

Kinetic and mechanism of the homogeneous, unimolecular elimination of α,β -unsaturated aldehydes in the gas phase

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ABSTRACT: The gas phase thermal decarbonylation of α,β -unsaturated aldehydes E-2-butenal and E-3-phenyl-2-methylpropenal was studied in a static system over the temperature range 380.5–490.0 °C and pressure range 55.5–150 Torr. The reactions are homogeneous and unimolecular and obey a first-order rate law. The rate coefficient is represented by the following Arrhenius equations:

$$\text{E-2-Butenal: } \log k_1 (\text{s}^{-1}) = (13.18 \pm 0.16) - (212.0 \pm 2.0) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$$

$$\text{E-3-phenyl-2-methylpropenal: } \log k_1 (\text{s}^{-1}) = (13.23 \pm 0.22) - (234.6 \pm 3.2) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$$

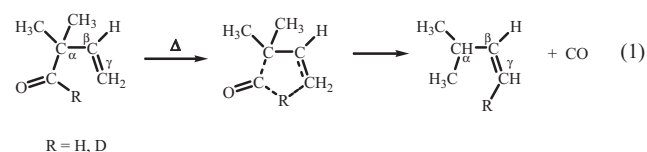
The elimination products of 2-butenal are propene and CO gas, while 3-phenyl-2-methylpropenal produces α -methylstyrene, *cis-trans*- β -methylstyrene, indan, and CO gas. Kinetic and thermodynamic parameters suggest these elimination reactions to proceed through a three-membered cyclic transition state type of mechanisms. However, a two steps mechanisms for the formation of a carbene type of intermediate through a four-membered cyclic transition structure can not be overlooked. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: gas phase elimination; pyrolysis; kinetics; mechanisms; 2-butenal; 3-phenyl-2-methylpropenal

INTRODUCTION

An important type of organic molecules, the aldehydes, have little been studied in thermal decomposition kinetics in the gas phase. This fact may be due to their tendency to oxidize in contact with air and to generally undergo a complex free radical chain processes.¹ Gas phase pyrolyses of saturated aldehydes such as propionaldehyde,^{2–8} acetaldehyde,^{9–24} and formaldehyde^{25–27} at temperatures of 450–600 °C showed to proceed through free radical reactions. An aldehyde with the CHO group attached directly to a π -system, that is, benzaldehyde^{28–32} at 550–1400 °C was described to undergo a radical mechanism to produce benzene and CO as primary products, while biphenyl and hydrogen gas as secondary products. The only work on the gas phase thermal decomposition of a β - γ -unsaturated aldehyde,

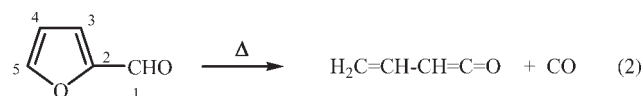
2,2-dimethyl-3-butenal, was reported by Crawford *et al.*³³ This compound, in a static system at 282–302 °C, yielded 2-methyl-2-butene and carbon monoxide. Additionally, the kinetic isotope effect of this elimination reaction gave a $k_H/k_D = 2.8$ at 296.9 °C (i.e., 7.2 at 25 °C). This result indicated that the H attached to the CO group of the aldehyde has been transferred during the process of decomposition. Since the reaction proved to be unimolecular and obeys a first-order rate law, the mechanism was described by a five-membered cyclic transition state type of mechanism as depicted in reaction (1)



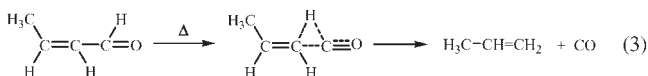
In the paper describing the pyrolysis of benzaldehyde in a flow system described of Grela and Colussi,³² 2-furaldehyde and 2-butenal were also examined. The

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2-furaldehyde suggested to proceed via a biradical mechanism in bond breaking of C₂—O or C₅—O [reaction (2)], while 2-butenal was demonstrated to be



a molecular process. 2-Butenal with mixed CHO and CDO in a ratio of 1:3 yielded the same product ratio. This means that H or D at the CO of the aldehyde are transferred to the β -position through a 1,2-migration. Therefore, the mechanism of gas elimination of 2-butenal suggested a concerted three-membered cyclic transition state structure as shown in reaction (3).

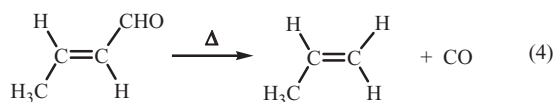


In view of little information on the thermolysis of α - β -unsaturated aldehydes, the present work aimed at examining in a static system, under homogeneous and molecular conditions, the gas phase elimination kinetics of 2-butenal and 3-phenyl-2-methylbutenal and to consider a reasonable mechanism of these reactions

RESULTS AND DISCUSSION

E-2-Butenal

The gas phase molecular elimination of this aldehyde was determined between the temperature range of 380.5 and 430.5 °C and pressure range of 55.5–150 Torr. The theoretical stoichiometry described in reaction (4) demands $P_f/P_0 = 2.0$, where P_f and P_0 are the final and initial pressures,



respectively. The average experimental results P_f/P_0 at four different temperatures and 10 half-lives for 2-butenal is 1.9 (Table 1). Additional examination of stoichiometry (4), up to 68% decomposition, was obtained by

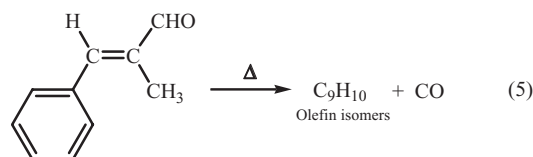
comparing the pressure measurements with the quantitative GLC analysis of olefin formation (Table 2).

The homogeneity of the reaction was studied by using a vessel with a surface-to-volume ratio 6 relative to the normal vessel, which had an $S/V = 1$ (Table 3). The packed and unpacked clean Pyrex vessels and the packed and unpacked Pyrex vessels seasoned with allyl bromide had no marked effect on the rate coefficients. The effect of the free radical inhibitor is described in Table 4. The kinetic determinations were carried out in the presence of at least 2 equivalent of toluene in order to suppress any possible free radical chain process of the substrate and/or products. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficients for the elimination reaction calculated from $k_1 = -(2.303/t) \log[(2P_0 - P_t)/P_0]$ were shown to be independent of the initial pressure of the substrate (Table 5), and the first-order plots of $\log[(2P_0 - P_t)]$ against time t are linear up to 68% reaction. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation is described in Table 6 (90% confidence limits from a least-squares procedure).

E-3-Phenyl-2-methylpropenal

The elimination kinetics of E-3-phenyl-2-methylpropenal was examined in the temperature range of 440.6–490.0 °C and pressure range of 62–142 Torr. The stoichiometry of reaction (5) requires



$P_f = 2P_0$. The actual average experimental value of P_f/P_0 at several different temperatures and 10 half-lives is 2.0 (Table 1). Additional verification of stoichiometry (5), up to 56% reaction, gave a good agreement between the extent of decomposition as predicted from pressure

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

Compound	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Aver.
E-2-Butenal	400.0	96	178	1.9	1.9
—	410.3	101	184.5	1.8	—
—	420.3	96	188.5	2.0	—
—	430.5	100.5	204	2.0	—
E-3-Phenyl-2-methylpropenal	470.2	103.2	203	2.0	2.0
—	480.2	92	186.5	2.0	—
—	490	99.9	204.5	2.1	—

Table 2. Stoichiometry of the reaction

Substrate	Temperatures (°C)	Parameter	Value				
E-2-Butenal	410.3	Time (min)	7	10	12	15	20
—	—	Reaction (%) (pressure)	32.8	43.4	51.5	56.3	68.3
—	—	Olefin (%) (GLC)	31.6	42.6	51.7	55.7	68.7
E-3-Phenyl-2-methylpropenal	470.2	Time (min)	6	10	15	20	35
—	—	Reaction (%) (pressure)	18.4	27.1	36.9	46.0	56.2
—	—	Olefin (%) (GLC)	18.7	25.2	34.5	45.2	55.2

Table 3. Homogeneity of the elimination reactions

Substrate	S/V (cm ⁻¹) ^a	$k_1 \times 10^4$ (s ⁻¹) ^b	$k_1 \times 10^4$ (s ⁻¹) ^c
E-2-Butenal at 410.3 °C	1	9.75	9.60
—	6	9.77	9.71
E-3-Phenyl-2-methylpropenal at 470.2 °C	1	5.73	5.66
—	6	5.75	5.72

^a S, surface area; V, volume.^b Clean Pyrex vessel.^c Vessel seasoned with allyl bromide.**Table 4.** Effect of free radical suppressor toluene on rates

Substrate	Temperature (°C)	P_s (Torr)	P_i (Torr)	P_i/P_s	$k_1 \times 10^4$ (s ⁻¹)
E-2-Butenal	410.3	103.5	—	—	11.4
—	—	104	56.5	0.5	9.72
—	—	150	151	1.0	9.67
—	—	99	159	1.6	9.52
—	—	97.5	197.5	2.0	9.71
—	—	100	245	2.5	9.51
—	—	107	307	2.9	9.65
—	—	101.5	346	3.4	9.74
E-3-Phenyl-2-methylpropenal	470.2	92	—	—	7.56
—	—	80.8	102	1.3	5.74
—	—	79.7	183.5	2.3	5.76
—	—	99.1	298	3.0	5.58
—	—	79.4	327	4.1	5.64
—	—	79.4	411	5.2	5.53

 P_s , pressure substrate; P_i , pressure inhibitor.**Table 5.** Invariability of the rate coefficients with initial pressure

Substrate	Temperature (°C)	Parameters	Value					
E-2-Butenal	410.3	P_0 (Torr)	55.5	82	94	108.5	130	150
—	—	$k_1 \times 10^4$ (s ⁻¹)	9.77	9.72	9.66	9.58	9.74	9.67
E-3-Phenyl-2-methylpropenal	470.2	P_0 (Torr)	62.7	79.4	86.4	91	108.8	142.3
—	—	$k_1 \times 10^4$ (s ⁻¹)	5.65	5.53	5.63	5.64	5.67	5.72

Table 6. The variation of the rate coefficients with temperatures

Substrate	Parameters	Value					
E-2-Butenal	Temperature (°C)	380.5	390.5	400.0	410.3	420.3	430.5
—	$k_1 \times 10^4$ (s ⁻¹)	1.70	3.22	5.51	9.60	16.40	27.40
Rate equation $\log k_1$ (s ⁻¹) = (13.18 ± 0.16) - (212.0 ± 2.0) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9998$							
E-3-Phenyl-2-methylpropenal	Temperature (°C)	440.6	450.7	460.2	470.2	480.2	490.0
—	$k_1 \times 10^4$ (s ⁻¹)	1.19	1.92	3.38	5.66	9.15	15.20
Rate equation $\log k_1$ (s ⁻¹) = (13.23 ± 0.22) - (234.6 ± 3.2) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9996$							

Table 7. Distribution of olefins at different percentages of the reaction at 470.2 °C

<i>t</i> (min)	% reaction	α -Methylstyrene	<i>Cis</i> - β -methylstyrene	<i>Trans</i> - β -methylstyrene	Indan
6	18.7	30.8	14.3	41.4	13.5
10	25.2	27.9	13.7	41.9	16.6
15	34.5	29.7	12.9	44.2	13.3
20	45.2	29.0	13.7	43.2	14.1
—	Average	29.4	13.7	42.7	14.4

measurements and the sum of quantitative chromatographic analyses of olefin products (Table 2).

The products formation of this substrate within the rate of coefficient determinations at different reaction percentages were analyzed at 470.2 °C (Table 7). As the extent of the reaction increases, the olefin distribution are nearly constant. This result appears to be due to the very rapid isomerization of the β -methylstyrene product. Moreover, Table 8 describes how the temperature influences, at 50% reaction, the process of olefin isomerization.

To give support to the above consideration, the equilibrium process of these products were verified by the approximate calculations using thermodynamic group additivity table³⁴ at 470.2 °C (743.35 K) (Table 9).

Tests for surface effects on the rate of elimination, the packed and unpacked clean Pyrex vessels, and the packed and unpacked Pyrex vessels seasoned with allyl bromide showed no effect, and the reaction may be said to be homogeneous in nature. The effect of different pro-

portions of the free radical inhibitor toluene is given in Table 4. This reaction has also been carried out in the presence of at least 2 equivalent of suppressor so as to inhibit any possible free radical chain process of the substrate and/or products. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The first-order rate coefficients of this aldehyde, calculated from $k_1 = -(2.303/t)\log[(2P_0 - P_t)/P_0]$ were found to be independent of the initial pressure of the substrate (Table 5). A plot of $\log [(2P_0 - P_t)]$ versus time *t* gave a good straight line up to 55% decomposition. The variations of the rate coefficient are described in Table 6. The results given in Table 6 lead, by using the least square procedure and 90% confidence limits, to the shown Arrhenius equation.

According to the kinetic and thermodynamic parameters of Table 10, the small negative value of the entropy of activation ΔS^\ddagger , together with the frequency

Table 8. Distribution of olefins at different temperature

Temperature (°C)	α -Methylstyrene	<i>Cis</i> - β -methylstyrene	<i>Trans</i> - β -methylstyrene	Indan
440.6	25.8	14.2	49.6	10.4
470.2	29.7	12.9	44.2	13.3
490.0	32.4	12.8	41.4	13.4

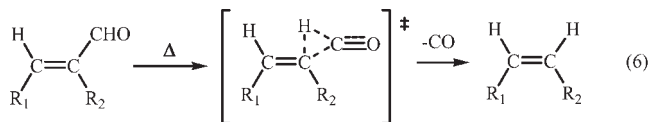
Table 9. Equilibrium mixtures from thermodynamic additivity³⁴ at 470.2 °C (743.35 K)

Temperature (°C)	α -Methylstyrene	<i>Cis</i> - β -methylstyrene	<i>Trans</i> - β -methylstyrene	Indan
470.2	12.1	38.8	34.9	14.2

Table 10. Kinetic and thermodynamic parameters at 440.6 °C

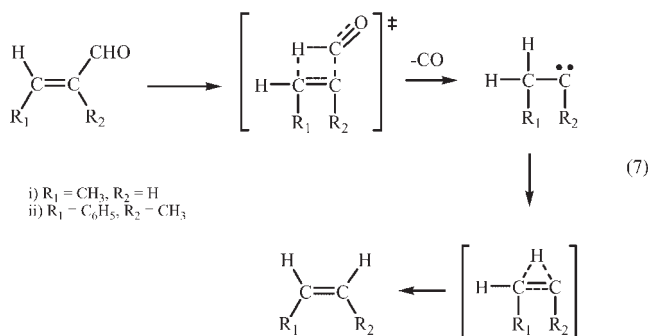
Substrate	$k_1 \times 10^4$ (sec ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i> (sec ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
E-2-Butenal	46.5	212.0 ± 2.0	13.18 ± 0.16	-8.2	209.7	215.5
E-3-Phenyl-2-methylpropenal	1.19	234.6 ± 3.2	13.23 ± 0.22	-7.1	228.7	233.8

factor of log A values (Table 10) of 13.18 and 13.23 implies a transition state of these elimination reaction of three- or four-membered cyclic structure.³⁴ Of these two structures, the most reasonable hypothesis is the concerted semi-polar three-membered cyclic transition state structure as described in reaction (6).



- i) $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$
 ii) $\text{R}_1 = \text{C}_6\text{H}_5$, $\text{R}_2 = \text{CH}_3$

This assumed mechanism may find support from the pyrolytic elimination of E-2-butenal in a flow system, with $E_a = 249.7 \text{ kJ/mol}$ and $\log A = 13.5$ at $770\text{--}900^\circ\text{C}$, proposed by Grela and Colussi.³² Otherwise, the formation of a four-membered cyclic transition structure [reaction (7)] may not be overlooked and implies the formation of a carbene type of intermediate and CO gas. Such intermediate may undergo a 1,2-hydrogen migration through a three-membered cyclic transition state to give the corresponding olefin.



- i) $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$
 ii) $\text{R}_1 = \text{C}_6\text{H}_5$, $\text{R}_2 = \text{CH}_3$

Because of resonance interaction towards the aromatic nuclei in 3-phenyl-2-methylbutenal of reaction (6), the electrons at the $\text{C}=\text{C}$ adjacent to the CHO are less available when compared to the electron release of the methyl group towards the $\text{C}=\text{C}$ in 2-butenal. This fact appears to cause to E-2-butenal to be faster in rate of decarbonylation than E-3-phenyl-2-methylbutenal (Table 10).

EXPERIMENTAL

The substrates E-2-butenal (Acros, 99.0% purity) and E-3-phenyl-2-methylpropenal (Acros, 99.8% purity) were used (GC-MS: Saturn 2000, Varian 3600X, with a DB-5MS capillary column $30 \text{ m} \times 0.25 \text{ mm}$ i.d., $0.25 \mu\text{m}$ film thickness). The quantitative chromatographic analyses of olefin products were determined by using a Gas Chromatograph Varian 3600X, with a DB-5MS capillary column $30 \text{ m} \times 0.53 \text{ mm}$ i.d., $1.5 \mu\text{m}$ film thickness. The identification of the product was made

by comparing with true authentic samples bought from Aldrich and in a GC-MS (Saturn 2000, Varian 3600 \times with a DB-5MS capillary column $30 \text{ m} \times 0.25 \text{ mm}$ i.d., $0.25 \mu\text{m}$).

Kinetics

The kinetic determinations were carried out in a static reaction system as described before.^{35–37} At each temperature, six to nine runs have been carried out in our experiments. The rate coefficients for the decomposition was calculated from the pressure increase manometrically. The temperature was maintained within $\pm 0.2^\circ\text{C}$ through control with a Shinko DIC-PS 23TR resistance thermometer and was measured with a calibrated iron–constantan thermocouple. No temperature gradient was observed along the reaction vessel. The substrates were all injected directly into the reaction vessel with a syringe through a silicone rubber septum. The amount of substrate used for each reaction was $\sim 0.05\text{--}0.1 \text{ mL}$.

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