Methoxy- and Aminoisocyanate

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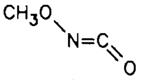
Methoxyisocyanate (**1**) can be prepared by photolysis of methyl azidoformate (**3**) or pyrolysis of *N*-methoxycarbonyl-*O*-methylhydroxylamine (**4**). Aminoisocyanate (**2**) is similarly formed on photolysis of carbamoyl azide (**12**) and pyrolysis of either methyl carbazate (**13**) or 3,4-diaminofurazan (**14**). The infrared spectra of **1** and **2** in an argon matrix at 10 K have been measured, and some of their properties are discussed.

Methoxy- und Aminoisocyanat

Methoxyisocyanat (**1**) kann durch Photolyse von Azidoameisensäure-methylester (**3**) oder Pyrolyse von *N*-Methoxycarbonyl-*O*-methylhydroxylamin (**4**) dargestellt werden. Aminoisocyanat (**2**) ist auf ähnliche Weise durch Photolyse von Carbamoylazid (**12**) und Pyrolyse von Carbazinsäure-methylester (**13**) oder 3,4-Diaminofurazan (**14**) zugänglich. Die IR-Spektren von **1** und **2**, aufgenommen in einer Argon-Matrix bei 10 K, werden diskutiert.

The interest in compounds such as methoxyisocyanate (**1**) or aminoisocyanate (**2**) dates back to the early days of chemistry. This interest was mainly due to the work of Curtius on the rearrangement of carbonylazides to isocyanates. In a short communication published in 1914, Curtius[1] divided carbonylazides into two groups: rigid azides, which do not undergo the Curtius rearrangement, and nonrigid ones, which rearrange, although no justification could be found for this different behavior[2]. Among the rigid carbonylazides were the alkyl azidoformates and alkyl-substituted carbamoylazides, which on decomposition did not give the expected isocyanates. Several attempts have been made to prepare alkoxyisocyanates[2-7] and aminoisocyanates[8-11], but without success. Only dimers (in the case of dialkylaminoisocyanates) or trimers (in the case of alkoxyisocyanates) could be isolated.



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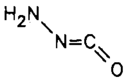

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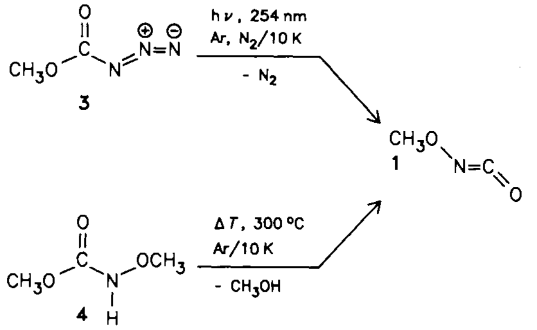
No theoretical calculations on **1** have been published to date, and the single reference to **2**[12] gives only a partially optimized structure assuming a planar amino group. This supposition seems to be incorrect[13].

Although our primary goal was the preparation of **1** and **2** as a basis for the search of the isomeric nitrile oxides (which should give **1** and **2** on matrix irradiation[14]) and not the study of the Curtius rearrangement or the chemistry of nitrenes, some interesting new results were obtained in these fields.

Methoxyisocyanate

From Methyl Azidoformate: Methoxyisocyanate (**1**) was prepared by photolysis of methyl azidoformate (**3**), isolated in an argon or nitrogen matrix at 10 K, or by pyrolyzing *N*-methoxycarbonyl-*O*-methylhydroxylamine (**4**) and condensing the pyrolysis products with a large excess of argon on a cesium iodide window held at 10 K.

The photolysis of **3** using the 254-nm line of a low-pressure mercury lamp proceeds almost quantitatively as long as sufficient argon is present to insure a good isolation.



Using a molar ratio for **3**:Ar of about 1:900, only small amounts of dimethyl azodicarboxylate (**7**) are formed as a secondary product, together with traces of formaldehyde and isocyanic acid.

Once formed, **1** is quite a stable compound. It remains unchanged after several hours of photolysis at 254 nm, and on careful heating of the matrix the argon can be selectively evaporated, leaving essentially pure methoxyisocyanate (**1**), which is stable up to at least 90 K.

Since it is known that azides are not only photolabile but also thermolabile, the flash vacuum pyrolysis of **3** was also examined. Quite surprisingly, only traces of **1** were found, independent of the temperature, pressure, or residence time used in the pyrolysis. Instead, carbon dioxide, isocyanic acid (**11**), formaldehyde, and methylene imine (**10**), together with small amounts of dimethyl azodicarboxylate (**7**), were the only detectable products. The ratios of carbon dioxide:methylene imine and isocyanic acid:formaldehyde did not change with temperature, but the ratio of (**8** + **10**):(**9** + **11**) decreased with increasing temperature. By measuring these ratios, or more exactly the ratios of the integrated infrared intensities, it could be deduced that the reaction leading to isocyanic acid and formaldehyde has a smaller activation energy than the reaction leading to carbon dioxide and methylene imine by about 2.4 kcal/mol.

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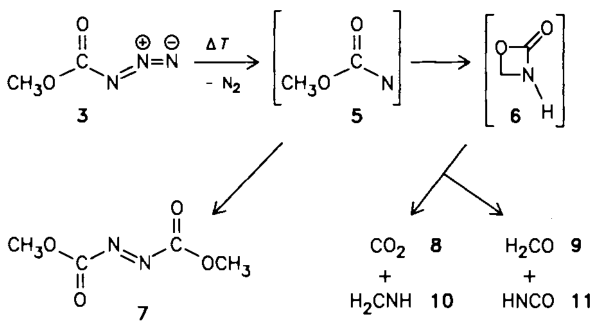
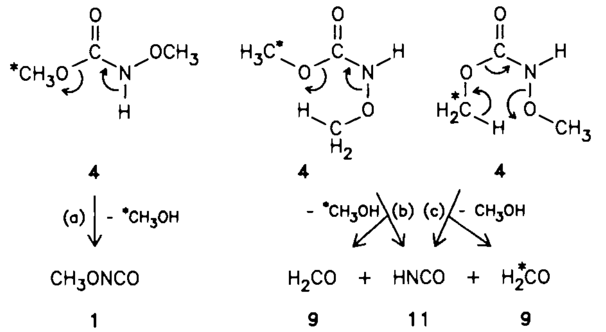


It is very difficult, relying only on the analysis of the reaction products, to get some insight into the decomposition mechanism of 3. The fact that photolysis and pyrolysis lead to completely different products seems to indicate two different primary reaction paths for 3. But even so, there are at least three alternatives: (a) The rearrangement and the expulsion of nitrogen could be concerted in both cases, but starting from different electronic states of 3 [S_0 for the thermal reaction and S_n ($n > 0$) for the photochemical reaction]. (b) The reaction could be stepwise in both cases but with nitrenes of different multiplicity as intermediates (a singlet nitrene for thermal and a triplet nitrene for the photochemical reaction). (c) The thermal reaction could be stepwise with singlet nitrene as an intermediate while the photochemical reaction would be concerted.

The first mechanism does not provide a convincing explanation for the formation of 7 (7 is only a side product in the vacuum pyrolysis. When the pyrolysis is effected at pressures above ca. 300 mbar, 7 becomes the main product). The second mechanism on the other hand implies that the intersystem crossing of singlet 5 to triplet 5 in the argon matrix must be faster than either the CH insertion or the recombination with N_2 (the photolysis of 3 proceeds at approximately equal rates in argon or nitrogen matrices), what seems unlikely. The third mechanism is the one which can rationalize the bulk of observations but still cannot explain the origin of the small amounts of 7, which are always observed as a byproduct not only in the pyrolysis but also in the photolysis of 3.

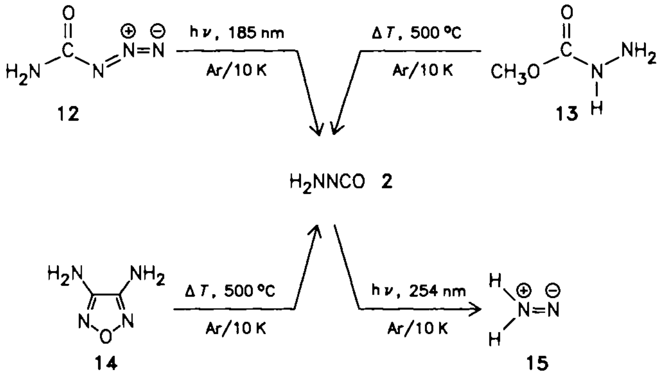
From N-Methoxycarbonyl-O-methylhydroxylamine: Methoxyisocyanate was also prepared by pyrolysis of *N*-methoxycarbonyl-*O*-methylhydroxylamine (4). This reaction is not as convenient as the photolysis of 3, since a very accurate control of temperature and residence time is needed in order to obtain good yields of 1. Using the conditions of flash vacuum pyrolysis (quartz tube, ⌀ = 0.5 cm, hot zone 5 cm, pressure ca. 10^{-5} Torr), no conversion of 4 is obtained at temperatures below 300°C. At temperatures above 400°C only small amounts of 1 could be detected, the main products being isocyanic acid (11), formaldehyde (9), and methanol. Unfortunately, at 300°C, where the best selectivity of 1 is achieved, the conversion is very small. To overcome this problem, we used a quartz tube packed with a small amount of quartz wool. This allows to increase the residence time without making any changes in the oven construction. In this way we were able to obtain an almost quantitative conversion of 4 to methoxyisocyanate and methanol. As side products only small amounts of isocyanic acid, formaldehyde, and unconverted 4 were observed.

These side products are by no means trivial, since again they can result from at least three different mechanisms. Formaldehyde (9) and isocyanic acid (11) can be formed either by the decomposition of methoxyisocyante [route (a)] or by one, or both, of the shown pericyclic fragmentations [routes (b) and (c)]. In order to gain some insight into the mechanism of formation of these side products, we also examined the pyrolysis of *N*-ethoxycarbonyl-*O*-methylhydroxylamine (ester methoxy in 4 replaced by an ethoxy group). The products predicted from mechanisms (a) and (b) are ethanol, formaldehyde, and isocyanic acid, and from mechanism (c) methanol, acetaldehyde and isocyanic acid. Actually, a mixture of all these products is obtained with still some methoxyisocyanate, when the pyrolysis is carried out at a temperature slightly above 300°C. This means that besides mechanism (c) at least another one is operating. Unfortunately, these experiments do not allow to distinguish between the two-step process (a) and the pericyclic pathway (b).



Aminoisocyanate

From Carbamoyl Azide: Aminoisocyanate (2) was prepared by photolysis of carbamoyl azide (12), isolated in an argon matrix at 10 K, or by pyrolyzing methyl carbazate (13) or 3,4-diaminofurazan (14) and condensing the pyrolysis products as described for 1.



The photolysis of carbamoyl azide in an argon matrix had already been examined by Dervan[11] who postulated the intermediacy of aminoisocyanate in the formation of aminonitrene (**15**). Indeed, when the 254-nm line of a low-pressure mercury lamp is used to photolyze **12**, only very small amounts of **2** can be obtained, the main product being carbon monoxide. We have found that using the 185-nm line (selected with an interference filter), the reaction can be stopped at the stage of aminoisocyanate. But since the use of very short wavelenghts has the disadvantage of producing matrices of very poor quality, we looked for another precursor, which could yield **2** on pyrolysis instead of photolysis. Pyrolysis of **12** itself requires a temperature of at least 700°C to obtain total conversion. Under these quite drastic conditions extensive fragmentation is observed. The main products are isocyanic acid, hydrazoic acid, hydrogen cyanide, and ammonia, together with traces of azodicarboxdiamide and aminoisocyanate.

From Methyl Carbazate: A more promising precursor was methyl carbazate (**13**). Indeed, when pyrolyzed at 500°C through a quartz tube filled with quartz wool, **13** cleanly eliminated methanol to give aminoisocyanate. Small amounts of isocyanic acid were the only side product. Using this procedure, very good samples of matrix-isolated aminoisocyanate could be produced, which allowed to study its photochemistry in some detail.

Aminoisocyanate is stable when irradiated at a wavelength of 185 nm or at wavelengths ≥ 366 nm. Irradiation at 254 nm induced a very rapid reaction (within a few minutes) to produce carbon monoxide and aminonitrene (**15**), which at this wavelenght reacts further to give molecular nitrogen and hydrogen atoms. These hydrogen atoms react with the carbon monoxide to give the formyl radical $H\dot{C}O$, formaldehyde, and the hydroxymethyl radical $H_2\dot{C}OH$. It is not possible to decide whether methanol is also produced since large amounts of it are always present as a byproduct from the preparation of aminoisocyanate. The fact that hydroxymethyl radicals are also formed shows that hydrogen atoms can diffuse in an argon matrix at 10 K. Otherwise only reduction products with up to two hydrogen atoms should have been observed.

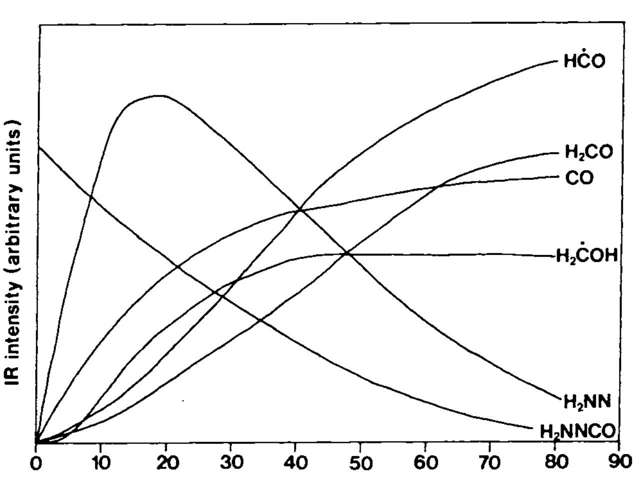


Figure 1. Time dependence of the IR intensities of the species involved in the 254-nm photolysis of aminoisocyanate. To preserve clarity, each curve was multiplied by a different arbitrary constant

The time evolution of the concentration of each species involved in the 254-nm photolysis of aminoisocyanate can be taken from Figure 1, where integrated IR intensities are plotted against the time of irradiation.

An unassigned band at 1288 cm^{-1} shows a time dependence similar to that of the hydroxymethyl radical. This absorption may be due to the methoxy radical $H_3CO^{\bullet}$. The IR spectrum of this radical has never been measured, but PE spectra[15] and laser fluorescence spectra[16], taken in the gas phase, predict an IR absorption at 1325 ± 30 cm^{-1} or 1380 ± 20 cm^{-1}, respectively. Although hydroxycarbene ($H-\bar{C}-OH$) could also account for this absorption this seems more unlikely than the methoxy radical, because a time dependence similar to that of formaldehyde, and not to that of the hydroxymethyl radical, would then be expected.

Under irradiation at a wavelenght of 313 nm, aminoisocyanate cleanly cleaves into **15** and CO. Since aminonitrene is photostable at 313 nm, high concentrations of it can be reached, although several hours of photolysis are needed to completely convert all aminoisocyanate. This allowed for the first time to study the photochemistry of aminonitrene; the results of this investigation are discussed in a subsequent paper[17].

From 3,4-Diaminofurazan: 3,4-Diaminofurazan (**14**) also yields aminoisocyanate, but with many more side products than **13**. On pyrolysis at 500°C through a quartz tube packed with quartz wool, **14** produces a mixture of aminoisocyanate, cyanamide, isocyanic acid, and hydrogen cyanide with small amounts of carbon monoxide, carbodiimide, and ammonia. A probable intermediate in this reaction is aminoformonitrile oxide, $H_2N-C\equiv N-O$, but no direct evidence for its formation could be found.

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Experimental

All starting materials except **4** and the corresponding ethyl ester were prepared as described in the literature and their purity tested by gas chromatography. Methyl azidoformate (**3**) was synthesized from methyl chloroformate and sodium azide as described by Forster[18]. Carbamoyl azide (**12**) was prepared by treating semicarbazide hydrochloride with sodium nitrite[19], and methyl carbazate (**13**) according to the procedure given by Diels[20]. 3,4-Diaminofurazan (**14**) was synthesized using the procedure of Coburn[21]. *N*-Methoxycarbonyl-*O*-methylhydroxylamine (**4**) and the *N*-ethoxy analog were prepared as described below.

N-Methoxycarbonyl-O-methylhydroxylamine (**4**): 12 mmol of *O*-methylhydroxylamine hydrochloride and 24 mmol of sodium hydroxide were each separately dissolved in 3 ml of water. Both solutions were cooled to −10°C and mixed. 12 mmol of methyl chloroformate was then very slowly added with stirring, not allowing the temp. to rise above 5°C. The reaction mixture was stirred for an extra 0.5 h at 0°C, the pH adjusted to 5−6 (if needed), and then extracted with five 10-ml portions of ether. The organic phase was dried with $CaCl_2$, and the ether evaporated in vacuo at a temp. below 10°C. The oily residue crystallized on cooling. Impure **4** must be purified by dissolving it in 2−3 ml of ether, drying with molecular sieve (3 Å) and diluting with 2−3 ml of dry pentane. On cool-

Table 1. Infrared spectra of methoxy- and aminoisocyanate

	CH_3ONCO (C_s)				H_2NNCO (C_s)		D_2NCNO (C_s)		$HDNNCO$ (C_1)	
Vibr.	$\tilde{\nu}$ [cm^{-1}]	Rel. Int.	Vibr.	Symm.[a]	$\tilde{\nu}$ [cm^{-1}]	Rel. Int.	$\tilde{\nu}$ [cm^{-1}]	Rel. Int.	$\tilde{\nu}$ [cm^{-1}]	Rel. Int.
	425	4.8	δ_{NCO}	A''	563	1.6	563	2.3	563	1.8
	510	6.6	δ_{NNC}	A'	642	2.2	638	3.3	641	0.7
	657	4.8	ν_{NN}	A'	844	0.6	843	3.0	835	1.1
	828	5.7	b)	–	1026	10.8	790	2.3	876	4.8
	1049	24.1	b)	–	1303	0.2	876	1.1	1124	2.1
ν^{as}_{NCO}	2115	2.9	δ_{NH_2}	A'	1612	1.7	1181	2.1	1391	0.9
	2152	16.5	ν^{as}_{NCO}	A'	2210	100.0	2213	100.0	2195	73.7
	2204	100.0			2262	52.7	2260	99.6	2242	100.0
			$\nu^{s}_{NH_2}$	A'	3297	0.1				
			$\nu^{as}_{NH_2}$	A''	3362	0.4				

[a] Symmetry is given only for [H_2]aminoisocyanate and [D_2]aminoisocyanate. All the vibrations of [D_1]aminoisocyanate have A symmetry. — [b] These vibrations can either be τ_{NH_2} A'', δ_{HNN} A', or ω_{NH_2} A'.

ing to −30°C, **4** separates as colorless crystals, which should be filtered under dry nitrogen because of its very high hygroscopicity, yield 67−73%. When pure and dry, **4** can be kept for several months at ca. 4°C, but it decomposes slowly at room temp. — MS: m/z (%) = 105 (14.5) [M^+], 74 (22.6), 59 (100). — IR[22]: $\tilde{\nu}$ = 3420 cm^{-1} (w, NH), 2962 (m, CH), 1790, 1767 (vs, CO), 1454 (s), 1355 (s), 1234 (vs), 1126 (s), 1076 (m), 964 (w), 783 (w), 740 (w).

N-Ethoxycarbonyl-O-methylhydroxylamine: Prepared as described for **4**, but using only 10 mmol of ethyl chloroformate instead of 12 mmol. Purification by fractional condensation (liquid at room temp.). — IR[22]: $\tilde{\nu}$ = 3410 cm^{-1} (w, NH), 2985 (m, CH), 1786, 1759 (vs, CO), 1446 (s), 1230 (vs), 1119 (s), 1070 (m), 955 (w), 775 (w).

Infrared Spectra: The reported infrared spectra were taken on a Bruker IFS 85 FT infrared spectrometer with a resolution of 0.5 cm^{-1} covering the range of 4000−300 cm^{-1}. For the matrix experiments the double-stage compressor "Displex Closed-Cycle Refrigeration System CS 202" from Air Products was used.

The observed spectra of methoxyisocyanate, aminoisocyanate and both deuterium-substituted isotopomers are given in Table 1. The assignments given for aminoisocyanate are based on the observed deuterium shifts and by comparison with theoretically computed spectra[23], and they should be considered as tentative. The intensities given are relative integrated intensities, and the band positions are derived from spectra taken at 0.5 cm^{-1} resolution and are rounded to the nearest wavenumber. Typical halfwidths of the given bands are 1 to 3 cm^{-1}.

The most interesting point to be noted in these spectra is the presence of more than one band in the region of the NCO asymmetric stretching vibration, where only one was to be expected. A matrix effect can be excluded in this case since nearly identical spectra are observed whether the matrix material is argon or nitrogen, and the splittings are anyhow too large to be due to a matrix effect. Typical matrix effects cause splittings of only a few wavenumbers, while the ones observed here are about 50 cm^{-1}. Although no bands could be found whose overtone or combination could cause a Fermi resonance with the asymmetric NCO stretching vibration (neither in aminoisocyanate nor in methoxyisocyanate), this seems to be the only acceptable explanation for the observed splittings. Ethoxyisocyanate shows also a structured band for the asymmetric NCO stretching mode but N,N-dimethylaminoisocyanate (generated by pyrolysis of N,N-dimethylcarbamoyl azide) shows only a single band at 2218 cm^{-1} when isolated in argon at 10 K. It is possible that similar splittings, which were observed for chloro- and bromoformonitrile oxide[14] and which were attributed to matrix effects, are indeed also due to Fermi resonance.

CAS Registry Numbers

1: 117775-56-1 / **2**: 67249-78-9 / **2** (N-d_2): 117775-57-2 / **2** (N-d_1): 117775-58-3 / **3**: 1516-56-9 / **4**: 66508-91-6 / **4** (Et ester): 3871-28-1 / **4** · HCl: 593-56-6 / **7**: 2446-84-6 / **12**: 13125-56-9 / **13**: 6294-89-9 / **14**: 17220-38-1 / $ClCO_2Me$: 79-22-1 / $ClCO_2Et$: 541-41-3

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