# Polarity Reversal Catalysis of Hydrogen Atom Abstraction Reactions

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Overall transfer of electron deficient hydrogen to the electrophilic t-butoxyl radical is catalysd by $Me_3N{\rightarrow}BH_2Hex^t$; hydrogen atom abstraction is actually brought about by the nucleophilic $Me_3N{\rightarrow}\dot{B}HHex^t$.

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Alkoxyl radicals are highly electrophilic species and their chemical reactivities are strongly influenced by polar effects.[1] Thus, the rates of similarly exothermic hydrogen-atom abstraction reactions (1) increase with the extent of stabilisation of the transition state (**1**) by electron transfer to the alkoxyl radical, as represented by inclusion of structure (**1c**). The contribution from (**1c**), and thus the rate of reaction (1), will increase with increasing stability of the cationic fragment $X^+$. An equivalent analysis may be given in the language of frontier molecular orbital theory.

$$RO^{\cdot} + HX \longrightarrow ROH + X^{\cdot} \qquad (1)$$

$$\underset{\textbf{(1a)}}{[RO^{\cdot}\,H\text{–}X} \longleftrightarrow \underset{\textbf{(1b)}}{RO\text{–}H\,{}^{\cdot}X} \longleftrightarrow \underset{\textbf{(1c)}}{R\bar{O}\colon H^{\cdot}\,X^{+}]}$$

Abstraction of an electron deficient hydrogen atom (*i.e.* when $X^+$ is relatively unstable and $X^-$ relatively stable) by an electrophilic radical such as $RO^{\cdot}$ could be effectively catalysed if the direct reaction (1) were to be replaced by two fast consecutive steps as illustrated in equations (2) and (3). Here

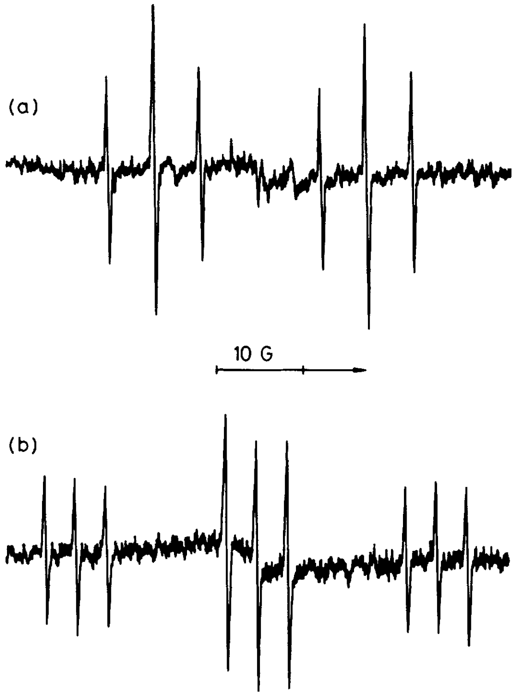


**Figure 1.** E.s.r. spectra obtained at 164 K during u.v. irradiation of cyclopropane–oxirane solutions containing di-t-butyl peroxide and acetonitrile, (a) without polarity reversal catalyst, (b) in the presence of trimethylamine–2,3-di-methylbutan-2-yl borane (0.1 M). 1G = $10^{-4}$ T.

the intermediate radical $Y^{\bullet}$ is nucleophilic (*i.e.* readily gives up an electron to form $Y^+$) and hence both reactions (2) and (3) would be facilitated by favourable polar effects.

$$\mathrm{RO^{\bullet} + \overset{\delta-\,\delta+}{H{-}Y} \xrightarrow{\text{fast}} ROH + Y^{\bullet}} \qquad (2)$$

$$\mathrm{Y^{\bullet} + \overset{\delta+\,\delta-}{H{-}X} \xrightarrow{\text{fast}} HY + X^{\bullet}} \qquad (3)$$

Making use of this principle, we have found that certain amine–alkylborane complexes act as catalysts for the abstraction of electron deficient hydrogen by t-butoxyl radicals.

U.v. photolysis of di-t-butyl peroxide (DTBP) in the presence of acetonitrile in cyclopropane solution, whilst the sample was in the microwave cavity of an e.s.r. spectrometer, afforded only a very weak spectrum of the cyanomethyl radical at 240 K, despite the fact that reaction (5) is appreciably exothermic [$DH^{\circ}$(Bu$^t$O–H) and $DH^{\circ}$(H–CH$_2$CN) are 440 and 389 kJ mol$^{-1}$, respectively[2]]. When this experiment was repeated in cyclopropane–oxirane solvent ([oxirane]/[MeCN] = 7.5), the e.s.r. spectrum of the oxiranyl radical was observed [equation (6)] and that of cyanomethyl was barely detectable (see Figure 1a). However, when trimethylamine–2,3-di-methylbutan-2-yl borane complex[3,4] (2) (0.1—1.0 M) was also present, the e.s.r. spectrum was strikingly different such that now only the cyanomethyl radical was detected (Figure 1b) although [oxirane]/[MeCN] was unchanged.

$$\mathrm{Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet}} \qquad (4)$$

$$\mathrm{Bu^tO^{\bullet} + MeCN \longrightarrow Bu^tOH + {}^{\bullet}CH_2CN} \qquad (5)$$

$$\mathrm{Bu^tO^{\bullet} + \overline{CH_2CH_2O} \xrightarrow{k} Bu^tOH + {}^{\bullet}\overline{CHCH_2O}} \qquad (6)$$

We attribute these results to catalysis of the overall transformation shown in equation (5) *via* the cycle of reactions (7) and (8). Reaction (7)[4] is very rapid compared with hydrogen abstraction from oxirane[5] ($k = 1.1 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 300 K), as evidenced by the detection of only the e.s.r. spectrum of the amine-boryl radical (3) [$a(^{11}\mathrm{B})$ 59.6, $a(\mathrm{H}_{\alpha})$ 10.0 G, $g$ 2.0022 at 208 K] during u.v. irradiation of an oxirane solution containing DTBP (15% v/v) and (2) (1.0 M).

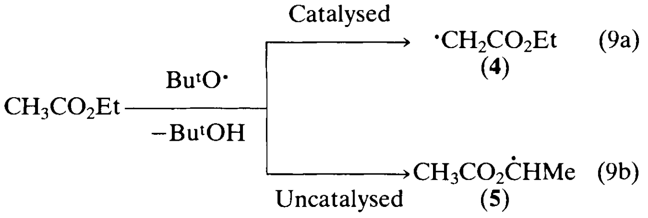
$$\mathrm{Bu^tO^{\bullet} + \underset{(2)}{Me_3N{\rightarrow}BH_2Hex^t} \longrightarrow Bu^tOH + \underset{(3)}{Me_3N{\rightarrow}\dot{B}Hex^t}} \qquad (7)$$

$$\mathrm{Me_3N{\rightarrow}\dot{B}HHex^t + MeCN \longrightarrow Me_3N{\rightarrow}BH_2Hex^t + {}^{\bullet}CH_2CN} \qquad (8)$$

$$\mathrm{Hex^t = Me_2CHCMe_2}$$

Reaction (8) is much faster than reaction (5) under the same conditions, presumably because of a favourable polar effect for abstraction of electron deficient hydrogen from the nitrile by the nucleophilic, metalloidal amine-boryl radical.[6] Assuming that to be rapid under our experimental conditions reaction (8) must be at least thermoneutral, these results set a lower limit for $DH^{\circ}$(B–H) in (2) of 389 kJ mol$^{-1}$. In fact, it seems likely[7] that the B–H bond in (2) is similar in strength to a secondary C–H bond in an alkane[2] (*ca.* 400 kJ mol$^{-1}$).

An intense, clean e.s.r. spectrum of the $\alpha$-(ethoxycarbonyl)-methyl radical[8] (4) was observed at *ca.* 190 K during u.v. irradiation of a cyclopropane solution containing ethyl acetate (1.0 M), (2) (0.1 M), and DTBP (15% v/v) [equation (9a)]. However, when the catalyst was omitted, a weaker spectrum assigned to the radical[9] (5) was observed in place of (4) and the cyclopropyl radical, formed by hydrogen abstraction from the solvent, was also detected.



$\mathrm{CH_3CO_2Et \longrightarrow {}^{\bullet}CH_2CO_2Et}$ (4) (9a)

$\mathrm{CH_3CO_2Et \longrightarrow CH_3CO_2\dot{C}HMe}$ (5) (9b)

In addition to furnishing a graphic example of polarity reversal catalysis, this result indicates that the B–H bond in (2) is probably stronger than the $\alpha$-C–H bond of ethyl acetate and suggests that the latter is weakened significantly because of stabilisation of (4) by conjugative delocalisation of the unpaired electron.[8]

The use of polarity reversal catalysis (*cf.* the concept[10] of 'umpolung') to increase the rates and to control the chemo- and regio-selectivities of free radical reactions could have many applications in organic synthesis. The principle could, of course, be extended to the catalysis of reactions of nucleophilic radicals at electron rich centres.

*Received, 12th May 1987; Com. 644*

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