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Photolysis of isothiocyanic acid HNCS in low-temperature matrices. Infrared detection of HSCN and HSNC isomers

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Abstract

A combination of matrix isolation technique and Fourier transform infrared spectroscopy has been used to study the low-temperature photochemistry of isothiocyanic acid HNCS. Near UV photolysis with a medium-pressure mercury lamp of the matrix isolated HNCS/DNCS precursor in nitrogen and argon led to the formation of two unobserved, so far, isomers: thiocyanic acid HSCN and isothiofulminic acid HSNC and their deuterated analogs. Both species are formed as primary products presumably via two reaction channels: formation of the [H···NCS] and hydrogen migration leading to the HSCN molecule and formation of the [HNC···S] followed by rearrangement to HSCN and HSNC species. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The isothiocyanic acid HNCS is a sulfur analog of the well-known isocyanic acid HNCO. Since the latter species plays an important role both in atmospheric and combustion processes it has attracted a considerable attention. The performed theoretical and experimental studies concern the structure, stability and photolytic behavior of HNCO and its structural isomers [1–11]. Much less is known so far about isothiocyanic acid HNCS and its isomers. The early theoretical work of Bak et al. [12] has predicted a stability of four isomers to increase in the following order: HCNS, HSNC, HSCN and HNCS. This trend agrees with the fact that isothiocyanic acid HNCS is the only hitherto spectroscopically described isomer. Several papers on infrared spectra of gaseous [13,14], solid and isolated in argon matrix [14] isothiocyanic acid have been published. Microwave studies of various isotopic species of HNCS have been performed and the structure of the molecule was evaluated [15,16]. Flash photolysis of HNCS was also reported [17]. Results of a detailed photoionization mass spectrometric studies are published as well [18].

In this Letter we report the infrared matrix isolation studies of the UV photolysis of isothiocyanic acid HNCS in solid argon and nitrogen.

2. Experimental

Gaseous HNCS was prepared in a vacuum line by treating KNCS kept at 0 °C with 60%

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H_3PO_4 (D_3PO_4). It was collected and shortly stored in 1 l bulb at low (less than 10 mbar) pressure. Gaseous mixtures of isothiocyanic acid with matrix gases (Ar or N_2) were prepared by standard manometric techniques. Their concentration ranged between 1/600 and 1/3000. The gas mixtures were condensed onto gold-plated copper mirror kept at 15 and 18 K for deposition of argon and nitrogen matrices, respectively. The temperature was maintained by means of a closed cycle helium refrigerator (Air Products, Displex 202A). Infrared spectra were recorded at 11 K in a reflection mode with a resolution of 0.5 cm^{-1} by means of a Bruker 113v FTIR spectrometer equipped with a liquid N_2 cooled MCT detector.

UV photolysis was performed by light from a medium-pressure mercury lamp (Philipps CS200W-2) equipped with water filter and glass longwavelength pass filters (Schott-WG 360, 345, 335, 305, 295 and 280 nm).

3. Results

The results of the UV photolysis of the isothiocyanic acid isolated in argon and nitrogen matrices will be presented. First, matrices were subjected to the full output of the mercury lamp. Additional experiments were performed using glass longwavelength pass filters to evaluate the threshold energy for the photolytic reaction. Details of the initial spectra, themselves of interest as well, will be the subject of a separate report [19]. The spectra of HNCS in solid argon are in good agreement with those previously published by Durig and Wertz [14].

When matrices containing HNCS/DNCS suspended in nitrogen or argon are subjected to the full output of the mercury lamp several new bands grow following photolysis. In nitrogen matrices four new absorptions appear for both HNCS and DNCS precursors as presented in Fig. 1. The most intense absorption in the HNCS experiments occurs at 2580.2 cm^{-1} and is accompanied by three much weaker features situated a few wavenumbers apart from the main peak. Another absorption is observed at 960.9 cm^{-1} with a weaker band at 965.9 cm^{-1}. The 2580.2 and 960.9 cm^{-1} bands have their deuterium counterparts at 1873.6 and 688.5 cm^{-1}, respectively, in the spectra recorded in the DNCS experiments. The other new absorptions observed at 2182.3 and 2065.9 cm^{-1} in the spectra with HNCS precursor are only slightly affected by deuteration; the bands are 0.5 cm^{-1} blue and 0.5 cm^{-1} red shifted, respectively, in the spectrum of deuterated sample. The relative intensities of the four bands at 2580.2, 2182.3, 2065.9 and 960.9 cm^{-1} remain constant during prolonged photolysis time but the 2065.9 cm^{-1} band decreases slightly with respect to the other three bands after matrix annealing. This behavior indicates that the bands at 2580.2, 2182.3 and 960.9 cm^{-1} belong to one product species while the 2065.9 cm^{-1} band to another photoproduct.

A corresponding set of bands was observed in argon matrices. The most intense bands after UV irradiation of HNCS/Ar matrices appeared at 2182.3 and 2064.2 cm^{-1} (Fig. 2a). They are slightly shifted on deuteration as shown in Fig. 2b, the 2182.3 cm^{-1} band moves by 0.7 cm^{-1} to higher wavenumbers while the 2064.2 cm^{-1} absorption is red shifted by 0.7 cm^{-1}. Two additional weaker absorptions were localized in the spectra of the irradiated HNCS/Ar matrices at 2581.0 and 959.7 cm^{1}. Their counterparts in the DNCS/Ar system were found at 1874.0 and 692.8 cm^{-1}, respectively.

Wavenumbers of the new absorptions mentioned above, observed in N_2 and Ar matrices, together with the assignment proposed in the following discussion are gathered in Table 1.

In some experiments weak and relatively broad absorptions appeared in the spectra after photolysis at 3217.7 cm^{-1} for HNCS/Ar, at 3287, 3224.0, 2050.3, 2029.0 cm^{-1} for HNCS/N_2 and at 1964.6 cm^{-1} for DNCS/N_2. The intensities of these bands grow with time during photolysis however they are not correlated one with another or with the absorptions described above. Probably they are due to some unidentified complexes formed between species present in the matrix.

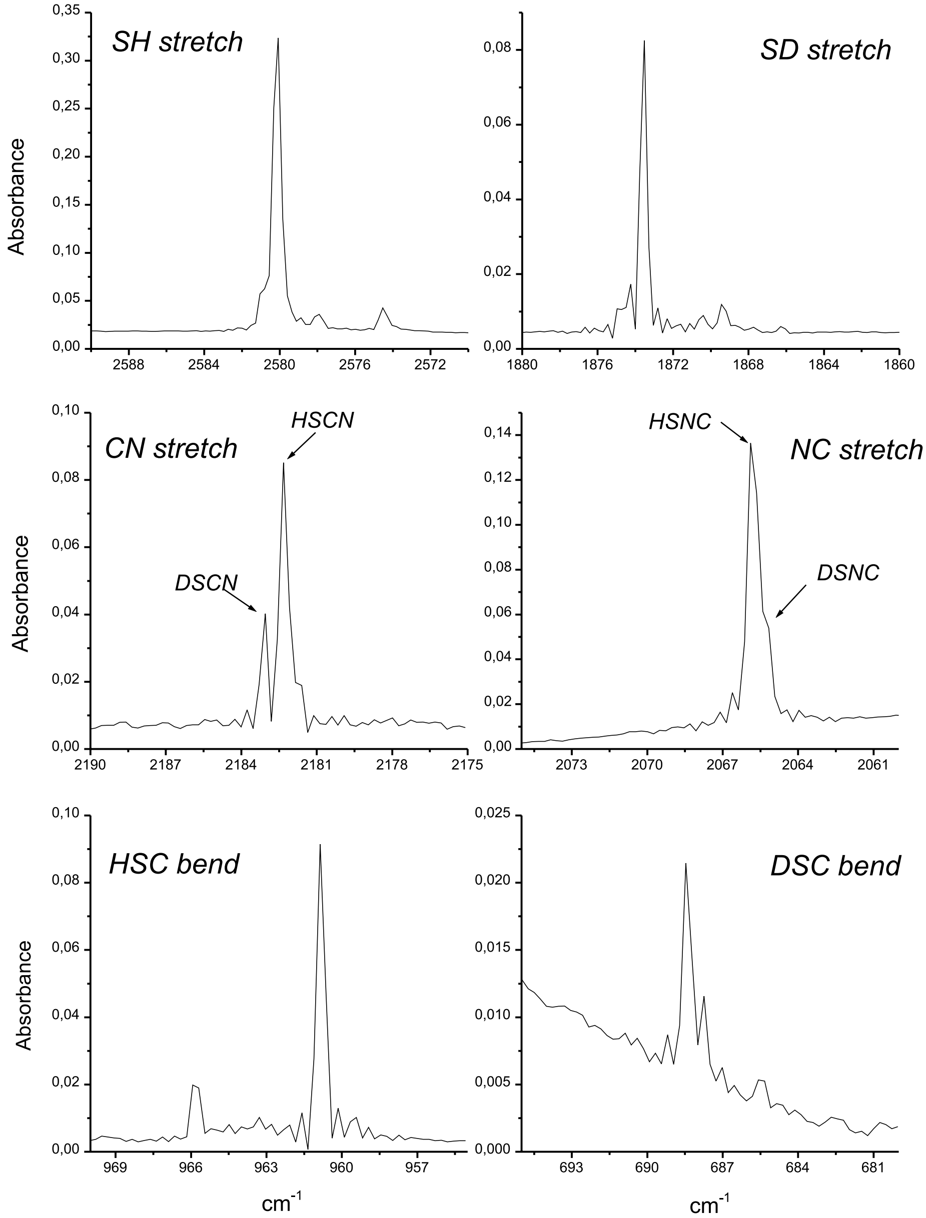

Fig. 1. New bands observed in the spectra recorded after 350 min UV photolysis of the matrix $(HNCS + DNCS)/N_2 = 1/1500$.

4. Discussion

4.1. Identification of new species

We assigned three bands at 2580.2, 2182.3, 960.9 cm^{-1} and at 2581.0, 2182.3, 959.7 cm^{-1} appearing in the spectra of photolyzed HNCS isolated in nitrogen and argon matrices, respectively, to one of the theoretically predicted but unobserved so far isomers of the HNCS molecule, namely, to *thiocyanic acid HSCN*. This assignment may be justified by the following arguments:

The 2580.2 and 2581.0 cm^{-1} bands appearing after photolysis of the HNCS/N_2 and HNCS/Ar

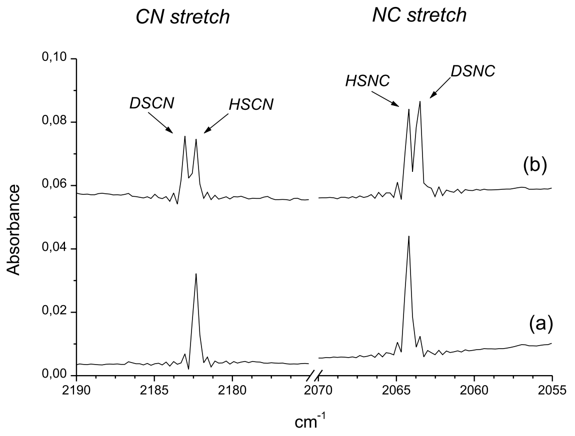

Fig. 2. ν(CN) and ν(NC) regions of the spectra recorded: (a) after 290 min of the UV photolysis of the matrices, HNCS/Ar = 1/2000; (b) after 260 min of the UV photolysis of the matrices, (HNCS + DNCS)/Ar = 1/2000.

matrices are situated in the range suitable for an SH stretching mode. Their counterparts in the DNCS/N_2 and DNCS/Ar systems, occurring respectively at, 1873.6 and 1874.0 cm^{-1}, show H/D isotopic ratio equal to 1.38 as expected for this type of mode. These features are assigned to the ν(SH) and ν(SD) modes of HSCN and DSCN acids. The above assignment finds support in the literature. Bohn et al. [20] have studied the cocondensation reaction products of H atoms with CS_2 in solid argon. They identified the HSCS radical as the major product. Isotopic data used for this system allowed to localize the SH stretching mode at 2527.5 cm^{-1} and its SD counterpart was found at 1805.3 cm^{-1}. In turn Moller et al. [21] performed an infrared investigation on the thionitrous acid isolated in argon matrices and observed the SH stretching mode at 2613.0 and 2566.0 cm^{-1} for *trans* and *cis* HSNO isomers, respectively.

The 960.9 and 959.7 cm^{-1} absorptions growing up during irradiation of the HNCS/N_2 and HNCS/Ar matrices are in the region anticipated for the HSC bending mode. These bands show a large H/D isotopic ratio of 1.38 (the ν(DSC) occurs at 688.5 and 692.8 cm^{-1} in N_2 and Ar, respectively), therefore H (or D) motion must be dominant. Bohn et al. [20] have identified the HSC bending vibration in argon isolated HSCS species at 941.4 cm^{-1} (at 713.8 cm^{-1} for DSCS, respectively), and a corresponding mode for CH_3SCH_2SH in solid Ar was reported by Li and Li [22] at 928 cm^{-1}. We assign the 960.9, 959.7 cm^{-1} and 688.5, 692.8 cm^{-1} features to the ν(HSC) and ν(DSC) bending modes in the thiocyanic acid HSCN/DSCN, respectively, in solid N_2 and Ar.

Table 2 gathers the frequencies of the ν(SH) stretching vibrations of various molecules isolated in argon matrices. The corresponding bending modes are given as well, whenever identified. The positions of the absorptions attributed to the HSCN in the studied matrices fit very well to this list.

The 2182.3 cm^{-1} absorption is assigned to the ν(CN) stretching mode in thiocyanic acid HSCN. This band is situated in the region characteristic for CN group [27–29]. For instance, Fraenkel and Haas [27] reported the CN stretching mode for ICN molecule in argon at 2171 cm^{-1}. The deuterium shift for the 2182.3 band is equal to 0.7 cm^{-1} and demonstrates that the species of interest con-

Table 1
New bands observed after photolysis of the HNCS/DNCS/N_2 and HNCS/DNCS/Ar matrices (cm^{-1})

HNCS/N_2	DNCS/N_2	HNCS/Ar	DNCS/Ar	Assignment
2580.9 sh	1874.3 sh			S-H, S-D stretch in HSCN, DSCN
2580.2 (5.9)	1873.6	2581.0 (0.4)	1874.0	
2577.9	1870.4			
2574.6	1869.4			
2182.3 (1.0)	2183.8	2182.3 (1.0)	2183.0	CN stretch in HSCN, DSCN
2065.9	2065.4	2064.2	2063.5	NC stretch in HSNC, DSNC
965.9	688.5		692.8	HSC, DSC bend in HSCN, DSCN
960.9 (1.1)	687.8	959.7 (0.15)		
	685.5			

Table 2
The S-H/S-D stretching and HSC/DSC or HSN bending frequencies of different SH containing molecules isolated in argon matrices

Molecule	S-H/νS-D stretch (cm^{-1})	HSC/DSC bend (cm^{-1})	Reference
HSCS/DSCS	2527.5/1805.3	941.4/713.8	[20]
H_2BSH	2574		[23]
H–C≡C–SH	2575		[24]
HSCN/DSCN	**2581.0/1875.0**	**959.5/692.0**	This work
$HSCH_2CH_2SH$	2586		[22]
C_2H_5SH	2597 (*trans*), 2600 (*gauche*)	869.8	[25]
CH_3SCH_2SH	2603	928	[22]
CH_3SH	2603.2	799.8	[25]
trans-HSNO	2613.0	877.5/724.0	[21,26]
cis-HSNO	2566.0	858.5/715.0	[21,26]

tains hydrogen atom that is directly bonded neither to N nor to C atom. For example, in HNCS, HCN molecules, in which hydrogen atom is directly bonded to CN group, the deuterium shift of the CN stretch frequency is equal to 42.2 and 164 cm^{-1} [30], respectively.

The remaining band showing up after photolysis at 2065.9 cm^{-1} (in nitrogen spectra) and at 2064.2 cm^{-1} (in argon spectra) is attributed to the NC stretching mode in the third undetected so far isomer of isothiocyanic acid: *isothiofulminic acid HSNC*. A small deuterium shift observed for this absorption (0.5 cm^{1} in N_2 and 0.7 cm^{-1} in Ar) is in agreement with the proposed assignment. The ν(NC) mode was reported in the literature to appear in the 2030–2120 cm^{-1} region [27,28]. Studies of various XCN–XNC pairs [27–29] revealed that the frequency difference between ν(CN) and ν(NC) stretching modes ranged between 110 and 200 cm^{-1}. In the present study the difference between ν(CN) in HSCN and ν(NC) in HSNC is equal to 116.4/118.1 cm^{-1} in solid nitrogen/argon, respectively.

The ν(NC) absorption is the only one identified for the isothiofulminic acid HSNC in the present study. The attempts to localize other modes of this isomer were unsuccessful which is probably due to the small yield of this species in the performed experiments and to small absorption coefficient of the other bands. It is worth noting that the SH stretching and HSC (HSN) bending modes are expected to be situated in the same regions for both HSCN and HSNC isomers. However, we assigned the absorptions appearing at ca. 2580 and 960 cm^{-1} to the thiocyanic acid HSCN (and not due to the isothiofulminic acid HSNC) on the basis of the following arguments:

1. Fraenkel and Haas [27] have pointed out that the transition dipole moment of the NC stretch in INC is much larger than in ICN molecule. If analogy holds for the HSCN, HSNC molecules, then the concentration of HSCN in the studied matrices is much larger than that of HSNC in spite of comparable intensities of the ν(CN) and ν(NC) absorptions.
2. The above conclusion is in agreement with recent ab initio calculations performed for HNCS and its isomers [31]. The results predict 40 times smaller intensity for the CN stretching mode in HSCN than for the NC stretching mode in HSNC while intensities calculated for other modes are of the same order of magnitude.

Weaker bands observed in addition to main peaks in the SH stretching and H–SC bending regions in nitrogen matrices (see Table 1) are assigned to the multiple trapping site effect and not to the corresponding modes in HSNC molecule.

It is worth mentioning that there are apparent variations in the relative intensities of the CN and SH stretching and HSC bending modes of the HSCN isomer depending on whether argon or nitrogen is used as matrix material. This effect is also shown in Table 1 where the relative intensities for these modes are given in parenthesis. The absorptions due to the SH stretching and HSC bending modes in nitrogen spectra are much stronger than their counterparts in argon. This may be due to the specific hydrogen bond interaction between HSCN and nitrogen cage.

4.2. HNCS photolysis and isomerization

The flash photolysis studies in the near UV [17] demonstrate that there are two dissociation channels for HNCS in the gas phase:

$$HNCS \rightarrow NCS + H \tag{1}$$

$$HNCS \rightarrow HNC + S(^3P) \tag{2}$$

accompanied by a fast secondary process:

$$S(^3P) + HNCS \rightarrow S_2(X^3\Sigma^-) + HNC$$

Upon irradiating HNCS with vacuum ultraviolet light [32] the third channel of dissociation is available according to the reactions:

$$HNCS \rightarrow NH(X^3\Sigma^-) + CS(A^1\Pi) \tag{3}$$

$$CS(A^1\Pi) \rightarrow CS(X^1\Sigma^+)$$

It is known that photolysis of molecules in matrices differs from that in the gas phase. One of the factors influencing the photolysis in matrices is cage effect which is responsible for trapping the produced photofragments and preventing them from being separated [9,33,34].

Fig. 3 presents a plot of the absorbance of the 1981.8 cm^{-1} band of HNCS, the 2182.3 cm^{-1} band of HSCN and the 2064.2 cm^{-1} band of HSNC as a function of the photolysis time during a single experiment in argon matrix. The intensities have been normalized to their own maximum absorbances within the experiment. Our results show that both HSCN and HSNC are the primary products of HNCS photodissociation with near UV light irradiation. The back reaction must not be of importance in the studied matrices since HNCS has not been reproduced during photolysis (opposite to that what was observed by Jacox and Milligan [1] for HNCO and HOCN species). According to Fig. 3 after prolonged photolysis there was a slight decrease of concentration of HSCN and HSNC photoproducts. However, no increase of the HNCS precursor was noticed neither secondary products were identified.

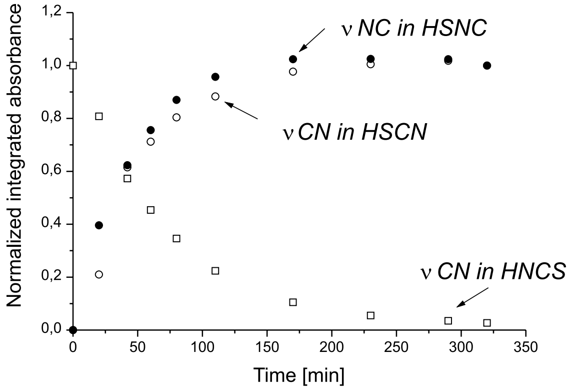

Fig. 3. A plot of the normalized integrated intensities of the 1981.8 cm^{-1} (ν(CN) of HNCS) (□), 2182.3 cm^{-1} (ν(CN) of HSCN) (○) and 2064.2 cm^{-1} (ν(NC) of HSNC) (●) bands versus the photolysis time for a single experiment in argon matrix.

The mechanism of HSCN and HSNC formation is of considerable interest. Taking into account two primary processes which occur in the gas phase (reactions 1 and 2) one may consider two different ways of the HNCS isomerization on near UV irradiation in matrices.

The first path may proceed via either formation of [H···NCS] pairs as observed in the gas phase or via a cyclic transition state [35]. In both cases the attachment of H atom to the sulfur atom of the NCS would lead to formation of HSCN and the H attachment to the nitrogen atom would reproduce HNCS. The formation of the isothiofulminic acid HSNC would require a rearrangement of the NCS species to CNS. The final products of the latter process are expected to be both HSNC and HCNS which are formed when hydrogen atom is attached to sulfur or carbon atoms, respectively.

The energy difference between HNCS/HSCN isomers was calculated to be ca. 21 kJ/mol [12]. However, the transition state for the 1,3 hydride transfer in the HNCS/HSCN system was found to be over 250 kJ/mol higher in energy than HSCN [35]. Even if the latter value is overestimated it is much too high to make the HNCS/HSCN isomerization energetically possible with the 300 nm radiation used. The second possibility – the formation of the [H···NCS] pairs seems to be more probable. Mechanism via pre-dissociation into [H···CNO] pairs was suggested by Bondybey et al. [3] for fulminic acid isomerization.

As stated above the formation of HSNC via rearrangement of NCS into CNS should be accompanied by HCNS formation. The latter isomer has not been identified in the studied matrices though it is predicted to have comparable stability to HSNC isomer and large intensities of the infrared absorptions [31]. The absence of HCNS isomer rather excludes the formation of the HSNC species via rearrangement of CNS.

The second dissociation channel that is observed in the gas phase, $HNCS \rightarrow HNC + S(^3P)$, may be responsible for the formation of both HSCN and HSNC isomers in the matrices. The reaction may proceed via [HNC···S] pairs followed by hydrogen migration and formation of [NC···SH] pairs which recombine to form HSCN or HSNC isomers.

By means of glass longwavelength filters the threshold energy for the photolytic reaction in argon and nitrogen matrices was estimated to be ca. 300 nm. There is no observable photolysis in argon matrix for $\lambda \geqslant 335$ nm, photolysis starts with a 305 nm cut-off filter, it remains slow when 295 and 280 nm cut-off filters are used and its rate increases apparently at shorter wavelength with full output of the mercury lamp.

The onset of the photolysis corresponds closely to the value of the threshold energy for the $HNCS \rightarrow NCS + H$ reaction that was evaluated to be 4.2 eV (294 nm) [18]. It suggests that this photodissociation channel is the source of thiocyanic acid HSCN. Simultaneously, the second photodissociation channel $HNCS \rightarrow HNC + S$ probably serves as a source of both thiocyanic HSCN and isothiofulminic HSNC acids.

5. Summary

1. The photochemistry of isothiocyanic acid HNCS/DNCS has been studied in argon and nitrogen matrices.
2. Several new absorptions grew in the regions of SH, SD, CN stretching and HSC, DSC bending modes.
3. Analysis of the band positions and their isotopic H/D shifts allowed us to conclude that near UV photolysis led to the formation of two unobserved so far isomers: thiocyanic acid HSCN and isothiofulminic acid HSNC and their deuterated analogs.
4. The two isomers are probably formed via two reaction channels:
   - formation of the [H···NCS] and hydrogen migration leading to the HSCN molecule;
   - formation of the [HNC···S] followed by rearrangement to HSCN and HSNC species.

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