3-Bromopropanoyl Isocyanate as an Acyclic Source of the Succinimidyl Radical

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Bromine-atom abstraction from 3-bromopropanoyl isocyanate (**1**) gives the 2-(isocyanatocarbonyl)ethyl radical (**2**) which undergoes cyclisation to form the succinimidyl radical.

Although the established chemistry of the succinimidyl radical ($S^{\bullet}$) is now quite extensive,[1—3] the nature of its electronic ground state is still uncertain and disagreement remains as to whether an excited electronic state of $S^{\bullet}$ can participate in thermal reactions of *N*-halogenosuccinimides. Thirty years ago, it was proposed[1] that the rearrangement of *N*-bromosuccinimide to 3-bromopropanoyl isocyanate (**1**) involves thermally induced ring-opening of $S^{\bullet}$ to form the 2-(isocyanatocarbonyl)ethyl radical (**2**) as a key step (Scheme 1). More recently, Skell *et al.*[4] have proposed that this ring-opening is also readily reversible with $k_1 \simeq k_{-1} \simeq 2 \times 10^7\ s^{-1}$ at ambient temperature, although kinetic data obtained by Walling *et al.*[5] require that k_1 is $\leqslant 2 \times 10^4\ s^{-1}$ under similar conditions.

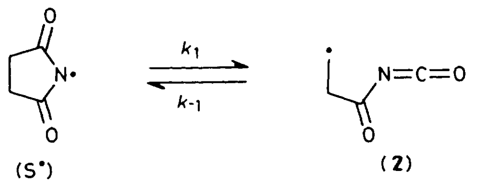
Whilst the e.s.r. spectrum of $S^{\bullet}$ in solution has never been detected, one assigned to this radical trapped in a rigid matrix has been interpreted in terms of an electronic ground state in which the unpaired electron is centred mainly on nitrogen in a π SOMO ($S^{\bullet}_{\pi}$).[6] This conclusion receives support from high-level *ab initio* m.o. calculations which predict a π ground state, although this is separated from the first excited state ($S^{\bullet}_{\sigma}$) by only 21.5 kJ mol^{-1}.[7] However, it has been pointed out[8,9] that the ring-opening process is stereoelectronically allowed only from $S^{\bullet}_{\sigma}$ and it follows that cyclisation of (**2**) should lead to this electronic state of the succinimidyl radical. Dewar and Olivella[9] have calculated that the ring-opening of $S^{\bullet}_{\sigma}$ to give (**2**) is exothermic by 30 kJ mol^{-1} and have estimated k_1 to be *ca.* $2.4 \times 10^4\ s^{-1}$ at 298 K, close to the maximum value proposed by Walling *et al.*,[5] although on the basis of these calculations endothermic cyclisation of (**2**) to give $S^{\bullet}_{\sigma}$ would be very slow under normal conditions. Symmetry forbidden ring-opening of $S^{\bullet}_{\pi}$ was predicted to be extremely slow at ambient temperature[9] and it has been suggested[3] that, whilst the electronic ground state is $S^{\bullet}_{\pi}$, the reported chemistry of $S^{\bullet}$ may be that of the first excited state, $S^{\bullet}_{\sigma}$.

Against this background, we considered it important to generate (**2**) by halogen abstraction from the acyclic (**1**) in order to confirm that this radical does cyclise to give $S^{\bullet}$ and thereby to establish (**1**) as a useful source of $S^{\bullet}$ for further investigations. *N*-Halogenosuccinimides undergo radical chain addition to simple alkenes, implying that the electrophilic $S^{\bullet}$ adds rapidly to the C=C bond.[10] Addition of a variety of types of radical to 1,1-di-t-butylethylene (**3**) yields relatively persistent adducts which are readily detectable by e.s.r. spectroscopy, although simple alkyl radicals do *not* add at a significant rate.[11] We reasoned that (**3**) should therefore act as a selective trap for $S^{\bullet}$ in the presence of (**2**).

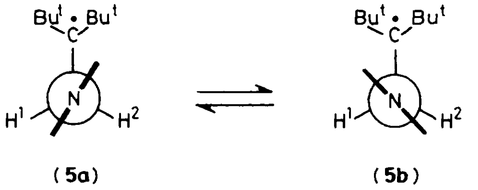
$$\text{S–Cl} \xrightarrow{h\nu} \text{S}^{\bullet} + \text{Cl}^{\bullet} \tag{1}$$

$$\underset{(\mathbf{3})}{\text{S}^{\bullet} + \text{Bu}^{t}_{2}\text{C=CH}_{2}} \longrightarrow \underset{(\mathbf{4})}{\text{Bu}^{t}_{2}\dot{\text{C}}\text{–CH}_{2}\text{S}} \tag{2}$$

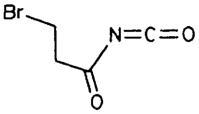
An intense e.s.r. spectrum (see Figure 1a) was observed during u.v. irradiation of a perdeuterioacetonitrile solution containing *N*-chlorosuccinimide (NCS; 0.2 M) and (**3**) (0.6 M) between 238 and 296 K. We assign this spectrum to the 1,1-di-t-butylalkyl radical (**4**) formed by addition of $S^{\bullet}$ to (**3**) [equations (1) and (2)]; the corresponding adduct of the



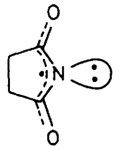
Scheme 1



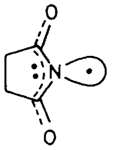
Scheme 2



(1)



$S_\pi^\bullet$



$S_\sigma^\bullet$

chlorine atom was not detected under the same conditions. When photolysis was interrupted at 263 K, decay of (**4**) was approximately first-order ($t_{\frac{1}{2}}$ *ca.* 18 s). The e.s.r. parameters [$a(2H_\beta)$ 13.57, $a(N_\beta)$ 6.97, $a(18H_\gamma)$ 0.37 G, and g 2.0025 at 261 K] are in accord with the proposed structure of (**4**); in common with other adducts of (**3**), the eclipsed conformation (**5**) about the C_α–C_β bond is preferred for steric reasons.[11] The lines associated with $M_I(2H_\beta) = 0$ are broader than the wing lines of the triplet, particularly at lower temperatures, indicating that the β-protons are non-equivalent. Out-of-phase modulation of the β-proton splittings is probably brought about by restricted motion around the N–C_β bond and inspection of molecular models suggests that rocking of the planar succinimide ring between the two minima (**5a**) and (**5b**) (Scheme 2) is a possible cause of the selective line broadening exhibited by this sterically congested radical.

The e.s.r. spectrum of (**4**) was also observed when S• was generated thermally in the presence of (**3**) by heating a Pr^nCN solution containing the alkene (0.7 M), NCS (0.2 M), and dibutanoyl peroxide (10% v/v) at 323—338 K [equations (3) and (4)]. Chlorine atom abstraction could also be effected with $Bu^tOCH_2^\bullet$ produced by thermal decomposition [equation (5)] of di-t-butyl hyponitrite (TBHN) in the presence of t-butyl methyl ether.

$$Pr^nC(O)O_2C(O)Pr^n \xrightarrow{\text{heat}} 2Pr^{n\bullet} + 2CO_2 \qquad (3)$$

$$Pr^{n\bullet} + S\text{–}Cl \longrightarrow S^\bullet + Pr^nCl \qquad (4)$$

$$Bu^tON{=}NOBu^t \xrightarrow{\text{heat}} 2Bu^tO^\bullet + N_2 \qquad (5)$$

A very similar spectrum of (**4**) (see Figure 1c) was recorded at 317 K during thermolysis of TBHN (0.4 M) in the presence of (**3**) (0.6 M), tributylphosphine–borane[12] (0.4 M), and (**1**) (0.8 M, prepared from silver cyanate and 3-bromopropanoyl bromide by a modification of the method described by Johnson and Bublitz)[1] in CD_3CN solvent. Abstraction of bromine from (**1**) gives (**2**) [equations (6) and (7)], which would react only slowly with the phosphine–borane[12] and must cyclise relatively rapidly to give S•. Presumably[8,9] the initial product of cyclisation is $S_\sigma^\bullet$, even if this is not the electronic ground state. The spectrum of (**4**) was also observed when the primary t-butoxyl radicals were generated photochemically from di-t-butyl peroxide (DTBP) in nitrile or alkane solvents and when bromine abstraction from (**1**) was brought about by trimethylstannyl radicals, produced by thermolysis of TBHN or photolysis of DTBP in the presence of $Me_3SnSnMe_3$, in heptane solvent. When t-butoxyl radicals were produced photochemically in CD_3CN or thermally in heptane, each containing (**1**) and $Bu^n_3P{\rightarrow}BH_3$ [but not (**3**)], a chain reaction ensued, presumably because S• abstracts hydrogen from the phosphine–borane [equation (8)]. Succinimide (S–H) was isolated by h.p.l.c. in *ca.* 25% yield [based on (**1**)] from the products of thermal reactions at 328 K.

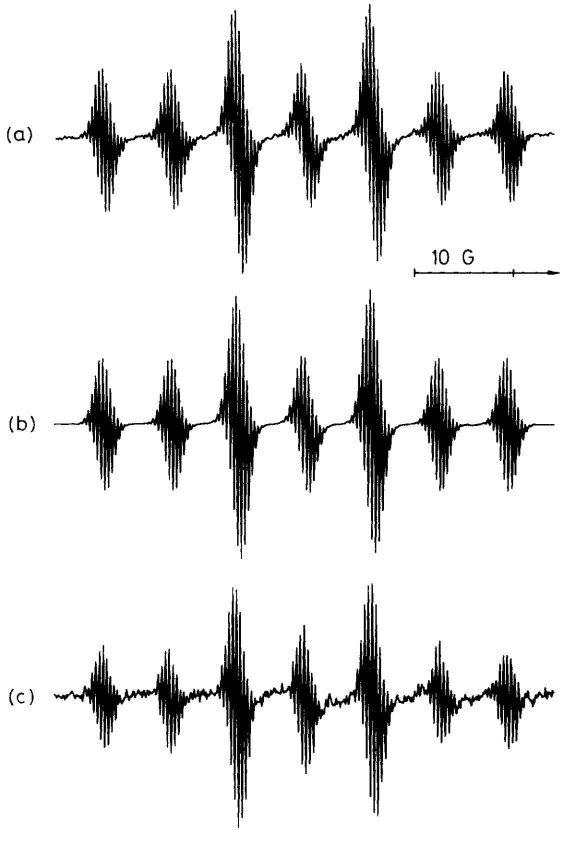


Figure 1. (a) E.s.r. spectrum of the radical (**4**) at 261 K obtained during u.v. irradiation of NCS and (**3**) in CD_3CN. (b) Computer simulation of (a) using the splitting constants given in the text. The peak-to-peak widths of the lines associated with $M_I(2H_\beta) = 0$ and ±1 are 0.21 and 0.17 G ($G = 10^{-4}$ T), respectively. (c) E.s.r. spectrum of the radical (**4**) at 317 K obtained during thermolysis of TBHN in the presence of (**1**), (**3**), and $Bu^n_3P{\rightarrow}BH_3$ in CD_3CN [$a(2H_\beta)$ 13.71, $a(N_\beta)$ 6.86, and $a(18H_\gamma)$ 0.38 G].

Much work still remains to be done with imidyl radicals and their open-chain isomers. It is clearly important to obtain

$$Bu^tO^\bullet + Bu^n_3P{\rightarrow}BH_3 \longrightarrow Bu^tOH + Bu^n_3P{\rightarrow}\dot{B}H_2 \qquad (6)$$

$$Bu^n_3P{\rightarrow}\dot{B}H_2 + BrCH_2CH_2C(O)NCO \longrightarrow Bu^n_3P{\rightarrow}BH_2Br + {}^\bullet CH_2CH_2C(O)NCO \qquad (7)$$

$$S^\bullet + Bu^n_3P{\rightarrow}BH_3 \longrightarrow S\text{–}H + Bu^n_3P{\rightarrow}\dot{B}H_2 \qquad (8)$$

e.s.r. spectra of S$^{\bullet}$ and of other imidyl radicals in fluid solution to determine their electronic configurations and to investigate possible medium effects on the nature of the electronic ground states.

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