A Flash Photolytic Study of Thiatriazoles and Mesoionic Oxathiazoles. The Thermal Decomposition of Nitrile Sulphides

By Arne Holm,* Chemical Laboratory II, Department of General and Organic Chemistry, University of Copenhagen, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Jørn J. Christiansen, Department of Chemistry, Royal Danish School of Educational Studies, Emdrupvej 115 B, DK-2400 Copenhagen, Denmark

Christian Lohse, Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

Benzonitrile sulphides have been generated by irradiation of 4-phenyl-1,3,2-oxathiazolylium-5-olate and of 5-aryl-1,2,3,4-thiatriazoles. Rate constants for the first-order decay of the nitrile sulphides were measured in 96% ethanol at 10—30 °C and the results used to calculate activation parameters, E_a 18.88 and 17.20 kJ mol^{-1} and $\Delta S\ddagger$ -121.8 and -132.7 J mol^{-1} K^{-1} for 4-BrC$_6$H$_4$CNS and 4-MeC$_6$H$_4$CNS, respectively. The decay reaction is 3—4 times slower in CCl$_4$. A Hammett ρ-value of 2.2 was calculated. Thermochemical relations between HCNS and the decomposition products, HCN and S, have been obtained by ab initio calculations. The mechanism of sulphur extrusion is discussed.

BENZONITRILE SULPHIDE has been generated photochemically from phenyl derivatives of thiatriazole, 1,3,4-oxathiazol-2-one, and 1,3,2-oxathiazolylium-5-olate.[1,†] It is characterized by its electronic spectrum EPA ‡ at 85 K, which remains unchanged for at least several hours. Warming caused no significant change in the spectrum, but crystallization of the glass took place around 140 K followed by melting and simultaneous formation of benzonitrile and elemental sulphur. Decomposition rates and relative stabilities of nitrile sulphides could consequently not be studied under these conditions, and we have used instead flash photolysis at room temperature.

Photochemical Results.—Photochemical formation of benzonitrile, benzonitrile sulphide, and phenyl isothiocyanate from 5-phenylthiatriazole ($\lambda_{max.}$ 280 nm), has been demonstrated to take place via excited singlet states.[1]

In the present studies thiatriazoles were irradiated as solutions in 96% ethanol in contact with air. Two types of thermal decay reactions were recognized depending on the concentration of the thiatriazole. In 10^{-3}—10^{-4}M-solutions a relatively slow decay process (lifetime ca. 50 ms) was observed corresponding to the formation of one or more species giving rise to absorptions in the region observed (ca. 340 to 700 nm) (see Experimental section). Continued irradiation caused a steady rise of the baseline. On the surmise that the decay process observed might be connected with production of elemental sulphur, a freshly prepared saturated solution of SCO in ethanol was irradiated under similar conditions to give species with the same lifetime and spectral properties as above. Photolysis of carbonyl sulphide, SCO, has been investigated in ethanol, alkanes, and acetonitrile.[2] The reaction leads to carbon monoxide and singlet sulphur atoms, S(^{1}D), with a quantum yield of 0.9, independent of the concentration of SCO (up to 0.7M). Spin inversion to triplet sulphur, S(^{3}P), takes place followed by S$_2$-formation and subsequent polymerisation to S$_8$ (Scheme 1).
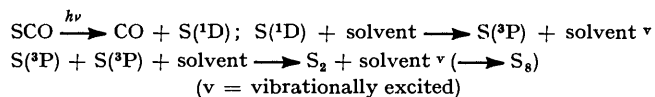
The allotropic species S$_2$, S$_3$, S$_4$ (chains),[3,4,5] and S$_6$ and

† Previously these compounds were named as 1,3,2-oxathiazolylio-5-oxides.

‡ Ether–isopentane–ethanol (5 : 5 : 2 v/v).

S$_7$ (rings)[6] give rise to absorptions in the u.v. and visible region, and we assume that the relatively slow decay process exhibited by all investigated thiatriazoles and SCO as well as 4-phenyl-1,3,2-oxathiazolylium-5-olate (see below) is associated with the above reaction of sulphur. The complicated processes from atomic sulphur to S$_8$ have been investigated in the gas phase,[7] and estimated lifetimes for the various allotropes vary from milliseconds (S$_2$)[8] to seconds (S$_6$).[9]

Weak signals (optical density ca. 0.01) due to a first-order decay process (lifetime ca. 1 ms) were observed upon irradiation of a highly dilute solution of thiatriazole (10^{-5} to 5×10^{-6}M) in 96% ethanol. Rate constants for

$$\text{SCO} \xrightarrow{h\nu} \text{CO} + \text{S}(^1\text{D}); \quad \text{S}(^1\text{D}) + \text{solvent} \longrightarrow \text{S}(^3\text{P}) + \text{solvent}^v$$
$$\text{S}(^3\text{P}) + \text{S}(^3\text{P}) + \text{solvent} \longrightarrow \text{S}_2 + \text{solvent}^v (\longrightarrow \text{S}_8)$$
$$(v = \text{vibrationally excited})$$

SCHEME 1

thermal decay processes of substituted thiatriazoles are shown in Table 1. 4-Phenyl-1,3,2-oxathiazolylium-5-olate apparently gives rise to the same intermediate as 5-phenylthiatriazole under similar conditions, as demonstrated by identical decay rates (Table 1). How-

TABLE 1

Rate constants for first-order decay of nitrile sulphides obtained by irradiation of 5-arylthiatriazoles and 4-phenyl-1,3,2-oxathiazolylium-5-olate (10^{-5}—5×10^{-6} M)

ArCNS	Precursor	k/s^{-1}	$t_{\frac{1}{2}}$/ms	Solvent	T/°C
Ar = Ph	Thiatriazole	3 181	0.22		
Ar = Ph	Oxathiazol-ylium-5-oxide	3 178	0.22		
Ar = 4-BrPh	Thiatriazole	3 275	0.21	96% EtOH	22.3
Ar = 4-MePh	Thiatriazole	1 534	0.45		
Ar = 4-MeOPh	Thiatriazole	799	0.87		
Ar = 4-MePh	Thiatriazole	512	1.35	CCl$_4$	24.0

ever, the signal-to-noise ratio proved even less satisfactory in this case than in the above measurements and it was not possible to make decay measurements with substituted 1,3,2-oxathiazolylium-5-olates. Decay rates of intermediates from flashing of thiatriazoles could also be measured in carbon tetrachloride but not in benzene or cyclohexane. Furthermore, in carbon tetrachloride,
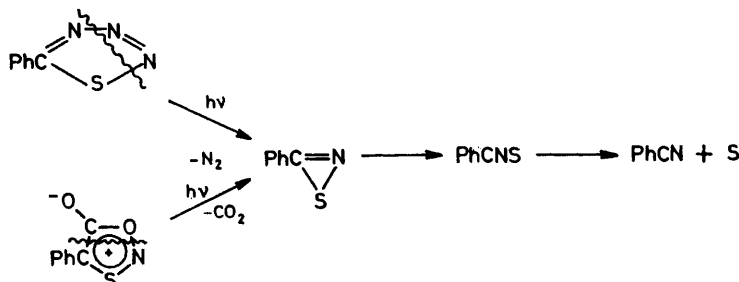
deviations from first-order kinetics were apparent at the beginning of the decay reaction. We consider the intermediates to be benzonitrile sulphides, as these are intermediates common to the two types of heterocyclic systems [10] (Scheme 2 *). Processes of higher order than unity ($nS \longrightarrow S_n$) are suppressed in the highly diluted solutions rendering it possible to observe the decay of the nitrile sulphides.

The nitrile sulphides generated at room temperature exhibited poorly defined, broad absorptions shifted by ca. 25 nm to longer wavelengths, compared with the well-defined absorption maxima recorded in EPA at 85 K (Table 2). However, spectral information below ca. 340

TABLE 2

Activation parameters for decomposition of nitrile sulphides at 25 °C in 96% ethanol

Compound	$E_a/$ kJ mol^{-1}	log A	$\Delta S^{\ddagger}/$ J mol^{-1} K^{-1}
4-BrC$_6$H$_4$CNS	18.88	6.86	−121.8
	±0.38	±0.07	±1.3
4-MeC$_6$H$_4$CNS	17.20	6.30	−132.7
	±5.4	±0.97	±18.4

nm could not be obtained, and although shifts to lower wavelengths may often be observed on cooling, it seems more reasonable to assume that the signals observed here belong to weak shoulders on the main absorption bands.

charges calculated *ab initio* for HCNS and HCN by the same uncontracted basis set as in ref. 11 are shown in Figure 1. We find that H–C is indicated to be the positive and N–S the negative end in HCNS. The Hammett ρ-value is in agreement with the increased electron density at the carbon atom in the transition state, resulting from transfer of the N–S bonding electrons to the nitrile group with formation of elemental sulphur. As reduction in hydrogen-bonding ability may

$$0.225 \quad 0.140 \quad -0.226 \quad -0.138 \quad \quad 0.187 \quad -0.030 \quad -0.157$$
$$\text{H} \longrightarrow \text{C} \equiv\!\equiv\!\equiv \text{N} \longrightarrow \text{S} \quad\quad \text{H} \longrightarrow \text{C} \equiv\!\equiv\!\equiv \text{N}$$
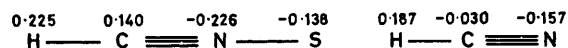
FIGURE 1 Calculated gross atomic charges of HCNS and HCN

be expected on going from the initial to the transition state, the nitrile sulphide should be more stable in protic than in non-protic solvents. However, the decay reaction is ca. 3—4 times slower in carbon tetrachloride than in ethanol, and deviations from first-order kinetics are observed. A direct involvement of ethanol in the transition state would result in pseudo-first-order kinetics which cannot be directly evaluated, but the activation entropy of ca. −125 J mol^{-1} K^{-1} (Table 2) is suggestive of a bimolecular reaction.[15] Electron donor–acceptor complex formation between sulphur and oxygen of the solvent ethanol may be one way to rationalize this

SCHEME 2

Thermal Reactions of Nitrile Sulphides and Supporting Theoretical Calculations.—A Hammett plot of log (k_{ArX}/k_{ArH}) against σ-values gives a straight line (r 1.001) for X = H, Me, and OMe, with a ρ-value of 2.2. For unknown reasons, the decay-rate constant for 4-bromobenzonitrile sulphide does not correlate with the other decay-rate constants, being only slightly greater than that of benzonitrile sulphide.

Ab initio calculations for HCNS by the LCAO–MO–SCF technique [11] indicate a linear geometry with an N–S bond distance of 1.678 Å and a dipole moment of 5.38 D, which may be compared with the experimental dipole moments of HCN (2.96 D) [12] and PhCN (4.14 D).[13] By use of known bond lengths [14] we estimate an N–S bond order of 1.0, indicating a single bond. Gross atomic

result. Unfortunately, rate measurements in the non-polar solvents are insufficiently reliable to allow further analysis of the solvent effects.

Sulphur formed in these reactions is most likely extruded as atoms, which in alcohols are kinetically important only in the S(^{3}P) state.[2] Cases of scavenging with S(^{3}P) are known. Thus ethylene sulphide [16] (gas phase) and thiocyanate ion [17] (solution) react with S(^{3}P) with formation of S$_2$. Scavenging of nitrile sulphide with sulphur atoms, leading to nitrile and S$_2$, will clearly give rise to kinetics of higher order than unity. However, first-order reactions are observed in ethanol, and the first-order rate constants are independent of the flash energy, as expected.

We may again compare the extrusion of sulphur from benzonitrile sulphide with extrusion from the unknown HCNS. The energy of the geometry-optimized HCNS has been estimated as −490.153 44 hartrees.[11] In order to make the best possible comparison, the energies of HCN (−92.767 64), S(^{3}P) (−397.400 28), and S(^{1}D)

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* Evidence has recently been obtained [10] for photochemical formation of thiazirines at 10 K in poly(vinyl chloride) film from thiatriazoles and other heterocyclic compounds. On warming, thiazirines rearrange to nitrile sulphides. The rate of rearrangement at 85 K in EPA-glass is so high that only nitrile sulphides are obtained on photolysis under these conditions.

$(-397.346\ 67\ H)$ have been calculated *ab initio*, applying the same uncontracted basis set as in ref. 11, and these have been used to obtain thermochemical relations between HCNS and HCN and S (Scheme 3). Most

SCHEME 3
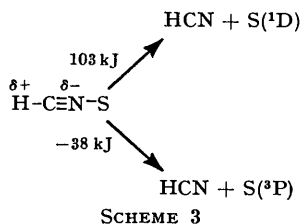
interestingly, the calculations indicate that extrusion of a singlet sulphur atom $S(^1D)$ from HCNS is endothermic to the extent of *ca.* 100 kJ. Formation of atomic sulphur in the ground state, $S(^3P)$, is exothermic to the extent of *ca.* 40 kJ, but it is spin-forbidden.

A singlet triplet crossing, which requires spin–orbit coupling,[18] may, however, take place.[19] We suggest tentatively that the nitrile sulphides extrude sulphur with spin inversion to form sulphur atoms in the triplet ground state.* Solvent effects on these systems are, however, clearly in need of detailed investigation.

TABLE 3

Absorption of nitrile sulphides generated by photolysis at room temperature in 96% ethanol and at 85 K in EPA

4-XArCNS	96% Ethanol at 295 K [a]/nm	EPA-glass at 85 K/nm
X = H	*ca.* 360vbr	242, 293, 317, 337 [1]
X = Br	*ca.* 370vbr	251, 300, 321, 343 [20]
X = MeO	*ca.* 345vbr	

[a] Absorptions were not recorded below 340 nm.

EXPERIMENTAL

Rate constants were obtained with flash-photolytic equipment designed for this study. The flash lamps were filled with air, and quartz–sodium bromide filters were used. Flash energies were 300—600 J. The monitoring light was

passed into a monochromator, through the reaction cell, and into a second monochromator with a photomultiplier on the exit slit. This optical system prevented photoisomerization by the 100 W quartz–iodine monitoring lamp. The region open to observations was *ca.* 340—700 nm. The rate constants were obtained, where possible, by measurements at wavelengths where only the thiatriazoles and oxa-thiazolylium-5-olate absorbed light. Lifetimes were reproducible to within 10%. Measurements were always taken using freshly prepared solutions.

* It has been shown that small amounts of episulphides are formed on irradiation of phenylthiatriazole in the presence of alkenes. These are considered to be the result of formation of triplet sulphur atoms. However, thermal decomposition of thiatriazoles leads to nitriles, nitrogen, and sulphur, but does not afford episulphides. These results have been explained in terms of differences in kinetic energy in the thermally and photo-chemically generated sulphur atoms.[20]

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