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Chlorine Kinetic Isotope Effects

Application of the Transition State Model to Thermolysis of Secondary and Tertiary Alkyl Chlorides

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Chlorine kinetic isotope effects in the thermolysis of 2-chloropropane and 2-chloro-2-methylpropane have been measured at temperatures between 250 and 441°C. The isotope effects are primary and they show normal temperature dependence. They increase with increasing methyl substitution on the central carbon atom. Model calculations using the heavy atom approximation theory show satisfactory agreement with the experimental data and with the observed temperature dependence. The participation of chlorine in the activated complex is the same for primary, secondary and tertiary alkyl chlorides and involves a combination of C—Cl stretching (3 %), C—C—Cl bending (2.7 %) and C—CH_3 shortening (4 %) from the ground state values.

Of all thermolytic gas phase reactions, the hydrogen chloride elimination from alkyl chlorides has probably been investigated in greatest detail. Studies have been made using several different practical and theoretical methods, the aim being to elucidate the structure of the transition state for these unambiguously unimolecular processes.[1] However, despite the large amount of information collected, no general agreement about the nature of the transition state has been achieved.

Heavy atom kinetic isotope effects have been found to provide a very sensitive and useful instrument for evaluating conflicting mechanistic explanations for reaction processes.[2, 3] Furthermore, the temperature dependence of kinetic isotope effects provides additional information that reduces the number of possible theoretical models. We have previously reported a study on chlorine kinetic isotope effects in chloroethane[4] and have now extended this work to secondary and tertiary alkyl halides. Gas phase pyrolysis of primary, secondary and tertiary alkyl halides yields hydrogen chloride and the corresponding alkene in each case and we based this investigation on the assumption that the mechanisms for all three might involve the same activated complex.

EXPERIMENTAL

2-Chloropropane was pyrolysed in a static system at temperatures in the range 352-441°C and 2-chloro-2-methylpropane was pyrolysed at temperatures between 250 and 343°C. Isotopic analyses were carried out, based on the hydrogen chloride produced.† The com-

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† In the case of 2-chloropropane and on the unreacted substrate in the case of 2-chloro-2-methylpropane.

petitive method was used to determine the changes in the isotope ratio from the initial natural abundance. Isotope ratios were measured using an AEI MS20 double collector mass spectrometer, the apparatus and techniques for the thermolysis and mass spectrometry and the procedure for calculating the experimental isotope effects for 2-chloropropane being identical to those previously described.[4, 5]

The ratio of isotopic rate constants from analysis of the substrate (2-chloro-2-methylpropane) was derived in the following manner. Consider the kinetics of a system undergoing a thermal unimolecular decomposition; the set of isotopically competitive reactions can be written schematically as

$$A_1 \xrightarrow{k_1} P_1 + Q \qquad (1a)$$

$$A_2 \xrightarrow{k_2} P_2 + Q \qquad (1b)$$

where the subscript 1 refers to the lighter isotopically substituted molecule and the subscript 2 to the heavier one. The rates of decomposition are expressed by two differential equations

$$-\frac{d[A_1]}{dt} = k_1[A_1] \qquad (2a)$$

$$-\frac{d[A_2]}{dt} = k_2[A_2] \qquad (2b)$$

of which the solutions give the expression for the kinetic isotope effect

$$\frac{k_1}{k_2} = \frac{\ln [A_1/A_{01}]}{\ln [A_2/A_{02}]} \qquad (3)$$

where $[A_{01}]$ and $[A_{02}]$ are the initial concentrations. Eqn (3) cannot be used directly in this form, since the observed quantities are $[A_2/A_1]/[A_{02}/A_{01}]$. If the fraction of decomposition is f, the remaining substrate is $(1-f)$, where

$$(1-f) = \frac{[A_1]+[A_2]}{[A_{01}]+[A_{02}]} = \frac{[A_2]R_0(1+R_f)}{[A_{02}]R_f(1+R_0)} \qquad (4)$$

TABLE 1(*a*).—EXPERIMENTAL CHLORINE KINETIC ISOTOPE EFFECTS IN 2-CHLOROPROPANE

temp. 440.9°C			temp. 394.9°C			temp. 351.8°C		
f	r	k^{35}/k^{37}	f	r	k^{35}/k^{37}	f	r	k^{35}/k^{37}
0.10	0.9967_0	1.0035_3	0.10	0.9964_1	1.0037_9	0.10	0.9962_4	1.0039_9
0.20	0.9968_3	1.0035_3	0.10	0.9961_9	1.0040_4	0.10	0.9961_6	1.0040_7
0.25	0.9970_1	1.0034_9	0.10	0.9960_9	1.0041_4	0.25	0.9971_1	1.0039_6
0.50	0.9977_7	1.0032_2	0.25	0.9967_7	1.0038_5	0.25	0.9962_1	1.0044_3
0.50	0.9975_6	1.0035_3	0.25	0.9970_2	1.0039_7	0.40	0.9965_3	1.0045_5
0.75	0.9981_7	1.0039_9	0.50	0.9971_8	1.0040_8	0.50	0.9970_1	1.0043_3
0.75	0.9981_2	1.0040_7	0.50	0.9971_1	1.0041_8	0.55	0.9973_4	1.0040_8
0.90	0.9989_4	1.0034_9	0.60	0.9976_3	1.0038_9	0.75	0.9979_4	1.0044_6
			0.75	0.9981_5	1.0040_2	0.75	0.9981_6	1.0039_8
			0.75	0.9981_0	1.0041_2			
			0.90	0.9989_9	1.0039_2			
			0.90	0.9989_4	1.0041_1			
mean k^{35}/k^{37} =			mean k^{35}/k^{37} =			mean k^{35}/k^{37} =		
	$1.0036_0 \pm 0.0002_1$			$1.00401_1 \pm 0.0001_1$			$1.0042_0 \pm 0.0002_1$	

TABLE 1(*b*).—EXPERIMENTAL CHLORINE KINETIC ISOTOPE EFFECTS IN 2-CHLORO-2-METHYLPROPANE

temp. 342.9°C			temp. 336.6°C			temp. 312.8°C		
f	r	k^{35}/k^{37}	f	r	k^{35}/k^{37}	f	r	k^{35}/k^{37}
0.11	1.0009_8	1.0084_8	0.12	1.0010_3	1.0083_4	0.10	1.0008_9	1.0082_5
0.13	1.0011_1	1.0083_2	0.12	1.0010_1	1.0081_0	0.10	1.0008_9	1.0085_2
0.13	1.0010_0	1.0075_4	0.13	1.0011_7	1.0081_6	0.10	1.0009_4	1.0089_6
0.22	1.0020_9	1.0084_3	0.13	1.0014_8	1.0100_2	0.15	1.0012_1	1.0073_8
0.25	1.0023_7	1.0083_0	0.17	1.0016_7	1.0090_0	0.15	1.0016_9	1.0099_4
0.25	1.0023_7	1.0082_9	0.20	1.0016_8	1.0075_1	0.15	1.0015_9	1.0098_8
0.25	1.0024_6	1.0086_0	0.25	1.0026_8	1.0093_8	0.19	1.0019_6	1.0088_1
0.40	1.0035_5	1.0069_7	0.25	1.0019_9	1.0069_6	0.20	1.0015_4	1.0068_9
0.40	1.0045_1	1.0089_0	0.27	1.0027_2	1.0088_3	0.20	1.0015_3	1.0072_5
0.40	1.0041_6	1.0082_1	0.27	1.0025_9	1.0084_1	0.20	1.0023_2	1.0099_1
0.50	1.0065_1	1.0094_3	0.33	1.0026_8	1.0066_5	0.40	1.0048_5	1.0095_5
0.50	1.0055_1	1.0079_8	0.33	1.0030_3	1.0074_8	0.40	1.0041_6	1.0082_1
0.50	1.0053_7	1.0077_7	0.33	1.0032_4	1.0080_2	0.40	1.0037_2	1.0071_0
			0.33	1.0032_5	1.0080_4	0.50	1.0061_0	1.0088_4
			0.40	1.0033_9	1.0076_7	0.50	1.0056_7	1.0082_0
			0.40	1.0045_3	1.0088_8	0.50	1.0052_3	1.0075_7
			0.40	1.0045_5	1.0089_4	0.50	1.0055_3	1.0079_9
			0.40	1.0034_9	1.0068_3			
			0.50	1.0061_8	1.0089_5			
			0.50	1.0060_7	1.0087_9			
			0.50	1.0049_2	1.0081_2			
			0.50	1.0050_1	1.0072_5			
mean k^{35}/k^{37} = $1.0082_3 \pm 0.0004_5$			mean k^{35}/k^{37} = $1.0082_0 \pm 0.0005_7$			mean k^{35}/k^{37} = $1.0084_3 \pm 0.0005_3$		

where $R_f = [A_2/A_1]_f$ and $R_0 = [A_{02}/A_{01}]$. By substituting $r = R_f/R_0$ and $S = (1+R_0)/(1+R_f)$, the final equation for the kinetic isotope effects is

$$\frac{k_1}{k_2} = \frac{\ln[(1-f)S]}{\ln[(1-f)rS]}. \tag{5}$$

The factor S is essentially a correction term and can be determined by direct measurement of the ratio of the relevant isotopic ion intensities. Since the quantities that were experimentally observed were r and f, the kinetic isotope effects for 2-chloro-2-methylpropane were calculated according to the above equation.

The experimental results are presented in table 1. At each temperature and fraction of reaction, ten individual measurements of r were carried out and the results averaged to give a single value of the isotope ratio. The standard deviations were then determined on six to eight such sets of ten experiments, where several values of r are reported for one f value, each r value represents 60-80 readings of the isotopic ratio.

THEORETICAL ANALYSIS

For the model calculations we adopted Bigeleisen's heavy atom approximation for the reduced ratios of isotopic partition functions.[3] The theory was outlined in our previous paper.[4] The complete evaluation of the rigid rotor approximation

(RRA) requires a knowledge of the geometries and vibrational frequencies of all normal modes for both the isotopic species, in both the ground state and the transition state. These data are not usually available and it is therefore necessary to use related approximations in the assignment of isotopic vibrational frequencies.

An investigation of the factors underlying isotope effect calculations reveals that the magnitude of primary isotope effects is influenced primarily by changes in those vibrational modes involving bonds directly attached to the isotopically substituted atom.[6] In our model, the methyl groups were replaced by point masses at the centres of gravity of the methyl groups. The chosen model of the activated complex was a planar ring structure, with relatively weak interactions between the hydrogen and chlorine atoms. The relative changes in the internal coordinates from the ground state were taken to be equal to those considered in the case of chloroethane.[4]

2-CHLORO-2-METHYLPROPANE

The structural parameters of 2-chloro-2-methylpropane used in these calculations were taken from the literature.[7] A model resembling methyl chloride was used in the evaluation of moments of inertia. Each methyl group was considered to have a mass of 15.024 amu and to be concentrated at the centre of the methyl trigonal pyramid that was placed at a distance of 0.79 nm along the extension of the C—C bond from the central carbon atom. A set of Cartesian coordinates were determined for this model, where the C—Cl bond was colinear with the X-axis. The same set was used for the ^{37}Cl model, since the C—Cl bond length was reported to vary by <0.01 nm on isotopic substitution. Sets of Cartesian coordinates for selected models of the activated complex were determined in a similar way to those for chloroethane, by varying the individual internal coordinates. The motions that were considered to undergo significant changes on thermal activation were C—Cl bond stretch, C—C—Cl bend and C—CH_3 bond shortening.

TABLE 2.—FREQUENCIES AND ISOTOPIC SPLITTINGS (cm^{-1}) FOR 2-CHLORO-2-METHYLPROPANE

ground state t-$C_4H_9^{35}Cl$	$\Delta\nu$	approximate description	model 8 5-$C_4H_9^{35}Cl^{\ddagger}$	$\Delta\nu^{\ddagger}$
585.0	2.7	C—Cl stretch	—	—
818.0	0.5	C—CH_3 stretch	838.2	0.60
370.0	3.8	CH_3—C—CH_3 deformation	358.2	2.2
1210.0	0.2	C—CH_3 stretch (degenerate)	1268.4	0.2
404.4	0.1	CH_3—C—CH_3 deformation (degenerate)	287.8	0.2
301.0	1.5	CH_3—C—Cl deformation	312.4	1.8

A vibrational analysis of the reduced model of 2-chloro-2-methylpropane in the ground state has been reported.[8] Of the nine normal vibrational modes of this model, three are doubly degenerate. For our calculations the frequencies in the activated complex were adjusted, either according to the rules of Pauling and Badger,[9] or they were calculated using Wilson's F.–G. matrix technique. The moments of inertia factor was evaluated by computer. The vibrational product and the excitation factors, which are temperature dependent, were calculated at temperatures equal to those of the experimentally determined isotope effects. The decomposition frequency was associated with the C—Cl stretch. The frequencies for the ground state and for the activated complex, together with their approximate descriptions, are listed in table 2.

2-CHLOROPROPANE

The model chosen for calculations on 2-chloropropane was intermediate between those of chloroethane and 2-chloro-2-methylpropane. The methyl groups were considered to have the combined masses of their atoms and to be placed at the centres of gravity. This reduced model has nine chlorine isotope dependent vibrational frequencies.[10] The isotopic shift has been reported for the C—Cl stretch [11] and the other shifts were estimated by analogy with models of chloroethane and 2-chloro-2-methylpropane. The frequencies used in the calculations for the ground state and the activated complex and the assignments of the fundamentals are summarised in table 3.

TABLE 3.—FREQUENCIES AND ISOTOPIC SHIFTS FOR 2-CHLOROPROPANE

ground state		approximate description	model 8	
ν_1	$\Delta\nu$		$\nu_1^{\ddagger}$	$\Delta\nu^{\ddagger}$
632.1	4.0	C—Cl stretch	—	—
317.0	1.5	C—C—Cl bend	310.0	1.9
337.0	1.5	C—C—Cl bend	355.3	1.9
888.0	0.5	C—CH_3 stretch	912.2	0.6
1160.1	0.3	C—C—C bend	1125.1	0.1
1061.1	0.3	C—C—C bend	1114.2	0.1
1260.0	0.2	H—C—Cl twist	1297.9	0.1
256.0	0.3	CH_3 torsion	265.8	0.4
423.5	3.0	C—C—C twist	294.8	2.1

DISCUSSION

Chlorine kinetic isotope effects in gas phase pyrolysis are generally small and rarely exceed half their theoretical maximum values, hence the C—Cl bond that is associated with the reaction coordinate is not completely broken in the activated complex. They do exhibit a definite dependence on temperature. The experimental k^{35}/k^{37} for 2-chloro-2-methylpropane are very close to those reported for chlorine kinetic isotope effects in solution.[12]

From the detailed calculation on chloroethane we concluded that the activated complex involves a combination of several internal modes. This inference also applies to 2-chloropropane and 2-chloro-2-methylpropane. Of the same complete set of models used for chloroethane, only model 8 agreed with both the experimental values of the kinetic isotope effect and the temperature dependence. Comparison of the experimental data and the calculated values is given in table 4 for 2-chloropropane and in table 5 for 2-chloro-2-methylpropane.

Calculations show that changes in internal coordinates cannot be larger than a few per cent. For a change in one mode of perhaps 10 %, it may be possible to define a structure for the transition state that would fit the experimental data at a given temperature. However, the model thus defined would require such fundamental changes to other parameters as to be unrealistic. Furthermore, such a model would not correspond to the observed temperature dependence. Thus the variation of kinetic isotope effects with temperature is considered to be a very important criterion when testing the validity of models of the activated complex.

In the expression for the rigid rotor approximation there are two terms that vary with temperature, the ZPE and the EXC factors. The change in the ZPE factor over a large temperature range is shown in fig. 1. A plot of ZPE against $1/T$ is linear, the gradient increasing with increasing complexity of the molecule. A similar plot of EXC against $1/T$ (fig. 2) shows an increasingly negative gradient with increasing molecular complexity. The combined contribution of these two terms to the temperature dependence is the product EXC × ZPE. Consequently, with their opposing

TABLE 4.—CHLORINE KINETIC ISOTOPE EFFECTS IN 2-CHLOROPROPANE

temperature/°C	experimental	model 8
440.9	$1.0036_0 \pm 0.0002_1$	1.003 62
394.9	$1.0040_1 \pm 0.0001_1$	1.003 89
351.8	$1.0042_0 \pm 0.0002_2$	1.004 13

TABLE 5.—CHLORINE KINETIC ISOTOPE EFFECTS IN 2-CHLORO-2-METHYLPROPANE

temperature/°C	experimental	model 8
342.9	$1.0082_3 \pm 0.0004_5$	1.008 23
336.6	$1.0082_0 \pm 0.0005_7$	1.008 27
312.8	$1.0084_3 \pm 0.0005_3$	1.008 43
287.7	$1.0086_8 \pm 0.0004_2$	1.008 65
249.6	$1.0090_0 \pm 0.0006_1$	1.009 01

TABLE 6.—TEMPERATURE INDEPENDENT FACTORS ($\nu^{\ddagger}_{1i}/\nu^{\ddagger}_{2i}$)

compound	extrapolated from exp. results	calculated [MMI/VP]
C_2H_5Cl	1.001 22	1.001 19
i-C_3H_7Cl	1.001 70	1.001 80
t-C_4H_9Cl	1.006 09	1.006 16

TABLE 7.—SUMS OF ISOTOPIC SHIFTS

	ground state $\Sigma(\nu_1-\nu_2)$	model 8 $\Sigma(\nu^{\ddagger}_1-\nu^{\ddagger}_2)$
C_2H_5Cl	7.6	6.13
i-C_3H_7Cl	10.1	6.05
t-C_4H_9Cl	10.6	5.73

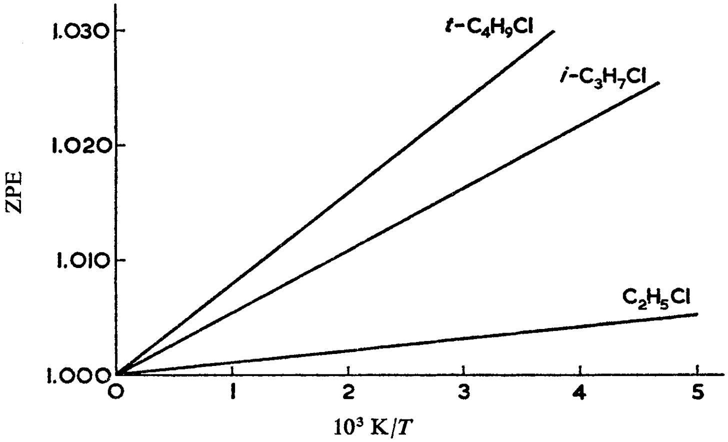

FIG. 1.—Temperature dependence of the ZPE factor.

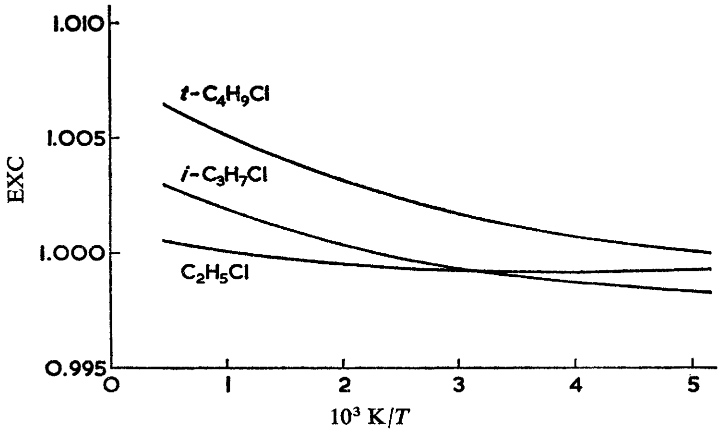

FIG. 2.—Temperature dependence of the EXC factor.

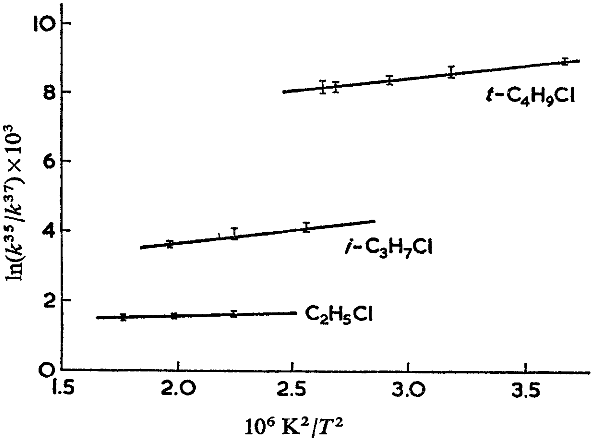

FIG. 3.—Temperature dependence of chlorine KIE.

gradients the chlorine isotope effects in the gas phase show only a small decrease as the temperature is increased (fig. 3), the most marked variation being for the most complex molecule, 2-chloro-2-methylpropane.

The other contribution to the calculated kinetic isotope effect comes from the temperature independent factor (TIF). One method of evaluating this from the experimental measurements is to extrapolate a plot of $\ln(k_1/k_2)$ against $10^3/T^2$ to zero.[6] The intercept is equal to the ratio of the decomposition frequencies, $\nu_1^{\ddagger}/\nu_2^{\ddagger}$. The theoretical values that were calculated for all three chloroalkanes using model 8 of the activated complex were found to be in very good agreement with those that were determined from the experimental data. A comparison of these temperature independent factors is presented in table 6.

In theoretical isotope effects, isotopic shifts have a much more significant effect on the temperature dependence than do the actual values of the vibrational frequencies. The adjustment of the ratios in the activated complex is therefore not critical, which is one of the advantages of using this theory. The sum of isotopic shifts in the ground state and in the activated complex is presented in table 7. It can be seen that the values calculated for model 8 of the activated complex are very similar for all three alkyl chlorides, regardless of the isotopic shifts in the ground state.

CONCLUSION

From this study of chlorine kinetic isotope effects in gas phase thermal decompositions and the model calculations it can be inferred that all alkyl chlorides involve the same type of activated complex. Chlorine participation involves a combination of bending and stretching modes. The geometric model of the activated complex that is in best agreement with the experimental results requires that the C—Cl bond be stretched by 3 %, the C—C—Cl angle be reduced by 2.7 % and the C—CH_3 bond length be shortened by 4 %, relative to their ground state values.

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