netically, as well as statically, plausible.

In review, the three steps of the proposed mechanism may be described as follows: (i) the adsorption–desorption process of Na^+; (ii) the diffusion process of methylammonium ion on the surface; (iii) the adsorption process of the methylammonium ion on the site in the cage (intracrystalline diffusion). The rate of this step may be controlled by the size of the cation.

In the present system, the negative log of the static equilibrium constant of the overall reaction, calculated from

$$K' = \frac{(\text{amount of A}^+ \text{ adsorbed})[\text{Na}^+]}{[\text{S}\cdot\text{Na}][\text{A}^+]} \qquad (13)$$

was determined to be $pK' = -1.4$. This value of the pK' obtained is nearly equal to that determined by Barrer et al.[7] only in clinoptilolite–methylamine system, $pK' = -1.1$. Certainly, the orderly agreement between both equilibrium constants does not validiate the proposed model, but should be noted by zeolite chemist. In the ion exchange, the entering process of the methylammonium ion into the cage can be separated by only the kinetic approach. On the other hand, the fact that the amounts of Na^+ released are greater than that of methylammonium ion adsorbed may be due to hydrolysis of the methylammonium ion in solution followed by hydronium ion exchange for Na^+. However, at the present pH, the hydronium ion seems not to be responsible for Na^+ release.

With respect to step a in reaction V, from the measurement of the concentration change of Na^+ in the present system, it was seen that the equilibration required 72 h, in agreement with the results of both Sherry et al.[2,11] and Barrer et al.[7] Moreover, from the kinetic results, the concentration dependences of the two relaxation times cannot be interpreted except for the case that step a is much slower than steps b and b′. Thus, the rate-determining step of the ion exchange in zeolite 4A can be attributed to step a. This result, furthermore, leads to the conclusion that the affinity of the site in the cage of zeolite 4A for small Na^+ may be stronger than that for the methylammonium ion.

It may be expected that much important information may be obtained from the dependences of the rate constants on various parameters. Similar kinetic studies for series of amines are now in progress, in order to obtain the dynamic information of amines in the cage of zeolite 4A, and with use of the proposed mechanism the interesting results will be reported in a subsequent paper.

Acknowledgment. The authors thank Toyo Soda Co. for the zeolite 4A.

Homogeneous Unimolecular Pyrolysis Kinetics of *o*-, *m*-, and *p*-Methyl-2-phenylethyl Chlorides

Gabriel Chuchani,* José D. Medina, Ignacio Martín, and José A. Hernandez A[1]

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 1010-A, Venezuela

(Received: April 10, 1981; In Final Form: July 6, 1981)

The pyrolysis kinetics of isomeric methyl-2-phenylethyl chlorides have been studied in a static system over the pressure range of 56–240 torr and the temperature range of 419–470 °C. These eliminations in seasoned vessels and in the presence of propene inhibitor are homogeneous and unimolecular, and follow a first-order rate law. The rate coefficients are given by the following Arrhenius equations: for *o*-methyl-2-phenylethyl chloride, $\log k_1\ (\mathrm{s}^{-1}) = (13.76 \pm 0.27) - (231.4 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$; for *m*-methyl-2-phenylethyl chloride, $\log k_1\ (\mathrm{s}^{-1}) = (12.84 \pm 0.26) - (219.2 \pm 3.5)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$; for *p*-methyl-2-phenylethyl chloride, $\log k_1\ (\mathrm{s}^{-1}) = (14.03 \pm 0.19) - (234.1 \pm 2.5)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$. The electron release of the methyl substituent, at the three isomeric positions of the benzene ring, is very weak and does not reinforce the phenyl participation in rate enhancement relative to 2-phenylethyl chloride.

Introduction

The occurrence of neighboring group participation in gas-phase elimination of 2-substituted ethyl chlorides[2–6] was to be expected on the basis of Maccoll's hypothesis,[7] where he proposed that the cyclic transition-state mechanism for alkyl halides pyrolysis is heterolytic in nature. These results have therefore inferred that anchimeric assistance in gas-phase reactions may be most effective[4] when (a) the transition state is very polar, (b) the participating atom is large and can therefore overlap, and (c) the participating atom is highly polarizable.

The phenyl group in $PhCH_2CH_2Cl$ was found to participate in the gas-phase pyrolysis of this halide.[3] The aromatic substituent causes a significant increase in the rate relative to ethyl chloride by an order of magnitude ascribed to the formation of a discrete phenonium ion in the transition state. Furthermore, the presence of the CH_3O group at the para position of the benzene ring in 2-phenylethyl chloride corroborated the above view where a corresponding augmentation in rate evinces the participation of the aromatic neighboring group in these reactions. An argument against the above consideration is that the acidity of the β hydrogen of the C_β–H bond adjacent to the benzene ring may assist these eliminations, yet, a

---

(1) Visiting Scientist, Facultad de Medicina, Universidad Central, Caracas.

(2) Chuchani, G.; Martín, I.; Bigley, D. B. *Int. J. Chem. Kinet.* **1978**, *10*, 649.

(3) Hernandez A., J. A.; Chuchani, G. *Int. J. Chem. Kinet.* **1978**, *10*, 923.

(4) Chuchani, G.; Martin, I.; Martin, G.; Bigley, D. B. *Int. J. Chem. Kinet.* **1979**, *11*, 109.

(5) Chuchani, G.; Hernandez A., J. A.; Martin, I. *Int. J. Chem. Kinet.* **1979**, *11*, 1279.

(6) Chuchani, G.; Martin, I.; Alonso, M. E.; Jano, P. *Int. J. Chem. Kinet.* **1981**, *13*, 1.

(7) Maccoll, A. *Chem. Rev.* **1969**, *69*, 33.

0022-3654/81/2085-3900$01.25/0

TABLE I: Rate Coefficients at Different Temperatures

			o-Methyl-2-phenylethyl Chloride				
temp, °C	430.1	435.3	440.2	445.1	450.1	460.0	470.1
$10^4 k_1$ (s^{-1})	3.72	4.84	6.77	8.46	11.68	18.77	30.89
			m-Methyl-2-phenylethyl Chloride				
temp, °C	430.1	435.1	440.2	445.1	450.2	460.1	470.2
$10^4 k_1$ (s^{-1})	3.60	4.76	6.23	7.98	10.21	16.75	27.57
			p-Methyl-2-phenylethyl Chloride				
temp, °C	419.2	430.2	440.0	444.9	449.4	459.1	466.0
$10^4 k_1$ (s^{-1})	2.30	4.52	7.60	9.81	12.78	21.57	30.46

reasonable explanation indicated that this phenomenon may be disregarded.

As phenyl participation has been reported in a couple of pyrolyses of phenylethyl chloride,[3] it seemed desirable to obtain additional data regarding the occurrence of anchimeric assistance in this type of compounds. Therefore, the present work aimed to study the kinetis of the gas-phase elimination of *o*-methyl-, *m*-methyl-, and *p*-methyl-2-phenylethyl chlorides.

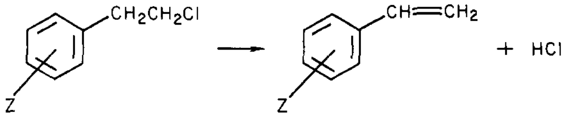
Experimental Section

The substrates *o*-methyl-, *m*-methyl-, and *p*-methyl-2-phenylethyl chlorides were prepared by treating the corresponding phenylethyl alcohol in dimethyl aniline with thionyl chloride as reported.[8] *o*-Methyl-2-phenylethyl chloride had a boiling point of 74 °C at 3.5 torr (lit. bp 96–97 °C at 15 torr[9]). *m*-Methyl-2-phenylethyl chloride had a boiling point of 73.5 °C at 3.5 torr. *p*-Methyl-2--phenylethyl chloride had a boiling point of 74 °C at 3.0 torr (lit. bp 81–85 °C at 10 torr[10]). These halides were distilled several times and the fraction over 99.0% purity (gas–liquid chromatography) was used (FFAP-7% Chromosorb W AW DMCS 80-100 mesh). The styrenes were prepared by the common method of treating the corresponding phenylethyl chloride with sodium ethoxide–ethanol solution. Thus, *o*-methylstyrene was prepared as described.[11] *m*-Methylstyrene had a boiling point of 60–61 °C at 11 torr (lit. bp 61–62 °C at 18 torr[12]). *p*-Methylstyrene had a boiling point of 53 °C at 3 torr (lit. bp 59–90 °C at 12 torr[12]). The above FFAP column was also used for the styrenes analyses. The identity of the phenethyl chlorides and the styrenes were additionally verified by mass spectrometry and by infrared and nuclear magnetic resonance spectroscopy.

The pyrolysis reactions were carried out in a static system in vessels previously seasoned by the product of decomposition of allyl bromide,[13,14] and in the presence of propene inhibitor. The halides were injected directly into the reaction vessel with a syringe through a silicone rubber septum.[15] The temperature was measured to better than ±0.2 °C with a calibrated platinum—platinum–13% rhodium thermocouple. The reaction vessel showed no temperature gradient at different points and the kinetic measurements were followed by monitoring the pressure increase.

Results and Discussion

The products of the gas-phase pyrolysis of ring-substituted methylphenylethyl chlorides (eq 1), in vessels previously seasoned with allyl bromide, are predominantly the corresponding substituted styrene and hydrogen chloride.



(1)

Z = o-CH_3, m-CH_3, and p-CH_3

The stoichiometry represented by eq 1 was proved by a series of reaction times of ten half-lives and at four different temperatures. In each case the final pressure, P_f, was found to be approximately double the initial pressure, P_0. Only a small departure from the required stoichiometry was found in *m*-methyl-2-phenylethyl chloride ($P_f/P_0 = 1.83$), due to the polymerization of the product *m*-methylstyrene. A further confirmation of the above stoichiometry is that the hydrogen chloride produced is equivalent to the pressure increase.

The eliminations were checked for homogeneity by using a vessel packed with glass tubing in which the surface-to-volume ratio has been increased by a factor of 6.14 compared with the unpacked vessel. The packed clean Pyrex vessel had only a little heterogeneous effect on the *o*-methyl-2-phenylethyl chloride. Yet, when the vessels are seasoned with allyl bromide no significant effect on the rate coefficients for pyrolysis of these chlorides was observed. The presence of a free-radical inhibitor such as propene showed no effect on the rates and no induction period was noticed.

The rate coefficients for the gas-phase elimination of these halides are independent over the initial pressure investigated and the first-order plots are found to be satisfactorily linear up to 70% decomposition. The temperature dependence of the rates of the reaction (Table I) have expressed in the following Arrhenius equations obtained by the least-squares procedure and 0.8 confidence coefficient:

o-methyl-2-phenylethyl chloride

$$\log k_1\ (\mathrm{s}^{-1}) = (13.76 \pm 0.27) - (231.4 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$$

m-methyl-2-phenylethyl chloride

$$\log k_1\ (\mathrm{s}^{-1}) = (12.84 \pm 0.26) - (219.2 \pm 3.5)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$$

p-methyl-2-phenylethyl chloride

$$\log k_1\ (\mathrm{s}^{-1}) = (14.03 \pm 0.19) - (234.1 \pm 2.5)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$$

In Table II, the rates of pyrolysis of the methyl- and methoxy-substituted 2-phenylethyl chlorides are compared with that of ethyl chloride. Even though the phenyl group

---

[8] Bergman, E.; Weizmann, A. *J. Org. Chem.* **1939**, *4*, 266.
[9] Baddeley, G.; Chadwick, J. *J. Chem. Soc.* **1951**, 368.
[10] Drake, N. L.; McVey, W. C. *J. Org. Chem.* **1939**, *4*, 464.
[11] Brown, R.; Moggridge, R. C. G. *J. Chem. Soc.* **1946**, 816.
[12] Titley, A. F. *J. Chem. Soc.* **1926**, 508.
[13] Maccoll, A. *J. Chem. Soc.* **1955**, 965.
[14] Maccoll, A.; Thomas, P. J. *J. Chem. Soc.* **1955**, 979.
[15] Bridge, M. R.; Davies, D. H.; Maccoll, A.; Ross, R. A.; Banjoko, O. *J. Chem. Soc. B* **1968**, 805.
[16] Evans, P. J.; Ichimura, T.; Tschiukow-Roux, E. *Int. J. Chem. Kinet.* **1978**, *10*, 855.

TABLE II: Kinetic Parameters of ZCH_2CH_2Cl at 440 °C

Z	10^4k_1, s^{-1}	rel rate per H	E_a, kJ/mol	log A, s^{-1}	ref
H	1.34	1.0	241.8 (±4.2)	13.84 (±0.20)	16
C_6H_5	7.73	8.6	220.9 (±4.6)	13.07 (±0.35)	3
o-$CH_3C_6H_4$	6.44	7.2	231.4 (±3.6)	13.76 (±0.27)	this work
m-$CH_3C_6H_4$	6.07	6.7	219.2 (±3.5)	12.84 (±0.26)	this work
p-$CH_3C_6H_4$	7.60	8.4	234.1 (±2.5)	14.03 (±0.19)	this work
p-$CH_3OC_6H_4$	12.00	13.3	228.4 (±4.6)	13.81 (±0.34)	3

assists the elimination in each of these halides, the electron release of the methyl group, at the three isomeric positions of the benzene ring, is apparently ineffective on the rate of dehydrohalogenation when compared to the unsubstituted 2-phenylethyl chloride. Within the experimental error, the reaction velocities are the same. Therefore, the effect of the CH_3 substituent appears to be weak in order to reinforce the phenyl assistance in rate augmentation in some of these methyl 2-phenylethyl chlorides. However, in the case of the p-methoxy substituent, its electron delocalization (+R effect) toward the aromatic nuclei causes a significant increase in rates by participation of the p-anisyl when compared with ethyl chloride and 2-phenylethyl chloride as already described.[3]

Steric Acceleration in the Pyrolysis Kinetics of 2-Substituted Ethyl Acetates

Ignacio Martîn[1] and Gabriel Chuchani*

Centro de Quîmica, Instituto Venezolano de Investigaciones Cientîficas, Apartado 1827, Caracas 1010-A, Venezuela

(Received: April 28, 1981; In Final Form: July 6, 1981)

The rates of elimination of several cyclo and branched alkyl substituents at the β carbon of ethyl acetates have been determined in a static system over the temperature range of 360–420 °C and pressure range of 34–337 torr. The reactions are homogeneous in both clean and seasoned vessels, follow a first-order rate law, and are unimolecular. The rate coefficients are given by the following Arrhenius equations: for 2-cyclohexylethyl acetate, $\log k_1\ (s^{-1}) = (13.30 \pm 0.28) - (208.1 \pm 3.4)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 2-cyclopentylethyl acetate, $\log k_1\ (s^{-1}) = (13.20 \pm 0.26) - (207.4 \pm 3.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 3-methyl-1-pentyl acetate, $\log k_1\ (s^{-1}) = (13.62 \pm 0.09) - (211.9 \pm 1.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 4-methyl-1-pentyl acetate, $\log k_1\ (s^{-1}) = (12.82 \pm 0.05) - (203.1 \pm 0.6)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$. The present data together with those reported in the literature give a good correlation line only, when plotting $\log k/k_0$ against Hancock's E_s^c values ($r = 0.916$, $\delta = -0.121$, and intercept = -0.020 at 400 °C). This work ratifies that steric acceleration is responsible for the rate of elimination of alkyl and several polar substituents interposed by at least three methylene groups with respect to C_α–O bond of ethyl acetates. Unreported E_s^c values of several substituents are defined.

Introduction

Linear correlation for the gas-phase elimination of aliphatic β-substituted ethyl acetates have been reported only recently.[2,3] The compiled data and experimental results in these works revealed the various type of effects of Z in $ZC_\beta H_2C_\alpha H_2OAc$. Thus, we have group A where β-alkyl groups and several polar substituents interposed by at least three methylene groups with respect to the C_α–O bond of the acetate enhanced the rate of the reaction due to steric acceleration. Plotting $\log k/k_0$ vs. E_s values gave an approximate linear relationship ($r = 0.914$ at 400 °C). Steric acceleration has already been described for β-substituted ethyl acetates.[4] However, when the phenyl substituent in 2-phenylethyl acetate is considered an exception due to benzylic weakening of the C_β–H bond[2] and it is excluded from this graph, the above linear relationship will give an unsatisfactory correlation coefficient ($r = 0.800$ at 400 °C). This result suggests that additional data are needed for a better correlation. For group B, polar β substituents with a strong electron-withdrawing effect slowed the pyrolysis rates of these acetates.[3] In spite of small differences in effects, the greater the electronegativity of the substituent the slower is the pyrolysis. These groups gave a good linear relationship by plotting $\log k/k_0$ against σ^* values with $\rho^* = -0.19$ at 400 °C ($r = 0.961$). Likewise, plotting $\log k/k_0$ vs. σ_I values also yielded a good straight line with $\rho_I = -1.03$ at 400 °C ($r = 0.960$). The negative slopes indicated the formation of a partial positive carbon atom in the transition state and that electronic factors influenced the process of elimination. The only exception of the CH_3S substituent, which caused a significant acceleration, was attributed to the participation of the neighboring sulfur atom of the methylthio group. This consideration was derived by analogy with the anchimeric assistance of the said CH_3S group on the pyrolysis rate of 2-methylthioethyl chloride in the gas phase.[5] For group C, multiple-bonded or π-bonded substituents adjacent to the β carbon of ethyl acetate produce a strong activation in elimination rates due to the –M or –R effect. This phenomenon has already been

---

(1) Taken from the thesis of Ignacio Martîn, submitted to the Faculty of IVIC, January 1981, in partial fulfillment of the requirements for the Degree of Magister Scientiarum.

(2) Chuchani, G.; Martîn I.; Avila, I. *Int. J. Chem. Kinet.* 1979, *11*, 561.

(3) Chuchani, G.; Martîn I.; Hernândez A., J. A.; Rotinov, A.; Fraile, G.; Bigley, D. B. *J. Phys. Chem.* 1980, *84*, 944.

(4) Burgh Norfolk, S. de; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 280.

(5) Chuchani, G.; Martin, I.; Bigley, D. B. *Int. J. Chem. Kinet.* **1978**, *10*, 649.

0022-3654/81/2085-3902$01.25/0 © 1981 American Chemical Society