Pyrolysis of Thio- and Isothiocyanates. II.[1a] Ethyl Thiocyanate

N. Barroeta and Allan Maccoll*

*Contribution from the Instituto Venezolano de Investigaciones Cientificas,
Caracas, Venezuela, and The Christopher Ingold Laboratories,
London, W.C.1, England. Received March 13, 1971*

Abstract: The gas-phase thermolysis of ethyl thiocyanate was investigated in the pressure range 25–350 mm by a conventional, static, manometric technique. The reaction can be represented by eq 1. The least-squares Arrhenius equation for the elimination reaction 1 is $k_1(\text{sec}^{-1}) = 10^{11.770\pm0.213} \exp(-40,510 \pm 576)/RT$ from 559 to 616°K. The values of the first-order rate constant are not affected by the nature of the walls or the surface to volume ratio of the reaction vessel, or by added olefinic inhibitors. The pyrolyses of ethyl-$1,1$-d_2, and ethyl-d_5 thiocyanates were also studied under the above conditions yielding the following Arrhenius equations: ethyl-$1,1$-d_2, $k_1(\text{sec}^{-1}) = 10^{11.992\pm0.193} \exp(-41,295 \pm 517)/RT$; ethyl-$d_5$, $k_1(\text{sec}^{-1}) = 10^{12.334\pm0.178} \exp(-43,390 \pm 495)/RT$. The mass spectrometric analysis of the ethylene produced in the pyrolysis of ethyl-$1,1$-d_2 thiocyanate showed it to be 95.6% $CH_2{=}CD_2$. The above results are interpreted in terms of a homogeneous, unimolecular mechanism in which the hydrogen and the thiocyanate group are eliminated from adjacent carbon atoms. The transition state is regarded as a cyclic structure with very little charge separation.

In recent years there has been an increasing interest in the problem of giving more detailed description[1] of the transition state of those gas reactions termed quasi-heterolytic.[2] On the other hand, advantage has been taken in solution of the use of bidentate nucleophiles like *p*-nitrobenzoate,[3] thiobenzoate,[4] and thiocyanate[5] when studying incipient ionization and internal return phenomena. With this background in mind we undertook the study of the thermal decomposition of organic thiocyanates which were both able to isomerize and to eliminate, a field so far untouched in the gas phase. In this paper we report on the thermal decomposition of ethyl thiocyanate, ethyl-d_5 thiocyanate, and ethyl-$1,1$-d_2 thiocyanate.

Results

Stoichiometry. The only products detected in measurable quantities during the first half-life of reaction were ethylene, thiocyanic acid, and, in much smaller amount, ethyl isothiocyanate. Furthermore, the infrared analysis of the gaseous products, taken at conversions of at least 30%, reveals only the presence of the "iso" form of thiocyanic acid HNCS. Traces of a group of unidentified, low boiling compounds which increased with time were also present from the start, but in no case did any of these account for more than 2% of the starting amount of thiocyanate, and these relatively high proportions were only attained at reaction times larger than five half-lives. Unpublished results seem to indicate that these come from the slow pyrolysis of thiocyanic acid itself. Ethyl isothiocyanate increased with time (Table I) in a sigmoid fashion from zero at the start to about 8% of total reaction at three

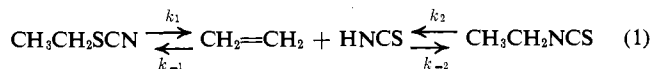Table I. Production of Isothiocyanate at 320° for an Initial Pressure of Thiocyanate of 100 mm

Time, min	% of reaction	Pressure of thiocyanate Apparent[a]	Pressure of thiocyanate Actual[b]	Pressure of isothio-cyanate	% of isomeri-zation
6	23.5	76.50	76.20	0.30	1.61
11	38.7	61.30	60.61	0.69	1.75
17	50.9	49.10	48.09	0.98	1.88
25	63.4	36.60	34.80	1.71	2.63
46	79.3	20.70	15.83	4.87	5.76
62	87.5	12.50	8.72	3.76	4.12
81	85.1	14.90	7.01	7.90	8.49

[a] As given by $2P_0 - P$. [b] From vpc analysis.

half-lives and from there on remained constant with in experimental error.

The total pressure of the system increased smoothly to values ranging from $1.70P_0$ to $2.00P_0$ depending on initial pressure and temperature. The implications of this will be discussed later. The correlations between the per cent of reaction as given by pressure measurement and that obtained from direct determination of thiocyanic acid (titrimetric) and ethyl thiocyanate (gas chromatographic) are given up to 65% reaction by the equations $P_1 = (1.012 \times 0.001)P_2$ and $P_1 = (0.968 \pm 0.017)P_3$, respectively, where P_1 is the per cent of reaction by pressure and P_2 and P_3 represent per cent of reaction by direct analysis of products.

On the basis of the above evidence it is concluded that the stoichiometry of the reaction under study can be represented by eq 1 and that the initial rate of pressure

$$\text{CH}_3\text{CH}_2\text{SCN} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{CH}_2{=}\text{CH}_2 + \text{HNCS} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{CH}_3\text{CH}_2\text{NCS} \quad (1)$$

increase provides a valid way to calculate k_1. It should be noted that k_2 in eq 1 has been independently evaluated[6] and is 14.7 times smaller than k_1.

Homogeneity. In a clean vessel, the rate constants obtained from consecutive runs do not show any "seasoning effects." Furthermore, the values are invariant to the nature and extent of the reactor surface. This was tested by comparing runs done in (a) clean

* Address correspondence to this author at the Department of Chemistry, University College, London, England.

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(5) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Amer. Chem. Soc.*, **87**, 1045 (1965).

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vessels and (b) vessels coated with the products of allyl bromide pyrolysis, the vessels having a surface/volume ratio of 1.0 cm^{-1}. To check the homogeneity further, runs were done in vessels with surface/volume ratios of 4.0 and 6.0 cm^{-1}. In no case did the rate constants from the packed vessels differ by more than the experimental error from those derived from the experiments in the unpacked vessel. The increase in surface/volume ratio was achieved by the use of concentric Pyrex tubes, mounted in the reactor vessel.

Effect of Added Substances. The pyrolysis of ethyl thiocyanate was conducted in the presence of cyclohexene, a chain inhibitor, and small amounts of allyl bromide and air which act as radical promoters (Table II). For larger concentrations of air a significant posi-

Table II. Action of Additives on the Pyrolysis of Ethyl Thiocyanate

T, °C	Additive	% additive	$10^4 k_1$, sec^{-1}	$\dfrac{k_1(\text{additive})}{k_1(\text{calcd})}$
298.7	Cyclohexene	14.8	1.87	0.97
298.7	Cyclohexene	35.6	1.95	1.01
298.7	Cyclohexene	95.8	1.90	0.99
337.5	Cyclohexene	25.7	18.2	0.98
337.5	Cyclohexene	44.9	18.3	0.99
337.5	Cyclohexene	101.4	18.8	1.02
293.0	Air	8.7	1.40	0.95
293.0	Air	19.9	1.50	1.02
327.0	Air	5.2	10.4	0.99
327.0	Air	26.5	10.6	1.01
327.0	Air	51.2	10.9	1.04
306.4	Allyl bromide	13.0	3.21[a]	1.05

[a] Corrected for the pressure increase due to allyl bromide alone.

tive effect, especially noticeable at the lower temperatures, is observed in the rate constants. Equally, larger concentrations of allyl bromide produce a marked effect on the rate constants but most likely a new reaction set in here as two new products (so far unidentified) were detected in the mixed pyrolysis.

Kinetic Results. The total pressure–time curve followed a first-order rate law up to 30–70% reaction depending on temperature and initial concentration of thiocyanate (Table III). At higher levels of de-

Table III. First-Order Rate Constants at 320.4° ($P_0 = 86.0$ mm)

Time, min	% reaction	$10^4 k_1$, sec^{-1}
2	8.2	7.08
5	19.5	7.20
8	29.0	7.08
10	35.0	7.15
14	45.3	7.18
18	53.8	7.16
20	57.0	7.04
24	63.4	6.96
30	70.8	6.83

composition the calculated first-order rate constants fell off with time due to the incursion of the reverse reaction. The first-order nature of the elimination is further demonstrated by the fact that the rate constants show no dependence on initial pressure of thiocyanate (Table IV). From the rate constant-temperature data of Table V the following Arrhenius eq I was calculated by means of a least-squares procedure.

Table IV. First-Order Rate Constants at Varying Initial Pressures at 306.4°

P_0, mm	32.6	59.8	86.0	114.0	162.0	222.2	257.5	345.0
$10^4 k_1$, sec^{-1}	3.30	3.36	3.47	3.47	3.38	3.26	3.33	3.18

Table V. Effect of Temperature on the Pyrolysis of Ethyl Thiocyanate

T, °K	No. of runs	Standard error, %	$10^4 k_1$, sec^{-1}
558.8	7	1.46	0.822
571.6	19	0.85	1.95
579.6	16	1.14	3.37
593.7	14	0.59	7.37
603.7	10	0.74	12.99
613.9	6	1.68	22.22
615.7	3	1.51	24.45

$$\log k_1(\text{sec}^{-1}) = (11.77 \pm 0.21) - (40,511 \pm 576)/2.303RT \quad \text{(I)}$$

Pyrolysis of Ethyl-$1,1$-d_2 Thiocyanate. This compound was pyrolyzed with initial pressure varying from 100 to 170 mm. Care was taken to keep conditions as near as possible to those used in the pyrolysis of the nondeuterated compound. The least-squares Arrhenius eq II was calculated from data in Table VI.

$$\log k_1(\text{sec}^{-1}) = (11.992 \pm 0.193) - (41,295 \pm 517)/2.303RT \quad \text{(II)}$$

Table VI. Variation of the Rate Constants with Temperature for Ethyl-$1,1$-d_2 Thiocyanate

T, °K	No. of runs	$10^4 k_1$, sec^{-1}	Mean dev, %
557.3	3	0.625	2.0
566.7	4	1.19	1.8
575.8	4	1.97	2.7
590.7	3	5.36	2.2
602.9	2	10.1	0.0
620.8	4	28.7	2.1

The ethylene produced in the elimination from this compound was analyzed by mass spectrometry and the following composition was found: $CH_2{=}CD_2$, 95.6%; $CH_2{=}CHD$, 3.7%; $CH_2{=}CH_2$, 0.7%.

Pyrolysis of Ethyl-d_5 Thiocyanate. The perdeuterated compound was pyrolyzed at initial pressures in the vicinity of 140 mm. From the temperature dependence of the rate constants (Table VII) the following

Table VII. Variation of the Rate Constants with Temperature for Ethyl-d_5 Thiocyanate

T, °K	No. of runs	$10^4 k_1$, sec^{-1}	Mean dev, %
575.5	4	0.703	4.7
594.9	3	2.53	0.5
605.1	4	4.57	1.0
615.1	3	8.50	1.2
629.9	4	19.3	3.3
642.7	4	35.6	3.4

Arrhenius equation was calculated by a least-squares procedure

$$\log k_1(\text{sec}^{-1}) = (12.334 \pm 0.178) - (43,390 \pm 495)/2.303RT \quad \text{(III)}$$

Rate Ratios for Isotopically Substituted Species.
From the rate constants calculated by means of the Arrhenius eq I, II, and III the isotope effects below were obtained (Table VIII).
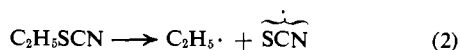
Table VIII. Relative Rates for Isotopic Substitution

T, °K	$\dfrac{k_1 \text{ for } C_2H_5SCN}{k_1 \text{ for } C_2H_3D_2SCN}$	T, °K	$\dfrac{k_1 \text{ for } C_2H_5SCN}{k_1 \text{ for } C_2D_5SCN}$
557.3	1.22	575.5	3.36
566.7	1.20	594.9	3.10
575.8	1.19	605.5	2.97
590.7	1.17	615.1	2.86
602.9	1.15	629.9	2.70
620.8	1.13	642.7	2.58

Discussion

From the shape of the pressure–time curve and the analysis of products during the early stages of the decomposition from which k_1 was obtained it can be concluded that the reaction under study is a clean reversible elimination of "thiocyanic acid" giving ethylene as the only hydrocarbon product. (As the two possible tautomers of this acid can be eliminated at the molecular level we want to emphasize that for "thiocyanic acid" we mean "the totality of acidic species of mass 59 which in aqueous solution give a positive test for thiocyanate anion.") Furthermore, it has been shown that the elimination is a homogeneous, first-order gas reaction.

Attention can now be focused on the mechanism and we first consider a long radical-chain process. Now the thiocyanate radical, being presumably resonance stabilized,[7,8] will not propagate such a radical chain efficiently, and experimentally we have noted the lack of inhibition by cyclohexene and the fact that the rate is not increased by moderated concentrations of allyl bromide or air. This evidence rules out a radical chain mechanism. On the other hand it still leaves open the possibility of a mechanism like

$$C_2H_5SCN \longrightarrow C_2H_5\cdot + \overset{\frown}{SCN} \qquad (2)$$

$$C_2H_5SCN + \overset{\frown}{SCN} \longrightarrow \dot{C}_2H_4SCN + HNCS \qquad (3)$$

$$\dot{C}_2H_4SCN + C_2H_5\cdot \longrightarrow C_2H_5SCN + C_2H_4 \qquad (4)$$

with reaction 2 as the rate-controlling step. The enthalpy of this reaction, which fixes a lower limit to the overall activation energy, can be estimated from the value 26.9 kcal mol^{-1} for the heat of formation of ethyl thiocyanate estimated from a consideration of the heat of formation of methyl isothiocyanate[7] and several approximate methods,[9] $H_f°(CH_3CH_2\cdot) = 25 \pm 1$ kcal mol^{-1} [10,11] and $H_f°(SCN) = 78 \pm 10$ kcal mol^{-1} [12] to give 76.1 ± 10 kcal mol^{-1} which is too high by far to account for the observed activation energy of 40.5

kcal mol^{-1}. This forces us to propose a molecular mechanism and here again two alternatives exist: the normal 1,2-elimination and a 1,1 elimination with simultaneous migration of a hydrogen atom from the adjacent methyl group.[13] Evidence for this type of mechanism has been presented for certain esters[14] and alkyl fluorides.[15] The relative magnitude of the intermolecular isotope effects obtained for ethyl-d_5 and ethyl-$1,1$-d_2 thiocyanates and most conclusively the fact that only dideuterio ethylene is formed from the latter clearly rules out the 1,1 elimination model.

The question now arises of the geometry of the transition state for the 1,2 elimination mechanism. As was implied above, two distinct structures can be formulated a priori: structure I leading to the production of thiocyanic acid, a species so far not identified in the gas phase,[16,17] and structure II leading to isothiocyanic acid. There are some observations in favor of structure II.

I   II
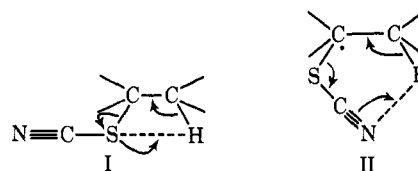
In the first place the result of the infrared analysis of the gaseous products points to the elimination of isothiocyanic acid. Secondly, when thiocyanates are pyrolyzed in the presence of olefins, isothiocyanates are predominantly formed as a result of the back addition of the acid.[12] This of course does not exclude the elimination of thiocyanic acid which then isomerizes to the isothiocyanic form. The necessary speed at which this isomerization must occur to render the former undectable seems unrealistic however. In this paper we then propose transition state II but recognize that more information is needed to reach a final choice. A very related problem has been considered by Shenkel, Hobrock, and Kiser[18] for the electron impact elimination process

$$C_2H_5NCS + e \longrightarrow HNCS^+ + C_2H_4 + 2e$$

and these authors reached the same conclusion.

The transition state appears to involve a highly synchronous process in the sense that both bond formation and bond breaking processes have progressed to about the same extent in the critical configuration. This follows from the smallness of the activation energy compared with the carbon–sulfur bond energy and from the effect of ethyl substitution on rate, namely a factor of 14 at 307°[19] which is not far from the magnitude of such effect found in typically homolytic reactions.[20,21]

The relatively large errors in the Arrhenius parameters of eq I and II from which the secondary isotope

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effects of Table VIII are computed do not warrant its discussion in terms of mechanism. The total d_5 isotope effect on the other hand is significant although we still feel that only qualitative conclusions can be drawn from it. The magnitude of such effect is in fact about the maximum one would expect for this kind of reaction from previous work on alkyl halides[22-24] and esters.[25] It implies a large degree of involvement of the hydrogen in the activation act.

Thermodynamics of the Elimination. In view of the fact of the variation of the ratio (final pressure)/(initial pressure) with initial pressure and temperature, we suggest the establishment of an endothermic equilibrium. Based on eq I, the equilibrium constant K_p can be written as

$$K_1 = \frac{P_{HNCS}P_{C_2H_4}}{P_{EtSCN}}$$

$$K_2 = \frac{P_{HCNS}P_{C_2H_4}}{P_{EtNCS}}$$

$$K_p = \frac{P_{HCNS}P_{C_2H_4}}{P_{EtSCN} + P_{EtNCS}}$$

with, of course, $K_p = K_1K_2/(K_1 + K_2)$. A preliminary calculation showed that $K_1 \gg K_2$ and so $K_p = K_2$. Values of $K_p = (P_f - P_0)^2/(2P_0 - P_f)$ are shown in Table IX. Reliable values for the thermodynamic

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Table IX. Equilibrium Constants for the Ethyl Thiocyanate Pyrolysis

T, °K	576.1	579.7	593.6	603.8	610.7
K_p	0.69	0.70	0.95	1.16	1.41

functions of the species involved in the equilibrium are not available in the literature.

Experimental Section

Ethyl Thiocyanate. A commercial sample from Eastman Organic Chemical, Rochester, N. Y., was purified by fractional distillation to give a compound 99.5% pure.

Ethyl-*1,1-d_2* Thiocyanate. This was prepared from ethyl-*1,1-d_2* bromide (98% isotopic purity) obtained from Merck Sharp and Dohme of Canada and potassium thiocyanate in dimethylformamide. After purification by standard procedures, the compound showed a chemical purity of 98.8%. Mass spectrometric analysis indicated that 97.7 molecules out of 100 are dideuterated.

Ethyl-*d_5* thiocyanate was prepared from the corresponding perdeuterated bromide (99% of isotopic purity). The sources of materials and the method of preparation were the same used for the previous compound. The isotopic purity of the final product was at least 98%. All compounds were analyzed by gas chromatography in a Perkin-Elmer F-11 flame ionization instrument, by nmr in a Varian A-60 spectrometer, and by ir in a Perkin-Elmer Model 337 grating spectrophotometer. Mass spectra were taken on a G.E.C.-A.E.I. MS-9 instrument.

Quantitative determinations of thio- and isothiocyanates were accomplished by gas chromatography using the method of internal standards and those of thiocyanic acid by titration with standard alkali. Details of the techniques are given elsewhere.[12]

The kinetic study was carried out in a standard, high-vacuum, all-glass system using the static manometric method. Temperature was kept constant within 0.2° by means of a RT-3R/2 temperature controller (A.E.I).

Thermal Decomposition of 2,2'-Diphenyl-2,2'-azohexafluoropropane

Joseph B. Levy* and Edward J. Lehmann

Contribution from the Department of Chemistry, The George Washington University, Washington, D. C. 20006. Received December 8, 1970

Abstract: Azohexafluorocumene (2,2'-diphenyl-2,2'-azohexafluoropropane) has been prepared from the corresponding amine and iodine pentafluoride. The thermal decomposition reaction in toluene solvent yields the rate expression $k = 10^{17.8\pm0.8} \exp(-32{,}800 \pm 1300)/RT$ sec^{-1}. The reaction products in toluene are 2-phenyl-2-*p*-(1,1,1,3,3,3-hexafluoro-2-propyl)phenylhexafluoropropane—the product of para coupling of the hexafluorocumyl radicals—and the products obtained by the coupling of benzyl and hexafluorocumyl radicals. The cage effect in toluene has been determined at 55° with iodine as a scavenger.

Azo compounds have been very widely used in the study of the reactions of free radicals.[1] The relationship between the radical-stabilizing effects of groups attached to the free radical center and the ease of decomposition of azo compounds has been pointed out[2,3] but

the nature of such groups has been confined to aryl, alkyl, cyano, and chloro.[4]

We report here on the synthesis and pyrolysis in benzene and toluene solution of azohexafluorocumene (2,2'-diphenyl-2,2'-azohexafluoropropane). The study was undertaken to investigate the effect of the trifluoromethyl group—a group which can be unequivocally

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