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Substituent Effects in the Gas-Phase Eliminations of α-Substituted Alkyl Chlorides

The Pyrolyses of 2-Chloro-3-Methylbutane and Pinacolyl Chloride

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Abstract

The gas-phase pyrolyses of 2-chloro-3-methylbutane and pinacolyl chloride in the temperature range of 345–390°C and pressure range of 60–220 mm Hg are homogeneous and unimolecular in a seasoned reaction vessel. The temperature dependence of the rate constants is given by the Arrhenius equations

$$\log k_1\ (\text{sec}^{-1}) = (13.80 \pm 0.24) - (49{,}700 \pm 700)\ \text{cal/mol}/2.303RT$$

and

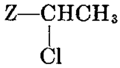
$$\log k_1\ (\text{sec}^{-1}) = (12.99 \pm 0.09) - (47{,}200 \pm 250)\ \text{cal/mol}/2.303RT$$

respectively. The Wagner–Meerwein rearrangement was not observed in these eliminations. Some correlations for the pyrolysis of α-substituted alkyl chlorides are presented and discussed. These facts are consistent with the heterolytic nature of the cyclic transition state mechanisms for these reactions.

Introduction

In view of the polar character and the analogy found between the unimolecular gas-phase elimination of alkyl halides and the solvolytic reactions of the corresponding substrates (S_N1 or E_1) in polar solvents [1], a few attempts of pyrolysis of Wagner–Meerwein type rearrangement-prone compounds were reported. Neopentyl chloride [2–4], which has no β-CH bond, was found to partially undergo a 1,2-methyl shift. A similar rearrangement has also been investigated where the thermal decomposition of bornyl [5] and isobornyl chlorides [1] gave the normal *cis*-elimination compound bornylene and the rearranged products camphene and tricyclene. Consequently, the present work was thought to be of interest at examining the pyrolyses of 2-chloro-3-methylbutane and pinacolyl chloride, since these compounds are known to rearrange in solution via a secondary carbonium ion [6–9]. However, if normal olefin-forming elimination of these halides occurs, then the effect of α-substituents Z in compounds of type (1)

(1)



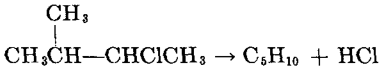
$$\mathrm{Z{-}CH(Cl)CH_3}$$

may well be correlated by a linear free energy relationship.

Results and Discussion

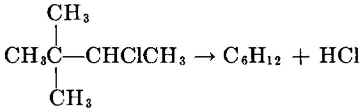
The stoichiometry based on reactions (2) and (3)

(2)



$$\mathrm{CH_3CH(CH_3){-}CHClCH_3 \rightarrow C_5H_{10} + HCl}$$

(3)



$$\mathrm{CH_3C(CH_3)_2{-}CHClCH_3 \rightarrow C_6H_{12} + HCl}$$

in vessels seasoned with the products of decomposition of allyl bromide, indicates that for long reaction times the final pressure P_f should be twice the initial pressure P_0. Experimentally, the average results of P_f/P_0 obtained out of five different temperatures were: 1.98 for 2-chloro-3-methylbutane [reaction (2)] and 1.96 for pinacolyl chloride (3-chloro-2,2-dimethylbutane) [reaction (3)]. An additional agreement of the stoichiometry was possible by comparing, within reasonable limits of analysis, the percentage decomposition as determined from pressure measurements with those obtained from the chromatographic analyses of the olefins. The hydrogen chloride evolved from the elimination reaction was removed by passing the gaseous mixture over soda lime. The alkyl chloride (2) yielded mainly 3-methyl-1-butene, 2-methyl-2-butene, and small amounts of 2-methyl-1-butene, whereas reaction (3) gave mostly 3,3-dimethyl-1-butene and little quantities of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

The homogeneity of these eliminations was examined by using a vessel of surface-to-volume ratio of 6.14 relative to the normal vessel. The packed and unpacked clean Pyrex vessel gave a dramatic change in rates and olefin distributions in both halides, thus suggesting that some heterogeneous effect on pyrolysis is taking place. However, when these vessels are seasoned with allyl bromide the reactions are homogeneous.

The analyses of the products of decomposition of both chlorides in an unpacked seasoned vessel are given in Table I. The pure olefins showed no change when pyrolyzed in a normal seasoned vessel during a period of half an hour and at 390°C. However, these results were compared with those obtained in the pyrolyses of the butanes–HCl gaseous mixtures (Table II), whereby it appears that hydrogen chloride is responsible for some of the isomerizations.

TABLE I. Distribution of olefins.

2-Chloro-3-methylbutane

Temperature (°C)	Time (min)	% Reaction	% 3-methyl-1-butene	% 2-methyl-2-butene	% 2-methyl-1-butene
360	23	50.2	22.5	21.4	3.6
370	13	49.9	24.4	21.2	3.2
390	4.25	51.1	25.2	18.5	1.1

Pinacolyl Chloride

Temperature (°C)	Time (min)	% Reaction	% 3,3-dimethyl-1-butene	% 2,3-dimethyl-2-butene	% 2,3-dimethyl-1-butene
345	59	50.3	46.1	2.4	3.0
360	23	50.0	44.8	3.8	2.9
380	7.5	54.4	41.0	3.9	2.6

Vessel surface-to-value ratio = 1 and seasoned with allyl bromide.

TABLE II. Isomerization of butene derivatives in a seasoned vessel.

Methylbutenes

Olefin	Time (min)	% 3-methyl-1-butene	% 2-methyl-2-butene	% 2-methyl-1-butene
3-methyl-1-butene	5	98.1	1.9	—
2-methyl-2-butene	5	2.0	88.0	10.0
2-methyl-1-butene	5	1.0	30.0	69.0

Dimethylbutenes

Olefin	Time (min)	% 3,3-dimethyl-1-butene	% 2,3-dimethyl-2-butene	% 2,3-dimethyl-1-butene
3,3-dimethyl-1-butene	4	99.8	0.2	—
2,3-dimethyl-2-butene[a]	4	—	93.9	3.2
2,3-dimethyl-1-butene[b]	4	—	9.4	85.3

Vessel surface-to-volume ratio = 1.
Proportion of olefin to HCl 1:1 and at 390°C.

[a] A mixture of 2.9% of chlorides was also produced.

[b] Yield of chloride mixture 5.3%.

TABLE III. Effect of cyclohexene on rates.

2-Chloro-3-methylbutane (370.2°C)			
P_c (mmHg)	217.5	109.9	92.0
P_i/P_c	—	0.97	2.35
$10^4 k_1$ (sec^{-1})	8.36	8.34	8.34
Pinacolyl Chloride (360.1°C)			
P_c (mmHg)	146.4	133.0	95.8
P_i/P_c	—	0.87	2.12
$10^4 k_1$ (sec^{-1})	5.02	5.04	5.11

P_c—pressure of the chloride; P_i—pressure of the cyclohexene inhibitor.

The reactions showed no induction period, and the addition of cyclohexene as chain inhibitor resulted in no significant effect in the reaction rate (Table III). Therefore these reactions are unimolecular.

The rates of decomposition are independent of the initial pressure of the chloride (Table IV), and the first-order log plots are satisfactory to 60% decomposition. The variation of the rate constants with temperature is shown in Table V.

From the experimental results, the following Arrhenius equations are obtained by means of a least square procedure. The errors were calculated with a confidence coefficient of 0.8:

2-chloro-3-methylbutane:

$$\log k_1(\text{sec}^{-1}) = (13.80 \pm 0.24) - (49{,}700 \pm 700)\ \text{cal/mol}/2.303RT$$

pinacolyl chloride:

$$\log k_1(\text{sec}^{-1}) = (12.99 \pm 0.09) - (47{,}200 \pm 250)\ \text{cal/mol}/2.303RT$$

The data listed in Tables I and II indicate that 2-chloro-3-methylbutane did not undergo a 1,2-methyl shift. The formation of 2-methyl-1-butene appears to be the product of isomerization through addition of HCl to the other unrearranged elimination product 2-methyl-2-butene. Very small quantities of rearranged dimethylbutenes from pinacolyl chloride are detected, and 2,3-

TABLE IV. Variation of rate constants with initial pressure.

2-Chloro-3-methylbutane (370.2°C)				
P_0 (mmHg)	63.0	117.1	149.0	217.5
$10^4 k_1$ (sec^{-1})	8.61	8.66	8.27	8.36
Pinacolyl Chloride (370.1°C)				
P_0 (mmHg)	113.7	135.0	151.7	164.9
$10^4 k_1$ (sec^{-1})	9.81	9.30	9.51	9.21

TABLE V. Variation of rate constants with temperature.

2-Chloro-3-methylbutane							
Temperature (°C)	345.15	350.12	355.14	360.12	370.21	380.06	390.06
10^4k_1 (sec^{-1})	1.74	2.50	3.27	4.53	8.39	14.98	27.54
Pinacolyl Chloride							
Temperature (°C)	345.04	350.13	355.08	360.14	370.10	380.09	390.13
10^4k_1 (sec^{-1})	2.06	2.80	3.77	5.22	9.46	15.67	28.25

dimethyl-1-butene apparently results from the HCl isomerization of 2,3-dimethyl-2-butene. The lack of Wagner–Meerwein rearrangements has also been observed in the pyrolysis of pinacolyl acetate [10], and consequently these results question any true ionic or ion-pair [11] type of mechanisms for these reactions.

A careful analysis of Table VI, where the comparative effect of substituents Z in compound type (1) is indicated, shows that three modes of electronic transmissions evidently take place. First, if the transition state for the elimination of these chlorides is represented by an elongation of the C-Cl bond and a subsequent polarization in the sense $C^{\delta+}$.....$Cl^{\delta-}$, then the +I inductive release of alkyl groups will tend to stabilize the partially positive charged carbon atom; thus enhancement of the reaction rate follows. This fact is best projected in Figure 1, where the Taft correlation is portrayed [22,23]. The sequence $Bu^t > Pr^i > Et > Me > H$ with $\rho^* = -3.55$ seems to support the assumed mechanism. Second, substituents of −I inductive effect must reduce the elongation and the degree of polarization of the C-Cl bond, which apparently is the rate-determining step of these reactions. Therefore, the decomposition rate has to be slower and the sequence MeCO > Cl > F is, as expected, very much in accord with their electronegative differences. These groups give a ρ^* value of −0.51 in Figure 1. The inflection point of the line at $\sigma^*(CH_3) = 0.0$ (Fig. 1) in two slopes may well be the result of small alterations in the polarity of the transition state due to changes in electron transmission at the α carbon. The $\sigma^*(Z)$ values for halogens were estimated from $\sigma^*(Z) = 2.7\ \sigma^*(ZCH_2)$. The reason why the H substituent gave a very low reactivity is due to the fact that generally primary halides are much slower in gas-phase elimination than secondary halides. Finally, the vinyl and phenyl groups with their π electrons and the MeO and EtO with their p electrons of the oxygen atom can greatly interact or delocalize with the empty p orbital of the adjacent carbon atom to the extent that a dramatic increase in rate is expected and obtained. It is reasonable to find that the sequence for elimination velocity is EtO > MeO > Ph > $CH_2 = CH$ > H, and their rate ratios relative to 1-phenylethyl chloride are correlated with σ_p^+ values [24] (Fig. 2). From these results it can

TABLE VI. Kinetic parameters for ZCHClMe elimination at 360°C.[a]

Z	10^4k_1 (sec^{-1})	10^4k_{Me} (sec^{-1})	Relative rate[b]	E_a (cal/mol)	log A (sec^{-1})	Reference
H	0.007	0.007	1	58,500 (±800)	14.05 (±0.26)	[12]
Me	1.01	0.51[c]	70	50,600 (±500)	13.47 (±0.17)	[13]
Et	3.33	1.43[d]	200	49,800 (±1000)	13.71 (±0.36)	[14]
Pr^i	4.43	2.04[e]	290	49,700 (±700)	13.80 (±0.24)	This work
Bu^t	5.00	4.50[f]	630	47,200 (±250)	12.99 (±0.09)	This work
$CH_2=CH$	4.09	4.09	570	48,700 (±500)	13.42 (±0.17)	[15]
Ph	13.58	13.58	1900	44,900 (±450)	12.63 (±0.17)	[16]
MeO	9,600.00	9,600.00	1.4×10^6	33,200 (±1100)	11.44 (±0.53)	[17]
EtO	12,700.00	12,700.00	1.8×10^6	30,700 (±1100)	10.70 (±0.52)	[18]
MeCO	0.066	0.066	9	49,200 (±1000)	11.80 (±0.33)	[19]
Cl	0.094	0.047[g]	7	52,900 (±1000)	13.23 (±0.33)	[20]
F	0.016	0.016[h]	2	57,400 (±1100)	14.02 (±0.30)	[21]

[a] The Arrhenius parameters were recalculated from data of cited references by the least square 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] Value estimated from 46% yield of 3-methyl-1-butene at 360°C.

[f] Yield of the 3,3-dimethyl-1-butene was 90% at 360°C.

[g] Rate for a single chlorine elimination.

[h] The competing elimination of HF from 1-chloro-1-fluoroethane is less than 1% at 360°C.

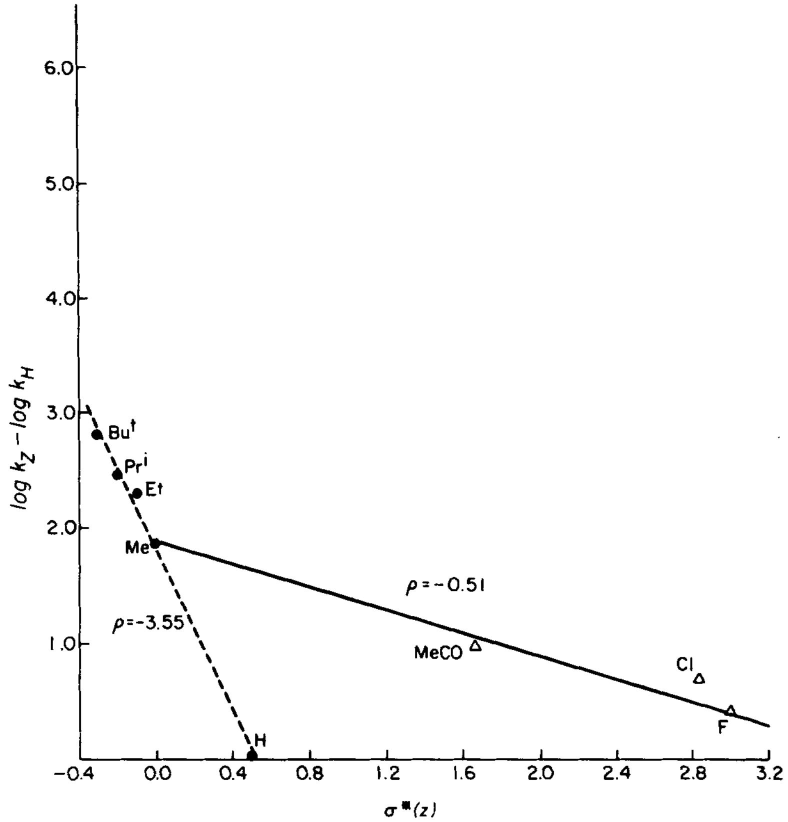


Figure 1. Slopes of relative rates versus $\sigma^*(Z)$ for electron releasing and withdrawing substituents Z in the pyrolysis of $ZCHClCH_3$.

be concluded that the greater the stabilization of the partially positive adjacent carbon atom by a substituent in the transition state, the faster the elimination rate. Further, the negative ρ values of Figures 1 and 2 confirm additionally the heterolytic nature of these reactions [1].

Although ion-pair reactions in the gas phase have been expected to give ρ values in the range of -3 to -5 [25], the results of the present work imply that this parameter should be more negative for this type of intermediate, since 2-chloro-3-methylbutane and pinacolyl chloride failed to rearrange.

Experimental

2-Chloro-3-methylbutane, boiling point 40–42°C at 50 mmHg (91°C at 753 mmHg [26]) and pinacolyl chloride (3-chloro-2,2-dimethylbutane), boiling point 30–32°C at 20 mmHg (109.9°C at 749 mmHg [27]), were obtained by the

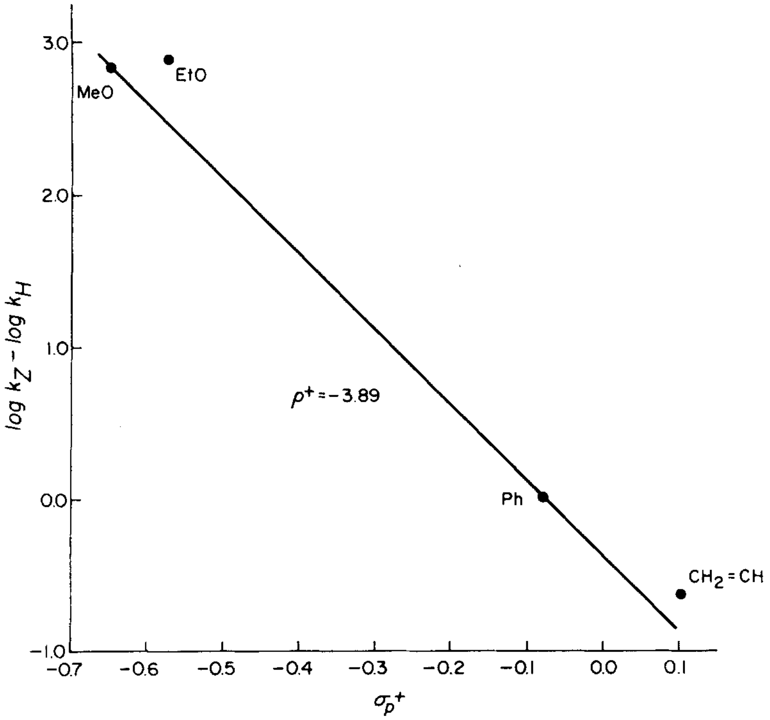


Figure 2. Slope of relative rate versus σ_p^+ for substituents Z with available p electrons in the pyrolysis of $ZCHClCH_3$.

treatment of the corresponding p-toluene sulphonyl ester derivatives with lithium chloride in dimethylformamide and hexamethylphosphoramide under vacuum as described recently [28]. The 2-chloro-3-methylbutane and pinacolyl chloride were distilled several times, and the fractions of 97% and 99% respectively, (gas–liquid chromatography) were used. The olefins 2,3-dimethyl-1-butene, 3-methyl-1-butene, and 2-methyl-1-butene were acquired from K & K Lab., Inc., whereas 2,3-dimethyl-2-butene, 3,3-dimethyl-1-butene, and 2-methyl-2-butene were from Aldrich Chemicals. These compounds were over of 99% purity and used as standard references. The starting materials and the products were determined quantitatively by the method of internal standard on a Perkin-Elmer F-11 gas chromatograph provided with a flame ionization detector. Di-isodecyl phthalate 5%-Chromosorb G.A.W. D.M.C.S. 60–80 mesh was used for the chloride and dimethylbutene analyses. Methylbutenes were analyzed quantitatively with a bis(2-methoxy ethyl)adipate 5%-Chromosorb G. A.W. D.M.C.S. 80–100 mesh column. The purity of the halides and products were additionally confirmed with a Varian MAT 111 mass spectrometer, and by infrared and nuclear magnetic resonance spectroscopy. The least square resonance calculations were made with a Digital PDP 1145 computer.

The chlorides were pyrolyzed in vessels seasoned by the products of decomposition of allyl bromide [29, 30] in a static system and the kinetics followed manometrically.

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