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Catalytic Metal-free Deoxygenation of Nitrous Oxide with Disilanes

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Supporting Information Placeholder

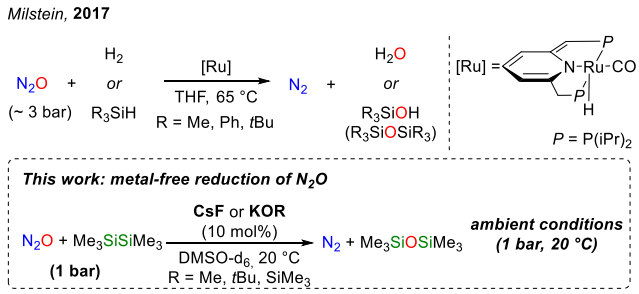
ABSTRACT: Due to its high kinetic stability, conditions to reduce the greenhouse gas N_2O are limited, hence requiring a better understanding of its chemistry and of the N–O bond cleavage. In this work, N_2O was deoxygenated under metal-free conditions. Using disilanes as reducing agents and a catalytic amount of fluoride anions or alkoxides allowed a mild reduction at ambient pressure and temperature. DFT calculations unveiled the mechanism, which shows a nucleophilic addition of a silyl anion to the central N atom of N_2O and release of N_2 from a pseudo-Brook rearrangement.
KEYWORDS: nitrous oxide, organocatalysis, reduction, fluoride, disilanes

In the natural nitrogen cycle, nitrous oxide, also called "laughing gas", is the last intermediate of the denitrification process, which transforms nitrates into atmospheric dinitrogen.[1] Because of human activities, such as agriculture, waste management, and industrial productions of adipic and nitric acid, its atmospheric concentration has significantly increased in the last centuries (20% since 1750),[2] raising environmental issues. N_2O is indeed the most potent ozone-depleting substance and a greenhouse gas,[3] estimated to be 298 times more potent than CO_2.[4] This has led to a growing interest in its chemical reactivity and to the development of end-of-the-pipe technologies to reduce industrial emissions.[5]

From a synthetic point of view, nitrous oxide is kinetically highly stable[6] and a poor ligand for transition metals.[7] Hence, reactions with this gas often require harsh conditions in presence of heterogeneous catalysts (typically >200 °C and >25 bar for alkenes oxidation).[8] Only few examples of reactions with N_2O occur under homogeneous and milder reaction conditions.[9] In most cases, N_2O has been used as an oxidant ($E°(N_2O/N_2) = 1.77$ V *vs* SHE)[10] and usually reacts with highly reactive organometallic species *via* oxygen atom transfer.[11] This reactivity has enabled the development of transition metal-catalyzed transformations where N_2O is deoxygenated in the presence of reductants such as Grignard reagents,[12] phosphines,[13] aldehydes,[14] alcohols[15] or CO.[16] Recently, Milstein and coworkers showed that the reduction of nitrous oxide can even be performed using H_2, with a PNP pincer ruthenium complex as catalyst (Scheme 1).[17] So far, there is however no example of metal-free deoxygenation of N_2O under mild conditions.

To better apprehend the reactivity of the N–O bond and overcome the kinetic stability of N_2O, we chose to use disilane derivatives as reducing agents. They are indeed efficient and mild deoxygenating agents due to the high oxophilicity of silicon, and easier to activate than hydrogen thanks to a lower bond dissociation energy (79.7 kcal.mol^{-1} in $Me_3SiSiMe_3$ *vs* 104 kcal.mol^{-1} in H_2).[18] Moreover, N_2O is known to react with tetramethylsilane in absence of catalysts but only under harsh conditions (>2 000 bar, >360 °C);[19] a transformation used for the passivation of electronical devices by chemical vapor deposition ("Semi Insulating Polycrystalline Silicon" (SIPOS)).[20] Milstein *et al.* have also used their ruthenium catalyst to perform N_2O reduction with hydrosilanes under milder reaction conditions (3.4 bar, 65 °C, Scheme 1).[17]

We show herein that the deoxygenation of N_2O can even be carried out under ambient conditions (1 bar, 20 °C) without any transition metal by using disilanes in the presence of a catalytic amount of fluoride anions or alkoxides (Scheme 1). Mechanistic investigations unveiled the mechanism at play in the N–O bond cleavage.



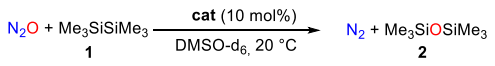
Scheme 1. Catalytic reduction of nitrous oxide with H_2 or organosilanes.

To start our investigations, we selected hexamethyldisilane (**1**) as a readily available and moisture stable reductant. Fluoride anions were screened as catalysts since they are known to efficiently activate disilanes.[21,22] Exposing a DMSO solution of disilane **1** to an atmosphere of N_2O (1 bar), in the presence of a catalytic amount of CsF (10 mol%), resulted in the formation of 77 % hexamethyldisiloxane (**2**) within 4 h at 20 °C. Analysis of the gas phase by gas chromatography (GC) indicated the quantitative conversion of N_2O into N_2 (N_2/N_2O 99:1) (Table 1, entry 1). No reaction took place without catalyst, even after 3 days (Table 1, entry 2).[23] Strictly anhydrous conditions were necessary to avoid the competitive deoxygenation of H_2O leading to H_2 production (Figure S8). Remarkably, the reaction could be scaled-up to 1.78 mmol of disilane **1** without any modification of the protocol, and furnished disiloxane **2** in 75% yield. Other alkali metal fluoride salts (LiF, NaF, KF) did not catalyze the reaction, certainly due to their lower solubilities (Table 1, entries 3-5). In contrast, with tetramethyl ammonium fluoride (TMAF), an anhydrous and solid surrogate of tetrabutyl ammonium fluoride, an increased activity was noted (Table 1, entry 6). The reaction proved to be however much slower with the moisture stable KHF_2 and tetrabutylammonium difluorotriphenyl-silicate (TBAT) as catalysts (Table 1, entries 7 and 8). In these latter cases, the fluoride anion is indeed not naked, and hence less reactive.

Disilanes can also be activated by non-fluorinated bases such as alkoxides.[24] In fact, both KOMe and KO*t*Bu catalyzed the reaction, leading to full conversion of N_2O within 1 h and 2 h, respectively (Table 1, entries 9 and 10). At this stage, KOMe and KO*t*Bu could act as precatalysts for the generation of a silanolate species.[21a,c] This hypothesis was validated by the successful use of $KOSiMe_3$ as a catalyst (Table 1, entry 11).

Interestingly, no reaction was detected in either THF or MeCN, even when 18-crown-6 was added to help solubilize CsF. In contrast, when a DMSO/THF 1:1 mixture was used as solvent, the reaction proceeded but required 48 h to reach full conversion, showing a detrimental effect of THF (Table S2). This observation was ascribed to a lower solubility of both the fluorinated base and N_2O in less polar solvents.

Table 1. Catalyst screening for the reduction of N_2O with disilane **1**.[a]



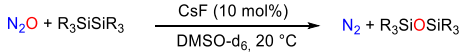
Entry	Cat.	Time	Conversion of **1** (%)[b]	Yield in **2** (%)[b]	N_2/N_2O [c]
1	CsF	4 h	92	77	99:1
2	-	3 days	0	0	5:95
3	LiF	24 h	12	0	10:90
4	NaF	24 h	8	0	5:95
5	KF	24 h	2	0	7:93
6	TMAF	1 h	100	76	97:3
7	KHF_2	24 h	35	2	25:75[e]
8[d]	TBAT	24 h	28	11	30:70
9	KOMe	1 h	98	85	100:0[e]
10	KO*t*Bu	2 h	92	62	100:0[e]
11	$KOSiMe_3$	4 h	86	80	90:10[e]

[a] Conditions: N_2O (1 bar, ≈2 mL), $(Me_3Si)_2$ (0.12 mmol), catalyst (12 µmol, 10 mol%), DMSO-d_6 (0.5 mL). [b] Conversions and yields measured by GC-MS analysis. Internal standard: 1,3,5-trimethoxybenzene. The difference between conversion and yield is ascribed to the volatility of the silylated compounds and to the production of Me_3SiF, Me_3SiOMe or $Me_3SiOtBu$ in the course of the reaction. [c] Corrected GC-ratios. Residual amount of N_2 from the atmosphere <10% [d] Scrambling of R_3Si residues: Ph_3SiF and $Ph_3SiOSiMe_3$ are detectable in GC-MS. [e] H_2 is also detected in GC (<2%). See SI for more details (p. S7).

To test the influence of the stereoelectronic properties of the silane reductant, the deoxygenation of N_2O was carried out with $(PhMe_2Si)_2$ (**3**) and $(Ph_2MeSi)_2$ (**4**) (Table 2, entries 2 and 3). Interestingly, the more Lewis acidic the disilane was, the faster the reaction proceeded, as reflected in the yields in the corresponding siloxanes, after 1 h, of 55%, 63% and 68%, for disilanes **1**, **3** and **4**, respectively (Table 2). In contrast, neither $(Bpin)_2$ nor $PhMe_2Si$–Bpin proved successful under these conditions.

Unfortunately, no intermediate could be either isolated or observed by NMR in the course of the reaction or through stoichiometric reactions. Hence DFT calculations were used (for computational details see SI, part V), to track how the N–O bond is cleaved under mild and metal-free conditions to promote the reduction of the kinetically stable N_2O molecule. According to the experimental results, CsF and $KOSiMe_3$ show a similar activity (Table 1, entries 1 and 11), and the latter was hence selected as a catalyst in the mechanism depicted in Scheme 2. The role of the fluoride anion (or alkoxides) as a precatalyst (mechanism A) or as a catalyst (mechanism B) is also explored, thereafter.

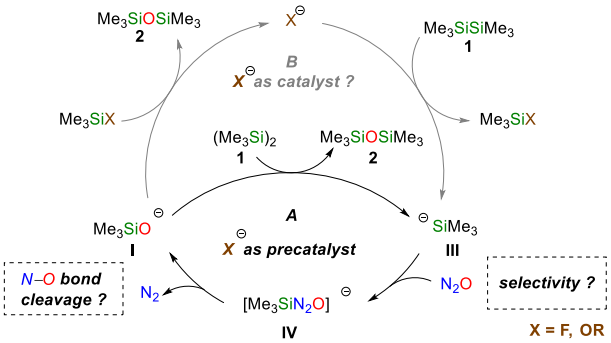
Table 2. Screening of disilanes for the reduction of N_2O[a]



Entry	R_3SiSiR_3	Yield[b] after 1 h	Final yield[b]	N_2/N_2O[c]
1	$(Me_3Si)_2$ (**1**)	55%	77% (4 h)	99:1
2	$(PhMe_2Si)_2$ (**3**)	63%	93% (3 h)	100:0
3[d]	$(Ph_2MeSi)_2$ (**4**)	68%	93% (2 h)	100:0

[a] Conditions: N_2O (1 bar, ca. 2 mL), R_3SiSiR_3 (0.12 mmol), catalyst (12 µmol, 10 mol%), DMSO-d_6 (0.5 mL). [b] Yields measured by GC-analysis (disilane **1**) or by NMR-analysis (compounds **3** and **4**). Internal standard: 1,3,5-trimethoxybenzene. [c] Corrected GC-ratios. Residual amount of N_2 from the atmosphere <10%. [d] To overcome the poor solubility of the starting material in DMSO, the reaction mixture was stirred 2 h at 20 °C under argon prior to adding N_2O. See SI for more details (p. S11).

The silanolate Me_3SiO^- (**I**) can react either with N_2O or with $(Me_3Si)_2$ (**1**). Whereas the activation barrier of the reaction with N_2O was high in energy ($\Delta G^{\ddagger}$= +44.4 kcal.mol^{-1}, Figure S10), the nucleophilic addition of silanolate **I** to disilane **1** appeared more favorable ($\Delta G^{\ddagger}$= +18.5 kcal.mol^{-1}). After release of the siloxane $(Me_3Si)_2O$ (**2**), it generates a highly nucleophilic Me_3Si^- anion (**III**), in an overall exergonic sequence (ΔG= –4.7 kcal.mol^{-1}) (Figure 1c). This result is supported by the observation in NMR of the instantaneous formation of $Me_3SiOSiMe_3$ (**2**) when $KOSiMe_3$ and disilane **1** are mixed (Figure S7).



Scheme 2. Two plausible mechanisms: with the fluoride anion or the alkoxides as precatalysts (A) or as catalysts (B).

In contrast to silanolate **I**, silyl anion **III** efficiently reacts with N_2O *via* a nucleophilic attack. Considering that the two degenerate LUMOs of N_2O are mostly developed on the two nitrogen atoms (Figure 1a), the nucleophilic attack can occur either on the central or the terminal nitrogen centers. Computational results show a significant difference in the activation barrier energy of both pathways: the nucleophilic attack of Me_3Si^- (**III**) on the central nitrogen is kinetically favored by 10.8 kcal.mol^{-1} (**TS$_3$** and **TS'$_3$**) and, under the applied conditions (20 °C), the attack on the terminal N atom is hardly accessible ($\Delta G^{\ddagger}$=+26.2 kcal.mol^{-1}). As such, the less stable $Me_3Si(N_2O)^-$ intermediate **IV** is the major product. Little is known about the ambivalent reactivity of N_2O as an electrophile. According to DFT calculations, metal-hydride complexes attack preferentially at the terminal nitrogen.[25] Likewise, non-metallic systems, such as *N*-heterocyclic carbenes reported by Severin *et al.*[26] or frustrated Lewis pairs,[27] have been experimentally shown to react *via* the terminal nitrogen of N_2O. The selectivity observed in our system is reversed and follows the principle of least nuclear motion,[28] with an addition of the silyl anion to the nitrogen atom bearing the highest positive charge and a corresponding transition state (**TS$_3$**) that minimizes the bond elongations in the N_2O fragment (Figure 1a and SI).

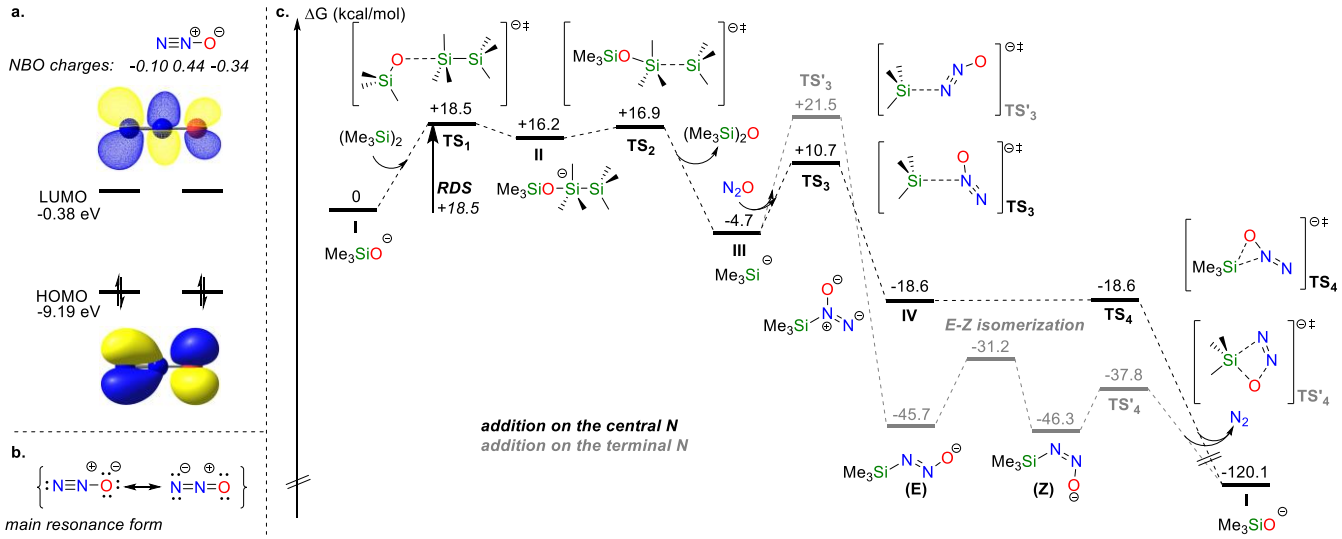


Figure 1. N_2O structure and computed mechanism. [a] NBO charges and frontier molecular orbitals of N_2O [b] Main resonance structures of N_2O [c] Reaction mechanism starting from silanolate **I**. Gibbs free energies in kcal.mol^{-1} computed at the B3LYP-D3/6-31G* (C,H,F,N,O) and B3LYP-D3/6-311+G** (Si) level of theory, using PCM=DMSO to account for solvation

From the $Me_3Si(N_2O)^-$ intermediate (**IV**), an essentially barrier-less and highly exergonic [1,2]-pseudo-Brook rearrangement occurs through the 3-center transition state **TS$_4$** ($\Delta G = -102$ kcal.mol^{-1}), in which the cleavage of the N–O bond is compensated by the synchronized formation of the stable Si–O bond, to release N_2. Such an intramolecular rearrangement has also been proposed for CO_2 reduction with disilanes by Skrydstrup *et al.*[21a,c] and in the reaction of KHMDS with N_2O to synthesize potassium azide, where a [1,4]-silicon shift has been suggested.[29] The overall reaction between N_2O and hexamethyldisilane (**1**) is thus highly exergonic by 120.1 kcal.mol^{-1}, and the first nucleophilic substitution at the silicon atom is the rate determining step (RDS), with an energetic barrier of 18.5 kcal.mol^{-1} (**TS$_1$**, Figure 1c).

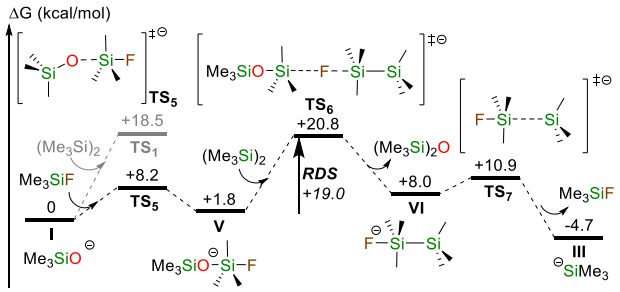


Figure 2. Possible pathway for the regeneration of silyl anion Me_3Si^- (**III**) in presence of a catalytic amount of fluoride anions. Gibbs free energies in kcal.mol-1 computed at the B3LYP-D3/6-31G* (C,H,F) and B3LYP-D3/6-311+G** (Si) level of theory, using PCM=DMSO to account for solvation.

With this mechanism in hands, we then investigated the role of the catalytic species, using the fluoride system as a model. Addition of F^- to the hexamethyldisilane reductant (**1**) generates the Me_3Si^- anion (**III**), in agreement with previous findings,[22] and this nucleophile is competent to deoxygenate N_2O as discussed there above. Yet, its regeneration can proceed *via* two different pathways: either through the route described in Figure 1c, where the fluoride anion is playing the role of a precatalyst (Scheme 2, A), or through a route involving an actual catalytic activity of F^- (Scheme 2, B). The latter implies the displacement of a fluoride anion from Me_3SiF, by the Me_3SiO^- silanolate (**I**). This reaction proceeds *via* an associative pathway, with the formation of a stable pentacoordinated intermediate **V** (Figure 2). The energy barrier involved in the regeneration of the free fluoride anion is computed at 20.8 kcal.mol^{-1}, 2.3 kcal.mol^{-1} greater than the energy span computed for the transformation catalyzed by the Me_3SiO^- silanolate. This small difference in energy suggests that F^- is a precatalyst in the reduction of N_2O by hexamethyldisilane.

In the reduction of N_2O with hexamethyldisilane (**1**), the formation and regeneration of the silyl anion Me_3Si^- (**III**) controls the rate of the reaction. The latter attacks N_2O preferentially at the central nitrogen and a subsequent barrier-less pseudo-Brook rearrangement releases N_2. This mechanism also explains the trend observed with phenyl substituted disilanes **2** and **3** (Table 2). Indeed, with the more acidic disilanes **2** and **3**, the rate of the reaction is no longer controlled by the regeneration of the silyl anion but by the addition of the silyl anion to N_2O, which involves low energy barriers of 15.0 kcal.mol^{-1} and 15.2 kcal.mol^{-1}, respectively (see SI, Figures S12,S13). Thanks to this lower energy span, phenyl substituted disilanes **2** and **3** react faster than disilane **1** (Table 2).

In summary, we have developed the first transition metal-free catalytic deoxygenation of N_2O. The kinetic stability of this gas has been overcome by using disilanes as mild reducing agents, under ambient conditions (1 bar, 20 °C), and in presence of catalytic amounts of fluoride anion or alkoxides. According to DFT calculations, the reaction proceeds through nucleophilic addition of a silyl anion to the central nitrogen of N_2O. The cleavage of the N–O bond then results from a pseudo-Brook rearrangement to release N_2 gas, triggered by the formation of a strong Si–O bond.

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Notes

The authors declare no competing financial interests.

ASSOCIATED CONTENT

Supporting Information

Detailed descriptions of experimental and computational methods are given in the Supporting Information, available free of charge on the ACS Publications website.

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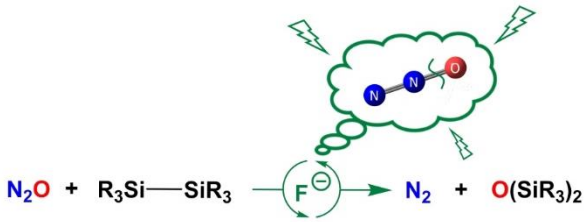
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