Kinetics of the Thermal Decompositions of 4-Chlorocyclohexene and 3-Chlorocyclohexene

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The gas-phase thermal decompositions of 4-chlorocyclohexene in the temperature range 320—370 °C and of 3-chlorocyclohexene in the range 250—310 °C are homogeneous and unimolecular in a ' seasoned ' reaction vessel. The rate constants for the elimination of hydrogen chloride are given by the equations $k_1 = 10^{13\cdot17 \pm 0\cdot25} \exp -(48{,}380 \pm 700)/RT\ \mathrm{s}^{-1}$ and $k_1 = 10^{11\cdot16 \pm 0\cdot22} \exp -(36{,}950 \pm 550)/RT\ \mathrm{s}^{-1}$ respectively. The double bond when β to the chlorine atom has no effect on the rate of elimination of hydrogen chloride but when α to it increases the rate *ca.* 100-fold.

MACCOLL [1] and his co-workers have shown that in the gas phase, just as in solution, studies of the effects of substituents α and β to halogen give a good insight into the mechanism involved in the molecular elimination of hydrogen halides from organic halides. We report the effects of unsaturation on the rate of elimination as represented in the compounds 4- and 3-chlorocyclohexene. The effects of α- and β-vinyl groups on halogen-acid elimination from straight-chain chloro- and bromo-hydrocarbons have been reported by Thomas.[2,3] Our results are consistent with the quasi-heterolytic transition state suggested by Maccoll and Thomas.[1]

EXPERIMENTAL

4-Chlorocyclohexene was prepared by chlorinating cyclohexane-1,4-diol with thionyl chloride [4] to give 4-chlorocyclohexanol and distilling this over potassium hydrogen sulphate. The olefin was purified by fractional distillation; b.p. 122—124 °C at 760 mmHg, 42—45 °C at 10 mmHg; n_D^{20} 1·4822 (lit.,[5] b.p. 60—61 °C at 43 mmHg; n_D^{20} 1·4822) (Found: Cl, 30·35. Calc. for C_6H_9Cl: Cl, 30·45%).

3-Chlorocyclohexene, prepared by chlorinating 3-hydroxycyclohexene with thionyl chloride,[1] had b.p. 145—147 °C at 760 mmHg; n_D^{20} 1·4883 (lit.,[5] b.p. 58 °C at 29 mmHg; n_D^{20} 1·4881) (Found: Cl, 30·25%). Cyclohexa-1,4- and -1,3-dienes were obtained from Aldrich Chemicals.

Procedure.—The parameters for the rate of reaction were obtained by use of a static gas-phase system. The reaction vessel was ' seasoned ' by the decomposition products of allyl bromide. The rate of elimination of hydrogen chloride was followed by measuring the rate of pressure increase with time. For 4-chlorocyclohexene, however, the reaction was followed by measurement of the hydrogen chloride produced by titration in aqueous media with borax solution. From the amount of borax solution used, the corresponding pressure of hydrogen chloride was read off a calibration curve. The rate coefficients (k_1) for the reaction were then calculated from equation (1) where

$$k_1 t = 2\cdot303 \log P_0/(P_0 - P_a) \qquad (1)$$

P_0 is the initial pressure and P_a the pressure of the hydrogen chloride produced at time t. With 3-chlorocyclohexene, the change of pressure with time was representative of the rate of reaction; this was established by comparing the percentage decompositions as determined from pressure measurements with those determined by titration. The rate constants were then calculated from plots of $\log(2P_0 - P_t)$ against t, P_t being the pressure at time t. The products of pyrolysis were analysed by g.l.c. The column used was 6 ft × 0·25 in of 20% (w/w) β,β′-oxydipropionitrile on Aeropak 30, 80—100 mesh.

RESULTS AND DISCUSSION

Pure samples of cyclohexa-1,4-diene with and without hydrogen chloride were left in the reaction vessel for very long periods at the temperatures at which the reactions were studied; analysis of the products (g.l.c., n.m.r.) showed benzene and traces of cyclohexene. Cyclohexa-1,3-diene treated similarly also gave mainly benzene and traces of cyclohexene. The product analyses for the chlorides are shown in Table 1. From these results we conclude that at these temperatures 4-chlorocyclohexene decomposes according to the Scheme and this is why pressure change was not used to determine the rate coefficients. The 1,3-diene, however, is sufficiently stable at the pyrolysis temperatures for pressure change to be used as a measure of the decomposition of the 3-chloro-compound. At higher

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[1] A. Maccoll, ' Theoretical Organic Chemistry,' Butterworths, London, 1958.

[2] P. J. Thomas, *J. Chem. Soc.*, 1959, 1192.

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

[4] Kamaluddin Ahmad, F. Merlin Bumpus, and F. M. Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 3392.

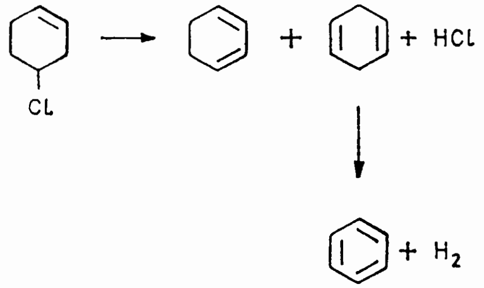
[5] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2161.

temperatures, however, the 1,3-diene may also decompose to give largely benzene and some cyclohexene. Our observations of the decompositions of the 1,4- and 1,3-dienes are in agreement with the studies of Benson *et al.*[6,7]

TABLE 1

Product analysis by g.l.c.

	4-Chlorocyclohexene		3-Chlorocyclohexene	
t/°C	361	383	340	383
Decomposition (%)	20	25	30	30
1,3-Diene (%)	79·6	75·4	100	96·1
1,4-Diene (%)	8·1	6·7		
Benzene (%)	12·2	17·4		3·5
Cyclohexene (%)	0·1	0·5		0·5



The homogeneity of the reactions was established by comparing the rates in unpacked (S/V 1·2 cm^{-1}) and packed (S/V 7·0 cm^{-1}) reaction vessels (Table 2). There was no dependence on pressure of the first-order rate coefficients (Table 3). The rates were not affected by the addition of cyclohexene as inhibitor (Table 4). The variation of the rate coefficients with temperature is shown in Table 5, and by the method of least squares, the Arrhenius equations (2) and (3) were evaluated for 4- and 3-chlorocyclohexene respectively.

$$k_1 = 10^{13\cdot17 \pm 0\cdot25} \exp - (48{,}380 \pm 700)/RT \text{ s}^{-1} \quad (2)$$

$$k_1 = 10^{11\cdot16 \pm 0\cdot22} \exp - (36{,}950 \pm 550)/RT \text{ s}^{-1} \quad (3)$$

TABLE 2

Homogeneity of the reaction

	4-Chlorocyclohexene (347·5 °C)		3-Chlorocyclohexene (255 °C)	
		Packed vessel		Packed vessel
10^5k_1/s^{-1}	12·5	12·8	7·00	7·12

TABLE 3

Dependence of k_1 on initial pressure

	4-Chlorocyclohexene (347·5 °C)			3-Chlorocyclohexene (268 °C)		
P_0/mmHg	70	109	150	60	105	140
10^5k_1/s^{-1}	12·4	12·6	12·6	17·8	17·7	18·0

TABLE 4

Effect of inhibitor (cyclohexene)

	4-Chlorocyclohexene (327 °C)			3-Chlorocyclohexene (247 °C)		
P_0/mmHg	120	80	50	105	70	73
P_i/P_0	0	0·84	1·50	0	0·95	1·50
10^5k_1/s^{-1}	3·80	3·70	3·60	4·60	4·60	4·55

From the results in Tables 1—5 we conclude that for the two chlorides the elimination is homogeneous and unimolecular. The Arrhenius parameters for some other secondary chlorides[3,8,9] and their relative rates at 360 °C are shown in Table 6. 4-Chlorocyclohexene decomposes at about the same rate as chlorocyclohexane. This is to be expected on the basis of the Maccoll–Thomas[1] hypothesis that the transition state involves the extension and polarisation of the C–Cl bond. That the double bond β to the halogen has no effect on the rate has also been observed by Thomas[2] in the case of $MeCHBr{\cdot}CH_2{\cdot}CH{=}CH_2$. The ratio of rate constants at 380 °C for the latter compound and $MeCHBr{\cdot}CH_2Me$ is 1·05 : 1.

TABLE 5

Effect of temperature on rate coefficients

4-Chlorocyclohexene

t/°C	327·0	347·5	367·0	369·0	373·0	393·1
No. of runs	6	4	4	5	3	4
10^5k_1/s^{-1}	3·70	12·5	44·0	50·6	72·0	194·0

3-Chlorocyclohexene

t/°C	247·0	255·0	268·0	276·0	279·2	297·2	308·9
No. of runs	5	6	5	4	5	4	3
10^5k_1/s^{-1}	4·40	7·00	17·9	26·0	34·7	100	192

TABLE 6

Arrhenius parameters and relative rates at 360 °C

Compound	log A	E/kcal mol^{-1}	10^4k_{360}/ s^{-1}	Relative rate
Cyclo-$C_6H_{11}Cl$ [a]	13·77	50·0	3·24	1·10
Bu^sCl [b]	13·62	49·6	3·16	1·07
$CH_2{=}CH{\cdot}CHClMe$ [c]	13·34	48·5	3·98	1·35
$CH_2{=}CMe{\cdot}CHClMe$ [c]	13·28	46·9	12·3	4·16
3-Chlorocyclohexene [d]	11·15	36·9	257	87·1
4-Chlorocyclohexene [d]	13·17	48·4	2·95	1·00

[a] Ref. 8. [b] Ref. 9. [c] Ref. 3. [d] This work.

The ratio of 4 : 1 of the diene products (1,3-diene : 1,4-diene) can be explained by the fact that after the extension and polarisation of the C–Cl bond, which is the rate-determining step, there are two possibilities as to the type of diene that could be formed. The 1,3-diene should be favoured as the result of allylic weakening of the β-carbon–hydrogen bond (position 3) thus facilitating the incipient conjugation in the 1,3-diene. That this is observed is further evidence in favour of this type of transition state (I). The small decrease in the activation energy is matched by a corresponding small decrease in the A factor.

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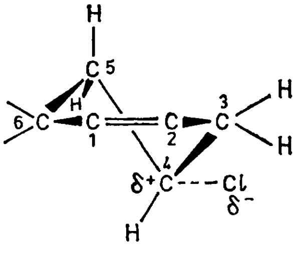
[6] S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 1967, **63**, 985.

[7] S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, 1967, **89**, 5351.

[8] E. S. Swinbourne, *Austral. J. Chem.*, 1958, **11**, 314.

[9] A. Maccoll and R. H. Stone, *J. Chem. Soc.*, 1961, 2756.

The large increase in rate in the 3-chlorocyclohexene is not unexpected because if the transition state is similar to (I) the reaction now involves an allylic carbon–halogen bond leading to the formation of a conjugated diene also with the possibility of the stabilisation of the transition state by incipient conjugation with the forming double bond. This effect must be very pronounced since it leads to a large decrease in the activation energy and hence fast decomposition, but it is in keeping with the general formulation for transition states in this type of reaction wherein the nature and environment of the carbon–halogen bond is of far greater importance than that of the eliminated hydrogen atom.



(I)

Thomas found that in the systems 3-chlorobut-1-ene and 3-chloro-2-methylbut-1-ene the α-vinyl groups do not increase the rates very much; however, it should be noted that in the case of 3-chloro-2-methylbut-1-ene (Table 6) there is a small decrease in activation energy. Our low activation energy may indicate that this type of incipient conjugation is much more favourable in the alicyclic system than in the straight chain.

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