Electronic Supplementary Material (ESI) for RSC Advances

Photodecomposition of *N*-hydroxyurea in argon matrices. FTIR and theoretical studies

Magdalena Sałdyka

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

E-mail: magdalena.saldyka@chem.uni.wroc.pl

Supplementary information: additional computational details

Figure S1 The optimized structures of the HNCO-NH_2OH complexes at the MP2/6-311++G(2d,2p) level of theory. The selected bond distances (in Å) and interaction energies ΔE^{CP} (in kJ mol^{-1}) are also presented; in parentheses the ΔE^{CP}_{ZPE} values (in kJ mol^{-1}) are given.

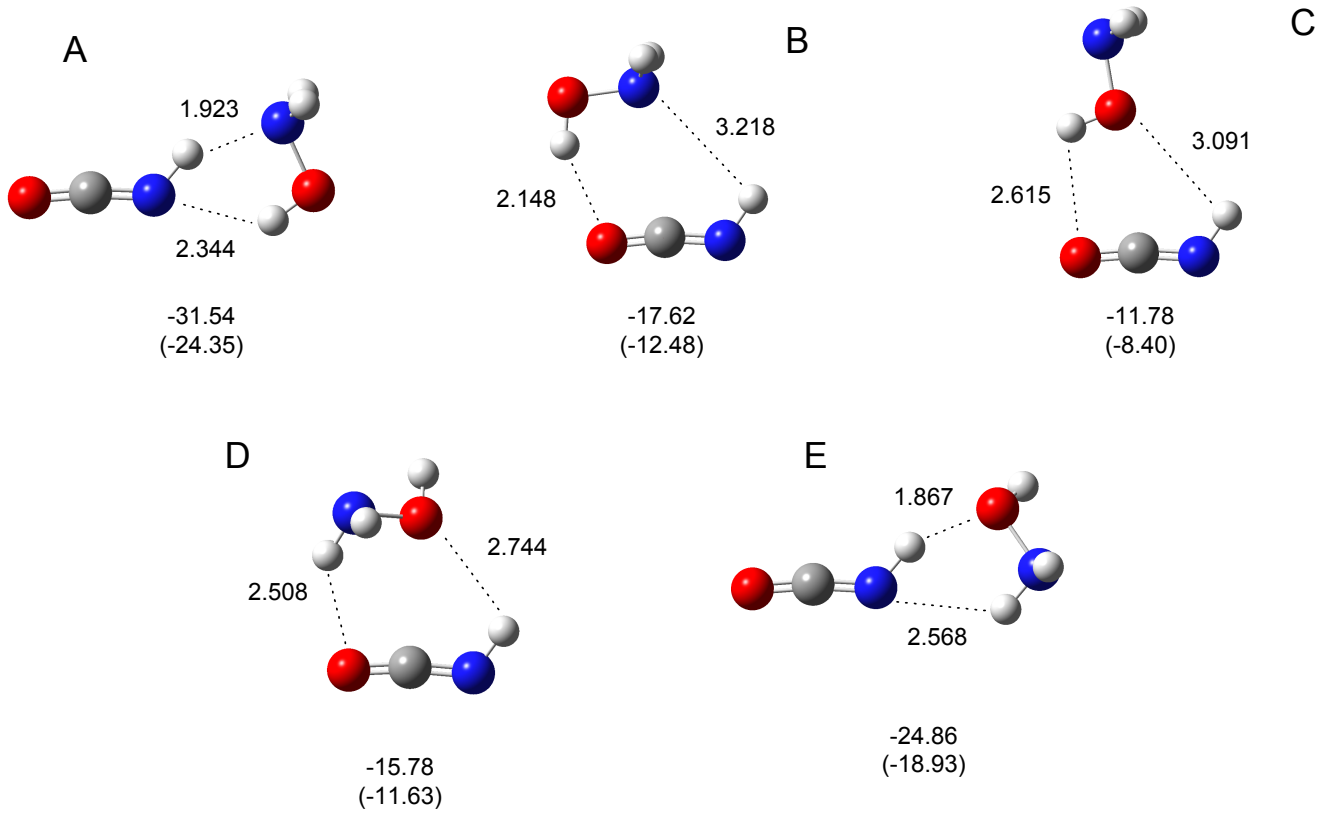

Table S1 Selected structural parameters[a] calculated for the HNCO-NH_2OH complexes at the MP2/6-311++G(2d,2p) level of theory

Property	A	B	C	D	E
r(NH(C))	1.0241	1.0045	1.0050	1.0061	1.0150 (1.0192)[b]
r(NC)	1.2166	1.2185	1.2198	1.2198	1.2172 (1.2166)
r(CO)	1.1757	1.1760	1.1745	1.1751	1.1754 (1.1761)
r(OH)	0.9641	0.9621	0.9604	0.9594	0.9600 (0.9632)
r(NO)	1.4407	1.4454	1.4478	1.4513	1.4518 (1.4467)
r(NH_a)	1.0123	1.0128	1.0122	1.0132	1.0143 (1.0177)
r(NH_b)	1.0123	1.0128	1.0122	1.0122	1.0123 (1.0153)
r((N)H···N), r((N)H···O)	1.9232	3.2185	3.0909	2.7444	1.9242 (1.8667)
r((O)H···N), r((O)H···O),	2.3446	2.1479	2.6151		
r((N)H_a···O), r((N)H_a···N)				2.5078	2.6362 (2.5684)
ϕ(HNC)	127.17	121.71	121.52	120.39	126.47 (126.90)
ϕ(OCN)	173.09	171.14	172.15	172.27	172.57 (172.58)
ϕ(NOH)	102.64	102.00	102.15	101.62	102.02 (102.14)
ϕ(H_aNO)	104.33	103.64	103.81	103.68	103.83 (103.75)
ϕ(NH···N), ϕ(NH···O)	147.88	99.60	98.45	109.51	152.93 (153.08)
ϕ(OH···N), ϕ(OH···O)	131.08	152.62	107.92		
ϕ(NH_a···O), ϕ(NH_a···N)				140.43	121.11 (121.09)
θ(NH···NH_a), θ(NH···OH)	-110.57	123.58	0.01	-124.78	117.18 (116.27)
θ(OH···NH), θ(OH···OC)	0.00	0.02	0.00		
θ(NH_a···OC), θ(NH_a···NH)				7.48	9.08 (8.11)

[a] the interacting atoms refer to the Figure S1; the bond distances are given in Å, the angles in degrees.
[b] the calculation performed at the aug-cc-pVTZ basis set.

Table S2 Wavenumbers and wavenumbers shifts (in cm^{-1}) calculated for the HNCO-NH_2OH complexes at the MP2/6-311++G(2d,2p) level of theory

	Monomer	**A**		**B**		**C**		**D**		**E**		**Assignment**
	ν	**ν**	**Δν**	**ν**	**Δν**	**ν**	**Δν**	**ν**	**Δν**	**ν**	**Δν**	
HNCO	3722 (172)[a]	3324 (1218)	-398	3711 (152)	-11	3706 (160)	-16	3692 (163)	-30	3500(517)	-222	νNH
	2308 (668)	2311 (713)	3	2302 (636)	-6	2305 (633)	-2	2301 (613)	-7	2311 (709)	3	ν_{as} NCO
	1289 (0,1)	1292 (9)	3	1289 (1)	0	1287 (0,3)	-2	1287 (0)	-2	1293 (7)	4	ν_{s} NCO
	813 (238)	972 (398)	159	820 (291)	7	831 (270)	18	842 (270)	29	898 (501)	85	δHNC
	630 (0,3)	742 86)	112	629 (2)	-1	628 (2)	-2	631 (0)	1	670 (20)	40	γNCO
	575 (75)	656 (10)	81	559 (76)	-16	564 (77)	-11	560 (80)	-15	641 (22)	66	δNCO
NH_2OH	3872 (53)	3795 (134)	-77	3828 (139)	-56	3858 (63)	-14	3869 (60)	-3	3865 (73)	-7	νOH
	3606 (6)	3606 (15)	0	3595 (8)	-11	3607 (7)	1	3604 (14)	2	3599 (20)	-7	ν_{as} NH_2
	3517 (0,6)	3518 (0)	1	3509 (0,5)	-8	3516 (0)	-1	3514 (3)	-3	3510 (33)	-7	ν_{s} NH_2
	1683 (17)	1682 (22)	-1	1684 (20)	1	1683 (22)	0	1688 (15)	5	1691 (15)	8	δNH_2
	1415 (27)	1478 (33)	63	1455 (46)	40	1417 (42)	2	1411 (25)	-4	1405 (26)	-10	δOH
	1336 (0)	1331 (0)	-5	1335 (0)	-1	1338 (0)	2	1349 (3)	13	1357 (1)	21	ρNH_2
	1164 (127)	1188 (154)	24	1184 (127)	20	1165 (149)	1	1175 (145)	11	1177 (137)	13	ωNH_2
	929 (11)	937 (172)	8	937 (8)	8	933 (11)	4	927 (10)	-2	927 (16)	-2	νNO
	434 (178)	404 (29)	-30	507 (165)	73	466 (170)	32	447 (179)	13	516 (190)	82	γOH
		575 (113)		-		-		-		-		intermolecular
	-	245 (1)	-	245 (72)	-	207 (104)	-	280 (103)	-	404 (43)	-	intermolecular
	-	234(33)	-	170 (19)	-	98 (8)	-	127 (1)	-	202 (26)	-	intermolecular
	-	124 (0)	-	156 (3)	-	94 (0)	-	109 (9)	-	138 (5)	-	intermolecular
	-	68 (2)	-	110 (2)	-	80 (0)	-	98 (0)	-	106 (0)	-	intermolecular
	-	14 (0)	-	83 (5)	-	40 (5)	-	58 (1)	-	57 (4)	-	intermolecular
	-			40 (4)		32 (0)		18 (1)		16 (0)		intermolecular

[a] The IR calculated intensities expressed in km mol^{-1}.

Table S3 Selected structural parameters[a] calculated for the N_2-H_2O-CO complexes at the MP2/aug-cc-pVTZ level of theory

Property	A	B	C
r(NN)	1.1141	1.1138	1.1138
r(OH(···N))	0.9612	0.9617	0.9629
r(OH(···C))	0.9641	0.9630	0.9613
r(CO)	1.1375	1.1376	1.1384
r((O)H···N)		2.3937	2.3502
r((O)H···C)	2.3645	2.3956	
r((H_2)O···C)			3.0898
r((H_2)O···N)	3.1365		
ϕ(HOH)	104.37	104.56	104.38
ϕ(OH···N)		160.34	165.96
ϕ(OH···C)	163.89	166.32	
ϕ(NN···H)		168.45	166.01
ϕ(OC···H)	167.26	171.73	
ϕ(NN···O(H_2))	97.79		
ϕ(OC···O(H_2))			101.82
θ(NN···HO)		-0.03	-0.01
θ(OH···CO)	-0.01	0.00	
θ(OC···OH)			0.30
θ(NN···OH)	-0.10		

[a] the interacting atoms refer to the Figure 6; the bond distances are given in Å, the angles in degrees.

Table S4 Wavenumbers (in cm^{-1}) of the N_2-H_2O-CO complexes calculated by the MP2/aug-cc-pVTZ method

A	B	C	Assignmt
3926 (141)[a]	3925 (254)	3935 (134)	$\nu_{as}H_2O$
3794 (69)	3804 (39)	3810 (34)	ν_sH_2O
1636 (58)	1638 (36)	1632 (71)	δH_2O
2123 (31)	2121 (33)	2115 (35)	νCO
2186 (0)	2189 (0.2)	2189 (0.3)	νN_2
352 (60)	340 (40)	286 (64)	intermolecular
226 (83)	259 (102)	188 (82)	Intermolecular
108 (5)	244 (114)	102 (3)	Intermolecular
103 (114)	103 (0.7)	96 (119)	Intermolecular
86 (7)	88 (0.8)	82 (1)	Intermolecular
70 (0)	59 (1)	68 (2)	Intermolecular
57 (16)	54 (2)	51 (10)	Intermolecular
49 (1)	44 (6)	50 (16)	Intermolecular
32 (0)	32 (13)	38 (0.7)	Intermolecular
30 (0)	10 (0)	31 (0.4)	intermolecular

[a] The IR calculated intensities expressed in km mol^{-1}.