

# Mechanism of reaction of nitrogen dioxide with alkenes in solution

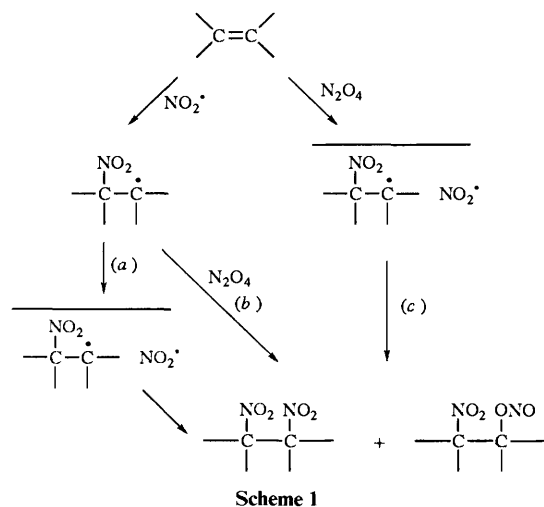
Julie Chatterjee,<sup>a</sup> Robert G. Coombes,<sup>\*†,a</sup> Julian R. Barnes<sup>b</sup> and Melanie J. Fildes<sup>b</sup>

<sup>a</sup> Department of Chemistry, City University, Northampton Square, London, UK EC1V 0HB

<sup>b</sup> Shell Research Ltd., Thornton Research Centre, PO Box 1, Chester, UK CH1 3SH

In spite of the observation of <sup>15</sup>N nuclear polarisation expected from the separate addition of two NO<sub>2</sub><sup>•</sup> radicals in the reaction of nitrogen dioxide with allylbenzene and some other alkenes, kinetic studies indicate that both NO<sub>2</sub><sup>•</sup> and N<sub>2</sub>O<sub>4</sub> are reactive species, each leading only to addition products.

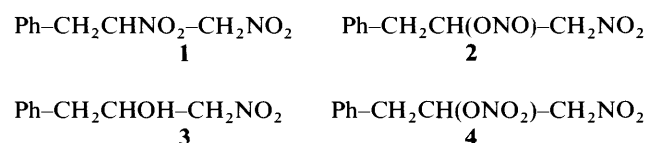
There are some unresolved aspects concerning the reactions of alkenes with nitrogen dioxide<sup>‡</sup> in solution. It has recently been demonstrated by studies of <sup>15</sup>N chemically induced dynamic nuclear polarisation (CIDNP) that a significant pathway for the addition reactions of 2-ethylbut-1-ene<sup>1,2</sup> and 2-methylpent-2-ene,<sup>2</sup> to form initially dinitro compounds and nitronitrites, involves the separate addition of two NO<sub>2</sub><sup>•</sup> radicals [Path (a), Scheme 1].<sup>2</sup> Earlier kinetic studies on a range of alkenes, however, had indicated<sup>3</sup> that the major pathway, certainly at higher nitrogen dioxide concentrations, is second order in [NO<sub>2</sub><sup>•</sup>] and this was attributed to initial attack by N<sub>2</sub>O<sub>4</sub> [Path (c), Scheme 1]. A further pathway<sup>2</sup> may involve reaction of the



intermediate carbon radical with N<sub>2</sub>O<sub>4</sub> [Path (b), Scheme 1]. The kinetic studies revealed a lowering of order at lower concentrations of nitrogen dioxide and evidence was presented which was interpreted as suggesting that hydrogen abstraction to form different products was the major reaction at low nitrogen dioxide concentrations for substrates with allylic hydrogen atoms, although such a pathway could not account for all the lowering of order. In the polarisation work<sup>2</sup> it was recognised that the overall <sup>15</sup>N polarisation observed could be that of Path (a) even if some of the reaction occurred by another pathway. A study of reaction with phenylethenes reports that a radical pathway is favoured although dinitro compounds are not listed amongst the identified products.<sup>4</sup> The present work was undertaken mainly with allylbenzene but also with 4-

phenylbut-1-ene, dodec-1-ene and phenylethene in order to assess the importance of the various possible pathways, particularly in allylbenzene where allylic reaction was expected to be facile.

Reaction of allylbenzene (0.01 mol dm<sup>-3</sup>) with nitrogen dioxide (0.1 mol dm<sup>-3</sup>) in cyclohexane at 30 °C for 1 h gave no sign of allylic substitution products. Initial products were the dinitro compound **1** (≈50%) and the nitronitrite **2** (≈43%) (from reaction of 7 × 10<sup>-3</sup> mol dm<sup>-3</sup> allylbenzene with 0.05 mol dm<sup>-3</sup> nitrogen dioxide in cyclohexane at 30 °C for 1 h). The nitronitrite subsequently reacts further to form the hydroxynitro compound **3** and some nitronitrate **4**. There was no significant change in the proportions of the products over the range of concentrations used in the kinetic studies.



Kinetic measurements were carried out by GLC on reactions at 30 °C with nitrogen dioxide in an excess ([N<sub>2</sub>O<sub>4</sub>] + 1/2[NO<sub>2</sub><sup>•</sup>] = 0.05–0.35 mol dm<sup>-3</sup> and [allylbenzene] = 4 × 10<sup>-3</sup>–1 × 10<sup>-2</sup> mol dm<sup>-3</sup>) in cyclohexane. First-order plots were linear over more than three half-lives and gave first-order rate coefficients (*k*<sub>obs</sub>/s<sup>-1</sup>). 4-Phenylbut-1-ene and dodec-1-ene were studied with quite similar results. Plots of *k*<sub>obs</sub> vs. [NO<sub>2</sub><sup>•</sup>] are given in Figs. 1 and 2 for allylbenzene and dodec-1-ene. The absence of light or oxygen and the variation of water content in the solvent medium did not have a significant effect on the rates of reaction for allylbenzene. In all three cases the kinetic results could be rationalised if contributions to the reaction rate from processes both first- and second-order in [NO<sub>2</sub><sup>•</sup>] were recognised.

$$k_{\text{obs}} = (k_2[\text{NO}_2^{\bullet}] + k_3[\text{NO}_2^{\bullet}]^2)$$

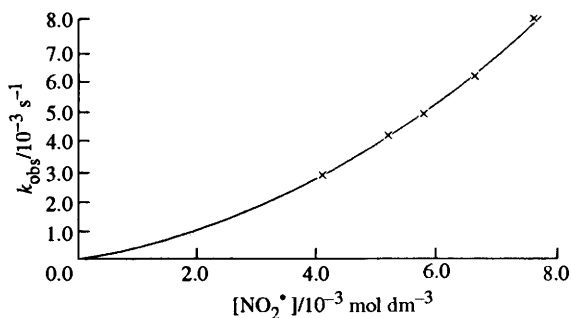
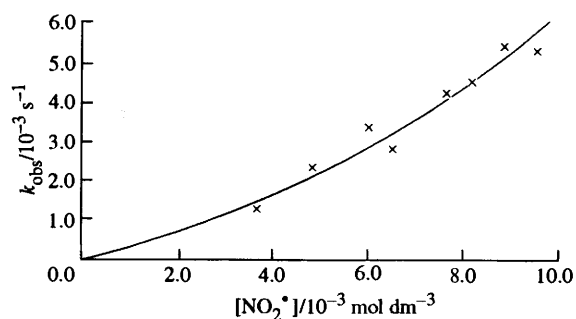
It is difficult to envisage a reaction involving NO<sub>2</sub><sup>•</sup> which is bimolecular in that species coexisting with a reaction which is unimolecular in the same species. A change in the rate limiting stage for reaction by Path (a) would lead to the second-order behaviour occurring at lower nitrogen dioxide concentrations. Accordingly the second-order dependence is attributed, as previously,<sup>3</sup> to bimolecular reaction with N<sub>2</sub>O<sub>4</sub>.

$$k_{\text{obs}} = k_2[\text{NO}_2^{\bullet}] + k_2'[\text{N}_2\text{O}_4] \\ (\text{where } k_2' = k_3K \text{ and } K = 2.64 \times 10^{-4} \text{ mol dm}^{-3} \text{ at } 30 \text{ }^\circ\text{C})^5$$

Measured values of *k*<sub>2</sub> are 0.26, 0.37 and 0.24 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and of *k*<sub>2</sub>' are 0.92 × 10<sup>-2</sup>, 1.3 × 10<sup>-2</sup> and 2.6 × 10<sup>-2</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for allylbenzene, 4-phenylbut-1-ene and dodec-1-ene,

<sup>†</sup> Present address: Department of Chemistry, Brunel University, Uxbridge, Middlesex, UK UB8 3PH.

<sup>‡</sup> The term nitrogen dioxide is used to describe the equilibrium mixture of NO<sub>2</sub><sup>•</sup> and N<sub>2</sub>O<sub>4</sub>. NO<sub>2</sub><sup>•</sup> and N<sub>2</sub>O<sub>4</sub> are used to describe the individual species.



**Figs. 1 and 2** Plots of  $k_{\text{obs}}$  vs.  $[\text{NO}_2^*]$  for the reactions of allylbenzene (Fig. 1) and dodec-1-ene (Fig. 2) with nitrogen dioxide in cyclohexane at 30 °C. (The lines are theoretical ones calculated as described in the text.)

respectively. The appropriate values were used to generate the curves shown in Figs. 1 and 2, illustrating the model's good agreement with the experimental data. However, in contrast to the earlier study<sup>3</sup> the first-order dependence is wholly attributed to Path (a) of Scheme 1 with the first stage rate limiting. The invariance of product proportions with nitrogen dioxide concentration suggests the presence of a common intermediate for the two pathways. The absence of allylic substitution products and the similarity of the  $k_2$  values for the three alkenes preclude allylic hydrogen abstraction being of importance even with allylbenzene. The reaction with styrene was too rapid for measurement by the technique employed.

Evidence concerning the nature of these reactions was then sought from CIDNP studies of the reactions using <sup>15</sup>N labelled nitrogen dioxide. <sup>15</sup>N NMR spectra were recorded during the reaction of allylbenzene (0.23 mol dm<sup>-3</sup>) with <sup>15</sup>N nitrogen dioxide (0.22 mol dm<sup>-3</sup>) in cyclohexane at ambient temperature. In the first spectrum of the nitro group region recorded after 1 min two absorption signals appeared at  $\delta$  4.9 and 7.8 (cf. Ph<sup>15</sup>NO<sub>2</sub> at  $\delta$  0.00), attributed to the 1-nitro groups of **1** and **2**, respectively. Both are enhanced by a factor of  $\approx 14$ . A third nitro group gives an emission signal enhanced by a factor of  $\approx 290$  at  $\delta$  13.1 attributed to the 2-nitro group of **1**. These peaks become progressively weaker over about 15 min and the final spectrum taken some time later shows unenhanced absorptions corresponding to the above three nitro groups together with one at  $\delta$  12.6 attributed to the nitro group of **3** and one at  $\delta$  196 attributed to the nitrite group of **2**. The assignments of the peaks were made by comparison of spectra

with those of product mixtures in which the presence of **1**, **3** and **4** had been established by various spectroscopic techniques. Small changes which occurred in the <sup>15</sup>N chemical shifts are attributed<sup>5</sup> to interaction with the medium. A point of note is that in the proton coupled <sup>15</sup>N spectra the primary nitro groups of **1** and **3** appeared as quartets ( $J_{\text{H-N}} = 1.9$  Hz) indicating similarity in the two- and three-bond coupling constants.

Similar CIDNP results were recorded for 4-phenylbut-1-ene and dodec-1-ene, the same pattern of enhanced absorptions, an enhanced emission and product peaks being observed. In the case of phenylethene no polarisation was observed, presumably because of the large rate of the reaction but a similar pattern of product peaks was obtained.

The CIDNP results make it clear that the behaviour previously reported<sup>1,2</sup> which indicates, by application of modified Kaptein's rules, that Path (a) is of significance, is general. Our kinetic results, however, enable us to estimate the contributions of Paths (a) and (b) to the overall reaction under the conditions of our CIDNP experiments. For allylbenzene at 25 °C  $k_2[\text{NO}_2^*] \approx 1.7 \times 10^{-3} \text{ s}^{-1}$  and  $k_2'[\text{N}_2\text{O}_4] \approx 2.0 \times 10^{-3} \text{ s}^{-1}$ . These pathways should have opposing consequences for <sup>15</sup>N nuclear polarisation<sup>1,2</sup> and it is clear that the consequences of Path (a) predominate even when the contributions of the two pathways to the reaction are comparable. This could be the case if the reaction of singlet radical pairs formed on Path (c) is rapid and faster than the rate of singlet to triplet interconversion to such an extent that any escape from the radical pair, necessary for polarisation, is minimised. With Path (a) the presence of some triplet radical pairs, formed on diffusion together of the radicals, which must undergo triplet to singlet interconversion before reaction may allow time for more escape from the cage and consequently greater polarisation.

We conclude that both NO<sub>2</sub><sup>\*</sup> and N<sub>2</sub>O<sub>4</sub> are significant reactive species towards alkenes forming addition products even when hydrogen abstraction might be expected to be facile. It was recognised earlier<sup>2</sup> that CIDNP results did not exclude other reaction pathways. Our results reinforce this reservation. Caution must be exercised in the interpretation of results from CIDNP experiments when alternative pathways are available. Observation of the pattern attributed to a particular pathway does not indicate that it is the only or even the major pathway.

The award of a research studentship by Shell Research Ltd to J. C. is gratefully acknowledged, as is the assistance of Dr S. R. Natrass with the CIDNP experiments and the advice and guidance of Dr R. C. Coy.

## References

- 1 J. L. Powell, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Chem. Commun.*, 1990, 402.
- 2 J. L. Powell, J. H. Ridd and J. P. B. Sandall, *Appl. Magn. Reson.*, 1993, **5**, 151.
- 3 D. H. Giamalva, G. B. Kenion, D. F. Church and W. A. Pryor, *J. Am. Chem. Soc.*, 1987, **109**, 7059.
- 4 D. K. Bryant, B. C. Challis and J. Iley, *J. Chem. Soc., Chem. Commun.*, 1989, 1027.
- 5 J. Chatterjee, PhD Thesis, City University, London, 1993.

Paper 5/00604J  
Received 1st February 1995  
Accepted 20th March 1995