JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 694–698
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.759

Kinetics and mechanisms of elimination of ethyl 3-phenyl and ethyl 3-methyl-3-phenyl glycidates in the gas phase

Gabriel Chuchani,* María Tosta, Alexandra Rotinov and Armando Herize

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

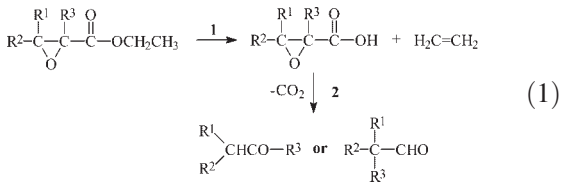
Received 7 December 2003; revised 30 January 2003; accepted 4 February 2003

ABSTRACT: The gas-phase elimination kinetics of the title compounds were examined in a static reaction system over the temperature range 350.2–399.7 °C and the pressure range 16.5–107 Torr (1 Torr = 133.3 Pa). The reactions are homogeneous, unimolecular and follow a first-order rate law. The rate coefficients are given by the following Arrhenius equations: for ethyl 3-phenylglycidate, $\log [k_1\ (s^{-1})] = (12.15 \pm 0.46) - (190.1 \pm 5.8)$ kJ mol^{-1} $(2.303\,RT)^{-1}$, and for ethyl 3-methyl-3-phenyl glycidate, $\log [k_1\ (s^{-1})] = (12.02 \pm 0.19) - (182.9 \pm 2.4)$ kJ mol^{-1} $(2.303\,RT)^{-1}$. The ethyl side of the ester is eliminated as ethylene through a concerted six-membered cyclic transtion state, while the unstable intermediate glycidic acid rapidly decarboxylates to give the corresponding substituted aldehyde. The glycidic acid appears to lose CO_2 gas by way of a five-membered cyclic transition state type of mechanism. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: gas-phase elimination; pyrolysis; mechanisms; ethyl 3-phenyl glycidate; ethyl 3-methyl-3-phenyl glycidate

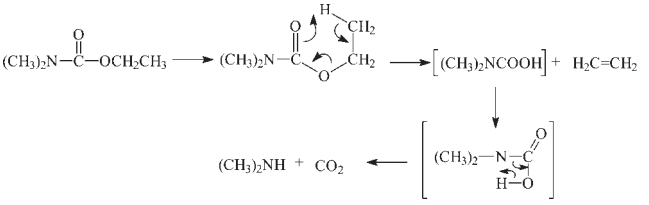
INTRODUCTION

An interesting review of glycidic esters and their conversions to aldehydes and ketones was presented by Newman and Magerlein[1] [reaction (1)]. These esters on alkaline hydrolysis and acidification yield the corresponding acids which generally are difficult to isolate [reaction (1), **step 1**]. Glycidic acids have been found to be unstable and decompose even at room temperature. However, the physical constants of a few high molecular weight member of these acids have been described.[2,3] The reaction of converting glycidic acids through decarboxylation into the aldehydes or ketones [reaction (1), **step 2**] is by heating to the decomposition point. In this respect, the above-mentioned review[1] reports several examples of pyrolyses or thermal decompositions of alkaline salts of these acids in the presence of a catalysts or heated in solvents.

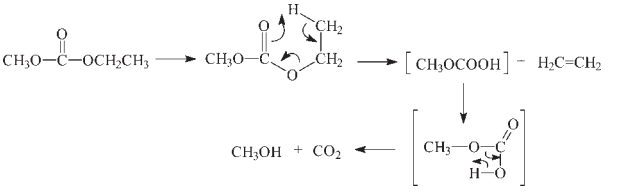


(1)

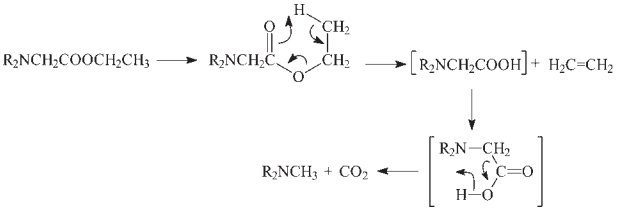
The process of removal of the alkyl side of the glycidic ethyl ester [reaction (1), **step 1**], followed by a rapid decarboxylation of the corresponding acid [reaction (1), **step 2**], may be associated with some analogous reactions undergoing a similar number of steps. Examples of such reactions are the homogeneous, unimolecular gas-phase elimination kinetics of ethyl carbamates[4] [reaction (2)], ethyl carbonates[5] [reaction (3)] and ethyl esters of amino acids[6,7] [reaction (4)]. According to reactions (2)–(4), the



(2)



(3)



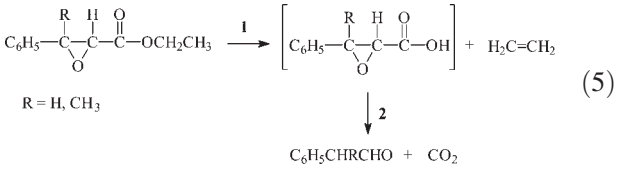
(4)

**Correspondence to:* G. Chuchani, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela.
E-mail: chuchani@quimica.ivic.ve

alkyl side of the ester is eliminated to the corresponding olefin, whereas the acid intermediate under the experimental conditions, decarboxylate to final products.The above information led to the present attempt to examine some glycidates eliminations in the gas phase. Two known compounds, ethyl 3-phenylglycidate and ethyl 3-methyl-3-phenylglycidate, on basic hydrolysis and acidification yielded the corresponding 2-phenylacetaldehyde[8,9] and 2-phenylpropionaldehyde,[10] respectively. Consequently, this work aimed at examining the gas-phase kinetics and mechanisms of these substrates and to compare the results, if any.

RESULTS AND DISCUSSION

The product formation in the molecular elimination of the ethyl glycidates in the gas phase can be described according to reaction (5).



(5)

The theoretical stoichiometry of reaction (5) demands that for a long reaction time $P_f/P_0 = 3$, where P_f and P_0 are the final and initial pressures, respectively. The average experimental result for P_f/P_0 at four temperatures and ten half-lives was nearly 3.0 (Table 1). The departure of P_f/P_0 to <3 for ethyl 3-methyl-3-phenylglycidate may be due to some polymerization of the corresponding aldehyde product. Additional examination for the verification of the stoichiometry of reaction (5), up to 60–70% reaction, was made by comparing the extent of decomposition of the substrate from pressure measurements with that obtained from quantitative gas-liquid chromatographic (GLC) analyses of the corresponding ethylene formation (Table 2).

Table 1. Ratio of rate of final pressure (P_f) to initial pressure (P_0)[a]

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
Ethyl 3-phenylglycidate	369.6	67	202	3.0	3.0
	379.9	76.5	222.5	3.0	
	389.9	74	211.5	2.9	
	399.7	69	216	3.1	
Ethyl 3-methyl-3-phenylglycidate	360.0	31.5	79	2.5	2.7
	370.6	12	32	2.7	
	380.2	22	61	2.8	
	391.1	35.5	98	2.8	

[a] Vessel seasoned with allyl bromide. 1 Torr = 133.3 Pa.

The effect of the surface area on the rate of elimination was tested by carrying out several runs in a vessel packed with small cylindrical glass balls, with a surface-to-volume ratio of 6 relative to that of the normal unpacked vessel, which is equal to 1. The rates of elimination of both substrates were unaffected in seasoned packed and unpacked vessels. However, clean packed and unpacked Pyrex vessels showed a significant heterogeneous effect on the rate coefficients (Table 3).

The effect of different proportions of the free radical inhibitor toluene on the elimination reactions is given in Table 4. 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 glycidic ethyl esters calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$ were found to be independent of the initial pressure (Table 5). A plot of $\log(3P_0 - P_t)$ against time t gave a good straight line up to 60–80% reaction. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation are given in Table 6 (90% confidence coefficients from a least-squares method). Therefore, these reactions, carried out in seasoned vessels and in the presence of the free radical inhibitor toluene, are homogeneous, unimolecular and follow a first-order rate law. The rate coefficient is expressed by the following Arrhenius equations:

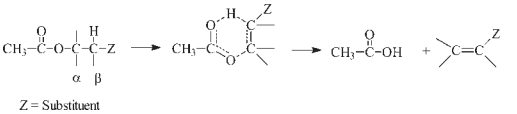
for ethyl 3-phenylglycidate:

$$\log[k_1(s^{-1})] = (12.15 \pm 0.46) - (190.1 \pm 5.8)\text{kJ mol}^{-1}(2.303\,RT)^{-1}$$

for ethyl 3-methyl-3-phenyl glycidate:

$$\log[k_1(s^{-1})] = (12.02 \pm 0.19) - (182.9 \pm 2.4)\text{kJ mol}^{-1}(2.303\,RT)^{-1}.$$

The kinetic and thermodynamic parameters are described in Table and Figures 1 and 2. The results for $\log A$ of 12.15 and 12.02 for the substrates listed in Table 7 are the commonly accepted values for a six-membered cyclic transition state mechanism for ester pyrolyses in the gas phase [reaction (6)].[11-13] Moreover, this mechanistic consideration is reinforced with a significant negative entropy of activation ($\Delta S^{\neq}$). Therefore, the first stage of elimination is the formation of ethylene and the corresponding glycidic acid [reaction (7), **step 1**)].



(6)

Unfortunately, the phenylglycidic acid intermediate, under the present reaction conditions, decarboxylates to give the corresponding aldehyde as described in

Table 2. Stoichiometry of the reaction

Substrate	Temperature (°C)	Parameter	Values				
Ethyl 3-phenylglycidate	390.1	Time (min)	3.5	4.5	7	10	12
		Reaction (%) (pressure)	24.6	30.2	43.8	55.9	64.1
		Ethylene (%) (GLC)	22.7	29.5	41.7	54.8	60.0
Ethyl 3-methyl-3-phenylglycidate	380.3	Time (min)	3	5.5	9	12	15
		Reaction (%) (pressure)	45.0	55.0	65.9	70.5	79.5
		Ethylene (%) (GLC)	44.5	56.4	69.2	73.4	77.5

Table 3. Homogeneity of elimination reactions

Substrate	S/V (cm^{-1})[a]	$10^4\ k_1$ (s^{-1})[b]	$10^4\ k_1$ (s^{-1})[c]
Ethyl 3-phenylglycidate at 390.1 °C	1	16.28	14.09
	6	22.72	13.87
Ethyl 3-methyl-3-phenylglycidate at 380.2 °C	1	25.56	24.91
	6	22.86	24.33

[a] S = surface area; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.

reaction (5). Attempts to prepare pure 3-phenylglycidic acid as reported[3] were unsuccesful, since this acid decomposes even at room temperature. Therefore, substrates <97.5% pure lead to unreliable and irreproducible kinetic results. To rationalize a reasonable mechanism for the formation of the final products from the glycidic acid intermediates, the tertiary carbon at the 3-position, rather than the secondary carbon at the 2-position, is more liable to a C—O bond polarization, in the sense of $C^{\delta+}\cdots O^{\delta-}$. Consequently, the oxygen becomes very nucleophilic in nature and may abstract the acidic H of the COOH through a five-membered cyclic transition state as shown in reaction (7), **step 2**.

Table 4. Effect of free radical inhibitor (toluene) on rates

Substrate	Temperature (°C)	P_s[a] (Torr)	P_i[b] (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
Ethyl 3-phenylglycidate	390.1	47	—	—	14.45
		85	63	0.7	13.91
		44.5	78	1.8	14.18
		53	106	3.8	14.40
Ethyl 3-methyl-3-phenylglycidate	380.2	20	—	—	26.31
		22	24	1.1	25.80
		21	72	2.3	25.73
		22	131	6.2	25.81

[a] P_s = pressure of the substrate.
[b] P_i = pressure of the inhibitor.

Table 5. Invariability of the rate coefficients with initial pressure[a]

Substrate	Temperature (°C)	Parameter	$10^4 k_1$ (s^{-1})				
Ethyl 3-phenylglycidate	390.1	P_0 (Torr)	44.5	53	78	85	107
		$10^4\ k_1$ (s^{-1})	14.18	14.45	14.18	13.91	14.03
Ethyl 3-methyl-3-phenylglycidate	380.2	P_0 (Torr)	16.5	30	47	58	67
		$10^4\ k_1$ (s^{-1})	25.31	25.90	26.32	25.80	25.71

[a] Vessel seasoned with allyl bromide.

Table 6. Variation of the overall rate coefficients with temperature

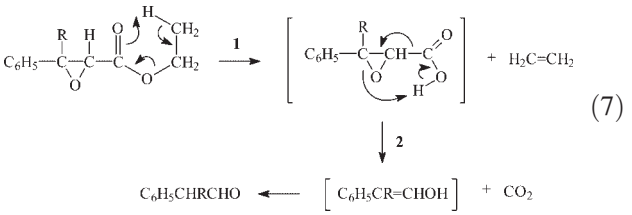
Substrate	Parameter	Value					
Ethyl 3-phenylglycidate[a]	Temperature (°C)	350.2	360.0	369.6	379.9	390.1	399.7
	$10^4\ k_1$ (s^{-1})	1.61	2.82	5.01	8.98	14.09	24.28
Ethyl 3-methyl-3-phenylglycidate[b]	Temperature (°C)	350.5	360.0	370.6	380.2	391.1	
	$10^4\ k_1$ (s^{-1})	5.47	8.51	15.41	25.81	40.21	

[a] Rate equation: $\log [k_1\ (s^{-1})] = (12.15 \pm 0.46) - (190.1 \pm 5.8)\ kJ\,mol^{-1}\ (2.303\,RT)^{-1}$; $r = 0.9980$.
[b] Rate equation: $\log [k_1\ (s^{-1})] = (12.02 \pm 0.19) - (182.9 \pm 2.4)\ kJ\,mol^{-1}\ (2.303\,RT)^{-1}$; $r = 0.9998$.

Table 7. Kinetic and thermodynamic parameters at 370 °C

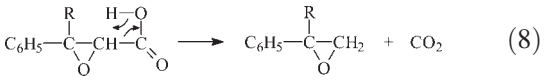
Substrate	$k_1 \times 10^4$ (s^{-1})	F_a (kJ mol^{-1})	Log A (s^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Ethyl 3-phenylglycidate	5.10	190.1 ± 5.8	12.15 ± 0.46	−27.2	184.8	202.3
Ethyl 3-methyl-3-phenylglycidate	15.41	182.9 ± 2.4	12.02 ± 0.19	−44.6	167.8	196.5

The aldehyde product is readily formed from isomerization of the corresponding enolic intermediate.



(7)

The alternative mechanism for the glycidic acid decomposition through decarboxylation as depicted in reaction (8) appears to be unlikely since the epoxy intemediate was not isolated. Moreover, most epoxy compounds undego isomerization and rearrangements at temperatures even higher than those employed in the present experiments.[14–16]



(8)

The *k*-value of ethyl 3-methyl-3-phenylglycidate is found to represent a nearly 2.9 times faster for rate than ethyl 3-phenylglycidate (Table 7). This result is surprising since the glycidic acid intermediates are unstable and decarboxylate very fast at the high working temperatures. Consequently, the difference in rates between the two esters may be deduced from the ethylene elimination [reaction (2), **step 1**], rather than the decarboxylation of the corresponding glycidic acid intermediate [reaction (2), **step 2**]. This means that the 3-phenyl oxiranyl substituent at the acid side of the ester should give a faster overall rate than the 3-methylphenyl oxiranyl substituent. Otherwise, it is possible to believe that such difference may be due to a concomitant fragmentation of the oxirane to generate the enol directly. Apparently, the greater substitution of the enol 3-methyl-3-phenyl substituent may provide an enhanced driving force for the reaction as compared with the 3-phenyl derivative. Accordingly, the enol would be more stabilized and if Hammond's postulate holds, then the activation barrier would be lowered and therefore result in a faster rate coefficient. Moreover, the result of a greater negative entropy of activation of the ethyl 3-methyl-3-phenylglycidate compared with ethyl 3-phenylglycidate suggests that the more concerted elimination of ethylene and then carbon dioxide to generate the enol intemediate appears to be rationalized by the experimental results (Table 7).

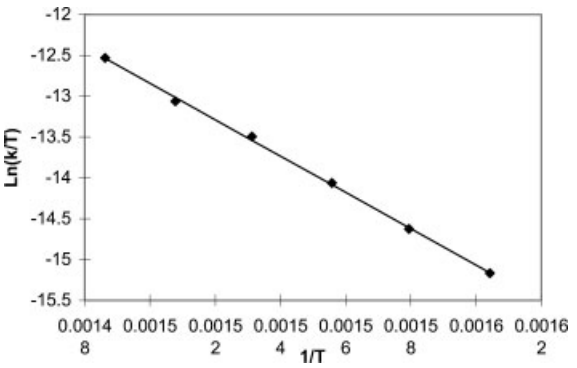


Figure 1. Kinetic plot to determine entropy and enthalpy of activation for the ethyl 3-phenylglycidate. $\ln(k/T) = \ln(k_B/\hbar) - \Delta S^{\#}/R - \Delta H^{\#}/RT$; slope −22225.3; intercept 20.49; $r = 0.9995$; $\Delta H^{\#} = 184.8$ kJ mol^{-1}; $\Delta S^{\#} = -27.15$ J mol^{-1}; $\Delta G^{\#} = 202.26$ kJ mol^{-1}

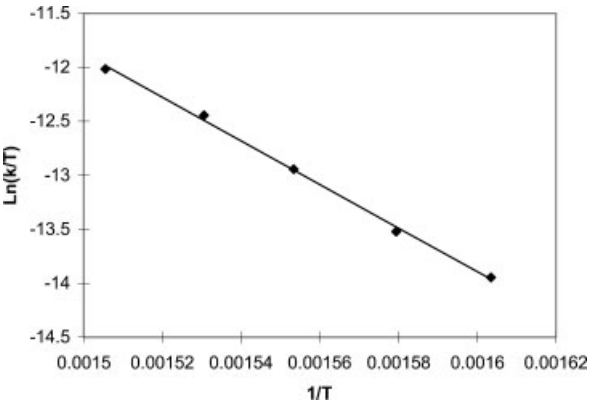


Figure 2. Kinetic plot to determine entropy and enthalpy of activation for the ethyl 3-methyl-3-phenylglycidate. $\ln(k/T) = \ln(k_B/\hbar) - \Delta S^{\#}/R - \Delta H^{\#}/RT$; slope −20182.6; intercept 18.40; $r = 0.9989$; $\Delta H^{\#} = 167.8$ kJ mol^{-1}; $\Delta S^{\#} = -44.55$ J mol^{-1}; $\Delta G^{\#} = 196.5$ kJ mol^{-1}

EXPERIMENTAL

Ethyl 3-phenylglycidate (Aldrich) and ethyl 3-methyl-3-phenylglycidate (Acros) were redistilled to >98.8% purity when analyzed by GC-MS (Saturn 2000, Varian) using a DB-5MS capillary column (30 × 0.25 mm i.d., 0.25 μm film thickness). Quantitative analysis of the product ethylene was performed by using a 3 m GC column of Porapak Q, 80–100 mesh. The verification of the substrates and identification of the products were carried out with the Varian Saturn GC-MS instrument with a DB-5MS capillary column.

Kinetics. The elimination kinetics were measured in a static reaction system as described.[17,18] The rate coefficients were determined manometrically with a precision of 0.5 mmHg. The temperature was controlled by a resistance thermometer controller, Shinko DIC-PS 25RT, and an Omega solid-state SSR240AC45, maintained within $\pm 0.2\,^{\circ}C$ and measured with a calibrated platinum–platinum-13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The ethyl glycidate substrates were injected (0.05-0.1 ml) directly into the reaction vessel with a syringe through a silicone-rubber septum.

REFERENCES

1. Newman MS, Magerlein BJ. *Organic Reactions*, vol. 5. Wiley: New York, 1949; 413–440.
2. Cagniant P. *Bull. Soc. Chim. Fr.* 1949; 847–853.
3. Deyrup JA, Moyer UV. *J. Org. Chem.* 1969; **34**: 1835–1840.
4. Chuchani G, Nuñez O, Marcano N, Napolitano S, Rodríguez H, Domínguez M, Ascanio J, Rotinov A, Domínguez RM, Herize A. *J. Phys. Org. Chem.* 2001; **14**: 146–158, and references cited therein.
5. Chuchani G, Marquez E, Herize A, Domínguez RM, Tosta M, Brusco D. *J. Phys. Org. Chem.* 2003; **16**: 839–848, and references cited therein.
6. Ensuncho A, Lafont J, Rotinov A, Domínguez RM, Herize A, Quijano J, Chuchani G. *Int. J. Chem. Kinet.* 2001; **33**: 465–471, and references cited therein.
7. Lafont J, Ensuncho A, Domínguez RM, Rotinov A, Herize A, Quijano J, Chuchani G. *J. Phys. Org. Chem.* 2003; **16**: 84–88.
8. Scheibler H, Tutundzitsch PS. *Chem. Ber.* 1931; **64**: 2916–2920.
9. Ruggli P, Hegedüs B. *Helv. Chim. Acta* 1942; **25**: 1285–1296.
10. Allen CFH, Van Allan J. *Org. Synth.* 1944; **24**: 87–88.
11. Taylor R. In *The Chemistry of the Functional Groups: Suplementary Volume B, Acid Derivatives*, Patai S (ed). Wiley: Chichester, 1979; 859–914.
12. Holbrook KA. In *The Chemistry of Acid Derivatives: Vapor and Gas Phase Reactions of Carboxylic Acids and Their Derivatives*, vol. 2, Patai S (ed). Wiley: Chichester, 1992; 703–746.
13. Chuchani G, Mishima M, Notario R, Abboud JLM. In *Advances in Quantitative Structure–Property Relationship*, vol. 2, Charton M, Charton BI, (eds). JAI Press: Stanford, 1999; 35–126.
14. Flowers MC, Parker RM, Voisey MA. *J. Chem. Soc. B* 1970; 239–243.
15. Flowers MC, Parker RM. *Int. J. Chem. Kinet.* 1971; **3**: 443– 452.
16. Flowers MC, Parker RM. *J. Chem. Soc. B* 1971; 1980–1988.
17. Maccoll A. *J. Chem. Soc.* 1955; 965–973.
18. Swinbourne E. *Aust. J. Chem.* 1958; **11**: 314–330.