Kinetics and Stereochemistry of Elimination Reactions in Tertiary Nitroalkanes: a Measure of the Nucleofugacity of Nitrite Ion from a Saturated Carbon

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Summary The reaction of methoxide ion in 50% (v/v) methanol–dimethyl sulphoxide with *p*-(2-methyl-2-nitropropyl)nitrobenzene and its derivatives shows that the elimination reaction taking place is a concerted anti-periplanar *E*2 process and that the nucleofugacity of nitrite ion in this system lies between that of bromide and chloride ions.

Elimination of nitrous acid from nitroalkanes has been used only to an extremely limited extent as a method for preparation of alkenes, despite its synthetic utility and apparent facility.[1] Since no quantitative studies on nitrous acid eliminations, except for indirect measurements on sequential elimination and addition reactions in 1,1,1-trinitroalkanes,[2] have been reported, and since we have observed ready elimination in 1-*p*-nitrophenyl-2-nitroalkanes[3] we studied this latter system in detail.

Elimination of nitrous acid from compounds (**1**)–(**3**) and (**6**) and of hydrogen halide from compounds (**4**) and (**5**) gave the second order rate constants listed in the Table. The products from these reactions, the styrene (**8**) from (**1**) and (**3**)–(**5**), the deuterio-styrene (**9**) from (**2**) and (**3**), and the (*E*)-styrene (**10**) from (**6**), were obtained in 93–98% yields. The large primary kinetic isotope effect (5—7)† indicates that the elimination involves a near concerted loss of the α-proton and the β-nitro group.[4]

$p\text{-}NO_2C_6H_4CR^1R^2CMeR^3X$

(**1**) $R^1 = R^2 = H,\ R^3 = Me,\ X = NO_2$
(**2**) $R^1 = R^2 = D,\ R^3 = Me,\ X = NO_2$
(**3**) $R^1 = H,\ R^2 = D,\ R^3 = Me,\ X = NO_2$
(**4**) $R^1 = R^2 = H,\ R^3 = Me,\ X = Br$
(**5**) $R^1 = R^2 = H,\ R^3 = Me,\ X = Cl$
(**6**) $R^1 = R^2 = H,\ R^3 = Bu^t,\ X = NO_2$
(**7**) $R^1 = H,\ R^2 = D,\ R^3 = Bu^t,\ X = NO_2$

$p\text{-}NO_2C_6H_4CR{=}CMe_2$

(**8**) R = H
(**9**) R = D

$(E)\text{-}p\text{-}NO_2C_6H_4CR{=}CMeBu^t$

(**10**) R = H
(**11**) R = D

The rates of reaction of (**1**), (**4**), and (**5**) give a measure of the relative nucleofugacity of nitrite, bromide, and chloride ions. The intermediate position of the nitrite ion ($Br^- > NO_2^- > Cl^-$) is surprising when one considers the generally accepted correlation of nucleofugacity with the strength of the conjugate acid of the leaving group.[5] This represents the first quantitative measure of the nucleofugacity of the nitrite ion. It is only recently that nitrite has been demonstrated as a leaving group in ionic bimolecular substitution reactions.[6]

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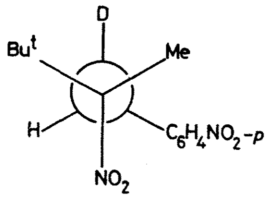
† The difference in the values of k_H/k_D obtained for compounds (**1**)—(**3**) are of the correct magnitude and direction for operation of a secondary (α) kinetic isotope effect (E. R. Thornton, *Ann. Rev. Phys. Chem.*, 1966, **17**, 349).

TABLE. Rate constants (l mol^{-1} s^{-1}) for the methoxide ion induced elimination reactions in compounds (**1**)—(**6**) in 50% (v/v) methanol–dimethyl sulphoxide at 20 °C.

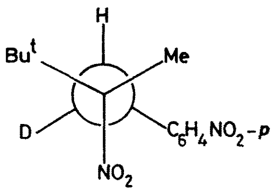
Compound	10^4k	k_H/k_D
(**1**)	31·7 ± 0·7	6·5 ± 0·4[a]
(**2**)	4·9 ± 0·2	
(**3**)	17·8 ± 0·5	5·2 ± 0·2[b]
(**4**)	310 ± 25	
(**5**)	11·2 ± 0·3	
(**6**)	3·7 ± 0·4	

[a] Calculated from k_H in (**1**) and k_D in (**2**). [b] Determined from the product ratio (**9**):(**8**); whence 10^4k_H and 10^4k_D in (**3**) are 30 ± 1 and 6 ± 1 l mol^{-1} s^{-1} respectively.

The stereochemistry of the nitrous acid elimination was readily demonstrated by competitive elimination of nitrous acid from the two diastereoisomers of (**7**), which gave mixtures of (**10**) and (**11**). These two diastereoisomers are shown in their preferred conformations (**12**) and (**13**).‡



(**12**)



(**13**)

The ratio of stereoisomers (**12**)/(**13**) varied as a function of percentage elimination as follows: 1·07 (0%), 1·29 (11%), 1·94 (18%), and 3·23 (48%). These results clearly demonstrate that not only is the reaction occurring *via* an antiperiplanar transition state but also that a substantial kinetic isotope effect is operating.

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‡ Assigned on steric grounds, and by ^{1}H n.m.r. spectroscopy.

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