^{15}N Nuclear Polarisation during Nitro-group Exchange Reactions on a σ-Complex formed by *ipso*-Attack

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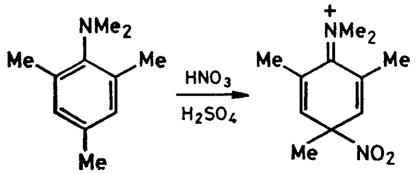
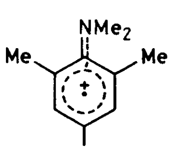
Summary The $^{15}NO_2$–$^{14}NO_2$ exchange reactions of the ion (**2**) with nitric acid give rise to either enhanced absorption or emission in the ^{15}N n.m.r. spectrum of the ion depending on the direction of the exchange.



(1) **(2)**



(3)

THE nitrous acid-catalysed reaction of the amine (**1**) with nitric acid in aqueous sulphuric acid to form the ion (**2**) has recently been reported.[1] The ion is a stable species and can be isolated as the hexafluorophosphate.[2] It does however undergo an exchange reaction with labelled nitric acid in aqueous sulphuric acid leading to an equilibrium distribution of the isotopic label.

When the ion (**2**) is formed using $H^{15}NO_3$, the beginning of the exchange reaction with $H^{14}NO_3$ leads to enhanced absorption in the ^{15}N n.m.r. spectrum of the ion. This can be seen by comparing the heights of the peaks (A) in spectra (a) and (b) (Figure). The concentration of the ^{15}N-labelled ion (**2**) in the solution giving spectrum (b) must be less than that in the original solution because of the obvious presence of $H^{15}NO_3$ formed in the exchange reaction [peak (B)]. When the ion (**2**) is prepared from $H^{14}NO_3$, the ^{15}N-labelled ion (**2**) formed at the beginning of the exchange reaction gives an emission spectrum (d). As equilibrium is approached, the ^{15}N n.m.r. spectrum of the ion (**2**) in both exchange reactions returns to its normal phase and intensity [spectra (c) and (e)].

The simplest interpretation of these results involves the intermediate formation of the radical cation (**3**) as shown in the Scheme. This interpretation is supported by the

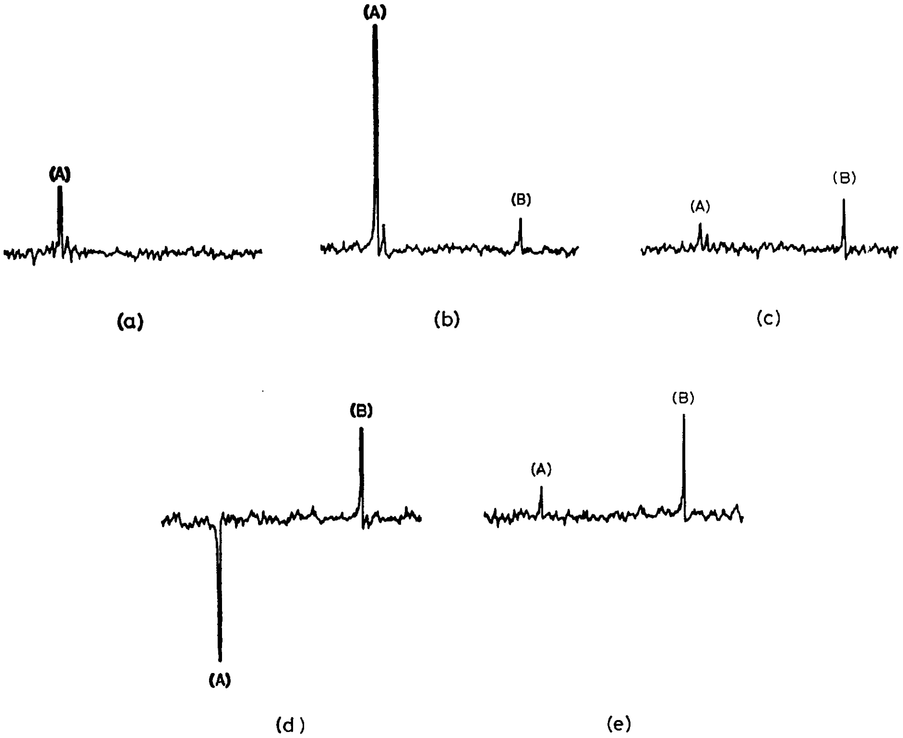
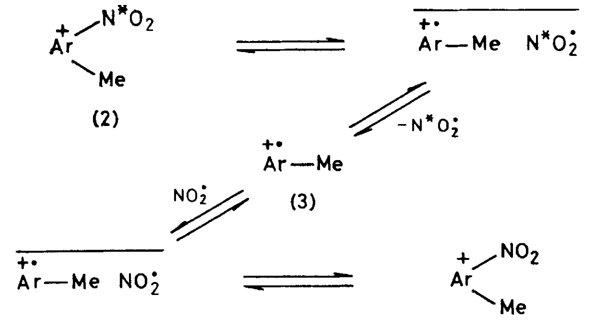


FIGURE. The ^{15}N n.m.r. spectra of solutions of the ion (**2**) (0·27 mol dm^{-3}) during ^{15}N exchange with nitric acid ([HNO_3] + [$H^{15}NO_3$] = 0·4 mol dm^{-3}) in 72·1% sulphuric acid at 0 °C. (A) = $^{15}NO_2$ group of ion (**2**); (B) = $H^{15}NO_3$. Peak (A) is 49·4 p.p.m. downfield from peak (B). (a) The ^{15}N labelled ion (**2**) before exchange; (b) the same during the first 19 min of exchange with $H^{14}NO_3$; (c) the same during the second 19 min of such exchange; (d) as (b) but for the exchange of the unlabelled ion with $H^{15}NO_3$; (e) as (d) but during the second 19 min of such exchange. All spectra involved 256 pulses with pulse angle 23° and pulse repetition time 4 s.

e.s.r. spectra of the reaction mixtures in the presence of hydrazine† for this is consistent with this radical cation and gives a *g*-value of 2·0032. On this interpretation, the ^{15}N nuclear polarisation arises from the partitioning of the radical pair $ArMe^{+\bullet}$ $NO_2^{\bullet}$ between combination and dissociation. The opposite consequences of this partitioning on the ^{15}N n.m.r. spectra in the two exchange experiments accord with Kaptein's rules[3] as modified to apply to ^{15}N nuclei.[4] When the ion (**2**) is initially labelled with ^{15}N, the n.m.r. spectrum of this ion during exchange is derived in part from material formed by the combination of a radical pair derived from a singlet precursor. When the ion (**2**) is initially unlabelled, the n.m.r. spectrum during exchange is that of a product formed from radicals that have diffused together.‡ The exchange of the NO_2 with the nitric acid presumably occurs *via* N_2O_4 since this exchange is stopped in the presence of hydrazine. The presence of nuclear polarisation prevents us from using the n.m.r. results to calculate the rate of the exchange reaction but it seems probable that most of the exchange occurs during the time of taking the first spectrum.



SCHEME

This work provides clear evidence that some, if not all, of the isotopic exchange occurs *via* the intermediate radical cation. It thus supports the interpretation of the 'cross-over experiments' involving isotopic exchange during concurrent [1,3] rearrangements of intermediates formed by *ipso*-attack.[1] The suggested source of the nuclear polarisation accords with that tentatively suggested to explain the CIDNP effect recently observed in the *para*-nitration of *NN*-dimethylaniline.[5]

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† The hydrazine presumably increases the equilibrium concentration of the radical cation by reducing that of dinitrogen tetroxide (hydrazine is a very effective trap for nitrous acid, D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1975, 655).

‡ The agreement with Kaptein's rules requires the reasonable assumption that the *g*-value of $NO_2^{\bullet}$ is less than that of the radical cation (see P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, 1967, p. 129). Certain higher values of *g* sometimes attributed to $NO_2^{\bullet}$ appear to derive from the association of $NO_2^{\bullet}$ with other molecules (B. H. J. Bielski, J. J. Freeman, and J. M. Gebicki, *J. Phys. Chem.*, 1968, **72**, 1721).

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