The Participation of Aromatic Neighboring Groups in Gas-Phase Elimination Reactions

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Abstract

The gas-phase pyrolysis of 2-chloroethylbenzene and *p*-methoxy-2-chloroethylbenzene was studied in a static system over the temperature range of 411°–471°C and a pressure range of 39–202 mm Hg. The reactions in seasoned vessels, with the propene inhibitor always present, were homogeneous, first-order, and unimolecular. The rate constants are given by the Arrhenius equation for 2-chloroethylbenzene:

$$\log k(\mathrm{sec}^{-1}) = (13.07 \pm 0.35) - (220.9 \pm 4.6)\mathrm{kJ/mol}/2.303RT$$

and for *p*-methoxy-2-chloroethylbenzene:

$$\log k(\mathrm{sec}^{-1}) = (13.81 \pm 0.34) - (228.4 \pm 4.6)\mathrm{kJ/mol}/2.303RT$$

The presence of phenyl substituents in the β position of ethyl chloride has been found to provide anchimeric assistance in these elimination reactions.

Introduction

The heterolytic nature of the transition state in the gas-phase pyrolyses of alkyl halides, already demonstrated by Maccoll [1], suggests that neighboring group participation in these types of reaction may be possible. Precisely this view has led to a recent successful result of the first convincing anchimeric assistance occurring to an alkyl halide, namely, 2-methylthioethyl chloride [2]. The latter compound was found to pyrolyze 234 times faster than ethyl chloride at 400°C. The large enhancement was explained in terms of participation of the easily polarizable neighboring sulfur atom of the SCH_3 group.

The β-phenylethyl system, especially with benzene sulfonate derivatives, has been found in reactions in solutions to be subject to anchimeric assistance by aryl participation [3, 4]. Therefore we wanted to further our study of neighboring group participation in gas-phase reactions with a similar

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type of compound. In this sense, the object of the present work is to determine the kinetics of the gas-phase elimination of 2-chloroethylbenzene and *p*-methoxy-2-chloroethylbenzene. The pyrolysis of the first-mentioned compound was reported at only one temperature [5a] and as a complete pyrolysis study in a micropulse reaction [5b].

Experimental

2-Chloroethylbenzene was acquired commercially (Aldrich) and redistilled. The fraction of 99.8% purity, as determined by gas–liquid chromatography, was used. Similarly, a commercial sample of styrene (Merck-Schuchard) was distilled several times and the fraction 98.6% (gas–liquid chromatography) was used. *p*-Methoxy-2-chloroethylbenzene was prepared by the addition of thionyl chloride to a mixture of *p*-methoxyphenethyl alcohol in dimethylaniline according to the procedure of Bergmann and Weizmann [6]. The boiling point was 132°C at 18 mm Hg; lit. 130°C at 20 mm Hg [7]. After several distillations, the *p*-methoxy-2-chloroethylbenzene used was 99.4% (gas–liquid chromatography) pure. *p*-Methoxystyrene was obtained by refluxing *p*-methoxy-2-chloroethylbenzene with a solution prepared from sodium and *n*-amyl alcohol [8]. The boiling point was 96°C at 17 mm Hg; lit. 91°C at 13 mm Hg [9]. This olefin was then fractionated several times until 99.4% purity (gas–liquid chromatography). The quantitative analyses of 2-chloroethylbenzene and styrene were done with a Perkin-Elmer F-11 chromatograph fitted with a flame ionization detector. The column used was Diisodecyl phthalate 5%-Chromosorb G A.W, D.M.C.S. 60–80 mesh. *p*-Methoxy-2-chloroethylbenzene and *p*-methoxystyrene were analyzed on a Hewlett-Packard 5700A chromatograph provided with a thermal conductivity detector. A column of Apiezon L 20%-Chromosorb P W A.W. 60–80 was used for these two compounds.

The hydrogen chloride quantitative titration was possible by separation from substrates and products using the trap-to-trap technique. The fraction of hydrogen chloride was trapped at −197°C, while the reagents and products were at −50°C. A solution of 0.0559 N of sodium hydroxide was then used for the acid titration.

The purity of the starting materials and products was also verified with a Hitachi-Perkin-Elmer RMU-6H mass spectrometer, by infrared Perkin-Elmer 577, and by nuclear magnetic resonance Varian A-60 spectroscopy. The least-squares calculations were carried out with a Digital PDP 1145 computer.

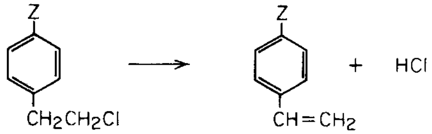
The substrates were injected directly into the reaction vessel through a silicon rubber septum. Extreme caution is necessary to avoid at minimum the introduction of air during injection of the chloride reagent. The oxygen of air tends to polymerize the styrene products under the conditions of the experiment.

The kinetic measurements were carried out in a static system in vessels seasoned by the products of decomposition of allyl bromide [10, 11], and the reaction was followed manometrically.

Results

The stoichiometry represented by Scheme 1 indicates that the ratio of the final pressure P_f to the initial pressure P_0 should be equal to 2. The average P_f/P_0 values at five different temperatures and ten halflives were 2-chloroethylbenzenes, 1.91, and *p*-methoxy-2-chloroethylbenzene, 2.59. The departure from the suggested stoichiometry is due to a small amount of polymerization of styrene in 2-chloroethylbenzene pyrolysis, whereas, in *p*-methoxy-2-chloroethylbenzene fragmentation and polymerization of the product *p*-methoxystyrene occurs. To confirm the above stoichiometry, the percentage decomposition of the chloride calculated from pressure measurements was found, as shown in Table I, to be in good agreement with that calculated from hydrogen chloride titration.

Scheme 1



The homogeneity of the reactions was examined by increasing the vessel in surface-to-volume ratio by a factor of 6.14. The rates were unaffected in seasoned vessels. Otherwise a small heterogeneous effect on the pyrolysis is found in clean packed and unpacked vessels. At all times a free radical inhibitor, propene, in an approximately 1:1 ratio in pressure with respect to the substrate, had to be used during the decomposition of these chlorides in order to avoid collateral reactions.

The rate constants of pyrolysis of these aromatic halides were found to be independent of their initial pressure. The first-order plots were satisfactorily linear up to 60% decomposition for 2-chloroethylbenzene and 40%

TABLE I. Stoichiometry of the reaction by acid titration.

	2-Chloroethylbenzene at 437.0°C					
Reaction (%)(press)	12.58	21.44	32.26	42.85	44.53	56.00
HCl titration (%)	12.31	21.08	32.35	41.94	44.89	54.88
	p-Methoxy-2-chloroethylbenzene at 422.0 °C					
Reaction (%)(press)	12.69	13.60	26.98	28.87	42.08	62.67
HCl titration (%)	12.93	13.32	24.56	29.69	41.18	60.66

for *p*-methoxy-2-chloroethylbenzene. The effect of temperatures upon the rate constants of these chlorides is shown in Table II.

The reliability of the rate constant values of Table II was checked in the following manner. (a) At 450°C, equal ratios of styrene with inhibitor or with inhibitor and HCl decompose in minute amounts up to 60% reaction of the 2-chloroethylbenzene. (b) At 452°C, equal ratios of *p*-methoxystyrene with inhibitor decompose 2.29 and 3.34% at 35 and 50% reaction, respectively, of the *p*-methoxy-2-chloroethylbenzene. Furthermore, the methoxystyrene with inhibitor and HCl gives 2.50 and 3.45% decomposition at 35 and 50% reaction of the substrate. Consequently the k values are within a reasonable limit of error in velocity constants.

The single k value reported for 2-chloroethylbenzene [5a] of 3.03×10^{-4} sec^{-1} at 698.7°K is quite close to the rate constant found in the present work, that is, 3.63×10^{-4} sec^{-1} at the same temperature. No comparison can be made with the pyrolysis results of the micropulse reaction [5b] since its kinetic parameters have been found to be considerably higher where some heterogeneous catalysis is taking place.

The data of Table II lead to the Arrhenius equation obtained by means of the least-squares procedure for 2-chloroethylbenzene: $\log k(\text{sec}^{-1}) = (13.07 \pm 0.35) - (220.9 \pm 4.6)$ kJ/mol/2.303 RT and for *p*-methoxy-2-chloroethylbenzene: $\log k(\text{sec}^{-1}) = (13.81 \pm 0.34) - (228.4 \pm 4.6)$ kJ/mol/2.303 RT. The errors were calculated with 80% confidence limits.

Discussion

Looking at Table III, when substituent Z in ZCH_2CH_2Cl is the aromatic ring, an increase in rate is observed relative to ethyl chloride. To explain this result, it seems reasonable to consider the neighboring phenyl group as providing anchimeric assistance to the elimination reaction. This interpretation may apparently find an objection in the sense that the hyperconjugative effect of the C_β-H bond adjacent to the benzene ring

Scheme 2

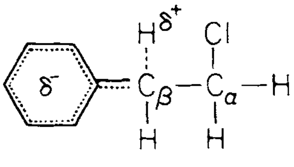


TABLE II. Variation of rate constants with temperature.

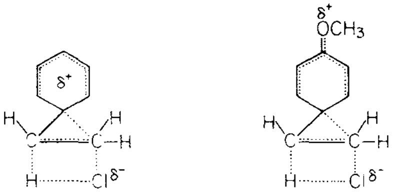
2-Chloroethylbenzene							
Temp. °C	422.0	432.1	437.0	442.0	450.8	461.1	471.0
$10^4 k(\text{sec}^{-1})$	2.83	4.99	6.52	8.30	13.10	22.90	34.50
p-Methoxy-2-chloroethylbenzene							
Temp. °C	411.8	423.5	432.2	443.5	452.4	461.9	471.3
$10^4 k(\text{sec}^{-1})$	2.51	4.35	7.60	13.55	22.40	35.50	60.03

TABLE III. Kinetic parameters of ZCH_2CH_2Cl at 440°C.

Z	kx10^4 (sec^{-1})	Rel. rate	Rel. rate per hydrogen	E_a (KJ/mol)	log A (sec^{-1})	Ref.
H	1.32	1	1	244.8(±3.4)	14.05(±0.26)	12
C_6H_5	7.76	5.9	8.8	220.9(±4.6)	13.07(±0.35)	This work
$CH_3OC_6H_4$	12.02	9.1	13.7	228.4(±4.6)	13.81(±0.34)	This work

(Scheme 2) can give rise to a greater acidity of the β hydrogen, and consequently a faster rate should be produced. The presence of the CH_3O group at the opposite side of the aromatic ring in phenylethyl chloride should lessen the C_β-H hyperconjugation. If this is so, the β-hydrogen decreases in acidity and the rate constant of *p*-methoxy-2-chloroethylbenzene should be much slower than 2-chloroethylbenzene. However, the experimental findings are quite to the contrary (Table III), and a significant increase in rate is obtained. The delocalization or +R effect of the OCH_3 group toward the benzene ring with the consequent augmentation in reaction velocity emphasizes the above assumption where the rate enhancement must therefore be aided by participation of the aromatic neighboring group. Therefore the order of reactivity shown in Table III results from the stabilization by partial bonding of the phenyl substituents to the $C^{\delta+} \ldots Cl^{\delta-}$ polarization in the transition state (Scheme 3):

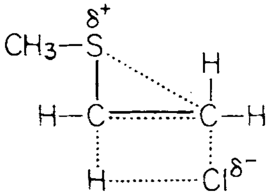
Scheme 3



The significantly lower *A* factor of 2-chloroethylbenzene with respect to that of ethyl chloride (Table III) is consistent with the proposed more rigid transition state in Scheme 3. The rate enhancement, due to a decrease in the energy of activation, can be the result of stabilization by aryl participation. In the case of the methoxy substituted compound, when compared to 2-chloroethylbenzene, a nearly equal E_a and an increase in *A* parameters are obtained. These data imply that electronic factors, mainly from the +R effect of the CH_3O substituent toward the benzene ring, contribute to the increase in rate.

The transition states as shown in Scheme 3 are similar to that proposed for the first reported convincing case of anchimeric assistance in a gas-phase reaction [2] with 2-methylthioethyl chloride (Scheme 4):

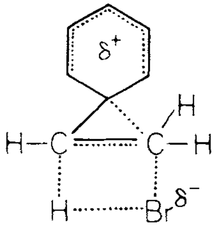
Scheme 4



Even though the relative rates of the chlorides (Table III) are not high by a factor of 234 as found in the pyrolysis of 2-methylthioethyl chloride relative to ethyl chloride at 400°C [2], it is possible to rationalize these results. The phenyl neighboring group is not as polarizable or highly nucleophilic for anchimeric assistance as the sulfur atom of the SCH_3 group.

The molecular gas-phase elimination of 2-bromoethylbenzene was reported at only one temperature [5a]. The first-order specific rate found at 385°C was $0.85\ (\pm 0.07) \times 10^{-4}\ \mathrm{sec}^{-1}$. If this single k value is compared to the estimated rate constant, as given in Table IV, the increase by a factor of 3.76 per hydrogen may also be indicative of participation of the neighboring phenyl group. Therefore the transition state can be represented as Scheme 5, which is similar to Scheme 3.

Scheme 5



The rate ratio of 2-bromoethylbenzene to ethyl bromide shows to be lower than the rate ratio of 2-chloroethylbenzene to ethyl chloride. Any argument with regard to this difference may be premature and speculative since the pyrolysis of 2-bromoethylbenzene was determined at only one temperature. However, the rate constant of 2-bromoethylbenzene is greater

TABLE IV. Comparative rates of ZCH_2CH_2Br at 385.5°C.

Z	$k \times 10^4$ (sec^{-1})	Relative rate per hydrogen	Ref.
H	0.34	1	[13]
C_6H_5	0.85	3.76	[5a]

TABLE V. Comparative rates of acetates at 427.2°C[a]

	$k \times 10^4$ (sec^{-1})	Relative rate per hydrogen
CH_3CH_2OAc	39.0	1
$C_6H_5CH_2CH_2OAc$	14.3	0.55
$CH_3OC_6H_4CH_2CH_2OAc$	12.4	0.48

[a] From [15]

than the rate of 2-chloroethylbenzene at 385.5°C, in accord with the relative rates of halides [14], RBr > RCl. 2-Bromoethylbenzene has also been pyrolyzed in a micropulse reactor [5b], where the presence of heterogeneous processes gives high *k* values. Therefore no comparison is possible.

Existing data on the rates of the gas thermal decomposition of some 2-substituted ethyl acetates [15] do not reveal participation of aromatic neighboring groups with compounds homologous to those studied in the present work (Table V). The lack of anchimeric acceleration of the phenyl groups appears to be impeded by the highly discrete semipolarity of the transition state of esters in contrast to the greater heterolytic nature of alkyl halides.

The gas-phase elimination of these chlorides gives place to believe that the C—Cl bond elongation in the sense of $C^{\delta+}\ldots Cl^{\delta-}$ polarization is the rate-determining step in the cyclic transition state of these reactions.

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