J. Chem. Soc. (B), 1971

# Strain Energy Effects in the Gas-phase Elimination Reactions of Cycloalkyl Chlorides

By M. Dakubu and J. L. Holmes,\* Chemistry Department, University of Ottawa, Ottawa 2, Ontario, Canada

The gas-phase thermal decompositions of cycloheptyl and cyclo-octyl chloride in a ' seasoned ' reaction vessel are homogeneous and unimolecular. Rate constants for their elimination of hydrogen chloride are given by the equations  $k_7 = 10^{12\cdot01} \pm 0.17$  exp - [43,620 ± 240]/RT s<sup>-1</sup> and  $k_8 = 10^{11\cdot88} \pm 0.22$  exp - [42,380 ± 340]/RT s<sup>-1</sup>. The relationship between these Arrhenius parameters and the difference in strain energy between the cycloalkanes and cycloalkenes is discussed.

ALTHOUGH there is a remarkable change in chemical reactivity with ring size,1-5 most studies of this topic have been confined to reactions in solution. The little

<sup>1</sup> H. C. Brown and O. Hans, J. Amer. Chem. Soc., 1956, 78,

<sup>8</sup> H. C. Brown and M. Borkowski, J. Amer. Chem. Soc., 1952, 74, 1894.

gas-phase work is mainly on the heats of hydrogenation of cycloalkenes.6,7

<sup>4</sup> E. W. Garbisch, jun., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, J. Amer. Chem. Soc., 1965, 87, 2932.
<sup>5</sup> C. S. Foote, J. Amer. Chem. Soc., 1964, 86, 1854.
<sup>6</sup> J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, J. Amer. Chem. Soc., 1969, 21, 268.

Chem. Soc., 1939, **61**, 1868. <sup>7</sup> M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, J. Amer. Chem. Soc., 1937, **59**, 831.

 <sup>2735.
 &</sup>lt;sup>2</sup> H. C. Brown, R. S. Fletcher, and R. B. Johannesen, J. Amer. Chem. Soc., 1951, 73, 212.

Maccoll et al.<sup>8,9</sup> studied the gas-phase elimination of halogen acid from cyclopentyl and cyclohexyl bromides, and Swinbourne<sup>10,11</sup> the corresponding chlorides. Both observed that the Arrhenius parameters for the cyclohexyl halides are close to those of the appropriate s-butyl compounds, whereas for the cyclopentyl compounds there is a small but significant drop in activation energy compared with that for the s-butyl compounds. When the present work was being prepared for publication, Herndon and Sullivan<sup>12</sup> reported results on the stirred flow pyrolyses of cyclochloroalkanes,  $C_5$  to  $C_8$ . We have studied the gas-phase pyrolyses of cycloheptyl and cyclo-octyl chlorides in a static system using the cyclohexyl chloride pyrolysis as an internal check against systematic errors. Larger-ring chlorides were not investigated owing to their low volatility. We find, in agreement with Herndon and Sullivan,<sup>12</sup> that the rate sequence is cyclohexyl < cyclopentyl < cycloheptyl < cyclo-octyl; however we observe larger decrements in the activation energies. We attempt to correlate these changes in activation energies with strain energy changes in going from the  $C(sp^3)$  to  $C(sp^2)$  hybridisation. This is the *I*-strain hypothesis of H. C. Brown.<sup>2</sup>

### EXPERIMENTAL

Cycloheptyl chloride, from Aldrich Chemicals, had  $n_{\rm p}^{20}$ 1.4750, b.p. 176-177 °C (Found: Cl, 26.4. Calc. for  $C_7H_{13}Cl: Cl, 26.8\%$ ). Cyclo-octyl chloride was prepared by chlorinating the alcohol with thionyl chloride 13 and had  $n_{\rm p}^{25}$  1.4820, b.p. 50—52° 10 mmHg (Found: Cl, 23.9. Calc. for  $C_8H_{15}Cl$ : Cl, 24.2%). Cycloheptene and cyclooctene were from Aldrich Chemicals.

Procedure.--All the reactions were carried out in reaction vessels which had been 'seasoned' by the decomposition products of allyl bromide.14 The rate of elimination was followed by measurement of the rate of pressure increase in a static system. However it was first verified that the method gives a true representation of the rate of reaction by comparing the percentage decomposition as determined from pressure measurements with that determined by titration of the hydrogen chloride produced. For both compounds the agreement between the two measurements was within 2%. The corresponding olefins were also kept in the reaction vessel both with and without hydrogen chloride during long periods. No pressure change was observed and g.l.c. (10% Apiezon M on Aeropak-30) showed that no new product was formed; analysis of pyrolysis products showed only the original chloride and the corresponding olefin. These checks indicated that the reaction involved only the elimination of the hydrogen chloride to yield an olefin (equation 1).

- <sup>8</sup> M. N. Kale and A. Maccoll, J. Chem. Soc., 1957, 5020.

- J. H. S. Green and A. Maccoll, J. Chem. Soc., 1957, 920, 99
   J. H. S. Green and A. Maccoll, J. Chem. Soc., 1955, 2499.
   E. S. Swinbourne, Austral. J. Chem., 1958, 11, 314.
   E. S. Swinbourne, J. Chem. Soc., 1960, 4668.
   J. M. Sullivan and W. C. Herndon, J. Phys. Chem., 1970, 005
- 74, 995. <sup>13</sup> Kamaluddin Ahmad, F. Merlin Bumpus, and F. M. Strong, 1048 70, 3392

# RESULTS AND DISCUSSION

If the elimination goes to completion then the ratio of the final  $(P_f)$  to the initial  $(P_0)$  pressure would be 2. The results for such measurements are shown in Table 1. The rate coefficients were calculated from plots of  $\log (2P_0 - P_i)$  against t,  $(P_i)$  being the total pressure at time t. The homogeneity of the reactions was established by comparing the rates of elimination in unpacked  $(s/v \ 1.2 \ cm^{-1})$  and packed reaction  $(s/v \ 7.0 \ reaction)$ 

#### TABLE 1

	Ratic	s of fina	l to initi	al pressu	res			
	Cycle	heptyl cl	nloride	Cyclo	clo-octyl chloride			
$\frac{\text{Temp.}/^{\circ}\text{C}}{P_{\text{f}}/P_{\text{0}}}$	$313.0 \\ 1.88$	$\begin{array}{r} 341 \cdot 0 \\ 1 \cdot 93 \end{array}$	$368.0 \\ 1.91$	$312.5 \\ 1.95$	344.0 1.96	$358.5 \\ 1.93$		
		Т	ABLE 2					
	The h	omogen	eity of tl	ne pyroly	vses			
	Cycloh (:	Cycloheptyl chloride (310·0 °C)			Cyclo-octyl chloride (302·0 °C)			
	(packed vessel)			(packed vessel)				
$10^{5}k/s^{-1}$	5.65	Į	5.75	7.35		$7 \cdot 3$		
		Т	ABLE 3					

#### Dependence of $k_1$ on initial pressure Cycloheptyl chloride Cyclo-octyl chloride (378-3 °C) (360·3 °C) 54.0 58.0 72.0 135 154 45.0 55.0 64.0 107.5 $P_0/\text{mmHg}$ 296 278 295 296 215 105k1/s-1 288236 220212

# TABLE 4

#### Effect of inhibitor

	Cycloheptyl chloride (355·5 °C)			Cyclo-octyl chloride (360·3 °C)			
$P_0/mmHg P_i/P_0 = 10^{5}k/s^{-1}$	69∙0 0 86∙0	62·0 1·30 91·0	84·5 1·40 87·0	$45.0 \\ 0 \\ 221$	$92.0 \\ 0.58 \\ 222$	$54.0 \\ 1.19 \\ 230$	$46.5 \\ 2.14 \\ 222$

### TABLE 5

## Variation of the rate coefficients with temperature

Cycloheptyl chloride

Temp./°C No. of runs $10^{5}k_{1}/s^{-1}$	$310.0 \\ 3 \\ 5.65$	${321 \cdot 0 \atop {3} \atop {11 \cdot 5}}$	$323.8 \\ 6 \\ 13.2$	$332 \cdot 8$ $4$ $23 \cdot 3$
Temp./°C No. of runs $10^{5}k_{1}/s^{-1}$	$egin{array}{c} 341\cdot0\5\38\cdot4 \end{array}$	$354{\cdot}6\3 85{\cdot}0$	$\begin{array}{r} 368 \cdot 0 \\ 7 \\ 163 \end{array}$	$378\cdot 3$ 7 287
	Cycle	o-octyl chlo	ride	
Temp./°C No. of runs $10^{5}k_{1}/s^{-1}$	$302 \cdot 0$ $4$ $7 \cdot 30$	$312.5 \\ 6 \\ 14.6$	$334.3 \\ 4 \\ 53.7$	${344 \cdot 0 \atop {3} \atop {87 \cdot 5}}$
Temp./°C No. of runs $10^{5}k$ ./s <sup>-1</sup>	346·5 5 109	$353.5 \\ 4 \\ 147$	$358.3 \\ 3$ 205	$360\cdot3$ $4$ $221$

cm<sup>-1</sup>) vessels (Table 2). The first-order rate coefficients did not show any significant dependence on the initial pressure (Table 3). The rates measured in the presence of cyclohexene<sup>15</sup> as inhibitor were in good agreement with values in absence of inhibitor (Table 4). The variations of rate constants with temperature are shown in Table 5. They lead to the Arrhenius equations

- <sup>14</sup> A. Maccoll, J. Chem. Soc., 1955, 965.
   <sup>15</sup> A. Maccoll and P. J. Thomas, J. Chem. Soc., 1957, 5033.

 TABLE 6

 Arrhenius parameters for s-butyl and cycloalkyl chlorides

		E	E_	$\overline{E}_{s}$	$\Delta E_{s}$	
Chloride	$\log A/s^{-1}$	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>	kcal mol <sup>-1</sup>	Ref.
s-Butyl	13.80	50.1		_		a. b
Cyclohexyl	13.83	50.1	0.0	1.4	0	11. •
Cyclopentyl	13.47	48.3	6.3	5.9	1.8	10
Cycloheptyl *	12.01	43.6	6.4	5.4	2.4	d
Cyclo-octyl	11.88	$42 \cdot 4$	9.9	6.0 *	5.3	d

 $E_s$  = strain energy in cycloalkane;  $\bar{E}_s$  = strain energy in cycloalkene;  $\Delta E_s = (E_s - \bar{E}_s) - [(E_s - \bar{E}_s) \text{ for cyclohexyl}].$ \* Value for *cis*-cyclo-octene.

<sup>a</sup> A. Maccoll and R. H. Stone, J. Chem. Soc., 1961, 2756. <sup>b</sup> H. Heydtmann and G. Rinck, Z. phys. Chem. (Frankfurt), 1961, **30**, 250. <sup>c</sup> W. C. Herndon, M. B. Henly, and J. M. Sullivan, J. Phys. Chem., 1963, **67**, 2842. <sup>d</sup> This work.

 $k_1 = 10^{12.01 \pm 0.17} \exp{-[42,620 \pm 240]/RT} \text{ s}^{-1}$  for cycloheptyl chloride and  $k_1 = 10^{11.88 \pm 0.22} \exp{-[42,380 \pm 340]/RT} \text{ s}^{-1}$  for cyclo-octyl chloride; the values of log A and E were determined by the method of least squares.

The rate of the pyrolysis of cyclohexyl chloride was measured at two temperatures to check for any systematic errors. The values found were at  $326\cdot5$  °C,  $k_1 = 3\cdot85 \times 10^{-5}$  s<sup>-1</sup> (calc.,<sup>16</sup>  $3\cdot72 \times 10^{-5}$  s<sup>-1</sup>);  $348\cdot0$  °C,  $k_1 = 14\cdot2 \times 10^{-5}$  s<sup>-1</sup> (calc.,<sup>16</sup>  $15\cdot1 \times 10^{-5}$  s<sup>-1</sup>).

The thermal decomposition of the two chlorides studied are homogeneous and unimolecular. The Arrhenius parameters for s-butyl chloride and the



Relative rates of hydrogen chloride elimination as a function of strain energy difference;  $\bigcirc$ , 300 °C;  $\triangle$ , 360 °C

cycloalkyl chlorides are shown in Table 6 together with ring strain energy data.<sup>17</sup>

The results shown in Table 6 indicate that there is a significant decrease in activation energy in the sequence s-butyl  $\approx$  cyclohexyl > cyclopentyl > cycloheptyl > cyclop-octyl. These changes are in the same sequence as change in  $\Delta E_s$  values. However the relationship between  $E_a$  and  $\Delta E_s$  is not linear. This could be due in part to the approximation we have made, namely that  $E_s$  is about the same for the cycloalkane and the corresponding chloride. We however find that there is an

<sup>16</sup> A. Maccoll, *Chem. Rev.*, 1969, **69**, 53. <sup>17</sup> S. W. Benson, 'Thermochemical Kinetics,' John Wiley, New York, 1968, p. 179.

approximately linear relationship between  $\log k$  (relative to cyclohexyl chloride) and  $\Delta E_s$ . This is shown in the Figure for two temperatures. These results show that the strain energy difference does correlate with the rate of the elimination and on this basis we predict that cyclononyl chloride, with  $\Delta E_{\rm s}$  between <sup>17</sup> 2.9 and 4.3 (considering both *cis*- and *trans*-cyclononene), will eliminate HCl more quickly than cycloheptyl chloride but more slowly than the cyclo-octyl compound. Our A factors are lower than those observed by Herndon and Sullivan<sup>12</sup> and do not therefore support their suggested loose, cyclic transition state. Our results show an appreciable lowering of the elimination activation energy which would not be expected if the nature of the C-Cl bond (*i.e.*, secondary) were the major energy-determining factor; presumably there is considerable participation of the  $\beta$ -hydrogen atoms in the transition state.

There are two possible ways that the strain energy can affect the activation energy. (i) The possibility that owing to the strain, the energy of the ground state of the chloride relative to the transition state is increased, hence the lowering of the activation energy; or (ii) the presence of the strain in the chloride ring facilitates the attainment of the geometry required by the transition state. (These possibilities, if operative, must be primary in effect, since the largest change in activation energy involved is 8 kcal mol<sup>-1</sup>.)

It is also of interest to examine the results in the light of the analogy suggested by Maccoll and Thomas<sup>18</sup> between gas-phase elimination and  $S_{\rm N}1$  reactions in polar solvents. Brown<sup>1</sup> and Winstein *et al.*<sup>19</sup> have investigated the  $S_{\rm N}1$  reaction of the toluene-*p*-sulphonates of cycloalkyl compounds. They observed an increase in rate in the same sequence we have reported, and these increases in rate are partially due to small decreases in activation energy. Our results further support the suggested analogy.

This work was financed by the National Research Council. One of us (M. D.) thank the Canadian International Development Agency for a Fellowship and the University of Ghana for leave-of-absence.

# [0/1819 Received, October 26th, 1970]

<sup>19</sup> S. Winstein, E. Grunwald, and L. Ingraham, J. Amer. Chem. Soc., 1948, **70**, 821; S. Winstein, B. K. Moore, E. Grun-Grunwald, H. W. Jones, J. Lorse, D. Irifan, and H. Marshall, *ibid.*, 1952, **74**, 1127.

<sup>&</sup>lt;sup>18</sup> A. Maccoll and P. J. Thomas, Nature, 1955, **176**, 392.