), 1457 (m), 1320 (s), 1278 (m), 1037 (m), 931 (m), 776 (m), 687 (m).

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