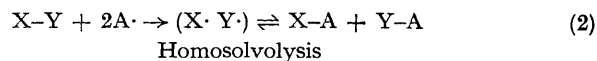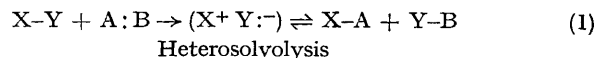# The Induced Homolysis of Bromotriphenylmethane by a Nitroxide

By Alan C. Scott and John M. Tedder

(Department of Chemistry, The University, St. Andrews, Fife KY16 9ST)

Summary The induced homolysis of bromotriphenyl-methane by di-t-butyl nitroxide has been observed by monitoring the decline of the nitroxide spectrum and the appearance of triphenylmethyl radical spectrum in an e.s.r. spectrometer.
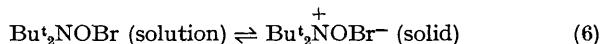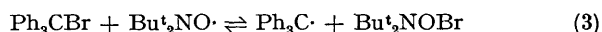
In previous communications[1] we distinguished between *heterosolvolysis* (reaction 1) in which the solvent (A:B) splits into A:$^-$ and B$^+$, and gives respectively a pair of electrons to an incipient cation and accepts a pair of electrons from an incipient anion, and *homosolvolysis* (reaction 2) in which the solvent (A·) transfers a single

$$X-Y + A:B \rightarrow (X^+ Y:^-) \rightleftharpoons X-A + Y-B \qquad (1)$$
Heterosolvolysis

$$X-Y + 2A· \rightarrow (X· Y·) \rightleftharpoons X-A + Y-A \qquad (2)$$
Homosolvolysis

electron to each fragment formed in the fission process. We presented chemical evidence for the homolysis of weak bonds using nitroxides as the solvolytic reagents. If the ideas we put forward are correct we should be able to detect reversible homolysis of such weak bonds by nitroxides, even though the nitroxide is not in vast excess, *i.e.* is not the solvent. We now report the direct detection of the induced homolysis of bromotriphenylmethane by di-t-butyl nitroxide. We have observed the gradual disappearance of the e.s.r. signal of the nitroxide and the concomitant appearance of the e.s.r. signal of the triphenylmethyl radical.

It is not possible to use pure nitroxide as solvent because the e.s.r. signal becomes saturated; we have therefore used the nitroxide (di-t-butyl nitroxide) dissolved in an inert solvent with bromotriphenylmethane as substrate also dissolved in the same solvent. When the two solutions are mixed the initial intense signals of the nitroxide decrease and eventually the signals of the triphenylmethyl radical start to appear. The overall equilibrium situation is quite complicated (reactions 3—6). The triphenylmethyl radical

$$Ph_3CBr + Bu^t_2NO\cdot \rightleftharpoons Ph_3C\cdot + Bu^t_2NOBr \qquad (3)$$

$$Ph_3C\cdot + Bu^t_2NO\cdot \rightleftharpoons Ph_3CONBu^t_2 \qquad (4)$$

$$Ph_3C\cdot + Ph_3C\cdot \rightleftharpoons Dimer \qquad (5)$$

$$Bu^t_2NOBr \text{ (solution)} \rightleftharpoons Bu^t_2\overset{+}{N}OBr^- \text{ (solid)} \qquad (6)$$

is only about 2·5% dissociated in benzene solution[2] and it appears that the O-triphenylmethyl-hydroxylamine (Ph$_3$-CONBu$^t_2$) is largely associated. This means that a considerable excess of triphenylmethyl bromide is required for the triphenylmethyl radical to be present in detectable concentrations. As the equations illustrate the nitroxide bromide is only slightly soluble in benzene and crystallises out of solution. A further complication is that although triphenylmethyl radicals will not abstract hydrogen atoms from the nitroxide, triphenylmethylperoxyl radicals do (reactions 7 and 8). For this reason it is extremely

$$Ph_3C\cdot + O_2 \rightleftharpoons Ph_3CO_2\cdot \qquad (7)$$

$$Ph_3CO_2\cdot + Bu^t_2NO\cdot \rightleftharpoons Ph_3CO_2H + Me_2C{=}CH_2 + Bu^tNO \qquad (8)$$

important that the experiments are performed in the complete absence of oxygen.

In a typical experiment solutions of bromotriphenylmethane (0·5 M in dry benzene) and di-t-butyl nitroxide (0·03 M in dry benzene) are carefully degassed before being mixed (*in vacuo*). The combined solution is placed in the cavity of the e.s.r. spectrometer and the spectra observed at regular intervals. The nitroxide signal[3] declines very rapidly to start with but eventually reaches a value of 10—20% of the original value after an hour and subsequently remains constant. The addition of further bromotriphenylmethane (0·25 mol. equiv.) causes a further decline in the nitroxide signal and the appearance of the triphenylmethyl spectrum[4] which intensifies with time as the nitroxide weakens further. The Figure shows the e.s.r.
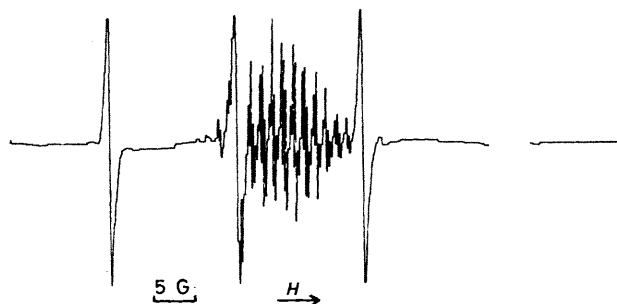

FIGURE. The e.s.r. spectrum of the reaction mixture after 72 h. The complex spectrum of Ph$_3$C· is superimposed on the simple triplet of Bu$^t_2$NO·.

spectrum of a typical reaction solution before the nitroxide signal has disappeared. Work is currently in progress to elucidate the relatively complex equilibria and to investigate the influence of the medium on the equilibria.

[1] H. Low, I Paterson, J. M. Tedder, and J. C. Walton, *J.C.S. Chem. Comm.*, 1977, 171; 'Radicaux Libre Organiques,' Proceedings of the 2nd International Symposium on Organic Free Radicals, Éditions du Centre Nationale de la Recherche Scientifique, Paris, 1977, pp.127—135.
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[4] H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, 1954, **22**, 1783.