

Thermolysis Reaction of 2-Acetyl-1-Oxo-Five-, Six-, and Seven-Membered Ring

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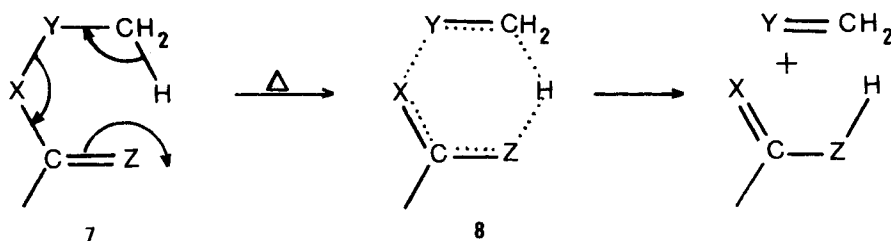
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Abstract

The rates of gas-phase thermolysis reactions of 2-acetylcyclopentanone 1, 2-acetylcyclohexanone 2, *N*-acetylcaprolactam 3, 2-acetylbutyrolactone 4, 2-acetyl-2-methylbutyrolactone 5, and 3-acetyl-2-oxazolidinone 6 have been measured over a temperature range of 50 K. They undergo unimolecular first-order elimination reactions for which $\log A = 11.7, 11.7, 11.2, 11.4, 11.5,$ and 11.1 s^{-1} and $E_a = 193.4, 189.5, 153.2, 201.0, 206.8,$ and $176.1 \text{ kJ mol}^{-1}$, respectively. The effect of the ring size together with the effect of a heteroatom in the ring on the rate of thermolysis reactions for compound 1–6 is the subject of this work. © 1995 John Wiley & Sons, Inc.

Introduction

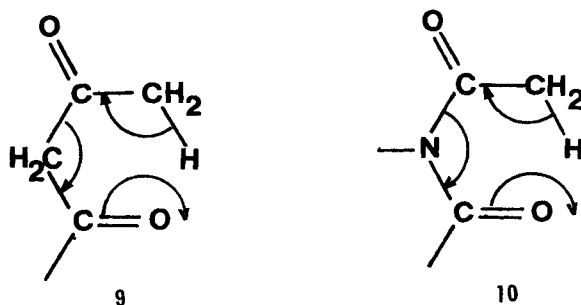
Gas-phase elimination reaction of compounds of general formula 7 (e.g., esters, iminoethers, and thioesters) are generally believed [1] to occur through the six membered transition state 8, Scheme I.



Scheme I

The rate of such reactions has been shown to depend on the acidity of hydrogen abstracted by atom Z and strength of X—Y bond. Although α -acyl-ketones 9 and *N*-acylamides 10 can decompose thermally in gas phase into enols and imidoles, respectively, Scheme II, their behavior in gas phase has received only limited attention.

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Scheme II

Bailey and co-workers [2,3] have shown that in cyclic and acyclic systems electronics factors influence the direction of elimination. Methyl *trans*-2-acetoxy-cyclohexanecarboxylate pyrolyzed to 97% of the conjugated ester and only 3% of the unconjugated isomer. Statistically, there are the same number of *cis*- β -hydrogens on either side of the acyl group.

Superimposed on this electronic effect, however, is a steric effect. The ratio of the exo to endo isomer formation is directly dependent on the ring size. 1-methylcyclohexyl acetate [4] pyrolyzes at 450°C to 24% methylenecyclohexane and 76% 1-methyl-cyclohexene. On the other hand, 1-methylcyclopentyl acetate yields exclusively 1-methylcyclopentene. About 25–30% more exo isomer was obtained when *cis*- and *trans*-1,2-dimethylcyclohexyl acetate were pyrolyzed, and as much as 30% exo isomer was obtained from *cis*-1,2-dimethylcyclopentyl acetate [5].

Thermolysis of the molecules investigated in this article takes place via formation of an endo isomer.

Results and Discussion

Table I summarizes the first-order rate coefficients of the gas-phase thermolysis reactions of compounds 1–6. Each rate coefficient represents an average of three kinetic runs, in agreement to within $\pm 2\%$ rate spread. The effect of temperature on the reactions, gave the Arrhenius parameters, which support the pathways proposed for these reactions. All compounds gave first-order straight line up to 80% reaction and no difficulty due to the molecularity of the reaction were encountered in the flow method.

The kinetic runs showed no adverse reactor–surface effects. The rates using an empty carbonized reaction vessel were compared with that of similar vessel packed with glass helices and this increase in the surface to volume of approximate nine-fold has not affected the rates. Since a six-fold change in the amount of substrate used per kinetic run gave no significant change in rate coefficient, these reactions were deemed to be first-order processes.

Arrhenius parameters in Table II are in agreement with the pathways proposed for these reaction.

Product analysis together with the kinetic data reveal that the thermolysis of these compounds takes place via six-membered transition state. The main features of the results are the following.

2-acetylcyclopentanone: The alignment of the acetyl and carbonyl group in this compound permits the thermolysis reaction to proceed via six-membered transition state to give ketene and 1-cyclopentenol.

TABLE I. Rate coefficient for thermolysis of 2-acetyl-1-oxo-saturated five, six, and seven membered ring.

Compound	T/K	$10^3 k/s^{-1}$
1	713.6	3.2
	723.6	5.5
	733.7	8.5
	743.4	13.4
	753.4	19.5
	758.0	24.7
	764.3	29.4
2	702.0	3.5
	713.7	6.0
	723.7	10.1
	733.1	13.6
	743.0	21.3
	752.9	31.9
3	574.7	1.7
	583.2	2.7
	590.5	4.0
	606.4	9.1
	610.0	10.9
	623.0	20.6
	633.1	31.9
4	773.0	5.8
	783.8	8.9
	793.6	12.7
	803.2	20.5
	813.4	27.8
	823.1	38.3
5	783.2	5.5
	793.9	9.1
	803.6	13.7
	813.7	18.9
	822.4	27.3
	833.5	37.3
6	684.1	3.8
	693.8	5.3
	703.5	9.2
	713.3	14.4
	722.1	18.9
	733.2	29.6
	742.0	42.4

2-acetylcyclohexanone: This is more reactive than the corresponding cyclopentanone by a factor of 1.7. This can be readily explained in terms of the formation of 1-cyclohexenol compared to 1-cyclopentenol.

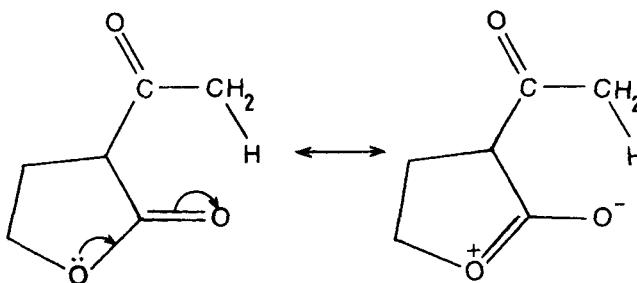
N-acetylcaprolactam: This compound stands out as being substantially more reactive. The "substituent" nitrogen in the ring produce a large rate acceleration.

TABLE II. Arrhenius parameters and rate data at 740 K for the thermolysis of 2-acetyl-1-oxo-saturated five, six, and seven membered rings.

Compound	$\log A(s^{-1})$	$E_a \text{ kJmol}^{-1}$	$10^3 k(s^{-1})$
2-acetylcyclopentanone	11.7 ± 0.0	193.4 ± 0.0	11.1
2-acetylcyclohexanone	11.7 ± 0.2	189.5 ± 2.8	18.4
<i>N</i> -acetylcaprolactone	11.2 ± 0.0	153.2 ± 0.4	2286
2-acetylbutyrolactam	11.4 ± 0.3	201.0 ± 4.4	1.6
2-acetyl-2-methylbutyrolactone	11.5 ± 0.4	206.8 ± 6.9	0.8
3-acetyl-2-oxazolidinone	11.1 ± 0.1	176.1 ± 0.3	42.4

This reactivity is derived in part from the increased ease of C—N bond cleavage compared to C—C cleavage in cycloalkanones 1 and 2. Kinetic data for the same effect was observed in the gas-phase elimination of diacetamide [6] which eliminates 9500 times faster than diacetylacetone [7] at 600 K. In accounting for the reactivity of *N*-acetylcaprolactam, we feel that during the elimination reaction a double bond is introduced into a seven-numbered ring and this process requires less energy than the same in five and six-membered rings. Another factor which could account for the high reactivity of this compound is that thermolysis produces imidole which requires less energy than the formation of enols in 1 and 2. C=N bond is 14.9 kcal stronger than C=C [8].

2-Acetylbutyrolactone: Although the protophilicity of atom Z in this compound is more than in 1, 2, and 3 as a result of oxygen atom lone pair resonance, Scheme III, the thermal decomposition of this compound is slower.



Scheme III

This could be attributed to the fact that the Y—X bond in this compound is less polar than the Y—X bonds in 1, 2, and 3 because the ester group in 4 is not as strongly electron attracting as a carbonyl group in 1, 2, and 3. This situation leads to less polarizability of Y—X bond in 4, thus rendering Y—X bondbreaking more difficult. This observation indicates that Y—X bond breakage is more important than C=Z attack on the β -hydrogen in this group of compounds.

2-Acetyl-2-methylbutyrolactone: This is less reactive than α -acetylbutyrolactone by a factor of 0.5. This can be explained in terms of the methyl substituent effect on the alignment of the participating atoms in the transition state.

3-Acetyl-2-oxazolidinone: This is more reactive than α -acetylbutyrolactone by a factor of 27. This can be readily explained in the manner used for the previously

observed nitrogen "substituent" effect, when comparing the reactivity of *N*-acetylcaprolactone with 2-acetylcyclohexanone, but the reactivity ratio of the last pair was of 81 order due to the differences in the ring size.

Experimental

Materials

2-acetylcyclopentanone, 2-acetylcyclohexanone, *N*-acetylcaprolactam, 2-acetylbutyrolactone, 2-acetyl-2-methylbutyrolactone, and 3-acetyl-2-oxazolidinone were all obtained from Aldrich. G. L. C. analysis of the reactants using a 9 ft column packed with 5% OV101 adsorbed on 100–120 mesh Chromosorb G, operated at 170°C, indicated to be 99% pure.

Kinetics

The flow system used in the kinetic determinations consists of a CDS custom made pyrolysis unit where the reaction takes place, coupled to a Varian 3300 gas chromatograph, equipped with a 2m × 1/8 o.d., 15% SE30 silicon column on Chromosorb W., AW 80–100 mesh size with flow rate of nitrogen carrier gas of 25–30 ml/min. The oven reactor consists of an insulated aluminium block, with a pyrex vessel of 19 cm length and 1.7 cm width, a platinum resistance thermometer, and a thermocouple connected to a Comark microprocessor. The internal surface of the reaction vessel has been deactivated by injecting 4–5 portions of 50 μ of allylbromide at 450°C in the absence of air. This process coated the internal surface of the reactor by a homogeneous carbon film [9]. 1–5 μ of a solution of compound in inert standard was injected into the reactor. Unreacted starting material and products were swept via a heated arm into GC oven.

The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to an internal standard. Analysis by gas chromatography allowed several kinetic runs to be performed at each temperature. The kinetic rate was obtained from the first-order expression $kt = l n a_0/a$ where t is the reaction time which is the residence time of the sample vapor in the pyrex reactor and determined by $t = P.V.T_m/P_m.G$ where P is the pressure in the reactor, V is the volume of reactor, T_m is the room temperature, P_m is atmospheric pressure, and G is the rate of carrier gas flow. The residence time is 40–43 sec. The Arrhenius parameters were obtained from a plot of $\log k$ vs. $1/T$ (K) (Fig. 1).

Product Analysis

Saturated solutions of substrates in chlorobenzene were passed down a reactor column packed with helices [10]. The column was heated to temperature comparable to those used in kinetic investigations. The products of pyrolysis were swept out using a stream of nitrogen, and the effluents were collected in cold traps. The product obtained from the pyrolysis of 1 was cyclopentanone, from 2, cyclohexanone, from 3, caprolactam, from 4, butyrolactone, from 5, 2-methylbutyrolactone, and from 6, 2-oxazolidinone. Ketene was identified as sodium acetate in a cold trap containing sodium hydroxide. The structures of the products were all confirmed by NMR and IR spectroscopy.

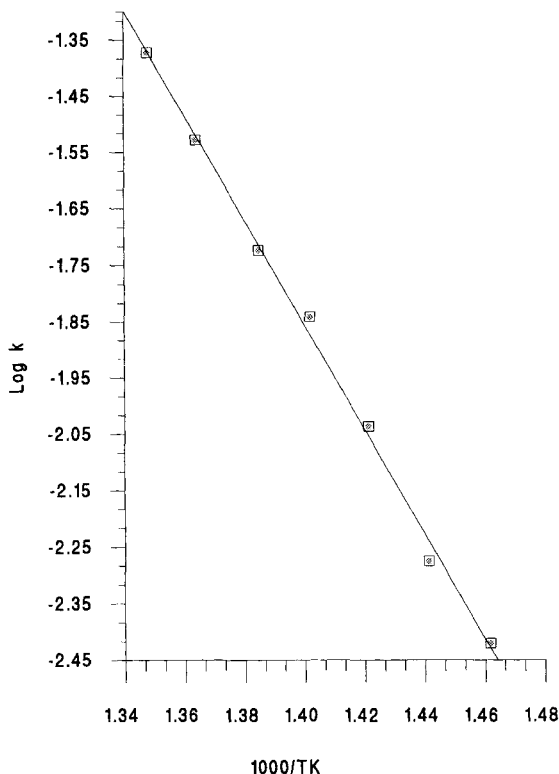


Figure 1. Arrhenius plot for 2-Acetyl-2-oxazolidone.

Acknowledgment

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