

## A New Kinetic Form for Nitrous Acid Catalysed Nitration: Second-order with respect to the Aromatic Compound

J. Ramón Leis,† M. Elena Pëna,† and John H. Ridd\*

Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ, U.K.

As the concentration of naphthalene is increased, the nitrous acid catalysed nitration of naphthalene in aqueous mixtures of acetic and sulphuric acid becomes second-order with respect to the naphthalene.

Aromatic nitration can give rise to a number of kinetic equations<sup>1,2</sup> but, in none of the established reaction paths, does the order with respect to the aromatic compound exceed unity. One reaction, however, provides evidence of a higher order, for the nitrous acid catalysed nitration of naphthalene in aqueous sulphuric acid has been reported to have an order of 1.5 with respect to the aromatic compound;<sup>3</sup> this was considered to derive from an initial electron transfer followed by an unspecified chain reaction.

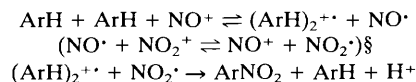
We have reinvestigated this reaction using the same method (u.v. spectroscopy)<sup>3</sup> but with aqueous mixtures of acetic and sulphuric acids as the solvent; more acetic acid is required when the higher concentrations of naphthalene are used. The

variation of the half-life with the concentration of naphthalene (Figure 1) under conditions where the nitric acid is present in large excess shows a transition from first-order to second-order kinetics with respect to naphthalene. ‡ An analysis of the initial rates leads to the same conclusion. The kinetic runs in each of the two sets shown in Figure 1 have been analysed by a computer program and the results accord with equation (1): thus, for  $[\text{ArH}] = 3.9 \times 10^{-5}$  to  $3.13 \times 10^{-4} \text{ mol dm}^{-3}$  (set A),  $k_1 = (1.45 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$  and  $k_2 = (14.9 \pm 2.4) \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$ .

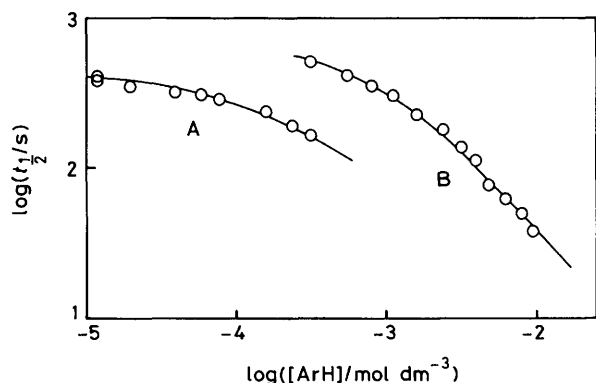
$$\text{Rate} = k_1[\text{ArH}] + k_2[\text{ArH}]^2 \quad (1)$$

The variation of  $k_1$  and  $k_2$  with the concentrations of nitrous and nitric acid has also been studied. For  $k_1$ , this variation shows the changes in the order with respect to nitrous and nitric acid characteristic of the two rate-determining stages in the mechanism for nitrous acid catalysed nitration put forward previously.<sup>2a</sup> The variation of  $k_2$  is very similar to that of  $k_1$  (illustrated with respect to nitrous acid in Figure 2). To explain the second term in equation (1), it is therefore necessary to show how a second molecule of naphthalene can be included in the earlier mechanism.

The proposed reaction path for the second-order term is shown in Scheme 1. The first stage, forming the cation radical of the  $\pi$ -dimer of naphthalene, is a known reaction<sup>4</sup> and, as before,<sup>2a</sup> the change in the rate-determining step from the first to the third stage of Scheme 1 explains the change in the order



Scheme 1

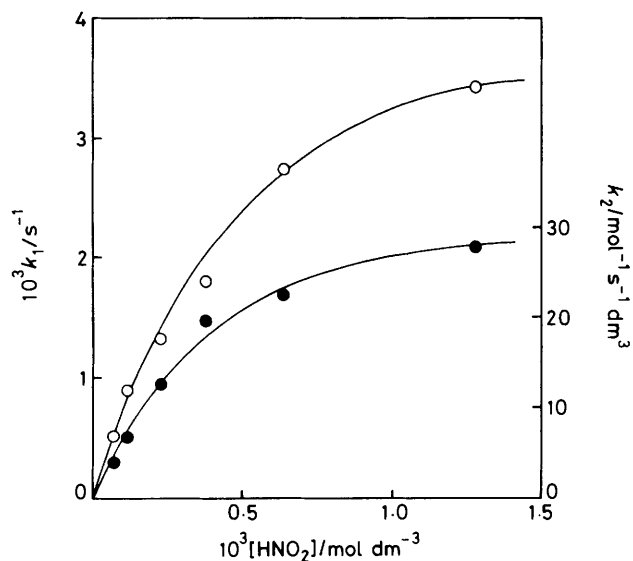


**Figure 1.** The variation of the half-life with the initial concentration of naphthalene. Series A:  $\text{H}_2\text{SO}_4$ , 52.2%;  $\text{HOAc}$ , 4.9%;  $[\text{HNO}_2] = 2.3 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{HNO}_3] = 0.01 \text{ mol dm}^{-3}$ . Series B:  $\text{H}_2\text{SO}_4$ , 46.5%;  $\text{HOAc}$ , 27.8%;  $[\text{HNO}_2] = 2.39 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{HNO}_3] = 0.084 \text{ mol dm}^{-3}$ . Temperature = 25 °C. The line for Series B is drawn to have a final slope of  $-1$ .

† Present address: Departamento de Química Física, Universidad de Santiago, E-Santiago de Compostela, Spain.

‡ At these acidities, the rate of reaction through the nitronium ion is too slow to be significant.

§ This stage shows the stoichiometry involved, not the mechanism.



**Figure 2.** The variation of  $k_1$  (open circles) and  $k_2$  (filled circles) with the initial concentration of nitrous acid.  $[\text{ArH}] = 3.13 \times 10^{-4} \text{ mol dm}^{-3}$ . The other conditions are as used for Series A (Figure 1).

with respect to nitrous acid (Figure 2). Such stabilisation of radical cations by  $\pi$ -dimerisation occurs widely,<sup>5</sup> even with hexamethylbenzene.<sup>6</sup> The present work therefore suggests that, for many of the more reactive aromatic compounds, reaction paths involving electron transfer in nitration will become more important as the concentration of the aromatic compound is increased, irrespective of the species accepting the electron.

Two of us (J. R. L. and M. E. P.) thank the Rectorado of the University of Santiago for financial support.

Received, 26th January 1988; Com. 8/00286J

### References

- 1 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, 1980, Ch. 7.
- 2 (a) M. Ali and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1986, 327; (b) U. Al-Obaidi and R. B. Moodie, *ibid.*, 1985, 467.
- 3 D. S. Ross, K. D. Moran, and R. Malhotra, *J. Org. Chem.*, 1983, **48**, 2218.
- 4 A. S. Morkovnik and O. Yu. Okhlobystin, *Zh. Obshch. Khim.*, 1985, **55**, 692.
- 5 A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **13**, 155.
- 6 W. Lau and J. K. Kochi, *J. Org. Chem.*, 1986, **51**, 1801.