RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2018, **8**, 19310

A combined experimental and DFT mechanistic study for the unexpected nitrosolysis of *N*-hydroxymethyldialkylamines in fuming nitric acid†

Yu Zhang, Po Zou, Yingbin Han, Yongliang Geng, Jun Luo* and Baojing Zhou*

Received 17th April 2018
Accepted 15th May 2018

DOI: 10.1039/c8ra03268h

rsc.li/rsc-advances

The reaction of dimorpholinomethane in fuming HNO_3 was investigated. Interestingly, the major product was identified as *N*-nitrosomorpholine and a key intermediate *N*-hydroxymethylmorpholine was detected during the reaction by ^{1}H-NMR tracking which indicates that the reaction proceeds *via* an unexpected nitrosolysis process. A plausible nitrosolysis mechanism for *N*-hydroxymethyldialkylamine in fuming nitric acid involving a HNO_3 redox reaction is proposed, which is supported by both experimental results and density functional theory (DFT) calculations. The effects of ammonium nitrate and water on the nitrosolysis were studied using different ammonium salts as additives and varying water content, respectively. Observations show the key role of ammonium ions and a small amount of water in promoting the nitrosolysis reaction. Furthermore, DFT calculations reveal an essential point that ammonia, merged from the decomposition of the ammonium salts, acts as a Lewis base catalyst, and the hydroxymethyl group of the substrate participates in a hydrogen-bonding interaction with the NH_3 and H_2O molecules.

Introduction

N-Nitramines and *N*-nitrosamines are present in a wide range of drug molecules, functional organic chemicals and energetic materials.[1] For example, some *N*-nitrosamines have biological activity and can be used in various treatments for illnesses including cancer, cardiovascular diseases, central nervous, and diseases related to immunity and physiological disorders.[2] *N*-Nitrosamines are valuable intermediates in organic synthesis[3] such as in application for the preparation of biologically important α-disubstituted hydrazines[4] and mesoionic-heterocyclic compounds like sydnones.[5] *N*-Nitrosamines can also be applied as a nitroso source to prepare aryl *C*-nitroso compounds in good yield through a Fischer-Hepp rearrangement.[6] Recently, *N*-nitroso functionality has emerged as a traceless directing group for the activation of inert C–H bonds in aryl rings by associating with transition metals.[7] Furthermore, some widely used explosives with excellent performances such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) belong to the *N*-nitramine group, which can be prepared from acetamides and *N*-nitrosamines through nitrolysis or oxidation.[8]

Interestingly, when nitryl chloride, nitrogen pentoxide, nitryl fluoride, nitronium fluoroborate and tetranitromethane were used for the *N*-nitration of secondary or tertiary amines at low temperatures, nitrosamine products were obtained with low yields.[9] Our group made efforts to synthesize HMX by nitrolyzing 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT) with traditional nitration systems such as fuming HNO_3, HNO_3–H_2SO_4, HNO_3–N_2O_5, and HNO_3–Ac_2O below 0 °C, but 1-nitroso-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (MNX) was achieved as the main product. Furthermore, NH_4NO_3 can inevitably improve the yield of MNX.[8f] Recently, the so called "small-molecule route" using urea as the starting material to prepare HMX *via* DPT has been thought to be a promising method for scale-up.[10] Although the development of various techniques has enhanced the yield of HMX by the nitrolysis of DPT, no significant progress in practical potential has been achieved.[11] The main reason is attributed to the ambiguity of the nitrolysis mechanism.[8e,8f] It's widely considered that the bridging methylene of the DPT is cleaved to produce an extremely active intermediate 1-hydroxymethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane.[12] The addition of NH_4NO_3 can hinder esterification (*O*-acetylation in HNO_3–Ac_2O and *N*-nitraton in fuming HNO_3) but promote dehydroxymethylation to improve the HMX yield.[8e,8f,11,12] However, there is no sufficient or direct experimental evidence to support the above mechanism because of the rapid reaction characteristics of the nitrolysis process, and the production of a complex by-product, and a short-lived intermediate.[12]

In this work, we selected a bridging methylene diamine dimorpholinomethane as a model substance and investigated

---

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: luojun@njust.edu.cn; bzhou@njust.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra03268h

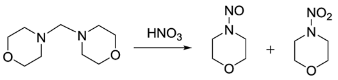
in detail its reaction in fuming nitric acid to mimic the nitrolysis of DPT. Interestingly, nitrosomopholine was obtained as the main product and the key intermediate *N*-hydroxymethylmorpholine was detected by ^{1}H-NMR tracking during the reaction. Based on experimental observations, a plausible mechanism for the nitrosolysis of *N*-hydroxymethyldialkylamines in fuming nitric acid is proposed. We further provide computational results for the possible reaction mechanism at the molecular level using the density functional theory (DFT), which is one of the popular routes to understand the course of an organic reaction.[13]

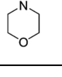
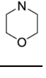
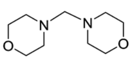
Results and discussion

Similar to DPT, dimorpholinomethane has the *N*,*N*′-methylene motif. Therefore, we first examined the reaction of the dimorpholinomethane with fuming nitric acid. To our surprise, *N*-nitrosomorpholine was obtained rather than *N*-nitromorpholine when the reaction was carried out at room temperature (Table 1, entry 1). Prolonging the reaction time increased the yield of *N*-nitrosomorpholine (entries 2, 3). A small amount of *N*-nitromorpholine was isolated after reacting for 12 hours (entry 3). When the reaction temperature was elevated from 25 °C to 40 °C, both of them were obtained with higher yields (entry 4). A further increase of the reaction temperature to 70 °C afforded a lower yield of *N*-nitrosomorpholine but a higher yield of *N*-nitromorpholine (entry 5). It is well known that NH_4NO_3 plays a key role in the nitrolysis of DPT.[11] Here, similarly, the yield of *N*-nitrosomorpholine increased dramatically when NH_4NO_3 was used as an additive to the reaction mixture (entry 6).

It is generally accepted that 1-hydroxymethyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane is a key intermediate during the nitrolysis of DPT in fuming nitric acid. Accordingly, we hypothesized that *N*-hydroxymethylmorpholine is the intermediate in the reaction of dimorpholinomethane in fuming nitric acid. To verify this, the reaction was performed at 0 °C for 10 minutes, then the reaction mixture was poured into ice water, extracted with cold dichloromethane, and washed with ice water to neutralise it. A yellow oily liquid was obtained by rotary evaporation at room temperature. According to the ^{1}H-NMR spectrum, three compounds can be identified (Fig. 1a). As shown in Fig. 1b, the chemical shifts of the dimorpholinomethane occur at 3.70–3.69, 2.91, 2.50 ppm.[14] Clearly, the mixture mainly consists of dimorpholinomethane. As shown in Fig. 1c, hydrogen atoms observed at 4.13, 3.74–3.69 and 2.72–2.67 ppm are assigned to *N*-hydromethylmorpholine.[14] Comparing Fig. 1a with 1c, we can distinguish *N*-hydromethylmorpholine from the mixture. However, *N*-nitromorpholine, whose chemical shift is at 3.83 ppm (Fig. 1d), is not found in the mixture. Moreover, comparing Fig. 1a with 1e, we found that the chemical shifts at 44.31–4.29, 3.91–3.86 and 3.68–3.66 ppm in the former spectrum belong to *N*-nitrosomorpholine.[14a] Thus, *N*-hydroxymethylmorpholine is formed during the reaction and nitrosolysis is predominant at room temperature in classical nitration systems.

Table 1 The results for the reaction of dimorpholinomethane in fuming HNO_3[a]



Substrate	Entry	Reactant system	T/°C	t/h	Yield[c]/%	
						
	1	HNO_3	25	1	10	0
	2	HNO_3	25	4	18	0
	3	HNO_3	25	12	25	5
	4	HNO_3	40	1	29	10
	5	HNO_3	70	1	15	16
	6	HNO_3/NH_4NO_3[b]	25	1	31	0

[a] Unless otherwise noted, dimorpholinomethane (5 mmol), fuming HNO_3 (200 mmol). [b] NH_4NO_3 (12.5 mmol). [c] Isolated yield.

Although *N*-hydroxymethylmorpholine was observed in the reaction, it is not clear whether it is an intermediate or a by-product. To shed some light on this, we prepared a mixture of *N*-hydroxymethylmorpholine and dimorpholinomethane as the substrate for the reaction. As shown in Table 2, *N*-nitrosomorpholine is still the major product in fuming nitric acid, and only 3% of *N*-nitromorpholine is obtained (entry 1). The yields of *N*-nitrosomorpholine and *N*-nitromorpholine increase with the elongation of the reaction time (entries 1–3). In contrast, with an elevation in the reaction temperature, the yield of *N*-nitrosomorpholine first increases and then decreases (entries 1, 4, 5). Once again, NH_4NO_3 significantly promotes nitrosolysis (entry 6). These observations are similar to those

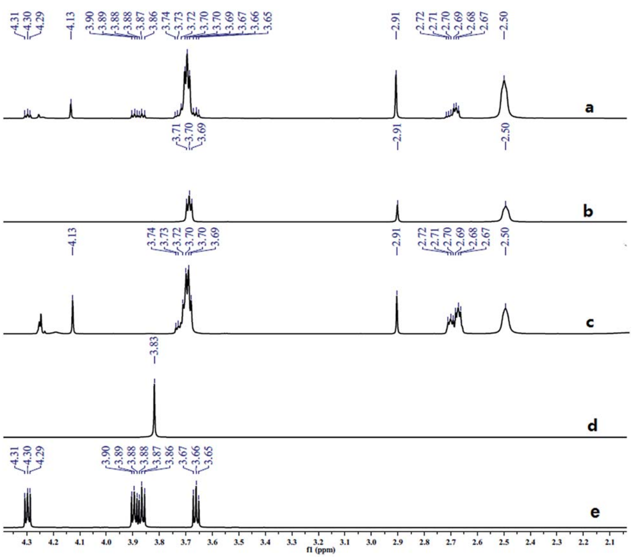
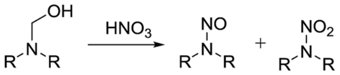
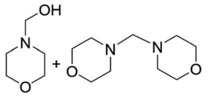
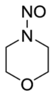
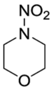
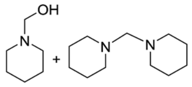
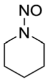
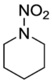
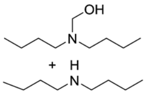
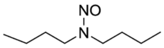
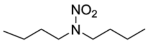


Fig. 1 ^{1}H-NMR spectrum of: (a) the product from the reaction of dimorpholinomethane in fuming HNO_3 at 0 °C for 10 minutes; (b) dimorpholinomethane; (c) the mixture of *N*-hydromethylmorpholine and dimorpholinomethane; (d) *N*-nitromorpholine; (e) *N*-nitrosomorpholine.

Table 2 The results for the reaction of *N*-hydroxymethyldialkylamines in fuming HNO_3[a]



Substrate[b]	Entry	Reactant system	Nitrosamine product	Nitrosamine yield[h]/%	Nitramine product	Nitramine yield[h]/%
	1	HNO_3		21		3
	2[c]	HNO_3		30		6
	3[d]	HNO_3		35		12
	4[e]	HNO_3		33		9
	5[f]	HNO_3		25		18
	6	HNO_3/NH_4NO_3[g]		51		2
	7	$HNO_3/(NH_4)_2SO_4$[g]		46		3
	8	HNO_3/NH_4Cl[g]		49		2
	9	HNO_3/CH_3COONH_4[g]		47		2
	10	HNO_3		21		0
	11	HNO_3/NH_4NO_3[g]		39		0
	12	HNO_3		19		4
	13	HNO_3/NH_4NO_3[g]		38		4

[a] Unless otherwise noted, fuming HNO_3 (200 mmol), $T = 25$ °C, $t = 1$ h. [b] Substrate (5 mmol), *n*(*N*-hydroxymethylmorpholine) : *n*(dimorpholinomethane) = 1 : 1.1, *n*(*N*-hydroxymethylpiperidine) : *n*(dipiperidinemethane) = 1 : 1.25, *n*(*N*-hydroxymethyldibutylamine) : *n*(dibutylamine) = 1 : 1.17. [c] $t = 4$ h. [d] $t = 12$ h. [e] $T = 40$ °C. [f] $T = 70$ °C. [g] NH_4NO_3 (12.5 mmol); NH_4Cl (12.5 mmol); CH_3COONH_4 (12.5 mmol); $(NH_4)_2SO_4$ (6.25 mmol). [h] Isolated yield.

made in the nitrosolysis of dimorpholinomethane. Thus, *N*-hydroxymethylmorpholine should be an intermediate in the reaction, rather than a by-product. The nitrosolysis of the mixture of *N*-hydroxymethylmorpholine and dimorpholinomethane was further carried out in fuming nitric acid/ammonium salts containing $(NH_4)_2SO_4$, NH_4Cl, and CH_3COONH_4. Similar to NH_4NO_3, these ammonium salts can also improve the yield of *N*-nitrosomorpholine (entries 7–9).

We further examined the nitrosolysis of the mixture of *N*-hydroxymethylpiperidine with dipiperidinemethane and that of *N*-hydroxymethyldibutylamine with dibutylamine in the fuming HNO_3, respectively. As shown in Table 2, the main products are identified to be *N*-nitrosamines[15] (entries 10, 12). To estimate the interference of dibutylamine, we calculated its amount in the mixture according to the proton NMR test. Then an equal amount of dibutylamine was used as the substrate for a reaction under common reaction conditions, which was monitored by gas chromatography. Only less than 4% *N*-nitrosodibutylamine (gas chromatography yield) was detected over 2 h. So we conclude that the *N*-nitrosodibutylamine is formed predominantly by the nitrosolysis of *N*-hydroxymethyldibutylamine. The achieved yield of *N*-nitrosopiperidine and *N*-nitrosodibutylamine in the fuming HNO_3/NH_4NO_3 system was 39% and 38% respectively, much higher than for the reactions without NH_4NO_3 (entries 10–13).

The influence of water on the nitrosolysis of the mixture of *N*-hydroxymethylmorpholine and dimorpholinomethane was evaluated by performing the reaction in water-containing nitric acid, which was prepared by the addition of different amounts of water into freshly prepared 100% HNO_3. As shown in Fig. 2, the yield of *N*-nitrosomorpholine first increases and then decreases with the increase of water content. The highest yield of 21% was obtained when *ca.* 5% water was added. Meanwhile, a small amount of *N*-nitromopholine was observed in all cases. These results suggest that *ca.* 5% water is optimal for the nitrosolysis of the mixture of *N*-hydroxymethylmorpholine and dimorpholinomethane.

Considering the fact that only very little HNO_2 and its analogues are present in fuming nitric acid, it is puzzling that the product is mostly *N*-nitrosamine in the above reactions. It is natural to surmise that a redox reaction has occurred. It is plausible that *N*-hydroxymethyldialkylamines react with NO^+ to

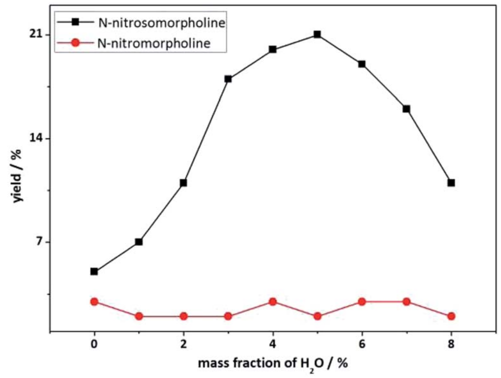


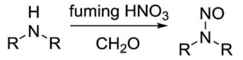
Fig. 2 The effect of water on the nitrolysis of *N*-hydroxymethylmorpholine.

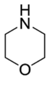
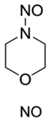
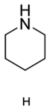
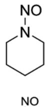
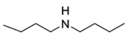
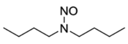
afford the *N*-nitrosoamines and release formaldehyde, which reduces nitric acid to nitrous acid. Then nitrous acid can be viewed as a catalyst. To further verify this viewpoint, three secondary amines were reacted in the fuming nitric acid with or without paraformaldehyde (Table 3). It turned out that *N*-nitrosamines were obtained in less than 6% yield in the absence of paraformaldehyde (entries 1, 3, 5). The addition of paraformaldehyde greatly increases the yield (entries 2, 4, 6). These results suggest that *N*-hydroxymethyldialkylamines are formed as the more active intermediates under the acidic conditions when paraformaldehyde is present.[13]

In the above reaction, some *N*-nitromorpholine was observed and its amount increased with the reaction time (Table 2, entries 1–3). To investigate whether it was formed from the nitrolysis of *N*-nitrosomorpholine, we monitored the reaction of *N*-nitrosomorpholine in fuming nitric acid at 40 °C by ^{1}H-NMR spectroscopy. As shown in Fig. 3a, no *N*-nitromorpholine was observed at the end of the feeding process (Fig. 3a). However, *N*-nitromorpholine gradually formed with an increase in the reaction time as indicated by the chemical shift of 3.83 ppm in Fig. 3b and c[15] and its proportion increased with the disappearance of *N*-nitrosomorpholine. After 6 hours, almost all of the *N*-nitrosomorpholine had been converted to *N*-nitromorpholine (Fig. 3d). On the other hand, some *N*-nitroamines may have been generated by the oxidation of the *N*-nitrosamines.[8] To examine this possibility, the reactions of nitrosomorpholine in 90% HNO_3, 80% HNO_3, 70% HNO_3, 60% HNO_3, and 50% HNO_3 were investigated. Almost no product, however, was detected even when the reaction temperature changed from 20 °C to 80 °C. Thus, we conclude that *N*-nitromorpholine is mainly formed through the nitrolysis of *N*-nitrosomorpholine in fuming nitric acid.

We further performed a computational study to investigate the reaction mechanism at the atomic level. Two reaction models were constructed. The first reactant model contained one *N*-hydroxymethyldialkylamine, one NH_3 and three H_2O molecules. In another reaction model, the NH_3 molecule was replaced by a H_2O molecule. Interestingly, we found that the free ammonia, formed from the unfavourable balance with NH_4^+ in an acidic environment, is a Lewis base catalyst, while water molecules are essential for the formation of the hydrogen bond (HB) adduct. A bicyclic ring was inferred from the bond angle of H_2O molecules. The optimized structures of the reactants, transition states (TSs), and products from the two reaction models in the presence (model a) or absence (model b) of NH_3 are compared in Fig. 4.

Table 3 The nitrosation of secondary amines is promoted by paraformaldehyde[a]



Substrate	Entry	n(substrate) : $n(CH_2O)$	Product	Yield[b]/%
	1 2	0 1 : 1		6 33
	3 4	0 1 : 1		4 51
	5 6	0 1 : 1		3 65

[a] Substrate (5 mmol), fuming HNO_3 (200 mmol) $T = 25$ °C, $t = 1$ h. [b] Isolated yield.

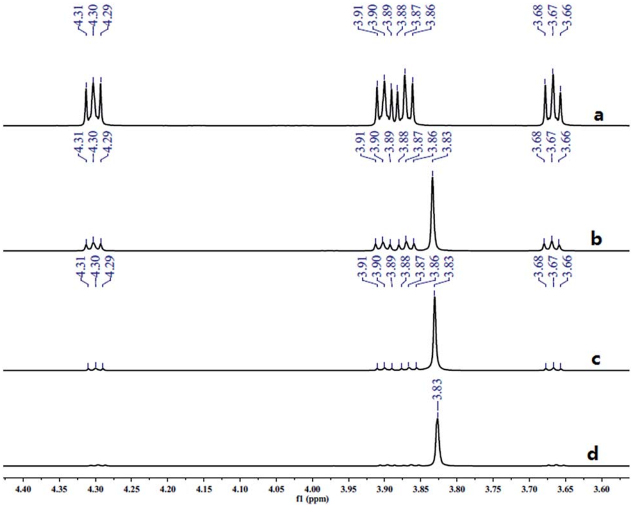


Fig. 3 ^{1}H-NMR spectra of samples taken from the reaction mixture at: (a) the end of the feeding process; (b) 2 hours; (c) 4 hours (d) 6 hours.

For both models, we found that NO^+ is not involved in the bicyclic ring formed from the HB interactions and it approaches the N atom in the substrate from the other side. In the TS, the N–N bond forms, and the C–N bond is breaking, while the H is transferring from the hydroxyl group to the NH_3 (model a) or H_2O molecule (model b), which suggests a synergistic mechanism. The computed relative Gibbs free energy profiles for models a and b are summarized in Fig. 5. For model a, the predicted Gibbs free energy of activation is 3.3 kcal mol^{-1}. For model b, the reaction barrier is 13.7 kcal mol^{-1}, which is 10.4 kcal mol^{-1} higher than that of model a. These results indicate that the NH_3 molecule plays the role of a catalyst. Therefore, the addition of NH_4^+ can significantly promote the nitrosolysis of *N*-hydroxymethyldialkylamines.

The gradual changes of the four chemical bonds along the reaction coordinate are illustrated in Fig. 6. First, the hydroxyl H is extracted by the N of ammonia, which leaves the negative charge on the *N*-hydroxymethyldialkylamine substrate. Then the electrophilic attack is initiated by NO^+ as indicated by its decreasing separation from the N atom of the substrate. When the N–N bond is half formed, the C–N and O–H bonds break, which leads to the formation of the products, *i.e.* nitrosamine, formaldehyde, and ammonium. The highly synchronous variations further indicate the concerted reaction mechanism for the nitrolysis of *N*-hydroxymethylmorpholine.

Based on our experimental and theoretical results and the related reports,[8e,8f,11,12] we propose a plausible mechanism for

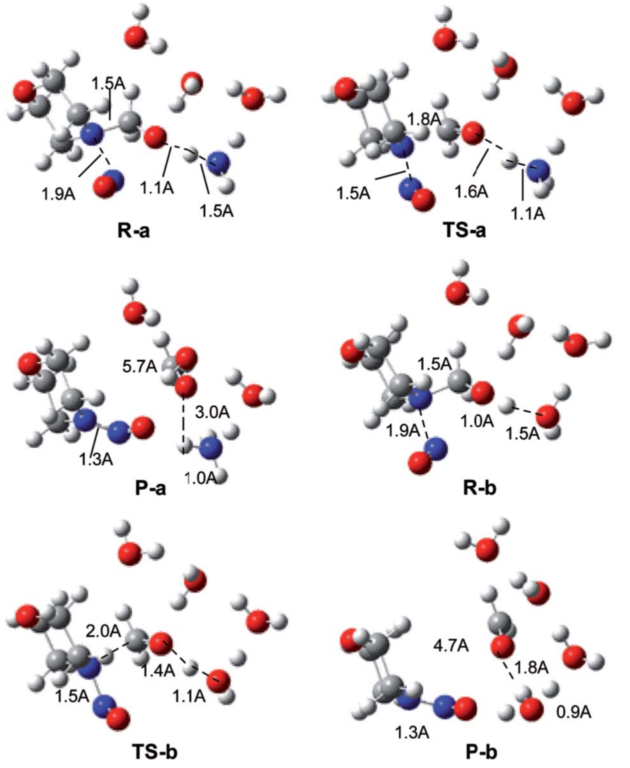


Fig. 4 Optimized structures for the two reaction models representing the nitrosolysis of *N*-hydroxymethylmorpholine. Model a contains an NH_3 molecule, while in model b, the NH_3 molecule is replaced by a H_2O molecule. O: red, C: dark grey, H: light grey, N: blue.

the formation of *N*-nitrodialkylamines from *N*-hydroxymethyldialkylamines in fuming nitric acid and an ammonium nitrate system (Scheme 1). First, a small amount of HNO_2 in fuming HNO_3 is converted to NO^+ and some free NH_3 emerges through the equilibrium reaction with NH_4NO_3. The substrate is conjoined to one ammonia and three water molecules by HB interactions to form the pre-reactive complex *in situ*. Then, the NH_3 abstracts the hydrogen from the hydroxyl group to increase the electron density of the tertiary N atom, which facilitates the attack of NO^+. Then *N*-nitrosamine forms along with the departure of formaldehyde. Subsequently, formaldehyde is oxidized by HNO_3 to form HCOOH.[16] Simultaneously, HNO_3 is reduced to HNO_2 to complete one nitrosolysis cycle. *N*-Nitramine is afforded from *N*-nitrosamine by the replacement of the nitroso group with a nitro group *via* a nitrolysis process.

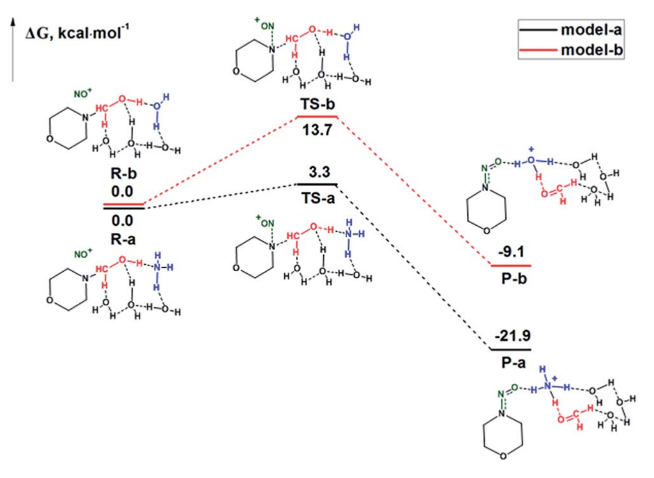


Fig. 5 Energy profile for the nitrosolysis of *N*-hydroxymethylmorpholine in the presence or absence of NH_3.

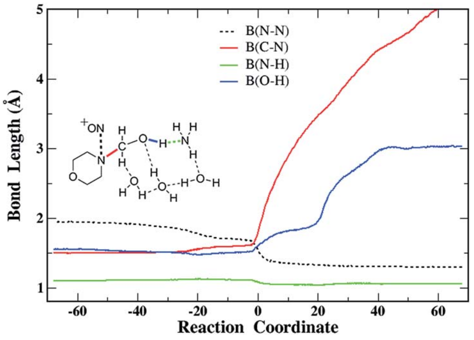
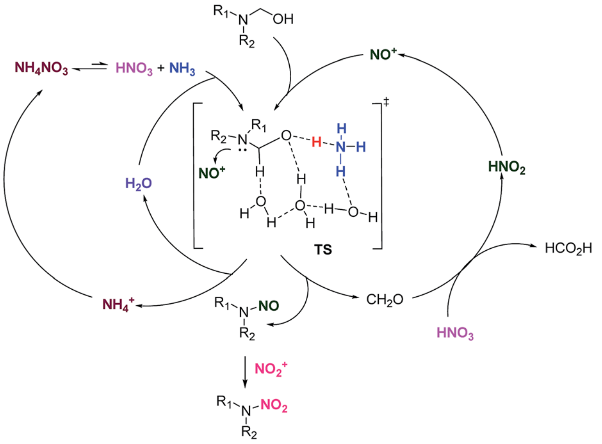


Fig. 6 Bond cleavages and formations along the IRC path of the nitrosolysis of *N*-hydroxymethylmorpholine.



Scheme 1 Possible reaction mechanism for the nitrosolysis of *N*-hydroxymethyldialkylamine.

Conclusions

We synthesized *N*-nitrosodialkylamines from *N*-hydroxymethyldialkylamines in fuming HNO_3 *via* nitrosolysis. The reaction mechanism at the molecular level was established based on experimental observations and DFT calculations and involves a redox reaction of HNO_3 to afford HNO_2. The DFT calculations indicate that the nitrosolysis reaction proceeds very smoothly with a rigid bicyclic transition state consisting of *N*-hydroxymethyldialkylamine, ammonia and water.

Experimental section

General procedure for the nitrosolysis of the mixture of *N*-hydroxymethyldialkamines in fuming nitric acid

The mixture of *N*-hydroxymethyldialkamines (5 mmol) was added in portions to fuming nitric acid (200 mmol) under vigorous stirring at 0 °C, and the reaction mixture was then warmed to a certain temperature. The reaction was quenched by being poured into ice water (20 mL). The resulting mixture was extracted with dichoromethane (3 × 30 mL). The combined organic layer was washed with saturated $NaHCO_3$ and dried with Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure to afford the crude product, and the desired product was obtained by column chromatography.

The same procedure as described above was used for the nitrosolysis of dimorpholinomethane.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was sponsored by Qing Lan Project of Jiangsu Province, P. R. China.

Notes and references

1 (*a*) R. N. Leoppky and J. R. Outram, *N-Nitroso Compounds: Occurrence and Biological Effects*, IARC Scientific Publishers, Lyon, 1982; (*b*) R. N. Loeppky and C. J. Michjda, *Nitrosamines and Related N-Nitroso Compounds: Chemistry and Biochemistry*, ACS Symposium Series, American Chemical Society, Washington DC, 1994; (*c*) S. Gupta, N. Muniyappan and S. Sabiah, *Green Chem.*, 2016, **18**, 2323–2330; (*d*) J. Zhang, J. Jiang and Y. Li, *J. Org. Chem.*, 2013, **78**, 11366–11372; (*e*) J. P. Agrawal and R. Hodgson, *Organic chemistry of explosives*, Wiley-VCH, New York, 2007; (*f*) B. Wang, X. Qi and W. Zhang, *J. Mater. Chem. A*, 2017, **5**, 20867–20873; (*g*) P. Yin and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, **54**, 14513–14517; (*h*) P. Yin, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2014, **53**, 12889–12892.

2 (*a*) P. G. Wang and M. Xian, *Chem. Rev.*, 2002, **102**, 1091–1134; (*b*) H. Kakeya, M. Imoto, Y. Takahashi, H. Naganawa, T. Takeuchi and K. Umezawa, *J. Antibiot.*, 1993, **46**, 1716–1719; (*c*) M. Li, S. M. Shandilya and M. A. Carpenter, *ACS Chem. Biol.*, 2012, **7**, 506–517; (*d*) C. T. Gnewuch and G. Sosnovsky, *Chem. Rev.*, 1997, **97**, 829–1013; (*e*) A. A. Rossini, A. A. Like and W. L. Chick, *Proc. Natl. Acad. Sci. U. S. A.*, 1977, **74**, 2485–2489; (*f*) H. Iimura, T. Takeuchi, S. Kondo and M. Matsuzaki, *J. Antibiot.*, 1972, **25**, 497–500; (*g*) W. D. Kumler and P. P. Sah, *J. Pharm. Sci.*, 1952, **41**, 375–379; (*h*) F. D. Popp, *J. Pharm. Sci.*, 1973, **62**, 679–680.

3 J. E. Saavedra, *Org. Prep. Proced. Int.*, 1987, **19**, 85–159.

4 (*a*) I. D. Entwistle, R. A. W. Johnstone and A. H. Wilby, *Tetrahedron*, 1982, **38**, 419–423; (*b*) F. W. Schueler and C. Hanna, *J. Am. Chem. Soc.*, 1951, **73**, 4996; (*c*) W. W. Hartman and L. J. Roll, *Org. Synth.*, 1933, **13**, 66–67; (*d*) R. L. Hinmap and K. L. Hamm, *J. Org. Chem.*, 1958, **23**, 529–531.

5 (*a*) D. L. Browne and J. P. A. Harrity, *Tetrahedron*, 2010, **66**, 553–556; (*b*) F. H. C. Stewart, *Chem. Rev.*, 1964, **64**, 129–147.

6 (*a*) D. L. H. Williams, *Tetrahedron*, 1975, **31**, 1343–1349; (*b*) I. Cikotiene, M. Jonusis and V. Jakubkiene, *Beilstein J. Org. Chem.*, 2013, **9**, 1819–1825.

7 (*a*) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu and J. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 468–473; (*b*) B. Q. Liu, C. Song, C. Sun, S. G. Zhou and J. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 16625–16631; (*c*) C. Wang and Y. Huang, *Org. Lett.*, 2013, **15**, 5294–5297; (*d*) J. Chen, P. Chen, C. Song and J. Zhu, *Chem.–Eur. J.*, 2014, **20**, 14245–14249; (*e*) T. Gao and P. Sun, *J. Org. Chem.*, 2014, **79**, 9888–9893; (*f*) Y. Wu, L. J. Feng, X. Lu, F. Y. Kwong and H. B. Luo, *Chem. Commun.*, 2014, **50**, 15352–15354; (*g*) F. Xie, Z. S. Qi, S. J. Yu and X. W. Li, *J. Am. Chem. Soc.*, 2014, **136**, 4780–4787; (*h*) S. Yu and X. Li, *Org. Lett.*, 2014, **16**, 1200–1203; (*i*) D. D. Li, Y. X. Cao and G. W. Wang, *Org. Biomol. Chem.*, 2015, **13**, 6958–6964; (*j*) J. Dong, Z. Wu, Z. Liu, P. Liu and P. Sun, *J. Org. Chem.*, 2015, **80**, 12588–12593; (*k*) Y. Liang and N. Jiao, *Angew. Chem., Int. Ed.*, 2016, **55**, 4035–4039; (*l*) L. Zhang, Z. Wang and P. Y. Guo, *Tetrahedron Lett.*, 2016, **57**, 511–2514.

8 (*a*) F. J. Brockman, D. C. Downing and G. F. Wright, *Can. J. Res.*, 1949, **27**, 469–474; (*b*) T. G. Bonner, R. A. Hancock and J. C. Robert, *J. Chem. Soc., Perkin Trans. 1*, 1974, **5**, 653–658; (*c*) W. E. Bachmann and E. L. Jenner, *J. Am. Chem. Soc.*, 1951, **73**, 2773–2775; (*d*) J. R. Wu, *Chin. J. Explos. Propellants*, 1989, **4**, 1–5; (*e*) W. J. Liu, Z. B. Xu, K. J. Cui and Z. H. Meng, *Propellants, Explos., Pyrotech.*, 2015, **40**, 645–651; (*f*) Y. Zhang, P. Zou and J. Luo, *Propellants, Explos., Pyrotech.*, 2017, **42**, 1208–1213; (*g*) N. V. Latypov, A. U. Wellmar and P. Goede, *Org. Process Res. Dev.*, 2000, **4**, 156–158; (*h*) Y. X. Ou, Z. Meng and J. Q. Liu, *Chem. Ind. Eng. Prog.*, 2007, **26**, 762–768.

9 (*a*) D. L. H. Williams, *Adv. Phys. Org. Chem.*, 1983, **19**, 381–428; (*b*) M. A. Ilyushin, E. L. Golod and B. V. Gidaspov, *Zh. Org. Khim.*, 1977, **13**, 11–17; (*c*) T. C. Bruice and S. L. Walters, *J. Am. Chem. Soc.*, 1971, **93**, 2269–2282; (*d*) A. Castonguay and H. V. Vunakis, *Toxicol. Lett.*, 1979, **4**, 475–480; (*e*) J. C. Bottaro, R. T. Schmitt and C. D. Bedford, *J. Org. Chem.*, 1987, **52**, 2292–2294; (*f*) O. V. Anikin, G. V. Pokhvisneva and D. L. Lipilin, *Russ. Chem. Bull.*, 2009, **58**, 2043–2046; (*g*) Y. D. Park, H. K. Kim and J. J. Kim, *J. Org. Chem.*, 2003, **68**, 9113–9115; (*h*) X. F. Chen, K. Yang and B. Z. Wang, *J. Phys. Chem. A*, 2013, **117**, 5007–5014; (*i*) Y. D. Liu and R. G. Zhong, *Chin. J. Struct. Chem.*, 2010, **29**, 421–431; (*j*) Z. Mao, H. Jiang and Z. Li, *Chem. Sci.*, 2017, **8**, 4533–4538; (*k*) J. Miao, Y. Y. Huo and X. Lv, *Biomaterials*, 2016, **78**, 11–19; (*l*) R. Azadi and K. Kolivand, *Tetrahedron Lett.*, 2015, **56**, 5613–5615.

10 (*a*) S. Radhakrishnan, M. B. Talawar and S. Venugopalan, *J. Hazard. Mater.*, 2008, **152**, 1317–1324; (*b*) S. Radhakrishnan, K. S. Kumar and T. Soman, *J. Energ. Mater.*, 2008, **26**, 102–114; (*c*) H. Y. Song, P. Wang, Z. X. Ge and Z. H. Meng, *Chin. J. Org. Chem.*, 2010, **30**, 414–418; (*d*) H. Qian, D. B. Liu and C. X. Lv, *Lett. Org. Chem.*, 2011, **42**,

184–187; (*e*) F. S. Toosi and M. Jadidoleslami, *Synth. React. Inorg. Met.-Org. Chem.*, 2016, **46**, 159–162.

11 (*a*) L. Chen, Z. M. Chen and X. H. Chen, *Chin. J. Explos. Propellants*, 1986, **3**, 1–5; (*b*) X. C. Huang, Z. H. Meng and Z. X. Ge, *Chin. J. Appl. Chem.*, 2013, **42**, 299–303; (*c*) M. H. Xi, *Chin. J. Energ. Mater.*, 1996, **4**, 57–61; (*d*) Q. L. Li, J. Chen and J. L. Wang, *Chin. J. Energ. Mater.*, 2007, **15**, 509–510; (*e*) Z. Y. He, J. Luo and C. X. Lv, *Bull. Korean Chem. Soc.*, 2011, **32**, 2677–2682; (*f*) H. Z. Zhi, J. Luo and G. A. Feng, *Chin. Chem. Lett.*, 2009, **20**, 379–382; (*g*) Z. Y. He, J. Luo and C. X. Lv, *Chin. J. Explos. Propellants*, 2010, **33**, 1–4.

12 (*a*) X. C. Huang, T. Yu and Z. X. Ge, *Chin. J. Energ. Mater.*, 2015, **23**, 1151–1154; (*b*) A. F. McKay, G. F. Wright and H. H. Richmond, *Can. J. Res.*, 1949, **27**, 462–468; (*c*) Z. Y. He, J. Luo and C. X. Lv, *Chin. J. Energ. Mater.*, 2012, **20**, 5–8; (*d*) S. Epstein and C. A. Winkler, *Can. J. Chem.*, 1952, **30**, 734–742; (*e*) Z. M. Si, S. H. Jin and L. J. Li, *Chin. J. Explos. Propellants*, 2011, **34**, 21–25; (*f*) L. Shi, Z. Gang and Y. Zhang, *Chin. J. Chem.*, 2010, **28**, 1553–1558; (*g*) S. L. Zhang, X. F. Xiong and Y. U. Tao, *Chem. J. Chin. Univ.*, 2012, **33**, 1444–1449; (*h*) Z. Y. He, J. Luo and C. X. Lv, *J. Explos. Propellants*, 2010, **33**, 1–4.

13 (*a*) S. Li, H. Tang and Y. Wang, *J. Mol. Catal. A: Chem.*, 2015, **407**, 137–146; (*b*) Y. Wang, L. Zheng, D. Wei and M. Tang, *Org. Chem. Front.*, 2015, **2**, 874–884; (*c*) Y. Wang, B. Wu, L. Zheng, D. Wei and M. Tang, *Org. Chem. Front.*, 2016, **3**, 190–203; (*d*) Y. Wang, M. Tang and D. Wei, *J. Org. Chem.*, 2016, **81**, 5370–5380.

14 (*a*) M. Turlington and L. Pu, *Org. Synth.*, 2010, **87**, 59–67; (*b*) T. Netscher, F. Mazzini and J. Roselyne, *Eur. J. Org. Chem.*, 2007, **7**, 1176–1183.

15 (*a*) J. Zhang, J. Jiang and Y. Li, *J. Org. Chem.*, 2013, **78**, 11366–11372; (*b*) I. V. Kuchurov, I. V. Fomenkov and S. G. Zlotin, *Russ. Chem. Bull.*, 2010, **59**, 2147–2150.

16 R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, 1967, **89**, 1827–1836.