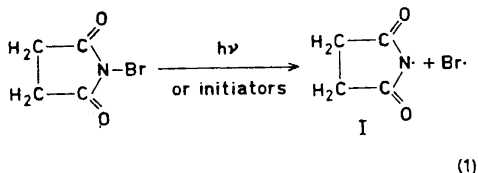


Trapping as Nitroxide Radicals of  
the Radicals Formed in Some  
Reactions of *N*-Bromosuccinimide,  
*N*-Bromotetramethylsuccinimide,  
*N*-Chlorosuccinimide and  
*N*-Bromophthalimide

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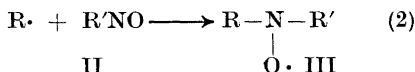
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It is now generally accepted that bromination by *N*-bromosuccinimide (NBS) proceeds via free radicals which are induced in a homolytic cleavage through the action of light or radical initiators.<sup>1-3</sup>



The propagation is thought to involve the abstraction of a hydrogen atom from the substrate HR, by either the succinimidyl radical (I) or Br·, to form the radical, R·.

In the presence of a suitable *C*-nitroso compound (II), many short-lived radicals R·, can be trapped and converted into the more stable corresponding nitroxide radicals (III), which, in the ESR spectra, exhibit secondary hfs characteristic for the trapped radicals.<sup>4-7</sup>



The following results were obtained when the trapping technique was applied to some reactions of NBS, *N*-chlorosuccinimide (NCIS), *N*-bromotetramethylsuccinimide and *N*-bromophthalimide.

*I. Radicals derived from the imides.* Irradiation with UV light of a solution of NBS, or NCIS and II (*t*-nitrosobutane) in CCl<sub>4</sub>, CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub> produced a nitroxide radical which exhibited the 3×3 line spectrum shown in Fig. 1. Evidently this spectrum is caused by the coupling of the

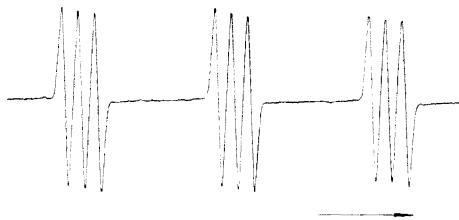
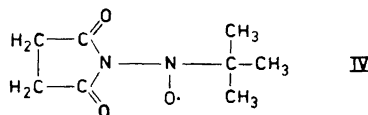


Fig. 1. ESR spectrum of the nitroxide radicals formed by the trapping of the succinimidyl radicals produced by photolysis of *N*-bromosuccinimide (NBS). Solvent: CHCl<sub>3</sub>.

unpaired electron with two non-equivalent <sup>14</sup>N nuclei (*a*<sub>1</sub><sup>N</sup>=16.4 g, *a*<sub>2</sub><sup>N</sup>=1.81 g) and is consistent with the trapping of the succinimidyl radical (I), produced as in eqn. (1), with the formation of the nitroxide radical (IV).



Spectra with almost identical coupling constants were obtained with *N*-bromotetramethylsuccinimide and *N*-bromophthalimide by the trapping of the tetramethylsuccinimidyl and the phthalimidyl radical, respectively. By the use of the nitroxide method, it was found that the phthalimidyl radical could also be produced from potassium phthalimide in CH<sub>2</sub>Cl<sub>2</sub> by oxidation with lead tetraacetate and UV irradiation.

After a prolonged irradiation by light, secondary nitroxide radicals were formed in some of the reaction mixtures. These radicals exhibited a 3×1 line spectrum with *a*<sup>N</sup>=7.5 g, and had a *g*-value somewhat larger than that of the nitroxide radicals described above, indicating the trapping of an acyl radical.<sup>8</sup> It is suggested that this radical has the structure O=C-CH<sub>2</sub>-CH<sub>2</sub>-N=C=O, and that it is formed by the splitting of one of the carbon-nitrogen bonds of the succinimidyl radical.<sup>2</sup>

As expected no radicals were observed from NBS or NCIS when polar solvents such as H<sub>2</sub>O or methanol were used.<sup>1-3</sup>

*II. Radicals produced by the abstraction of hydrogen atoms from olefinic substances.* By the use of the nitroxide method, radicals have been trapped which are formed by the abstraction of a hydrogen atom in the reaction between the *N*-halogen imides and a variety of olefinic substances such as 2-propen-1-ol, 2-buten-1-ol, 2-propenenitrile, 6-methyl-5-hepten-2-one, 3-methyl-2-cyclopenten-2-ol-1-one, cyclopentene, cyclohexene, 1-methyl-1-cyclohexene, or *d*-limonene. With an excess of the olefinic compounds the nitroxide radicals formed from these substances were found to dominate over the species (IV) derived from the trapping of the succinimidyl radicals. In several cases the radicals could be identified by the secondary hfs of the corresponding nitroxide radicals.

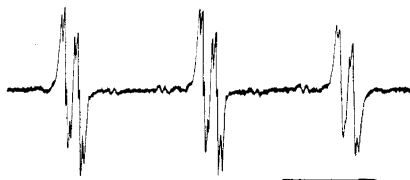


Fig. 2. ESR spectrum of the nitroxide radicals formed by the trapping of the radicals produced in the reaction between 2-propen-1-ol and *N*-chlorosuccinimide (NCIS). Solvent:  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was irradiated by UV light.

Fig. 2 shows the spectrum of the nitroxide radicals obtained with 2-propen-1-ol and NCIS ( $a^N = 14.9$  g). The secondary doublet splitting ( $a^H = 1.43$  g) indicates the trapping of a radical with the structure  $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H} - \text{OH}$ , though the structure  $\dot{\text{C}}\text{H} = \text{CH} - \text{CH}_2 - \text{OH}$  is a possible alternative. However, the former structure is supported by the result obtained with 2-buten-1-ol and NCIS, which also gave rise to a nitroxide radical with a doublet splitting ( $a^N = 14.9$  g,  $a^H = 1.43$  g) indicating the trapping of  $\text{CH}_3 - \text{CH} = \text{CH} - \dot{\text{C}}\text{H} - \text{OH}$  radicals.

In other cases the structure of the trapped radical was uncertain, as no complete analysis of the secondary hfs was possible.

In view of the possible selective survival of certain nitroxide species, and the different ability of the *C*-nitroso compound (II) to trap different species of short-lived radicals,<sup>4-7</sup> it should be emphasized that

the nitroxide radicals actually observed do not necessarily represent the intermediate radicals of the main path of the reaction between *N*-halogen imides and the olefinic substances concerned.

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### Relative Thermodynamic Stabilities of 4-Methylene-1,3-dioxane and the Isomeric 4-Methyl-1,3-dioxene-(4) and the Kinetics of Their Hydrolytic Cleavage

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In a recent study of five-membered cyclic vinyl ethers<sup>1</sup> it was found that the kinetic behavior depended greatly on the site of unsaturation; 4-alkylidene dioxolanes were cleaved in acid solutions