An *Ab Initio* Calculation of the Acid-catalysed Hydrolysis of *N*-Nitrosoamines. A Hypothesis on the Rate-determining Step†

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The molecular geometries and energies of H_2NNO, MeNHNO, and Me_2NNO and their *N*- and *O*-protonated species have been calculated using *ab initio* methods. The *N*-protonated species $[NH_3NO]^+$ is found to be the more stable when electron correlation effects are taken into account (by 3—4 kcal mol^{-1}). Substitution on nitrogen by Me groups successively favours *O*-protonation (by 9—10 kcal mol^{-1} for each Me group) so that $[Me_2NNOH]^+$ is more stable than $[Me_2NHNO]^+$. The N–N bond is surprisingly long in the *N*-protonated species $[NH_3NO]^+$ (1.971 Å) which resembles an amine-stabilized nitrosonium ion, but progressively shortens on substitution (to 1.587 Å in Me_2NHNO^+). No evidence is found for stabilized complexes formed by preassociation between the nitrosamines and H_3O^+; proton transfer to N or O occurs without a barrier. Dissociation of $[R_2NHNO]^+$ to the fragments R_2NH and NO^+ is in all cases difficult (>30 kcal mol^{-1}) and increases with Me substitution. Solvation of the protonated substrate at the amino nitrogen raises the dissociation barrier further but a second water molecule solvating the nitrogen of the forming nitroso group facilitates dissociation (by *ca.* 10 kcal mol^{-1}). The results are interpreted in terms of the rate-determining step for denitrosation being fragmentation of this intermediate.

Ever since the discovery by Magee and Barnes [1] nearly 30 years ago that *N*-nitrosodimethylamine is carcinogenic in rats, an enormous number of experimental studies on the formation, structures, and reactivity of nitrosoamines have been reported.[2–7] In particular, the kinetics and possible mechanisms of denitrosation reactions of these important compounds have been investigated in detail by Williams and his co-workers.[8–13] Let us summarize first the experimental findings on this problem. In general, the rate constant of the acid-catalysed hydrolysis (or denitrosation) of nitrosoamines increases on the one hand with the acidity of the reaction medium, and on the other hand with the reactivity and concentration of a non-basic nucleophilic catalyst such as halide anions, thiocyanate anion, or thiourea [Y^- in equation (1)]. Hydrolysis also takes place

$$R_2N\text{–}N{=}O \underset{(a)}{\overset{H^+}{\rightleftharpoons}} [R_2NHN\text{–}O]^+ \xrightarrow[(b)]{Y^-} R_2NH + NOY \quad (1)$$

even in the absence of an added nucleophile; hence the solvent molecules can also act as catalysts. In contrast, the catalytic effect of nucleophiles (Y^-) may disappear at high concentration. Moreover, substituent effects at the amino nitrogen-atoms are found to be small.

From these facts, Williams *et al.*[13] have recently proposed that the rate-determining step of denitrosation reactions may be either the initial protonation of substrates [step (a), equation (1)] or the formation of amines [step (b), equation (1)] depending upon the concentration of nucleophilic species.

Accordingly, a change from general acid catalysis (with hydrogen transfer as rate-limiting step) at high concentration to specific hydrogen ion catalysis at low concentration also occurs. These authors[13] have consequently proposed a mechanism which involves successively three steps [equation (2)]: (a) a preassociation of reactants ($R_2NN{=}O + HA$) forming an intermediate (**I**); (b) a proton transfer to the amino nitrogen-atom constituting the rate-limiting step; and (c) a nucleophilic attack on the *N*-protonated intermediate finally leading to amines.

$$\begin{array}{l} R_2N\text{–}N{=}O \rightleftharpoons R_2N\text{–}N{=}O\cdot HA \rightleftharpoons \\ \quad + \\ \quad HA \qquad\qquad (\mathbf{I}) \\ \qquad\qquad\qquad R_2NH\text{–}NO^+ \xrightarrow{Y^-} R_2NH \\ \qquad\qquad\qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad\quad A^- \qquad\quad NO^+ \end{array} \quad (2)$$

Nevertheless, the nature of the hypothetical intermediate (**I**) has not been detailed, nor has the rate-limiting step definitely been proven. Williams and his co-workers have, in fact, stated (in ref. 13), 'Intermediate (**I**) is believed to be a hydrogen-bonded species which then leads to the *N*-protonated form'.

It would seem, therefore, of interest to determine the most likely structures of such an intermediate, if any, by means of *ab initio* calculations. In recent work, we have shown that the dissociation of the most stable protonated nitrous[14] and nitric[15] acid leading to the production of NO^+ and NO_2^+, respectively, may constitute the rate-limiting steps in nitrosation or nitration reactions.

The present work aims to determine various protonated forms of the prototype $H_2N\text{–}N{=}O$ species as well as its interaction with the simplest acid, H_3O^+. Furthermore, structures of protonated species of *N*-nitrosomethylamine ($CH_3NHN{=}O$) and *N*-nitrosodimethylamine [$(CH_3)_2NN{=}O$] have also been examined. Overall, we propose an alternative mechanism for the acid-catalysed hydrolysis of nitrosoamines.

Calculations

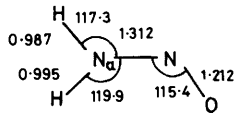
The molecular geometries of the species considered were optimized with the 4-31G basis set[16] making use of the force method with analytical gradient as implemented in the MONSTERGAUSS program.[17] As a test case, the relative energies between neutral and protonated $H_2NN{=}O$ species have been determined from single-point calculations at the SCF

† *Non-SI unit employed*: 1 cal mol^{-1} = 4.184 J mol^{-1}.

Table 1. Total energies (a.u.) of the neutral (**1**) and protonated (**2**)—(**4**) H_2N–N=O considered at different levels of calculations

Method[a]	(1)	(2)	(3)	(4)
HF/4-31G	−184.538 66	−184.852 56	−184.820 16	−184.837 88
HF/6-31G*	−184.824 88	−185.143 07	−185.110 93	−185.136 15
HF/6-31G**	−184.833 05	−185.157 82	−185.123 36	−185.146 76
HF/6-31++G**	−184.841 45	−185.161 27	−185.126 97	−185.149 28
MP2/4-31G	−184.897 67	−185.204 76	−185.197 04	−185.230 98
MP2/6-31G*	−185.330 87	−185.638 42	−185.627 51	−185.652 43
MP3/6-31G*	−185.332 27	−185.647 62	−185.626 70	−185.647 69
MP4/6-31G*	−185.343 98	−185.657 47	−185.637 67	−185.665 10
ZPE[b]	22.7	32.0	32.2	29.9

[a] Using 4-31G-optimized geometries given in Figure 1. [b] Zero-point vibrational energies at HF/4-31G in kcal mol^{-1}.



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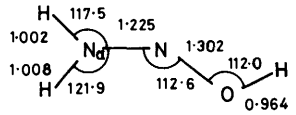

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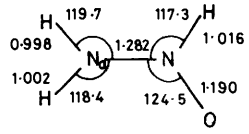

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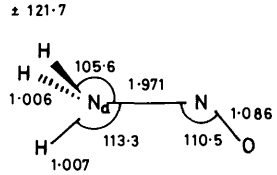

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Table 2. Proton affinities (kcal mol^{-1}) of H_2N–N=O at different sites

Method	*O*-Protonation (**2**)	*N*-Protonation (**3**)	N_a-Protonation (**4**)
HF/4-31G	−197.0	−176.6	−187.8
HF/6-31G*	−199.7	−179.5	−195.3
HF/6-31G**	−203.8	−182.2	−196.8
HF/6-31++G**	−200.7	−179.2	−193.1
MP2/4-31G	−192.7	−187.9	−209.1
MP2/6-31G*	−193.0	−186.1	−201.8
MP3/6-31G*	−197.9	−184.8	−192.9
MP4SDQ/6-31G*	−196.7	−184.3	−201.5
MP4SDQ/6-31++G**[a]	−197.7	−184.0	−199.3
Estimated[b]	−188.4	−174.5	−192.1

[a] Using the additivity relationship, PA(MP4/6-31++G**) ≃ PA(MP4/6-31G*) + PA(HF/6-31++G**) − PA(HF/6-31G*), *cf.* ref 23. [b] Including MP4SDQ/6-31++G** and ZPE values.

level using different gaussian basis sets: 6-31G*[18] (polarization *d*-functions for N and O), 6-31G** (polarization *d*-functions for N and O and *p*-functions for H), 6-31++G**[19] (the 6-31G** plus a set of diffuse *s*, *p*-functions on N and O and *s*-functions on H) employing their 4-31G-optimized geometries. The correlation energies have also been calculated *via* the Møller–Plesset perturbation theory to second (MP2), third (MP3), and fourth (MP4SDQ) order[20] using the HF/6-31G** wavefunctions as references and with the aid of the GAUSSIAN-82 program.[21] Harmonic vibrational frequencies were computed with the 4-31G basis set. For larger species, only single points at the HF/6-31G* level were considered.

Results and Discussion

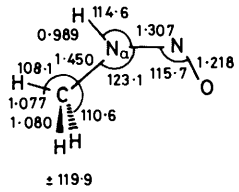
Optimized structures for H_2NNO (**1**) and for the *O*- (**2**), *N*- (**3**), and N_a- (**4**) protonated species are shown. Their total energies calculated at different levels of theory are listed in Table 1.

The major feature of note is the lengthening of the N–N bond in (**4**). In effect, this species is a nitrosonium ion (NO^+) solvated strongly by the NH_3 group. This is directly analogous to the protonated nitrous acid $[H_2O \cdots NO]^+$ species.[14]

The proton affinities of the *O*-, *N*-, and N_a-sites are summarized in Table 2. The following points are noted. (a) The central nitrogen (*N*-) is the least basic site and this is independent of the method used. (b) The proton affinities of the N_a- and *O*-sites are much closer and the order does vary with the method.

At the SCF level, *O*-protonation is favoured over *N*-protonation. The extension of the basis set (polarization *p*-functions on H and diffuse functions) exerts only a small effect on the proton affinities although it seems to slightly disfavour the N_a-protonation (values in Table 2 at higher levels using HF/4-31G-geometries). When electron correlation is however taken into account by means of the Møller–Plesset perturbation theory, then the N_a-protonated species becomes consistently more stable. This shows that, contrary to the earlier suggestion of Reynolds and Thomson,[22] the correlation correction is not negligible for these systems. It is somewhat striking that at the MP3/4-31G level, the *O*-protonated species (**2**) is still found to be lower in energy than the N_a-protonated (**4**).[22] Our best values including relative energies at MP4SDQ/6-31++G** plus zero-point energies corrections (Table 2) estimate that N_a-protonation is favoured over *O*-protonation by 3—4 kcal mol^{-1}.

In order to determine the effect of substituents on nitrogen on the ease of protonation at the various sites, the *N*-methyl (**5**) and the *NN*-dimethyl (**9**) densities were also examined. The results obtained for the structures displayed in structures (**5**)—(**12**) are summarized in Table 3. As expected, the presence of one methyl group enhances the ease of protonation of the nitrosoamines and the second methyl group continues this trend. The largest effect is on the *O*- (and to a lesser extent *N*-protonation) rather than on N_a-protonation in spite of the fact that this is the site of the substituent change. Such an effect is not surprising however. For instance, a detailed analysis on charge distributions in (**1**), (**5**), and (**9**) previously showed that the net charge on the NO group increases by successive methyl substitution and that this increase is almost entirely due to the net charge on O.[23] The extra stabilization energy is *ca.* 9—10 kcal mol^{-1} for the *O*-proton affinity for each methyl group, while for N_a-protonation the increased stabilization is less than half of this. The result is that, at the HF/6-31G* level, there is now a marked preference (15 kcal mol^{-1}; Table 3) for the *O*-protonation of the dimethylnitrosoamine. The obvious question is to what extent



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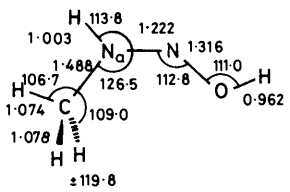

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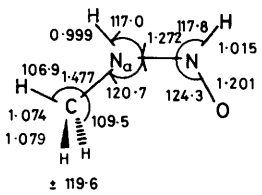

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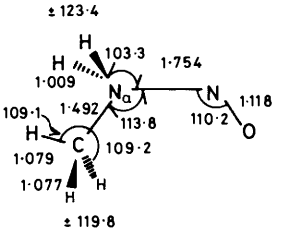

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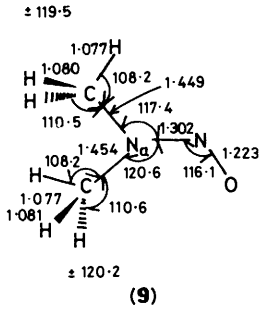

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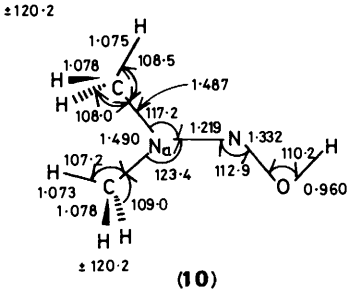

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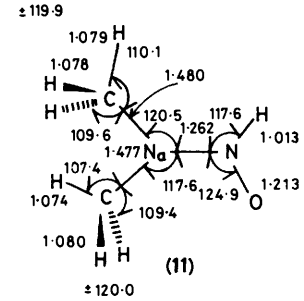

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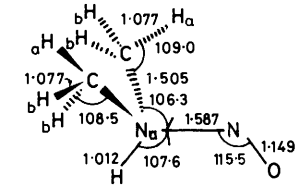


∠ CNNO = ± 119·1
∠ HαCNC = ± 59·3
∠ HbCNHα = ± 120·2

(12)

the correlation correction modifies this stability ordering. According to the changes which occur in the case of H_2NNO species, it is possible that the *O*-protonated species (**10**) might remain of lower energy than the N_a-protonated species (**12**) even when correlation energies are included in the calculations. Nevertheless, without explicit calculations we hesitate to predict too far.

The molecular geometries of the neutral molecules have been discussed in detail in an earlier work.[23] With regard to the N_a- and *O*-protonated species, the most notable structural changes are as follows. (a) *O*-Protonation produces a notable shortening of the N_a–N bond [compare (**2**) with (**1**), (**6**) with (**5**), and (**10**) with (**9**)] with a concomitant lengthening of the N–O bond. However, the methyl groups exert almost no effect on this alteration. (b) N_a-Protonation produces a lengthening of the N_a–N but the effect is markedly less as the nitrogen is substituted by methyl groups: N_a–N bond lengths in (**4**), (**8**), and (**12**) are 1.971, 1.754, and 1.587 Å, respectively. Such a trend is consistent with the gas-phase relative basicities of amines. As a matter of fact, the nitrogen atoms in the amines become more negatively charged; thus the complexes formed between them and the NO^+ cation become in turn stronger.

Table 3. Total energies (a.u.) and proton affinities (in kcal mol^{-1}, in parentheses) of CH_3–NH–N=O and $(CH_3)_2$N–N=O calculated at HF/4-31G and HF/6-31G*

Species[a]		HF/4-31G	HF/6-31G*
CH_3–NH–N=O			
Neutral	(**5**)	−223.513 26	−223.859 30
O-Protonated	(**6**)	−233.844 52 (−207.9)	−224.193 33 (−209.6)
N-Protonated	(**7**)	−223.810 37 (−186.4)	−224.159 91 (−188.6)
N_a-Protonated	(**8**)	−223.818 92 (−191.8)	−224.169 73 (−194.8)
$(CH_3)_2$N–N=O			
Neutral	(**9**)	−262.485 34	−262.890 89
O-Protonated	(**10**)	−262.832 55 (−217.9)	−263.238 88 (−218.4)
N-Protonated	(**11**)	−262.794 41 (−193.9)	−263.202 08 (−195.9)
N_a-Protonated	(**12**)	−262.801 31 (−198.3)	−263.213 44 (−202.4)

[a] Using HF/4-31G-optimized geometries given in structures (**5**)—(**12**).

Table 4. Total energies (a.u.) of NO^+ and NH_3 fragments and dissociation energies of the N_a-protonated $NH_2N{=}O$ (**4**) calculated at different levels of theory

Method[a]	NO^+	NH_3	ΔE[d]
HF/4-31G	−128.669 66	−56.106 69	38.6
HF/6-31G*	−128.909 42	−56.179 59	29.6
HF/6-31G**	−128.909 42	−56.191 63	28.7
HF/6-31++G**	−128.912 25	−56.198 39	24.2
MP2/4-31G	−128.938 12	−56.221 91	44.5
MP2/6-31G*	−129.234 39	−56.348 52	43.6
MP3/6-31G*	−129.221 95	−56.360 07	41.2
MP4/6-31G*	−129.236 58	−56.362 70	41.3
ZPE[b]	3.9	22.8	26.7
Estimated[c]			32.7

[a] Using HF/4-31G geometries of NO^+ and NH_3. [b] Zero-point vibrational energies at HF/4-31G in kcal mol^{-1}. [c] Including the estimated MP4SDQ/6-31++G** values (see text) and ZPE contributions. [d] $\Delta E = E(NO^+ + NH_3) - E$(**4**) in kcal mol^{-1}.

We have also calculated the energies of dissociation of the N_a-protonated species (**4**), (**8**), and (**12**) to NO^+ and NH_3, CH_3NH_2, and $(CH_3)_2NH$, respectively (Tables 4 and 5).

With respect to the HF/6-31G** values, extension of the basis set lowers the dissociation energy whereas the correlation effect tends to increase it. Despite the fact that the absolute value varies considerably as the method used is changed, the trend is clear. The overall dissociation energy is high. Our best estimate provides a dissociation energy of 32.7 kcal mol^{-1} for (**4**) into fragments NH_3 and NO^+ (Table 4, MP4SDQ/6-31++G** plus ZPEs). Table 5 indicates that this quantity increases by 5—10 kcal mol^{-1} for each additional methyl group. Accordingly, it is difficult to envisage spontaneous dissociation occurring (yielding unsolvated nitrosonium ion NO^+).

In order to gain some further information on the solvation process, the interaction between protonated species with water molecules has been examined. Structures (**13**) and (**14**) display geometries of the complexes between (**2**) and (**4**) and the water molecules, respectively optimized at HF/4-31G. It should be pointed out that these stationary points are also found to be the minima resulting from the interaction between H_2NNO (**1**) and the H_3O^+ ion. In other words (**13**) and (**14**) are the common

Table 5. Total energies (a.u.) of CH_3NH_2 and $(CH_3)_2NH$ fragments and dissociation energies (kcal mol^{-1}) of N_a-protonated $CH_3NH{\cdot}N{=}O$ (**8**) and $(CH_3)_2NN{=}O$ (**12**)

Energy[a]	HF/4-31G	HF/6-31G*
CH_3NH_2	−95.071 66	−95.206 91
$(CH_3)_2NH$	−134.040 19	−134.237 08
$CH_3NH_2 + NO^+$	−223.741 32	−224.116 33
$(CH_3)_2NH + NO^+$	−262.709 85	−263.146 50
ΔE_1[b]	48.7	33.5
ΔE_2[c]	57.4	42.0

[a] Using 4-31G-optimized geometries. [b] $\Delta E_1 = E(CH_3NH_2 + NO^+) - E(\mathbf{8})$. [c] $\Delta E_2 = E[(CH_3)_2NH + NO^+] - E(\mathbf{12})$.

single minima of two groups of fragments.[24] Accordingly, there is no intermediate (**I**), as proposed by Williams and his co-

$$H_2NNO + H_3O^+ \rightleftharpoons \begin{cases} (\mathbf{13}) \longleftarrow H_2NNOH^+ + H_2O \\ \qquad\qquad (\mathbf{2}) \\ (\mathbf{14}) \longleftarrow H_3NNO^+ + H_2O \\ \qquad\qquad (\mathbf{4}) \end{cases}$$

workers,[13] formed from a model of the preassociation of reactants. The proton transfer from the acid H_3O^+ to nitrosoamine takes place in a fast step. We examine here only the energetic data of the N_a-protonated species (**14**).

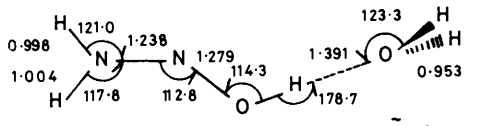
At the HF/4-31G level, (**14**) lies 27.2 and 23.1 kcal mol^{-1} below the fragment (**1**) + H_3O^+ and (**4**) + H_2O respectively.[25] It dissociates into NO^+ and the complex $NH_3{\cdot}H_2O$ by means of a dissociation energy of 58.1 kcal mol^{-1} (HF/4-31G), *ca.* 20 kcal mol^{-1} larger than that of (**4**) at the same level of theory (Table 4). This indicates that structure (**14**) does not participate in the dissociation process.

Structures (**15**) and (**16**) display the geometries of the complexes between (**4**) and (**14**) with the water molecule at the central nitrogen cation, respectively. Note that the intermolecular distances become appreciably stretched. Of particular interest are the dissociation of these species into fragments. The dissociation energies of (**15**) and (**16**) into NH_3 ($NO^+{\cdot}H_2O$) and ($NH_3{\cdot}H_2O$) ($NO^+{\cdot}H_2O$) are calculated to be 26.4 and 39.8 kcal mol^{-1}, respectively, at the HF/4-31G level. With respect to that of the unsolvated species (**4**) (38.6 kcal mol^{-1}), the latter is slightly higher, whereas the former is significantly reduced. These data confirm that on the one hand the solvation at hydrogen atoms of amine groups is unlikely and on the other hand, the solvation of NO^+ is important.

Therefore it is tempting to conclude that during a catalysed hydrolysis of nitrosoamines, the complex between the hydrated nitrosonium ion, H_2ONO^+, and the amine group which is formed after a fast proton transfer to nitrosoamines plays a central role. The fragmentation of this complex appears to be the rate-determining step of the overall process.

Such fragmentations with appreciable dissociation energies are reflected in the strong catalysis of hydration of nitrosoamines by added nucleophiles.

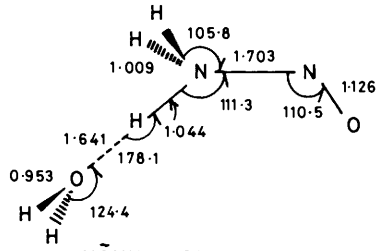
At high added nucleophile concentration, denitrosation becomes independent of the concentration of the nucleophile [Cl^-, Br^-, $SC(NH_2)_2$, SCN^- • • •][13] added. There is also a (small) primary isotope effect which is also consistent with *general acid* catalysis at least being partly rate determining. With the less basic nitrosoamines (*e.g.* nitrosoamides and nitrososulphonamides) such general acid catalysis is observed even at low added nucleophile concentration. Under these experimental conditions, the rate of denitrosation shows only a small dependence on the substituent present in aliphatic



HÕHO = ± 86·1

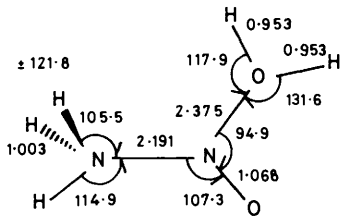
(**13**)

HÑNO = ± 121·9

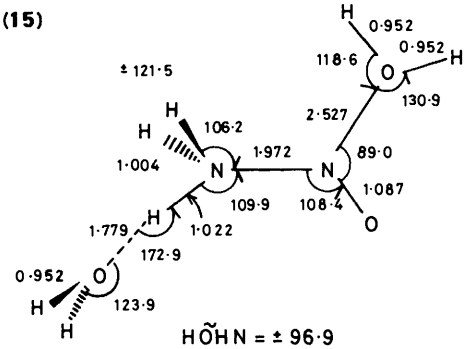


HÕHN = ± 91·4

(**14**)



(**15**)



HÕHN = ± 96·9

(**16**)

nitrosoamines, or in the *p*-position in aromatic nitrosoamines;[13] this observation is consistent with the small change in the charge on nitrogen on protonation (at N_a) of the nitrosoamine which we have calculated.

In conclusion there is no evidence for the formation of complexes of any stability between NH_2NO and H_3O^+; direct proton transfer (to N or O) occurs without the energy barrier. The species formed $[H_2O{\cdot}NH_3NO]^+$ on transfer to N_a is quite stable and does not undergo rapid spontaneous decomposition (as does *e.g.* $\overset{+}{N}H_3$–CO_2^- in carbamate hydrolysis[25] and thus requires preassociation of the acid). Moreover in the mechanism proposed by Williams,[13] the rapid subsequent step involves (bimolecular) reaction with the nucleophile, Y^- [equation (2)]; thus the reaction is not directly comparable to carbamate hydrolysis. However, association of a nucleophile (H_2O was used in the present work) with the central nitrogen does reduce the barrier to dissociation and this provides a useful model for the transfer of an NO^+ group from ammonia to water in the protonated nitrosamine.

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