Do Deprotonated Amidoximes Undergo the Tiemann Rearrangement in the Gas Phase?

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The Tiemann rearrangement in the condensed phase involves base-catalysed transformation of suitably substituted amidoximes to ureas, *e.g.*

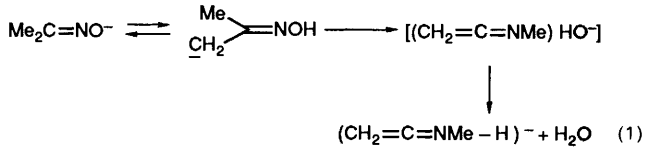
$$R^1(NH_2)C{=}NOR^2 \xrightarrow{\text{base}} NH{=}C{=}NR^1 \xrightarrow{H_2O} R^1NHCONH_2$$

In contrast, deprotonated amidoximes, in the gas phase, undergo only minor reaction through Tiemann intermediates. Instead, they decompose by loss of hydroxylamine, *e.g.*

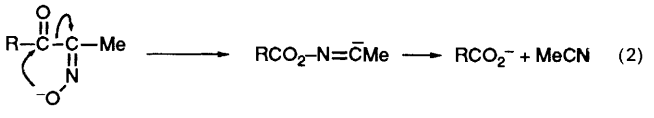
$$^-NHC(Me){=}NOH \longleftrightarrow NH{=}C(Me) - \bar{N}OH \longrightarrow [(MeCN)^-NHOH] \longrightarrow {}^-CH_2CN + NH_2OH$$

a process substantiated by ^{15}N and ^2H labelling and product-ion studies.

We have proposed that the collision-induced loss of water from deprotonated oximes in the gas phase is best rationalised by a negative ion Beckmann rearrangement [eqn. (1)].[1] However, deprotonated oximes sometimes undergo other rearrangements in preference to the Beckmann rearrangement. For example, α-oximino carbonyl compounds undergo the cyclisation/dissociation shown in eqn. (2).[2] There are also other oximes, which because of their structural features, cannot undergo the negative ion Beckmann rearrangement. In such cases, other rearrangement reactions are observed: one example is shown in eqn. (3).[1]



(1)



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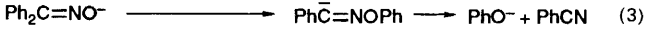

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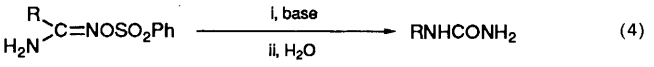

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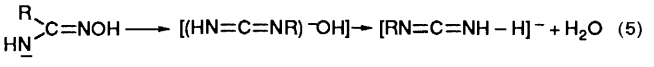


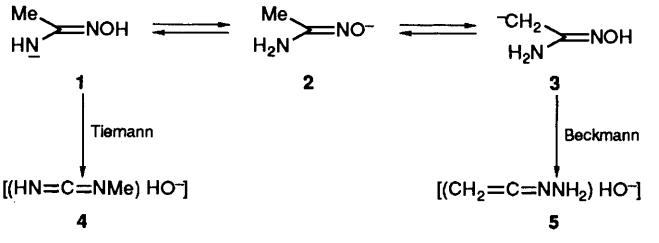
(5)

There is a base-catalysed solution reaction that is very similar to the proposed gas phase negative ion Beckmann rearrangement. This reaction, called the Tiemann rearrangement, involves the conversion of suitably substituted amidoximes to urea derivatives. The reaction was first reported one hundred years ago and is summarised in eqn. (4).[3,4] If this reaction occurs in the gas phase with deprotonated amidoximes, then it is analogous to the negative ion Beckmann rearrangement and a major fragmentation should be loss of water [see eqn. (5)]. In this paper we explore the collision-induced dissociations of deprotonated amidoximes and cognate systems with a view to determining whether there is a correlation between the gas and condensed-phase reactivities for this system.

Results and Discussion

The collisional activation mass spectra of a variety of deprotonated amidoximes are recorded in Table 1 and Figs. 1 and 2. Tandem mass spectra (MS/MS/MS) of selected daughter ions are collected in Table 2.

The reaction between, for example, $Me(NH_2)C{=}NOH$ and a strong base (in this case NH_2^-) is expected to result in deprotonation at a number of sites. The various ΔH°_{acid} values (the energy necessary to effect the transformation $HA \longrightarrow H^+ + A^-$) of the neutral are not known but relative values may be estimated. For example, (i) $\Delta H^\circ_{acid}[Me(NH_2)C{=}NOH]$ should be similar to the value for a primary amide or urea ($\simeq$1510 kJ mol^{-1}),[5] (ii) $\Delta H^\circ_{acid}[Me(NH_2)C{=}NOH]$ should be comparable to $\Delta H^\circ_{acid}(Me_2C{=}NOH)$ = 1532 kJ mol^{-1},[6] and (iii) $\Delta H^\circ_{acid}[CH_3(NH_2)C{=}NOH]$ and $[(CH_3)_2C{=}NOMe]$ (1560 kJ mol^{-1})[7] should be almost the same. Therefore, NH_2^- [$\Delta H^\circ_{acid}(NH_3)$, 1689 kJ mol^{-1}][8] will deprotonate the neutral to form **1**, **2** and **3** (Scheme 1) although **1** might be the most prevalent ion. In addition, it is quite possible that **1**, **2** and **3** will interconvert by proton transfer under conditions of collisional activation (*cf.* ref. 1).



Scheme 1

Table 1 Collisional activation mass spectra of deprotonated amidoximes $[R^1(R^2R^3N)C{=}NOH - H]^-$

Precursor Ion			Loss							Formation				
R^1	R^2	R^3	H$^\bullet$	NH_3	H_2O	$R^{2\bullet}$	R^2R^3NH	R^2NO	NH_2OH	CNO^-	$^-NHC{\equiv}N$	NH_2O^-	CN^-	HO^-
Me	H	H[a]	See Fig. 1											
Me	Me	Me	10		8	100	21						1	10
Et	H	H	15	2	6				100		1	1		
Pr	H	H[b]	39		1				100		3	1	1	
Ph	H	H[c,d]	100		14			8	89	1	1	0.5	1	
Ph	Me	Me[e]	100		3	65	32			1				

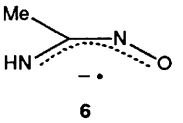
[a] The spectrum of $[Me(ND_2)C{=}NOD - D]^-$ is as follows [*m/z* (loss) abundance]: 74(H$^\bullet$)17, 73(D$^\bullet$)96, 56(HOD)9, 55(D_2O)7, 42(33)8, 41(H_2DNO)-29, 40(HD_2NO)100, 26(CH_3D_2O)3 and 18($C_2H_3DN_2$)0.5. [b] This spectrum shows a peak corresponding to loss of C_2H_5 (6%) (*cf.* ref. 1). [c] The spectrum of $Ph(NH_2)C{=}NO^-$ [from $Ph(NH_2)C{=}NOSiMe_3$ by nucleophilic displacement with NH_2^-] is as follows: 134(H$^\bullet$)100, 117(H_2O)8, 104(HNO)6, 102(NH_2OH)62 and 41(C_6H_6)1. Thus deprotonation at N and O produce species which equilibrate on collisional activation. [d] The spectrum of $[Ph(ND_2)C{=}NOD - D]^-$ is as follows: 135(H$^\bullet$)100, 118(HOD)13, 117(D_2O) < 5[e], 103(H_2DNO)48 and 102(HD_2NO)32. [e] Not resolved.

Table 2 MS/MS/MS data for daughter ions (see the Experimental section for details of the MS/MS/MS method)

Parent ion (*m/z*)	Daughter ion [(*m/z*), loss]	Spectrum type	Spectrum[a]
$[Me(NH_2)C{=}NOH - H]^-$ (73)	[(55), H_2O]	CA[b]	54(H$^\bullet$)10, 53(H_2)22, 40(NH)100, 26(CH_3N)21
		CR	54(18), 53(100), 41(40), 40(56), 39(18), 38(14), 29(15), 28(38), 27(26), 26(14), 15(6), 14(5)
	[(42), HNO]	CR	42(52), 41(100), 40(74), 39(28), 38(14), 28(20), 27(21), 26(19), 25(4), 15(15), 14(6)
	[(40), NH_2OH]	CA	39(H$^\bullet$)100, 26(CH_2)14
		CR	40(100), 39(45), 38(30), 28(4), 27(1), 26(16), 25(2), 24(1), 14(1)
$^-CH_2CN$[c] (40)		CA MS/MS	39(H$^\bullet$)100, 26(CH_2)9
		CR MS/MS	40(100), 39(40), 38(28), 28(3), 27(1), 26(14), 25(2), 24(1), 14(1)
$[Ph(NH_2)C{=}NOH - H]^-$ (135)	[(117), H_2O]	CA[d]	116(H$^\bullet$)100, 90(HCN)68, 41(C_6H_4)45, 26(C_6H_5N)8
	[(104), HNO]	CA[d]	102(H_2)100, 76(CH_2N)71
	[(102), NH_2OH]	CA	101(H$^\bullet$)100, 26(C_6H_3N)20
$(C_6H_4)^-CN$[e] (102)		CA MS/MS	101(H$^\bullet$)100, 26(C_3H_3N)25
		CR MS/MS	101(80), 100(15), 99(18), 98(23), 87,86(10),[f] 76(58), 74(100), 61,62[f](20), 50(40), 37,38[f](8), 25,26[f](2)
$[Ph(NMe_2)C{=}NO^-]$ (163)	[(118), Me_2NH]	CA[d]	92(O)15, 90,89[f](CO,CHO$^\bullet$)82, 42(C_6H_4)100
[*o*-$CN(C_6H_4)O^-$] (118)		CA MS/MS[d]	117(H$^\bullet$)100, 92(O)2, 90(CO)32, 89(CHO$^\bullet$)25, 66(52)3, 63(55)6, 42(C_6H_4)4, 26(C_6H_{40})1

[a] Collisional activation [*m/z* (loss) abundance]: for charge reversal [*m/z* (abundance)]. [b] Spectrum very weak. [c] Formed by deprotonation of acetonitrile. [d] The charge reversal spectra are very complex and are not recorded. [e] Prepared by deprotonation of benzonitrile. [f] Prepared by deprotonation of 2-hydroxybenzonitrile.

Loss of Water.—Loss of water is a minor process for all all $[R^1(R^2R^3N)C{=}NOH - H]^-$ species (Table 1, Figs. 1 and 2). The process is most noticeable in Figs. 1 and 2: the relative abundances are 13 and 14% respectively. Loss of water could occur by a Tiemann rearrangement (**1** ⟷ **4**, Scheme 1) or by a Beckmann-type rearrangement (**3** ⟷ **5**). The Tiemann intermediate **4** should lose water to yield $(HN{=}C{=}NMe - H)^-$, while the analogous loss from the Beckmann intermediate **5** will form $(CH_2{=}C{=}NNH_2 - H)^-$.* The collisional activation and charge reversal (positive ion)[9] tandem mass spectra (MS/MS/MS) for the appropriate daughter ion (*m/z* 55, Fig. 1) are listed in Table 2, but do not distinguish between the two structures. In contrast, the ion $[Ph(NH_2)C{=}NOH - H]^-$ (Fig. 2) cannot undergo the Beckmann rearrangement. In this case, the CA MS/MS/MS data (Table 2) for daughter ion *m/z* 117 are consistent with Tiemann product $(C_6H_4)^-N{=}C{=}NH$. In particular, the ion loses CNH (to form $C_6H_4N^{\bullet-}$) and C_6H_4 (to yield ^-NHCN). We conclude that the Tiemann reaction is, at best, a minor process of deprotonated amidoximes in the gas phase.



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Other Fragmentations: Loss of Hydroxylamine.—All deprotonated amidoximes eliminate H$^\bullet$; labelling data in Table 1 indicate that for $[Me(NH_2)C{=}NOH - H]^-$, loss of H$^\bullet$ forms predominantly the resonance stabilised radical anion **6**. Loss of H$^\bullet$ from the methyl group is minor in comparison. The most interesting fragmentations of deprotonated amidoximes are the major loss of NH_2OH together with minor loss of HNO (see Fig. 1). We propose that these reactions are interrelated. We

* Labelling data (Table 1) indicates that $[Me(ND_2)C{=}NOD - D]$ loses both HOD and D_2O. Thus the HO^- of the decomposing complex [**4** and/or **5**, Scheme 1] is effecting deprotonation at both nitrogen and carbon.

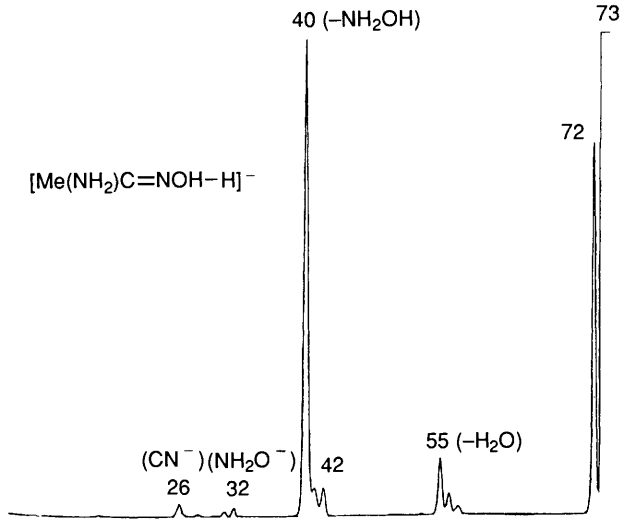


Fig. 1 Collisional activation mass spectrum of $[Me(NH_2)C{=}NOH - H]^-$

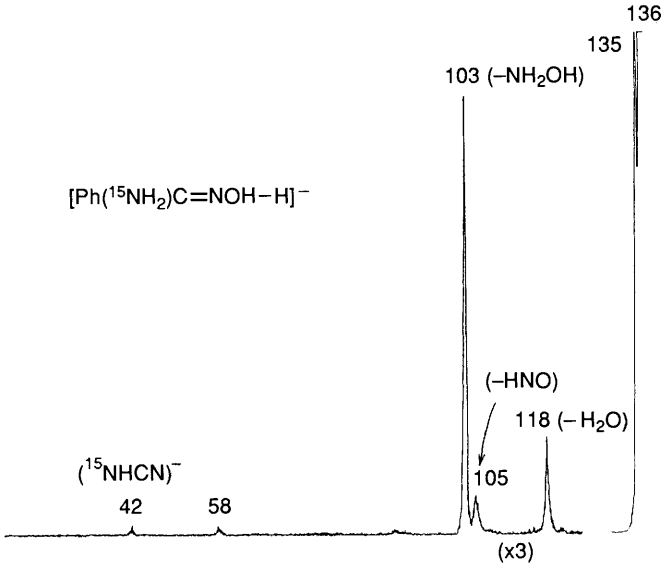
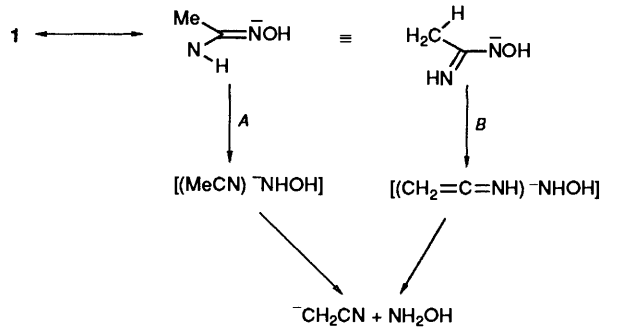


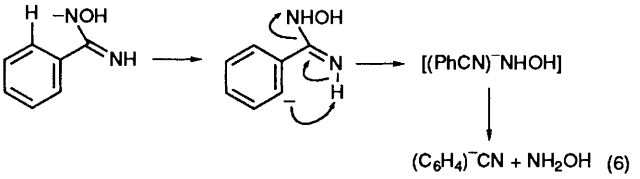
Fig. 2 Collisional activation mass spectrum of $[Ph(^{15}NH_2)C{=}NOH - H]^-$

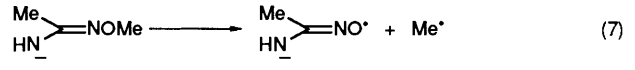
need a ^{15}N-labelled derivative in order to determine which nitrogen is lost in these processes. The most informative derivative would be $Me(^{15}NH_2)C{=}NOH$: unfortunately we were unable to prepare this neutral. However, $[Ph(NH_2)C{=}NOH - H]^-$ also loses NH_2OH and HNO, and in this case we were able to synthesise $Ph(^{15}NH_2)C{=}NOH$. The spectrum (Fig. 2) of the deprotonated ion shows losses of unlabelled NH_2OH, and HNO. Thus it is the nitrogen of the oxime group that is involved in the losses of NH_2OH and HNO. The spectrum (Table 1) of $[Me(ND_2)C{=}NOD - D]^-$ shows major loss of 'HD_2NO' together with minor loss of 'H_2DNO'. The structure of the product ion formed by loss of NH_2OH from $[Me(NH_2)C{=}NOH - H]^-$ is $^-CH_2CN$, as demonstrated by comparison of MS/MS/MS data with the spectra of deprotonated acetonitrile (Table 2). Mechanistic proposals are shown in Scheme 2: proton transfer from the imine position (route A) is the predominant process. The associated hydride transfer, involving loss of HNO, could occur from either ion/neutral complex shown in Scheme 2.

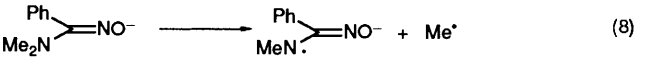
The product ion formed by loss of NH_2OH from $[Ph(NH_2)C{=}NOH - H]^-$ is $(C_6H_4)^-CN$ as evidenced by the data listed in Table 2. However, $[Ph(ND_2)C{=}NOD - D]^-$ eliminates more 'H_2DNO' than 'HD_2NO' (see Table 1 and *cf.* Scheme 2). Thus the predominant fragmentation route for the methyl derivative (route A, Scheme 2) is the minor process for the phenyl analogue. The major process must involve proton transfer from the ring followed by a second proton transfer as shown in eqn. (6).*

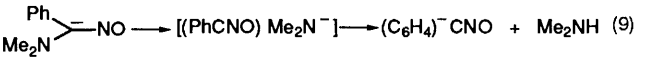


Scheme 2









Fragmentations of N- *and* O-*Substituted Amidoximes.*— The spectra of deprotonated *N*- and *O*-substituted amidoximes are recorded in Tables 1 and 3, and two representative spectra are reproduced in Figs. 3 and 4. These spectra are different from those considered previously, and are often dominated by competitive losses of H• and the substituent attached to N or O. Both processes form resonance stabilised anions: for example, eqn. (7) (see also Fig. 3) and eqn. (8) (Table 1). The other major fragmentation of $Ph(Me_2N)C{=}NO^-$ is shown in eqn. (9).†

Processes resulting in the loss of hydroxylamine are either minor or do not occur. The spectrum of the OMe derivative

* Small peaks at *m/z* 32 are observed in some spectra (see *e.g.* Fig. 1). This corresponds to a deprotonated hydroxylamine, but the ion cannot be NHOH since the electron affinity of •NHOH is negative (–17 kJ mol^{-1}).[10] The species must be NH_2O^- which has been observed before.[11] The electron affinity of NH_2O• is close to zero,[10] and it is presumably formed from an ion complex of the type shown in Scheme 2. For example, for $[Me(NH_2)C{=}NOH - H]^-$, the reaction may be $[(MeCN)^-NHOH] \longrightarrow [^-CH_2CN\ (NH_2OH)] \longrightarrow [(MeCN)\text{-}NH_2O^-] \longrightarrow NH_2O^- + MeCN$. For this process to occur, the initial complex must have an excess energy of at least 70 kJ mol^{-1} (*i.e.* the ΔH°_{acid} values of MeCN, N*H*$_2$OH and NH$_2$O*H* are, respectively, 1560,[12] 1670[10] and 1630[10] kJ mol^{-1}).

† We suggest that the product ion is deprotonated benzonitrile *N*-oxide. The precursor compound is relatively unstable and we were unable to obtain its spectrum. However the product ion does not correspond to the isomeric deprotonated *o*-hydroxybenzonitrile (Table 2).

Table 3 Collisional activation mass spectra of deprotonated amidoxime *O*-methyl ethers

Precursor (*m*/*z*)	Spectrum [*m*/*z* (loss or formation) abundance]
$Ph(\bar{N}H)C{=}NOMe$ (149)	148($H^{\bullet}$)48, 134($Me^{\bullet}$)100, 117(MeOH)4, 104(CH_3ON)2, 102($MeONH_2$)2
$(C_6H_4)^{-}(NMe_2)C{=}NOMe$ (177)	176($H^{\bullet}$)86, 162($Me^{\bullet}$)8, 146($MeO^{\bullet}$)5, 91[$(C_6H_4)^{-}Me$]100, 42(CNO^{-})5

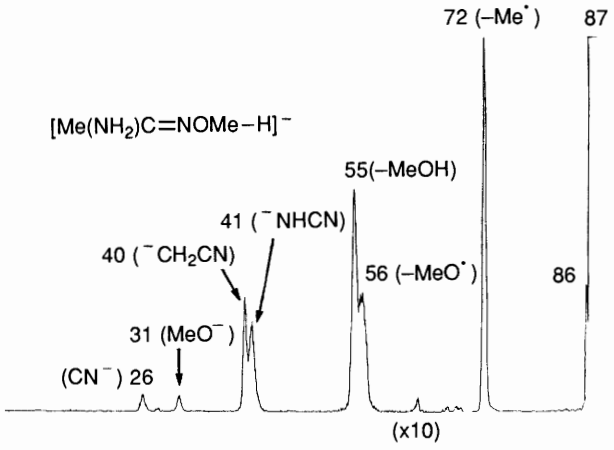


Fig. 3 Collisional activation mass spectrum of $[Me(NH_2)C{=}NOMe - H]^{-}$

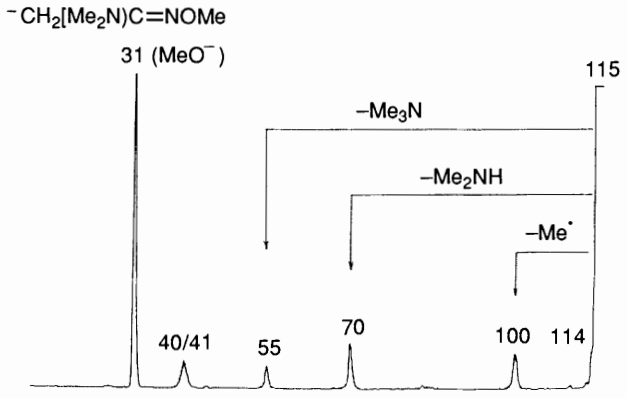


Fig. 4 Collisional activation mass spectrum of $^{-}CH_2(NMe_2)C{=}NOMe$

$$^{-}CH_2(Me_2N)C{=}NOMe \longrightarrow [(CH_2{=}C{=}NOMe)Me_2N^{-}] \longrightarrow HC{\equiv}C{-}\bar{N}OMe + Me_2 \quad (10)$$

$$CH_2{=}C{=}NO^{-} + Me_3N \quad (11)$$

$$MeO^{-} + CH_2{=}C{=}NNMe_2 \quad (12)$$

shown in Fig. 3 shows only minor loss of $MeONH_2$, while *N*-disubstituted amidoximes cannot lose NH_2OH. Similarly, the Tiemann reaction is at best a very minor process. For example, the loss of MeOH illustrated in Fig. 3 is minor.

Finally, when both N and O are fully alkylated, some spectacular rearrangement reactions are observed. The species shown in Fig. 4 fragments almost exclusively by the Beckmann rearrangement, eliminating Me_2NH [eqn. (10)], Me_3N [eqn. (11)] and forming MeO^{-} [eqn. (12)]. The corresponding phenyl derivative can only deprotonate on the phenyl ring, and thus cannot undergo any of the major processes so far described in this paper. Instead, it fragments by an unusual methyl migration to form $(C_6H_4)^{-}Me$ (base peak of spectrum, see Table 3).

In conclusion, the Tiemann reaction is a minor process of deprotonated amidoximes and their *O*-methyl ethers in the gas phase. The characteristic decomposition channel of amidoximes is loss of hydroxylamine [Scheme 2 and eqn. (6)].

Experimental

Collisional activation mass spectra (MS/MS) were recorded using a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical-ionisation mode.[13] All slits were fully open to obtain maximum sensitivity and to minimise energy resolution effects.[14] The chemical ionisation slit was used in the ion source, ionising energy 70 eV (tungsten filament); ion source temperature 180 °C, accelerating voltage 7 kV. Deprotonation of all neutrals was effected by NH_2^{-} (from NH_3). The initial measured source pressure of NH_3 was 1×10^{-5} Torr (1 Torr = 133.332 Pa). The substrate pressure (liquids introduced through the septum inlet at 150 °C; solids through the direct probe with no heating) was typically measured at 5×10^{-7} Torr. The estimated total pressure in the ion source is 10^{-1} Torr. The pressure of helium just outside the second collision cell was 2×10^{-7} Torr measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of *ca.* 10%, and corresponds to essentially single collision conditions.

Consecutive collision induced dissociation spectra (MS/MS/MS)[15] and charge-reversal[9] MS/MS/MS spectra were measured with a Kratos MS 50 TA instrument previously described.[15] Neutral substrates were deprotonated by MeO^{-} (from MeONO[16]) in a Kratos Mark IV chemical-ionisation source ion source temperature 100 °C, electron energy 280 eV, emission current 500 μA and accelerating voltage 8 kV. Samples were introduced through an all-glass heated inlet system at 100 °C. The indicated source pressure of substrate was 2×10^{-5} and of methyl nitrite 1×10^{-6}, giving an estimated source pressure of *ca.* 10^{-1} Torr. The indicated pressure of helium in the collision cells was 2×10^{-6} Torr, giving a decrease in the main beam signal of 30%.*

The following compounds are all known and were prepared by reported methods: ethanamide oxime,[17] propanamide oxime,[17] butanamide oxime,[18] benzamide oxime,[19] *N*,*N*-dimethylbenzamide oxime,[20] *N*,*N*-dimethylethanamide oxime,[20]

* The tandem MS/MS/MS experiments were carried out as follows. The MS 50 TA instrument is a three-sector instrument of geometry EBE. The daughter ion in question (say for a process A ⟶ C formed by collisional activation in the first collision cell) is mass selected by magnet B (MS/MS). The ion C then passes into the second collision cell, and subsequent decompositions (MS/MS/MS, either negative or positive as appropriate) are monitored by scanning the third sector (E).

benzamide *O*-methyloxime,[21] *N,N*-dimethylbenzamide *O*-methyloxime[22] and benzamide *O*-trimethylsiloxyoxime.

Ethanamide O-*Methyloxime* [$MeC(NH_2)$=NOMe].—This was prepared using a standard procedure.[21] The reaction product was purified by flash chromatography over silicic acid in dichloromethane. Yield 70%, b.p. 40–41 °C/0.5 mmHg. The material is not particularly stable when exposed to the atmosphere (Found: $M^{\cdot+}$, 88.0637. $C_3H_8N_2O$ requires 88.0633); δ($CDCl_3$, 300 MHz): 1.85 (3 H, s), 3.77 (3 H, s) and 4.53 (2 H, s); δ_C 16.96 (CH_3), 60.76 (CH_3) and 150.24 (CN).

The Labelled Compounds.—(i) *Ethan*[$^2H_2$]*amide* [^{2}H]*oxime* [$CH_3(ND_2)$C=NOD] *and benz*[$^2H_2$]*amide* [^{2}H]*oxime* [$Ph(ND_2)$C=NOD]. These were prepared by allowing the appropriate unlabelled compound (100 mg) to stir in D_2O (10 cm^3) for 1 h. Evaporation of the solvent *in vacuo* yielded the appropriate labelled derivative ($^2H_3$ > 95%).

(ii) [$^{15}N_1$]*Benzamide oxime* [$Ph(^{15}NH_2)$C=NOH]. This was prepared by a standard route.[20] A mixture of benzohydroximoyl chloride[24] and $^{15}NH_3$ (Aldrich, ^{15}N = 98%) in methanol was allowed to stir at −78 °C for 12 h; m.p. = 77–78 °C, ^{15}N = 98%.

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