107. HNO, an Intermediate in (Light-induced) Rearrangement Reactions of Nitrosooxy Compounds and Nitrosamines

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Summary

IR-spectroscopic investigations of light-induced rearrangement reactions of nitrosooxymethane (CH_3ONO), nitrosooxyethane (CH_3CH_2ONO) and *N,N*-dimethylnitrosamine ($(CH_3)_2NNO$) in low-temperature rare-gas matrices have established that these molecules are transformed in two photolysis steps to the previously unknown *C*-nitroso compounds nitrosomethanol ($CH_2(OH)(NO)$), 1-nitrosoethanol ($CH_3CH(OH)(NO)$), and methyl(nitrosomethyl)amine ($CH_2(NO)(NH)CH_3$). Evidence for a similar rearrangement reaction has been advanced for *N*-nitrosopyrrolidine ($(\overline{C_4H_8N}NO)$) which is converted to *C*-nitrosopyrrolidine ($(\overline{C_3H_6CH(NO)(N}H))$). The matrix-isolation technique in combination with wavelength-selective irradiation allowed to trap and characterize an intermediate of the rearrangement which revealed to be a nitroxyl (HNO) complex ($CH_2O...HNO$, $CH_3CHO...HNO$, $CH_3N=CH_2...HNO$, and $\overline{C_3H_6CH=N}...HNO$). Since these findings have a close resemblance with rearrangement reactions of more complex nitrosooxy compounds, nitrosamines, or nitrosohydrazines used in organic synthesis, it is suggested that also in these reactions nitroxyl is present as an intermediate species.

Introduction. – The interest in the chemistry of nitrosooxy compounds and nitrosamines has gradually increased during the last ten years, not only because of their high carcinogenicity [1][2] but also because of their usefulness as reagents for organic synthesis [3]. Their reaction behavior, which has been studied under a variety of conditions, involves in a number of cases an intramolecular rearrangement. The intermediate steps of this reaction are, however, still subject to speculation [4][5].

For nitrosooxy compounds, nitrosamines, or nitrosohydrazines the common feature of the rearrangement reaction is the exchange of a hydrogen atom and a nitroso group [4] as shown in *Eqn. 1*. In an attempt to observe intermediates of this exchange

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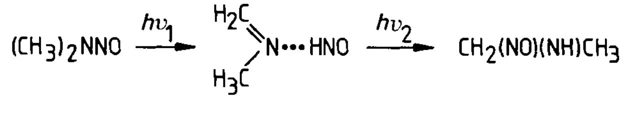
reaction, we investigated by IR-spectroscopic methods the light-induced rearrangement reaction of nitrosooxymethane, nitrosooxyethane, *N,N*-dimethylnitrosamine, and *N*-nitrosopyrrolidine in low-temperature rare-gas matrices. It is shown that these molecules are transformed into the previously unknown *C*-nitroso compounds *via* a HNO-complex.

Experimental. – Apparatus and methods employed in this study are described in [6]. In short, a mixture of the matrix gas (Ar, SWWL) and the nitroso compound (N) in a mole-fraction ratio Ar/N ≈ 1000 was deposited at about 20 K onto a cold target (CsI-window). The IR spectra were recorded between 170 and 4000 cm^{-1} with a *Perkin-Elmer 580B* spectrometer. Photolysis was conducted with a 580-W high-pressure Hg arc lamp *(Osram HBO)* using a water filter and either a monochromator or suitable cut-off filters. The monochromator (*f*/4.0, focal length 220 mm) equipped with 5-mm slits provided a bandpass of ± 10 nm. Nitrosooxymethane and nitrosooxyethane were synthesized according to the method of *Hartung & Crossley* [7]. These compounds as well as *N,N*-dimethylnitrosamine *(Merck)* and *N*-nitrosopyrrolidine *(Fluka)* were purified by distillation.

Results and Discussion. – In a previous study it was shown that wavelength-selective photolysis of nitrosooxymethane in an Ar matrix produces formaldehyde and nitroxyl [8–10]. These products form a well-isolated 1:1 complex, $CH_2O...HNO$, in the matrix cage [9][10]. Further irradiation, either into the absorption of the formaldehyde moiety with $\lambda_{exc} = 345$ nm or into the absorption of the nitroxyl part of the complex with $\lambda_{exc} \approx 650$ nm led to the previously unknown species nitrosomethanol in two distinct rotameric conformations [11], *cf. Eqn. 2*. The 345-nm excitation produces the *trans*-species while with $\lambda_{exc} \approx 650$ nm the *cis*-rotamer is formed. To firmly establish the intermediate step $CH_2O...HNO$ as well as the structure and vibrational spectra of the new photoproduct nitrosomethanol, experiments were performed on eight isotopomers. Together with extensive *ab initio* and normal-coordinate calculations we achieved an unequivocal assignment of the fundamental vibrations of the complex [9] and the nitrosomethanol conformers [12]. Very recently this rearrangement reaction has been reported to occur in the photodecomposition of nitromethane in solid Ar, where nitrosooxymethane is formed in a primary step [13]. On this firm basis provided by the nitrosooxymethane results, the identification of the products of similar light-induced rearrangements was considerably facilitated, *cf. Eqn. 2–4*.

$$CH_3\text{-}ONO \xrightarrow{h\nu_1} CH_2O\cdots HNO \xrightarrow{h\nu_2} \underset{\textit{cis}\text{ and }\textit{trans}}{CH_2(OH)(NO)} \qquad (2)$$

$$CD_3CH_2\text{-}ONO \xrightarrow{h\nu_1} CD_3CHO\cdots HNO \xrightarrow{h\nu_2} \underset{\textit{cis}}{CD_3CH(OH)(NO)} \qquad (3)$$



$$(CH_3)_2NNO \xrightarrow{h\nu_1} (H_2C)(H_3C)N\cdots HNO \xrightarrow{h\nu_2} CH_2(NO)(NH)CH_3 \qquad (4)$$

Irradiation of CH_3CH_2ONO into the S_1 $(n\pi^*) \leftarrow S_0$ absorption band at 365 nm produces a complex between acetaldehyde and nitroxyl, $CH_3CHO...HNO$ *(Eqn. 3)*. The pertinent vibrational frequencies of this complex are summarized in *Table 1*. The assignments are based on the well-known frequencies of the monomeric species HNO, $H^{15}NO$ [14], and CH_3CHO [15], and on a comparison with the $CH_2O...HNO$ complex

Table 1. *Vibrational Frequencies* ($\tilde{\nu}$, cm^{-1}) *of Complexed and Monomeric Acetaldehyde*[a]) *and Nitroxyl in an Ar Matrix at 12 K*

Assignment	CH_3CHO Complexed (this work)		CH_3CHO monomer (this work)		Assignment	HNO Complexed (this work)		$H^{15}NO$ Complexed (this work)	HNO Complexed to CH_2O [9]	HNO Monomer [14]	$H^{15}NO$ Monomer [14]
	$\tilde{\nu}$	%-rel. Abs.	$\tilde{\nu}$	%-rel. Abs.		$\tilde{\nu}$	%-rel. Abs.	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$
$2\nu_9$ (A')	1780	2	1748[b])	70	ν_1	2810	6	2804	2804	2717	2710
ν_4 (a')	1733	100	1726.5[b])	100	ν_2	1575	100	1565.5	1571	1563	1549.5
ν_5 (a')	1429	24	1426.5	74	ν_3	1509	13	1487	1509	1505[c])	1487[c])
ν_6 (a')	1400	3	1398	30							
ν_7 (a')	1352	40	1348.5	56							
ν_8 (a')	1123	33	1111	84							
ν_9 (a')	890	1	871	7							
ν_{10} (a')	521.5	17	506	36							

[a]) The IR spectrum of monomeric CH_3CHO recorded in an Ar matrix has been found to correspond well with the gas-phase spectrum [15]. The assignment of the latter has been adopted. The CH-stretching region has not been included in the *Table*, since it is strongly perturbed by *Fermi* resonances [15].

[b]) The $2\nu_9$ and ν_4 absorptions of the monomer appear as a strong and broad ($\approx$ 50 cm^{-1}) *Fermi* resonance doublet. The linewidths seem to be dominated by the width of the broad ν_9 absorption.

[c]) Ar matrix containing $\approx$ 5‰ N_2.

[9]. With deuteration on C(*β*) of nitrosooxyethane (CD_3CH_2ONO), it was demonstrated that the nitroxyl hydrogen atom is furnished exclusively from the C(*α*)-atom since only the complex $CD_3CHO...HNO$ was formed. In a second photolysis step, selective excitation of either the CH_3CHO (λ_{exc} = 345 nm [16]) or the HNO ($\lambda_{exc} \approx$ 650 nm [17]), part of the complex led to the new compound 1-nitrosoethanol, but in contrast to nitrosomethanol [11][12], in one single conformation *(Eqn. 3)*. Examination of some group frequencies of $CH_3CH(OH)(NO)$ in comparison with those of *trans*- and *cis*-$CH_2(OH)(NO)$, as given in *Table 2*, indicates the former compound to exist in an

Table 2. *Characteristic Vibrational Frequencies* ($\tilde{\nu}$, cm^{-1}) *of Nitrosomethanol*[a]) *and 1-Nitrosoethanol in an Ar Matrix at 12 K*

trans-$CH_2(OH)(NO)$		*cis*-$CH_2(OH)(NO)$		*cis*-$CH_3CH(OH)(NO)$		Assignment
$\tilde{\nu}$	%-rel. Abs.	$\tilde{\nu}$	%-rel. Abs.	$\tilde{\nu}$	%-rel. Abs.	
3638	31	3477.5	34	3458.5	30	OH-str
1555	57	1559[b])	18	1552	57	NO-str
1106.5	100	1130.5	100	1176.3[d])	100	CO-str
				1080 999	40 26	CH_3-rock[c])
847	4	792	26	793.5[d])	32	CNO-bend, CN-str
220	29	346.5	19	326[d])	27	OH-tors
386.5	31	334	5	303.5	11	OCN-sciss

[a]) Taken from [12].

[b]) In *Fermi* resonance with $2\nu_8$ and $\nu_8 + \nu_9$ [12].

[c]) For comparison *cf.* ethanol [28]: CH_3-rock 1083.2 (A"), 1025.0 (A') cm^{-1}.

[d]) Site structures: 1182, 787, 318.5 cm^{-1}. Site conversion takes place by annealing the matrix to $\approx$ 25 K.

intramolecularly H-bonded cyclic structure. With respect to this structure, the reduction of the OH-stretching frequency of 180 cm^{-1} in 1-nitrosoethanol relative to *trans*-nitrosomethanol is particularly informative [18]. We have previously reported [11] that irradiation of the $CH_2(OH)(NO)$ isomers with $\lambda_{exc} \approx 650$ nm (*trans*-form) or $\lambda_{exc} = 510$ nm (*cis*-form) induces a *trans*→*cis* or a *cis*→*trans* isomerization, respectively, and that during the *cis*→*trans* rotamerization a small fraction of the molecules (≈ 5–10%) is reconverted to the H-bonded complex, *cis*-$CH_2(OH)(NO) \xrightarrow{510\ nm} H_2CO...HNO$. In the case of *cis*-nitrosoethanol (cyclic structure), irradiation at 510 nm ($S_1(n\pi^*) \leftarrow S_0$ [19]) does not produce another rotamer but reforms completely the H-bonded complex, *cis*-$CH_3CH(OH)(NO) \xrightarrow{510\ nm} CH_3CHO...HNO$.

The photolysis of *N,N*-dimethylnitrosamine at 365 nm ($S_1(n\pi^*) \leftarrow S_0$) in an Ar matrix leads to a complex between methylenemethylamine and nitroxyl, $CH_3N=CH_2...HNO$ *(Eqn. 4)*, as has been recently demonstrated by a detailed IR analysis on six isotopic dimethylnitrosamine modifications [20]. We have now irradiated the complexed nitroxyl at about 650 nm and obtained the previously unknown molecule methyl(nitrosomethyl)amine $CH_2(NO)(NH)CH_3$ *(Eqn. 4)*. The assignment of the IR spectrum of this species [21] was made by investigation of the vibrational shifts upon (D_6)- and ^{15}N-substitutions and by comparison with the spectrum of the related dimethylamine [22] and *N*-methylnitroamine [23] compounds *(cf. Table 3)*. Methyl(nitrosomethyl)amine can exist in different rotameric conformations. At 12 K one conformer, here called A, is preferentially formed. When gradually raising the matrix temperature to ≈ 30 K a second isomer, denoted B, is produced from species A. Recooling the matrix to 12 K stabilizes conformer B. The vibrational frequencies of the two isomers are listed in *Table 3*. Irradiation with IR light ($\lambda \geqslant 2\mu$) converts B to A by a photochemical isomerization reaction. Examples of IR-induced photoisomerizations

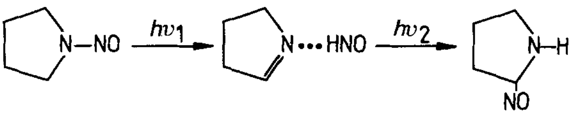
Table 3. *Characteristic Vibrational Frequencies* ($\tilde{\nu}$, cm^{-1}) *of Methyl(nitrosomethyl)amine in an Ar Matrix at 12 K*

$CH_2(NO)(NH)CH_3$ (this work)				$(CH_3)_2NH$[b]) [22]	CH_3NHNO_2[b]) [23]	Assignment
	Conformer A		Conformer B[a])			
	$\tilde{\nu}$	%-rel. Abs.	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	
	3399	4	3393	3374	3438	NH-str
(ND:	2537)			(2565)	(2518)	
	1551.5	100	1567.5			NO-str
(^{15}NO:	1540.5)					
	1483	19	1486	1483	1470	CH_3-def
	1455	23	1465	1467	1454	
	1428	2	1428	1445	1434	
	1314	11	1308			2 × NH-bend
	1105	16	1102			CH_3-rock
	821	4	761			CNO-bend, CN-str
	662	91	657	735	618	NH-bend
(ND:	540)			(440)	(592)	
	318	15	308			NCN-sciss

[a]) Many absorptions of B overlap with absorptions of A.
[b]) Gas phase.

have recently been reviewed and the photophysical processes involved have been discussed in some detail [24]. Although it is difficult to specify the exact conformations of these rotamers, one might speculate that conformer B possesses the O–N–C–N molecular frame in the *cis*-conformation while species A conforms to the *trans*-isomer. With this respect the 761 cm^{-1} absorption of the B form (821 cm^{-1} in A) may be interpreted to represent a CNO-bending/CN-stretching mode similarly to the one of *cis*-(*trans*-)$CH_2(OH)(NO)$ molecule, where this mode is found at 755 cm^{-1} (847 cm^{-1}). The slightly lower N–H stretching frequency of B could signify a weak H-bond interaction between the N–H and N=O functional groups. Another indication for such a structure is provided by the slightly higher N=O stretching frequency of B (1567.5 cm^{-1}) as compared to that of A (1551.5 cm^{-1}) thus paralleling similar findings in *cis*- and *trans*-$CH_2(OH)(NO)$ (1559, 1555 cm^{-1}, respectively [12]).

Photodecomposition of the larger nitroso compound *N*-nitrosopyrrolidine was briefly examined under similar conditions. In a first photolysis step ($\lambda_{exc} = 365$ nm) complexed HNO is formed as revealed by the absorptions at 2730.5 (ν_1), 1563 (ν_2), and 1511.5 cm^{-1} (ν_3). Assuming the photolytic transformations to occur analogously to those of the above discussed examples *(Eqn. 2–4)*, the complex partner of nitroxyl is pyrrolidineimine. We have not attempted to analyze the complex IR spectrum of the imine, but the strong absorption at 1636.5 cm^{-1} is considered to signify a C=N functional group (*e.g.* 1659 cm^{-1} in $CH_3{-}N{=}CH_2$ [25]). In a second photolysis step using red light (600 nm), all the IR absorptions pertaining to the presupposed $\overline{C_3H_6CH{=}N}$...HNO complex disappeared, while new absorption bands grew in simultaneously. Among these absorptions the ones at 1541, 564.5, and 382 cm^{-1} might be attributed to the N=O- and CN-stretching vibrations, and to the CNO-bending (NCN-scissoring) mode, respectively (similar frequencies of *trans*-$CH_2(OH)(NO)$ are 1555, 542, and 386.5 cm^{-1} [12]). Based on these findings we are inclined to suggest that a reaction sequence similar to the one found for the aforementioned compounds occurs also in the transformation of nitrosopyrrolidine *(Eqn. 5)*.



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The similarity between the rearrangement reactions of the small nitroso compounds in Ar matrices with those of the more complex molecules in solution is intriguing. In a detailed mechanistic study of the widely used *Barton* reaction, HNO has been proposed to occur as a reaction intermediate [26]. In the photolysis of *e.g.* 6*β*-nitrosooxy-5*α*-cholestan-3-yl acetate a nitroso group is exchanged intramolecularly with a hydrogen atom of the C(19)-CH_3 group leading to a nitrosoalcohol *(cf. Eqn. 1)*. The latter reacts further to the more stable oxime. In their study, *Barton et al.* proposed a concerted photochemical elimination mechanism for the formation of the 6-ketone and nitroxyl even before the typical H/NO exchange. HNO was indirectly identified by the UV spectrum of the dianion of hyponitrous acid (HO–N=N–OH) which is known to be formed by dimerization of HNO in solution [27]. Our matrix results are in full accordance with these findings, thus supporting the suggestion that primary HNO formation might be an important step also in other rearrangement reactions of nitrocooxy compounds, nitrosamine, and nitrosohydrazine.

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