



Homogeneous, unimolecular gas-phase pyrolysis kinetics of 4- and 2-hydroxyacetophenone

Yeljair Monascal^{a,b}, Eliana Gallardo^a, Loretta Cartaya^b, Alexis Maldonado^b,
Yenner Betancurt^a, Gabriel Chuchani^{b,*}

^a Departamento de Química, Instituto Universitario de Tecnología "Dr. Federico Rivero Palacios", Km 8, Carretera Panamericana, Caracas, Venezuela

^b Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C), Apartado 21827, Caracas 1020A, Venezuela

ARTICLE INFO

Article history:

Received 15 December 2016

Received in revised form 19 January 2017

Accepted 20 January 2017

Available online 20 February 2017

Keywords:

Pyrolysis kinetics

Mechanism

2-Hydroxyacetophenone

4-Hydroxyacetophenone

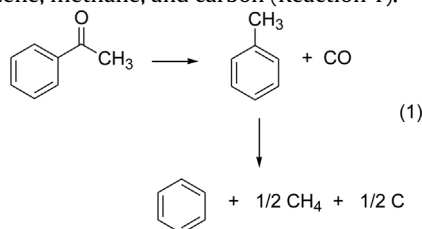
ABSTRACT

The pyrolysis kinetics of 4- and 2-hydroxyacetophenones in the gas phase were determined in a static system, where the reaction vessel was deactivated with allyl bromide, and in the presence of the free radical inhibitor propene when necessary. The working temperature range was 464–485 °C, and the pressure range was 44–133 Torr. The reactions were found to be homogeneous and unimolecular and to obey a first-order rate law. The products for 4-hydroxyacetophenone are phenol and ketene, while for 2-hydroxyacetophenone are phenol and ketene, with smaller amounts of phenyl acetate and benzofuran. The Arrhenius expression of the pyrolyses was found for 4-hydroxyacetophenone: $\log k_1$ (s^{-1}) = $(13.83 \pm 0.08) - (258.1 \pm 1.1) \text{ kJ mol}^{-1} (2.303RT)^{-1}$ ($r = 0.9999$); for 2-hydroxyacetophenone: $\log k_1$ (s^{-1}) = $(13.81 \pm 0.43) - (251.9 \pm 6.2) \text{ kJ mol}^{-1} (2.303RT)^{-1}$ ($r = 0.9991$). Deacetylation may be considered as the primary reasonable mechanism, and the process appears to proceed through a semi-polar concerted four-membered cyclic transition state.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

It is rather curious that an early interesting investigation on the thermal decomposition of acetophenone [1] has not promoted further investigation on the gas-phase pyrolysis of substrates having the acyl group adjacent to a π -system or directly attached to an unsaturated hydrocarbon. The pyrolysis kinetic of this substrate at 570–630 °C, and 15–150 mmHg, yielded toluene and CO gas [1]. The intermediate toluene undergoes a subsequent decomposition to give benzene, methane, and carbon (Reaction 1).

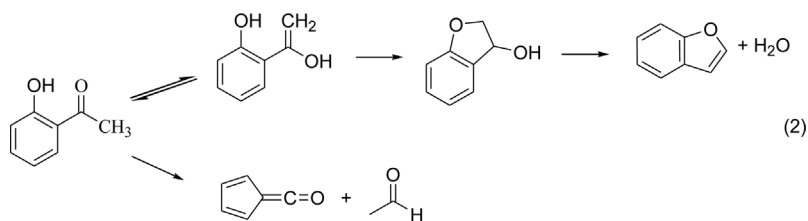


The reaction was found to be homogeneous, absence of free radical process, i.e., molecular in nature, and nearly to a first-order rate law. The estimated activation energy was approximately 70 kcal/mol (292.8 kJ/mol). The mechanism of this decomposition was not described.

Another investigation of a substituted acetophenone was the flash thermolysis of 2-hydroxyacetophenone, where the products were measured using mass spectrometry [2]. The decomposition process was found to proceed through two parallel reactions. The main pathway was thought to proceed through rearrangement with subsequent dehydration to give benzofuran, whereas the minor pathway for decomposition was thought to occur by the probable elimination of acetaldehyde to finally produce cyclopentadienylidene carbonyl as shown in Reaction (2). They were able to support the suggested mechanism obtained from thermolytic fragmentation of 2-hydroxyacetophenone.

* Corresponding author.

E-mail address: chuchani@ivic.gob.ve (G. Chuchani).



The acetyl group attached to an adjacent C=C bond as in 4-methylpent-3-ene-2-one, known as mesityl oxide, was found to pyrolyze at the temperature of 412–490 °C [3]. This substrate was found to decarbonylate to give methane as major product together with methylbutene isomers and isobutene. However, the initial rate of this process up to 20% appears to obey a first-order rate law and expressed by the equation $k_1 = 10^{14.22} \exp(-63,240/RT) \text{ s}^{-1}$, that is, $\log k_1 (\text{s}^{-1}) = \log 14.22 - (264.5 \text{ kJ/mol}) (2.303RT)^{-1}$. Furthermore, this thermal decomposition beyond the initial rate undergoes a radical process and a Rice-Herzfeld chain was proposed (Scheme 1).

Considering the lack of information about the gas-phase pyrolysis of molecules possessing an acyl group directly attached to a π -system or adjacent to C=C double bond of an unsaturated hydrocarbon, the present work was addressed to find a reasonable decomposition pathway for these types of compounds. Consequently, a static reaction system with deactivated reaction vessels was used in the presence of a free radical inhibitor. The pyrolysis experiments were performed in an apparatus explained in detail in the supplementary material of this article and in references 4–7 along with its figure as referred before [4–7]. The substrates to be examined are 2- and 4-hydroxyacetophenone.

2. Experimental

The substrates 2-hydroxyacetophenone (99.8%) and 4-hydroxyacetophenone (99.2%) were bought from Aldrich. The products of decomposition were phenol, purchased from Riedel de Haen, and phenyl acetate from Aldrich. The identities of the starting materials and products were examined and identified by GC/MS (Varian, Saturn 2000). Capillary column DB – 5MS. 30 m \times 0.250 mm id. 0.25 μm . The product phenol was determined quantitatively using a Hewlett Packard gas Chromatograph Model 5710A with a column of 10% SP 1200 1% H_3PO_4 /Chrom WAW 80/100 mesh. Ketene product was detected through formation of acetic acid in the chromatogram when introducing the reaction mixture in a few drops of water.

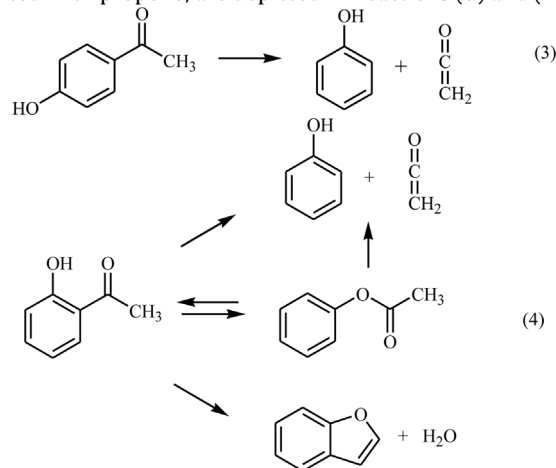
2.1. Kinetic

The experiments were carried out in a static system described with the figure of the apparatus (Supplementary) as reported [4–7]. The reaction vessel was deactivated with the products of decomposition of allyl bromide [8] to avoid surface effect. The decomposition of 4-hydroxyacetophenone did not required the presence of the free radical inhibitor propene, while 2-hydroxyacetophenone needed the presence of at least twice the amount of the suppressor propene. The estimation of the rate coefficients of the substrates were made manometrically and/or by percentage decomposition of the sub-

strate. The temperature was controlled by a SHINKO DIC-PS 23TR resistance thermometer controller, maintained ± 0.2 °C, and measured with calibrated Iron Constantan thermocouple attached to a Digital Multimeter Omega 3465B. Different points along the reaction vessel showed no temperature gradient when measured with a thermometer introduced around the heated aluminum block. The 4-hydroxyacetophenone dissolved in pyridine and the liquid 2-hydroxyacetophenone were injected directly into the reaction vessel through a silicone rubber septum. The amount of the substrate used for each reaction was ≈ 0.03 – 0.1 ml.

3. Results and discussions

The decomposition products of the gas-phase pyrolysis of 4-hydroxyacetophenone and 2-hydroxyacetophenone, in a static system, deactivated with allyl bromide, and the latter substrate inhibited with propene, are depicted in Reactions (3) and (4).



The stoichiometries of Reactions (3) and (4) suggest that the final pressure P_f should be twice the initial pressure P_0 . The average experimental results from P_f/P_0 values and two different temperatures and ten half-lives were: 2.08 for 4-hydroxyacetophenone and 1.95 for 2-hydroxyacetophenone (Table 1).

Additional verification of the stoichiometries represented in Reactions (3) and (4) is given in Table 2. For 4-hydroxyacetophenone, up to 60% reaction, good agreement is found between the decomposition of the starting material as predicted from pressure measurements and from the amount of quantitative analyses of the product phenol. With regard to 2-hydroxyacetophenone, a quantitative chromatographic analyses of the reacted amount of the substrate were determined.

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

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Aver.
4-Hydroxyacetophenone	480.0	54	111	2.06	2.08 \pm 0.03
	485.0	61	128	2.10	
2-Hydroxyacetophenone	480.2	43	83	1.93	1.95 \pm 0.02
	485.4	50	98	1.96	

P_0 = initial pressure, P_f = final pressure.

Download English Version:

<https://daneshyari.com/en/article/5134622>

Download Persian Version:

<https://daneshyari.com/article/5134622>

[Daneshyari.com](https://daneshyari.com)