

Catalysis by hydrogen chloride in the gas-phase elimination kinetics of 2-phenyl-2-propanol and 3-methyl-1-buten-3-ol

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ABSTRACT: A homogeneous, molecular, gas-phase elimination kinetics of 2-phenyl-2-propanol and 3-methyl-1-buten-3-ol catalyzed by hydrogen chloride in the temperature range 325–386 °C and pressure range 34–149 torr are described. The rate coefficients are given by the following Arrhenius equations: for 2-phenyl-2-propanol $\log k_1$ (s^{-1}) = $(11.01 \pm 0.31) - (109.5 \pm 2.8) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$ and for 3-methyl-1-buten-3-ol $\log k_1$ (s^{-1}) = $(11.50 \pm 0.18) - (116.5 \pm 1.4) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$. Electron delocalization of the $\text{CH}_2=\text{CH}$ and C_6H_5 appears to be an important effect in the rate enhancement of acid catalyzed tertiary alcohols in the gas phase. A concerted six-member cyclic transition state type of mechanism appears to be, as described before, a rational interpretation for the dehydration process of these substrates. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: elimination; gas-phase kinetics; hydrogen chloride catalyst; mechanism; 3-methyl-1-buten-3-ol and 2-phenyl-2-propanol

INTRODUCTION

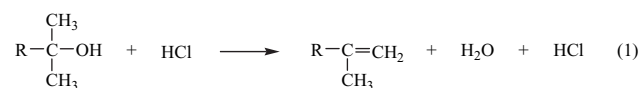
Experimental gas-phase elimination kinetics of aliphatic alcohols are known to be difficult and they proceed from a radical chain to a molecular mechanism when changing from primary to tertiary carbon.¹ The temperature needed for dehydration of these alcohols is from 500 °C and up. Along this line of work, few alcohols were reported to dehydrate on acid catalyzed homogeneous, unimolecular elimination in the gas phase. The acid catalysts of these molecules are found to be carried out well below 100 °C when compared to the uncatalyzed dehydration process and the activation energy reduced to about 125 kJ mol^{-1} . The mechanism for the acid catalyzed dehydration of *tert*-butyl alcohol (Scheme 1) has already been described by Maccoll and Stimson.²

Further investigations on the molecular elimination of tertiary alcohol catalyzed by HBr and/or HCl^{3-8} considered steric acceleration as a reasonable explanation for rate enhancement in the dehydration process. These reactions were believed to proceed through a six-member cyclic transition state type of mechanism. Steric factor

was believed to be the mechanism of the acid catalyzed tertiary alcohols; however, electronic effect was not ignored. Consequently, the present work aimed at studying the elimination kinetics of acid catalyzed tertiary alcohols with an unsaturated or π -bond substituent that may well delocalize their electrons to the positive carbon reaction center. The substrates to be examined are 2-phenyl-2-propanol and 3-methyl-1-buten-3-ol.

RESULTS AND DISCUSSION

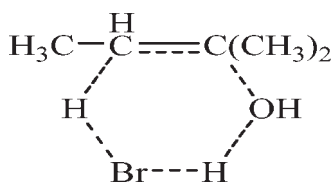
The elimination process of both tertiary alcohols catalyzed with HCl gas, in a static system, and the reaction vessel was seasoned with products of decomposition of allyl bromide, which is a polymeric carbon coat. Under this condition the gas-phase elimination of these substrates produces water and the corresponding olefin, as described in reaction (1):



R: $\text{CH}_2=\text{CH}$, C_6H_5

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Scheme 1

Stoichiometry (1) requires that, for long reaction times, $P_f = 2P_0$, where P_f and P_0 are the final and initial pressure, respectively. The average experimental results for P_f/P_0 values at five different temperatures and 10 half-lives were 1.9 for 2-phenyl-2-propanol and 1.7 for 3-methyl-1-buten-3-ol (Table 1).

The departure from $P_f/P_0 = 2.0$ may be attributed to a small polymerization of the corresponding olefin product and possibly to dead-space errors. Verification of stoichiometry (1) was made by comparing the percent decomposition of the tertiary alcohol substrate from pressure measurements against chromatographic analyses of the corresponding olefin products (Table 2).

To examine the homogeneity of these reactions several runs were carried out in a vessel with a surface-to-volume ratio of about 6.0 relative to that of the normal vessel,

Table 1. Ratio of final (P_f) to initial pressure P_0 of the substrate^a

Substrate	Temperature (°C)	P_0 (torr)	P_f (torr)	P_f/P_0
2-Phenyl-2-propanol ^b	340.1	71	133	1.9
	340.0	62	115	1.9
	356.3	52	95	1.8
	386.2	70	129	1.9
	386.1	72.0	133	1.9
3-Methyl-1-buten-3-ol ^b	326.1	89	150	1.7
	370.6	84	144	1.7
	371.0	94	162	1.7
	384.4	88	150	1.7
	384.4	82	140	1.7

^a Seasoned vessel.

^b Presence of HCl gas pressure $\approx 3P_0$.

Table 2. Stoichiometry of the reactions^a

Substrate	Temperature (°C)	Time (min)	% Olefin (GC)	% Olefin (pressure)
2-Phenyl-2-propanol	340.5	10	27.7	29.2
		12	32.5	34.1
		14	40.8	38.5
		16	43.9	42.3
		15	30.0	28.9
3-Methyl-1-buten-3-ol	355.5	6	11.2	11.9
		9	19.0	18.4
		12	25.3	23.9
		15	30.0	28.9
		15	30.0	28.9

^a Seasoned vessel and in the presence of HCl gas pressure.

which is equal to 1. The normal Pyrex vessel seasoned with allyl bromide had no effect on the rate coefficients (Table 3). Yet, the clean packed, unpacked, and seasoned packed Pyrex vessels showed an extremely fast increase in pressure which could not be measured in a very short time. These results indicate a significant heterogeneous effect.

The absence of a free radical chain reaction was verified by carrying out several runs in the presence of different proportions of toluene as inhibitor (Table 4).

The pseudo-first-order rate law given in Eqn (1), the rate coefficient k_0 is not independent of the HCl pressure as a catalyst, this means variation of P_{HCl} gives different values of k_0 (Table 5, column 4). Consequently, the true rate coefficient is obtained by dividing k_0 by P_{HCl} (Table 5, column 5) and Eqn (1) changes into Eqn (2)

$$k_0 = P_{\text{HCl}}k_1 = \left(\frac{1}{t}\right) \ln \frac{P_0}{2P_0 - P_T} \quad (1)$$

$$k_1 = \left(\frac{1}{t}\right) \left(\frac{1}{P_{\text{HCl}}}\right) \ln \frac{P_0}{2P_0 - P_T} \quad (2)$$

The rate coefficients of these eliminations were found, at constant HCl pressure, to be invariant to initial pressures (Table 6) and the pseudo-first-order rate was calculated from Eqn (2).

The variation of the rate coefficients with temperatures is shown in Table 7. The results given in Table 7 lead, by using the least-squares procedure and 90% confidence limits, to the shown Arrhenius equations.

Steric acceleration was considered to be an important factor in the rate enhancement of the gas-phase elimination kinetics of acid catalyzed alkyl branched tertiary alcohols.^{7,8} However, the present results and the analysis of the data described in Table 8 suggest the electronic factor to be responsible for rate increase. Scaled Dreiding Stereo Models reveals that substituent such as $\text{CH}_2=\text{CH}$ has less steric influence than CH_3CH_2 and $\text{CH}_3\text{CH}_2\text{CH}_2$. This fact leads to believe that electronic transmission of alkyl substituents affects the rate of elimination through strong sigma bonds, while resonance interaction of the vinyl and phenyl substituents

Table 3. Rate coefficient in seasoned normal ($S/V = 1.0$) Pyrex vessels

Substrate	Temperature ($^{\circ}\text{C}$)	P_{HCl} (torr)	P_0 (torr)	$10^7 k/P_{\text{HCl}}$ ($\text{torr}^{-1} \text{s}^{-1}$)	k_1 ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
2-Phenyl-2-propanol	340.4	264	71	13.9 ± 0.1	50.6 ± 3.3
	340.0	262	71	13.2 ± 0.2	50.2 ± 1.2
	340.5	237	72	13.7 ± 0.6	52.7 ± 2.5
3-Methyl-1-buten-3-ol	325.8	231	97	6.0 ± 0.3	22.3 ± 1.1
	325.7	238	97	6.0 ± 0.1	22.3 ± 0.4
	325.8	245	88	6.1 ± 0.3	22.7 ± 0.9

S = surface; V = volume.

Table 4. Effect of the inhibitor toluene on rates^a

Substrate	P_i (torr)	P_0 (torr)	P_i/P_0	$10^7 k_1/P_{\text{HCl}}$ ($\text{torr}^{-1} \text{s}^{-1}$)	k_1 ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
2-Phenyl-2-propanol at 356.2°C	—	63	—	20.7 ± 0.6	81.9 ± 2.0
	80	67	1.2	20.7 ± 0.9	81.1 ± 3.5
	117	59	2.0	20.7 ± 0.9	80.1 ± 1.9
	123	45	2.7	20.9 ± 0.6	82.1 ± 2.2
3-Methyl-1-buten-3-ol at 384.2°C	—	89	—	44.0 ± 0.8	182.1 ± 3.7
	53	81	0.7	44.1 ± 0.7	181.5 ± 2.7
	106	81	1.3	44.4 ± 1.5	181.9 ± 6.0
	168	78	2.1	44.6 ± 1.4	181.0 ± 7.0

In the presence of HCl gas $\cong 3P_0$.

P_0 = pressure of the substrate; P_i = pressure of toluene inhibitor.

^a Vessel seasoned with allyl bromide.

Table 5. Effect of hydrogen chloride on the rate of dehydration

Temperature ($^{\circ}\text{C}$)	P_{HCl} (torr)	P_0 (torr)	$10^4 k_0$ (s^{-1})	$10^7 k_1/P_{\text{HCl}}$ ($\text{torr}^{-1} \text{s}^{-1}$)
2-Phenyl-2-propanol				
	356.1	335	63	7.0 ± 0.1
	356.2	296	67	6.4 ± 0.7
	356.1	282	73	4.1 ± 0.6
	356.0	274	70	5.8 ± 0.1
3-Methyl-1-buten-3-ol	356.0	205	68	4.3 ± 0.2
	370.4	306	93	8.9 ± 0.2
	370.5	222	93	8.7 ± 0.4
	370.7	202	92	5.7 ± 0.2
	370.4	81	94	2.3 ± 0.1
370.4	73	95	2.1 ± 0.1	28.9 ± 1.1

Table 6. Variation of rate coefficient with initial pressure of the substrate^a

Temperature ($^{\circ}\text{C}$)	P_{HCl} (torr)	P_0 (torr)	P_{HCl}/P_0	$10^7 k_1/P_{\text{HCl}}$ ($\text{torr}^{-1} \text{s}^{-1}$)	k_1 ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)
2-Phenyl-2-propanol					
	356.1	296	67	20.7 ± 0.4	81.1 ± 1.6
	356.3	309	52	20.5 ± 0.2	82.2 ± 1.4
	356.1	261	48	21.3 ± 0.3	83.6 ± 1.0
3-Methyl-1-buten-3-ol	356.0	300	34	21.5 ± 0.2	83.5 ± 0.5
	384.5	282	149	44.6 ± 1.5	185.0 ± 6.0
	384.7	263	94	44.8 ± 0.9	183.8 ± 3.9
	384.4	296	89	44.0 ± 0.8	182.1 ± 3.7
384.4	301	82	3.7	44.6 ± 0.5	183.4 ± 1.2

^a Seasoned vessel.

Table 7. The variation of the rate coefficients with temperatures

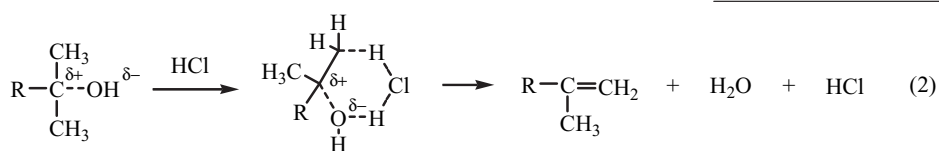
Substrate	Parameters		Value			
2-Phenyl-2-propanol	Temperature (°C)	325.2	340.5	356.2	371.2	386.2
	$10^7 k_1/P_{\text{HCl}}$ (torr ⁻¹ s ⁻¹)	8.5 ± 0.4	13.4 ± 0.4	20.6 ± 0.6	31.6 ± 0.9	51.8 ± 0.9
	k_1 (cm ³ mol ⁻¹ s ⁻¹)	29.6 ± 1.6	50.5 ± 2.1	81.5 ± 1.9	129.0 ± 3.7	213.0 ± 5.3
Rate equation $\log k_1$ (s ⁻¹) = $(11.01 \pm 0.31) - (109.5 \pm 2.8) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$, $r = 0.9996$						
3-Methyl-1-buten-3-ol	Temperature (°C)	325.8	340.4	355.5	370.5	384.2
	$10^7 k_1/P_{\text{HCl}}$ (torr ⁻¹ s ⁻¹)	6.0 ± 0.2	10.1 ± 0.3	17.1 ± 0.6	28.7 ± 1.0	44.5 ± 1.2
	k_1 (cm ³ mol ⁻¹ s ⁻¹)	22.4 ± 0.8	39.0 ± 2.0	66.8 ± 2.5	115.1 ± 4.0	182.4 ± 4.5
Rate equation $\log k_1$ (s ⁻¹) = $(11.50 \pm 0.18) - (116.5 \pm 1.4) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$, $r = 0.9999$						

Table 8. Kinetic and thermodynamic parameters of R(CH₃)₂COH catalyzed with HCl at 380 °C

Z	k_1 (cm ³ mol ⁻¹ s ⁻¹)	E_a (kJ mol ⁻¹)	$\log A$ (s ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	References
CH ₃	22.9	136.8	12.30	-16.51	131.4	143.2	3
CH ₃ CH ₂	28.8	142.2	12.83	-6.36	136.8	141.0	5
CH ₃ CH ₂ CH ₂	43.7	145.3 ± 2.4	13.26	1.87	139.8	141.0	8
CH ₂ =CH	151.4	116.5 ± 1.4	11.50 ± 0.18	-31.86	111.1	131.9	a
C ₆ H ₅	177.8	109.5 ± 2.8	11.01 ± 0.31	-41.20	104.2	131.1	a

a, This work.

explains the importance of stabilization of the partial positive carbon reaction center in the transitions state for a greater ease of dehydration. The mechanism can be described as in reaction (2)

R: CH₂=CH, C₆H₅

3700 (column: 3% OV – 17 Gas Chromosorb Q 80/100 mesh, 2 m), while for 2-methyl-1,3-butadiene by employing Varian 3600× (DB-5 capillary column 30 m × 0.53 mm i.d., 0.53 μm).

EXPERIMENTAL

2-Phenyl-2-propanol (99% purity, Air Product) and 3-methyl-1-buten-3-ol (99% purity, Air Product) were used. Pure HCl gas was bought from Matheson. The purity of these substrates was checked by GC-MS: Saturn 2000, Varian, with a DB-5MS capillary column 30 m × 0.25 mm i.d., 0.25 μm film thickness. The products 2-phenylpropene and 2-methyl-1,3-butadiene were identified in a GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column 30 m × 0.25 mm i.d., 0.25 μm. The quantitative analyses of the products; for 2-phenylpropene by using a Gas Chromatograph Varian

Kinetics

The tertiary alcohols were pyrolyzed in a static system^{9–11} with the reaction vessel seasoned with allyl bromide and in the presence of the catalyst HCl gas. The rate coefficients were determined by pressure increase manometrically. The temperature was controlled by a Shinko DC-PS resistance thermometer controller maintained at ±0.2 °C and measured with a calibrated Iron Constantan thermocouple. No temperature gradient was found along the reaction vessel. All substrates were injected directly into the reaction vessel with a syringe through a silicone rubber septum. The

amount of substrate used for each reaction was ~0.05–0.2 ml.

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