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Synthesis and structure of a product of interaction of acetonitrile with hydrogen bromide, $[H_2N{=}C(Me){-}NH{-}C(Me)Br_2]Br$

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A mixture of solid products was obtained upon absorption of dry HBr by MeCN. One of the products, $[H_2N{=}C(Me){-}NH{-}C(Me)Br_2]Br$, was isolated as white single crystals and characterized by X-ray diffraction analysis.

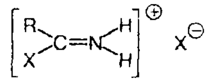
Key words: acetonitrile, hydrogen bromide, X-ray diffraction analysis.

It is well known that in many cases hydrogen halides act as specific catalysts of reactions of nitriles. For example, the Pinner reaction (preparation of salts of imino esters), the Hoesch reaction (preparation of salts of ketimines), the Gattermann and Stephen reactions (preparation of salts of aldimines), and a number of other reactions of nitriles are performed with the participation of hydrogen halides and do not proceed when alternative protic or aprotic acids are used.[1] Therefore, from the first work[2] and on, the direct reactions of nitriles with hydrogen halides attracted the continuing interest of chemists involved in studies of problems of catalysis.[1–4]

Previously, it was believed that complexes containing only one molecule of hydrogen halide are formed upon dissolution of hydrogen halides in nitriles.[2] However, subsequent studies (primarily, studies of fusibility curves of binary systems) demonstrated that a number of compounds of different stoichiometric compositions can exist: $RCN \cdot HX$ (**1**)[5], $RCN \cdot 2HX$ (**2**)[5,6], $2RCN \cdot HX$ (**3**)[7], $2RCN \cdot 2HX$ (**4**)[7], $2RCN \cdot 3HX$ (**5**)[3,5,7], $RCN \cdot 5HX$ (**6**)[5], and $RCN \cdot 7HX$ (**7**)[5] (R = Me, X = Cl or Br). The melting points of most of them are below room temperature. Hydrochloride derivatives have received the most study by ^1H NMR and IR spectroscopy. Products of hydrolysis and alcoholysis of these derivatives were isolated and characterized.[1,7,8]

Two schemes of interactions of nitriles with hydrogen halides were reported in the literature.[1] The first scheme, which was suggested based on the UV spectra and on the analysis of the data on the conductivity, assumes that the nitrilium cation $[RC{\equiv}NH]^+$ and the polymeric anion $X(HX)^-_n$ are formed in solutions.[9] According to the second scheme (IR spectral studies), the solutions contain the imonium halide cation and the halide anion solvated by molecules of hydrogen halide.[3]

The structural studies of single crystals of composition **2** (X = Cl (neutron diffraction study)[5] or Br (X-ray diffraction analysis)[10]) confirmed the formation of the imonium halide cation.



In this work, we report the results of the structural study of the compound $2RCN \cdot 3HX$ (**5a**, R = Me and X = Br), which was formed in the reaction mixture of MeCN and HBr. This mixture is used for studying the catalytic reaction of carbonylation of acetylene in the presence of palladium complexes.[11]

Experimental

Hydrogen bromide was prepared by bromination of anthracene according to a procedure reported previously.[12] Reagent-grade bromine and anthracene were used without additional purification. To purify hydrogen bromide from traces of Br_2, it was passed through a U-tube filled with anthracene at a rate of ~1.7 mol $L^{-1}h^{-1}$ and then through a Drechsel bottle, which contained MeCN (chemically pure, 11.5 mL) and was cooled with ice (~0 °C). When HBr contacted with MeCN, a finely dispersed precipitate immediately formed in the central tube of the bottle. After 20 min, 0.026 moles of HBr per mole of MeCN were absorbed. Under the above-mentioned conditions, hydrogen bromide was absorbed completely (not determined with the use of wet litmus paper as it left the bottle).

The solution of HBr in MeCN containing a white amorphous precipitate was kept at –20 °C. After 12 days, colorless transparent crystals of compound **5a** precipitated on the walls and in the central tube. The structure of **5a** was studied.

We failed to analyze the finely dispersed precipitate that formed initially because the compound decomposed ("disappeared") in the course of filtration *in vacuo* with the use of a water aspirator pump. Apparently, the instability of the compound and its disappearance from the filter are associated with its decomposition to the initial reagents, which is typical of nitrilium salts and, probably, of the imonium halide cation.

The colorless crystals are more stable but very hygroscopic (rapidly ran in air). Because of this, we failed to obtain reproducible results of elemental analysis and potentiometric titration.

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Table 1. Crystallographic parameters for compound **5a**

Molecular formula	$C_4H_9Br_3N_2$
Space group	$P2_1/n$
a/Å	8.235(2)
b/Å	9.832(4)
c/Å	11.430(5)
α/deg	90
β/deg	102.06(2)
γ/deg	90
V/Å^3	905.0(6)
Z	4
ρ_{calc}/g cm^{-3}	2.384
Radiation	Mo-Kα (λ = 0.71073 Å)
θ-2θ scanning range (deg)	3—54
Number of measured reflection	1302
Number of reflections with $I > 4\sigma$	1239
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
R	0.034
R_w	0.043

X-ray diffraction analysis of compound 5a. Single crystals of compound **5a** (mounted in air) were glued to glass needles using rapidly solidifying epoxy resin. Then the crystals were rapidly transferred on a diffractometer equipped with a low-temperature unit. The X-ray diffraction data were collected on an automated four-circle Siemens P3/PC diffractometer at −112 °C. The structure was solved by direct methods, which allowed us to reveal all nonhydrogen atoms. Absorption correction (μ = 133 cm^{-1}) was applied using the program described in Ref. 13. After anisotropic refinement of the nonhydrogen atoms, the position of all hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (PC version).[14] The crystallographic parameters and the details of the refinement are given in Table 1. The principal geometric characteristics of the molecule are listed in Tables 2 and 3. The atomic coordinates are given in Table 4.

Results and Discussion

According to the data of X-ray diffraction analysis, compound **5a** is *N*-(α,α-dibromoethyl)acetamidine hydrobromide (Fig. 1) formed as a result of co-condensation of two acetonitrile molecules with three molecules of hydrogen bromide.

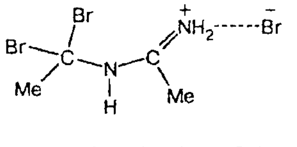


Table 2. Principal bond lengths (d) in molecule **5a**

Bond	d/Å	Bond	d/Å
Br(2)—C(2)	1.967(6)	Br(3)—C(2)	1.981(6)
N(1)—C(2)	1.428(9)	N(1)—C(4)	1.356(9)
N(1)—H(1A)	0.895(24)	N(2)—C(4)	1.303(9)
N(2)—H(21)	1.063(30)	N(2)—H(22)	0.812(28)
C(1)—C(2)	1.526(9)	C(1)—H(1B)	0.929(24)
C(1)—H(1C)	0.882(31)	C(1)—H(1D)	0.983(29)
C(3)—C(4)	1.487(10)	C(3)—H(3A)	1.021(30)
C(3)—H(3B)	0.909(24)	C(3)—H(3C)	0.880(28)

Table 3. Principal bond angles (ω) in molecule **5a**

Angle	ω/deg
C(2)—N(1)—C(4)	126.9(7)
C(4)—N(1)—H(1A)	117.4(21)
C(4)—N(2)—H(22)	129.2(21)
C(2)—C(1)—H(1B)	107.0(20)
H(1B)—C(1)—H(1C)	114.9(26)
H(1B)—C(1)—H(1D)	108.3(23)
Br(2)—C(2)—Br(3)	108.0(4)
Br(3)—C(2)—N(1)	111.7(5)
Br(3)—C(2)—C(1)	107.7(6)
C(4)—C(3)—H(3A)	110.3(16)
H(3A)—C(3)—H(3B)	110.4(25)
H(3A)—C(3)—H(3C)	111.1(26)
N(1)—C(4)—N(2)	123.8(8)
N(2)—C(4)—C(3)	119.7(7)
C(2)—N(1)—H(1A)	115.7(21)
C(4)—N(2)—H(21)	119.5(15)
H(21)—N(2)—H(22)	111.3(24)
C(2)—C(1)—H(1C)	107.6(18)
C(2)—C(1)—H(1D)	106.2(18)
H(1C)—C(1)—H(1D)	112.4(26)
Br(2)—C(2)—N(1)	111.0(5)
Br(2)—C(2)—C(1)	108.8(5)
N(1)—C(2)—C(1)	109.6(7)
C(4)—C(3)—H(3B)	109.5(20)
C(4)—C(3)—H(3C)	107.1(20)
H(3B)—C(3)—H(3C)	108.4(23)
N(1)—C(4)—C(3)	116.5(7)

Table 4. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (U_{eq}× 10^3) for compound **5a**

Atom	x	y	z	U_{eq}/Å^2
Br(1)	−3383(1)	5970(1)	3811(1)	18(1)
Br(2)	2189(1)	10487(1)	4544(1)	22(1)
Br(3)	492(1)	7634(1)	3693(1)	19(1)
N(1)	3736(9)	8411(7)	3478(5)	15(1)
N(2)	2094(9)	9420(7)	1775(5)	19(1)
C(1)	3435(11)	7920(10)	5491(7)	25(1)
C(2)	2644(10)	8557(8)	4290(6)	15(1)
C(3)	4853(10)	8649(8)	1693(7)	18(1)
C(4)	3464(10)	8839(8)	2326(7)	15(1)

Compound **5a** was formed due to dimerization of the CN fragments of two MeCN molecules, which resulted in a new N—C bond (N—C, 1.356(9) Å). In one of the MeCN molecules, the central carbon atom is bound to two bromine atoms to form CBr_2Me (Br—C, 1.967(6) and 1.981(6) Å; C—CH_3, 1.526(9) Å). The nitrogen atom (C—N, 1.428(9) Å) is bound to one hydrogen atom (N—H 0.89(2) Å). In the second MeCN molecule, the nitrogen atom is terminal. Two hydrogen atoms are attached to this nitrogen atom (N—H, 1.06(3) and 0.81(3) Å) and the nitrogen atom forms a double bond with the carbon atom (C—NH_2, 1.303(9) Å). The formally terminal nitrogen atom is positively charged

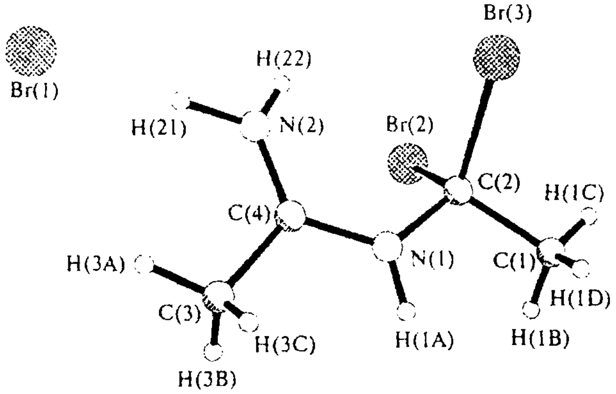
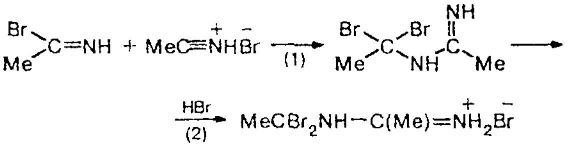


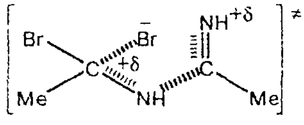
Fig 1. Structure of compound **5a**.

and the NH_2^+ fragment interacts with the Br^- anion through the N—H...Br hydrogen bond (2.43(1) Å), which leads to the substantial elongation of one N—H bond of the NH_2 fragment. At the same time, it should be noted that the $C=NH_2$ and C—NH bond lengths have similar values, which is, most likely, indicative of delocalization of the positive charge to form the amidine system $N\!=\!\overset{+}{C}\!=\!N$.

Based on the available data on the formation of the 1 : 1 products and the products containing two or more nitrile molecules as well as on our observational data on the course of formation of adduct **5a**, two schemes of cocondensation of MeCN and HBr can be suggested.

Scheme 1



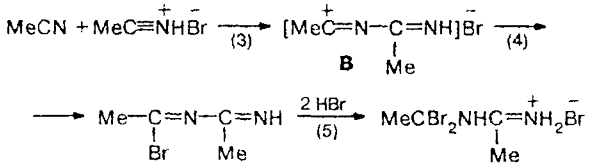


A

Apparently, the stage (1) proceeds through transition state **A**.

The second scheme involves the stage of interaction of nitrilium bromide with the MeCN molecule to form ionic adduct **B** (3). Then, intramolecular conversion (4) occurs followed by addition of two HBr molecules (5).

Scheme 2



The second scheme provides an explanation for the formation of trimeric imino derivatives in the system $RCN—HBr—SbBr_3$ [15,16] by the addition of the third MeCN molecule to adduct **B**. Note that the polymeric anion $(HBr)_nBr^-$ can serve as a source of HBr in these reactions.

When studying catalytic reactions in nitriles, which are used as solvents, possible interactions of nitriles with hydrogen halides should be taken into account. In particular, the effect of the concentration of HBr on the course of the catalytic reaction of carbonylation of acetylene cannot be revealed because products of addition of HBr to nitriles readily form.[11]

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