drawn. Both activation energies are of the order to be expected for ultrafast reactions.

From the measured broadening, rate constants can be calculated through the relation

 $k_{\rm f}=2\pi cA$

The rate constants are collected in Table I. It is seen that their magnitudes considerably exceed the diffusion-controlled limit. Such high rate constants are consistently found in picosecond kinetics⁷ and are explained by noting that the reactions dealt with do not involve diffusion but rather repeated dissociation and association of nearby species.

Our rate constant for H_2SO_4 , $17 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C, is rather larger than the room-temperature rate constants obtained by Chen and Irish, $6.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, and by Ikawa et al., $4.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This discrepancy does not seem to result from a systematic difference between Raman and IR results since the D_2SO_4 rate constant of Chen and Irish, $10.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, agrees with our 25 °C rate constant of $8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ (being, if anything, *larger* than our value). We cannot, at present, offer an explanation of the disagreement beyond noting that in many cases our solutions differ in composition from those used by the previous workers (containing, e.g., no K^+ or NH_4^+) and that intuition would favor $k_{H^+} > K_{D^+}$, as we do find. Further work on the influence of added ions is clearly indicated and we plan to carry it out.

Two other points which require comment are the following: The possibility of an alternative mechanism

$$SO_4^{2-} + HSO_4^{-} \rightleftharpoons HSO_4^{-} + SO_4^{2}$$

for proton transfer must be considered. Our experimental reason for preferring proton exchange between sulfate ion and hydronium as the cause for line broadening, rather than exchange with bisulfate, is the lack of broadening of the lines of the latter.

Still another mechanism for apparent line broadening would be the partial lifting of degeneracy of the ν_3 triply degenerate band (which is the 1100-cm⁻¹ line) through interaction with neighbors. We consider this possibility unlikely in view of the fact that only H⁺ (or D⁺) is found to cause broadening and the overall consistency of the interpretation in terms of kinetic broadening.

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Registry No. H_3O^+ , 13968-08-6; D_3O^+ , 24847-51-6; SO_4^{2-} , 14808-79-8.

Correlation of Alkyl and Polar Groups in the Gas-Phase Pyrolysis Kinetics of α -Substituted Ethyl Chlorides

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The kinetics of the gas-phase pyrolysis of several secondary chlorides were determined in a static system over the temperature range of 369.9-490.1 °C and the pressure range of 28-298 Torr. The reactions in seasoned vessels, with the free radical suppressor propene and/or toluene always present, are homogeneous and unimolecular and obey a first-order rate law. The observed rate coefficients are represented by the following Arrhenius equations: for 2-chloropropionitrile, log k_1 (s⁻¹) = $(13.45 \pm 0.57) - (236.1 \pm 8.2)$ kJ mol⁻¹; for methyl 2-chloropropionate, log k_1 (s⁻¹) = $(12.22 \pm 0.54) - (217.0 \pm 7.4)$ kJ mol⁻¹ (2.303RT)⁻¹; for methyl 3-chlorobutyrate, log k_1 (s⁻¹) = $(13.65 \pm 0.39) - (214.9 \pm 5.0)$ kJ mol⁻¹ (2.303RT)⁻¹. The data of this work together with those reported in the literature confirm previous correlations that α -alkyl substituents of ethyl chloride give a good straight line, when log k/k_0 vs. σ^* values ($\rho^* = -3.58 \pm 0.24$, correlation coefficient = 0.996, and intercept = -0.0066 at 360 °C) are plotted, while α -polar substituents give rise to an inflection point at σ^* (CH₃) = 0.00 into another straight line ($\rho^* = -0.46 \pm 0.06$, correlation coefficient = 0.972, and intercept = -0.017 at 360 °C). Several other polar α -substituents have been found to enhance the dehydrochlorination process by means of their electron delocalization or resonance effect. Revising a work reported on the pyrolysis kinetics of pinacolyl chloride, a Wagner-Meerwein rearrangement appears to be a reasonable explanation for the formation of about 12% of the 2,3-dimethylbutene products.

Introduction

The Taft correlation for the gas-phase pyrolysis of aliphatic primary² and tertiary³ chlorides were considered as additional evidence of Maccoll's theory⁴ on the polar nature of the transition state for alkyl halide pyrolyses in the gas phase. This conclusion was derived from the fact that if the transition state for the pyrolysis of these halides is represented by the elongation of the C-Cl bond and a subsequent polarization in the sense C^{δ^4} -...Cl^{δ^7}.

then the +I inductive electron release of alkyl substituents will tend to stabilize the partially charged carbon reaction center; thus enhancement of the reaction rates follows. In the case of substituents of -I, electron-withdrawing effect must reduce the elongation and the degree of polarization of the C-Cl bond, which is the rate-determining step of these reactions. Therefore, the elimination rates will be slower and the sequence very much in accord with their electronegative differences.

Prior to these investigations, a linear Taft correlation of alkyl groups and a very small population of polar substituent at the α -carbon of ethyl chloride pyrolyses were also described.⁵ The Taft plot for alkyl substituents gave a straight line of $\rho^* = -3.55$ at 360 °C and another slope at $\sigma^*(CH_3) = 0.00$ and for very few

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⁽¹⁾ Taken from the thesis of Rosa M. Dominguez, submitted to the Faculty of IVIC, February 1986, in partial fulfillment of the requirements for the Degree of Magister Scientiarum.

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polar substituents a ρ^* of -0.51 at 360 °C. Because of this, it was thought to be of interest to study the effect of several other polar substituents in this type of secondary alkyl halides. The data that will be examined in the present work, together with those obtained in recent years from the literature, will provide a wide range of substituent effects, and at the same time, may lead to more and better information regarding the mechanisms of secondary alkyl chloride pyrolyses in the gas phase.

Experimental Section

2-Chloropropionitrile. This compound was prepared from cyanohydrin (Aldrich) in pyridine with thionyl chloride⁶ (bp 110 °C at 630 Torr; lit.⁷ 123 °C at 760 Torr). The fraction of 99.8% purity (GLC: FFAP (7%)-Chromosorb G AW DMCS, 80-100 mesh) was used. Acrylonitrile (Aldrich) was analyzed in the FFAP column.

Methyl 2-Chloropropionate. The fraction of 98.8% purity of this substrate (Aldrich) (GLC: diisodecyl phthalate (5%)-Chromosorb G, 60-80 mesh) was used. Methyl acrylate (Aldrich) was analyzed in the diisodecyl phthalate column, and vinyl chloride (Matheson) in a Porapak Q column.

Methyl 3-Chlorobutyrate. 3-Chlorobutyric acid was treated with methanol, in the presence of Merck Acid-Resin S 1080 G1 as described⁶ (bp 78 °C at 50 Torr; lit.⁸ bp 155–6 °C at 760 Torr; purity, 99.7% (GLC: FFAP column)). The product methyl trans-2-butenoate (methyl crotonate) was made by mixing ethyl crotonate with methanol as reported⁶ (bp 65-6 °C at 100 Torr; lit.⁹ 118-120 °C at 760 Torr) and analyzed in the diisodecyl phthalate column. Methyl 3-butenoate was obtained from vinylacetic acid with methanol in Merck Acid-Resin S 1080 G1 (bp 76 °C at 120 Torr; lit.¹⁰ 133-4 °C at 760 Torr) and analyzed in the diisodecyl phthalate column.

Kinetics. The pyrolyses experiments were carried out in a static system with the reaction vessel seasoned with allyl bromide.⁴ The rate coefficients were determined manometrically and/or by chromatographic analysis of the unreacted chloride substrate and/or HCl titration. The temperature was found to be within ± 0.2 °C when measured with a calibrated iron-constantan thermocouple. The reaction vessel showed no temperature gradient at different points, and the substrate was injected directly into the vessel through a silicon rubber septum.

Results and Discussion

The products of the gas-phase pyrolysis of several α -substituted ethyl chlorides, in a static system, seasoned with allyl bromide, and in the presence of the radical chain inhibitor propene, are predominantly the corresponding olefin and hydrogen chloride (eq 1).

$$CH_{3}CHZ \longrightarrow CH_{2}=CHZ + HCI \qquad (1)$$

$$| (1)$$

$$CI$$

$$Z = CN, COOCH_{2}, CH_{2}COOCH_{2}$$

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TABLE I: Distribution of Olefins at Different Pyrolysis Temperatures of Methyl 3-Chlorobutyrate

		yield, %	
temp, °C	methyl trans-2- butenoate	methyl cis-2- butenoate	methyl 3-butenoate
380.4	57.6	19.7	22.7
400.3	56.7	19.0	24.3
420.2	54.2	20.6	25.2

TABLE II: Variation of Olefin Formation from Percentage Pyrolysis of Methyl 3-Chlorobutyrate at 400.3 °C

time, min	reaction, %	methyl trans-2-butenoate	methyl cis-2-butenoate	methyl 3-butenoate
2	10.7	56.7	19.6	23.7
5	29.1	55.7	20.0	24.3
10	41.4	57.1	19.2	23.8
15	63.6	56.7	19.0	24.2
20	69.9	57.4	18.6	24.0
25	77.9	56.5	18.6	24.9

TABLE III: Equilibrium Mixtures from Thermodynamic Group Additivity at 701.05 K (427.9 °C)

methyl	methyl	methyl	
trans-2-butenoate	cis-2-butenoate	3-butenoate	
42.2%	37.7%	20.1%	

The stoichiometry described by eq 1 implies $P_f = 2P_0$, where $P_{\rm f}$ and P_0 are the final and the initial pressures, respectively. The average experimental results of P_f/P_0 values at four different temperatures and ten half-lives was 1.67 for 2-chloropropionitrile, 2.64 for methyl 2-chloropropionate, and 2.03 for methyl 3chlorobutyrate. A significant departure from P_f/P_0 for 2chloropropionitrile results from the small polymerization of the product acrylonitrile. However, the departure found in methyl 2-chloropropionate was due to the decomposition of the primary product methyl acrylate as described in eq 2.

$$CH_2 = CHCOOCH_3 \longrightarrow CH_2 = CHCOCI + CH_3OH$$

$$\downarrow \qquad (2)$$

$$CH_2 = CHCI + CO$$

Additional verification of the stoichiometry of eq 1 was made as follows: For 2-chloropropionitrile, up to 60% reaction, there is a good agreement between the chromatographic analyses of the reacted amount of the chloropropionitrile with that obtained by titration of HCl with 0.05 N sodium hydroxide solution. The quantitative titration of HCl agrees reasonably with either the pressure increase or the chromatographic analysis up to 55% decomposition of the reacting substrate methyl 2-chloropropionate. Finally, the stoichiometry for methyl 3-chlorobutyrate, up to 80% reaction, was checked by comparing the extent of decomposition from pressure measurement with that obtained from the chromatographic analyses of the unsaturated ester product or by the reacting amount of substrate.

2-Chloropropionitrile gave, up to 60% decomposition, mostly acrylonitrile and HCl gas, while methyl 2-chloropropionate, up to 55% reaction, yielded mainly methyl acrylate, HCl, and very small amounts of methanol and vinyl chloride. The primary products of methyl 3-chlorobutyrate were, up to 80% reaction, methyl cis- and trans-2-butenoate, methyl 3-butenoate, and HCl.

Tables I and II suggest that the formation of the olefinic esters from the gas-phase molecular elimination of methyl 3-chlorobutyrate proceeded with kinetic control. To support this conclusion, each olefin product under the condition of experiments was introduced into the reaction vessel in the presence of HCl and at different temperatures. None of the olefins isomerized; only methyl cis-2-butenoate (methyl isocrotonate) yielded nearly 2% of the trans isomer (methyl crotonate). The lack of an equilibrium process among these methyl butenoates was verified by the approximate calculation using the thermodynamic group additivity table²⁵ at 701.05 K (427.9 °C) (Table III).



Figure 1. log k_Z/k_{CH_3} against σ^* -values for electron-releasing and -withdrawing substituents in the pyrolysis of ZCHClCH₃ at 360 °C. The lines were drawn by the least-squares procedure.

The homogeneity of these reactions was examined under the inhibitor propene in a vessel with a surface-to-volume ratio of 6.0 times greater than that of a normal vessel which is equal to one. The packed and unpacked clean Pyrex vessel had a marked effect on the rates. However, when the packed and unpacked vessels were seasoned with allyl bromide, no significant effect on the rate coefficient of these organic halides was obtained. The rate coefficients are reproducible with a standard deviation not greater than $\pm 5\%$ at a given temperature.

The pyrolyses of these halides, in seasoned vessels, had to be carried out in the presence of at least the equivalent amount of the inhibitor propene and/or toluene.

The first-order rate coefficients were found to be independent of the initial pressures. The logarithmic plots are linear up to 60% decomposition for 2-chloropropionitrile, 55% for methyl 2chloropropionate, and 80% for methyl 3-chlorobutyrate. The temperature dependence of the rate coefficients is given in Table IV.

The results of Table IV are expressed, when the least-squares procedure and 0.8 confidence coefficient are used by the following equations:

2-chloropropionitrile:

 $\log k_1 (s^{-1}) =$

$$(13.45 \pm 0.57) - (236.1 \pm 8.2) \text{ kJ mol}^{-1} (2.303RT)^{-1}$$

methyl 2-chloropropionate:

 $\log k_1 (s^{-1}) =$

 $(12.22 \pm 0.54) - (217.0 \pm 7.4) \text{ kJ mol}^{-1} (2.303RT)^{-1}$

methyl 3-chlorobutyrate:

 $\log k_1 (s^{-1}) =$

 $(13.65 \pm 0.39) - (214.9 \pm 5.0) \text{ kJ mol}^{-1} (2.303RT)^{-1}$

Table V lists a considerable numbers of substituent effects in the gas-phase dehydrochlorination of α -substituted ethyl chlorides. As before,⁵ the log k_{rel} of alkyl substituents (1–6, Table V) when plotted against σ^* -values²⁶ gave a very good straight line with ρ^*

TABLE IV: Variation of the Rate Coefficients with Temperature

		2.01	loronro	nionitril	<u> </u>		
temp, °C	450.9	460.2	465.8	469.0	475.2	480.2	490.1
$10^4 k_1, s^{-1}$	2.72	4.15	5.51	6.80	9.05	11.51	20.34
		Methyl	2-Chlor	opropio	nate		
temp, °C	424.7	430.0	440.0	450.3	460.4	469.7	
$10^4 k_1$, s ⁻¹	0.94	1.29	1.94	3.13	5.66	9.48	
		Methy	l 3-Chlo	orobutyr	ate		
temp, °C	369.9	380.4	389.5	400.3	405.0	410.2	420.2
$10^4 k_1$, s ⁻¹	1.61	2.86	5.14	10.12	12.00	17.28	28.67

SCHEME I



 $= -3.58 \pm 0.24$, r = 0.996, and intercept = -0.0066 at 360 °C (Figure 1). This means that branching of alkyl groups at the α -carbon of ethyl chloride enhances the pyrolysis rates due to their electron-releasing effect (+I effect). The negative value of ρ^* implies that a positively charged carbon atom in the transition state is the limiting factor in these reactions. The Taft plot for several electron-withdrawing substituents (7-13, Table V) gives rise to an inflection point of the line at $\sigma^*(CH_3) = 0.00$ into another good straight line with $\rho^* = -0.46 \pm 0.06$, r = 0.972, and intercept = 0.017 at 360 °C (Figure 1). The negative slope of -0.46 suggests a very small polarization of C^{b^+} Cl^{b^-} bond in the transition state. The present work confirms the correlation found in a previous study of the gas-phase pyrolysis of α -substituted ethyl chlorides.⁵ Figure 1 is similar to those Taft correlations found in the gas-phase pyrolysis of β -substituted ethyl chlorides² and α -substituted tertiary chloride,³ where the electron-releasing alkyl groups (+I effect) give one slope and the electron-withdrawing polar groups (-I effect) another slope at $\sigma^*(CH_3) = 0.00$. The inflection point at $\sigma^*(CH_3) = 0.00$ into two slopes can reasonably be explained, as already advanced^{2,3} in terms of a slight alteration

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no.	Z	$10^4 k_1, s^{-1}$	$10^4 k_{\rm CH_3}$, s ⁻¹	rel rate ^b	$E_{\rm a}$, kJ mol ⁻¹	$\log A$, s ⁻¹	$\log k_{\rm Z}/k_0$	σ*	ref
1	н	0.008	0.008	1	241.8 ± 4.2	13.83 ± 0.20	-1.805	0.49	11
2	CH ₃	1.02	0.51°	64	211.6 ± 2.8	13.47 ± 0.22	0.000	0.00	12
3	CH ₃ CH ₂	3.31	1.42 ^d	178	211.7 ± 3.5	13.99 ± 0.29	0.444	-0.10	13
4	CH ₃ CH ₂ CH ₂	3.97	1.71 ^e	214	212.1 ± 1.7	14.10 ± 0.10	0.525	-0.115	14
5	(CH ₃) ₂ CH	4.51	2.07 ^f	259	207.8 ± 2.0	13.80 ± 0.21	0.608	-0.19	5
6	(CH ₃) ₃ C	5.13	4.62 ^g	578	197.3 ± 2.6	12.99 ± 0.22	0.958	-0.30	5
7	Cl	0.063	0.032 ^h	4	224.0 ± 1.7	13.28 ± 0.13	-1.203	2.94	15
8	F	0.018	0.018 ⁱ	2	239.7 ± 4.4	14.02 ± 0.28	-1.453	3.08	16
9	Cl ₃ C	0.084	0.057 ^j	7	225.1	13.50	-0.952	2.65	17
10	CH3CO	0.068	0.068	8	205.3 ± 4.1	11.77 ± 0.31	-0.875	1.65	18
11	CH₃OCO	0.021	0.021	3	217.0 ± 7.4	12.22 ± 0.54	-1.386	$(2.78)^{k}$	this work
12	NC	0.009	0.009	1	236.1 ± 8.2	13.45 ± 0.57	-1.754	3.64	this work
13	CH ₃ OCOCH ₂	0.83	0.20'	25	214.9 ± 5.0	13.65 ± 0.39	-0.407	$(1.03)^{m}$	this work
14	CH ₂ =CH	4.02	4.02	503	203.8 ± 2.0	13.42 ± 0.16	0.896		19
15	$CH_2 = C(CH_3)$	12.65	12.65	1581	197.4 ± 7.6	13.39 ± 0.64	1.394		19
16	cis-CH ₃ CH==CH ⁿ	1040.00	1040.00	130000	131.3 ± 5.1	9.85 ± 0.46	3.308		20
17	trans-CH ₃ CH=CH	41.85	41.85	5231	196.8 ± 3.5	13.86 ± 0.26	1.914		20
18	CH₃CH —CHCH—CH	320.00	320.00	40200	144.5 ± 4.6	10.43 ± 0.41	2.799		21
19	C ₆ H ₅	13.62	13.62	1703	187.8 ± 1.9	12.63 ± 0.16	1.426		22
20	CH3O	9400.00	9400.00	1.2×10^{6}	139.0 ± 4.7	11.44 ± 0.50	4.263		23
21	CH ₃ CH ₂ O	12600.00	12600.00	1.6×10^{6}	128.2 ± 4.5	10.68 ± 0.51	4.394		24

^a The Arrhenius parameters were whenever possible recalculated from the reported data of the cited reference by the least-squares procedure. The confidence coefficient used to determine the errors was 0.8. ^b The comparative rates were rounded off. ^c Rate toward a single methyl group. ^d Value based on 43% yield of 1-butene at 360 °C. ^e Assuming an approximately 43% yield of 1-pentene at 360 °C. ^f Value estimated from 46% yield of 3-methyl-1-butene at 360 °C. ^g Yield of 3,3-dimethyl-1-butene at 360 °C. ^h Rate for a single chlorine elimination. ⁱ The competing elimination of HF from 1-chloro-1-fluoroethane is less than 1% at 360 °C. ^j Value derived from 68.2% yield of 1,1,1-trichloro-2-propene. ^k σ^* -value estimated from $\sigma_{I}(CH_2COOCH_3) = 0.17$, using equations $\sigma_{I}(Z) \simeq 0.45\sigma^*(CH_2Z)$ and $\sigma^*(Z)/\sigma^*(CH_2Z) = 2.7$. ⁱ Value from 24.2% yield of the terminal olefin. ^m σ^* -value estimated as in k. ⁿ The significant high rate was explained in terms of a six-membered cyclic transition state.

TABLE VI: Extrapolation of ρ^* -Values for Alkyl Substituents

compd		ρ*			
(Z = alkyl)	300 °C	360 °C	440 °C		
ZCH ₂ CH ₂ Cl	-1.46	-1.32	-1.17^{a}		
ZCHCICH,	-3.95	-3.58 ^b	-3.18		
$Z(CH_3)_2CCl$	-4.75°	-4.30	-3.82		

^a Value from ref 2. ^b Value of the present work. ^c Value from ref 3.

in the polarity of the transition state due to changes of electronic transmission at the carbon reaction center. Therefore, a simultaneous effect may be operating during the process of decomposition, particularly with the polar electron-withdrawing substituents. This means that polar groups destabilize the reaction center, while the hydrogen of the adjacent CH_3 to Z (Scheme I) becomes more acidic and thus assists the leaving chloride atom. Such a phenomena leads to the pyrolysis rates being similar or slightly higher with respect to the unsubstituted compound, Z = H, i.e., ethyl chloride (1, Table V).

Substituents with π - or p-electrons (14–21, Table V) directly attached to the reaction center may delocalize their electrons (resonance effect) with the positively charged carbon atom in the transition state. Consequently, these substituents cannot be plotted in Figure 1, and they should be correlated with electrophilic substituent constant σ^+ -values. However, σ^+ -parameters have only been defined for substituents on the benzene ring and not adjacent to the reaction site. Even though steric factors can simultaneously interfere with delocalization, the effect of these substituents is polar in nature.

The slopes of the lines from the gas-phase pyrolysis of primary, secondary, and tertiary chlorides indicate by extrapolation $(\rho_{T_2}/\rho_{T_1} = T_1/T_2)$ that the positive nature at the carbon reaction center of the C-Cl bond in the transition state increases from primary to tertiary carbon atom⁴ (Tables VI and VII).

A few years ago, a work on the gas-phase pyrolysis of pinacolyl chloride⁵ (6, Table V) reported the absence of a Wagner-Meerwein rearrangement during the decomposition process. According to this paper, the reaction as described in eq 3 showed no changes of olefin products distribution at three different temperatures.

$$\begin{array}{l} (CH_3)_3CCHClCH_3 \rightarrow (CH_3)_3CCH=CH_2 + \\ (CH_3)_2C=C(CH_3)_2 + HCl + (CH_3)_2CHC(CH_3)=CH_2 (3) \end{array}$$

TABLE VII: Extrapolation of ρ^* -Values for Polar Substituents

compd	ρ*			
(Z = polar)	300 °C	360 °C	440 °C	
ZCH ₂ CH ₂ Cl	-0.37	-0.32	-0.30ª	
ZCHCICH ₃	-0.51	-0.46^{b}	-0.41	
$Z(CH_3)_2CCl$	-0.73°	-0.63	-0.59	

^aValue from ref 2. ^bValue obtained in this work. ^cValue from ref 3.

Apparently, the yields of the dimethylbutenes proceeded by a kinetic control. Moreover, the authors of the said paper were very cautious to rationalize the formation of about 12% of the 2,3-dimethylbutenes. From a careful analysis of their results, it is reasonable to assume a Wagner-Meerwein rearrangement during the dehydrohalogenation process of pinacolyl chloride in the gas phase. In this sense, the reaction may be described as going in two pathways (eq 4).



The main olefin product 3,3-dimethyl-1-butene, formed through the normal four-centered cyclic transition state, did not isomerize to the 2,3-dimethylbutenes,⁵ while 2,3-dimethyl-1-butene isomerized little to 2,3-dimethyl-2-butene. Consequently, the yields of the 2,3-dimethylbutenes, which appear to be formed by a

The correlations obtained in the gas-phase pyrolyeses of aliphatic primary, secondary, and tertiary chlorides support Maccoll's theory on the heterolytic nature of the transition state for alkyl halide pyrolysis in the gas phase.⁴

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Kinetic Study of the Complexations of Cryptand 222 with Alkaline Earth Ions by the **Conductance Stopped-Flow Method**

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Two relaxation steps are observed in the complexation reaction between alkaline earth ions (Ca^{2+} , Sr^{2+} , and Ba^{2+}) and cryptand 222 using the conductance stopped-flow (CSF) method. The faster relaxation step (relaxation time τ_1) shows a large amplitude of conductance change, and the reciprocal value $(1/\tau_1)$ increases linearly with the concentration of cryptand under the condition [cryptand] \gg [metal ion]. The slower relaxation step (relaxation time (τ_2)) shows a relatively small amplitude, and its reciprocal value $(1/\tau_2)$ first increases and then levels off with increase in the concentration of cryptand. We propose a reaction mechanism involving three steps; the faster step of the encounter reaction observed is a cleavage of the coordinated water molecules from a metal ion. The slower step is an inclusion of a metal ion into the cavity of cryptand. There exists another step prior to the faster step that is a conformational change of cryptand but is too fast to observe by the CSF method. Thermodynamic parameters of the faster and the slower steps are evaluated and these values support the proposed mechanism. Ionic radii of alkaline earth ions show a great influence on the faster and the slower steps.

Introduction

The formation of stable complexes of the synthetic macrobicyclic ligand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8] hexacosane (cryptand 222) with alkali and alkaline earth ions was first described by Lehn and co-workers^{1,2} and the chemical properties of the cryptand have been extensively studied by many researchers.³⁻⁵ They insist in their reports that cryptand has a conformational rearrangement (endo-endo ≈ exo-exo) in the position of lone pairs of nitrogen atoms.^{1,2} Kinetic studies of complexation of cryptands with alkali ions and Ti⁺ using ¹H NMR⁶ or ²³Na NMR,⁷ with Li⁺ using ⁷Li NMR,⁸ and with alkaline earth ions using potentiometric titration⁶ or the stopped-flow method in the presence of metal indicator⁹ have been reported. But the direct analysis by a spectrophotometric method has not been carried out owing to the lack of significant visible or ultraviolet spectral changes. The CSF method is a convenient technique for kinetic analyses of ionic reactions such as the present complexations because most ionic reactions are accompanied by a significant change in conductance in the course of the reaction. Recently we constructed several types of CSF apparatus and applied them to various ionic reaction systems including metalmacroion complexations and macrocation-macroanion complexations (polyelectrolyte complex).¹⁰⁻¹⁶

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Recently Cox and co-workers have measured the dissociation rates (k_d) of metal cryptates in various kinds of solvents from the change in conductance caused by the addition of excess acid to the cryptate solution and evaluated the apparent second-order rates of complex formation with eq $1,^{17-21}$ where K is a stability constant.

$$k_{\rm f} = k_{\rm b} K \tag{1}$$

The complexations of cryptand with metal ions were analyzed as one-step reactions hitherto. However, other complexations, such as valinomycin and crown ether with metal ions, were reported to have at least two steps.

In this report we observed two relaxation steps in the complexation reaction, which suggests that this reaction has at least two more steps in addition to the rapid conformational change of the cryptand molecule.

Experimental Section

Materials. Cryptand 222 was obtained from Merck and used without further purification. All other reagents were of guaranteed grade. $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$ were dissolved in water that was deionized and distilled just prior to use. The pH of each solution was maintained higher than 11.0 in order to fully deprotonize the cryptand molecule.

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