Inorganic Chemistry Communications 13 (2010) 622–624

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Unexpected formation of ammonium thiocyanate from the reaction of aqueous hydroxylamine with carbon disulfide

Muddamarri Hanumantha Rao [a], Raghavaiah Pallepogu [b], Krishnamurthi Muralidharan [a,b,*]

[a] *Advanced Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad 500046, India*
[b] *School of Chemistry, University of Hyderabad, Hyderabad 500046, India*

ARTICLE INFO

Article history:
Received 31 October 2009
Accepted 1 March 2010
Available online 6 March 2010

Keywords:
Ammonium thiocyanate
Carbon disulfide
Hydroxylamine
Hydroxy isothiocyanate

ABSTRACT

Reaction of aqueous hydroxylamine with carbon disulfide in acetonitrile or in tetrahydrofuron unprecedentedly results in the formation of ammonium thiocyanate and sulfur.

Hydroxylamine and its derivatives are versatile chemicals as they have innumerable applications in the fields ranging from synthetic organic chemistry to propellants science and technology. Hydroxylamine is used as reducing agents in a variety of organic and inorganic reactions [1–3]. Further, hydroxylamine nitrate (HAN), a derivative of hydroxylamine has been used for applications that include equipment decontamination in nuclear industry and also as aqueous or solid propellants [4–6].

Synthetic utility of the reactions between carbon disulfide and N-nucleophiles to form wide range of organosulfur compounds are well known [7]. Carbon disulfide is known to deoxygenate tertiary amine N-oxides to tertiary amines [8] and N, N-disubstituted hydroxylamines to secondary amines [9]. However, the products formed from the reaction of aqueous hydroxylamine with carbon disulfide are a matter of debate for a long time.

In one of the earlier report [10] on reaction of hydroxylamine with carbon disulfide, formation of yellow solution has been observed which subsequently turned red following which sulfur precipitated out. In another report, reaction of hydroxylamine hydrochloride with carbon disulfide in presence of triethylamine yielded hydroxyimidodithiocarbonates after alkylation [11]. Since the earlier reports did not describe the compound obtained other than sulfur and hydroxyimidodithiocarbonates, we were interested to reinvestigate the products obtained in the reaction of hydroxylamine with carbon disulfide.

A recent report described quantitative conversion of carbon dioxide into isocyanate and symmetrical carbodiimide under mild condition via a metathetical reaction [12]. As it is known that the carbon–sulfur double bond energy is lesser than that of carbon–oxygen double bond, we were interested to investigate the possibility of formation of N,N′-dihydroxy carbodiimide from the reaction of hydroxylamine with carbon disulfide.

In our study, we have reacted aqueous hydroxylamine with carbon disulfide in three different mole ratios (1:1, 2:1 and 1:2) respectively in acetonitrile as well as in tetrahydrofuron [13]. In all these reactions, irrespective of the stoichiometry of the reactants, ammonium thiocyanate, NH_4SCN, (yield: 42–50%) and sulfur (30–38% yield) were obtained. Furthermore, a reaction was carried out by producing the hydroxylamine *in-situ* [1] by reacting hydroxylamine hydrochloride with sodium butoxide in dry *n*-butanol and then it was reacted with carbon disulfide. This reaction under strictly anhydrous condition also produced the ammonium thiocyanate, but in relatively lesser yield. This indicates that the water did not participate in the reaction but help to increase the solubility of hydroxylamine in the reaction medium. Other side products were also formed in these reactions as has been observed from ^{1}H and ^{13}C NMR spectral data of the reaction mixture. Attempt to isolate any of these side products was not successful probably due to the instability of these products.

When carbon disulfide was added to the solution of aqueous hydroxylamine in acetonitrile or tetrahydrofuron at 0–5 °C, evolution of a gas was observed. The IR spectrum of collected gaseous products showed a signal at 1047 cm^{-1} matching C S (stretching). It may be due to the formation of COS or COS_2 [8,9]. As the temperature was allowed to rise to room temperature, a crystalline yellow precipitate was started forming from the reaction mixture whose melting point

---

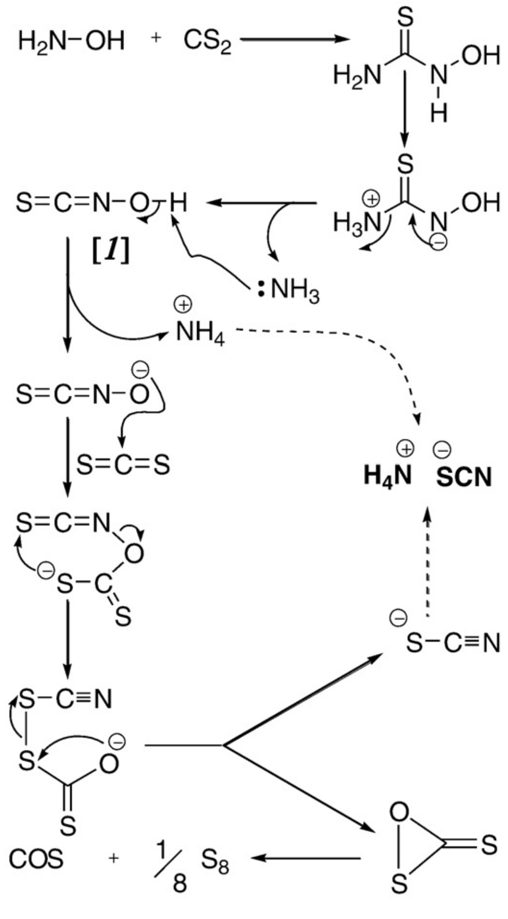
* Corresponding author. School of Chemistry, University of Hyderabad, P O. Central University, Gachibowli, AP 500046, India. Tel.: +91 40 23134819; fax: +91 40 2301 2460.
E-mail address: kmsc@uohyd.ernet.in (K. Muralidharan).

1387-7003/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2010.03.003

was close to that of sulfur (mp. 115 °C). The reaction was continued at room temperature until the evolution of gas and further precipitation ceased (2–3 h). The precipitate obtained was confirmed as sulfur from the unit cells obtained from single crystal X-ray diffractometer [14]. This observation is in consistent with the earlier report [10].

The precipitate was filtered off and the clear solution was kept in refrigerator maintained at 7 °C. After two days, some more sulfur precipitated which was removed by filtration. After four days a white crystalline solid also precipitated from the reaction mixture. The solid was washed with ethylacetate, dried under vacuum. NMR (in DMSO-D6) and IR spectra of this solid sample was obtained which indicated the formation of ammonium thiocyanate [15]. Later, the formation of ammonium thiocyanate was also confirmed by single crystal X-ray diffraction technique.

To find any of the species involved in the plausible mechanism, the progress of the reaction was monitored by liquid chromatography coupled with electron spray mass spectroscopy (LCMS) at different time intervals. The recorded LCMS at first and second hours showed strong signals corresponding to *m*/*z* values of 75 and 59. This may be due to SCNOH and protonated SCN respectively. The LCMS recorded after 5 h showed few more less intense signal with higher *m*/*z* value (see Supplementary information). Based on our observations as well as reports on similar reactions [7,16], we propose to explain the formation of ammonium thiocyanate and sulfur as shown in Scheme 1. The formation of hydroxylthiourea shown in the step 1 of the mechanism is well established in similar reactions [7,11,16]. Ammonia being a very good leaving group, could facilitate the formation of hydroxy isothiocyanate, S C N–OH (**1**). The corresponding mass observed in the LCMS of the reaction mixture also supports the formation of compound **1**.



Scheme 1. Plausible mechanism for the formation of ammonium thiocyanate.

Alkoxy and aryloxy isothiocyanates (RO–N C S) were unknown until a recent report on preparation of methoxy isothiocyanate (CH_3–O–N C S) by flash vacuum thermolysis at 400 °C and isolation of it in argon matrix. The methoxy isothiocyanate was reported to be stable only up to −153 °C (120 K) [17]. The fragmentation pattern of this compound in collision induced mass spectrum and charge reversal mass spectrum have also been reported recently in which fragment peak corresponding to $(SCNO)^-$ ion is observed predominantly [18]. Hence it can be presumed that compound **1** is the one of the species involved in the mechanism.

The formation of oxathiranethione (COS_2) proposed in this mechanism is already been described in literature [8,9]. The IR spectrum of collected gas from our reaction also suggested the same. Albeit the structure of COS_2 is unknown, it is known to decompose to yield sulfur and carbonylsulfide (COS). Thus the proposed mechanism shown in Scheme 1 could explain the formation of ammonium thiocyanate as well as sulfur.

The ammonium thiocyanate obtained in this reaction afforded an opportunity to reinvestigate the structure of it [19]. The ammonium thiocyanate crystallizes in a cetrosymmetric monoclinic $P\,2_1/c$ space group with all atoms located in general positions. The X-ray crystal structure (Fig. 1) of ammonium thiocyanate shows a ammonium cation and a thiocyanate anion in the asymmetric unit and there are four such units in the unit cell. The crystal structure analysis of ammonium thiocyanate reveals that, the two components are interlinked by strong N–H···N and weak N–H···S types of hydrogen bonding interactions [20]. The relevant hydrogen bonding parameters of ammonium thiacyanate with symmetry codes are summarized in the supplementary information.

In conclusion we have studied the reaction of aqueous hydroxylamine with carbon disulfide in three different mole ratios and proposed a mechanism for the formation of ammonium thiocyanate and sulfur from these reactions. The structure of ammonium thiocyanate has also been reinvestigated.

Acknowledgement

The authors gratefully acknowledge School of Chemistry, University of Hyderabad for infrastructure and support of the DRDO, India in the form of grant to ACRHEM. The authors also acknowledge Dr. R. Balamurugan and Dr. V. Baskar, School of Chemistry, University of Hyderabad for useful discussions.

Appendix A. Supplementary material

Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-770160. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.03.003.

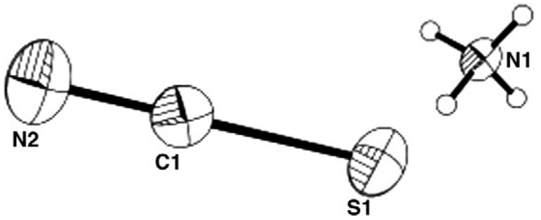


Fig. 1. Thermal ellipsoidal plot of compound $[SCN][NH_4]$ with atom labeling scheme. Displacement ellipsoids are drawn at 30% probability level except for the H atoms, which are shown as circles of arbitrary radius. [Bond Lengths: C–S; 1.641 Å and C–N; 1.152 Å].

References

[1] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd Ed.Elsevier, New Delhi, 2005 pp 431.

[2] (a). J. Moran, J.Y. Pfeiffer, S.I. Gorelsky, A.M. Beauchemin, Org. Lett. 11 (2009) 1895;
(b). J. Moran, S.I. Gorelsky, E. Dimitrijevic, M.-E. Lebrun, A.-C. Be´dard, C. Se´guin, A.M. Beauchemin, J. Am. Chem. Soc. 130 (2008) 17893;
(c). V. Manivannan, J.B. Goodenough, Mater. Res. Bull. 33 (1998) 1353.

[3] L.A. Voloboueva, D.W. Killilea, H. Atamna, B.N. Ames, FASEB J. 21 (2007) 4077.

[4] (a). Y. Huang, H. Gao, B. Twamley, J.M. Shreeve, Chem. Eur. J. 15 (2009) 917;
(b). K. Muralidharan, B.A. Omatowa, B. Twamley, C. Piekarski, J.M. Shreeve, Chem. Commun. (2005) 5193.

[5] D.G. Harlow, R.D. Felt, S. Agnew, J.M. Mc Kibben, R. Garber, M. Lewi, Online, U. S. Department of Energy, 1998, p. 2, http://www.hss.energy.gov/healthsafety/wshp/chem_safety/docs/ hydroxylamine.pdf.

[6] M.I. Papadaki, E. Pontiki, L. Liu, W.J. Rogers, M.S. Mannan, J. Chem. Eng. Data 54 (2009) 2616.

[7] W.-D. Rudorf, J. Sulfur Chem. 28 (2007) 295.

[8] M.F. Zipplies, M.-J. De Vos, T.C. Bruice, J. Org. Chem. 50 (1985) 3228;
(b). T. Yoshimura, K. Asada, S. Oae, Bull. Chem. Soc. Jpn 55 (1982) 3000.

[9] M.A. Schwartz, J. Gu, X. Hu, Tetrahedron. Lett. 33 (1992) 1687.

[10] J.A. Pierce, Ind. Eng. Chem. Anal. Ed. 1 (1929) 227.

[11] (a). C.W. Voigt, G. Gattow, Z. Anorg. Allg. Chem. 438 (1978) 195;
(b). M. Pallas, F. Geissler, W. Kalkofen, Z. Chem. 20 (1980) 207;
(c). M. Pallas, F. Geissler, W. Kalkofen, Z. Chem. 20 (1980) 257.

[12] U.J. Kilgore, F. Basuli, J.C. Huffman, D.J. Mindiola, Inorg. Chem. 45 (2006) 487.

[13] Aqueous hydroxylamine (50%) (1.85 mL, 30.25 mmol for 1:1 reaction; 3.71 mL, 60.5 mmol for 2:1 reaction) was dissolved either in acetonitrile or in tetrahydrofuron in a two neck RB flask equipped with gas inlet and outlet and then the carbon disulfide (0.793 mL, 13.10 mmol) was added drop wise to it at ice temperature. The temperature was allowed to rise to room temperature over period of 45 min. Then the reaction was stirred at room temperature for 3 h. The reactions were worked up as described vide-supra.

[14] Sulfur unit cells: Orthorhombic, a = 10.4623(6) Å, b = 12.8625(8) Å, c = 24.4788 (14) Å.

[15] NMR (DMSO-D6): ^{1}H, δ 7.0 ppm ($^+NH_4$); ^{13}C, δ 130.7 ppm ($^-$SCN).

[16] (a). S. Kim, Ch.J. Lim, S.-E. Song, H.-Y. Kang, R.D. Haugwitz, Synlett (2001) 688;
(b). R.D. Haugwitz, Liebigs Ann. Chem. 731 (1970) 171.

[17] A.T. Bech, R. Flammang, C.Th. Pedersen, M.W. Wong, Curt Wentrup, J. Chem. Soc., Perkin Trans. 2 (1869).

[18] S. Dua, M.J. Maclean, M. Fitzgerald, A.M. McAnoy, J.H. Bowie, J. Phys. Chem. A 110 (2006) 4930.

[19] (a). Z.V. Zvonkova, G.S. Zhdanov, Z. Fizicheskoi 23 (1949) 1495;
(b). V.E. Zavodnik, Z.V. Zvonkova, G.S. Zhdanov, E.G. Mirevich, Kristallografiya 17 (1972) 107.

[20] G.R. Desiraju, T, The weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, Steiner, 1999.