Pyrolysis of Thiocyanates and Isothiocyanates. Part IV.† Effect of Structure on Thiocyanate Elimination

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The mechanistic study of the pyrolysis of thiocyanates has been continued with the detailed kinetic investigation of the gas-phase elimination of isopropyl, t-butyl, and but-3-enyl thiocyanates for which the Arrhenius equations are: $k_1 = 10^{12\cdot27} \exp(-39{,}330/RT)$ s^{-1}, $k_1 = 10^{12\cdot28} \exp(-37{,}370/RT)$ s^{-1}, and $k_1 - 10^{12\cdot34} \exp(-41{,}879/RT)$ s^{-1} respectively. Rate data at one temperature were also obtained for n-propyl and 2-phenylethyl thiocyanates. The structure and character of the transition state for this reaction, which is believed to be homogeneous and unimolecular, is discussed and a six-centre concerted mechanism is suggested

We have shown that the gas-phase thermolysis of ethyl[1] and s-butyl[2] thiocyanates is a homogeneous, reversible elimination of ' thiocyanic acid ' occurring by a molecular mechanism. Further, experiments with deuteriated ethyl thiocyanates[1] and [2-^{2}H$_1$]s-butyl thiocyanate[3] led us to conclude that the reaction is a 1,2-elimination with appreciable carbon–hydrogen bond-breaking in the transition state. However, two main questions regarding mechanism remained unanswered, namely, the electronic requirements of the reaction centre and the detailed structure of the transition state. The present results will allow us to give a clearer account of the former and to discuss more fully the latter.

RESULTS

Stoicheiometry and Kinetics.—As for other thio- and isothio-cyanates investigated in our laboratories, the stoicheiometry can be represented by equation (1) where $k_1 \gg k_{-1}$. The possible complications in the study of

$$\mathrm{C}_n\mathrm{H}_m\mathrm{SN} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C}_{n-1}\mathrm{H}_{m-1} + \mathrm{HNCS} \qquad (1)$$

reaction (1), namely the incursion of back addition (reaction -1), the slow decomposition of the acid, and, in the specific case of but-3-enyl thiocyanate, the dimerisation of butadiene, only became significant in the later stages of the reaction. This favourable circumstance allowed us to use the initial rate (*e.g.*, the first 20—50% reaction depending on the conditions) of total pressure increase to calculate k_1. The suggested stoicheiometry was established, besides chemical characterisation of the mixture by standard instrumental techniques, through direct determination of at least two components in equation (1). It was found that the percentage of reaction calculated from manometric readings and from direct determination of reactant

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† Part III, N. Barroeta, A, Maccoll, M. Cavazza, L. Congiu, and A. Fava, *J. Chem. Soc.* (*B*), 1971, 1267.

[1] N. Barroeta and A. Maccoll, *J. Amer. Chem. Soc.*, 1971, **93**, 5787.

[2] N. Barroeta, A. Maccoll, M. Cavazza, L. Congiu, and A. Fava, *J. Chem. Soc.* (*B*), 1971, 1264.

[3] N. Barroeta, A. Maccoll, and A. Fava, unpublished results.

and/or products showed a 1 : 1 correlation within experimental error as shown in Table 1 where the regression coefficients between the percentage of reaction by pressure (P_1) and by direct analysis (P_2) are given. Throughout this paper the errors are calculated as the standard deviation from the mean. The three reactions reported follow the general pattern of thiocyanate pyrolysis, namely: (*a*) the total pressure increases smoothly to a final value of 1·80—2·00 times the initial pressure depending upon compound, initial concentration, and temperature; (*b*) high-sensitivity gas chromatography reveals a very clean reaction during the first half-life of the elimination. In later stages of the reaction, several compounds of low molecular weight become noticeable although their proportions are widely erratic between runs and presumably come from initial impurities of the reactant and secondary reactions of the products. Exceptions are the isomeric isothiocyanates which increase steadily from the beginning of the reaction to near equilibrium values at four or more half-lives of elimination, and have been demonstrated [2,4] to come from reaction (−1). A typical example is shown for isopropyl thiocyanate in Figure 1. This suggests that the acid present in the mixture is the isothiocyanic form. In order to check this possibility ethyl, isopropyl, t-butyl, and but-3-enyl thiocyanates were pyrolysed to *ca.* 20% reaction, whereupon the mixture was taken out of the vessel. After removal of the unchanged material by selective condensation, the gaseous products were expanded in a 10 cm i.r. gas cell and the spectrum taken. This spectrum agrees completely with one constructed from the published spectrum [5] of HNCS and the spectrum of the olefin, prepared by known methods.

TABLE 1

The ratio $P_1 : P_2$ determined from product analysis

Thiocyanate pyrolysed	Compound determined directly		
	Reactant [a]	Olefin [b]	Acid [c]
Isopropyl	0·951 ± 0·046 (10, 75) [d]	1·037 ± 0·062 (6, 75)	0·991 ± 0·017 (5, 70)
t-Butyl			1·016 ± 0·020 (9, 80)
But-3-enyl	0·963 ± 0·040 (18, 50)		1·032 ± 0·058 (40, 55)

[a] Determined by g.l.c. by use of the Internal Standard method. [b] Determined by *V–P–T* measurements. [c] Titrated with standard alkali. [d] Figures given in parentheses represent the number of degrees of freedom and the extension of linearity of the correlation (given as percentage of reaction) respectively.

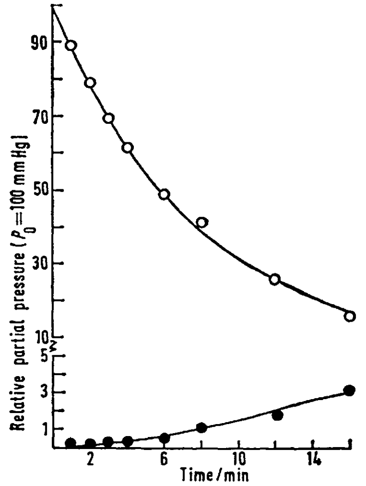

FIGURE 1 Reaction profile for pyrolysis of isopropyl thiocyanate and isothiocyanate at 300·6 °C; ○, Pr$^{\rm i}$SCN; ●, Pr$^{\rm i}$NCS

As several of the substrates currently under study in our laboratory yield buta-1,3-diene as one product and some of its thermal reactions are potential sources of complications in the study of unsaturated compounds like but-3-enyl thiocyanate, we decided to look more closely at the pyrolysis of butadiene under our working conditions. The full results will be published elsewhere, but at the temperatures at which but-3-enyl thiocyanate was pyrolysed, the only important reaction of butadiene is dimerisation to vinylcyclohexene, but even this reaction had progressed to no more than *ca.* 2% during the first half-life of the elimination at the highest temperature at which the latter reaction can be measured.

Once the total pressure of the system was proved to be a valid measurement of the extent of reaction, as explained above, first-order rate constants were calculated from the initial rate of pressure increase. About 12 pressure readings were taken for each run and the rate constants were calculated from the equation $\ln(2P_0 - P_t) = -k_1t + \ln P_0$. The standard error of k_1 for a collection of runs at the same temperature and varying initial pressures was *ca.* 3—4%. The calculated first-order rate constants are independent of concentration as shown in Table 2.

TABLE 2

Effect of concentration on calculated first-order rate constants

Thiocyanate	Initial pressure (mmHg)	10^4k_1/s^{-1}
Pr$^{\rm i}$ at 277·7 °C	31·5	4·62
	62·5	4·74
	111·0	4·76
	145·0	4·70
	221·0	4·64
	247·0	4·64
	275·0	4·90
Bu$^{\rm t}$ at 274·9 °C	32·7	23·8
	51·8	24·9
	85·5	24·2
	94·0	24·3
	122·3	24·2
	128·6	24·6
	149·0	24·6
	227·2	24·3
But-3-enyl at 296·4 °C	35·5	5·70
	68·0	5·26
	103·0	5·72
	121·8	5·70
	184·0	5·36
	248·5	5·88
	280·0	5·84
	305·0	5·47

TABLE 3

Arrhenius parameters for thiocyanate pyrolysis

Thiocyanate	*a*	*b*	$\log_{10}(A/\mathrm{s}^{-1})$	E_a/kcal mol^{-1}	Ref.
Pr$^{\rm i}$	8	10	12·27 ± 0·15	39·33 ± 0·38	This work
Bu$^{\rm t}$	11	3	12·28 ± 0·32	37·37 ± 0·79	This work
But-3-enyl	7	10	12·84 ± 0·27	41·87 ± 0·70	This work
Et	7	10	11·77 ± 0·21	40·51 ± 0·58	1
Bu$^{\rm s}$	7	10	1·230 ± 0·16	38·82 ± 0·40	2

[a] Number of points used in the correlation. [b] Mean number of runs averaged at each temperature.

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[4] N. Barroeta, Ph.D. Thesis, University of London, 1968.

[5] C. Reid, *J. Chem. Phys.*, 1950, **18**, 1512.

In order to ascertain the dependence of the specific rate constant on temperature, the data were fitted, by the least-squares method, to Arrhenius equations in the usual form. These results are summarised in Table 3 together with previous data for comparison.

Attempts to Influence the Velocity of the Reaction.—In order to ascertain the most important characteristics of the mechanism, several diagnostic tests were conducted in which the effect of added substances and the extent and nature of the reaction vessel's surface on reaction velocity was investigated. Some representative results of the experiments carried out with olefinic inhibitors and air are presented in Table 4 while results where the surface : volume ratio of the vessels was varied are shown in Table 5.

TABLE 4

Effect of additives on the pyrolysis of thiocyanates

Additive [a]	Additive (%)	t/°C	k(additive)/ k(no additive)
	Isopropyl thiocyanate		
C	44·0	277·9	1·017
C	124·4	277·9	1·013
C	170·0	300·7	1·015
P	164·1	289·7	0·988
A	6·4	289·7	1·052
A	16·7	289·7	0·964
	t-Butyl thiocyanate		
C	88·8	259·5	0·950
C	145·3	259·5	1·000
C	238·9	259·5	1·024
	But-3-enyl thiocyanate		
C	37·5	264·6	1·057
C	168·8	264·6	1·057
C	74·0	284·7	0·955
C	201·0	284·7	1·000
A	23·6	264·6	0·960
A	28·4	284·8	1·014
A	9·5	318·0	1·012

[a] A, air; C, cyclohexene; P, propene.

TABLE 5

Effect of reaction vessel conditions on specific rate [a]

Surface [b]	t/°C	Effect on rate [c]
	Isopropyl thiocyanate	
P	258·6	0·975
P	276·9	0·986
S	291·0	0·974
S	300·6	1·011
	t-Butyl thiocyanate	
S	236·8	1·042
S	258·81	0·995
S	274·94	0·986
	But-3-enyl thiocyanate	
P	269·3	1·098
T	269·3	0·995
T	289·1	1·027
T	300·8	1·015

[a] Surface: volume ratio 6·8 throughout. P = Clean Pyrex glass; S = 'seasoned' by the allyl bromide method followed by repeated pyrolysis of isopropyl thiocyanate; T, 'seasoned' by repeated pyrolysis of isopropyl thiocyanate. [c] Given as the ratio of the rate constant for runs in the packed vessel to those obtained in a 'normal vessel' of $S/V = 1{\cdot}0$ cm^{-1}.

These reactions are neither affected by the addition of radical-chain inhibitors, nor show the oxygen effect. Further, they are unaffected by the nature and the extent of the surface of the walls of the reaction vessel. There is an important exception to the latter statement, however, in that the reaction of t-butyl thiocyanate is strongly catalysed by clean Pyrex glass surfaces. Starting with a new vessel, the specific rate falls abruptly within the first few runs and only attains a reproducible value after repeated pyrolysis. This effect was more pronounced as the surface : volume ratio was increased. Nevertheless the products were the same irrespective of the nature and extent of surface.

DISCUSSION

In previous papers [1,2] we disclosed the main features of the mechanisms for the reactions of ethyl and s-butyl thiocyanates and discussed the implications of the observed effect of several parameters on rate. As the present results do not contradict the main conclusions of those papers we assume that we are dealing with a homogeneous molecular reaction. In spite of the resemblance in many chemical properties displayed by thiocyanates and organic halides in solution, a distinct property of the thiocyanate reaction in the gas phase appears to be the constancy of mechanism. It is established that, for example, for gaseous alkyl bromides, relatively small changes in structure can lead to completely different mechanisms. Thus n-propyl,[6] isopropyl,[7] and allyl [8] bromides decompose by radical-chain, molecular, and radical-non-chain mechanisms respectively, whereas thiocyanates seems to adhere to the molecular mechanism. This indicates an inherent tendency of the latter to reorganise valence states internally in a more or less synchronous manner instead of breaking particular bonds, either homolytically or heterolytically. This reorganising tendency seems to be maintained even in solution in polar solvents as illustrated by the finding that the isomerisation and other thermal reactions of organic thiocyanates in solution avoid the formation of free ions except perhaps in a few very special cases.[9,10] It has also been shown that allyl thiocyanates enter readily into six-membered transition states to produce rearranged isothiocyanates.[11] The geometry of these transition states is formally the same as the one we believe is operating in the elimination as shown in Figure 2. This formulation is favoured, although not proved, by: (*a*) the structure of the acid eliminated is that of isothiocyanic acid as shown by i.r. analysis of gaseous products; (*b*) the addition of acid produced to added olefins yields almost exclusively isothiocyanates as expected for the addition of isothiocyanic acid to double bonds; [4] and (*c*) the electronic distribution within the thiocyanate moiety, as indicated

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[6] J. T. D. Cross and V. R. Stimpson, *Austral. J. Chem.*, 1968, **21**, 973.

[7] A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 1955, 979.

[8] A. Maccoll, *J. Chem. Soc.*, 1955, 965.

[9] N. Barroeta, A. Maccoll, M. Cavazza, L. Congiu, and A. Fava, in preparation.

[10] L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, 1969, **91**, 2961, and references therein.

[11] A. Fava, in 'Organic Sulfur Compounds,' ed. N. Kharasch and C. Meyers, Pergamon, 1966.

by dipole moment[12] and atomic charge,[13] suggests a higher activity of the nitrogen atom toward hydrogen abstraction. However, the actual situation might not be a perfectly developed six-membered structure as the initial interaction of the hydrogen atom is likely to occur with the π cloud of the C–N bond from a not perfectly planar configuration. The hydrogen atom would afterward progressively ' fall ' toward the nitrogen as the rehybridisation in the thiocyanate group proceeds.

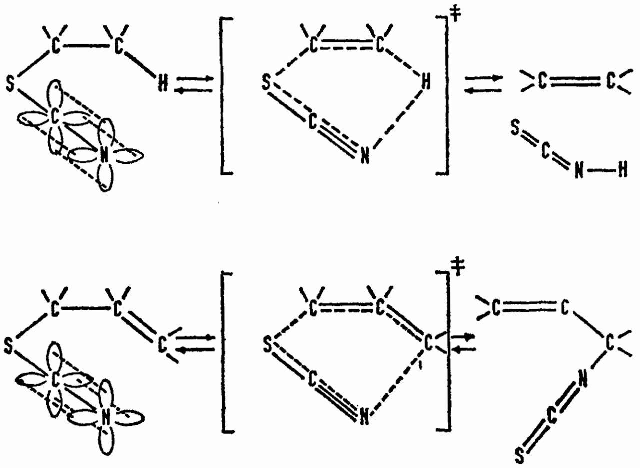

FIGURE 2 The transition states for elimination and isomerisation

Table 6 summarises all the data now available on reactivity of organic thiocyanates. For comparison some representative relative rate values for a moderately polar gas reaction, such as the pyrolysis of esters, as well as relative rates for a quasi-heterolytic reaction such as the pyrolysis of alkyl halides are also included in Table 6. On the basis of the same criteria used to evaluate the degree of polarity of the latter reactions[14,15] the pyrolysis of thiocyanates appears to be a highly concerted reaction with very little charge separation. Maccoll[14] has shown that in the case of chlorides and bromides, β-vinyl and phenyl substitution do not increase the reaction rate to any greater extent than that obtained for a methyl group, which implies that conjugation with the incipient carbon–carbon double bond is not important. In the case of thiocyanates the effects of the β-vinyl and phenyl groups, although relatively small, are significant and indicate substantial double-bond formation in the transition state.

TABLE 6

Relative rates at 307·4 °C[a]

Radical	Leaving group SCN	OAc	Br
Et[b]	1·00	1·00	1·00
$\mathrm{Pr^i}$	8·70	34·5	278·8
$\mathrm{Bu^t}$	49·1	3700·0	80,220·0
$\mathrm{Pr^n}$[c]	1·56	0·84	5·67
$\mathrm{Bu^s}$	14·8	17·2	682·0
But-3-enyl	3·64	—	—
2-Phenylethyl[c]	3·52	5·75	—

[a] Data for acetates and bromides are ' preferred ' values in the compilation by Benson and H. O'Neal, U.S. Department of Commerce, NSRDS–NBS 21, 1970. [b] Rates are given relative to ethyl radical for each kind of compound. [c] Runs were only made at 307·4 °C in order to get an experimental value of k_1.

In conclusion, the gas-phase elimination of organic thiocyanate can be formally regarded as a highly concerted reaction proceeding through a six-centred transition state to give olefins and isothiocyanic acid at moderate temperatures.

EXPERIMENTAL

Reagents.—The thiocyanates were prepared by the alkali-metal thiocyanate–organic bromide method[16] and roughly purified to the point where the isomeric isothiocyanates were the main impurities. These were then removed by selective formation of thioureas and the remaining thiocyanate finally purified by fractional distillation under reduced pressure to yield a product of 99% purity or better.

All other reagents were commercial products purified according to common practice.[17]

Analytical.—Thiocyanates were analysed by g.l.c. on a variety of columns, but the more useful were found to be the 15%, 6 ft × ⅛ in, dinonyl phthalate and diethylene glycol on 80—100 mesh Chromosorb X.

Isopropyl thiocyanate and but-3-enyl thiocyanate were determined by use of toluene and cumene as internal standard with a thermal conductivity detector. The calibration factors (f) (defined by the expression: pressure compound/pressure standard = f × area compound/area standard) were: 2·165 ± 0·019 and 1·107 ± 0·019 respectively.

Olefins were determined as follows: the total mixture was removed from the reaction vessel and passed through a 1-ft column filled with soda-lime and then through a trap at −80 °C. The olefin fraction was finally condensed at liquid-nitrogen temperature in a calibrated bulb, where it was then brought to room temperature and its amount computed from V–P–T measurements. Gases from this bulb were taken for qualitative analysis, mainly by i.r. and g.l.c.–m.s. combination.

For the acid determinations, the total mixture was condensed in a special trap containing about 15 cm³ of a 10% aqueous solution of ethanol and titrated with standard alkali. Blank experiments showed no interference by the unchanged thiocyanates.

Apparatus.—The reaction vessel was a Pyrex glass cylinder, 5 cm in length and of 238 ml capacity, which was attached to a conventional vacuum line and separated from a mercury manometer by means of an optical glass diaphragm gauge.

The furnace was an electrically heated aluminium block whose temperature was kept constant within 0·2 °C with an RT3 proportional temperature controller from Associated Electrical Industries Ltd., Harlow, England.

[1/1581 *Received*, 1*st September*, 1971]

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