g), and 13.71 g of viscous red-brown liquid were obtained. From the latter, crystalline needles separated on standing.

The entire 13.20 g of the liquid containing some needle crystals was dissolved in benzene and submitted to column chromatography as above to afford three main fractions using benzene and then methanol as an eluent: **i**, 9.00 g (red-brown liquid), **ii**, 0.18 g (light brown liquid), **iii**, 3.06 g (by flushing with absolute methanol, viscous dark grown liquid); recover 95.9%.

From the nmr spectrum of **i** (CCl$_4$), δ 7.21 and 7.16 (broad, 12.2), 4.42 (s, 0.7), 3.49 and 3.44 (s, 2.9), 2.04 (s, 1.9), and 1.79 ppm (s, 2.0), the composition of the mixture was estimated as dibenzyl sulfide (28.6 mol %), methyl benzyl sulfide (46.4 mol %), and unreacted benzyl chloride (25.0 mol %).

Fraction **i** (3.22 g) was dissolved in 4 ml of absolute ethanol, and 3 ml of methyl iodide was added. After standing at room temperature overnight, white needle crystals separated from the dark red-brown supernatant. Another 1 ml of methyl iodide was added, and the fraction was left overnight again. The fine white needles were filtered and washed with absolute ethanol to yield 2.35 g of trimethylsulfonium iodide, mp 209–215° with sublimation (95% ethanol) (lit.[10] 203–207°), nmr (D$_2$O) δ 2.92 ppm (s). The nmr and ir spectra were identical with those reported for trimethylsulfonium iodide.[10]

To the dark red-brown mother liquid, ether was added to yield white needle crystals. A total of 800 ml of ether was used until no further precipitate occurred to give 1.15 g of the crystals, identified as **dimethylbenzylsulfonium iodide**. Recrystallization afforded flat needles: mp 99–101°; nmr (D$_2$O) δ 7.57 (s, 5 H), 4.61 (s, 2 H), and 2.83 ppm (s, 6 H).

Anal. Calcd for C$_9$H$_{13}$SI: C, 38.58; H, 4.69; I, 45.29; S, 11.45. Found: C, 38.63; H, 4.82; I, 45.36; S, 11.61.

After solvent evaporation, the mother liquid afforded 2.79 g of highly lachrymatory dark red-brown liquid, which was not further studied (presumably benzyl iodide).

A 3.06-g sample of **iii** was dissolved in CCl$_4$ to give white needle crystals on standing (0.92 g). Solvent evaporation and addition of 95% ethanol gave an additional 0.83 g of the crystals. Recrystallization afforded white wooly needle crystals of **methylsulfonylbenzylphenylmethane** (I), mp 120–122° (CCl$_4$).

Anal. Calcd for C$_{15}$H$_{16}$SO$_2$: C, 69.18; H, 6.21; S, 12.31. Found: C, 69.06; H, 6.21; S, 12.47.

The mother liquid was condensed to give 1.24 g of red-brown liquid (showing sulfoxide by ir) which was dissolved in 30 ml of glacial acetic acid and oxidized with 6 ml of 50% H$_2$O$_2$ to yield 1.00 g of yellow oily solid. Recrystallization gave white needle crystals of **methylsulfonyldibenzylphenylmethane** (II), mp 165–168° [95% ethanol, followed by petroleum ether (bp 60–110°)–CHCl$_3$].

Anal. Calcd for C$_{22}$H$_{22}$SO$_2$: C, 75.38; H, 6.34; S, 9.15. Found: C, 75.38; H, 6.37; S, 9.16.

Reaction of DMSO with NaI.—By heating for 39 min at 80°, 6.10 g of NaI was dissolved in 40 ml of redistilled dimethyl sulfoxide. No precipitate appeared on standing at room temperature for a week. However, when the concentration was higher, *e.g.*, 10 g of NaI in 40 ml of dimethyl sulfoxide, colorless crystals appeared. The solution was poured into 100 ml of benzene to yield 13.71 g (theory, 12.5 g) of white solid after filtration under N$_2$. Recrystallization from absolute ethanol afforded hygroscopic white needles, mp 144–147°.

Anal. Calcd for C$_4$H$_{12}$IONaS$_2$: C, 15.69; H, 3.96; I, 41.45; Na, 7.51; S, 20.94. Found: C, 15.56; H, 3.79; I, 41.50; Na, 7.41; S, 20.75.

Registry No.—Dimsyl ion, 13810-16-7; dimethyl sulfoxide, 67-68-5; I, 15733-05-8; II, 20505-04-8; methyl benzyl sulfone, 3112-90-1; NaI·2CH$_3$SOCH$_3$, 4659-76-1; dimethyl benzyl sulfonium iodide, 20483-21-0.

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[10] R. Kuhn and H. Trischmann, *Ann. Chem.*, **611**, 117 (1958).

The Thermal Decomposition of β-Hydroxy Ketones

B. L. Yates and J. Quijano

Departamento de Química, Universidad del Valle, Cali, Colombia

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β-Hydroxy ketones decompose thermally to mixtures of aldehydes and ketones in a reaction that is the reverse of the aldol condensation. A study has been carried out of the kinetics of the thermal decomposition of some β-hydroxy ketones in xylene solution. The results indicate that the reaction is unimolecular and involves a cyclic transition state. Comparison of the rates of decomposition of the different β-hydroxy ketones indicates that little charge separation is obtained during the breaking of the carbon–carbon bond in the transition state.

β-Hydroxy ketones decompose thermally[1] to give mixtures of aldehydes and/or ketones in a reaction which is the reverse of the aldol condensation. A kinetic study of the pyrolysis of 4-hydroxy-4-methyl-2-pentanone in the gas phase[2] showed that the decomposition is homogeneous and follows first-order kinetics, and it was proposed that the reaction involves a six-membered cyclic transition state. As a further test of this mechanism, we have carried out a study of the products and kinetics of the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone in dilute xylene solution. It would be expected[3] that, if in the gas phase the pyrolysis of 4-hydroxy-4-methyl-2-pentanone does involve a cyclic intramolecular mechanism, the same reaction carried out in nonpolar solvent would involve a similar type of mechanism, thus giving rise to similar products and first-order kinetics.

Furthermore, no kinetic measurements have been carried out for the thermal decomposition of other β-hydroxy ketones.

We have therefore studied the kinetics of the thermal decomposition of 4-hydroxy-3-methyl-2-pentanone and 4-hydroxy-2-pentanone, in order to examine the influence of the differently substituted methyl groups on the mechanism and velocity of pyrolysis.

Discussion

Quantitative analysis, using gas–liquid chromatography, of the products of the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone in dilute xylene solution showed that acetone is by far the principal product of the reaction, being obtained in a yield of >95%, although a small amount (<5% in total) of two other unidentified products was also observed.

The rate of decomposition of the 4-hydroxy-4-methyl-2-pentanone was followed using glpc, by measuring both the rate at which acetone is formed and the rate of disappearance of the 4-hydroxy-4-methyl-2-pentanone.

[1] C. D. Hurd, "The Pyrolysis of Organic Compounds," The Chemical Catalog Co., Inc., Reinhold Publishing Corp., New York, N. Y., 1929, p 164.

[2] G. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 2067 (1965).

[3] S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 506.

It was found by both methods that the decomposition followed good first-order kinetics for at least three half-lives, and that furthermore the first-order rate constants obtained by each method were in very good agreement. The determined rate constants are listed in Table I.

Table I

Rates of Pyrolysis of Some β-Hydroxy Ketones at Different Temperatures

β-Hydroxy ketone	$k \times 10^{-4}$ sec^{-1} at 148.7°	160.7°	179.4°	206.5°
4-Hydroxy-2-pentanone	...	0.141	0.530	3.62
4-Hydroxy-4-methyl-2-pentanone	0.126	0.373	1.55	10.0
4-Hydroxy-3-methyl-2-pentanone	0.100	...	1.03	8.20

They were found to be reproducible to within ±4%, and rate constants determined at different temperatures were found to follow a good Arrhenius relationship. The derived activation parameters can be seen in Table II. Assuming that the rate constants are accurate to ±4%, the energy and entropy of activation are estimated to be accurate to within ±1.0 kcal and ±1.6 eu, respectively.

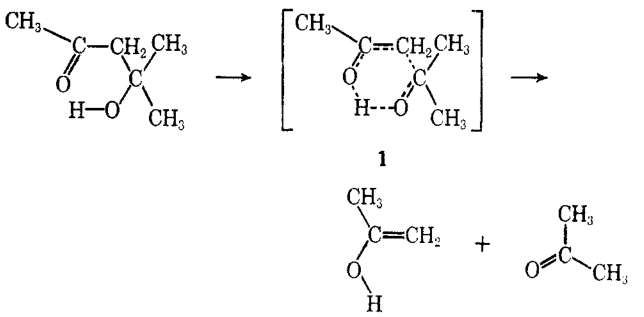
Table II

Activation Parameters for the Pyrolysis of Some β-Hydroxy Ketones

β-Hydroxy ketone	E_a (kcal/mol) (±1.0 kcal)	$\log_{10} A$ (±0.34)	$\Delta S^{\ddagger}$ (eu) (±1.6 eu)
4-Hydroxy-2-pentanone	30.2	10.24	−12.6
4-Hydroxy-4-methyl-2-pentanone	31.1	11.12	−8.7
4-Hydroxy-3-methyl-2-pentanone	31.0	10.96	−9.4

The first-order rate constants showed little variation with the initial concentration of the 4-hydroxy-4-methyl-2-pentanone: at a temperature of 179.5° and initial concentrations of the β-hydroxy ketone of 2, 4, 6, 8, and 10% (v/v), the values of the first-order rate constants obtained for the decomposition were 1.52, 1.55, 1.57, 1.49, and 1.50 × 10^{-4} sec^{-1} respectively. Also, the reaction does not appear to be influenced by surface effects. In ampoules packed with glass wool which increased the surface area of the reaction vessel by a factor of at least 15, the rate of decomposition of the 4-hydroxy-4-methyl-2-pentanone was found to be 1.48 × 10^{-4} sec^{-1}, compared with 1.55 × 10^{-4} sec^{-1} in an unpacked vessel.

These results indicate that, as was found for the reaction in the gas phase, the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone in dilute xylene solution is a homogeneous first-order reaction which gives acetone as practically the only product. The entropy of activation for both reactions is very similar: −8.3 eu for the reaction in the gas phase and −8.7 eu for the reaction in solution. These values are typical of those reactions that are thought to involve cyclic transition states,[4] and it would thus appear that, in solution, 4-methyl-4-hydroxy-2-pentanone decomposes through the cyclic six-membered transition state 1 similar to the one previously proposed[2] for its decomposition in the gas phase.



1

As would be expected[3] for such intramolecular unimolecular reactions, the presence of a nonpolar solvent does not have a great influence on the velocity of the reaction. The energies of activation for the decomposition in the gas phase and in solution are 32.2 and 31.2 kcal respectively, giving extrapolated first-order rate constants for the decomposition in the gas phase and in solution of 5.37 and 6.76 × 10^{-4} sec^{-1} respectively at 200°. It can thus be seen that the results obtained for the reaction in solution are in agreement with the mechanism previously proposed for the reaction in the gas phase, the reaction involving a cyclic six-membered intramolecular transition state in both phases.

Similar first-order kinetic results were also obtained for the two other β-hydroxy ketones studied, 4-hydroxy-2-pentanone and 4-hydroxy-3-methyl-2-pentanone. These compounds were found to decompose thermally to mixtures of acetone and acetaldehyde and acetaldehyde and methyl ethyl ketone respectively. In both cases it was determined by glpc that the products were obtained in yields of >95%, although, as in the case of 4-hydroxy-4-methyl-2-pentanone, small quantities (<5%) of other products were also obtained. The decomposition of both compounds followed good first-order kinetics up to >3 half-lives, with the first-order rate constants showing a reproducibility of ±4%. Rate constants determined at different temperatures were found to follow good Arrhenius relationships, and the derived energies and entropies of activation can be seen in Table II. Again, the rate of decomposition was shown not to depend on the initial concentration of the β-hydroxy ketone.

As in the case of 4-hydroxy-4-methyl-2-pentanone, the entropies of activation for the decomposition of 4-hydroxy-2-pentanone and 4-hydroxy-3-methyl-2-pentanone were found to be negative, −12.6 and −9.4 respectively. These entropies of activation, together with the first-order kinetics and the nature of the products, would seem to indicate that 4-hydroxy-2-pentanone and 4-hydroxy-3-methyl-2-pentanone decompose thermally through a six-membered cyclic transition state similar to that proposed for the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone.

Compared with 4-hydroxy-2-pentanone, 4-hydroxy-3-methyl-2-pentanone and 4-hydroxy-4-methyl-2-pentanone have a methyl group substituted on either side of the breaking carbon–carbon bond. Comparing the rates of decomposition of these two β-hydroxy ketones

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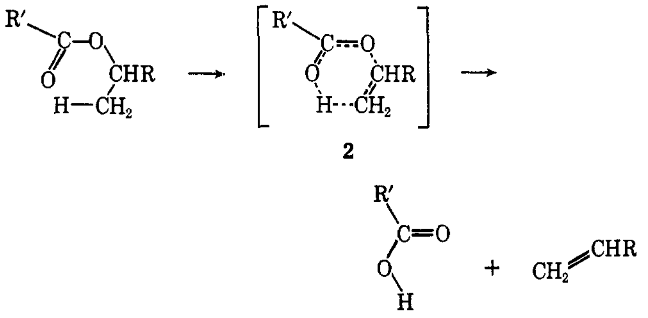
(4) See ref 3, p 257.

with that of 4-hydroxy-2-pentanone it can be seen that the methyl groups do not have a great influence on the rate of decomposition. For example, at 179.5° the relative rates of decomposition of 4-hydroxy-4-methyl-2-pentanone, 4-hydroxy-3-methyl-2-pentanone and 4-hydroxy-2-pentanone are 2.9:1.9:1.0.

It is of interest to compare the effect of methyl groups in the pyrolysis of β-hydroxy ketones with their effects in two other pyrolytic reactions that are thought to involve analogous cyclic six-membered transition states, the pyrolysis of esters 2[5] and β-hydroxy olefins 3.[6]



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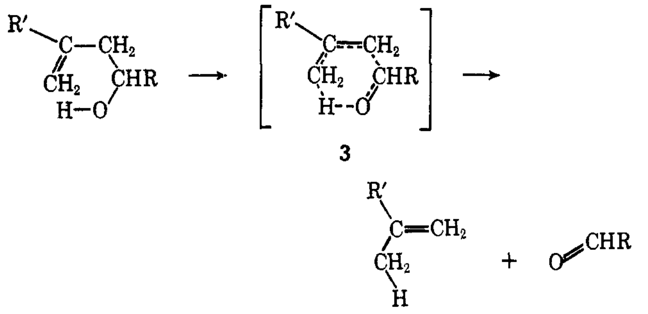

3

In the case of the esters, the relative rates of pyrolysis of ethyl, isopropyl, and *t*-butyl formate at 650°K are 1:18:760,[7] while the relative rates of pyrolysis at the same temperature of the β-hydroxy olefins 3-buten-1-ol, 4-penten-2-ol, and 2-methyl-4-penten-2-ol are 1:2.9:5.4.[6] It can thus be seen that branching at the α-carbon of the esters (*i.e.*, the carbon of the bond C-O) has a much greater effect than the corresponding substitutions in the case of the β-hydroxy ketones and β-hydroxy olefins. Part of the effect must be statistical, there being more hydrogens available for reaction in the case of the more highly branched esters. Nevertheless, the effect is much greater than can be accounted for on a purely statistical basis, and it has been suggested[8] that some carbonium ion character is developed by the α-carbon during the breaking of the C–O bond. In the case of the pyrolysis of the β-hydroxy olefins and β-hydroxy ketones, the effect of the extra methyl group is much less, which would seem to indicate that much less charge is developed during breaking of the C–C bond in these two reactions. This is reasonable when one considers that, in the breaking of the carbon–oxygen bond in ester pyrolysis, two atoms of different electronegativity are involved, whereas in β-hydroxy olefin and β-hydroxy ketone pyrolysis the breaking of the carbon–carbon bond involves two atoms of identical electronegativity.

This conclusion, of course, is only valid if the transition state in ester pyrolysis does indeed develop some carbonium ion character. For example, it has been suggested[9] that the rate-enhancing influence on ester pyrolysis of extra methyl groups on the α-carbon could be accounted for by the increased stability of the olefin being formed. However this view has been disputed,[10] and in any case this effect would also be expected to have a similar influence on the rate of pyrolysis of the β-hydroxy olefins, whereas in fact, as can be seen from the rates of pyrolysis of the β-hydroxy olefins given above, increased methyl substitution on the breaking C–C bond has only a small effect on the rate of pyrolysis of the β-hydroxy olefin. It would thus seem that, in the pyrolysis of β-hydroxy olefins and β-hydroxy ketones, little charge is developed during the breaking of the carbon–carbon bond, whereas in ester pyrolysis some charge is developed during the breaking of the C–O bond.

Experimental Section

4-Hydroxy-4-methyl-2-pentanone was obtained commercially, while 4-hydroxy-2-pentanone and 4-hydroxy-3-methyl-2-pentanone were obtained by the aldol condensation[11] of acetaldehyde and acetone and acetaldehyde and methyl ethyl ketone respectively. All the β-hydroxy ketones were distilled carefully before use and their purity checked by glpc using a 5-ft 10% tricresyl phosphate column, and by infrared spectroscopy.

As solvent, Matheson Coleman and Bell purified-grade xylene was used. It was fractioned before use using a 4-ft packed glass column.

The reaction was carried out in sealed glass ampoules made from capillary tubing. The sealed ampules containing the β-hydroxy ketone in xylene solution were placed in a boiling solvent thermostat bath whose temperature was checked using a N. B. S. standardized thermometer, allowances being made for variation in atmospheric pressure. At regular intervals the ampoules were removed and the amount of acetone or methyl ethyl ketone produced was determined by glpc, using benzene as an internal standard, on a 5 ft column of 10% tricresyl phosphate on Chromosorb W. The rate of decomposition of each of the β-hydroxy ketones was also determined by observing the rate of disappearance of the β-hydroxy ketone, again by glpc using a 5-ft 10% tricresyl phosphate column with mesitylene as an internal standard.

Registry No.—4-Hydroxy-2-pentanone, 4161-60-8; 4-hydroxy-4-methyl-2-pentanone, 123-42-2; 4-hydroxy-3-methyl-2-pentanone, 565-79-7.

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