Kinetics and Mechanism of the Nitrosation of Methylhydrazine and *NN*-Dimethylhydrazine

By **John R. Perrott, Geoffrey Stedman,*** and **Miss Nermin Uysal,** Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

The nitrosation of methylhydrazine and *NN*-dimethylhydrazine proceeds through their conjugate acids, and occurs with either the nitrosonium ion or nitrosyl halides as electrophilic reagents. For methylhydrazine the products show that sizeable proportions of both possible conjugate acids must exist in solution. In the presence of a substantial concentration of nitrous acid a secondary reaction can occur, resulting in the destruction of the primary methylnitrosohydrazine, and the formation of methanol, dinitrogen, and nitrogen(I) oxide. A dinitroso-intermediate is probably involved.

In a previous paper we argued [1] that the nitrosation of hydrazine proceeded through the hydrazinium ion, at a rate close to the encounter limit when the electrophile was the nitrosonium ion. An extension of this work to the methylhydrazines appeared to be of potential value as the primary product, a methylnitrosohydrazine, has been isolated in some cases,[2] whereas for hydrazine its formation has to be inferred. A comparison of the kinetics of nitrosation of hydroxylamine and its methyl derivatives had earlier proved very fruitful in understanding the mechanism.[3]

EXPERIMENTAL

Materials.—Methylhydrazine was purified by treatment of the sulphate with hot ethanol, and by recrystallisation. *NN*-Dimethylhydrazine was purified by distillation in a nitrogen atmosphere, b.p. 63° at 760 mmHg. All other chemicals were AnalaR materials of the purest grade available.

Kinetic Methods.—The kinetics were studied by following changes in the u.v. spectra in the range 340—380 nm as a function of time, using a Unicam SP 700 or SP 500 instrument with thermostatted cell compartment. Rapid reactions were started by injecting one reagent by syringe through a small hole in the cell compartment lid. Solutions were buffered with excess of perchloric acid. For *NN*-dimethylhydrazine there were complications because of secondary reactions involving the nitroso-compound initially formed, and kinetic measurements were based upon the initial rates of change of absorbance. Particular care was necessary to avoid spurious changes in absorbance due to oxidation; careful degassing of the solutions by bubbling dinitrogen through them before the reaction started was helpful. Some measurements were made using a colorimetric method of analysis for nitrous acid, similar to that used previously for hydroxylamine.[4]

Product Analyses.—^{1}H N.m.r. spectra were run on a Varian HA-100 instrument, using t-butyl alcohol as internal standard. Gas analyses were carried out using a standard Warburg method, with magnetic stirring. Mass spectra were run on an MS9 instrument.

RESULTS

Products.—*Methylhydrazine.* The stoicheiometry and reaction products were found to vary with the concentration of reagents, particularly of nitrous acid, and we first consider reaction at low (10^{-4}—10^{-3} mol dm^{-3}) concentrations. The stoicheiometry was $\Delta[HNO_2]/\Delta[CH_3NHNH_2,H^+] = 1.0$. The u.v. spectrum of the infinity solution was very similar to that of an *N*-nitroso-compound with peaks at 380 (ε 41) and 249 nm (3 000). Gas was evolved in the same reaction, and mass spectrometric analysis showed the presence of nitrogen(I) oxide with possibly some dinitrogen. A preliminary analysis by i.r. again showed the presence of nitrogen(I) oxide. Analysis using a Warburg apparatus gave a yield of 68.9% gas [assumed to be nitrogen(I) oxide] based upon the original nitrite; the yield was constant over the acidity range $[H^+] = 0.01$—0.1 mol dm^{-3}. All of these results refer to a relatively rapid reaction that is complete in *ca.* 20—30 min under typical conditions ($[H^+] = 0.01$, $[CH_3NHNH_2,H^+] = 0.005$, $[HNO_2] = 0.000\,5$ mol dm^{-3}; 25°). When the reaction solution is allowed to stand over some hours a second, much slower reaction occurs. The characteristic u.v. peaks disappear and there is a further slow evolution of gas, corresponding to a yield of 23.6%, which is again independent of acidity. Thus the total amount of gas evolved is 92.5% overall. Mass spectrometric analysis again showed the presence of nitrogen(I) oxide in the gas evolved in this second reaction.

We set out in equations (1) and (2) our suggestions for

$$CH_3NHNH_2,H^+ + HNO_2 \longrightarrow CH_3N(NO)NH_2 + H_3O \quad 31\% \quad (1)$$

$$CH_3NHNH_2,H^+ + HNO_2 \longrightarrow (CH_3NH_3^+) + N_2O + H_2O \quad 69\% \quad (2)$$

the stoicheiometry of the first reaction. Methylamine has been entered in parentheses because we do not have any *direct* evidence for its formation. The possible trace of dinitrogen may arise from a small amount of secondary nitrosation to form $CH_3N(NO)NHNO$, which breaks down to form dinitrogen as one of its products (see below).

The reaction at higher reagent concentrations follows a quite different stoicheiometry. Experiments were carried out with an excess of methylhydrazine and with concentrations large enough (up to 0.6 mol dm^{-3}) to give products readily detectable by ^{1}H n.m.r. It was hoped in this way to identify the methylammonium ion. Spectra were run at frequent intervals after mixing, but no change was observed in the spectrum with time; the final products were formed completely within 15 min of mixing. There was no sign of peaks due to the methylammonium ion or to methylnitrosohydrazine, the only species detectable being

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[1] J. R. Perrott, G. Stedman, and N. Uysal, *J.C.S. Dalton*, 1976, 2058.

[2] P. A. S. Smith, 'Open Chain Nitrogen Compounds,' 1966, Benjamin, New York, Vol. II, p. 500.

[3] M. N. Hughes, T. D. B. Morgan, and G. Stedman, *J. Chem. Soc.* (*B*), 1968, 344.

[4] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 2824.

methanol and unchanged methylhydrazine. The yield of methanol based upon methylhydrazine consumed was 97%, and the ratio of nitrite consumed to methylhydrazine consumed was 2.0. This last number is probably somewhat unreliable because the formal initial concentrations of nitrous acid were in the range 0.2—0.4 mol dm^{-3}, and there must be some losses by self-decomposition. Gas was evolved in this reaction and mass spectrometric analysis showed the presence of dinitrogen and nitrogen(I) oxide. We propose the main reaction involved is (3).

$$2HNO_2 + CH_3NHNH_2,H^+ \longrightarrow CH_3OH + N_2 + N_2O + H_2O + H_3O^+ \quad (3)$$

For concentrations between these two extreme intermediate stoicheiometries were found. Some analyses were carried out by a pH titrimetric method and gave values of $\Delta[HNO_2]/\Delta[CH_3NHNH_2,H^+]$ in the range 1.3—1.6, while analyses by the colorimetric method for nitrite gave $\Delta[HNO_2]/\Delta[CH_3NHNH_2,H^+] = 1.3$—1.7. Mass spectrometric analyses showed both dinitrogen and nitrogen(I) oxide to be present in the gas evolved.

NN-*Dimethylhydrazine*. Experiments at low concentrations of nitrous acid gave a product with a u.v. spectrum like that of an *N*-nitroso-compound with peaks at 365 ($\varepsilon > 17$) and 232 nm (> 258). This species decomposed at an appreciable rate and no attempt was made to correct for this decomposition, so the extinction coefficients are very much minimum values. The final solution showed ^{1}H n.m.r. spectrum that was characteristic of the dimethylammonium ion, while the evolved gas had a mass spectrum showing nitrogen(I) oxide to be present. These are the products generally found [5] for the reactions of *NN*-dialkylhydrazines with nitrous acid, though other products have been reported for particular systems.[6]

Kinetics.—Methylhydrazine. Reaction was followed by u.v. spectrophotometry, in solutions containing at least a five-fold excess of methylhydrazine over nitrite. Individual runs gave good pseudo-first-order plots, and by varying the acidity and methylhydrazine concentrations the rate law was found to be $v = 127[H^+][HNO_2][CH_3NHNH_2,H^+]$ mol dm^{-3} at 25° and 0.3 ionic strength. The activation energy (14—43°) was 46 kJ mol^{-1}. Added chloride, bromide, and thiocyanate ions catalysed the reaction as has previously been observed for hydrazine [1] and the methylhydroxylamines,[3] and the same form of rate law was established for bromide catalysis, $v = k_4^{Br}[H^+][HNO_2][Br^-][CH_3NHNH_2,H^+]$. Assuming the same kinetic form for chloride and thiocyanate we find k_4^X as 1 780 (Cl), 3 500 (Br), and 7 090 (SCN). Results for the uncatalysed reaction are in Table 1.

TABLE 1

First-order rate constants for the nitrosation of the methylhydrazinium ion at 25° and 0.3 ionic strength

$10^3[CH_3NHNH_2,H^+]$/mol dm^{-3}	2.2	3.1	4.4	5.8	2.2
$10^2[H^+]$/mol dm^{-3}	1.0	1.0	1.0	1.0	2.0
10^3k_1/s^{-1}	2.8	3.6	5.8	8.2	5.9
$k_1([H^+][CH_3NHNH_2,H^+])^{-1}$/dm^6 mol^{-2} s^{-1}	128	115	132	141	135
$10^3[CH_3NHNH_2,H^+]$/mol dm^{-3}	2.2	2.4	2.4	2.4	
$10^2[H^+]$/mol dm^{-3}	4.0	6.0	8.0	10.0	
10^3k_1/s^{-1}	9.9	17.3	27.6	31.0	
$k_1([H^+][CH_3NHNH_2,H^+])^{-1}$/dm^6 mol^{-2} s^{-1}	112	120	143	129	

The kinetics of the second, slow reaction, in which the characteristic u.v. peaks of the primary product disappeared were followed spectrophotometrically. Individual runs gave good first-order plots of log $(A - A_\infty)$ *versus* time, and the first-order rate constants k_1 fitted the equation $10^4k_1 = 1.22 + 1.03[H^+]$ at 25°. Similar rate constants were obtained whether the run was followed by the disappearance of the peak at 380 or 249 nm, but because of the danger of overlapping absorptions at short wavelengths we prefer the data obtained at 380 nm. Measurements over the range 25—45° gave Arrhenius activation energies of 96 and 107 kJ mol^{-1} respectively for the first and second terms.

NN-*Dimethylhydrazine*. Reaction could be followed by u.v. spectrophotometry, but unless particular care was taken the results were complicated by side reactions forming strongly absorbing species, probably oxidation products of dimethylhydrazine. It was found to be much more satisfactory to follow the disappearance of nitrous acid colorimetrically. The rate law found was $v = k[H^+][HNO_2][(CH_3)_2NNH_2,H^+]$ with $k = 25.4 \pm 1.6$ dm^6 mol^{-2} s^{-1} (u.v. method) at 25° and 0.3 ionic strength, $k_D/k_H = 1.5$, while by the colorimetric method k was found to be 32.2 ± 1.3. Reaction was catalysed by added chloride, bromide, and thiocyanate ions, and the rate of the catalysed reaction was shown to be first order with respect to the concentration of catalytic anion. Assuming the form of rate equation found for hydrazine, methylhydrazine, and the hydroxylamines we obtain k_4^X/dm^9 mol^{-3} s^{-1} of 3 430 (Cl), 9 850 (Br), and 22 900 (SCN) at 25°. Experimental results are in Table 2.

TABLE 2

First-order rate constants for the reaction of nitrous acid with *NN*-dimethylhydrazine at 25° and 0.3 ionic strength

$10^3[Cl^-]$/ mol dm^{-3}	10^3k_1/ s^{-1}	$10^3[Br^-]$/ mol dm^{-3}	10^3k_1/ s^{-1}	$10^3[SCN^-]$/ mol dm^{-3}	10^3k_1/ s$^-$
0	(1.69)	0	(1.69)	0	(1.69)
10	3.56	4	3.80	1	2.84
20	5.24	8	5.37	3	5.00
30	6.73	10	6.53	5	7.42

$[(CH_3)_2NNH_2,H^+] = 10^{-3}$ mol dm^{-3}; $[H^+] = 0.05$ mol dm^{-3}.

DISCUSSION

It is well established that it is possible to isolate *N*-nitroso-derivatives of methyl- and *NN*-dimethylhydrazine from reaction mixtures containing nitrosating agents, and the u.v. spectra of our reaction solutions confirm this. The kinetic form of the rate laws found are those expected [7] for an electrophilic nitrosation by the nitrosonium (or nitrous acidium ion) or a nitrosyl halide. From the rate law the monoprotonated methylhydrazine is the nucleophile, but for unsymmetrically substituted compounds there is a complication as there

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[5] I. T. Millar and H. D. Springall, 'Sidgwicks Organic Chemistry of Nitrogen,' Clarendon, Oxford, 1966, 3rd edn., p. 506; ref. 2, p. 129.

[6] P. G. Gassman and K. Shudo, *J. Amer. Chem. Soc.*, 1971, **93**, 5899.

[7] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

are two basic sites in the free base. Thus the methylhydrazinium ion may exist as $CH_3\overset{+}{N}H_2NH_2$ (I) or $CH_3NH\overset{+}{N}H_3$ (II). It is generally thought that the alkylated nitrogen is the more basic, and there is i.r. evidence to confirm this.[8] We have examined the ^1H n.m.r. spectra of solutions of methylhydrazine in concentrated perchloric acid, but have only observed a single methyl signal. Thus either one tautomer is present in large excess, or the rate of exchange is fast on the n.m.r. timescale. The products of nitrosation of the two tautomers would be $CH_3NHNHNO$ and $CH_3N(NO)NH_2$ respectively, and the former of these by a further proton transfer could give rise to methyl azide or dinitrogen and *N*-methylhydroxylamine [reaction (4)].

Audrieth states [9] that aryl and alkylnitrosohydrazines when heated in inert solvents break down readily to give nitrogen(I) oxide and the corresponding amine, but that if the decomposition is permitted to occur in acidic or basic solution the corresponding azides are obtained. This is certainly true for the aryl compounds, but Smith comments [10] that the reaction between nitrous acid and alkylhydrazines is not a good method for preparing alkyl azides. Our i.r. and mass spectrometric analyses show that nitrogen(I) oxide is the main product, though we have detected a peak at *m*/*e* 57 probably due to methyl azide. This is certainly a minor product, $<10\%$. Nitrenium ions have been detected [6] as intermediates in the reaction of nitrous acid with special *NN*-dialkylhydrazines. We looked for *N*-methylhydroxylamine by ^1H n.m.r. without success. We consider that the 69% yield of gas arises from the nitrosation of ion (I) leading to $CH_3NHNHNO$ and thence to nitrogen(I) oxide, but we have not been able to find any direct evidence for the methylammonium ion at the low concentrations where a 1 : 1 stoicheiometry was found. If this explanation is accepted then the yield of $CH_3N(NO)NH_2$ is 31%. For most of our experiments the reaction was too fast to allow the kinetics to be followed by liberation of gas because the rate of equilibration between the vapour and liquid phases was not great enough. However at the lowest acidity studied, $[H^+] = 0.005$ mol dm^{-3}, the first-order rate constant for the build-up of pressure was very close to the first-order rate constant determined by u.v. spectroscopy. This suggests that $CH_3NHNHNO$ must tautomerise quite rapidly, and that it does not build up to a sizeable concentration in solution.

The rate constant of 127 dm^9 mol^{-3} s^{-1} represents the combined reactivity of both tautomers (I) and (II). This figure is not much below the value of 611 for the hydrazinium ion, which is thought [1] to be close to the encounter rate. For species as reactive as this there is a levelling effect on reactivity differences due to substituent effects, and although simple arguments suggest that (II) should be more reactive than (I), we suggest that the difference is unlikely to be a large one. Thus the fact that we observe yields of nitrogen(I) oxide and $CH_3N(NO)NH_2$ comparable in order of magnitude implies that there must be corresponding proportions of (I) and (II) in solution, despite earlier assumptions that (I) was in large excess over (II). This is consistent with recent work by Condon *et al.*[11] who have analysed the heats of hydration of a series of alkylhydrazines in terms of σ^* constants and hydration parameters depending upon the number of hydrogen atoms on each nitrogen of an alkylhydrazinium ion. From their data they predict the relative basicities of the two nitrogens in methylhydrazine, and they calculate that there should be 72% (I) and 28% (II). The close agreement with our figure of 69% is clearly fortuitous but they agree with us that there should be a sizeable proportion of the less stable tautomer. If we accept Condon's figure of 72%, this implies that (I) and (II) are equally reactive, which seems slightly surprising. Reactivity differences would be expected to show up more clearly with a less reactive electrophile such as one of the nitrosyl halides. However attempts to observe a difference in the yield of $CH_3N(NO)NH_2$ when reaction was catalysed by chloride, bromide, or thiocyanate were inconclusive. The yield of gas liberated in the first reaction did decrease somewhat to *ca.* 64%, in the presence of substantial concentrations of sodium chloride, bromide, or thiocyanate. As (I) is expected to be less reactive than (II), this is the direction expected for nitrosation by a less reactive electrophile. As however it was necessary to add quite large concentrations of sodium halides in order to divert a large proportion of the reaction to the nitrosyl halide mechanism, up to 0.8 mol dm^{-3}, there may be masking complications due to specific salt effects. The evidence is not very strong.

The same difficulty arises with *NN*-dimethylhydrazine. Condon's calculations suggest that there should be 70% of the $(CH_3)_2\overset{+}{N}HNH_2$ tautomer. In the original i.r. study [8] the fact that there were two strong bands above 3 100 cm^{-1} was interpreted as showing that $(CH_3)_2\overset{+}{N}HNH_2$ must be present; it was argued that $(CH_3)_2N\overset{+}{N}H_3$ could only account for one such band. This argument still stands, though Evans and Kynastons' assumption that they were dealing with a single tautomer now looks very suspect.

TABLE 3

Rate constants for the nitrosation of hydrazine and the methylhydrazines by various electrophiles at 25°

Electrophile		$NH_3NH_2^+$	CH_3NHNH_2,H^+	$(CH_3)_2NNH_2,H^+$
$NO^+/H_2NO_2^+$	k_3	611	127	32
ONCl	k_4^{Cl}	(1 140)	1 780	3 430
ONBr	k_4^{Br}	(1 140)	3 500	9 850
ONSCN	k_4^{SCN}	(5 720)	7 090	22 900
	pK_a	8.07	7.87	7.21

If there is a sizeable proportion of $(CH_3)_2NHNH_3^+$

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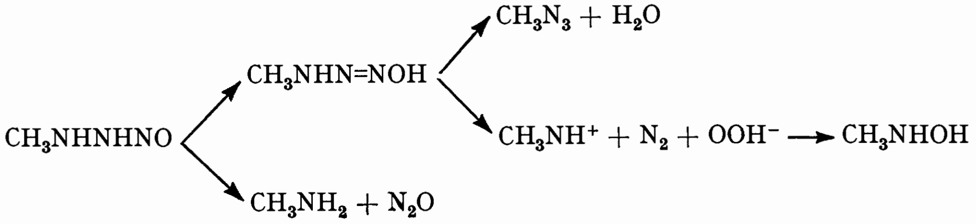
[8] R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 1963, 3151.

[9] L. F. Audrieth, *J. Phys. Chem.*, 1930, **34**, 538.

[10] Ref. 2, p. 129.

[11] F. E. Condon, R. T. Reece, D. G. Shapiro, D. C. Thakker, and T. B. Goldstein, *J.C.S. Perkin II*, 1974, 1112.

then nitrosation would presumably produce $(CH_3)_2\overset{+}{N}(NO)NH_2$ which might denitrosate, or rearrange to $(CH_3)_2NNHNO$. The reactivities of the various compounds studied are compared in Table 3. The best data for the halide-catalysed nitrosation of the hydrazinium ion was obtained at 0°, while the results at 25° were less complete. For this reason these entries in the Table are in parentheses. This shows a remarkable contrast in behaviour; for neutral nitrosating agents there is an increase in reactivity as methyl substitution increases, whereas for a cationic reagent the reactivity generally decreases. For the hydrazinium ion it was shown [1] that the neutral nitrosating agents reacted at very much less than the encounter rate. Increasing electron density on the nitrogen bearing the lone pair should produce an increase in reaction rate, and this accounts for the increasing values of k_4^{X} with increasing methyl substitution. The cause of the decrease in k_3 with increasing methyl substitution is not understood. The methylnitrosohydrazines are thought to be weak bases, and so two protons must be lost in the conversion of the methylhydrazinium ion to its *N*-nitroso-derivative. It might be argued that electron release by the methyl group to the nitrogen makes proton loss more difficult. However as we think that the rates are not much below the encounter rate this is hardly a satisfactory explanation. Furthermore the solvent isotope effect is close to what would be expected for a pre-equilibrium proton transfer, as required by an encounter controlled reaction. It also begs the question of why this effect does not show up for nitrosation by neutral nitrosyl compounds, and why the conjugate acids of the methylhydrazines increase in acidity with increasing methyl substitution.[12] Another explanation is that the transition state bearing a double positive charge will be much more strongly solvated than the reactants, and the methyl groups would sterically hinder solvation. If, however, we are thinking of a reaction close to the encounter limit then this suggests that the simple expression for the effect of charge on the encounter rate based upon the distance of closest approach [13] is not adequate.



(4)

Turning now to the reactions that follow the initial nitrosation, we first consider the disappearance of $CH_3N(NO)NH_2$. This process involves the formation of nitrogen(I) oxide, and it is significant that the total yield in the first and second reactions is close to 100%. We suggest that the second reaction is the rate determining rearrangement of $CH_3N(NO)NH_2$ to $CH_3NHNHNO$, followed by a rapid breakdown as shown in reaction (4). It is known that rearrangements of the type $R^1N(NO)NHR^2$ to $R^1NHN(NO)R^2$ can occur in acid media.[14] Although the rate law for the disappearance of $CH_3N(NO)NH_2$ contained two terms, one independent of acidity and one acid catalysed there was no variation in yield of gas with acidity, so we assume that both terms refer to the formation of $CH_3NHNHNO$. The observation of a peak at *m/e* 57 at high acidities indicates the possibility of an acid-catalysed decomposition leading to methyl azide. For the reaction of methylhydrazine and nitrous acid at high concentrations the most significant fact seems to be that there is no sign of $CH_3N(NO)NH_2$ or $CH_3NH_3^+$ among the products. It might be argued that methylamine and nitrous acid have reacted to form methanol and dinitrogen. However the kinetics of this reaction have been investigated and at the concentrations studied such a reaction would take many hours to go to completion, whereas the ^1H n.m.r. spectra show that reaction is complete within 15 min. Another possibility, reaction (5) between methyl azide

$$CH_3N_3 + HNO_2 + H^+ \longrightarrow [CH_3NNNNO]^+ \xrightarrow{H_2O} CH_3OH + N_2 + N_2O + H^+ \quad (5)$$

and nitrous acid is excluded by the fact that this is a very slow process.[15] Thiele in his original work on the nitrosation of the alkylhydrazines stated [14] that in acidic media nitrous acid reacts with nitrosomethylhydrazine and destroys it, with the evolution of gas. He suggested the reaction sequence (6). For *NN'*-

$$RNHNH_2 \longrightarrow RN(NO)NH_2 \longrightarrow RN(NO)N(NO)H \longrightarrow RN(NO)H + N_2O \longrightarrow RN{=}NOH \quad (6)$$

dimethylhydrazine he suggested that further action of nitrous acid upon $CH_3N(NO)NHCH_3$ formed $CH_3N(NO)N(NO)CH_3$. These ideas fit in well with our own observations; we suggest that not only does $CH_3N(NO)NH_2$ react in the manner but so also does the intermediate $CH_3NHNHNO$ that we have assumed to exist. If it were trapped in this fashion it would not be able to break down to form methylamine. In experiments that we have carried out [16] on a range of substituted phenylhydrazines reacting with excess of nitrous acid we have obtained large yields of the corresponding diazonium

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[12] Ref. 2, p. 121.

[13] E. F. Caldin, 'Fast Reactions in Solution,' Blackwell, Oxford, 1964, p. 12.

[14] J. Thiele, *Annalen*, 1910, **376**, 264.

[15] R. C. Thompson, personal communication.

[16] G. Stedman and N. Uysal, unpublished work.

ion. By analogy we suggest that for methylhydrazine $CH_3N(NO)NHNO$ tautomerises to $CH_3\overset{+}{N}(=NOH)\overset{-}{N}NO$ which loses nitrogen(I) oxide to form an unstable diazonium ion which in turn reacts with the solvent to form methanol and dinitrogen.

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