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Reaction Profiles in Sulfur–Nitrogen Chemistry
I. The Isomerization of *cis* Thionylimide, HNSO, to *cis* Thiazyl-S-hydroxide, HOSN

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A study of the energy changes which occur in the course of the isomerization of cis thionylimide to cis thiazyl-S-hydroxide has been carried out using MNDO molecular orbital calculations. The reaction is characterized by a standard enthalpy change of 3–7 kcal/mol. The reaction proceeds through a cyclic transition state with an enthalpy of activation of 76 kcal/mol. The nature of electronic structures of the reactant and product molecules and the transition state complex have been studied using energy localized molecular orbitals. The transition state was found to be a cyclic structure wherein the hydrogen atom is about equally bonded to both the oxygen and nitrogen atoms.

Introduction

The chemical system of empirical formula HOSN has been known for many years. Readily synthesized by the gas phase reaction of thionyl chloride and ammonia [1, 2], the reaction product has been characterized as the *cis* form of thionylimide, OSNH. The infrared spectrum of this material has been extensively studied [3–6]. The same materials react in condensed medium to yield a material which has been suggested to be thiazyl-S-hydroxide, HOSN, and also characterized thionylimide, OSNH [7]. The situation is further complicated by the presence of additional reactions which result in polymeric reaction products such as a tetrameric molecule $(OSNH)_4$ of unknown structure [8]. Since this laboratory has an interest in the study of these later polymerization reactions, it was of interest to study first the basic monomeric materials which might be present in the system.

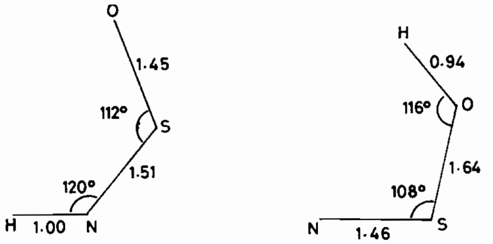

Fig. 1. Structures for the *Cis* Forms of Thionylimide and Thiazyl-S-hydroxide.

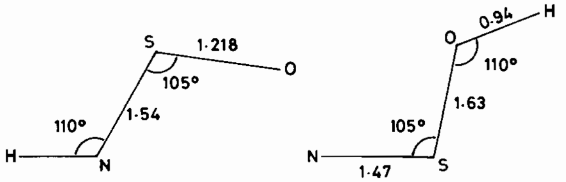

Fig. 2. Structures for the *Trans* Forms of Thionylimide and Thiazyl-S-hydroxide.

Calculations

MNDO type molecular orbital calculations were carried out for the system discussed in this paper by the methods described by Dewar *et al.* [9]. The electronic structure of the reactant molecule, product molecule, and transition state were studied using energy localized molecular orbitals (LMOs) calculated by a modified method of Edmiston and Ruedenberg starting from the CNDO/2 canonical M.O.s [10, 11].

Thermodynamics of the HOSN–OSNH System

The molecules thionylimide and thiazyl-S-hydroxide can, in principle, exist in both *cis* and *trans* conformations. In Table I are listed the structures

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TABLE I. Heats of Formation for Thionyimide and Thiazyl-S-hydroxide.

	ΔH_f° (kcal/mole)	Structure		
Cis Forms				
Thionylimide	41.7	d_{N-H}	1.00	∠HNS 120°
		d_{N-S}	1.51	∠NSO 112°
		d_{S-O}	1.45	
Thiazyl-S-hydroxide	47.7	d_{N-S}	1.46	∠NSO 108°
		d_{S-O}	1.63	
		d_{H-O}	0.94	∠SOH 116°
Trans Forms				
Thionylimide	44.7	d_{N-H}	1.00	∠HNS 110°
		d_{N-S}	1.54	∠NSO 105°
		d_{S-O}	1.48	
Thiazyl-S-hydroxide	48.8	d_{N-S}	1.47	∠NSO 105°
		d_{S-O}	1.63	
		d_{H-O}	0.94	∠SOH 110°

(see Figs. 1 and 2) of lowest total energy for the *cis* and *trans* forms of each, together with a description of their structure. In general thiazyl-S-hydroxide possesses a lower enthalpy of formation than thionylimide in both the *cis* and *trans* forms. The energetic difference between *cis* and *trans* forms of the same molecule are calculated to be in the range of 1–3 kcal/mol and cannot be taken as significant. The isomerization energy for the reaction (imide) → (hydroxide) is calculated to be 3.0–7.1 kcal/mol depending upon which conformations are employed for the reactants and products. Both molecules possess strongly positive enthalpies of formation.

The Transition State

The reaction passes through a transition state diagrammed in Fig. 3. The heat of formation of the transition state is 117.6 kcal/mol yielding an enthalpy of activation of 75.8 kcal/mol for the isomerization reaction. The activated complex is cyclic in structure, very slightly non planar with a O–H distance of 1.36 Å, an N–H distance of 1.38 Å, a S–N distance of 1.51 Å and a S–O distance of 1.57 Å. The sulfur–oxygen distance is somewhat longer than that found in sulfur trioxide (1.43 Å) [12], and more closely resembles that found in the $S_2O_6^{2-}$ ion (1.50 Å) [13] indicating that the transition state is probably best viewed as possessing a S–O single bond. The S–N distance of 1.51 Å is indicative of a S–N bond of some multiple bond character probably about a full double bond. The hydrogen oxygen distance of 1.36 Å is representative of a single bond 'stretched out' about 35% from its normal equilibrium value of about 1.00 Å. The hydrogen–nitrogen distance of 1.38 Å is also about 35% longer than that normally associated with a N–H single bond. Geometrically the transition state appears to be a cyclic structure, H–O–S–N, wherein the hydrogen nitrogen and hydrogen oxygen bonds are about one third longer than normal single bonds, while the sulfur–oxygen bond approximates a normal single bond and the N–S bond has distinct π character. This picture is also supported by the results of a set of energy localized molecular orbital calculations, which were started from the CNDO/2 canonical M.O.s appropriate to the structure shown in Fig. 3. The results of these calculations, as carried out by a

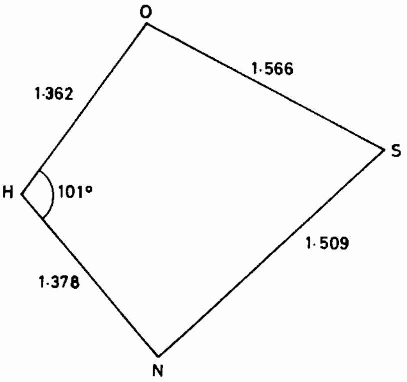

Fig. 3. Structure of the Transition State.

TABLE II. Localized Molecular Orbitals for Transition State.

CNDO/2 Atomic Charge	Localized Orbitals Type	A.O. Coefficient		% Localization[a]
H 0.254				
N -0.225	H–O_σ bond	1s	0.38202	96.99
S +0.383		2s	0.39970	
O -0.412		$2p_x$	0.12876	
		$2p_y$	-0.80471	
	S–O_σ bond	3s	0.27165	95.48
		$2p_x$	0.70827	
		2s	-0.21657	
		$2p_x$	-0.57868	
		$2p_y$	-0.16360	
	S–N_σ bond	2s	0.33200	99.21
		$2p_y$	0.61725	
		3s	0.27913	
		$3p_x$	-0.11798	
		$3p_y$	0.63956	
	H–N_σ bond	1s	0.45648	96.78
		2s	0.34584	
		$2p_x$	-0.79282	
		$2p_y$	-0.10594	
	N lone pair	2s	0.79402	99.61
		$2p_x$	0.40229	
		$2p_y$	0.45145	
	S lone pair	3s	0.83809	99.32
		$3p_x$	0.33344	
		$3p_y$	0.42887	
	O lone pair	$2p_z$	0.98432	96.89
	O lone pair	2s	0.83929	99.82
		$2p_x$	-0.41421	
		$2p_y$	0.34953	
	S–N π bond	$2p_z$	0.58283	99.17
		$3p_z$	0.80754	

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[a] For definition, see R. R. Adkins and A. G. Turner, *J. Am. Chem. Soc., 100,* 1383 (1978).

previously published method are shown in Table II [14]. The only pi type localized orbital obtained is the bond between nitrogen and sulfur. Lone electron pair orbitals are obtained for nitrogen and sulfur, one orbital each; and for oxygen, two lone pair orbitals.

TABLE III. Electronic Structure of the Reactant and Product Molecules.

Gross Atomic Charge	Localized Orbitals Type	A.O. Coefficients		% Localization
Reactant – NSOH				
N -0.246				
S +0.423	N–Sσ	2s	0.33372	99.66
O -0.323		$2p_x$	0.19641	
H +0.146		$2p_y$	-0.55744	
		3s	0.35355	
		$3p_x$	-0.17187	
		$3p_y$	0.61757	
	S–Oσ	3s	0.19377	97.97
		$3p_x$	0.57881	
		2s	0.36034	
		$3p_x$	0.68309	
	H–Oσ	1s	0.65152	99.36
		2s	0.35002	
		$2p_x$	0.23728	
		$2p_y$	0.62472	
	lone pair N	2s	0.86957	99.72
		$2p_x$	-0.15600	
		$2p_y$	-0.46557	
	lone pair S	3s	0.82299	99.55
		$3d_{z^2}$	-0.20386	
		$3d_{xz}$	-0.52597	
	lone pair O(1)	2s	0.76654	99.62
		$2p_x$	0.32630	
		$2p_y$	-0.54966	
	lone pair O(2)	$2p_z$	0.99142	98.29
	N–Sπ	$2p_x$	0.89681	
		$2p_y$	0.31215	
		$3p_x$	0.21485	
		$3d_{x^2-y^2}$	0.14817	
		$3d_{xy}$	0.13729	
	N–Sπ	$2p_z$	0.50465	99.28
		$3p_z$	0.85911	
Product – HNSO				
H +0.0963				

(continued overleaf)

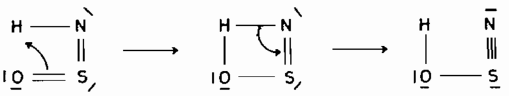
TABLE III. *(continued)*

Gross Atomic Charge	Localized Orbitals Type	A.O.	Coefficients	% Localization
N −0.279	H–Nσ	1s	0.67010	98.26
S +0.599		2s	0.36065	
O −0.416		$2p_x$	−0.63489	
	N–Sσ	2s	0.34125	99.30
		$2p_x$	0.22461	
		$2p_x$	0.54666	
		3s	0.33582	
		$3p_x$	−0.38648	
		$3p_x$	−0.51496	
	S–Oσ	3s	0.34297	98.63
		$3p_x$	−0.43478	
		$3p_y$	0.51074	
		2s	0.25628	
		$2p_x$	0.36329	
		$2p_y$	−0.47023	
	lone pair O(1)	2s	0.91889	98.81
		$2p_x$	−0.23546	
		$2p_y$	−0.31349	
	lone pair O(2)	$2p_x$	0.78105	96.09
		$2p_y$	0.59235	
	lone pair N	2s	0.72369	98.32
		$2p_x$	0.33500	
		$2p_y$	−0.58928	
	lone pair S	3s	0.77172	99.38
		$3p_x$	0.63106	
	S–Nπ	$2p_z$	0.79144	96.40
		$3p_z$	0.58109	
	S–Oπ	$3p_z$	0.36371	97.69
		$2p_z$	0.90189	

We established that we are dealing with a true transition state and not an arbitrary maxima in the potential energy surface, by carrying out a normal coordinate analysis and obtaining one negative force constant corresponding to a large frequency [15]. This corresponds to motion along the reaction coordinate. The reaction coordinate is a combination of motions which in effect translates the proton in the xy plane between the nitrogen and the oxygen atoms. The remaining vibrational motions are predicted to have frequencies of 765, 1132, 1250, 1342, and 2117 cm^{-1}, respectively. These frequencies generally span the region where N–S and S–O motions are known to absorb [16]. For example tetrasulfur dinitride exhibits vibrational structure in the range of 600– 1200 as do several other sulfur nitrides, *e.g.* S_4N_4, S_2N_2, S_4N^-, $S_3N_3^-$.

Electronic Structures

In Table III are presented the calculated localized orbitals for the reactant and product molecules. This information together with localized orbitals for the transition state provide a very clear picture of the alterations that occur in the electronic structure of the system as it passes from the reactant state to the product state. The reaction can be symbolically described as wherein a sulfur–oxygen pi bond is



opened up and the electron pair is utilized to form a partial single bond between the oxygen atom and the hydrogen atom. Simultaneously the hydrogen–nitrogen single bond begins to weaken (lengthen). The product state is achieved by a complete breaking of the N–H bond, formation of the O–H bond, and formation of a sulfur–nitrogen π type bond. The transition state clearly shows the intermediate stage obtained in adjustment of the electronic structure of the system. Specifically the nitrogen hydrogen distance in thionylimide starts out at 1.00 Å and lengthened to 1.38 Å in the transition state. It attains a value of 2.57 Å in the product, thiazyl-S-hydroxide. The oxygen–hydrogen distance can also be followed through the course of the reaction. It starts at 1.48 Å in the reactant, thionylimide, attains a value of 1.36 Å in the transition state and ends up at 0.94 Å for the O–H single bond in thiazyl-S-hydroxide. The presence of the relatively strong hydrogen bonding interaction between the proton and the oxygen atom in the imide is probably a factor in the dictation of the transition state attained by the system.

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