

THERMAL CHEMISTRY PATHWAYS OF ESTERS AND KETONES

by

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INTRODUCTION

The work described is a continuation of our studies of the thermal chemistry pathways of reactive oxygenates important in fossil fuel hydrocarbons. Esters and ketones are pyrolysis products from carboxylic acids. Ketones have been found to be important components of hydroxyrolysis oils from low rank coals, fossil fuels known to contain substantial amounts of carboxylate functionality.

THERMAL CHEMISTRY PATHWAYS OF ESTERS

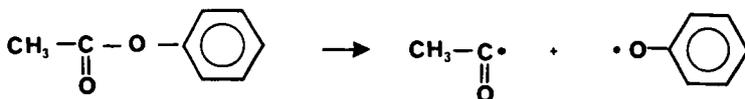
Conventional organic chemistry textbook wisdom describes ester pyrolysis only in terms of olefin elimination, and this only with esters of carboxylic acids. Noller (1) states that "when esters that have hydrogen on the β -carbon of the alkoxy group are heated to 500°C, a molecule of acid is lost with the formation of an olefin". This process is called pyrolytic cis-elimination. The situation with esters lacking β -hydrogens is less well studied and even the textbook cases are somewhat more complex than described.

Hexyl acetate. Hexyl acetate eliminates acetic acid to form 1-hexene according to the textbook mechanism, but this is not the only thermal chemistry event. Our thermal studies were carried out both in a flash pyrolysis unit (Figure 1) and in batch autoclaves. Conditions were set to achieve conversion levels of 10-60%. The thermal chemistry mechanisms are independent of unit. Using the flash pyrolysis unit and establishing a vapor residence time of ~ 1-2 sec, the major components in the gas phase products included hydrogen, methane, ethylene, propylene, water, carbon dioxide, and surprisingly carbon monoxide along with the anticipated 1-hexene (Table I). Experiments at equivalent conditions showed that acetic acid produces acetone, water and carbon dioxide as major products. Since, as we will show below, ketones thermally decarbonylate, the thermal conversion of hexyl acetate proceeds through 1-hexene and acetic acid. Acetic acid itself is thermally reactive and produces water and acetone. The ketone decarbonylates to produce the carbon monoxide observed. Finally, the 1-hexene slowly cracks and according to the results of Rebeck (2) produces C_1 - C_5 products with a relatively high yield of propylene. Our results are fully consistent with this picture.

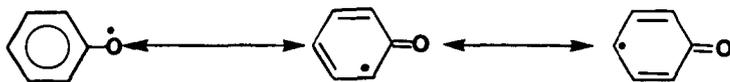
Methyl acetate. This ester does not have the structural properties required for pyrolytic cis-elimination, and at the 18% conversion level produces acetone, methanol and water as the major liquid phase products. This would indicate acyl oxygen, rather than alkyl oxygen, cleavage.

Phenyl acetate. Phenyl acetate unimolecularly decomposes only at the acyl oxygen site due to the influence of the aryl ring. As expected, the only major organic liquid products of any consequence are phenol >>> benzene. The unimolecular rate constant for phenyl acetate decomposition is 0.35 min^{-1} s. 0.44 min^{-1} for benzoic acid decomposition under similar conditions (3), (4).

A new mechanism is proposed to account for reaction products when olefin elimination is not feasible due to structural constraints. This proposed mechanism is shown in Scheme I for phenyl acetate. Cleavage at the phenolic position has been shown to be a favored pathway in the thermolysis of benzyl phenyl ether (5). ArO-H and $\text{ArCH}_2\text{-H}$ bonds are similar in strength, and



it is reasonable to invoke phenoxy radical formation in the thermal chemistry of phenyl acetate. A contributing driving force for this cleavage reaction at the benzylic position is the enhanced stability of benzyl and/or phenoxy radicals through delocalization of the free electron.

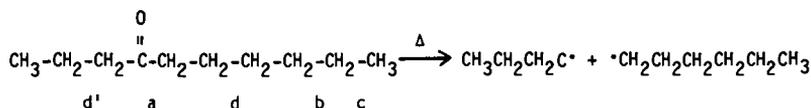


THERMAL CHEMISTRY PATHWAYS OF KETONES

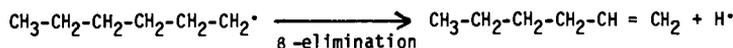
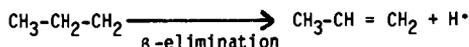
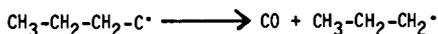
4-Decanone. Treatment of this internal ketone at 600°C in the flash pyrolysis unit led to conversion levels of 18%. The major fragmentation products (accounting for 85% of the converted ketone) were ethylene, propylene, carbon monoxide and 1-hexene (Table II). The rate constant for the unimolecular decomposition of 4-decanone was calculated to be $\sim 7.9 \text{ min}^{-1}$. This experimentally determined activation energy implies a radical chain, since there is no bond this weak ($\sim 36 \text{ kcal/mol}$) in the system. A mechanism which accounts for all of the observed products is shown in Scheme II.

SCHEME II

Initiation



Radical Elimination Reactions



Cleavage at the (b) or (c) bonds can lead to octenones and nonenones and to methane and ethane/ethylene, all identified in the product. Acetone arises from a sequence of reactions ultimately resulting in cleavage at the d and d' positions.

2-Decanone. The activation energy was calculated to be ~ 38 Kcal/mol for the unimolecular decomposition of this ketone with a rate constant at 600°C of ~11 min⁻¹. Table III presents the product data for the thermolysis of 2-decanone at 550 and 650°C. Here, as found with the 4-isomer, carbon monoxide is a significant product, thus confirming the statement made earlier that acyl radicals decompose releasing carbon monoxide. Ring closure to form aromatic rings becomes an important pathway by 650°C as does formation of solid carbonaceous material.

Aliphatic ketones are formed from the pyrolysis of carboxylic acids. They, in turn, decompose thermally to lighter olefins and acetone, and at sufficiently severe conditions to methane, carbon monoxide and coke.

1-Tetralone. A cyclic ketone such as 1-tetralone undergoes a different sequence of thermal transformations. Tetralin, naphthalene and 1-naphthol are the major liquid products when 1-tetralone is treated at 425°C under an inert atmosphere. When hydrogen is present the yields of tetralin and naphthalene increase, consistent with results published earlier (Table IV).

Acknowledgements

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TABLE I
PYROLYSIS OF HEXYL ACETATE
550°C, ~1-2 SEC. RESIDENCE TIME, HELIUM SWEEP GAS

Gas Analysis, Relative Mole %

<u>H₂</u>	<u>CO</u>	<u>CO₂</u>	<u>CH₄</u>	<u>C₂H₄</u>	<u>C₂H₆</u>	<u>C₃H₆</u>	<u>C₃H₈</u>	<u>C₄'S</u>	<u>C₅'S</u>	<u>C₆'S</u>	<u>H₂O</u>
39	12	12	7.7	3.7	-	4.4	1.1	1.8	-	10	5.2

TABLE II
4-DECANONE THERMOLYSIS
600°C, ~1-2 SEC. VAPOR RESIDENCE TIME
3.8g FEED, HELIUM SWEEP GAS

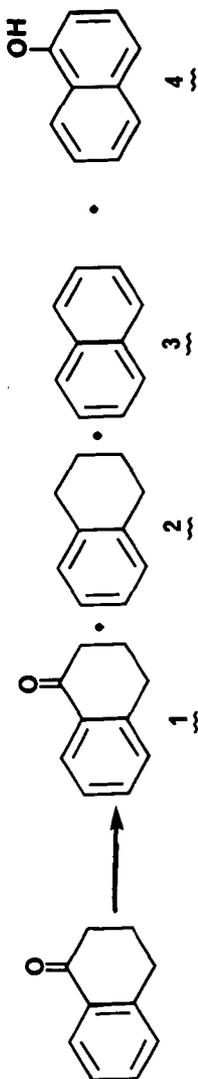
<u>Yields</u>	<u>g</u>	<u>% of Starting Feed</u>
Solid	0.02	0.53
Liquid	3.27	86.3
4-Decanone	3.11	82.1
Acetone	0.024	0.62
1-Hexene	0.049	1.3
n-Hexane	0.002	0.05
Nonenones	0.021	0.56
Others	0.064	1.7
Gases	0.48	12.7
H ₂	0.002	0.05
CH ₄	0.050	1.3
C ₂ H ₆	0.035	0.9
C ₂ H ₄	0.12	3.1
C ₃ H ₈	0.005	0.12
C ₃ H ₆	0.10	2.8
C ₄ 's	0.038	1.0
C ₅ 's	0.014	0.4
CO	0.11	2.8
H ₂ O	0.07	0.2
Total Recovered	3.77g	99.4

TABLE III
2-DECANONE PYROLYSIS
 1-2 SEC. VAPOR RESIDENCE TIME

Yields	3.73 g Feed			
	g	550°C	650°C	
		% of Starting Feed	g	% of Starting Feed
Solid	0.09	2.4	0.45	12.1
Liquid	3.67	98.4	1.81	48.5
2-decanone	3.59	96.2	1.23	33.1
acetone	-	-	0.036	1.0
1-hexene	0.003	0.07	0.039	1.1
n-hexane	-	-	0.011	0.31
2-hexenes/C ₆ H ₆	tr	tr	0.101	2.71
1-heptene	0.022	0.61	0.093	2.89
n-hexane	-	-	0.009	0.25
2-heptenes/C ₇ H ₈	-	-	0.051	1.37
1-octene	0.029	0.80	0.091	2.45
n-octane	tr	tr	0.010	0.27
2-octenes/EB,XYL	-	-	0.047	1.25
CH ₃ CO ₆ ⁼ or CH ₃ CO-cyclohexyl	tr	tr	0.015	0.40
others	0.034	0.93	0.87	2.34
Gases	0.093	2.5	0.84	22.5
H ₂	0.005	0.1	0.112	3.0
CH ₄	0.013	0.3	0.115	3.1
C ₂ H ₆	-	-	0.053	1.4
C ₂ H ₄	0.015	0.4	0.108	2.9
C ₃ H ₈	0.001	tr	0.097	2.6
C ₄ 's	0.008	0.2	0.033	0.9
C ₅ 's	0.024	0.6	0.003	0.1
CO	0.023	0.6	0.303	8.1
H ₂ O	0.004	0.1	0.009	0.2
<u>TOTAL RECOVERED</u>	3.85	103.2	3.10	83.1

TABLE IV

THERMAL CHEMISTRY OF α -TETRALONE



Reaction Atmosphere	Wt. % of Liquids			
	1	2	3	4
3 MPa He	28	19	20	25
3 MPa H ₂	8	52	29	-
5 MPa H ₂	2	56	35	-