The Mechanism of Addition of Nitrogen Dioxide to Alkenes. Evidence from ^{15}N Nuclear Polarisation

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The ^{15}N nuclear polarisation in the dinitro and nitro-nitrito products from the addition of nitrogen dioxide to 2-ethylbut-1-ene is consistent with the separate addition of two nitrogen dioxide radicals.

The formation of dinitro-compounds by the addition of nitrogen dioxide† to alkenes is currently considered to occur *via* at least two mechanisms. The mechanism first proposed[1] involves the reversible addition of molecular nitrogen dioxide to the alkene to give the more stable of the two possible radicals followed by the addition of a second nitrogen dioxide molecule to this radical. More recently, however, the kinetics of the reaction in more concentrated solutions (>0.1 mol dm^{-3} in nitrogen dioxide) have led to the suggestion that the intial reaction of the alkene is with molecular dinitrogen tetroxide to form the same radical pair.[2] These reaction paths are shown for addition to 2-ethylbut-1-ene in Scheme 1.

Although the same radical pair (**1**) is involved in the two reaction paths, the implications of these paths for any possible ^{15}N nuclear polarisation in the product are very different. This arises because the radical pair from path (a) is formed by diffusion and hence the radicals have uncorrelated spins (an F precursor),[3] while that from path (b) must be initially in a singlet state (an S precursor).[3] The application of Kaptein's Rules[3] as modified to apply to ^{15}N nuclear polarisation[4] leads to the predicted phases of ^{15}N nuclear polarisation shown in Table 1. These predictions assume that the sign of ($g_{NO_2} - g_{RH}$) for the two components of the radical pair is negative[5] and that the hyperfine coupling constant for the nitrogen atom in the alkyl radical is also negative: this second point follows from the negative magnetogyric ratio for the ^{15}N nucleus and the results of MNDO calculations.

Table 1. Predicted and observed phases of ^{15}N nuclear polarisation in the dinitroproduct (**2**). The subscripts indicate the carbon atom to which the nitrogen atom is bonded.

	N_1	N_2
F Precursor	Enhanced absorption	Emission
S Precursor	Emission	Enhanced absorption
Observed	Enhanced absorption	Emission

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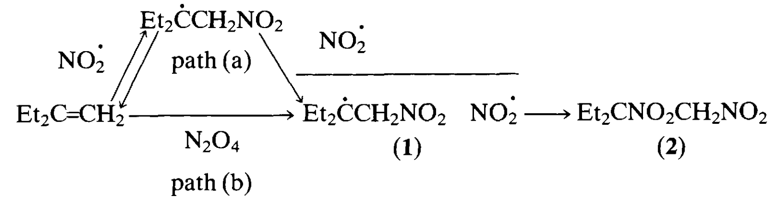
† The term 'nitrogen dioxide' without the qualification 'molecular' is used to refer both to this species and to the various forms of the dimer in equilibrium with it.



Scheme 1

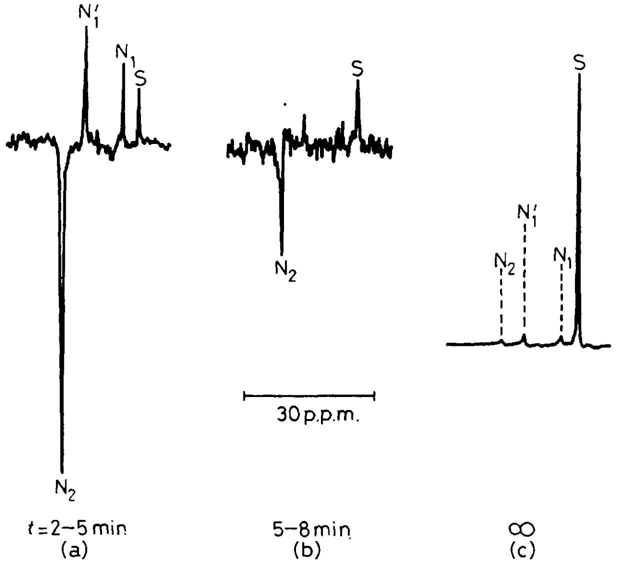


Figure 1. ^{15}N NMR signals observed during the mixing of a solution of 2-ethylbut-1-ene (1.0 mol dm^{-3}) with an equal volume of a solution of ^{15}N-nitrogen dioxide (1.0 mol dm^{-3}), both in n-hexane as solvent. The signals N_1 (δ 3.0 p.p.m.) and N_2 (δ 15.0 p.p.m.) refer to the nitrogen atoms attached to carbon atoms 1 and 2 in the dinitrocompound, signal N_1' (δ 11.5 p.p.m.) comes from the nitro-group in the other major product (1-nitro-2-nitrito-2-ethylbutane). Signal S comes from the external standard (^{15}N-nitrobenzene in n-hexane). The chemical shifts are measured from the standard (high field negative). The spectra involved 28 pulses [(c) > 3000 pulses], pulse repetition time 6.4 s, pulse angle 45°.

A ^{15}N-labelled sample of the dinitrocompound (**2**) has been prepared and the ^{15}N NMR signals assigned on the basis of the proton coupling observed in the high resolution spectra: the peak N_1 is a triplet and the peak N_2 a quintet. The observation of ^{15}N nuclear polarisation in the product of the addition reaction proved difficult because of the speed of the reaction but polarisation was observed when the reagents were allowed to mix within the NMR spectrometer. A solution of the substrate in n-hexane was frozen in an NMR tube so as to leave a coaxial cylindrical cavity; this was then filled with a solution of nitrogen dioxide in the same solvent and the tube contents were then refrozen. On bringing to the temperature of the NMR probe, the solutions melted and the reaction began. The resulting spectra are shown in Figure 1.

The comparison of the intensities of the resulting signals with the standard (^{15}N-nitrobenzene in an outer coaxial tube) shows clearly that the early signals are strongly polarised with the phases expected from an F precursor and hence from reaction by path (a) (see Table 1). The fact that the signals for N_1 and N_2 are of opposite phase shows that the polarisation cannot arise in some other process and be carried over into the dinitroproduct. The enhanced absorption signal (N_1') seen for the nitro-group in the nitro-nitrite [$Et_2C(ONO)CH_2NO_2$, see Figure 1] indicates that this compound, which is formed concurrently with the dinitroproduct, is also derived from the radical pair from path (a).

We thank Dr. B. P. Roberts for helpful comments. This work has been carried out with the support of the Procurement Executive, Ministry of Defence.

Received, 30th November 1989; Com. 9/05129E

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