Gas-phase Thermal Unimolecular Isomerizations of Acetylcyclopropane. Part II.[1] Determination of the Rate Constants

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The gas-phase thermal reactions of acetylcyclopropane and 2,3-dihydro-5-methylfuran have been studied in the temperature range 672—731 K. Acetylcyclopropane isomerizes by four parallel routes to yield (1) 2,3-dihydro-5-methylfuran, (2) *cis*-pent-3-en-2-one, (3) *trans*-pent-3-en-2-one, and (4) pent-4-en-2-one. Reaction (1) is reversible and the other reactions are essentially irreversible. The sole observable reaction of 2,3-dihydro-5-methylfuran is a reversible isomerization to acetylcyclopropane [reaction (−1)]. The experimentally determined Arrhenius relationships for the first-order rate constants are: $\log k_1/\text{s}^{-1} = 13{\cdot}89 \pm 0{\cdot}22 - (231{\cdot}2 \pm 2{\cdot}9\ \text{kJ mol}^{-1})/\theta$, $\log k_{-1}/\text{s}^{-1} = 14{\cdot}85 \pm 0{\cdot}22 - (241{\cdot}0 \pm 2{\cdot}9\ \text{kJ mol}^{-1})/\theta$, and $\log (k_2 + k_3 + k_4)/\text{s}^{-1} = 14{\cdot}4 - (243{\cdot}5\ \text{kJ mol}^{-1})/\theta$, where $\theta = 2{\cdot}303\,RT$. These parameters can be rationalized by a diradical mechanism in which a stabilization energy of *ca*. 30 kJ mol^{-1} (7 kcal mol^{-1}) in the alkylacetonyl radical is operative.

THE kinetic parameters for the thermal isomerizations of vinylcyclopropanes and the thermal decompositions of vinylcyclobutanes have been rationalized on the basis of diradical mechanisms,[2] and thermochemical kinetic analyses of the diradical models yield values for the resonance energy in the alkyl-substituted allyl radical which are in good agreement with those obtained from iodine-atom abstraction methods.[3] Diradical analyses of the decompositions of carbonyl-substituted cyclobutanes,[2] however, indicate appreciably higher values for the resonance energy in the alkylacetonyl radical than those obtained by the iodine-atom technique.[4]

The present study was undertaken to determine the energetic effect of the carbonyl group in the reactions of the carbonyl analogue of isopropenylcyclopropane.

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[1] Part I, A. T. Cocks and K. W. Egger, preceding paper.

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

[3] D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

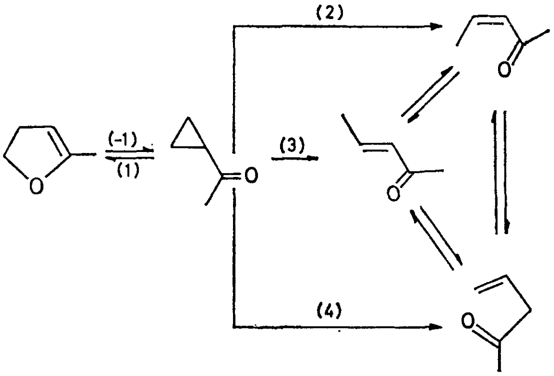
[4] R. K. Solly, D. M. Golden, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1970, **2**, 381.

EXPERIMENTAL

Materials and experimental techniques used in this study were identical to those described previously.[1]

RESULTS

In the range 672—731 K, acetylcyclopropane isomerizes reversibly to 2,3-dihydro-5-methylfuran and irreversibly to *cis*- and *trans*-pent-3-en-2-one and pent-4-en-2-one by parallel reaction paths. In the same range, the sole detectable reaction of 2,3-dihydro-5-methylfuran is the reversible isomerization to acetylcyclopropane. Under the experimental conditions employed, the pentenones undergo slow interconversion, and some decomposition to lower molecular-weight hydrocarbons and carbon monoxide occurs. The overall reaction scheme is shown in (1).



(1)

Extensive preliminary experiments indicated that in ' aged ' vessels, the primary reactions were homogeneous [1] and independent of reactant pressure above 4 Torr.* The primary isomerizations appear, therefore, to be first-order unimolecular processes at their high-pressure limits. The interconversion of the pentenones did, however, appear to have a heterogeneous component.

The integrated rate equations for scheme (1), obtained by the method outlined previously,[1] are shown in (2)—(4) for experiments starting with acetylcyclopropane and in (5)—(7) for experiments starting with 2,3-dihydro-5-methylfuran. Starting with acetylcyclopropane:

$$A/A_0 = A_A = \frac{(a + p + k - 1)}{2p} \exp-(a + p)t + \frac{(p - a + k - 1)}{2p} \exp-(a - p)t \qquad (2)$$

$$B/A_0 = B_A = 1 + \frac{(k_t - a - p)}{2p} \exp-(a - p)t - \frac{(k_t + p - a)}{2p} \exp-(a + p)t \qquad (3)$$

$$C/A_0 = C_A = \frac{k_1}{2p} [\exp-(a - p)t - \exp-(a + p)t] \qquad (4)$$

Starting with 2,3-dihydro-5-methylfuran:

$$A/C_0 = A_C = \frac{k_{-1}}{2p} [\exp-(a - p)t - \exp-(a + p)t] \qquad (5)$$

$$B/C_0 = B_C = 1 + \frac{(a - p)}{2p} \exp-(a + p)t - \frac{(a + p)}{2p} \exp-(a - p)t \qquad (6)$$

$$C/C_0 = C_C = \frac{(k_{-1} + p - a)}{2p} \exp-(a + p)t + \frac{(a + p - k_{-1})}{2p} \exp-(a - p)t \qquad (7)$$

where A, B, and C are the concentrations of acetylcyclopropane, total pentenones, and 2,3-dihydro-5-methylfuran respectively (subscript 0 refers to initial concentrations),

and $k_t = k_2 + k_3 + k_4$, $a = (k_1 + k_{-1} + k_t)/2$,

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

The evaluation of the equilibrium constant from (4) and (5) has been discussed previously.[1] Another useful ratio, k_{-1}/k_t, can be obtained from (3), (5), and (6), for a given time, and the resulting expression is shown in (8).

$$k_{-1}/k_t = A_C/(B_A - B_C) \qquad (8)$$

Attempts to evaluate this ratio from experiments conducted for equal times at the same temperature starting with both acetylcyclopropane and 2,3-dihydro-5-methylfuran gave scattered results which showed no systematic variation with temperature or primary conversion below 50%. The mean value obtained was 4·5 with a standard deviation of ±1·2. The high scatter observed is due to the large errors involved in $(B_A - B_C)$ which is the small difference between minor products. Above *ca.* 50% primary decomposition, there was evidence for decomposition of the pentenones and hence, kinetic runs were normally restricted to below 50% conversion.

Two methods, both involving some approximation, were used to evaluate the rate constants in the system.

In method I, k_1 and k_{-1} were obtained from studies of the isomerization of 2,3-dihydro-5-methylfuran at low conversion. Under these conditions, the perturbation due to the further reaction of acetylcyclopropane is small and the rate constants can be evaluated from the normal reversible first-order kinetic equations, using equilibrium constants determined previously.[1] Rate constants obtained by this method were consistent for reactions up to *ca.* 60% approach to equilibrium, and the values for k_1 are shown in the Table together with relevant experimental details. From these values k_t was calculated from (2)—(7) by iteration using the Newton–Raphson procedure.[5] This method is a severe test of the data as all errors are reflected in k_t, and only equation (2) yielded consistent rate constants. This is not surprising as A_A is the only reaction mixture component directly affected by k_t which could be measured with reasonably high precision. Values for k_t obtained from A_A are also listed in the Table.

In method II, k_1 and k_{-1} were expressed in terms of k_t by using the equilibrium constants k_{-1}/k_1 [1] and the mean ratio k_{-1}/k_t of 4·5. This method artificially equates the temperature dependences of k_{-1} and k_t. Rate constant k_t was then determined from equations (2), (4), (5), and (7) by iteration. Because of the greater inherent experimental error in the measurement of the pentenones, no use was made of equations (3) and (6). Equations (2) and (7) yielded consistent values for k_t, but the results from (4) and (5) were more scattered and the mean values tended to be generally *ca.* 20% lower than those from (2) and (7). A lowering of the equilibrium constant by *ca.* 10% would produce good agreement between the two sets of values, but the larger experimental errors in A_C and C_A with respect to those for A_A and C_C do not permit a meaningful refinement of the equilibrium constant. Values for k_t and the derived values for k_1 obtained from (2) and (7) are shown in the Table.

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* 1 Torr = (101·325/760) kN m^{-2}.

[5] R. A. Buckingham, ' Numerical Methods,' Pitman, London, 1962, p. 255.

Rate constants for the isomerization of acetylcyclopropane

		$k_t \times 10^4/s^{-1}$			$k_1 \times 10^4/s^{-1}$		
Temp./K	Time/min	Method I	Method II(A)[a]	Method II(C)[b]	Method I	Method II(A)[a]	Method II(C)[b]
672·1	120	0·276	0·288			0·810	
672·8	30			0·279	0·787		0·785
672·9	90	0·310	0·309			0·869	
673·2	90			0·322	0·931		0·906
673·5	30	0·410	0·351			0·981	
673·8	120			0·375			1·05
674·8	60			0·332	0·947		0·928
674·9	60	0·357	0·354			0·989	
679·0	45			0·418	1·16		1·15
680·1	60			0·557			1·54
680·3	45	0·486	0·490			1·35	
681·0	30	0·469	0·498			1·37	
681·0	15			0·525	1·44		1·44
681·2	15	0·449	0·498			1·37	
681·3	30			0·526	1·45		1·44
682·3	60	0·593	0·577			1·57	
702·7	10			1·78	4·70		4·66
704·0	15			1·34			3·49
704·1	15	2·04	2·06			5·36	
704·1	10	2·09	2·09			5·44	
704·3	10			2·25	5·94		5·85
704·6	10	2·37	2·25			5·85	
705·3	20	2·52	2·43			6·28	
706·1	20			4·50[c]			11·6[c]
720·8	5	5·49	5·45			13·6	
721·0	5			5·48	14·0		13·7
721·1	4	5·47	5·48			13·7	
721·1	4			5·44	13·8		13·6
722·6	3	5·68	5·86			14·6	
722·7	3			5·63	14·1		14·0
723·5	6			6·57			16·3
723·6	6	6·70	6·54			16·3	
729·9	5			9·14			22·4
730·0	5	10·9	10·4			25·4	
730·3	4			6·72			16·4
730·5	4	10·1	9·76			23·9	
730·7	3			9·16	22·9		22·4
730·8	3	9·40	9·28			22·7	
731·6	2			8·94	22·0		21·9
731·8	2	9·30	9·64			23·6	

[a] Starting with acetylcyclopropane. [b] Starting with 2,3-dihydro-5-methylfuran. [c] Not included in least-squares analysis.

From the Table, it can be seen that rate constants obtained by methods I and II are in good agreement. The Arrhenius relationships derived from these data are given by (9)—(14).

Method I:

$$\log k_1/\text{s}^{-1} = 13{\cdot}89 \pm 0{\cdot}22 - (231{\cdot}2 \pm 2{\cdot}9\ \text{kJ mol}^{-1})/\theta \quad (9)$$

$$\log k_t/\text{s}^{-1} = 14{\cdot}40 \pm 0{\cdot}33 - (243{\cdot}5 \pm 4{\cdot}2\ \text{kJ mol}^{-1})/\theta \quad (10)$$

Method II, A_A:

$$\log k_1/\text{s}^{-1} = 14{\cdot}03 \pm 0{\cdot}14 - (232{\cdot}9 \pm 1{\cdot}9\ \text{kJ mol}^{-1})/\theta \quad (11)$$

$$\log k_t/\text{s}^{-1} = 14{\cdot}33 \pm 0{\cdot}15 - (242{\cdot}7 \pm 2{\cdot}0\ \text{kJ mol}^{-1})/\theta \quad (12)$$

Method II, C_C:

$$\log k_1/\text{s}^{-1} = 13{\cdot}74 \pm 0{\cdot}24 - (229{\cdot}2 \pm 3{\cdot}2\ \text{kJ mol}^{-1})/\theta \quad (13)$$

$$\log k_t/\text{s}^{-1} = 14{\cdot}04 \pm 0{\cdot}24 - (239{\cdot}1 \pm 3{\cdot}3\ \text{kJ mol}^{-1})/\theta \quad (14)$$

where $\theta = 2{\cdot}303\,RT$ and the quoted errors are standard deviations.

The equations agree within the standard deviations, and those from method I mav be taken as representative. The corresponding equation for k_{-1} is shown in (15). From

$$\log k_{-1}/\text{s}^{-1} = 14{\cdot}85 \pm 0{\cdot}22 - (241{\cdot}0 \pm 2{\cdot}9\ \text{kJ mol}^{-1})/\theta \quad (15)$$

(10) and (15), the value of k_{-1}/k_t over the experimental temperature range varies from 4·3 to 4·5, in good agreement with the mean value observed.

The error limits given in the Arrhenius relationships refer only to the random deviations. The assumptions made in deriving these equations would tend to introduce systematic errors as would any calibration factor inaccuracies. These errors are unlikely to exceed ±20% for the rate constants and would affect only the A-factors in equations (9) to (14) (±0·1 in log A).

The interconversion of the pentenone isomers and their decomposition render an exact solution for the component rate constants of k_t impossible. At very low conversions, the ratios of *cis*-pent-3-en-2-one to *trans*-pent-3-en-2-one to pent-4-en-2-one are 4 : 1 : 5. At higher conversions, the *trans*-pent-3-en-2-one predominates. If the low conversion ratios are taken to be representative of the unperturbed formation from acetylcyclopropane alone at the mid-temperature of the study, the approximate Arrhenius equations can be obtained from the mid-temperature value of k_t and estimates of the A-factors. Semi-empircal predictions of the A-factors of analogous hydrocarbon reactions [2] indicate that reasonable A-factors for k_2, k_3, and k_4 would be 13·8, 13·2, and 14·6 respectively. The resulting Arrhenius equations are:

$$\log k_2/\text{s}^{-1} = 13{\cdot}8 - (241\ \text{kJ mol}^{-1})/\theta \quad (16)$$

$$\log k_3/\text{s}^{-1} = 13{\cdot}2 - (241\ \text{kJ mol}^{-1})/\theta \quad (17)$$

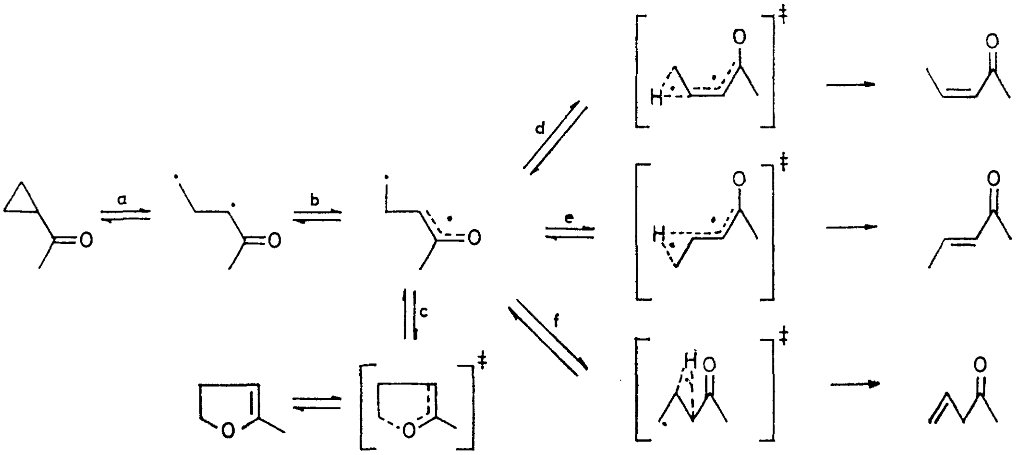
$$\log k_4/\text{s}^{-1} = 14{\cdot}6 - (250\ \text{kJ mol}^{-1})/\theta \quad (18)$$

An Arrhenius plot calculated from the sum of these rate constants over the experimental temperature range yields a line with curvature small enough to be readily masked by experimental errors, and gives the values, $\log A = 14{\cdot}5$, $E_a = 245$ kJ mol^{-1} in good agreement with (10).

DISCUSSION

By analogy with the thermal reactions of vinylcyclopropanes, the isomerizations of acetylcyclopropane would be expected to occur *via* a diradical mechanism. Support for this mechanism is provided by the fact that the A-factor for the isomerization to 2,3-dihydro-5-methylfuran ($10^{13{\cdot}9}$ s^{-1}) is identical to that observed in the analogous isomerization of isopropenylcyclopropane to 1-methylpentene.[6] The high A-factor for the reverse reaction is also indicative of a diradical pathway, as are the observed isomeric reaction products.

The diradical scheme for the isomerizations of acetylcyclopropane is shown in (19). The activation energies are, therefore, the sums of the energies for the steps to the appropriate transition state. Step a, the hypothetical ring opening without participation of the carbonyl group, should be the same as that for methylcyclopropane (222 kJ mol^{-1}).[2] The energy involved in step b (X kJ mol^{-1}) is the stabilization energy of the alkylacetonyl radical. The energy required for ring closure, step c, is unlikely to be substantially different from that in the hydrocarbon case (35 kJ mol^{-1}), as strain energies for oxygen containing ring systems are very similar to those for the analogous hydrocarbon compounds.[2]



(19)

The activation energy for the isomerization to 2,3-dihydro-5-methylfuran is, therefore, estimated to be $222 - X + 35 + 4$ (*cis* correction)$^2 = 261 - X$ kJ mol^{-1}. From the observed value of 231·2 kJ mol^{-1}, the stabilization energy X is calculated to be *ca.* 30 kJ mol^{-1} or 7 kcal mol^{-1}.

The energy required for 1,2-hydrogen transfer in hydrocarbon radicals is 45 kJ mol^{-1}.[2] In the vinylcyclopropanes, this energy is modified in step d to take into account non-planarity in the transition state. In the present case, however, steric interactions in the transition state leading to *cis*-pent-3-en-2-one are likely to be less severe than in the corresponding hydrocarbon reaction and hence, little change from 45 kJ mol^{-1} is expected.

From the isomerizations to both *cis*- and *trans*-pent-3-en-2-one, therefore, X is given by:

$$-X/\text{kJ mol}^{-1} = 241 \text{ (activation energy)} - 222 \text{ (step a)} - 45 \text{ (step d or e)} \quad (20)$$

The stabilization energy in the alkylacetonyl radical is thus estimated to be 26 kJ mol^{-1} (6 kcal mol^{-1}). This value is in good agreement with that obtained from the dihydromethylfuran pathway but is less reliable as it depends on estimated A-factors.

A value for the stabilization energy can also be obtained from the parameters for the isomerization to pent-4-en-2-one, but this requires one further assumption. For the analogous hydrocarbon paths, it appears that half the stabilization energy is lost in the transition state,[2] and assuming this to apply also to the oxygen compound, relationship (21) is obtained. This yields

$$-X/2 = (250 - 222 - 45) \text{ kJ mol}^{-1} \quad (21)$$

a stabilization energy of 34 kJ mol^{-1} (8 kcal mol^{-1}), again in good agreement with the values calculated from the other paths.

The rate data for the thermal isomerizations of acetylcyclopropane are thus consistent with a diradical mechanism in which a stabilization energy of *ca.* 30 kJ mol^{-1} in the alkylacetonyl radical is operative. This value is in good agreement with those obtained from diradical analyses of the decompositions of carbonyl-substituted cyclobutanes (32—36 kJ mol^{-1}),[2] but it is appreciably larger than those obtained by halogen atom techniques for the methylacetonyl radical (11 kJ mol^{-1} or 2·7 kcal mol^{-1})[4] and the unsubstituted acetonyl radical (0 kJ mol^{-1}).[7,8]

The low values obtained from the halogen-atom work have been rationalized on the basis of the large difference in stability (*ca.* 88 kJ mol^{-1}) between the two canonical forms of the radical.[4] Whilst this simple valence-bond

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[6] H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 1962, 3981.

[7] R. K. Solly, D. M. Golden, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1970, **2**, 11.

[8] K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1970, **92**, 5541.

picture certainly predicts a lowering of the stabilization energy with respect to that found in more symmetrical delocalized radicals such as methylallyl (52 kJ mol^{-1} or 12·5 kcal mol^{-1}) [3] or 2-aza-allyl (*ca.* 60 kJ mol^{-1} or 14·5 kcal mol^{-1}),[9] it can yield no quantitative information on the expected magnitude, and does not rule out the values found from diradical analyses.

The discrepancy between the halogen-atom work and the diradical analyses for the carbonyl-substituted cyclobutanes could be explained if, in the cyclobutane reactions, *ca.* 50% decomposition occurred *via* a concerted process,[4] and it is conceivable that the presence of the carbonyl group might favour a concerted path in the isomerizations of acetylcyclopropane. However, it is unlikely that the energetic effect of a carbonyl group would be the same for such widely differing reactions as cyclobutane decompositions and cyclopropane isomerizations if concerted processes were operative. It is also of interest to note that the agreement between observed relative rates for cyclization and isomerization to linear products, and those predicted from a diradical model, is closer for acetylcyclopropane than for the analogous hydrocarbons.

In the case of acetylcyclopropane there is another possible explanation for the disagreement with iodine-atom work. Theoretical considerations [10] lead to the prediction that unsaturated groups in a conjugated position to a cyclopropane ring should strengthen the opposite bond and weaken the adjacent bonds in the ring. It is conceivable, therefore, that the ' stabilizing ' effect observed for acetylcyclopropane is in reality due to a destabilization of the ground state. Recent microwave studies,[11] however, have indicated that the length of the bond opposite the formyl group in formylcyclopropane, although shorter than the corresponding bond in methylcyclopropane, is not significantly different to that in vinylcyclopropane. As the kinetic parameters for the isomerizations of vinyl cyclopropanes are compatible with the well-established methallyl resonance energy,[3] it would appear that any ground-state bond weakening is small. The apparent stabilization energy derived from the acetylcyclopropane data is, therefore, unlikely to contain a significant contribution from ground-state effects.

Consideration of the likely errors involved in the experimental data and the assumptions involved in the diradical analyses for the carbonyl-substituted ring compounds results in a lower limit for the alkylacetonyl radical stabilization energy of *ca.* 21 kJ mol^{-1} (5 kcal mol^{-1}). The maximum value, within the experimental error, for the stabilization energy, in the methylacetonyl radical derived from iodine-atom studies [4] is also 21 kJ mol^{-1}. However, this limiting value does not take account of possible errors in the assumption that the activation energy for the reaction of HI with the methylacetonyl radical is 4 ± 4 kJ mol^{-1}. This value has not been determined directly and has been assumed to be independent of the nature of the radical in all iodine-atom studies.[3] There is evidence, however, that for some radicals, a value of at least 17 kJ mol^{-1} is appropriate,[12] which, if applicable to the methylacetonyl radical, would give good agreement with the diradical analyses.

[2/1872 *Received, 7th August*, 1972]

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[9] A. T. Cocks and K. W. Egger, *Internat. J. Chem. Kinetics*, 1972, **4**, 169.

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

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

[12] K. W. Egger and M. Jola. *Internat. J. Chem. Kinetics*, 1970, **2**, 265.