Gas-phase Thermal Unimolecular Isomerizations of Acetylcyclopropane. Part I. The Equilibrium between 2,3-Dihydro-5-methylfuran and Acetylcyclopropane

By **Alan T. Cocks** and **Kurt W. Egger,*** Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich, Switzerland

Contrary to earlier literature reports, the isomerization of 2,3-dihydro-5-methyl furan to acetylcyclopropane has been found to be a reversible process. Equilibrium constants for the temperature range 673—731 K have been obtained from the kinetically complex acetylcyclopropane isomerization system and yield the van't Hoff relationship

$$\log K = 0{\cdot}96 \pm 0{\cdot}25 - (9{\cdot}6 \pm 3{\cdot}3\ \text{kJ mol}^{-1})/\theta,\ \text{where}\ \theta = 2{\cdot}303\,RT$$

This is in good agreement with estimates based on thermodynamic group additivity concepts, and indicates that any interaction between the carbonyl group and the cyclopropane ring has little overall effect on the stability of acetylcyclopropane.

THE thermal isomerization of 2,3-dihydrofuran to formylcyclopropane is reversible,[1] whereas the corresponding isomerization of 2,3-dihydro-5-methylfuran has been reported to be irreversible.[2,3] However, preliminary studies of the thermal reactions of acetylcyclopropane revealed this latter report to be in error, and the present paper reports a quantitative investigation of the equilibrium between 2,3-dihydro-5-methylfuran and acetylcyclopropane. The relative stabilities of these compounds are of interest as they provide a quantitative estimate of the effect of carbonyl group–cyclopropane interaction on thermodynamic stability, and a knowledge of the equilibrium constants is important for the evaluation of the rate constants involved in the thermal reactions of acetylcyclopropane.[4]

EXPERIMENTAL

Materials.—Acetylcyclopropane was obtained from Fluka AG, and 2,3-dihydro-5-methylfuran was obtained from Aldrich-Europe. Both materials were better than 99·5% pure (g.l.c.) after distillation on the vacuum line.

Apparatus and Procedure.—The conventional static reaction system used for the kinetic measurements was essentially the same as that described previously.[5] A cylindrical 1-l Pyrex reaction vessel was normally employed. For heterogeneity tests, this was replaced by a similar vessel packed with thin-walled Pyrex tubes giving a surface to volume ratio 14 times that of the unpacked vessel. Pressures in the reaction system were measured with a pressure transducer.

Reactant was introduced into the reaction vessel in the gas phase from a storage bulb. At the end of a kinetic run, the contents of the reaction vessel were shared with an evacuated gas-pipette of *ca.* 150 ml volume. To avoid condensation problems, the gas-pipette and connecting tubing on the vacuum line were maintained at *ca.* 70 °C. The contents of the gas pipette were analysed by gas-chromatography using a Carlo–Erba Fractovap G 1 instrument fitted with a Hewlett–Packard gas sampling valve. The sampling valve and 5 ml stainless-steel sampling loop were heated to *ca.* 70 °C.

A 9 m × 4 mm stainless-steel column packed with 15% Carbowax 20 M on 80—100 Celite operated at 80 °C gave a good separation of the components of the reaction mixture, although some problems were encountered with slight peak-tailing. Signals from the flame-ionization detector were integrated using an Infotronics CRS 208 electronic integrator. The calibration factor for 2,3-dihydro-5-methylfuran with respect to acetylcyclopropane was found to be 1·30 ± 0·03 from standard mixtures which covered a large absolute and relative concentration range. Pure samples of the pentenones were not available and the calibration factors were assumed to be unity. Analysis of liquid mixtures of mixed pentenones (90% pure) and acetylcyclopropane indicated that this assumption was valid.

Duplicate analyses of reaction mixtures generally agreed

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[1] C. L. Wilson, *J. Amer. Chem. Soc.*, 1947, **69**, 3002.

[2] H. Normant, *Bull. Soc. chim. France*, 1951, 115.

[3] D. M. A. Armitage and C. L. Wilson, *J. Amer. Chem. Soc.*, 1959, **81**, 2437.

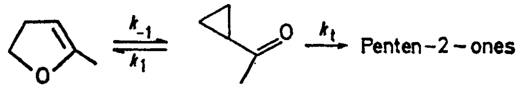
[4] A. T. Cocks and K. W. Egger, following paper.

[5] K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.

within 0·5% for the major components (reactants) and within 3% for the minor components (products). Reaction products were isolated by preparative g.l.c. separation of the reaction mixture using an F + M 810 instrument fitted with a 3 m × 6 mm column packed with 33% Carbowax 20 M on 60—80 Chromosorb P, and were identified by n.m.r. spectroscopy (including double irradiation and europium shift).

RESULTS

In the temperature range 673—731 K, acetylcyclopropane isomerizes reversibly to 2,3-dihydro-5-methylfuran and irreversibly to penten-2-ones (1). In the same range, the sole reaction of 2,3-dihydro-5-methylfuran appears to be the reversible isomerization to acetylcyclopropane.



(1)

Extensive preliminary experiments established that the rates of decomposition of acetylcyclopropane and 2,3-dihydro-5-methylfuran were independent of initial pressure in the range 4—60 Torr * and subsequent runs were carried out with initial pressures in the range 6—16 Torr.

Initial runs with 2,3-dihydro-5-methylfuran in the packed reaction vessel resulted in greater apparent conversion than that obtained in the unpacked vessel for an equal time. After ' ageing ' the vessel by conducting several pyrolyses to high conversions, however, good agreement between conversions for 2,3-dihydro-5-methylfuran and for acetylcyclopropane in packed and unpacked vessels was observed. Any heterogeneous component of the primary reactions is, therefore, small under the experimental conditions employed. It should be noted, however, that 2,3-dihydro-5-methylfuran appears to be susceptible to heterogeneous decomposition by ' unaged ' surfaces, as decomposition on several g.l.c. columns was observed. No evidence for decomposition on the column used for analyses in this study was apparent.

At long reaction times, the pentenones were found to undergo slow decomposition to yield low molecular-weight products. Runs to determine equilibrium constants were, therefore, restricted to *ca.* 50% primary isomerization to avoid problems associated with this secondary decomposition. Under these conditions, mass balances checked by an internal standard technique, were found to be satisfactory.

The kinetic differential equations describing reaction system (1) are:

$$\frac{dA}{dt} = k_{-1}[C] - (k_1 + k_t)[A] \qquad (2)$$

$$\frac{dB}{dt} = k_t[A] \qquad (3)$$

$$\frac{dC}{dt} = k_1[A] - k_{-1}[C] \qquad (4)$$

where [A] denotes the concentration of acetylcyclopropane, [B] the total concentration of the pentenones, and [C] the concentration of dihydromethylfuran. For reactions starting with pure A or C, the concentration of C is given by the stoicheiometric relationship $[C] = [A]_0 - [A] - [B]$ or $[C] = [C]_0 - [A] - [B]$ respectively. Substitution of this relationship into the differential equation for (A) followed by a second differentiation produces a simple second-order differential equation. This method was used by Rakowski [6] to obtain the general solution for the equations of consecutive reversible reactions, but there appears to be a sign error in the general solution given for a three-component system. In the specific case of the present study, the second-order equation is readily solved by insertion of the appropriate boundary conditions and hence, the integrated forms of (2)—(4) can be easily obtained. The important quantities for the determination of the equilibrium constants are the concentrations of C starting with A and A starting with C, and the appropriate integrated equations are:

$$\frac{[C]}{[A]_0} = C_A = \frac{k_1}{2p}[\exp-(a-p)t - \exp-(a+p)t] \qquad (5)$$

and

$$\frac{[A]}{[C]_0} = A_C = \frac{k_{-1}}{2p}[\exp-(a-p)t - \exp-(a+p)t] \qquad (6)$$

where

$$a = \frac{k_1 + k_{-1} + k_t}{2} \quad \text{and} \quad p = (a^2 - k_{-1}k_t)^{\frac{1}{2}}$$

For equal times, the equilibrium constant $K_{-1,1} = k_{-1}/k_1$, is given by the ratio A_C/C_A, and can thus be determined by pyrolysis of acetylcyclopropane and 2,3-dihydro-5-methylfuran for identical times at the same temperature. The results from this method are shown in the Table together with relevant experimental details. In some cases, small corrections for temperature differences were necessary.

Equilibrium constants for the isomerization of 2,3-dihydro-5-methylfuran to acetylcyclopropane

Temp./K	Time/min	k_{-1}/k_1
672·8	30	1·38
673·2	90	1·60
673·8	120	1·80
674·8	60	1·56
679·0	45	1·64
680·1	60	1·78
681·0	15	1·49
681·3	30	1·75
702·7	10	1·63
704·0	15	1·56
704·3	10	1·91
706·1	20	1·87
721·0	5	1·84
721·1	4	1·91
722·7	3	1·88
723·5	6	1·89
729·9	5	1·90
730·3	4	1·62
730·7	3	1·77
731·6	2	1·76

The values obtained for the equilibrium constant show a fairly large random scatter (up to ±10%) due partly to analytical errors involved in measuring C_A and A_C at small extents of reaction and partly to errors introduced in the handling procedures. The van't Hoff relationship derived from the data in the Table is given as

$$\log K_{-1,1} = 0·96 \pm 0·25 - (9·6 \pm 3·3\ \text{kJ mol}^{-1})/\theta \qquad (7)$$

where $\theta = 2·303\,RT$ and the quoted errors are standard deviations. The maximum likely error [7] in the enthalpy term is ±7·5 kJ mol^{-1}.

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* 1 Torr = (101·325/760) kN m^{-2}.

[6] A. Rakowski, *Z. Phys. Chem.*, 1907, **57**, 321.

[7] S. W. Benson, ' The Foundation of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 91.

DISCUSSION

The discrepancy between the present work and earlier reports [2,3] with respect to the reversibility of the isomerization of 2,3-dihydro-5-methylfuran to acetylcyclopropane is probably due to heterogeneous effects in the earlier work which was carried out using reactors packed with glass chips.[3]

The earlier work also reported that 2,3-dihydro-5-methylfuran was in equilibrium with *ca.* 2% of the 5-methylene isomer. Under the conditions used in the present study in which the decomposition route *via* acetylcyclopropane is relatively fast, this equilibrium was not detectable and would not be expected to influence the determination of the equilibrium constant between the dihydromethylfuran and acetylcyclopropane to a measurable extent.

The reversibility found in the carbonyl-substituted cyclopropane–dihydrofuran systems is in contrast to the behaviour observed in analogous hydrocarbon systems in which the isomerizations of vinylcyclopropanes to cyclopentenes are essentially irreversible.[8] In the case of the oxygen compounds, the formation of the five-membered ring is disfavoured, with respect to the corresponding hydrocarbon reaction, because of the large difference in thermodynamic stability between the vinyl ether and carbonyl structures. From the principles of thermodynamic group additivity,[9] the enthalpy of formation and entropy of 2,3-dihydro-5-methylfuran are estimated to be $-122{\cdot}6$ kJ mol^{-1} and 335 JK^{-1} mol^{-1} respectively. The corresponding values for acetylcyclopropane are estimated to be $-107{\cdot}5$ kJ mol^{-1} and 353 JK^{-1} mol^{-1}, yielding the calculated van't Hoff relationship (8) for the equilibrium between 2,3-dihydro-5-methylfuran and acetylcyclopropane. This equation is in

$$\log K_{-1.1} = 0{\cdot}94 - 15{\cdot}1 \text{ kJ mol}^{-1}/\theta \qquad (8)$$

excellent agreement with that obtained by experiment, considering the experimental errors and the uncertainties in the ' group ' values, for oxygen compounds.

It has been proposed, on theoretical grounds, that a π-system in a conjugated position with respect to a cyclopropane ring should strengthen the opposite bond and weaken the adjacent bonds in the ring,[10] and recent microwave studies [11] have confirmed the predicted shortening of the opposite bond in the case of carbonyl substitution. As the thermodynamic group additivity method takes no account of cyclopropane–π-system interactions, the good agreement between observed and calculated van't Hoff relationships for the acetylcyclopropane–2,3-dihydro-5-methylfuran system indicates that this interaction does not greatly affect the overall stability of the cyclopropane.

[2/1871 *Received, 7th August,* 1972]

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[8] S. W. Benson and H. E. O'Neal, ' Kinetic Data on Gas Phase Unimolecular Reactions,' NSRDS-NBS21, Nat. Bur. Standards, 1970.

[9] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

[10] R. Hoffmann, *Tetrahedron Letters*, 1970, 2907.

[11] R. E. Penn and J. E. Boggs, *J.C.S. Chem. Comm.*, 1972, 666.