

The Reaction of Phenylethenes with NO₂

Duncan K. Bryant, Brian C. Challis,* and Jim Iley

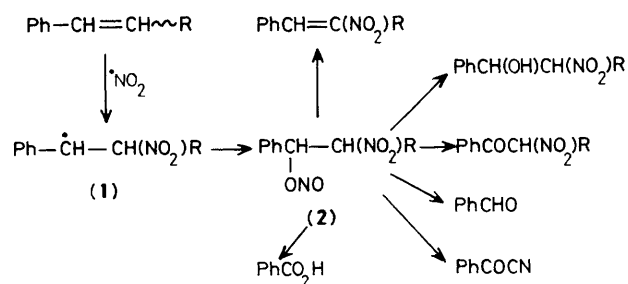
POCRG, Chemistry Department, The Open University, Milton Keynes, MK7 6AA, U.K.

Nitrogen dioxide reacts with phenylethenes to yield several products [PhCHO, PhCOCN, PhCO₂H, PhCH=CHNO₂, PhCOCH₂NO₂, PhCH(OH)CH₂NO₂] that can be explained by radical addition of two NO₂ molecules; the relevance of these reactions to the formation of nitropolycyclic aromatic hydrocarbons in the environment is discussed.

The reaction of nitrogen dioxide, or its dimer dinitrogen tetroxide, with polycyclic aromatic hydrocarbons (PAHs) and other unsaturated systems is of considerable interest to the formation of various environmental toxicants.^{1–5} Many of the more reactive PAHs such as phenanthrene and the higher acenes have carbon–carbon bonds with considerable alkenic character but they are still somewhat unreactive towards gaseous NO₂ (see later). Here, in an attempt to probe the alkenic reactivity of PAHs towards NO₂, we report on the reactions of various phenylethenes. In recent studies, Pryor and his colleagues have stressed the importance of allylic-H abstraction for the reaction of alkenes with NO₂,⁶ but this pathway is not relevant to our substrates or PAHs.

Thus, the reaction of styrene (0.1 M) in carbon tetrachloride with NO₂ (10 000 p.p.m.) at 25 °C readily gives rise to a similar array of products (Table 1) under aerobic and anaerobic conditions. The formation of these products can be explained

best by the formation of the 2-nitro-1-phenylethyl nitrite intermediate (2) (Scheme 1). Various substituted styrenes and stilbenes react similarly, and we believe that the radical addition shown is the preferred pathway.



Scheme 1. Reaction of NO₂ with PhCH=CHR.

Table 1. Product distribution from the reactions of PhCH=CHR with NO₂ at 25 °C.^a

| Product | Yield/% | | |
|------------------------------|--------------------|------------------|------------------|
| | R = H | R = <i>E</i> -Ph | R = <i>Z</i> -Ph |
| PhCHO | 9 (7) ^b | 58 | 39 |
| PhCOCN | 1 (1) | — | — |
| PhCO ₂ H | 1 (5) | 2 | — |
| PhCH=C(R)NO ₂ | 12 (1) | 16 | 33 |
| PhCOCH(R)NO ₂ | 29 (31) | — | — |
| PhCH(OH)CH(R)NO ₂ | 24 (33) | — | — |
| PhCOCOR | — | 4 | 13 |
| Unidentified products | 24 (22) | 20 | 15 |

^a Identified by g.c./m.s. by comparison to authentic materials.^b Figures in parenthesis under N₂ (anaerobic).**Table 2.** Relative reactivities of ArCH=CHR towards NO₂.

| Ar | R | Reactivity relative to styrene |
|---|--------------|--------------------------------|
| 4-MeOC ₆ H ₄ | H | 2.00 |
| 4-MeC ₆ H ₄ | H | 1.41 |
| Ph | H | 1.00 |
| 4-ClC ₆ H ₄ | H | 0.71 |
| 4-CNC ₆ H ₄ | H | 0.26 |
| 4-NO ₂ C ₆ H ₄ | H | 0.13 |
| Ph | <i>E</i> -Ph | 0.58 |
| Ph | <i>Z</i> -Ph | 0.06 |

Further evidence for the radical pathway comes from the reactivities of a number of *p*-substituted styrenes towards NO₂, relative to styrene itself. These are given in Table 2. The resulting Hammett plot yields a value of ρ of -0.91 ($r^2 = 0.99$), which is rather small and indicates that a carbocation intermediate is unlikely to be involved (such electrophilic

reactions have ρ values *ca.* -4^7). Indeed, recent work on the formation of benzylic radicals reports a Hammett ρ value of -0.66 .⁸ We thus infer that the β -nitrophenethylradical (**1**) is formed in these reactions (Scheme 1). Further, there is no evidence (compare aerobic with anerobic conditions) of significant interception of (**1**) by dioxygen.

Reactions of *Z*- and *E*-1,2-diphenylethene with NO₂ yield a spectrum of products similar to those of styrene (Table 1), with reactivities relative to styrene of 0.58 and 0.06, respectively. The low reactivity of the *E*-isomer, which has a more conjugated double bond than the twisted *Z*-isomer, as it can adopt a coplanar conformation, indicates that the extent of conjugation is crucial to the rate of reaction. This is further demonstrated by the cyclic analogue of the *Z*-isomer, phenanthrene, which can only adopt a coplanar arrangement of the double bonds and is unreactive to NO₂ ($<10\,000$ p.p.m.). Interestingly, phenanthrene reacts readily with N₂O₄ in solution to form 9-nitrophenanthrene. Environmental ring nitration of PAHs is therefore most unlikely to occur *via* radical addition of NO₂, and an electron transfer mechanism (if the half-wave oxidation potential of the PAH is low enough) or reaction with N₂O₄ are more probable pathways.

Received, 22nd March 1989; Com. 9/01240K

References

- 1 J. A. DiPaulo, A. J. DeMannis, A. J. Chow, F. L. Garner, R. C. Martin, and J. Doniger, *Carcinogenesis*, 1983, **4**, 357.
- 2 L. Eberson and F. Radner, *Acta Chem. Scand., Ser. B.*, 1985, **39**, 34.
- 3 W. A. Pryor, J. P. Stanley, E. Blair, and G. B. Cullen, *Arch. Environ. Health*, 1976, **31**, 201.
- 4 D. H. Giamalva, G. B. Kenion, D. F. Church, and W. A. Pryor, *J. Am. Chem. Soc.*, 1987, **109**, 7059.
- 5 R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.*, 1984, **16**, 697.
- 6 W. A. Pryor, J. W. Lightsey, and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 6685 and references cited therein.
- 7 H. C. Brown and Y. Okamoto, *J. Org. Chem.*, 1957, **22**, 485.
- 8 S. Kim, H. Koo, and S. Choi, *Tetrahedron Lett.*, 1985, **26**, 891.