Gas-Phase Pyrolytic Reaction of 3-Phenoxy and 3-Phenylsulfanyl-1-propanol Derivatives: Kinetic and Mechanistic Study

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ABSTRACT: 3-Phenoxy-1-propanols **1a–c** and 3-phenylsulfanyl-1-propanols **2a–c** containing primary, secondary, and tertiary alcohols were prepared and subjected to gas-phase pyrolysis in a static reaction system. Pyrolysis of 4-phenyl-1-butanol **3**, 2-methyl-3-phenyl-1-propanol **4**, and 2-methyl-3-phenylpropanoic acid **5** was also studied, and results were compared with those obtained for compounds **1–3**. The pyrolytic reactions were homogeneous and followed a first-order rate equation. Analysis of the pyrolysate showed the products to be phenol (from **1a** to **1c**), thiophenol (from **2a** to **2c**), and toluene (from **3** to **5**) and carbonyl compounds. The kinetic results and product analysis of each of the nine investigated compounds are rationalized in terms of a plausible transition state for the elimination pathway. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 40: 51–58, 2008

INTRODUCTION

We have reported the kinetics and mechanism of thermal gas-phase elimination of α-substituted carboxylic acids [1]. Product analysis and kinetic results lend support to a reaction pathway involving a five-membered cyclic transition state previously suggested by Chuchani et al. [2] for other different α-substituted carboxylic acids (Scheme 1).

The order of reactivity of the aryl group is —OPh > —SPh > —NPh; this order corresponds to the trend expected for the nature of incipient phenol, thiophenol, and aniline [3].

A dramatic change in the reactivity is observed when the acidity of the incipient hydrogen is reduced by replacing the carboxylic acid proton with an alcohol hydroxyl hydrogen; a relative rate factor

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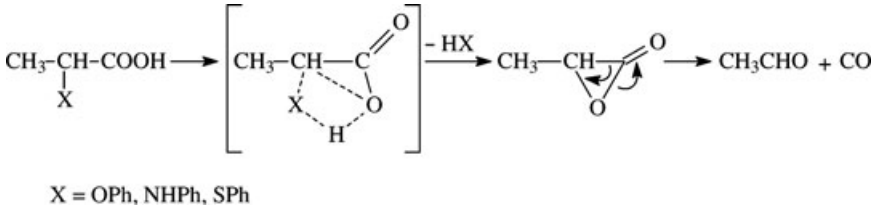
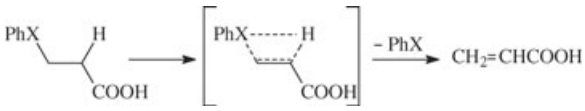


Scheme 1

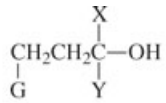


Scheme 2

of 2×10^3 is obtained when the rate of pyrolysis of 2-phenoxypropanoic acid and 2-phenoxy-1-propanol was compared [1].

Later, we studied the kinetic and mechanism of thermal gas-phase elimination of β-substituted acids [4]. Product analysis and theoretical calculation suggested a reaction mechanism compatible with a thermal retro-Michael reaction pathway involving a four-membered cyclic transition state (Scheme 2).

To investigate further in this elimination reaction, in the present study we examined the result of the kinetic and product analysis of the thermal gas-phase elimination reaction of 3-phenoxy-1-propanol **1a**, 4-phenoxy-2-butanol **1b**, 4-phenoxy-2-methyl-2-butanol **1c,** and their phenylsulfanyl derivatives **2a–c**. The pyrolysis of 4-phenyl-1-butanol **3**, 2-methyl-3-phenyl-1-propanol **4**, and 2-methyl-3-phenylpropanoic acid **5** was also investigated (Scheme 3).



Compound	G	X	Y
1a	OPh	H	H
1b	OPh	H	Me
1c	OPh	Me	Me
2a	SPh	H	H
2b	SPh	H	Me
2c	SPh	Me	Me
3	CH_2Ph	H	H
4	CH_3CHCH_2OH CH_2Ph		
5	$CH_3CHCOOH$ CH_2Ph		

Scheme 3 Substrates investigated in the study.

EXPERIMENTAL

General

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz superconducting NMR spectrometer. Mass spectra were measured on VG Autospec-Q (high-resolution, high-performance, tri-sector GC/MS/MS), and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode.

Synthesis

***3-Phenoxy-1-propanol* (1a).** A solution of 3-phenoxypropionic acid [5a] (1.66 g, 10 mmol) in dry ether (20 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (0.50 g, 13 mmol) in dry ether (100 mL) at rate sufficient to maintain reflux. After the addition was over, the reaction mixture was heated under reflux for 4 h and then cooled to room temperature. The excess hydride was decomposed by dropwise addition of water, and the resulting white suspension was filtered off. The filtrate was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to afford 1.2 g (80%) of **1a** [5b]. ^1H NMR ($CDCl_3$): δ 2.01 (quint, 2H, $J = 6.0$, CH_2), 3.04 (br, 1H, OH), 3.85 (t, 2H, $J = 6.0$, CH_2), 4.11 (t, 2H, $J = 6.0$, CH_2), 6.94 (d, 2H, $J = 8.0$), 6.98 (t, 1H, $J = 7.4$), 7.32 (t, 2H, $J = 7.8$). MS: $m/z = 152$ (M^+, 70%).

***4-Phenoxy-2-butanol* (1b).** To a solution of 4-phenoxybutan-2-one [6] (1.63 g, 10 mmol) in methanol (20 mL), cooled at 0°C, $NaBH_4$ (0.50 g, 15 mmol) was added portionwise with stirring. The reaction mixture was then stirred at room temperature for 1 h, and the solvent was then removed in vacuo. The product was extracted with ether (3×50 mL), washed with water, and dried over anhydrous sodium sulfate. The solvent was then removed in vacuo to give colorless oily product, yield 1.0 g (60%), which was purified by silica gel column chromatography, using EtOAc-pet. ether (60–80) as an eluent [$R_f = 0.37$ EtOAc-pet. ether 60–80 (1:4)]. ^1H NMR ($CDCl_3$): δ 1.29 (d, 3H, J 6.2,

CH_3), 1.95 (q, 2H, $J = 6.3$, CH_2), 2.24 (br, 1H, OH), 4.12 (m, 2H), 4.20 (m, 1H, CH—OH), 6.93 (d, 2H, $J = 8.3$), 6.98 (t, 1H, $J = 7.2$), 7.30 (t, 2H, $J = 8.0$). ^{13}C NMR ($CDCl_3$): δ 23.8 (CH_3), 38.1 (CH_2), 65.9 (CH_2), 66.4 (C—OH), 113.6 (2CH), 121.0 (CH), 129.6 (2CH), 158.8 (C). MS: $m/z = 166$ (M^+, 90%), 107 (30%), 94 (100%).

***4-Phenoxy-2-methyl-2-butanol* (1c).** To a solution of CH_3MgI (freshly prepared from 1.0 g Mg and 2.5 mL CH_3I in 40 mL dry ether) was added methyl 3-phenoxypropionate [4] (1.8 g, 10 mmol) in dry ether (20 mL) portionwise at room temperature with stirring under nitrogen atmosphere. The reaction mixture was heated under reflux for 24 h. After cooling at room temperature, the mixture was quenched with saturated aqueous ammonium chloride solution and the ethereal layer was separated and the aqueous layer was further extracted with ether (3×50 mL). The combined ethereal extracted was dried over anhydrous sodium sulfate. The solvent was then removed in vacuo to give colorless oil, yield 1.2 g (66%), which was purified by silica gel column chromatography using $CHCl_3$-pet. ether (60–80) as an eluent [$R_f = 0.7$ $CHCl_3$:pet. ether 60–80 (1:9)] [7]. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 6H, $2CH_3$), 2.03 (t, 2H, $J = 6.2$), 2.10 (br, 1H, OH), 4.21 (t, 2H, $J = 6.2$), 6.94 (d, 2H, $J = 8.2$), 6.99 (t, 1H, $J = 7.3$), 7.29 (t, 2H, $J = 7.9$). ^{13}C NMR ($CDCl_3$): δ 30.2 ($2CH_3$), 42.2 (CH_2), 65.6 (CH_2), 71.0 (C—OH) 115.1 (2CH), 121.6 (CH), 130.1 (2CH), 159.1 (C—O). MS: $m/z = 180$ (M^+, 30%), 94 (100%).

***3-Phenylsulfanyl-1-propanol* (2a).** A solution of 3-phenylsulfanylpropanoic acid [8a] (3.64 g, 0.02 mol) in dry ether (20 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (0.76 g, 20 mmol) in dry ether (100 mL) at rate sufficient to maintain reflux. After the addition was complete, the reaction was refluxed for 4 h and then cooled to room temperature. The excess hydride was decomposed by dropwise addition of water, and the resulting white suspension was filtered off. The filtrate was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to afford yellow oil; yield 2.5 g (71%), which was purified by vacuum distillation (lit. [8b] bp 105°C, 0.1 mm). ^{1}H NMR ($CDCl_3$): δ 1.90 (quint, 2H, $J = 6.4$, CH_2), 2.10 (br, 1H, OH), 3.05 (t, 2H, $J = 7.0$, CH_2), 3.78 (t, 2H, $J = 6.0$, CH_2), 7.20 (t, 1H, $J = 7.2$), 7.30 (t, 2H, $J = 7.6$), 7.38 (d, 2H, $J = 7.8$). ^{13}C NMR ($CDCl_3$): δ 30.8, 32.2, 61.9, 126.6, 129.5, 129.8, 136.8. MS: $m/z = 168$ (M^+, 80%).

***4-Phenylsulfanyl-2-butanol* (2b).** To a solution of 4-phenylsulfanyl-2-butanone [9] (1.82 g, 10 mmol) in methanol (20 mL), $NaBH_4$ (0.50 g, 15 mmol) was added portionwise at room temperature with stirring. The reaction mixture was then stirred at room temperature for 1 h, and the solvent was then removed in vacuo. The product was extracted with ether (3×50 mL), washed with water, and dried over anhydrous sodium sulfate. The solvent was then removed in vacuo, and the remaining colorless oily product, yield 1.4 g (60%), was purified by silica gel column chromatography using EtOAc–hexane as an eluent, ($R_f = 0.24$ EtOAc:hexane 1:4). ^{1}H NMR ($CDCl_3$): δ 1.20 (d, 3H, $J = 6.2$, CH_3), 1.76 (m, 2H, CH_2), 2.63 (s, 1H, OH), 3.04 (m, 2H, CH_2), 3.94 (sextet, 1H, $J = 6.2$, CH–O), 7.19 (t, 1H, $J = 7.2$), 7.30 (t, 2H, $J = 7.5$), 7.35 (d, 2H, $J = 7.7$). ^{13}C NMR ($CDCl_3$) δ: 24.1 (CH_3), 30.6 (CH_2), 38.7 (CH_2), 67.4 (C—OH) 126.5 (CH), 129.6 (4CH), 137.0 (C). MS: $m/z = 182$ (M^+, 90%), 123 (50%), 110 (100%).

***2-Methyl-4-phenylsulfanyl-2-butanol* (2c).** To a solution of thioanisole (1.2 mL, 10 mmol) in dry THF (40 mL) at −78°C and *n*-BuLi in hexanes (5.6 mL, 2.0 M), 2,2-dimethyloxirane (1.2 mL, 14 mmol) was added dropwise over several minutes. The reaction mixture was then allowed to slowly warm to room temperature and stirred over night at room temperature before quenching with 10% HCl. The organic layer was extracted with ether, dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to give the crude product as yellow oil, yield 1.6 g (79%) [7,10a,b], which was purified by silica gel column chromatography using EtOAc–hexane as an eluent solvent ($R_f = 0.3$ EtOAc:hexane 1:9). ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 6H, $2CH_3$), 1.59 (br, 1H, OH), 1.83 (m, 2H, CH_2), 3.05 (m, 2H, CH_2), 7.20 (t, 1H, $J = 7.2$), 7.30 (t, 2H, $J = 7.6$), 7.36 (d, 2H, $J = 7.9$). ^{13}C NMR ($CDCl_3$): δ 28.5 (CH_2), 29.3 ($2CH_3$), 42.7 (CH_2), 70.8 (C-OH), 125.9 (CH), 128.8 (2CH), 128.9 (2CH), 136.4 (C). MS: $m/z = 196$ (M^+, 80%), 109 (100%).

***4-Phenyl-1-butanol* (3).** This compound was purchased from Merck (Schuchardt OHG, Germany).

***2-Methyl-3-phenyl-1-propanol* (4).** To a suspension of lithium aluminum hydride (0.20 g, 5 mmol) in dry THF (20 mL), 2-methyl-3-phenylpropionic acid [11] (0.33 g, 2 mmol) in THF (10 mL) was added dropwise with stirring at rate sufficient to keep the solution refluxing. After complete addition, the reaction mixture was heated under reflux for 3 h. The mixture was cooled to room temperature, hydrolyzed with water (5 mL) and extracted with ethyl acetate (3×20 mL), dried with anhydrous sodium sulfate, and the solvent was evaporated in vacuo to give 2.5 g (83%) as pure product [12]. ^{1}H

NMR ($CDCl_3$): δ 0.92 (d, 3H, $J = 6.6$, CH_3), 1.98 (m, 1H, CH), 2.41 (dd, 1H, $J = 13.3$, 8.0), 2.78 (dd, 1H, $J = 13.3$, 6.0), 3.24 (br, 1H, OH), 3.49 (m, 1H), 3.56 (m, 1H), 7.20 (d, 2H, $J = 7.3$) 7.23 (t, 1H, $J = 7.6$). 7.61 (t, 2H, $J = 7.5$). MS: $m/z = 150$ (M^+, 80%), 92 (90%).

2-Methyl-3-phenylpropionic Acid (5). A mixture of diethyl 2-benzyl-2-methylmalonate [11a] (5.0 g, 19 mmol), KOH (5g, 89 mmol) in water (20 mL) was heated under reflux for 20 h. The reaction mixture was then diluted with water (20 mL), and the resulting ethanol was removed in vacuo. The residue was cooled in ice, and conc. H_2SO_4 (5 mL) was added. The reaction mixture was heated under reflux for 3 h, cooled to room temperature, and extracted with ether (3×50 mL). The ethereal extract was then dried over anhydrous sodium sulfate, and the solvent was then removed in vacuo to give the crude product as colorless oil, yield 2.4 (77%), which was purified by column chromatography using ether–pet. ether 60–80 as an eluent, ($R_f = 0.8$ ether:pet. ether 60–80 1:1) [11b]. ^{1}H NMR ($CDCl_3$): δ 1.22 (d, 3H, $J = 6.9$,CH_3), 2.72 (dd, 1H, $J = 8.0$, 13.3, CH), 2.80 (sext, 1H, $J = 6.9$ CH), 3.12 (dd, 1H, $J = 6.0$, 13.3,CH), 7.23 (d, 2H, $J = 8.0$), 7.27 (t, 1H, $J = 7.0$), 7.34 (t, 2H, $J = 7.3$), 10.5 (br, 1H, OH).^{13}C NMR ($CDCl_3$): δ 16.4 (CH_3), 39.2 (CH_2), 41.2 (CH), 126.4 (CH), 128.4 (2CH), 129.0 (2CH), 138.9 (C), 182.3 (CO). MS: $m/z = 164$ (M^+, 50%), 92 (90%).

Product Analysis

The reactor used for kinetic and product analysis is a Chemical Data System (CDS) custom-made pyrolyzer consisting of an insulated aluminum alloy block fitted with a platinum resistance thermocouple connected to a Comark microprocessor thermometer for reactor temperature readout, accurate to <0.5°C. The alloy was chosen for its high-thermal conductivity and low-temperature gradient, and may be heated for up to 530°C. The temperature of the reactor was controlled by means of a Eurotherm 093 precision temperature regulator to provide 0.1°C incremental change. The reaction tubes were Pyrex, 8-cm length for kinetic runs and 12 cm for product analysis, having internal and outside diameters of 1.5 and 1.7 cm, respectively.

A quantity of 0.2 g of the substrate was introduced in the reaction tube, cooled in liquid nitrogen, sealed under vacuum (0.06 mbar), and put in the pyrolyzer for 900 s at a temperature comparable to that used for complete pyrolysis in the kinetic studies. The content of the tubes was then analyzed by ^{1}H NMR and LCMS to characterize the consistituents of the pyrolysate. Percent yields were determined from ^{1}H NMR.

Kinetics and Data Analysis

Stock solution (7 mL) was prepared by dissolving 5–10 mg of the substrate in acetonitrile to give a concentration of 1×10^3 to 2×10^3 ppm. An internal standard was then added, and the amount of which was adjusted to give the desired peak area ratio of substrate to standard (2.5:1). The solvent and standard were selected to be stable under the conditions of pyrolysis, and because they do not interact or react with either substrate or product. The internal standards used in the present study were chlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene. Each mixture was filtered before use to ensure a homogeneous solution.

The ratio of the amount of substrate with respect to the internal standard was calculated from the ratio of the substrate peak area to the peak area of the internal standard. The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to the internal standard as follows: An aliquot part (0.2 mL) of each solution, containing the substrate and the internal standard, was pipetted into the pyrolysis tube, which was then cooled in liquid nitrogen and sealed at reduced pressure (0.28 mbar). The tube was then placed in the pyrolyzer for 6 min under nonthermal conditions (ambient temperature). A sample was then analyzed using Water's HPLC consisting of Water's HPLC pump (model 515) and Water's UV/vis detector (model 2487). HPLC columns used were Supelco LC-8, LC-18, and ABZ+ (25-cm length, 4.6-mm internal diameter, and 54-μm pore size). The wavelength of the detector $\lambda = 250$–260 nm was used to calculate the standardization value (A_0). Several HPLC measurements were obtained with an accuracy of $\geq$2%. The temperature of the pyrolysis block was then raised until ca. 10% pyrolysis of the substrate was deemed to occur over 900 s interval; the HPLC measurements were carried out as above. This process was repeated after each ca. 10°C rise in the reaction temperature until >95% reaction was achieved. The relative ratios of the sample and the internal standard (A) at each reaction temperature was calculated for a minimum of two kinetic runs, made at each of these temperatures that were in agreement within ±2% to ensure reproducible values of A [13,14]. The rate coefficients at $T = 600$ K were calculated using the kinetic relation $\log k = \log A - E_a/2.303\,RT$, where $\log A$ and E_a are the Arrhenius parameters obtained for the substrates. The limits of error in Table I represents the correction of statistical values. A typical Arrhenius plot for the pyrolysis of compound **1a** is shown in Fig. 1.

Table I Rate Coefficients, $k/(s^{-1})$, and Arrhenius Parameters of Compounds **1–5**

Compound	T (K)	$10^4\ k$ (s^{-1})	log A (s^{-1})	E_a (k J mol^{-1})	$K_{600\ K}$ (s^{-1})
1a	681.85	1.615	11.33 ± 0.12	197.41 ± 1.72	1.39×10^{-6}
	704.15	4.931			
	714.15	7.530			
	724.45	12.61			
	734.65	19.63			
	744.15	29.96			
1b	607.45	0.738	4.065 ± 0.31	95.55 ± 4.02	5.52×10^{-5}
	626.05	1.079			
	644.65	2.011			
	653.25	4.088			
	700.55	8.749			
	719.25	11.35			
	734.05	19.85			
1c	509.25	1.042	9.127 ± 0.94	127.33 ± 9.76	1.10×10^{-2}
	519.15	1.959			
	539.25	8.855			
	559.25	15.64			
	579.05	40.34			
2a	691.75	2.658	11.44 ± 0.143	199.10 ± 1.97	1.31×10^{-6}
	709.95	6.164			
	718.85	9.393			
	728.15	14.76			
	737.55	22.34			
	746.95	33.93			
2b	632.45	2.264	6.984 ± 0.26	128.62 ± 3.25	6.14×10^{-5}
	644.85	3.563			
	658.15	6.305			
	684.15	15.43			
	710.55	32.37			
2c	538.85	2.297	6.215 ± 0.27	101.58 ± 3.06	2.36×10^{-3}
	564.75	7.219			
	578.15	10.09			
	591.15	17.87			
	604.15	25.89			
	614.15	39.87			
3	731.65	4.161	8.48 ± 0.196	166.21 ± 2.85	1.04×10^{-6}
	744.45	6.764			
	757.75	10.47			
	770.45	16.02			
	783.65	26.06			
4	712.25	3.424	10.09 ± 0.45	185.10 ± 6.24	9.63×10^{-7}
	722.15	4.942			
	734.65	8.887			
	745.85	14.98			
5	624.40	8.430	12.44 ± 0.39	173.63 ± 4.79	2.10×10^{-3}
	634.10	16.06			
	639.00	19.09			
	644.00	23.45			
	649.00	26.98			
	653.60	36.47			
	658.20	49.27			

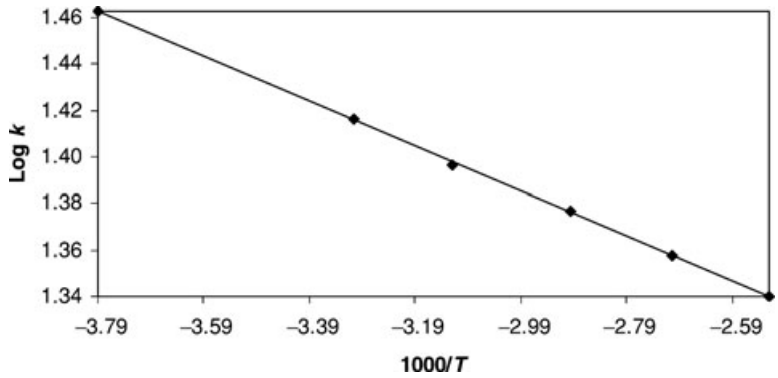


Figure 1 Arrhenius plot for the pyrolysis of 2-phenoxy-1-ethanol **1a**.

RESULTS AND DISCUSSION

Synthesis

The required substrates **1, 2, 4**, and **5** were prepared and fully characterized by NMR and MS, as described in the Experimental section. Compound **3** was purchased from Merck.

Kinetic Analysis

The kinetic data on the gas-phase elimination of compounds **1–5** are summarized in Table I. The reactions followed first-order kinetics. Each rate constant at a given temperature represents an average of at least two measurements in agreement within ±2% rate spread. The Arrhenius plots were strictly linear over >95% reaction.

Reaction Products and Mechanism

To ensure complete substrate pyrolysis, reactions for product analysis were carried out at temperatures exceeding those required for 98% reaction as per kinetic measurements. Absence of substrates from product mixtures was further confirmed by inspection of data on reaction products; the pyrolysates were analyzed using LCMS and ^{1}H NMR. Typical representative results are shown in Table II.

***3-Phenoxy-1-propanol* (1a), *4-Phenoxy-2-butanol* (1b), *and 2-Methyl-4-phenoxy-2-butanol* (1c).** The pyrolysates from **1a–c** were ascertained to be phenol together with CH_2O from **1a**, CH_3CHO from **1b**, and $(CH_3)_2CO$ from **1c**. These results could be fully explained on the basis of a reaction mechanism with a cyclic six-membered TS (Scheme 4).

Analysis of the kinetic results reported in Scheme 4, using the proposed reaction mechanism for **1a–c**, namely (3-phenoxy) primary, secondary, and tertiary alcohols, reflects the influence of the methyl group on the reactivity of alcohols **1a–c**. Tertiary alcohol is more reactive than its primary and secondary counterparts by a factor of 8×10^3 and 39, respectively. This appreciable rate enhancement $3^\circ > 2^\circ > 1^\circ$ is systematic and consistent with the stabilizing electron-donating effects of the methyl groups on the stability of the transition state by stabilizing the partial charge development at the carbon atom.

***3-Phenylsulfanyl-1-propanol* (2a), *4-Phenylsulfanyl-2-butanol* (2b), *and 2-Methyl-4-phenylsulfanyl-2-butanol* (2c).** The products of the gas-phase elimination reaction of **2a–c** were identified as thiophenol together with CH_2O from **2a**, CH_3CHO from **2b**, and $(CH_3)_2CO$ from **2c**. This indicates similar thermal behavior with their 3-phenoxy counterparts **1a–c** (Scheme 5).

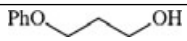
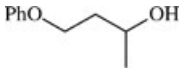
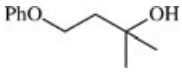
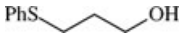
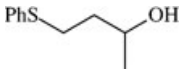
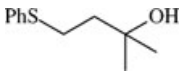
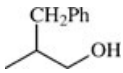
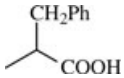
The reactivity order of this series **2a–c** parallels that of **1a–c**. The most reactive substituted alcohol is the tertiary. It is 2×10^3 and 38 times more reactive than its primary and secondary analogues, respectively. This lend support to the electron-donating effect of the methyl group in stabilizing the TS and, hence, enhancing the reaction rate.

***4-Phenyl-1-butanol* (3).** The pyrolysate from this compound consists of toluene and CH_2O, suggesting a similar mechanistic pathway to its oxygen and thio analogues **1** and **2**. The rate constant at 600 K is 1.04×10^{-6} s^{-1}.

To facilitate comparison, the rate constants, $k/(s^{-1})$, of gas-phase elimination reaction at 600 K of compounds **1–3** are compiled in Scheme 6.

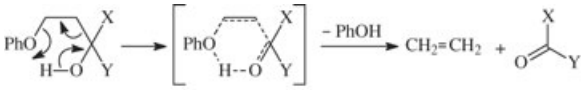
The analysis of the rate data shows that the influence of the aryl substituents (—OPh, —SPh, and —CH_2Ph) on the reactivity of the present alcohol is not significant in magnitude. The hydroxyl (OH) function of the alcohols

Table II Pyrolysis Products of Compounds **1–5** and Percentage Yield

Number	Compound	Product (% Yield)		
1a		PhOH (77)	CH_2O (22)	$CH_2{=}CH_2$
1b		PhOH (73)	CH_3CHO (29)	$CH_2{=}CH_2$
1c		PhOH (81)	$(CH_3)_2CO$ (17)	$CH_2{=}CH_2$
2a		PhSH (82)	CH_2O (27)	$CH_2{=}CH_2$
2b		PhSH (87)	CH_3CHO (16)	$CH_2{=}CH_2$
2c		PhSH (91)	$(CH_3)_2CO$ (22)	$CH_2{=}CH_2$
3		$PhCH_3$ (90)	CH_2O (23)	$CH_2{=}CH_2$
4		$PhCH_3$ (88)	CH_3CHO (13)	CO
5		$PhCH_3$ (79)	CH_3CHO (13)	CO

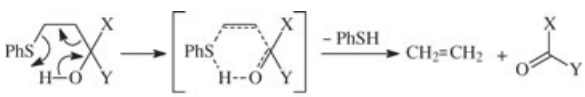
1–3 is equivalent; hence, the influence of this function on the molecular reactivity of alcohols **1–3** should be equivalent. This lend support to the importance of the OH bond breaking (Scheme 6) to the overall reactivity of the alcohols under study; the effect of this bond on molecular reactivity provides an explanation for the comparable rate constant of the gas-phase elimination reaction of alcohols **1–3**.

On the other hand, the TS proposed involves C—X bond breaking, one would expect that compound **3** (X = CH_2) would be less reactive than compound **1** (X = O) and **2** (X = S). Although it is not significant, it is of interest here to note that the results of the theoretical ab initio calculations show gas-phase thermodynamic stabilities of the arene fragments to be in order of $PhNH_2$ > $PhCH_3$ ≅ PhOH > PhSH [4], so the thermodynamic stability of $PhCH_3$ in the gas-phase elimination reaction compensates the lower polarity of the (C—X) bond in compound **3**. It is worth mentioning that the rate constant of the gas-phase elimination reaction of 3-anilino-1-propanol at 600 K is 5.95×10^{-5}. This is 42- to 45-times faster than the rate constant of the gas-phase elimination of phenol and toluene from compounds **1** and **3**, respectively. This confirms further the importance of thermodynamic stability of arene produced from the reaction rate.



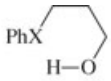
	X	Y	$k_{600\,K}(s^{-1})$
1a	H	H	1.39×10^{-6}
1b	H	Me	5.52×10^{-5}
1c	Me	Me	1.10×10^{-2}

Scheme 4 Gas-phase elimination of **1a–c** and the rate constant at 600 K.



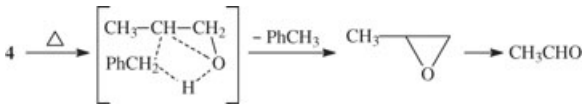
	X	Y	$k_{600\,K}(s^{-1})$
2a	H	H	1.31×10^{-6}
2b	H	Me	6.14×10^{-5}
2c	Me	Me	2.36×10^{-3}

Scheme 5

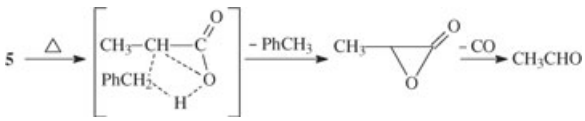


Compound	X	$k_{600\,K}(s^{-1})$
1a	O	1.39×10^{-6}
2a	S	1.31×10^{-6}
3	CH_2	1.04×10^{-6}
	NH	5.95×10^{-6}

Scheme 6 Rate constants at 600 K for compounds **1–3** and 3-*N*-phenyl aminopropanol.



Scheme 7



Scheme 8

***2-Methyl-3-phenyl-1-propanol* (4).** Product analysis revealed formation of $PhCH_3$ and CH_3CHO from compound **4**, at a rate constant of 9.63×10^{-7} at 600 K. Identity of the products suggests the mechanistic pathway that is shown in Scheme 7.

To prove this mechanism, we have prepared and pyrolyzed 2-methyl-3-phenylpropanoic acid **5**, and the pyrolysates were ascertained to consist of toluene $PhCH_3$ and CH_3CHO. This suggests a mechanistic pathway similar to 2-methyl-3-phenylpropanol **4** (Scheme 8) with a rate constant of 9.12×10^{-4} at 600 K. This high reactivity of 3-phenylpropanoic acid **5** of 947 relative to 2-methyl-3-phenylpropyl alcohol **4** is attributed to the increase in the acidity of the incipient hydrogen by replacing an alcohol hydroxyl hydrogen by a carboxylic acid proton; such an increase in the rate of reaction was observed when the reactivity of 2-phenoxypropanoic acid was compared with 2-phenoxy-1-propanol. 2-Phenoxy-1-propanol and 2-*N*-phenylamino-1-propanol were compared with the reactivities of 2-phenoxypropanoic acid and 2-*N*-phenylaminopropanoic acid, respectively [1].

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