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POSSIBLE REACTION MECHANISMS OF HYDROGEN CYANIDE FORMATION FROM OXIME BLOCKED ISOCYANATES AND RELATED ORGANIC COMPOUNDS DURING TOTAL CYANIDE ANALYSIS

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Frequent reports by paint manufactures of hydrogen cyanide detection in waste contaminated with oxime blocked isocyanates lead to an investigation of possible hydrogen cyanide generating reaction pathways. GC-MS is empolyed to analyze traces of byproducts of the total cyanide analysis. A Beckmann Rearrangement of oxime blocked isocyanates has been detected. The formation of α-ketocyanides and their hydrolysis to free hydrogen cyanide is reported as the key compound that leads to hydrogen cyanide generation. Hydrogen cyanide yields from the reaction of NO_x or hydroxylamine with ketones, alcohols, amines, peptides, EDTA, ascorbic acid and cyanides. The presence of an organic phase improves hydrogen cyanide yields. A sample pretreatment for oxime blocked isocyanate samples is described.

KEY WORDS: Total cyanide analysis; hydrogen cyanide generation; blocked isocyanates; oximes; ketones; α-ketocyanides

INTRODUCTION

The total cyanide analysis method is based on the distillation of hydrogen cyanide from an acidic condenser solution into an alkaline receiver solution. The method has been introduced several decades ago to analyze waste water from metallurgic plants (hardening of steel by cyanides). Since then the analysis of waste water became a general environmental issue, which lead to the analysis of more samples with a larger content of organic substances. In this process an increasing number of hydrogen cyanide false detections has been reported. Recently it has been described that this

observation seems to be connected to the presence of hydroxylamine or nitrite ions in the analytical mixture[1,2].

Oxime blocked isocyanates generate free hydroxylamine via hydrolysis in water. They are widely used to cure resins and are favorably applied in water based coatings. During the application of these coatings waste water is generated. In this waste water hydrogen cyanide has been detected by using the total cyanide analytical method.

We will discuss possible reaction mechanisms of ketones, amines and blocked isocyanates with hydroxylamine or nitrite in the total cyanide analytical method that can lead to hydrogen cyanide formation as well as we will give some ideas how to avoid this misdetection in case of analyzing oxime blocked isocyanates.

EXPERIMENTAL METHODS

Apparatus

For the determination of hydrogen cyanide, we used the same distillation equipment and reagents as they are required by the Japanese Industrial Standard (JIS -K0102–38.1). It has been shown that the employment of other methods, like the one of the International Standard Organization or the Standard Methods of the USA lead in principle to the same results[2].

To support suggested reaction mechanisms, we employed packed column gas chromatography with a flame ionization detector as well as capillary gas chromatography coupled with a mass spectrometer (GC-MS). With the GC-MS method the substances have been identified by comparing the collected MS-data with a mass spectral data base.

Reagents

A list of all reagents used or cited and their abbreviations is given in Table 1. Of all investigated samples only IPDI-MEKO has been synthesized at the Daicel-Hüls Laboratory. All other sample were supplied by Aldrich or Wako Pure Chemicals.

To prepare IPDI-MEKO, 2.01 mol of MEKO per 1 mol IPDI are used. While the IPDI is stirred well, MEKO is added in a way that the temperature does not exceed 80°C. After all MEKO has been added, the mixture is kept at 70°C for 2 more hours and than cooled.

PROCEDURE

To determine the amount of generated hydrogen cyanide we[6] used an apparatus according to the JIS standard. Into this apparatus 1g of the sample was added to 240 ml water and 10 ml concentrated H_3PO_4, which provides a highly acidic solution (pH 2). Any other chemicals added are listed in the Tables 2 to 6. In most cases the organic samples were not soluble in water. To handle some of the samples more easily, they

Table 1 List of all reagents used or cited and their abbreviations

Abbreviation	*Reagent*
AN	Acetonitrile
Ascorb-Ac	Ascorbic acid
BA	n-Butyl alcohole
BMG	Butyl monoglycolether
CyH	Cyclohexanone
CyHO	Cyclohexanon oxime
DIBA	Diisobutyl amine
DIPK	Diisopropyl ketone - 2, 4-Dimethyl-3-Petanone
DMK	Dimethyl ketone (Acetone)
DMKO	Dimethyl ketoxime (Acetonoxime)
DTBK	Ditertierbutyl ketone - 2, 2, 4, 4-Tetramethyl-3-Petanone
EDTA	Ethylene diamine tetra acetic acid
FAO	Formaldehyd oxime
Gly	Glycine
HDA	Hexamethylendiamine
HDI	Hexamethylendiisocyanate
IPA	Isopropyl alcohol
IPDA	Isophorondiamine
IPDI	Isophoronediisocyanate
MEK	Methylethyl ketone
MEKO	Methylethyl ketoxime
MeOH	Methanol
PCy	Pyruvocyanide - Acetyl cyanide
TDI	Toluoldiisocyanate

have been dissolved in methanol before they were added to the flask. Despite the methanol content, most samples still phase separated and established an organic phase.

The distillation is carried out at temperatures a little above 100°C. 80 ml distillate is distilled into an alkaline receiver, with a pH of at least 12 by using 20 ml of 0.5N NaOH. The cyanide ion in the distillate was determined by the 4-pyridine carboxylic acid-pyrazolone method[3]. The detection limit set by the JIS standard is 5 μg CN^-/100 ml distillate in the receiver.

RESULTS AND DISCUSSION

Oxime Blocked Isocyanates and the Formation of Hydrogen Cyanide

The data presented in Table 2 clearly indicates that only oxime blocked isocyanates generate hydrogen cyanide. Alcohol secondary or amine blocked or free isocyanates do not generate hydrogen cyanide.

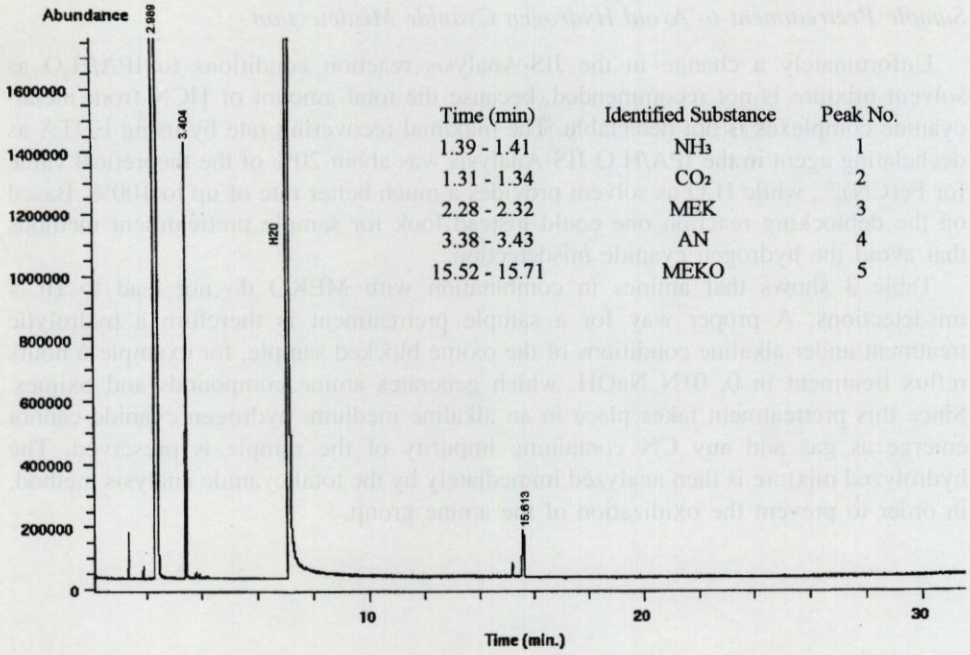
To get an insight into the complex chemistry that takes place, we investigated the alkaline JIS-Method distillate by GC-MS (Figure 1). It had to be distilled again, to remove inorganic components, such as NaOH. One could also think of collecting the distillate in a neutral and cooled receiver, but this would not cover any side reaction that might take place in the alkaline receiver.

Table 2 CN^- Detection test results for blocked or partially blocked isocyanates

Sample	*Reference*	*Amount (g)*	*NH_2OH ·HCl (g)*	*$NaNO_2$ (g)*	*EDTA (g)*	*Reducing or Additional Agent*	*CN^- (µg/100 ml) (distillate)*	*Yield per mol Sample*
IPDI	6	1.0	–	–	–	–	< 5	
	2	1.0	–	–	–	–	0.9	
	6	1.0	–	–	1.0	–	< 5	
	6	1.0	–	–	1.0	1 g $NH_4SO_3NH_2$	< 5	
	2	1.0	0.1	–	–	–	1.4	
	2	1.0	1.0	–	–	–	1.9	
	2	1.0	–	0.1	–	–	< 0.5	
	2	1.0	–	1.0	–	–	0.8	
	5	0.6	0.5	–		0.3g H_2N-NH_2	< 1	
IPDI+ MEKO	5	1.0	–	–	–	–	5 – 20	
IPDI+ MEKO+ MeOH	5	1.0 1.0 5.0	–	–	–	–	50 – 100	
IPDI-MeOH+ MEKO+ MeOH	5	1.5 1,0 4.5	–	–	–	–	< 1.0	
IPDI-DMKO	2	1.0[1]	–	–	–	–	124	1.69‰
IPDI-MEKO	6	1.0[1]	–	–	–	–	25	0.18‰
	6	1.0[1]	–	–	–	–	53	0.390‰
	6	1.0[1]	0.5	–	–	–	27	0.20‰
	6	1.0[1]	–	0.5	–	–	700	5.12‰
	2	1.0[1]	–	–	–	–	294	2.15‰
	6	1.0[1]	–	–	1.0	–	62	
	6	1.0[1]	–	–	1.0	1 g $NH_4SO_3NH_2$	140	
	6	1.0[1]	–	–	1.0	3 g $NH_4SO_3NH_2$	67	
IPDI-CyHO	2	1.0[1]	–	–	–	–	129	2.14‰
IPDI-BA	2	1.0[1]	–	–	–	–	1.1	
IPDI-DIBA	2	1.0[1]	–	–	–	–	0.6	
HDI	2	1.0	–	–	–	–	< 0.5	
	2	1.0	0.1	–	–	–	1.9	
	2	1.0	1.0	–	–	–	2.2	
	2	1.0	–	0.1	–	–	2.9	
	2	1.0	–	1.0	–	–	4.8	
HDI-MEKO	2	1.0[1]	–	–	–	–	301	3.81‰
TDI	2	1.0	–	–	–	–	< 0.5	
TDI-MEKO	2	1.0[1]	–	–	–	–	78.3	1.01‰

[1] The sample was dissolved in 5 ml methanol before it was put into the flask.

The identified samples in Figure 1 are NH_3, CO_2, MEK, AN, water and MEKO. Since we detected MEK and MEKO, one has to assume that IPDI-MEKO hydrolyses and /or deblocks under the experimental conditions. These reactions release MEKO or MEK. Due to the acidic reaction conditions about 90% of the free MEK-oxime will hydrolyse[7], so that NH_2OH and MEK result as final reaction products. These two substances could distill separately into the alkaline receiver, where they react again to MEKO. MEKO can also directly distill over. The deblocked and therefore free NCO-



Time (min)	Identified Substance	Peak No.
1.39 - 1.41	NH_3	1
1.31 - 1.34	CO_2	2
2.28 - 2.32	MEK	3
3.38 - 3.43	AN	4
15.52 - 15.71	MEKO	5

Figure 1 GC-MS 1-Distillate out of 100 ml - NaOH receiver in JIS K0102-38.1
Instrument : Hewlett Packard 5989A
Column : J&B-DB-WAX (0.25 mmø *30 m; 25 μm PEG-20M coating)
Inj. Temp. : 250°C
Column Temp. : 50°C – > 200°C; 5°C/min; 5 min init. time
Ion Source Temp. : 200°C
Separator Temp. : 100°C
Carrier Gas : He; 1 ml/min

group will hydrolyse under the experimental conditions by cleaving of CO_2 and releasing the free Amine – IPDA. These reactions explain the presence of CO_2, MEK and MEKO in Figure 1. The origin of NH_3 and AN is due to side reactions.

Deblocking Reaction of Oxime Blocked Isocyanates

For IPDI-MEKO it is uncertain whether the sample hydrolyses or deblocks at the JIS-Analysis reaction conditions. Since the deblocking reaction is temperature sensitive, an experimental setup with a changed boiling temperature should help to address this question. By using BMG/H_2O (1/1) instead of H_2O in the JIS-Analysis we detected a boiling temperature range between 120–150°C and an increased amount of generated hydrogen cyanide, while the usage of IPA/H_2O (7/3) lead to a boiling temperature range between 70–82°C and no detected hydrogen cyanide. We therefore believe that IPDI-MEKO deblocks before its constituents hydrolyse.

Sample Pretreatment to Avoid Hydrogen Cyanide Misdetection

Unfortunately a change in the JIS-Analysis reaction conditions to IPA/H_2O as solvent mixture is not recommended, because the total amount of HCN from metal-cyanide complexes is not detectable. The maximal recovering rate by using EDTA as dechelating agent in the IPA/H_2O JIS-Analysis was about 20% of the theoretical value for $Fe(CN)_6^{2-}$, while H_2O as solvent provides a much better rate of up to 100%. Based on the deblocking reaction one could instead look for sample pretreatment methods that avoid the hydrogen cyanide misdetection.

Table 3 shows that amines in combination with MEKO do not lead to HCN misdetections. A proper way for a sample pretreatment is therefore a hydrolytic treatment under alkaline conditions of the oxime blocked sample, for example 6 hours reflux treatment in 0, 01N NaOH, which generates amine compounds and oximes. Since this pretreatment takes place in an alkaline medium, hydrogen cyanide cannot emerge as gas and any CN^- containing impurity of the sample is preserved. The hydrolyzed mixture is then analyzed immediately by the total cyanide analysis method, in order to prevent the oxidization of the amine group.

Table 3 CN^- generation originated by amine compounds

Sample	*Reference*	*Amount (g)*	*NH_2OH ·HCl (g)*	*$NaNO_2$ (g)*	*EDTA (g)*	*Reducing or Additional Agent*	*CN^- (µg/100 ml) (distillate)*	*Yield per mol Sample*
IPDA	6	1.0	–	–	–	–	< 5	
	6	1.0	–	0.5	–	–	9.7	
	2	1	0.1	–	–	–	< 0.5	
	2	1	1	–	–	–	< 0.5	
	2	1.0	–	0.1	–	–	3.7	
	2	1.0	–	0.5	–	–	21	
	2	1.0	–	1	–	–	28.7	0.18‰
IPDA+ MEKO	5	1.0[1)]	–	–	–	–	< 5	
HDA	2	1.0	0.1	–	–	–	< 0.5	
	2	1.0	1.0	–	–	–	< 0.5	
	2	1.0	–	1.0	–	–	< 0.5	
	2	1.0	–	0.5	–	–	12.7	
	2	1.0	–	1.0	–	–	17.7	
$(H_2N\text{-}CH_2)_2\text{-}CO$	6	1.0	–	–	–	–	< 5	
Diaminoacetone	6	1.0	0.5	–	–	–	38	0.12‰
Gly	6	1.0	–	–	–	–	< 5	
	6	1.0	0.5	–	–	–	< 5	
	6	1.0	–	0.5	–	–	< 5	
Gly-Me-Est.	6	1.0	–	–	–	–	< 5	
	6	1.0	0.5	–	–	–	< 5	
	6	1.0	–	0.5	–	–	60	0.20‰

[1)] The sample was dissolved in 5 ml methanol before it was put into the flask

Redox – Reaction of NH_2OH – Generation of NO_x During the JIS-Analysis

The presence of NH_3 in Figure 1 is due to the instability of NH_2OH, which disproportionates into NH_3 and N_2O under acidic conditions[8] (see Figure 2).

The complete redox degradation of NH_2OH under acidic conditions leads mostly to NH_3 and N_2O (A), with HNO as possible intermediate product. Under alkaline conditions NH_2OH disproportionates to NH_3 and N_2.

The total reaction equation under acidic conditions utilizes 4 molecules of NH_2OH, which have to share a small reaction compartment inside the aqueous solution. It is improbable that this happens. Therefore an intermediate step can be favored, where two NH_2OH molecules react to NH_3 and HNO[12,13]. HNO can be regarded as a nitrogen analog compound to formaldehyde. It is quite reactive and instable. In water it forms a hydrate, which is mostly protonated at pH 2 (B). In alkaline solutions $HN(OH)_2$ reacts with NH_2OH to N_2, while the protonation of NH_2OH suppresses this reaction and leads the formation N_2O (C), probably via HO-N = N-OH. The dehydration of HO-N = N-OH is irreversible and at 100°C / pH 2 assumed to be fast. It is also reported that traces of HNO_2 emerge due to the disproportionation of two molecules $HN(OH)_2$ (D).

NH_3 can act only as a reducing agent, but it's EMF is so high that it can be regarded as inert under the JIS-Analysis reaction conditions. An investigation of N_2O as reactive species in the JIS-Analysis concluded also in an inert behavior of this gas[9]. Therefore NH_2OH; the instable HNO and traces of HNO_2 are favorable nitrogen sources for the generation of hydrogen cyanide from oxime blocked isocyanates.

A calculation based on the IPDI-MEKO / $NaNO_2$ and IPDI-MEKO HCN yields in Table helps to estimate the amount of generated HNO_2. If HNO_2 is the main reagent for the HCN generation, about 10% of all free NH_2OH in this example has to be converted into HNO_2 and to react before it is reduced by NH_2OH to HO-N = N-OH. A 10% conversion rate seems to be quite big for a side reaction that ought to yield only traces.

For NH_2OH one can say that the direct reaction of $NH_2OH_2^+$ with a target molecule is not neglectable, but it tends to yield small amounts of HCN, even if the reaction of

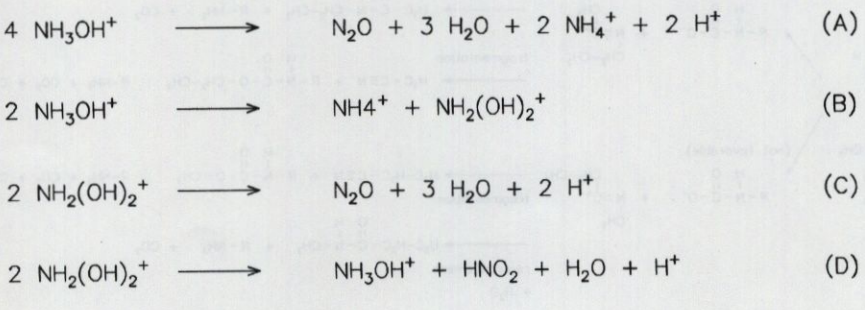


Figure 2 Redox reactions of hydroxylamine

$NH_2OH_2^+$ with a target molecule takes place (Table 3 – Diaminoacetone oxidation by NH_2OH compared with IPDI-MEKO in Table 2). Therefore the main reaction pathway to HCN should follow the HNO route.

AN Generation via Beckmann Rearrangement

Up to now we explained the presence of NH_3, CO_2, MEK and MEKO in Figure 1, but the presence of AN has not been explained yet. It is likely that AN derives from a Beckmann Rearrangement of oxime blocked isocyanates[10] (see Figure 3).

This reaction of oximes is well known in combination with p-toluolsulfonic acid. The GC-MS data indicates that isocyanates can act as elimination group as well with a final product mixture of nitriles, amides, urethanes, amines and alcohols. Figure 4 supports this reaction mechanism by the detection of N-Ethylacetamide. Ethanol has also been detected in the diluted diethyl ether extract of the experiment described in Figure 4, but it can be also an impurity of the extraction agent diethyl ether.

The amine-isocyanate reaction builds up an insoluble precipitate crosslinked via urea bridges, which forms the white sludge in the flask after the JIS-Analysis of oxime blocked isocyanate compounds has been finished. This very quick amine-isocyanate reaction might not take place in the ion pair arrangement during the Beckmann Rearrangement. Therefore urethanes with a relatively low vapor pressure (detectable by capillary GC) are formed.

It is possible to detect small amounts of isophorone based derivatives in an alkaline diethyl ether extract of the flask content after the JIS-Analysis of IPDI-MEKO, which are probably the assumed urethanes. This is unusual, since normally isocyanates react much quicker with amines than with water or alcohols.

Urethanes (Table 2 – IPDI-MeOH), Amines (Table 3 – IPDA), AN and N-Ethylacetamide (Table 6) do not generate significant amounts of HCN in the JIS-Analysis in the presence of NH_2OH. This can be different in mixtures with other

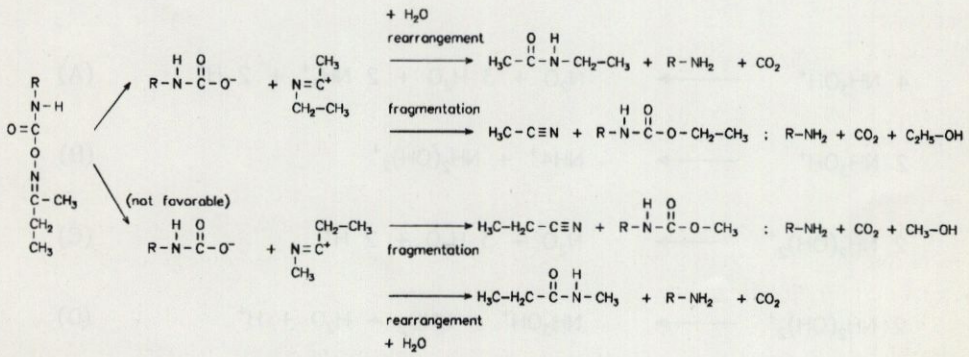


Figure 3 Beckmann rearrangement of oximes

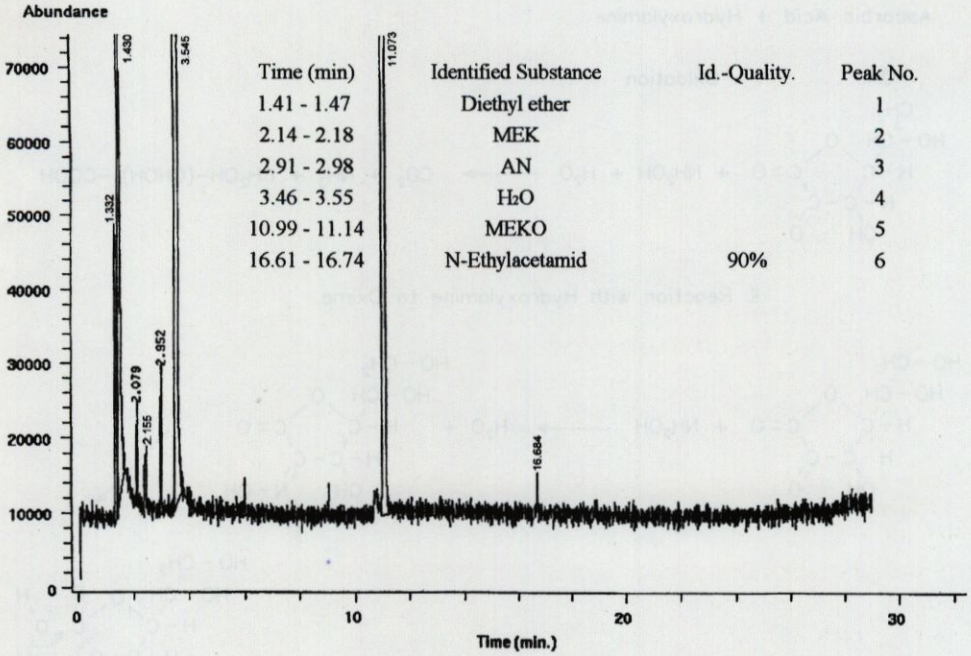


Figure 4 Organic phase GC-MS of alkaline (pH 11) 100 ml aqueous phase / 50 ml diethyl ether extract; 10 fold concentrated by evaporation of diethyl ether to a final sample size of 5 ml; out of 5g IPDI-MEKO; 2.5g $NH_2OH{\cdot}HCl$; 10 ml H_3PO_4; 240 ml H_2O; 4h reflux treatment.

Instrument	: Hewlett Packard 5989A
Column	: J&B-DB-WAX (0.25 mmø *30 m; 25 μm PEG-20M coating)
Inj. Temp.	: 250°C
Column Temp.	: 50°C – > 200°C; 5°C/min; 0 min init. time
Ion Source Temp.	: 200°C
Separator Temp.	: 100°C
Carrier Gas	: He; 1 ml/min

compounds, but at first it is better to work with a simplified system to establish a reaction mechanism. Also this simplified system has to yield detectable amounts of byproducts caused by this reaction mechanism. Therefore oximes were investigated.

Oximes and the Generation HCN

All investigated ketoximes and aldoximes are water soluble. As Table 4 shows, FAO generates a high amount of HCN under all listed reaction conditions. We believe that this is due to a dehydration reaction of HO-N = CH2 to HCN by elimination of water at elevated temperatures and acidic conditions.

The other oximes generate relatively high amounts of HCN in combination with Ascorbic Acid, which has been utilized as reducing agent in the JIS-CN Analysis. Today NH_4-SO_3NH_2 is used to decompose NO_2^-. The reaction of NH_2OH with Ascorbic Acid occurs in the way described in Figure 5.

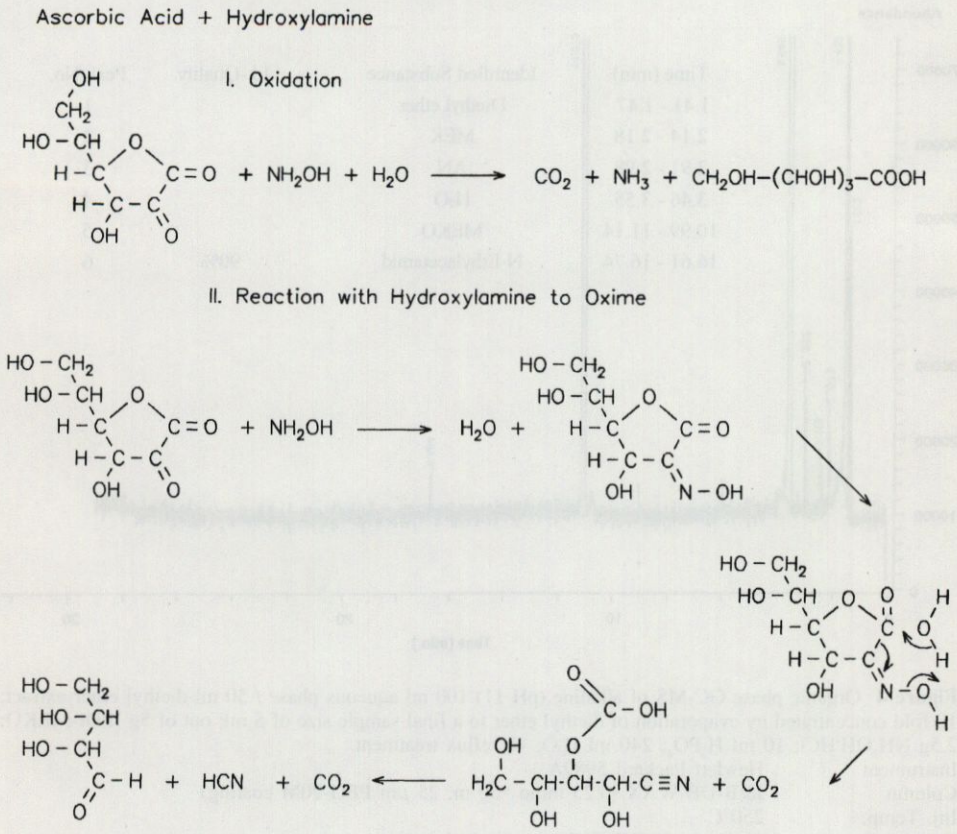


Figure 5 HCN generation by reaction of ascorbic acid with hydroxylamine

As instable intermediate product occurs a cyanhydrine, which hydrolyses under acidic conditions to HCN and an aldehyde.

Based on Table 4 it follows for the generation of HCN from EDTA that it is puzzling that EDTA does not generate HCN despite the relative large NH_2OH content (about 0, 32 g NH_2OH) in the experiments of Table 4. In Table 6 about 0, 25 g NH_2OH lead to the generation of a significant amount of HCN. One difference between these two experiments is the additional Cl^- content in Table 6, which might catalyze the EDTA degradation. This assumption is not confirmed by the MEKO/EDTA/NaCl experiment in Table 4. Another difference is the presence of MEK in the MEKO/EDTA/NaCl experiment, which therefore hinders the reaction of NH_2OH or its derivates with EDTA in the solution or on the flask surface.

Furthermore Table 4 shows that the HCN generation from IPDI-MEKO does not singly derive from MEKO or any other oxime in the absence of an organic phase. In the presence of an organic phase a generation of HCN out of oximes is possible, if the oxime is dissolved in the water phase (Table 4 – Placcel 320 and octacosane

Table 4 CN^- formation caused by oxime compounds

Sample	*Reference*	*Amount (g)*	*$NH_2OH \cdot HCl$ (g)*	*$NaNO_2$ (g)*	*EDTA (g)*	*Reducing or Additional Agent*	*CN^- (µg/100 ml) (distillate)*	*Yield per mol Sample*
NH_2OH . HCl	–	–	–	–	–	–	–	
w% NH_2OH:51								
FAO	4	0.5	–	–	–	–	470	1.57‰
	4	0.5	–	–	1.0	–	517	
	4	0.5	–	–	–	1 g $NH_4SO_3NH_2$	584	
	4	0.5	–	–	–	1 g Acorb-Ac	1060	
DMKO	4	1.0	–	–	–	–	< 0.5	
w% NH_2OH:45	2	1.0[1]	–	–	–	–	0.9	
Tbp.:135 °C	4	1.0	–	–	1.0	–	0.6	
	4	1.0	–	–	–	1 g $NH_4SO_3NH_2$	< 0.5	
	4	1.0	–	–	–	1 g Acorb-Ac	363	
MEKO	4	1.0	–	–	–	–	< 0.5	
w% NH_2OH:38	2	1.0[1]	–	–	–	–	0.6	
Tbp.: 152 °C	6	0.5	–	0.5	–	–	260	
	4	1.0	–	–	1.0	–	1.2	
	6	1.0	–	–	1.0	–	< 5	
	6	1.0	–	–	–	0.62 g NaCl	< 5	
	4	1.0	–	–	–	1 g $NH_4SO_3NH_2$	< 0.5	
	4	1.0	–	–	–	1 g Acorb-Ac	401	
	6	–	–	–	–	4 g Placcel 320	< 5	
	6	0.5[2]	–	–	–	4 g Placcel 320	< 5	
	6	0.5[2]	0.5	–	–	4 g Placcel 320	< 5	
	6	0.5[2]	–	0.5	–	4 g Placcel 320	62	0.40‰
	6	0.5[3]	–	–	–	4 g Placcel 320	36	0.23‰
	6	0.5	–	–	–	4 g Octacosane	9.1	0.06‰
	6	1.0	–	–	–	4 g Octacosane	9.7	0.03‰
	6	0.5	0.5	–	–	4 g Octacosane	8.2	0.05‰
CyHO	4	1.0	–	–	–	–	< 0.5	
w% NH_2OH:29	2	1.0[1]	–	–	–	–	1.0	
Tbp.: 208 °C	4	1.0	–	–	1.0	–	1.1	
	4	1.0	–	–	–	1 g $NH_4SO_3NH_2$	0.5	
	4	1.0	–	–	–	1 g Acorb-Ac	202	

[1] The sample was dissolved in 5 ml method before it was put into the flask
[2] MEKO has been dissolved in Placcel 320 (Polycaprolacton) before the analysis
[3] MEKO was placed in the flask, then H_3PO_4/H_2O was added and after 10 min waiting and dissolving MEKO in the acidic solution Placcel 320 was added

experiments). From this result it also follows, that the HCN yield depends on the interface surface area between the organic and the water phase. This explains the deviations between the HCN yields out of different IPDI-MEKO analysis runs in Table 2.

IPDI-MEKO phase separates during the JIS-Analysis, which promotes the HCN generation but still does not explain a feasible reaction pathway. Since the hydrogen cyanide yield of the NH_2OH/ketone systems are quite low and improve only in mixtures a more simplified system with better yields should be the better choice.

HCN Formation Based on Ketones

The generation of HCN out of organic compounds in the presence of NO_x has been reported many times[1, 2, 9]. Especially the $NaNO_2$/ketone system yields higher amounts of HCN, therefore it should serve as a base for a feasible reaction pathway. $NaNO_2$ leads to the formation of HNO_2 at acidic conditions. HNO_2 is also generated by redox reactions out of most other NO_x samples except N_2O. Therefore $NaNO_2$ provides a general base for further discussions of all NO_x derivatives.

Table 5 mainly indicates that the combination of ketones with $NaNO_2$ leads to HCN formation. To get an idea of the involved reaction mechanisms GC-MS has been performed. Figure 6 shows the total ion chromatogram (TIC) of MEK plus $NaNO_2$.

The diethyl ether peak in Figure 6 is due to the extraction solvent, all other peaks result from degradation products of MEK as shown in Figure 7.

Table 5 CN^- generation based on ketone compounds

Sample	*Reference*	*Amount (g)*	*NH_2OH ·HCl (g)*	*$NaNO_2$ (g)*	*EDTA (g)*	*Reducing or Additional Agent*	*CN^- (µg/100 ml) (distillate)*	*Yield per mol Sample*
DMK	6	1.0	–	–	–	–	< 5	
	6	1.0	–	–	1.0	–	< 5	
	6	1.0	0.5	–	–	–	< 5.	
	6	1.0	0.5	–	1.0	–	< 5	
	6	1.0	–	0.5	–	–	460	
	6	1.0	–	0.5	1.0	–	1300	
MEK	6	1.0	–	–	1.0	–	< 5	
	2	1.0	0.1	–	–	–	< 0.5	
	2	1.0	0.5	–	–	–	< 0.5	
	2	1.0	1.0	–	–	–	< 0.5	
	2	1.0	–	0.05	–	–	245	
	2	1.0	–	0.2	–	–	3720	
	2	1.0	–	0.5	–	–	5140	
	6	1.0	–	0.5	–	–	3700	10.7‰
CyH	2	1.0	0.1	–	–	–	< 0.5	
	2	1.0	0.5	–	–	–	< 0.5	
	2	1.0	1.0	–	–	–	< 0.5	
	2	1.0	–	0.05	–	–	19.7	
	2	1.0	–	0.2	–	–	69.6	
	2	1.0	–	0.5	–	–	134	0.49‰
DIPK	6	1.0	0.5	–	–	–	< 5	
	6	1.0	0.5	–	1.0	–	6.5	
	6	1.0	–	0.5	–	–	130	0.54‰
	6	1.0	–	0.5	1.0	–	950	
DTBK	6	1.0	0.5	–	–	–	< 5	
	6	1.0	0.5	–	1.0	–	< 5	
	6	1.0	–	0.5	–	–	< 5	
	6	1.0	–	0.5	1.0	–	950	

[1] The sample was dissolved in 5 ml methanol before it was put into the flask

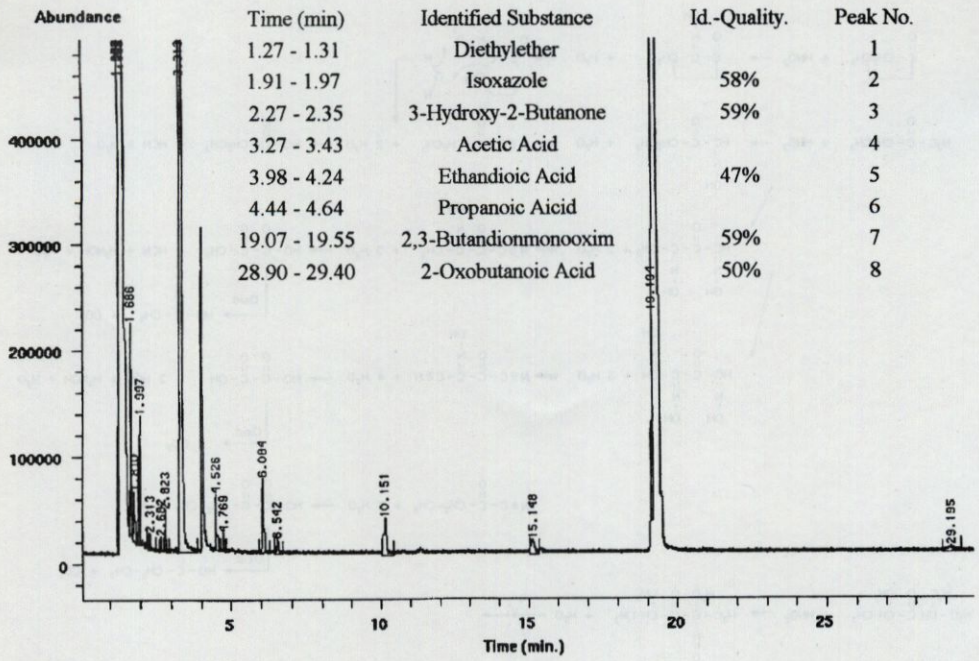


Figure 6 Organic phase GC-MS of neutral (pH 7) 100 ml aqueous phase / 50 ml diethyl ether extract; 20 fold concentrated by evaporation of diethyl ether to a final sample size of 2.5 ml; out of distillate from 1 g MEK; 1 g $NaNO_2$; 10 ml H_3PO_4; 240 ml H_2O; 1h reflux treatment; 2 h distillation. (The extraction was performed in order to remove NO_x in the distillate)

Instrument	: Hewlett Packard 5989A
Column	: J&B-DB-WAX (0.25 mmø *30m; 25μm PEG-20M coating)
Inj. Temp.	: 250°C
Column Temp.	: 120°C; 0°C/min
Ion Source Temp.	: 200°C
Separator Temp.	: 100°C
Carrier Gas	: He; 1 ml/min

In the reaction pathway of ketones with NO_x the NO_x first attacks the α-carbon atom to the carbonyl carbon. The reaction leads to a dion-monooxime or trion-dioxime. These α-diketone or α-triketone derivates can cause C-C bond cleavages by hydrolysis ($CyH/NaNO_2$). This reaction or the H_2O elimination out of CH = N-OH yield α-keto-cyanides, which then are hydrolyzed to α-keto-carbon-acids (R-CO-COOH) by releasing of NH_3 or carbon-acids by releasing HCN.

Furthermore NO_x partly oxidizes these compounds up to decarboxylated derivatives. Some of these compounds have been identified in Figure 6. 2-Oxobutanoic - Acid (C_2H_5-CO-COOH) could be the nitrile hydrolysis product of 2-Oxobutan-1-nitrile (R-CO-CN) or the product of hydrolyzed and oxidized 2-Oxobutan-1-aldoxime (R-CO-CNOH). Propanoic Acid could result from the decarboxylation of 2-Oxobutanoic Acid or the hydrolysis of 2-Oxobutan-1-nitrile. The last reaction cleaves of HCN. Overall the GC-MS data supports the postulated reaction mechanism quite well.

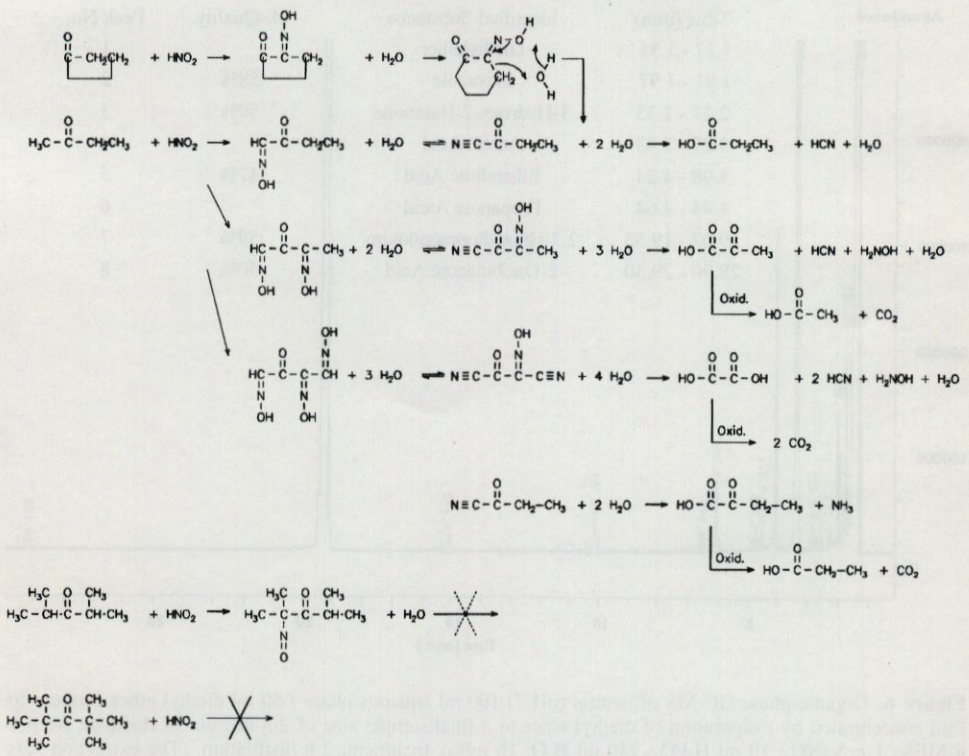


Figure 7 Oxidation of ketones by HCN generation therefrom

This postulated reaction pathway should be truncated by an introduction of substituents to the carbon atoms adjacent to the carbonyl carbon atom. A complete substitution with methyl groups provides indeed a HCN free distillate (DTBK in Table 5), while one remaining hydrogen atom decreases the detected amount significantly (DIPK in Table 5).

The DTBK result in Table 5 also indicates the degradation of EDTA by NO_x[9], while the DIPK experiment suggests a degradation of EDTA by NH_2OH.

Since the presence of an organic phase supports the formation of HCN in the presence of NH_2OH, it has to be explained why the more hydrophobic ketones, like CyH, DIPK and DTBK, do not cause any HCN detection. For DIPK and DTBK this result is understandable, since DTBK is inert and DIPK probably reacts with NH_2OH to an α-ketoamine ($R_2C(NH_2)$-CO-R) or with HNO to an di-α-ketoamine ($NH(R_2C$-$CO\text{-}R)_2$). Both amines cannot be transformed into cyanides, since the amine carbon atom has no further hydrogen atoms. Any traces of HNO_2 (Chapter 4) are to small for a HCN generation with DIPK.

CyH could be derivatized by NH_2OH or HNO to an α-ketoimine, which is then hydrolyzed to an α-diketone, that could react with NH_2OH to an α-ketoxime, which could lead to a C-C bond cleavage and the formation of HCN. Since there are many

step involved in this reaction pathway and since the formation of an oxime in an acidic medium is unfavorable, the yield of generated α-ketoxime seems to be to small to generate more than 5 μ-g HCN/100 ml.

Hydrolysis of α-Keto-Cyanides

The key reaction for the HCN generation by No_x and ketones is the hydrolysis of α-keto-cyanides (R-CO-CN). This reaction is similar to the hydrolysis of carbon-acid chlorides (R-CO-CI), which results in the formation of HCI and a carbon acid (R-COOH). The total reaction pathway could be also regarded as somewhat analogous to the "Haloform" reaction, where α-methyl ketones split of chloroform by treatment with HOCl[7].

To prove this R-CO-CN hydrolysis, the JIS-Analysis of PCy has been investigated. The result in Table 6 indicates that about 95% of PCy is hydrolyzed by cleaving of HCN. The well known nitrile hydrolysation[7] is only a minor side reaction.

Table 6 CN^- detection from various intermediate and additive compounds

Sample	*Reference*	*Amount (g)*	*NH_2OH ·HCl (g)*	*$NaNO_2$ (g)*	*EDTA (g)*	*Reducing or Additional Agent*	*CN^- (μg/100 ml) (distillate)*	*Yield per mol Sample*
EDTA	3	1.0	0.1	–	*	–	1.8	
	3	1.0	0.5	–	*	–	50.5	0.54‰
	3	1.0	–	0.1	*	–	142	
	3	1.0	–	0.5	*	–	380	4.11‰
Ascorb-Ac	3	1.0	0.1	–	–	*	79	
	3	1.0	0.5	–	–	*	116	
	3	1.0	–	0.1	–	*	16.4[2]	
	3	1.0	–	0.5	–	*	54.4[2]	
PCy	6	1.0	–	–	–	–	375000	958‰
	6	1.0	0.5	–	–	–	351000	
	6	1.0	–	0.5	–	–	335800	
	6	1.0	–	0.5	1.0	–	373000	
AN	6	1.0	–	–	1.0	–	< 5	
	6	1.0	0.5	–	–	–	< 5	
	6	1.0	0.5	–	1.0	–	< 5	
	6	1.0	–	0.5	–	–	12	
	6	1.0	–	0.5	1.0	–	710	
2 mol AN	6	1.0	–	–	–	–	< 5	
1 mol IPDA	6	1.0	0.5	–	–	–	< 5	
	6	1.0	0.5	–	1.0	–	< 5	
2 ml AN	6	1.0	–	–	–	–	< 5	
1 mol IPDA	6	1.0	–	–	1.0	–	< 5	
2 mol MEKO	6	1.0	–		1.0	–	< 5	
N-Ethyl-acetamide	6	1.0	–	–	–	–	< 5	
	6	1.0	0.5	–	–	–	< 5	
	6	1.0	–	0.5	–	–	21	

[1] The sample was dissolved in 5 ml methanol before it was into the flask
[2] NO_2^- has been detected

This α-keto-cyanide-hydrolyzation should also be the key in understanding the HCN formation out of oxime blocked isocyanates.

General Reaction Scheme for the Formation of α-Keto-Cyanides

The elctrophilic addition of HNO_2 to C = C double bonds is known[7]. It is possible to carry out the same reaction with NH_2OH or HNO. At first an elctrophilic N^+ species has to be generated by adding H^+ to HNO_2, $HN(OH)_2$ or NH_2OH (see Figure 8).

The partially positive nitrogen atom attacks a C-H acidic compound. Possible reaction partners are shown in Figure 9.

Species A derives from MEKO blocked isocyanates, where the oxime nitrogen will be protonated at pH 2, which will promote the double bond shift. Species B derives from MEK, C is based on N-ethyl-acetamide, D on a primary or secondary cyanide and E on EDTA. The nucleophilic carbon atoms of these C-H acidic compounds react with the electrophilic N^+ atoms as shown in Figure 10.

In this way α-methyl- or α-methylene- or with NO_x even α-CHR_2 – carbonyl or carbonyl analog compounds generate HCN in the JIS-Analysis. In the case of α-methylene- or α-CHR_2 – carbonyl compounds C-C bond cleavages have to take place, which should hinder the reaction and decrease the reaction yield. That this C-C bond cleavage occurs is supported by the IPDI-CyHO sample in Table 2 or the DIPK sample in Table 5. Also in the case of EDTA in Table 6 a C-N single bond has to be cleaved to allow the completion of the suggested reaction (see Figure 11).

Although AN cannot be regarded as carbonyl analog compound it causes the formation of HCN in combination with NO_x in almost the same way (see Figure 12).

Since there is at least one oxidation step involved in the NH_2OH reaction pathway to the target molecule structure α-keto-cyanide, an experiment to prove this oxidation step seemed to be feasible. For this reason diaminoacetone has been investigated. The

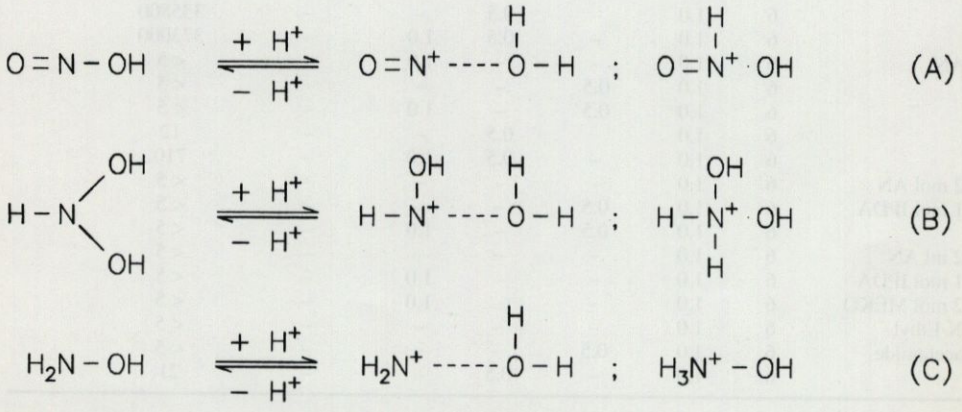


Figure 8 Formation of an electrophilic nitrogen atom under acidic conditions

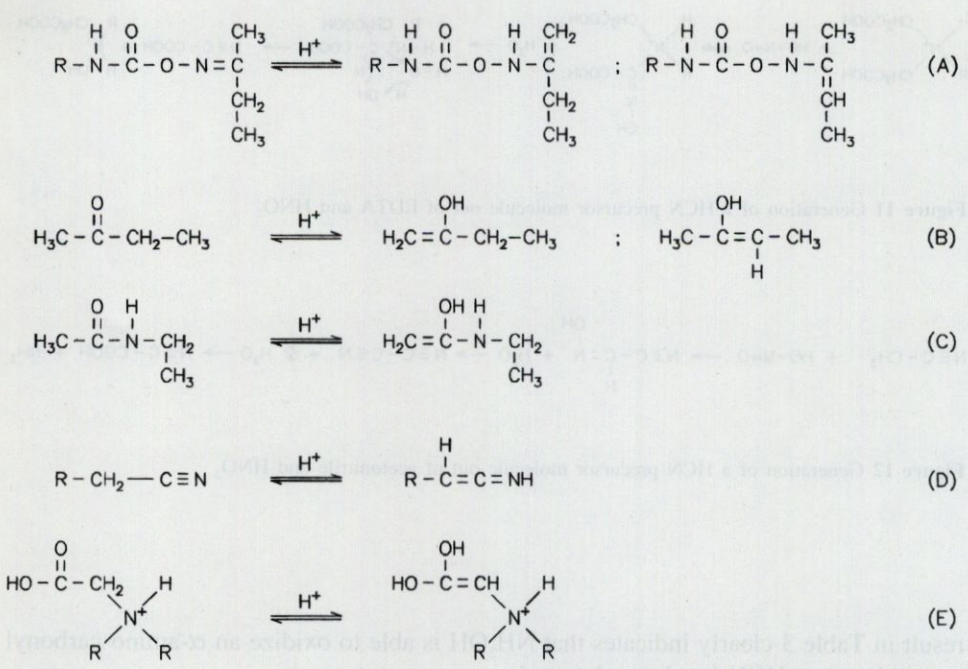


Figure 9 Formation of various nucleophilic reaction partners under acidic conditions

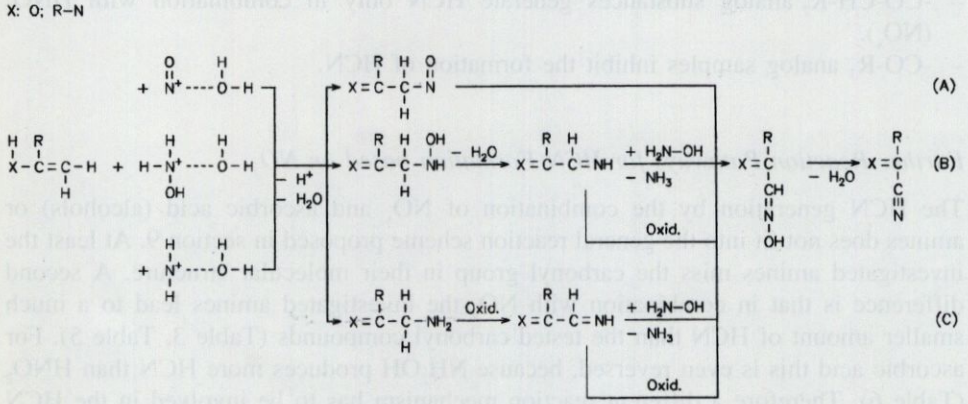


Figure 10 Reaction of an electrophilic nitrogen atom with a nucleophilic partner that yields α-Ketocyanides

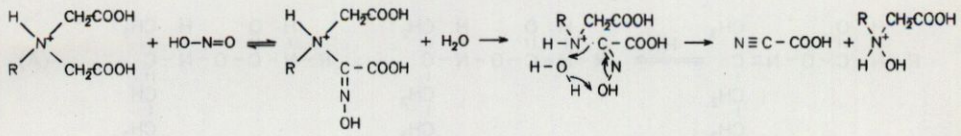


Figure 11 Generation of a HCN precursor molecule out of EDTA and HNO_2

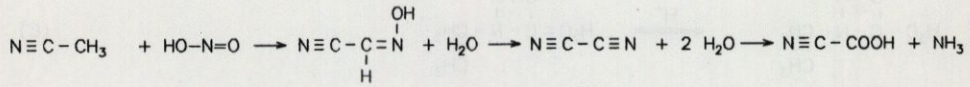


Figure 12 Generation of a HCN precursor molecule out of acetonitrile and HNO_2

result in Table 3 clearly indicates that NH_2OH is able to oxidize an α-amino-carbonyl group, because HCN has been detected.

After all these tested samples one finds as qualitative reactivity estimation (R-aliphatic hydrocarbon):

- NH_2OH causes less HCN generation than HNO_2.
- -CO-CH_3 analog compounds give the best HCN yields.
- -CO-CH_2-R analog samples decrease the HCN yields by one order of magnitude.
- -CO-CH-R_2 analog substances generate HCN only in combination with HNO_2 (NO_x).
- -CO-R_3 analog samples inhibit the formation of HCN.

Further Reaction Pathways for HCN Formation based on NO_x

The HCN generation by the combination of NO_x and ascorbic acid (alcohols) or amines does not fit into the general reaction scheme proposed in section 9. At least the investigated amines miss the carbonyl group in their molecular structure. A second difference is that in combination with NO_x the investigated amines lead to a much smaller amount of HCN than the tested carbonyl compounds (Table 3, Table 5). For ascorbic acid this is even reversed, because NH_2OH produces more HCN than HNO_2 (Table 6). Therefore a different reaction mechanism has to be involved in the HCN generation process. We believe that this reaction mechanism is based on the Barton-Reaction[11]. The reaction mechanism for amines (and alcohols) is shown in Figure 13.

There are different opportunities to generate HCN, but for us this looks the most probable one. At first the amine and HNO_2 forms a diazo compound, which is very

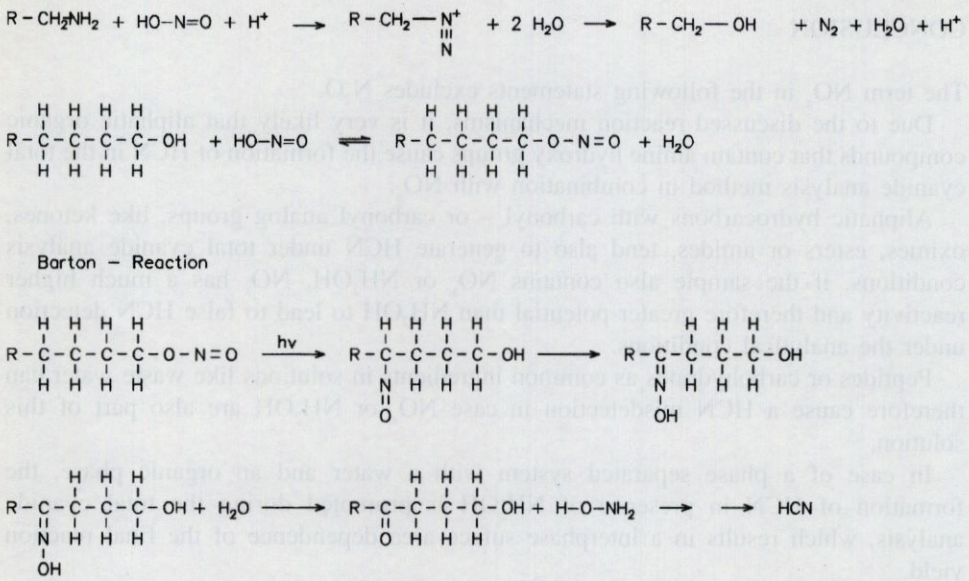


Figure 13 Generation of a HCN out of amines and HNO_2

reactive and gets hydrolyzed easily. The resulting alcohol is then esterificated by HNO_2. This nitrous acid ester is light sensitive and enables an addition of a N = O radical to the aliphatic hydrocarbon chain. This leads to an oxime or after its hydrolyzation to a ketone. From here the reaction mechainism of section 9 can be applied.

A different reaction mechanism for amines would be the oxidation of the amine group by NO_x. The result could be a cyanide, which is then derivatized according chapter 9 to an α-keto-cyanide. Furthermore one could think of an nitrous acid amide instead of an ester, which already could perform the Barton Reaction. Both alternatives seem to be rather unlikely, since the formation of a diazo compound should be the main reaction mechanism.

Ascorbic acid primarily reduces HNO_2 to NO_x or N_2O. But the reaction product of this reduction or ascorbic acid itself can be regarded as an alcohol, which reacts in the same way as the alcohol in the above proposed mechanism.

One reason for the smaller HCN yield caused by the combination of HNO_2 and amines or ascorbic acid should be the reduction of HNO_2 to N_2 or N_2O and hence the reduction in the available amount of HNO_2. Much more limiting should be the availability of photons, which are necessary to start the Barton Reaction. Since the brightness differs often between each analytical run or different laboratories, one should also expect a broad range in the amount of detected HCN in different experiments.

CONCLUSION

The term NO_x in the following statements excludes N_2O.

Due to the discussed reaction mechanisms, it is very likely that aliphatic organic compounds that contain amine hydroxy groups cause the formation of HCN in the total cyanide analysis method in combination with NO_x.

Aliphatic hydrocarbons with carbonyl – or carbonyl analog groups, like ketones, oximes, esters or amides, tend also to generate HCN under total cyanide analysis conditions, if the sample also contains NO_x or NH_2OH. NO_x has a much higher reactivity and therefore greater potential than NH_2OH to lead to false HCN detection under the analytical conditions.

Peptides or carbohydrates as common ingredients in solutions like waste water can therefore cause a HCN misdetection in case NO_x or NH_2OH are also part of this solution.

In case of a phase separated system with a water and an organic phase, the formation of HCN in presence of NH_2OH is promoted during the total cyanide analysis, which results in a interphase suface area dependence of the final reaction yield.

A suggestion to avoid the HCN misdetection by a sample pretreatment of oxime blocked isocyanates with caustic soda has been made.

Since the JIS-Analysis method is very similar to other used distillation methods to detect HCN in water, like ISO or ASTM methods, it is very likely that other methods also cause a detection of HCN, which has probably not been in the sample before the analysis started.

Acknowledgements

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