On the Electron Impact Induced Hydroxyl Loss from *o*-Nitrostyrene†

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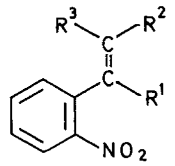
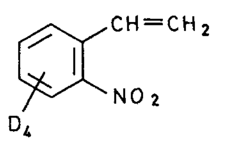
Unimolecular hydroxyl (OD˙) loss from regio- and stereo-specifically labelled *o*-nitrostyrenes 1a, 1c and 1d results in the formation of an ion which upon collisional activation gives identical mass spectra. Suggestions are made which aim at explaining: (i) the loss of stereochemical integrity of the diastereotopic methylene hydrogens in the course of hydroxyl elimination; and (ii) to account for the collision induced losses of CO and HNC from the [M−hydroxyl]$^+$ ion.

The unexpectedly rich gas phase chemistry of ionized nitroarenes is intimately connected with the name of John H. Beynon, and our present understanding of many of its features is mainly due to his work. By performing exact mass measurements in the early sixties,[1] investigating labelled compounds,[2] determining the kinetic energy releases associated with unimolecular decomposition,[3] and studying dissociations induced either by inelastic collisions of ions with target molecules[4] or photon absorption[5] in this work, Beynon and coworkers also introduced new methodologies into mass spectrometry which have proved extremely valuable for fundamental studies. In fact, his work on the mass spectrometric behaviour of nitroarenes constitutes a hallmark for in-depth mechanistic investigations which have themselves prompted related studies in many other laboratories.

Of particular interest in this context is the loss of hydroxyl radical from appropriately *ortho*-substituted nitroarenes whose prototype, that from *o*-nitrotoluene, was first studied as early as 1959 by Beynon, Lester and Williams,[6] and later by other groups.[7] Hydroxyl loss from ionized nitrobenzene derivatives is now regarded as paradigmatic for the operation of an *ortho* effect,[8] although there are many systems known in which OH˙ loss does occur from *meta*- and *para*-substituted benzene derivatives.[9]

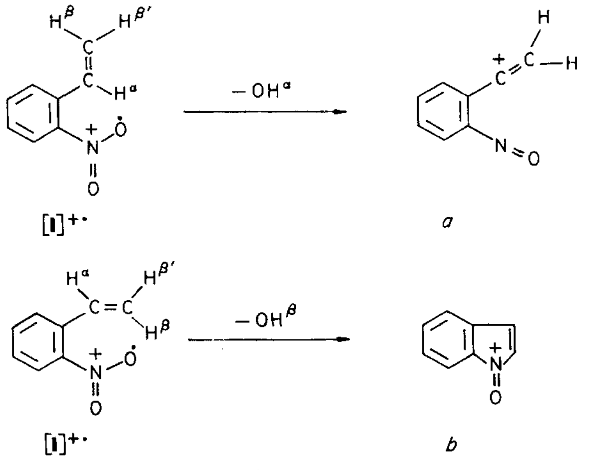


	R1	R2	R3
1	H	H	H
1a	D	H	H
1b	H	D	D
1c	H	H	D
1d	H	D	H



1e

We wish to report results on the unimolecular hydroxyl loss from the molecular ion of *o*-nitrostyrene (**1**) ($R^1 = R^2 = R^3 = H$), another classical case for the (potential) operation of an *ortho* effect. Our study complements the early work of Middleton *et al.*[10] on the mass spectrometric behaviour of *ar*-nitrostyrenes. The molecular ion of **1** undergoes unimolecular loss of OH˙ (40% rel. int.), and the investigation of the D-labelled isotopomers **1a** and **1b** revealed[10] that the hydrogen of the hydroxyl radical originated predominantly (i.e. 76%) from the β-position and 18% from C(α). The origin of the remaining 6% could neither be accounted for (discrimination of OD˙ loss due to the operation of a kinetic isotope effect or contribution of the arene hydrogens?), nor could the diastereotopic hydrogens of C(β) be differentiated with respect to their relative contributions to OH˙ loss. Moreover, this previous study did not attempt to substantiate the inference of two different product ion structures (*a* and *b*) as a result of H(α) and H(β) abstraction (only *cis* site accessible), respectively (Scheme 1). It is obvious that confirmation of the formation of two different



Scheme 1

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† See Ref. 13.

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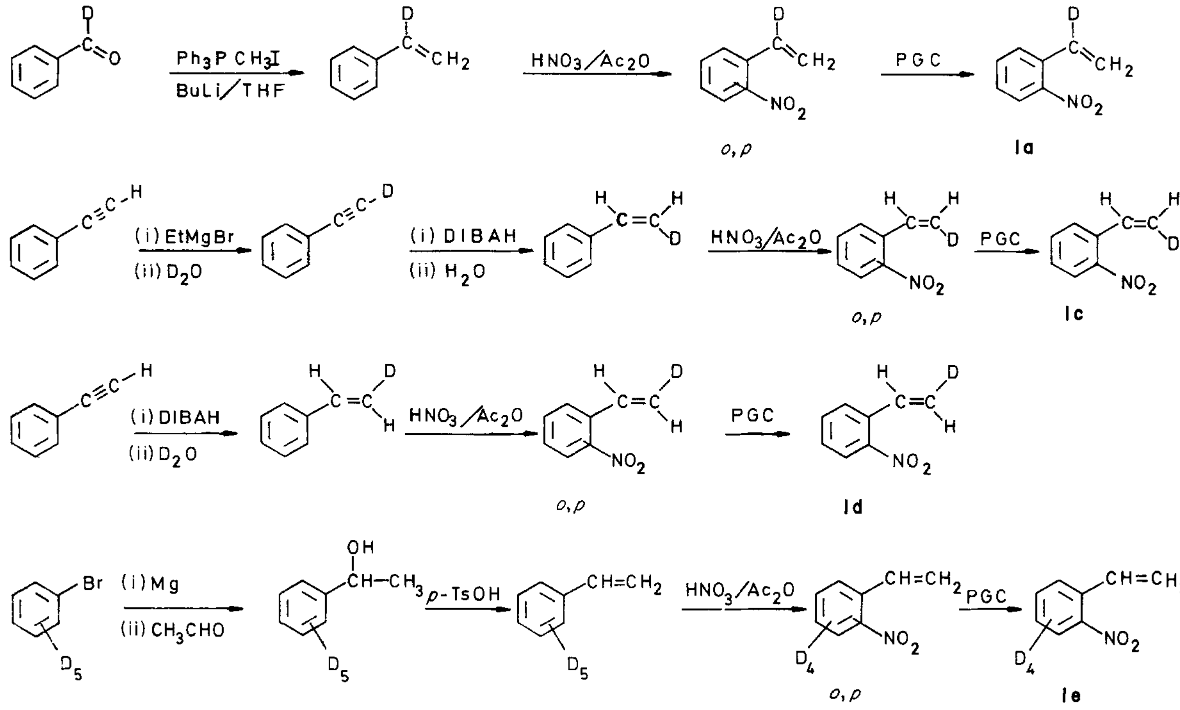
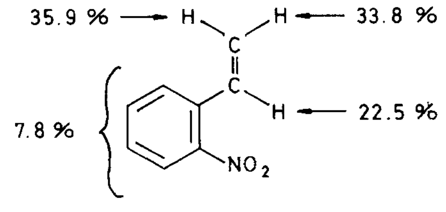


Scheme 2

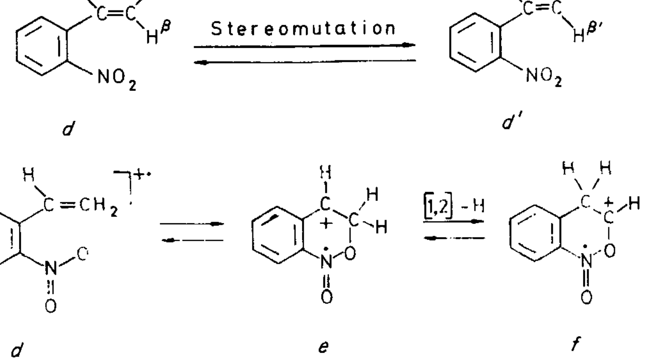
structures for the $[M-OD]^+$ ions from **1a** and **1b** could be taken as strong evidence for the operation of (at least) two independent competing decomposition channels. Moreover, it may be of interest to know whether there is a preference of R^3 over R^2 to be eliminated as $OH^{\cdot}$ as should be the case, as long as there is no stereomutation around the carbon–carbon double bond making the diastereotopic hydrogens R^2/R^3 indistinguishable. Probing this question requires, of course, investigation of stereospecifically labelled *o*-nitrostyrenes, as for example **1c** and **1d**. In fact, there is ample evidence[11] from theoretical work that the barrier for rotation around the carbon–carbon double bond is substantially lower for alkene carbon radicals when compared with their neutral counterparts.

As part of a comprehensive study[9b,c] of the mass spectrometric behaviour of *nitro*-substituted arenes we have, among other substrates, synthesized, by unambiguous, well-established methods (Scheme 2),[9b,c] the regio- and stereo-specifically labelled compounds **1a**, **1c** and **1d** and, in addition, the ring-labelled isotopomer, **1e**. As mandatory for a mechanistic study all the compounds in Scheme 2 were fully characterized by spectroscopic techniques, in particular NMR spectroscopy, in order to ensure their stereochemical integrity. Moreover, heating of the nitrostyrenes under reflux as well as separation of the *ortho*/*para* mixtures, obtained in the nitration, by preparative gas chromatography (PGC) did not give rise to exchange of hydrogen within the vinyl group. Thus, one has to conclude that the vinylic hydrogens are both positionally and stereochemically stable under thermal excitation.

The mass spectrometric analysis (70 eV electron impact) of **1a**, **1c**, **1d** and **1e**, respectively, revealed that the hydroxyl hydrogen originated from the sites of the molecular ion to the extents given in formula *c*. In agreement with Middleton's observation the hydrogen eliminated as a hydroxyl radical is preferentially supplied by the vinyl group, although the arene ring, in total, contributes as much as 7.8%. Undoubtedly, the most striking result is the nearly equal contribution of both (in the neutral molecule diastereotopic) hydrogens of C(β). This requires, of course, an equilibration of the two hydrogens $H^{\beta}/H^{\beta'}$ prior to hydroxyl loss, because in a stereochemically intact vinyl group no *trans* hydrogen ($H^{\beta'}$) of ion *d* (Scheme 3) is



c



Scheme 3

geometrically accessible to the NO_2 function. There are two obvious models by which such equilibration can be brought about. Mechanistically more simple, a stereomutation of the ionized carbon–carbon double bond, e.g. process $d \rightleftarrows d'$ (Scheme 3), could take place without affecting the positional integrity of $H(\alpha)$. A feasible, alternative isomerization involves neighbouring group participation by the NO_2 group in the course of an attack at the stereochemically intact double bond ($d \rightleftarrows e$); thereby, a carbenium centre is generated which, *per se*, could initiate facile, reversible [1, 2]-hydride shifts ($e \rightleftarrows f$). The latter (or similar processes, as for example attack of the NO_2 group at $C(\alpha)$) reactions would, to some degree, result in the loss of both positional and stereochemical indentity of all three vinylic hydrogens. The very same situation would naturally arise if an isomerization nitro $\rightleftarrows$ nitrito ($RNO_2^{+\cdot} \rightleftarrows RONO^{+\cdot}$) precedes the processes depicted in Scheme 3 (see below, Scheme 5). From the labelling data alone it is not easy to decide which mechanism(s) is operative. The contribution to the hydroxyl formation by $C(\alpha)$ is somewhat smaller than that of $C(\beta)$ (22.5% versus 33.8% and 35.9%, respectively). This disparity could be readily accounted for by two distinctly different elimination routes ($[\mathbf{1}]^{+\cdot} \rightarrow a$ and $[\mathbf{1}]^{+\cdot} \rightarrow b$), as invoked by Middleton,[10] which are preceded by a simple stereomutation of the carbon–carbon double bond ($d \rightleftarrows d'$). Alternatively, one may argue that hydroxyl loss occurs from a common precursor, which makes all vinylic hydrogens largely indistinguishable. At first sight, the data given in formula *c* seem to be in favour of the first model, although the observed differences may also well be due to: (i) isotope effects; and (ii) combinations of several competing elimination processes.

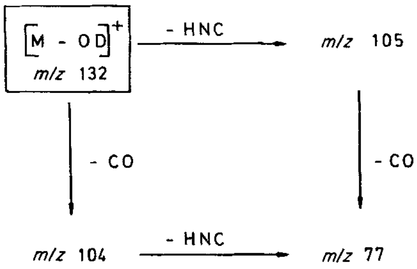
Table 1. Collision induced dissociations of $[\mathbf{M}-\mathbf{OD}]^+$ ions (m/z 132) generated from 1a, 1c and 1d,[a] and kinetic energy release, $T_k^{0.5}$, for the process $[\mathbf{M}]^{+\cdot} \rightarrow [\mathbf{M}-\mathbf{OD}]^+$

	1a	1c	1d
m/z = 132	38.9	39.2	40.2
105	2.1	2.0	2.2
104	35.9	36.6	36.2
77	23.1	22.2	21.4
$T_k^{0.5}$ (kJ mol^{-1})[b]	20.7	33.1	23.4
n	2.1	2.0	2.2

[a] Data are expressed in % total ion current.

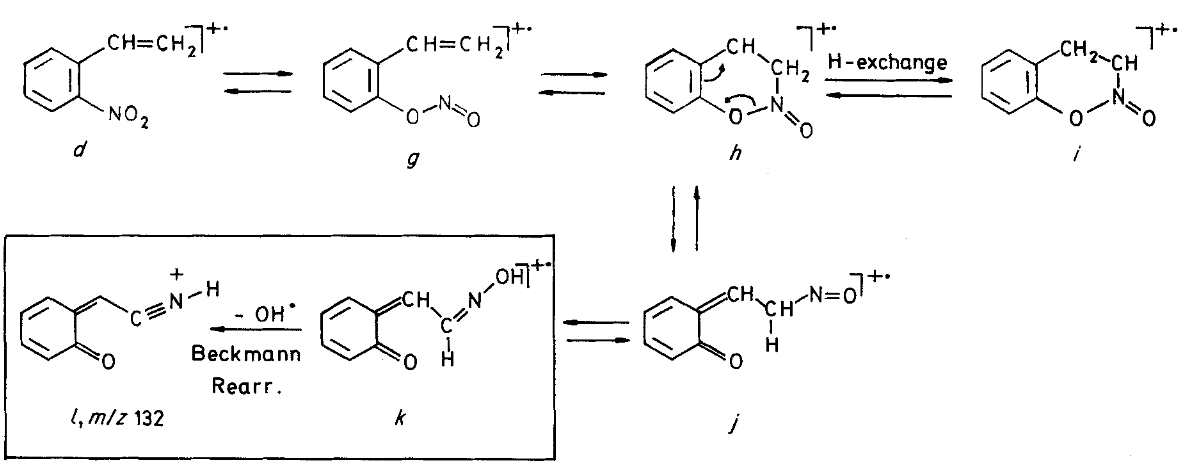
[b] All signals for the reaction $[M]^{+\cdot} \rightarrow [M-OD]^+$ are of pure Gaussian type with n values[12] given in the table.

However, evidence for the second model, i.e. the loss of hydroxyl from $[M]^{+\cdot}$ via formation of a single fragment ion structure irrespective of the origin of the hydroxyl hydrogen ($C(\alpha)$ or $C(\beta)$), is provided by the collision induced dissociation (CID) of the $[M-OD]^+$ ions (m/z 132) generated from **1a**, **1c** and **1d**, respectively. The CID spectra given in Table 1 are, within experimental error, identical for the three mass-selected parents, pointing to the formation of a common ion structure for the long-lived daughter ion, which itself undergoes the collision induced decomposition outlined in Scheme 4. Although the present data do certainly exclude the mechanisms suggested in the literature[10] and outlined in Scheme 1, they do not provide us with unambiguous evidence for a specific structure of the $[M-OD]^+$ ion and the detailed pathway via which the ion is generated. The observed collision induced losses of HNC and CO do, however, point to a structure from which upon excitation these two neutrals may be eliminated (*l*, Scheme 5). Some chemically reasonable rationalization is given in Scheme 5, requiring, however, future investigation in order to be verified.



Scheme 4

We have also determined the kinetic energy releases $T_k^{0.5}$, associated with $OD^\cdot$ losses from the molecular ions of **1a**, **1c** and **1d**, respectively. The data, which are compiled in Table 1 are, unfortunately, of no help in obtaining deeper insight into the course of hydroxyl



Scheme 5

loss from ionized *o*-nitrostyrene. This is not entirely surprising in view of the complex pathways which the molecular ions have to follow.

EXPERIMENTAL

Full mass spectra were recorded on a Varian CH 7 mass spectrometer (ionizing energy 70 eV, emission current 300 μA, ion source temperature 200 °C, direct sample insertion). Kinetic energy release measurements were performed by using a Varian MAT 711 instrument. The collision induced dissociations of the $[M-OD]^+$ ions were recorded in an on-line GC/MS/MS experiment operating a Finnigan Triple-Stage-Quadrupole (TSQ) mass spectrometer under the following conditions: ionizing energy 70 eV, emission current 250 μA, ion source temperature 200 °C. For mass selection of the $[M-OD]^+$ ion Q_1 was set at m/z 132 and Q_3 repetitively scanned over the mass range 20–200 in order to record collision induced fragment ions. Krypton (pressure *c*. 1 mTorr) is used as a collision gas in Q_2 (RF only mode; collision energy 15 eV). GC conditions were as follows: glass capillary column 20 m × 0.3 mm, SE-54, helium as carrier gas, temperature 60–200 °C (2 °C/min).

As already mentioned, all compounds, described in Scheme 2, were obtained by well-established procedures and fully characterized by means of spectroscopic methods.[9b,c] Only for the products **1a**, **1c**, **1d** and **1e** are the relevant ^{1}H NMR data given (EM 390 Varian: δ values, tetramethylsilane as internal standard).

2-Nitro-[α-D]-styrene (1a). dd 7.90 (1H) $J = 7.5$ and 2 Hz; m 7.66–7.23 (3H); m 5.77–5.60 (1H); m 5.50–5.37 (1H). $D_1 = 98\%$.

2-Nitro-(Z)-[β-D]-styrene (1c). dd 7.90 (1H) $J = 7.5$ and 2 Hz; m 7.67–7.23 (3H); d 7.18 (1H) $J = 11$ Hz; d 5.43 (1H) $J = 11$ Hz. $D_1 = 98\%$.

2-Nitro-(E)-[β-D]-styrene (1d). dd 7.90 (1H) $J = 7.5$ and 2 Hz; m 7.80–7.30 (3H); d 7.18 (1H) $J = 16$ Hz; d 5.67 (1H) $J = 16$ Hz. $D_1 = 98\%$.

[3, 4, 5, 6-D_4]-2-Nitrostyrene (1e). dd 7.20 (1H) $J = 17$ and 11 Hz; d 5.70 (1H) $J = 17$ Hz; d 5.47 (1*H*) $J = 11$ Hz. $D_4 = 99\%$.

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