Interconversion of Carbocations, Free Radicals and Carbanions in Nitroxide Solutions

By Hari Singh and John M. Tedder†
(*Department of Chemistry, The University, St. Andrews, Scotland* KY16 9ST)

Summary Both triphenylmethyl anions and cations are converted into triphenylmethyl radicals when dissolved in solutions containing di-t-butyl nitroxide; when oxygen is admitted both solutions yield triphenylmethylperoxyl radicals, but in the carbocation system the nitroxide is decomposed while in the carbanion system it is regenerated.

We have described how compounds with weak bonds may be solvolysed to yield radicals when treated with solvents containing unpaired electrons, and we have compared this homosolvolysis [reaction (1)] with the more common heterosolvolysis [reaction (2)], which involves the transfer of electron pairs.[1] If the solute is already ionised one-electron transfers convert cations or anions into radicals by the donation or acceptance of single electrons. At first sight it might appear that either the carbocation (R^+) or the carbanion ($R{:}^-$) would exchange electrons with the solute radical ($A\cdot$) but not both. However careful consideration shows that this is not necessarily so, and experimentally it is found that both triphenylmethyl perchlorate and sodium triphenylmethide react with di-t-butyl nitroxide to yield the triphenylmethyl radical. When benzene is the co-solvent and the nitroxide is in a deficiency triphenylmethyl perchlorate reacts slowly (over 2 days) while sodium triphenylmethide reacts within minutes, both reactions occurring at ambient temperatures. However the rate of reaction probably depends partly on solubility and in both cases when the triphenylmethyl salts ($Ph_3C^+ClO_4^-$ and $Ph_3C^-Na^+$) are in excess, the nitroxide signal is completely replaced by that of the triphenylmethyl radical. The Figure shows how these, at first sight unexpected, electron transfers occur.

$$\underset{\text{(solute)}}{RX} + \underset{\text{(solvent)}}{2A\cdot} \rightleftharpoons \underset{\substack{\upharpoonleft\downharpoonright \\ R\text{–}A}}{R\cdot\,\cdot A} + \underset{\substack{\upharpoonleft\downharpoonright \\ X^+A^-}}{X\cdot\,\cdot A} \qquad (1)$$

$$\underset{\text{(solute)}}{RX} + \underset{\text{(solvent)}}{AB} \rightleftharpoons \underset{\substack{\upharpoonleft\downharpoonright \\ A\text{–}X}}{A^+\,{:}X^-} + \underset{\substack{\upharpoonleft\downharpoonright \\ B\text{–}R}}{B{:}^-\,R^+} \qquad (2)$$

$$\underset{\text{(solute)}}{R^+\,{:}X^-} + \underset{\text{(solvent)}}{A\cdot} \longrightarrow R\cdot + A^+\,{:}X^- \qquad (3)$$

$$\underset{\text{(solute)}}{R{:}^-\,M^+} + \underset{\text{(solvent)}}{A\cdot} \longrightarrow R\cdot + A{:}^-\,M^+ \qquad (4)$$

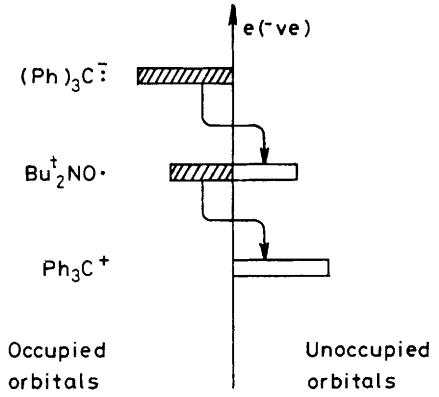
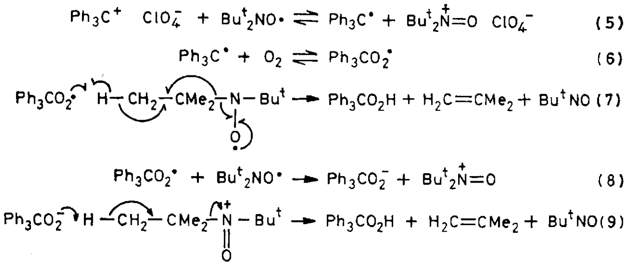


Figure. Energy levels and electron transfers between the triphenylmethyl anion and cation and the di-t-butylnitroxide radical.

Triphenylmethyl radicals do not react with unchanged di-t-butyl nitroxide,[1,2] but if air is admitted to a solution of triphenylmethyl prepared by the homosolvolysis of triphenylmethyl perchlorate (or bromotriphenylmethane) using di-t-butyl nitroxide, attack occurs rapidly [reaction (5)]. The triphenylmethyl radicals react as expected with oxygen [reaction (6)] and the resultant triphenylmethylperoxyl radicals react further with the nitroxide to yield triphenylmethyl hydroperoxide, 2-methyl-2-nitrosopropane, and isobutene. There are two possible mechanisms, hydrogen abstraction [reaction (7)] or proton transfer [reactions (8) and (9)]. We have previously found that a large number of radicals formed by homosolvolysis in di-t-butyl nitroxide solutions react further with the nitroxide to yield 2-methyl-2-nitrosopropane, isobutene, and the hydrocarbon (R–H) and in our previous papers we have assumed that a one-electron transfer, *i.e.* hydrogen abstraction, was involved.[1-3] We now have evidence that in some cases at least proton transfer is the mechanism of the subsequent reaction. If we take a solution of triphenylmethyl radicals prepared by treating the carbanion with nitroxide and then pass air or oxygen through the solution



$$Ph_3C^+\ \ ClO_4^- + Bu^t{}_2NO\cdot \rightleftharpoons Ph_3C^\cdot + Bu^t{}_2\overset{+}{N}{=}O\ \ ClO_4^- \qquad (5)$$

$$Ph_3C^\cdot + O_2 \rightleftharpoons Ph_3CO_2^\cdot \qquad (6)$$

$$Ph_3CO_2^\cdot\ \ H\text{–}CH_2\text{–}CMe_2\text{–}\underset{\substack{| \\ O\cdot}}{N}\text{–}Bu^t \longrightarrow Ph_3CO_2H + H_2C{=}CMe_2 + Bu^tNO \qquad (7)$$

$$Ph_3CO_2^\cdot + Bu^t{}_2NO^\cdot \longrightarrow Ph_3CO_2^- + Bu^t{}_2\overset{+}{N}{=}O \qquad (8)$$

$$Ph_3CO_2^-\ H\text{–}CH_2\text{–}CMe_2\text{–}\underset{\substack{\| \\ O}}{\overset{+}{N}}\text{–}Bu^t \longrightarrow Ph_3CO_2H + H_2C{=}CMe_2 + Bu^tNO \qquad (9)$$

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† Visiting Professor, La Trobe University, Bundoora, Victoria 3083, Australia.

no 2-methyl-2-nitrosopropane or isobutene is formed and instead the nitroxide is regenerated and the sodium salt of the hydroperoxide is formed. We can depict these steps as in reactions (10)—(12). The fact that triphenylmethylperoxyl radicals are present in this experiment and yet no hydrogen abstraction from the nitroxide is observed shows that when bromotriphenylmethane (or triphenylmethyl perchlorate) are homosolvolysed in the presence of oxygen the subsequent attack on the nitroxide must involve the proton-transfer mechanism.

$$\mathrm{Ph_3C{:}^- \, Na^+ + Bu^t_2NO\cdot \rightleftharpoons Ph_3C\cdot + Bu^t_2NO^- \, Na^+} \quad (10)$$

$$\mathrm{Ph_3C\cdot + O_2 \rightarrow Ph_3CO_2\cdot} \quad (11)$$

$$\mathrm{Ph_3CO_2\cdot + Bu^t_2NO^- \, Na^+ \rightarrow Ph_3CO_2Na^+ + Bu^t_2NO\cdot} \quad (12)$$

The only remaining question is whether the proton-transfer mechanism is always involved or whether the hydrogen-abstraction mechanism can also occur. Phenyl and *p*-nitrophenyl radicals, prepared by homosolvolysis using a nitroxide, predominantly couple with the nitroxide to yield the hydroxylamine [reaction (13)], but 2,4-dinitrophenyl radicals yield 1,3-dinitrobenzene and the nitroxide decomposition products ($\mathrm{Bu^tNO + CH_2{=}CMe_2}$).[3] This was attributed to the latter radical being more reactive, but it now appears that it is due to the more electrophilic character of the radical favouring proton transfer. Probably both mechanisms occur, with the proton-transfer mechanism predominating with electrophilic radicals and at low temperatures.

$$\mathrm{Ar\cdot + Bu^t_2NO\cdot \rightleftharpoons Bu^t_2NOAr} \quad (13)$$

$$\mathrm{Ar = Ph \text{ or } \mathit{p}\text{-}O_2NC_6H_4}$$

The experimental technique has been described in previous papers.[1–3] All the e.s.r. spectra were measured on a Decca X3 instrument.

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