Pyrolysis of Thio- and Isothio-cyanates. Part V.† The Pyrolysis of But-3-enyl and 1-Methylprop-2-enyl Isothiocyanates

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The homogeneous thermal elimination of isothiocyanic acid from but-3-enyl and 1-methylprop-2-enyl isothiocyanates has been investigated in the ranges 30—300 mmHg and 240—390 °C. The primary process is unimolecular, although secondary reactions of the products are more extensive than in the case of the isothiocyanates previously studied. The temperature dependences of the rate constants are given by equations (i) and (ii) for the but-3-enyl and 1-methylprop-2-enyl cases respectively. The increased reactivity brought about by unsaturation in the carbon skeleton is due mainly to the allylic weakening of the carbon–nitrogen bond whereas conjugation with the forming double bond is unimportant.

$$\log_{10} k_1/\mathrm{s}^{-1} = 12{\cdot}40 \pm 0{\cdot}20 - (45{,}040 \pm 320)/2{\cdot}303\,RT \text{ cal mol}^{-1} \qquad \text{(i)}$$

$$\log_{10} k_1/\mathrm{s}^{-1} = 11{\cdot}84 \pm 0{\cdot}30 - (37{,}550 \pm 750)/2{\cdot}303\,RT \text{ cal mol}^{-1} \qquad \text{(ii)}$$

In Parts I [1] and III [2] we have dealt with the effect of methyl substitution on thermal stability of alkyl isothiocyanates and as a result we have assigned these compounds an intermediate position between the pyrolysis of alkyl halides and cyclobutanes, which exemplify the extremes of the so-called 'spectrum of polarities' [3] in the transition state.

In this paper we discuss the effect of a double bond suitably located to the bonds to be broken and the developing unsaturation in the transition state. This problem has been treated by several authors for reactions of alkyl halides, both in solution [4] and in the gas phase.[5-7]

RESULTS

All the evidence supports equation (1) as the best representation of the stoicheiometry of the primary reaction in the pyrolysis of both but-3-enyl and 1-methylprop-2-enyl isothiocyanates. This is followed by the back addition of isothiocyanic acid to buta-1,3-diene and by the pyrolysis of the latter to give a complex mixture of hydrocarbons, the most abundant of which is 4-vinylcyclohexene, although methane, ethane, propane, butenes, cyclohexane, and benzene amongst other unidentified substances were detected in reaction times greater than three half lives. Besides the above hydrocarbons carbon disulphide was also produced, especially at the highest temperatures and apparently came from some reaction of isothiocyanic acid, as it was always present as an impurity when the latter was prepared by independent methods. Even at low conversion (*ca.* <25%) as much as seven unidentified substances of low retention time, some of which were detected in the starting material, were present in the reaction mixture. Nevertheless, in no case did the total chromatographic area of these 'by-products' exceed 3% of the area corresponding to the main product buta-1,3-diene. The product analysis was complicated by the rapid addition of the acid to buta-1,3-diene occurring in the liquid phase during the trapping procedure and leading to several species which are easily interconverted *via* allylic isomerisation.[8]

$$\mathrm{C_4H_7{\cdot}NCS} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH_2} + \mathrm{HNCS} \qquad (1)$$

In view of the above difficulties, the kinetic study was limited to the first 25% of reaction. The total pressure of the system is a valid measure of the extent of reaction (Table 1) and first-order rate constants were calculated in the usual way. The validity of the assumed first-order kinetics was confirmed by the fact that the rate constants were independent of initial pressure within the range 30—300 mmHg.

TABLE 1

The ratio % reaction by pressure: % reaction by product analysis

Isothiocyanate	Direct determination of * Reactant [a]	 Olefin [b]	 Acid [c]
$CH_2{=}CHCH_2CH_2NCS$		1·030 ±0·028 (50,4)	1·009 ±0·045 (50,15)
$CH_2{=}CHC(NCS)H{-}Me$	1·044 ±0·086 (50,9)		0·997 ±0·021 (60,17)

[a] Determined by g.l.c. by using toluene as internal standard. [b] Determined by *V–P–T* measurements. [c] Titrated with standard alkali.

* The first figure in parentheses is the % reaction to which the correlation applies. The second figure in parentheses is the number of determinations carried out.

The reactions studied are homogeneous, unimolecular decompositions in the sense that they are insensitive to changes in the nature of the vessel surfaces and geometry of the reactor (Table 2). Also they are insensitive to the addition of radical promoters and inhibitors as has been ascertained for other isothiocyanates. For example the pyrolysis of 1-methylprop-2-enyl isothiocyanate was not influenced by the addition of 300% cyclohexene or 32% air.

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† Part IV, N. Barroeta, V. De Santis, and R. Mazzali, *J.C.S. Perkin II*, 1972, 769.

[1] N. Barroeta, A. Maccoll, and A. Fava, *J. Chem. Soc.* (*B*), 1969, 347.

[2] N. Barroeta, A. Maccoll, M. Cavazza, L. Congiu, and A. Fava, *J. Chem. Soc.* (*B*), 1971, 1267.

[3] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33.

[4] C. A. Vernon, *J. Chem. Soc.*, 1954, 423.

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[6] P. J. Thomas, *J. Chem. Soc.* (*B*), 1967, 1238.

[7] C. J. Harding, Ph.D. Thesis, University of London, 1968.

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The results of those experiments in which the effect of temperature on rate was investigated are summarised in Table 3. A least-squares treatment led to the Arrhenius equations (2) and (3) for the but-3-enyl and 1-methylprop-2-enyl case respectively.

$$\log_{10}k_1/\text{s}^{-1} = 12{\cdot}40 \pm 0{\cdot}20 - (45{,}040 \pm 320)/2{\cdot}303\,RT \text{ cal mol}^{-1} \quad (2)$$

$$\log_{10}k_1/\text{s}^{-1} = 11{\cdot}84 \pm 0{\cdot}30 - (37{,}550 \pm 750)/2{\cdot}303\,RT \text{ cal mol}^{-1} \quad (3)$$

TABLE 2

Effect of the condition of the reaction vessel on the rate constants

Isothiocyanate	Nature of surface	SV^{-1}/ cm^{-1}	t/°C	Influencing factor *
But-3-enyl	Clean Pyrex glass	6	335·4	1·01
But-3-enyl	After repeated pyrolysis	6	362·3	1·05
1-Methylprop-2-enyl	Clean Pyrex glass	4	272·1	0·994
1-Methylprop-2-enyl	After repeated pyrolysis	4	294·3	1·02
1-Methylprop-2-enyl	After repeated pyrolysis	4	246·4	0·985
1-Methylprop-2-enyl	Clean Pyrex glass	6	25·0	0·936
1-Methylprop-2-enyl	After repeated pyrolysis	6	282·2	1·03

* Defined as the ratio of the $k_{1\,\text{exp}}$ to the $k_{1\,\text{calc}}$ with the aid of the Arrhenius equation obtained from runs in a 'normal vessel' of S/V 0·95 cm^{-1}.

Preliminary Results for But-2-enyl Isothiocyanate.—As the 1-methylprop-2-enyl isothiocyanate used for the kinetic experiments contained 1·0% of the but-2-enyl isomer a small amount of this was pyrolysed to ascertain any influence it might have. Besides isothiocyanic acid the other main product was again buta-1,3-diene although but-1-ene reached the abnormally high level of 6·8% of total hydrocarbon. Traces of methane, ethane, and butane were also present. Determination of first-order rate constants from the initial rate of pressure increase in the temperature range 280—330 °C allowed the calculation of the approximate Arrhenius parameters log A/s^{-1} = 11·7 and E_a = 39·1 kcal mol^{-1}. With these data we confirmed that no correction was needed for the small amount of but-2-enyl isomer present.

TABLE 3

Effect of temperature on rate constants

t/°C	Number of runs	10^4k_1/s^{-1}
	But-3-enyl isothiocyanate	
323·5	7	0·844 ± 0·020
337·8	13	2·21 ± 0·097
348·7	10	4·47 ± 0·183
357·1	10	7·27 ± 0·131
369·5	8	15·2 ± 0·272
380·0	5	14·2 ± 1·49
386·6	5	32·5 ± 1·97
	1-Methylprop-2-enyl isothiocyanate	
244·6	7	0·902 ± 0·021
255·7	15	2·11 ± 0·044
265·6	18	3·80 ± 0·146
271·5	10	5·84 ± 0·228
278·3	11	9·04 ± 0·217
288·9	13	16·8 ± 0·442
298·9	11	30·1 ± 1·06

DISCUSSION

In previous papers [1,2,9] we have discussed in some detail the mechanistic implications of the observed effects on the rate of several factors, such as nature and extent of reaction vessel surface, additives, and temperature. We have also considered the kind and distribution of products and the effect of methyl substitution on reactivity. All this evidence has given support to important conclusions about the structure and polar character of the transition state. We now concentrate on how the influence of a double bond close to the reaction centre fits into this picture.

Several observations emerge from the relative rates shown in Table 4 which can be summarised as follows.

TABLE 4

Summary of kinetic data for isothiocyanates

Isothiocyanate	log$_{10}$ (A/s^{-1})	E_a/ kcal mol^{-1}	Relative rate at 307 °C	Ref.
Ethyl (I)	12·4	45·4	1·00	1
Isopropyl (II)	13·0	42·9	33·4	1
s-Butyl (III)	12·5	41·3	37·2	2
1-Methylprop-2-enyl (IV)	11·8	37·6	241·0	This work
But-3-enyl (V)	12·4	45·0	1·31	This work
But-2-enyl (VI)	11·7	39·1	47·0	This work

(*a*) The substitution of a methyl by a vinyl group in the α-position brings about an increase in rate of 7·2 as given by the ratio (IV) : (II). A similar factor (6·5), and perhaps a better comparison, is obtained by the relative rate of (IV) to (III) where a double bond has been introduced in the same basic structure. These overall relative reactivities should be considered carefully however; for example, the ratio (IV) : (II), although it is enhanced by a factor of 100 which comes from the activation energy term in favour of the allylic compound, it is reduced to the quoted value by a factor of 14 from the entropy term. The corresponding factors for the chlorides [3,10,11] are 5·5 and 1·1 (a factor of 2·4 is obtained when a methyl group is substituted in t-butyl chloride). This effect is stronger in the isothiocyanate, although we realise that for α-vinylation, not only the allylic weakening of the bonds to be broken but also incipient conjugation with the double bond being formed might be important. (*b*) The rate ratio (V) : (I) tells us that this conjugation or even the homolytic weakening of the β-carbon–hydrogen bond are of negligible importance and in fact the Arrhenius parameters (Table 4) are

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[9] N. Barroeta and A. Miralles, *J. Org. Chem.*, 1972, **37**, 2255.
[10] W. Tsang, *J. Chem. Phys.*, 1964, **41**, 2487.
[11] W. Tsang, *J. Chem. Phys.*, 1964, **40**, 1171.

the same within experimental error. This implies that the α-vinyl group exerts its influence, mainly through allylic weakening of the carbon–nitrogen bond and this is reflected in the differences in Arrhenius parameters. While substitution of α-methyl by α-vinyl in the chlorides lowers log A and E_a by 0·37 and 2·3 kcal mol^{-1} respectively, the same changes are 1·16 and 5·3 kcal mol^{-1} for isothiocyanates.

It has been pointed out[2] that, contrary to the alkyl halides the correlation E_a *vs.* $D_{R^+X^-}$ for isothiocyanates is of the form $E_a = b + mD_{R^+X^-}$. This equation has been interpreted by one of us (N. B.) as 'the operation of two interaction mechanisms' which finds a quantitative expression in a 'linear combination of two model transition states'. Following this reasoning one is tempted to put $b = nD_{R-X}$ in the above equation although we feel that much more data is needed to check all the implications of this assumption.

Finally we think that the results obtained with but-2-enyl isothiocyanate, incomplete as they are, deserve some comment. Harding[12] has suggested that in the case of the chlorides, whenever the hydrogen atom available for 1,2-elimination is vinylic, and a hydrogen is available on C-4, this is preferentially eliminated with a synchronous migration of the double bond in a six-centre transition state. The formation of buta-1,3-diene from but-2-enyl isothiocyanate and the approximate Arrhenius parameter obtained, are highly suggestive of this kind of mechanism, although until data from deuteriated compounds are available we can not be certain about this point. Although no effort was made to produce a sterically pure compound our sample seemed to be practically pure *trans*-but-2-enyl isothiocyanate. This follows from comparison of its n.m.r. spectrum with those from *cis*- and *tran*-but-2-ene and, more importantly, from an analysis of the reactivity itself.

A comparison of the data collected by Harding for allylic chlorides and our data on isothiocyanates shows that the effect of vinylation on rate is about the same for both classes of compounds. On the other hand the relative positions of the double bond and the leaving group are responsible for relatively large differences in reactivity. Thus, the relative rates for pyrolysis of 1-methylprop-2-enyl, *cis*-but-2-enyl, and *trans*-but-2-enyl chlorides at 361 °C are 1 : 9 : 0·18.[12] The rate of pyrolysis of but-2-enyl isothiocyanate is 0·19 at 307 °C relative to the 1-methylprop-2-enyl compound. This evidence strongly indicates that the compound is in the *trans*-configuration. Initially no rapid reaction was observed that could be attributed to a significant amount of the *cis*-isomer.

EXPERIMENTAL

Reagents.—1-Methylprop-2-enyl isothiocyanate was prepared from but-2-enyl bromide by substitution with sodium thiocyanate followed by isomerisation in boiling acetone. After a first distillation it contained 10% but-2-enyl isothiocyanate as the main impurity detectable by g.l.c. A final purity of 99% was obtained by fractional distillation under reduced pressure. The following derivatives were prepared: α-naphthylthiourea, m.p. 143·5 °C (lit.,[13] 129—130 °C) (Found: C, 70·7; H, 6·2; N, 10·7; S, 12·2. Calc. for $C_{15}H_{16}N_2S$: C, 70·3; H, 6·3; N, 10·9; S, 12·5%); *p*-tolylthiourea, m.p. 129·5 °C (lit.,[13] 125 °C) (Found: C, 65·8; H, 7·3; N, 12·7; S, 14·6. Calc. for $C_{12}H_{16}N_2S$: C, 65·5; H, 7·3; N, 12·7; S, 14·5%). But-3-enyl isothiocyanate was obtained from but-3-enylamine according to the procedure of Ettlinger and Hodgkins.[14] The amine was in turn prepared *via* a modified Gabriel synthesis[15] from the corresponding bromide which was a commercial product. The product used for the kinetic study was at least 99% pure. But-2-enyl isothiocyanate was separated by preparative g.l.c. from the 1-methylprop-2-enyl isothiocyanate. Its *p*-tolylthiourea derivative had m.p. 80 °C (lit.,[13] 81—82 °C) (Found: C, 65·6; H, 7·3; N, 12·7. Calc. for $C_{12}H_{16}N_2S$: C, 65·5; H, 7·3; N, 12·7%).

Analytical.—All reactants and products, both primary and the more important secondary ones were thoroughly analysed by g.l.c.–m.s., n.m.r., and i.r. spectroscopy. The last of these was particularly useful in the identification of isothiocyanic acid[16] in the gaseous products. The details of the analytical techniques and apparatus were reported in previous papers of this series.

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