

Phenyl Migration in the Molecular Pyrolytic Elimination of 1-Chloro-2-methyl-2-phenylpropane in the Gas Phase†

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The elimination of kinetics of 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) in the gas phase were examined over a temperature range of 420–475 °C and a pressure range of 34–134 Torr. The reaction, in seasoned static vessels and in the presence of a free radical suppressor, is molecular in nature and follows a first-order rate law. The Arrhenius equation for the elimination was found to be: $\log(k_1/s^{-1}) = (13.47 \pm 0.62) - (227.8 \pm 8.7) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. A Wagner–Meerwein phenyl migration was the prevailing pathway in the rearrangement process. This work provides strong evidence for an intimate ion-pair type of mechanism.

The participation of an intimate ion-pair type of mechanism for the pyrolyses of alkyl halides in the gas phase must be considered if molecular rearrangement takes place under such conditions. Neopentyl chloride, containing no C_β-H, gave a simultaneous process¹ in a seasoned vessel at 444 °C, in which 75% of the formation of methylbutenes resulted from a homogeneous, unimolecular Wagner–Meerwein migration of the methyl group. However, about 24% of the overall decomposition was heterogeneous in nature.

Further examination of the neopentyl chloride pyrolysis,² over the temperature range of 410–496.6 °C, showed that the reaction occurred *via* two concurrent mechanisms: (a) a unimolecular Wagner–Meerwein rearrangement of the methyl group to produce methylbutenes, and (b) a radical chain process. The molecular reaction was shown to constitute 30–40% of the overall decomposition.

In this line of work, deuteriated [1,1-²H₂]neopentyl chloride was pyrolysed under maximal inhibition of cyclohexene at 445 °C.³ The formation of the rearrangement products [3,3-²H₂]-2-methylbut-1-ene and [3-²H]-2-methylbut-2-ene suggested an intimate ion-pair type of mechanism. Moreover, the rate coefficients for neopentyl chloride decomposition, in seasoned vessels and in the presence of cyclohexene inhibitor, were also measured over a range of 54 °C.

The decomposition of neopentyl bromide, in a static seasoned vessel and under maximal inhibition of cyclohexene, was a homogeneous molecular process with a first-order rate law.⁴ The yields of 2-methylbutene obtained suggested a Wagner–Meerwein rearrangement and a highly polar cyclic transition state mechanism.

Whitmore⁵ refluxed neat 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) in the liquid phase at 135 °C for 44 h and observed the exclusive formation of phenyl Wagner–Meerwein rearrangement products. Only 74% of the substrate was converted, 2-methyl-3-phenylprop-2-ene (36.5%), 2-methyl-3-phenylprop-1-ene (23%) and 2-chloro-2-methyl-3-phenylpropane (8.9%). The latter halide product was apparently obtained by addition of HCl to 2-methyl-3-phenylprop-2-ene in the reaction mixture.

In view of the rearrangements observed in the gas phase pyrolyses of neopentyl chloride and bromide, and because the phenyl ring is a better migrating group than methyl, as already described,⁵ the present work aimed at examining the pyrolytic elimination from 1-chloro-2-methyl-2-phenylpropane in the gas phase.

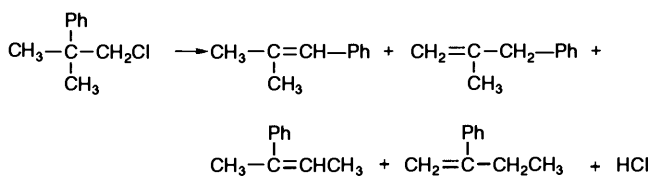
Experimental

1-Chloro-2-methyl-2-phenylpropane (neophyl chloride) was acquired from Aldrich, distilled repeatedly and the fraction of greater than 99.0% purity (GLC) was used. The column for quantitative analyses was 10% Dow Corning 200/100–Chromosorb W AW DMCS 80–100 mesh. The identities of the substrates and products were checked with a mass spectrometer and by IR and NMR spectroscopy.

The chloride reagent was pyrolysed in a static system, in the presence of a free-radical inhibitor (toluene or propene). The reaction vessel was seasoned with the product of decomposition of allyl bromide. The rate coefficients were estimated by pressure increase and/or by the sum of the chromatographic analyses of the olefinic products. No temperature gradient was observed in the reaction vessel, and the temperature was controlled by a resistance thermometer controller type SHINKO DIC-PS 25RT maintained within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. The halide substrate was injected directly into the reaction vessel with a syringe through a silicone rubber septum.

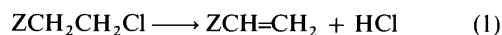
Results and Discussion

The experimental stoichiometry for the gas phase elimination of 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) is described by Scheme 1. The reaction in a static system in vessels



Scheme 1

seasoned with allyl bromide, and in the presence of a free radical suppressor (toluene or propene), was examined. The average results of the final pressure P_f , over the initial pressure P_o , at five different temperatures and ten half-lives are given in Table 1. The theoretical stoichiometry of the normal gas phase, homogeneous unimolecular dehydrochlorination of alkyl chloride [reaction (1)] demands $P_f/P_o = 2$. The small departure from



$P_f = 2P_o$ at 475.5 °C appears to be due to a slight

† Non-S.I. unit employed: 1 Torr = 133.322 Pa.

decomposition of one of the unsaturated products. Additional verification of the stoichiometry, up to 60% reaction, the extent of pyrolysis as predicted from pressure measurements, was found to be in good agreement with the sum of the chromatographic analyses of the aromatic unsaturated products (Table 2).

The breakdown of the chromatographic analyses of the elimination products under these conditions are given in Tables 3 and 4. Within experimental error, the distribution of products does not vary at a given temperature as a function of extent of reaction, and varies very insignificantly as a function of temperature. Accordingly, it is not unreasonable to believe that the formation of the olefinic products proceeds under kinetic control.

The products' distributions obtained for experiments

Table 1 Ratios of final pressure to initial pressure^a

<i>T</i> /°C	<i>P</i> ₀ /Torr	<i>P</i> _f /Torr	<i>P</i> _f / <i>P</i> ₀	Average <i>P</i> _f / <i>P</i> ₀
440.4	56	115	2.05	2.05
451.6	55	110	2.00	
462.1	62	120	1.94	
467.0	45	88	1.96	
475.5	64	146	2.28	

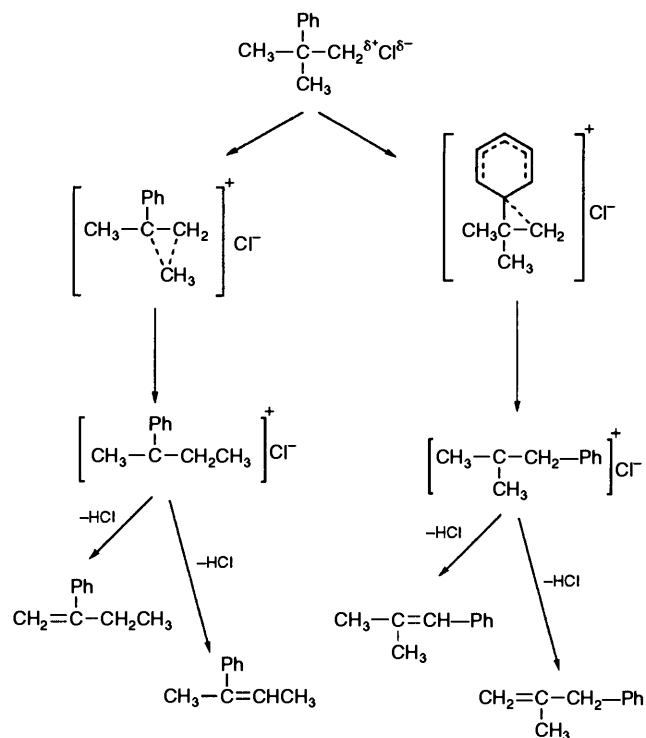
^a In the presence of toluene or propene.

Table 2 Stoichiometry of the reaction at 440.4 °C

<i>t</i> /min	Extent of reaction (%)	Product formation determined by chromatographic analysis (%)
6	21.7	20.7
12	36.4	37.1
18	45.5	43.0
24	58.2	59.6

employing packed and clean unpacked vessels (see Table 5) are rather different from the analyses described in Tables 3 and 4. Such results may be attributed to some heterogeneous effects. However, the yields of olefins in the packed seasoned vessels are very similar to those shown in Tables 3 and 4.

The distribution of products obtained for clean packed and clean unpacked vessels as described in Table 5 is very similar



Scheme 2

Table 3 Product distribution (%) at different extents of reaction at 451.6 °C

Extent of reaction (%)	2-Methyl-3-phenyl-prop-1-ene	2-Methyl-3-phenyl-prop-2-ene	2-Phenyl-but-1-ene	2-Phenyl-but-2-ene
23.3	67.9	27.8	3.2	1.1
34.3	68.1	27.1	3.5	1.2
41.1	67.0	28.6	3.3	1.1
48.4	68.8	27.2	3.0	1.0

Table 4 Product distribution (%) at different reaction temperatures

<i>T</i> /°C	2-Methyl-3-phenyl-prop-1-ene	2-Methyl-3-phenyl-prop-2-ene	2-Phenyl-but-1-ene	2-Phenyl-but-2-ene
428.0	70.4	28.5	0.6	0.5
440.4	71.6	25.8	1.7	0.9
451.6	68.8	27.2	3.0	1.1
467.0	68.8	29.3	2.2	0.7
475.5	67.8	29.3	1.5	0.5

Table 5 Distribution of products (%) in packed and clean unpacked vessels at 440.4 °C^a

Vessel	Surface area-to-volume ratio/cm ⁻¹	2-Methyl-3-phenyl-prop-1-ene	2-Methyl-3-phenyl-prop-2-ene	2-Phenyl-but-1-ene	2-Phenyl-but-2-ene
Clean unpacked	1	38.5	59.9	0.5	1.1
Clean packed	6	36.0	62.4	0.6	1.0
Seasoned packed	6	67.6	32.4	trace	trace

^a In the presence of toluene inhibitor.

Table 6 Effect of toluene inhibitor on rates

P_s/Torr^a	P_i/Torr^b	P_i/P_s	$k_1/10^{-4} \text{ s}^{-1}$
81	—	—	<i>c</i>
134	111.5	0.8	6.44
84	157	1.9	6.29
79	249	3.2	6.32
49.5	198	4.0	6.25

^a P_s pressure of the substrate. ^b P_i pressure of toluene inhibitor. ^c The k_1 -values tend to decrease which may be to the polymerization of the olefinic products.

Table 7 Variation of rate coefficient with initial pressure at 440.4 °C

P_o/Torr	$k_1/10^{-4} \text{ s}^{-1}$
34.5	6.17
52.0	6.25
78.5	6.32
84.0	6.29
134.0	6.44

Table 8 Variation of rate coefficient with temperature

$T/^\circ\text{C}$	$k_1/10^{-4} \text{ s}^{-1}$
420.8	2.14
428.0	3.19
440.4	6.17
451.6	10.83
462.1	18.52
467.0	24.35
475.2	39.55

Table 9 Arrhenius parameters and comparative rates at 440 °C

Compound	$k_1/10^{-5} \text{ s}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	Ref.
$(\text{CH}_3)_3\text{CCH}_2\text{Cl}$	0.74	251.0 ± 6.7	13.26 ± 0.35	2
	0.68	258.7 ± 8.4	13.78 ± 0.60	3
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	12.59	247.0 ± 5.0	14.2 ± 0.3	4
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{CCH}_2\text{Cl}$	60.26	227.8 ± 6.9	13.47 ± 0.49	This work

to the 61.3 to 38.7% relationship obtained for 2-methyl-3-phenylprop-2-ene to 2-methyl-3-methyl-3-phenylprop-1-ene by Whitmore.⁵ This means that boiling the chloride substrate in the liquid phase causes a heterogeneous effect from the glass reaction vessel.

The homogeneity of the elimination process was examined by carrying out several runs in a packed vessel with a surface area-to-volume ratio of six, as compared to that of the normal vessel,

with a ratio of one. Only the unpacked vessels seasoned with allyl bromide exhibited homogeneous reactions. The packed and clean unpacked vessels caused the olefinic products to polymerize, suggesting an appreciable surface effect.

The effect of the addition of an efficient free radical chain suppressor such as toluene is shown in Table 6, and no induction period was observed. The kinetic determinations were carried out in the presence of at least an equal amount of toluene to inhibit any possible radical processes of the substrate and/or products. The k -values are reproducible with a relative standard deviation not greater than $\pm 5\%$ at a given temperature.

The rate coefficients were independent of changes in the initial pressure of the substrate, and the first order plots gave good straight lines up to 60% decomposition (see Table 7). The temperature dependence of this reaction, in seasoned vessels and in the presence of toluene or propene inhibitors (see Table 8) can be expressed in the Arrhenius-type equation (2), where a 90% confidence limit is being quoted.

$$\log(k_1/\text{s}^{-1}) = 13.47 \pm 0.49 - \frac{(227.8 \pm 6.9) \text{ kJ mol}^{-1}}{2.303 RT} \quad (2)$$

The formation of products described in Tables 3 and 5 insinuates an unequivocal preference and predominance for phenyl migration in the gas phase pyrolysis of 1-chloro-2-methyl-2-phenylpropane; methyl migration is of little significance, accounting for less than 5% of the products. This result confirms that the phenyl ring, through π -bond participation, is a better migrating group than methyl. The homogeneous molecular rearrangements of this elimination reaction may be explained in terms of an intimate ion-pair, as represented in Scheme 2.

Because the carbocationic reaction centre is more stabilised through participation of the phenyl group, the overall rate constant is expected to be faster than for the previously reported neopentyl halide pyrolyses. The comparative rates given in Table 9 confirm this consideration.

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