Homosolvolysis

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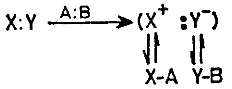
Summary Nitroxides when used as solvents have been found to promote the homolysis of weak bonds.

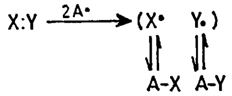
In a normal solvolysis the solvent provides electron pairs for the incipient cation and accepts electron pairs from the incipient anion.[1] For example tetramethylammonium chloride undergoes solvolysis in dinitrogen tetroxide to yield nitrosyl chloride and tetramethylammonium nitrate [equation (1)].

$$\begin{array}{ccccc} Me_3NCl & + \; N_2O_4 & \longrightarrow & Me_3NNO_3 & + \; NOCl \\ X:Y & A:B & & X:A & Y:B \end{array} \qquad (1)$$

The solvent splits heterolytically into $A:^-$ and B^+ which give a pair of electrons to the incipient cation and accept a pair of electrons from the incipient anion respectively. It would seem reasonable to describe such a process a heterosolvolysis [equation (2)]. If we wish to have the corresponding homosolvolysis we require to have a system which can accept a single electron from a fragment and donate an electron to another fragment [equation (3)]. Such solvents can be found in stable nitroxides which are easily prepared and are liquid at room temperature.[2] Just as in a heterosolvolysis the bond broken will be one which already has polar character, so in homosolvolysis bond fission will occur where the bond is weak and the incipient radicals stable. There is a further analogy; in heterosolvolysis the incipient ions may be strong electrolytes or weak electrolytes. In the former case the new molecules X–A and Y–B will largely exist in the ionised form whereas if they are weak electrolytes X–A and Y–B will exist mainly in the covalent form. In a similar way during a homosolvolysis the molecules X–A and Y–A may redissociate into radicals (like the

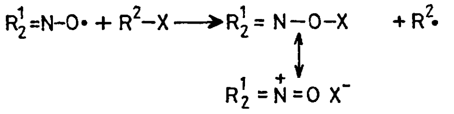


(2)



(3)

strong electrolytes) or remain as stable molecules. We have studied a number of different homosolvolyses using di-t-butyl nitroxide[3] and 2,2,6,6-tetramethyl-4-piperidone N-oxide[4] as solvents.



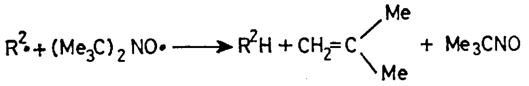
$$R^1_2{=}N{-}O\cdot + R^2{-}X \longrightarrow R^1_2{=}N{-}O{-}X + R^{2}\cdot \leftrightarrow R^1_2{=}\overset{+}{N}{=}O\ X^- \quad (4)$$

(I)

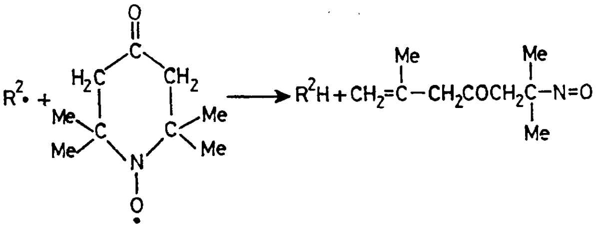
$$R^2\cdot + R_2{=}N{-}O\cdot \longrightarrow R^1_2{=}N{-}O{-}R^2 \quad (5)$$

(II)

Our studies include reactions in which R^2 is alkyl, allyl, benzyl, benzoyloxy, or succinimidyl, and where X has been a halogen (Br or I) or, in the case of benzoyloxy, where it has been benzoate [equations (4) and (5)]. Secondary and tertiary alkyl bromides and iodides react very slowly when dissolved in excess of nitroxide at room temperature; the reaction is considerably faster with allyl and benzyl bromides and the nitroxide bromide (I) crystallises out. With a two-fold excess of the nitroxide the reaction reaches an equilibrium stage after which no further salt precipitates. The addition of further nitroxide or further alkyl halide results in more precipitation. In one set of experiments, with allyl bromide the nitroxide salt was filtered off as fast as it was formed and further allyl bromide was added. Ultimately all the nitroxide was consumed. The O-allyl and O-benzyl hydroxylamines (II) correspond to weak electrolytes and remain undissociated at room temperature. The nitroxides themselves are very susceptible to hydrogen abstraction [equations (6) and (7)] and elevation of the temperature leads to dissociation of the O-substituted hydroxylamine and subsequent hydrogen abstraction. When N-bromosuccinimide or benzoyl peroxide dissolve in an excess of the nitroxides at room temperature, very rapid reactions ensue. The succinimidyl radical and the benzoyloxyl radical both behave like strong electrolytes and do not combine with the nitroxide, but instead both radicals abstract hydrogen as fast as they are formed to yield, respectively, succinimide and benzoic acid together with the appropriate nitroso-compounds depending on which nitroxide was the solvent. The succinimide reaction is complicated by N-bromosuccinimide promoting the decomposition of the nitroxide bromide to yield 2-bromo-2-methyl- and 2-methyl-2-nitroso-propane.



$$R^2\cdot + (Me_3C)_2NO\cdot \longrightarrow R^2H + CH_2{=}C(Me)_2 + Me_3CNO \quad (6)$$



(7)

The scope of the homosolvolytic reaction seems very wide indeed and we have qualitative evidence of similar reactions with acid chlorides, sulphonyl chlorides, azo-compounds, and even esters and ketones.

In heterosolvolysis the dielectric constant of the solvent is important in determining the extent of solvolysis. It may well be that in homosolvolysis the presence of paramagnetic species promotes solvolysis by facilitating the uncoupling of bonding electron pairs.

The homosolvolyses using di-t-butyl nitroxide have been performed at room temperature (*ca.* 25 °C), while those with 2,2,6,6-tetramethylpiperidone N-oxide were performed at the m.p. of nitroxide (35 °C). The reaction with N-bromosuccinimide is extremely rapid and needs to be controlled by cooling; the reaction with benzoyl peroxide is also fast and goes to completion in a few minutes (the yield of purified benzoic acid was 95%). The homosolvolysis of allyl bromide and benzyl bromide proceeds more slowly, the first crystals of the nitroxide bromides appearing after *ca.* 2 h, the equilibrium being established after 36 h. The position of the equilibria depend on the relative concentrations of the reactants and solvent [allyl bromide + 2,2,6,6-tetramethylpiperidone N-oxide (1 : 1) → 15% conversion at 40 °C].

All the experiments were carried out on a vacuum line with carefully degassed materials. Similar reactions take place in the atmosphere but they may be more complicated when oxygen is present. In all cases the major products have been identified and fully characterised (mass and n.m.r. spectroscopy, m.p. and mixed m.p., and analysis). Because the reactions have been carried out in an excess of nitroxide it is possible that minor additional side reactions have occurred. However, allowing for the difficulties in isolating products from the unchanged nitroxides the material balances indicate that if there are such side reactions they represent a very small contribution to the overall process.

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