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Isomerization of 2-Methyl-4,5-dihydrofuran. Studies with a Single-Pulse Shock Tube

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The isomerization of 2-methyl-4,5-dihydrofuran was studied behind reflected shock waves in a pressurized driver single-pulse shock tube over the temperature range 805–1030 K and densities of approximately ~3 × 10^{-5} mol/cm^3. Two isomerization products, acetylcyclopropane and 3-penten-2-one, are obtained in the isomerization. Acetylcyclopropane is formed in an irreversible process from 2-methyl-4,5-dihydrofuran. It further isomerizes, at higher temperatures, to *cis*- and *trans*-3-penten-2-one. At high temperatures where the conversion of 2-methyl-4,5-dihydrofuran is high, the main source for 3-penten-2-one is acetylcyclopropane. At lower temperatures 3-penten-2-one is formed mainly by a direct isomerization of 2-methyl-4,5-dihydrofuran. A small concentration of decomposition products, mainly methane and ethane, are also found in shock mixtures of 2-methyl-4,5-dihydrofuran, particularly at high temperatures. The Arrhenius relations for the three aforementioned processes are as follows: 2-methyl-4,5-dihydrofuran → acetylcyclopropane, $k_1 = 10^{15.4}\exp(-56.8 \times 10^3/RT)$ s^{-1}; 2-methyl-4,5-dihydrofuran → 3-penten–2–one, $k_2 = 10^{15.7}\exp(-63.6 \times 10^3/RT)$ s^{-1}; acetylcyclopropane → 3-penten-2-one, $k_3 = 10^{14.4}\exp(-58.3 \times 10^3/RT)$ s^{-1}, where R is expressed in units of cal/(K mol).

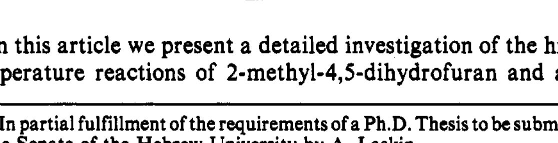
Introduction

We have recently published detailed investigations on the shock-initiated reactions of four oxygen-containing five-membered rings: furan,[1] tetrahydrofuran,[2] 2,3-dihydrofuran,[3] and 2,5-dihydrofuran.[4] Whereas furan and tetrahydrofuran are very stable ring structures, the dihydrofuran rings are considerably less stable and tend to react at much lower temperatures.

The main reaction in 2,5-dihydrofuran is elimination of a hydrogen molecule from H atoms in the C(2) and C(5) positions to form furan with a small extent of ring decomposition compared to the rate of hydrogen elimination. Propylene was found to be the major decomposition product.[4] The major reaction in 2,3-dihydrofuran is an isomerization to cyclopropanecarboxaldehyde with further isomerization to crotonaldehyde.[3] It could not be established in that study whether the latter was formed also directly from 2,3-dihydrofuran or only from cyclopropanecarboxaldehyde.

There are two detailed low-temperature investigations on the reactions of 2-methyl-4,5-dihydrofuran and acetylcyclopropane[5,6] where Arrhenius rate parameters were reported for the temperature range 670–730 K. An attempt was made to determine the equilibrium constant for 2-methyl-4,5-dihydrofuran → acetylcyclopropane, but the data obtained were highly scattered and unreliable.[5] An important issue in the investigation was a discussion of the reversibility of this reaction, and the conclusion reached suggested a back-reaction. This observation, which was in contradiction to earlier findings,[7,8] could not be corroborated also in the present investigation.

The main purpose of the present investigation is to establish the exact mechanism of the interconversion in the system 2-methyl-4,5-dihydrofuran, acetylcyclopropane, and 3-penten-2-one. Specifically, to verify or rebut a contribution from reaction 2 in this system:



(I)

In this article we present a detailed investigation of the high-temperature reactions of 2-methyl-4,5-dihydrofuran and acetylcyclopropane over the temperature range 805–1030 K. The mechanism is established, Arrhenius rate parameters for the various reactions are given, and the formation of decomposition products at higher temperatures is briefly mentioned.

Experimental Section

Apparatus. The isomerization of 2-methyl-4,5-dihydrofuran was studied behind reflected shocks in a 2-in.-i.d. pressurized driver single-pulse shock tube made of "Double Tough" Pyrex tubing. The driven section was 4 m long including a 30-cm test section. The driver had a maximum length of 2.7 m and could be tuned in 1-in. steps in order to obtain the best cooling conditions. A 36-L dump tank was connected to the driven section at a 45° angle toward the driver, near the diaphragm holder, in order to prevent reheating of the reaction mixture by reflection of transmitted waves. The driven section was separated from the driver by a Mylar polyester film of various thickness depending upon the desired shock strength.

Prior to performing an experiment, the tube and the gas handling system were pumped down to ~3 × 10^{-5} Torr. Postshock gas samples were collected in 150 cm^3 glass bulbs from an outlet in the test section near the end plate of the driven section and were transferred to the gas chromatograph for analysis.

Reflected shock temperatures were calculated from the extent of conversion of an internal standard which was added to the reaction mixture, using the relation

$$T = -(E/R)/\ln\{-(1/At)\ln(1-\chi)\} \qquad \text{(II)}$$

where E is the activation energy of the standard reaction, A is its preexponential factor, t is the reaction dwell time, and χ is the extent of decomposition of the internal standard defined in this case as $\chi = [C_3H_6]_t/([C_3H_6]_t + [C_3H_7Cl]_t)$. In studies where the starting material was 2-methyl-4,5-dihydrofuran the decomposition of 2-chloropropane was used as an internal standard ($A = 10^{13.8}$ s^{-1}, E = 50.87 kcal/mol[9]). When acetylcyclopropane was the starting material and an internal standard for somewhat higher temperature was needed, 1-chloropropane was used ($A = 10^{12.98}$ s^{-1}, E = 52.92 kcal/mol[10]). Both compounds yield propylene and hydrochloric acid in pure unimolecular reactions.

Reflected shock densities were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. The latter were measured with two high-frequency pressure transducers placed 230 mm apart near the end plate of the driven section. A third transducer

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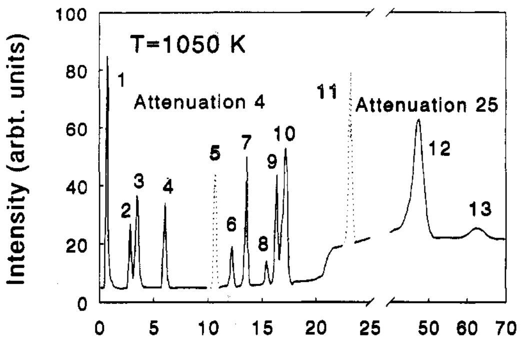


Figure 1. Gas chromatogram of a postshock sample of acetylcyclopropane, showing the isomerization and the decomposition products. The shock temperature is 1050 K. The dashed lines are peaks of the internal standard and its decomposition product propylene. The decomposition products are (1) methane, (2) ethylene, (3) ethane, (4) acetylene, (5) propylene, (6) allene, (7) propyne, (8) butane, (9) butene, (10) vinylacetylene, (11) 1-chloropropane, (12) acetylcyclopropane, (13) 3-penten-2-one.

placed at the center of the end plate provided measurements of the reaction dwell times (approximately 2 ms) with an accuracy of approximately 5%. Cooling rates were approximately 5×10^5 K/s. A detailed description of the tube and its mode of operation was given in an earlier publication.[11]

Materials and Analysis. Reaction mixtures containing 0.3% 2-methyl-4,5-dihydrofuran + 0.1% 2-chloropropane and 0.3% acetylcyclopropane + 0.1% 1-chloropropane in argon were prepared by injecting approximately 140 μL of the 2-methyl-4,5-dihydrofuran or acetylcyclopropane and 40 μL of chloropropane into 12-L glass bulbs which were then filled with argon to 1 atm. Both the bulbs and the vacuum line were pumped down to better than 2×10^{-5} Torr before the preparation of the mixtures.

1-Chloropropane and 2-chloropropane were obtained from Aldrich Chemical Co. Their listed purities were as follows: 2-methyl-4,5-dihydrofuran 99.8%, acetylcyclopropane 99.8%, 1-chloropropane 99%, and 2-chloropropane better than 99% pure. Argon was Matheson ultrahigh-purity grade, listed as 99.9995%, and helium was Matheson pure grade, listed as 99.999%.

The gas chromatographic analyses of the postshock mixtures were performed on a 2-m Porapak N column connected to a flame ionization detector (FID). The identification of the reaction products was based on their GC retention times and was also assisted by Hewlett-Packard Model 5970 mass selective detector. Sensitivity ratios of the different compounds were determined from standard mixtures. A typical chromatogram of a shocked mixture of 0.3% acetylcyclopropane in argon heated to 1050 K is shown in Figure 1. The peaks drawn in broken lines are those of the internal standard and its decomposition product, and are not part of the acetylcyclopropane decomposition.

GC peak areas were integrated with a Spectra Physics Model SP4200 computing integrator and were transferred to an IBM/PC for data reduction and graphical presentation.

Results

TABLE 1: Product Distribution (percent) in the Isomerization of 2-Methyl-4,5-dihydrofuran[a]

T_5, K	A	B	C	D
816	99.72	0.28		
842	99.54	0.46		
854	98.50	1.50		
877	97.11	2.89		
881	96.17	3.83		
881	96.70	3.30		
885	93.89	6.11		
896	94.44	5.56		
896	95.40	4.60		
896	96.22	3.78		
899	93.60	6.40		
901	93.20	6.80		
906	94.37	5.63		
915	87.32	11.70	0.87	0.10
917	90.42	8.87	0.71	
920	77.69	21.24	0.97	0.10
921	82.77	16.40	0.73	0.10
926	80.84	19.16		
926	82.27	17.73		
927	80.16	19.77		0.07
936	74.16	24.63	1.21	
946	69.98	27.80	2.10	0.12
946	71.94	26.32	1.74	
951	66.45	31.36	2.19	
954	61.32	36.30	2.25	0.13
959	53.29	44.32	2.23	0.16
963	53.0	43.32	3.49	0.19
963	60.29	36.96	2.75	
967	54.05	42.60	3.35	
968	54.86	40.78	4.19	0.16
970	37.86	56.73	5.00	0.41
975	48.06	46.40	5.16	0.38
978	32.95	62.92	3.66	0.47
998	19.22	69.80	10.33	0.64
1000	12.11	77.45	10.45	
1003	18.12	70.19	10.85	0.84
1006	10.78	78.52	9.89	0.81
1017	6.74	79.00	12.78	1.48
1020	4.67	76.43	17.27	1.64
1029	2.71	77.01	18.56	1.72
1030	2.22	73.20	22.55	2.03
1033	1.24	76.91	19.23	2.61

[a] A, 2-methyl-4,5-dihydrofuran; B, acetylcyclopropane; C, 3-penten-2-one; D, total decomposition.

Product Distribution in the Thermal Reactions of 2-Methyl-4,5-dihydrofuran. Some 40 experiments were carried out with 2-methyl-4,5-dihydrofuran as the starting material and 2-chloropropane as the internal standard, covering the temperature range 805–1030 K. Details of the experimental conditions of this series of experiments and the product distribution are given in Table 1. Figure 2 gives a graphical presentation of the distribution of the isomers and the extent of total decomposition. As can be seen, the extent of decomposition vs isomerization is minimal up to almost complete conversion of 2-methyl-4,5-dihydrofuran to its isomers. The main products are methane and ethane. Over the temperature range covered in this series of experiments, the main isomerization product is acetylcyclopropane. 3-Penten-2-one does not appear before 930 K and at much lower concentrations. The fact that the concentration of 3-penten-2-one increases with increasing acetylcyclopropane concentration (Figure 2) where that of 2-methyl-4,5-dihydrofuran goes almost

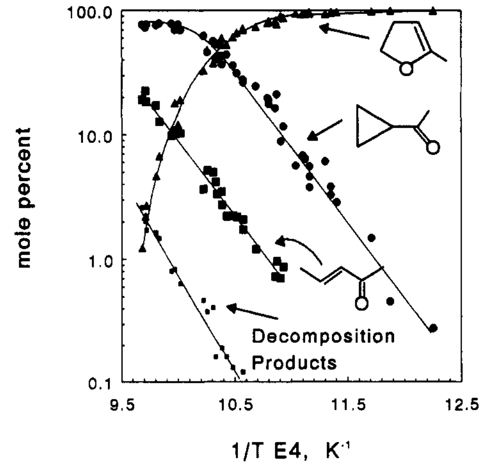


Figure 2. Product distribution in postshock samples of 2-methyl-4,5-dihydrofuran, showing the isomerizations and the extent of total decomposition.

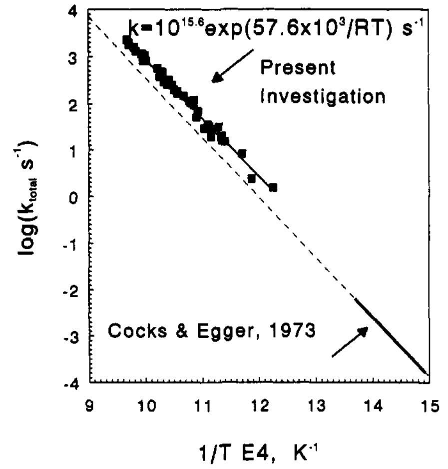


Figure 3. Plot of log k_{total} vs $1/T$. k_{total} corresponds to the total isomerization of 2-methyl-4,5-dihydrofuran. The low-temperature data are shown for comparison.

to zero clearly suggests, as has been assumed in the past, that 3-penten-2-one is formed by opening of the cyclopropane ring. It is not clear however, at this stage, whether it can be formed also directly from the 4,5-dihydrofuran ring. As has been mentioned before, one of the main aims of this investigation is to establish the precise mechanism of this $CH_3C_4H_3O$ system.

Figure 3 shows an Arrhenius plot for the total first-order disappearance of 2-methyl-4,5-dihydrofuran calculated from the relation

$$k_{\text{total}} = -\ln\{[\text{2-methyl-4,5-dihydrofuran}]_t/[\text{2-methyl-4,5-dihydrofuran}]_0\}/t \qquad \text{(III)}$$

k_{total} is equal k_1 if reaction 2 (Scheme I) does not exist and is equal to $k_1 + k_2$ if 3-penten-2-one is formed also from 2-methyl-4,5-dihydrofuran directly. The rate constant obtained at low temperatures by Cocks and Egger[5] for the same process is also shown for comparison. The comparison is made with the sum of k_1 and k_{-1}, where k_{-1} is the back reaction for the isomerization of 2-methyl-4,5-dihydrofuran to acetylcyclopropane. Cocks and Egger assumed that reaction 1 (Scheme I) should be treated kinetically as a reversible reaction. This assumption is not supported however in the present investigation as no 2-methyl-4,5-dihydrofuran was obtained in the isomerization of acetylcyclopropane. The data points obtained in this investigation are slightly higher than the low-temperature data, but the agreement, altogether, is quite reasonable. The high-temperature rate constant is given by $k_{\text{total}} = 10^{15.60}\exp(-57.6 \times 10^3/RT)$ s^{-1}.

On the assumption that all the reactions involved are irreversible, the equations that describe the kinetics of the reaction scheme I are the following:

$$\alpha = [A]/[A]_0 = \exp[-(k_1 + k_2)t] \qquad \text{(IV)}$$

$$\beta = [B]/[A]_0 = \frac{k_1}{k_3 - (k_1 + k_2)}\{\exp[-(k_1 + k_2)t] - \exp(-k_3t)\} \qquad \text{(V)}$$

$$\gamma = [C]/[A]_0 = 1 + \frac{1}{k_3 - (k_1 + k_2)}[k_1 \exp(-k_3t) - (k_3 - k_2)\exp(-k_1 + k_2)t] \qquad \text{(VI)}$$

where $k_1 + k_2$ stands for k_{total}. If k_2 is equal to zero, then the equations reduce to the simple A → B → C set of reactions.

Since γ is nothing but $1 - (\alpha + \beta)$, we have here two equations with three unknowns. We therefore proceeded to determine k_3 independently.

TABLE 2: Product Distribution (percent) in the Isomerization of Acetylcyclopropane[a]

T_5, K	A	B	C	T_5, K	A	B	C
918	98.96	1.04	0.0	1018	84.46	14.32	1.22
931	98.46	1.54	0.0	1021	81.84	16.90	1.26
940	97.91	1.95	0.14	1021	82.55	16.33	1.12
947	97.76	2.24	0.0	1026	79.91	18.83	1.26
948	97.68	2.14	0.18	1026	80.72	17.77	1.51
952	96.91	2.85	0.24	1029	78.68	19.38	1.94
961	96.43	3.37	0.20	1036	76.35	21.78	1.87
968	95.60	4.12	0.28	1043	74.74	22.36	2.90
969	95.29	4.48	0.23	1049	69.89	26.93	3.18
972	95.14	4.58	0.28	1052	68.54	27.74	3.72
975	94.97	5.03	0.0	1055	67.38	27.58	5.04
977	94.27	5.43	0.30	1056	58.73	37.87	3.40
978	94.17	5.48	0.35	1060	66.72	26.72	6.57
978	93.84	5.87	0.29	1060	63.05	32.67	4.28
981	93.32	6.33	0.35	1062	62.83	31.98	5.19
986	92.96	6.63	0.41	1072	56.24	37.02	6.74
992	91.51	8.24	0.25	1080	45.61	41.86	12.53
998	89.38	10.12	0.50	1081	51.30	38.81	9.89
1004	88.73	10.83	0.44	1103	30.68	56.91	12.41
1007	87.80	11.53	0.66	1103	30.53	55.55	13.92
1009	87.64	11.68	0.68	1120	18.56	52.39	29.05
1017	83.86	15.24	0.89	1130	17.15	56.10	26.75
1017	83.82	15.32	0.86	1131	19.00	55.46	25.54

[a] A, acetylcyclopropane; B, 3-penten-2-one; C, total decomposition.

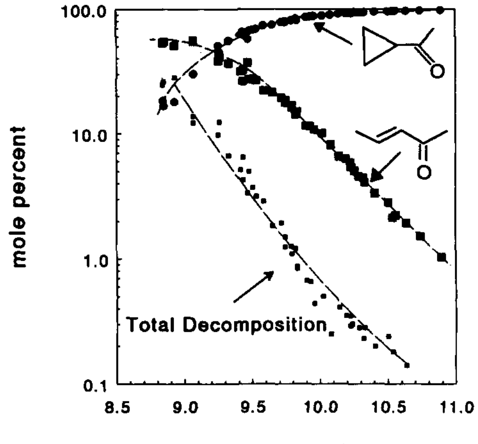


Figure 4. Product distribution in shocked samples of acetylcyclopropane showing the isomerization and the extent of total decomposition.

Rate Constant for the Isomerization Acetylcyclopropane → 3-Penten-2-one. Some 40 experiments were performed with acetylcyclopropane as the starting material and 1-chloropropane as the internal standard, covering the temperature range 920–1050 K. Details of the experimental conditions of this set of experiments and the product distribution are given in Table 2. Figure 4 shows a graphical presentation of the isomerization as well as the overall extent of decomposition. Here the decomposition is considerably higher than the one shown in Figure 2 as the temperature range covered in this set of experiments is higher. To determine the rate constant of the isomerization as a simple irreversible first-order process, we used data points below 1025 K where the extent of decomposition does not exceed 2% out of 25% conversion of the reactant. This is shown in Figure 5, where log k_3 is plotted against reciprocal temperature. As can be seen, there is very good agreement with the low-temperature data of Cocks and Egger[5,6] although the slope at the higher temperatures is somewhat smaller. We believe that the Arrhenius parameters obtained in the low-temperature range, namely, $k_3 = 10^{14.4}\exp(-58.3 \times 10^3/RT)$ s^{-1} are good as they extrapolate very well to the high-temperature range of this investigation and they are compatible with other substituted cyclopropane → propylene isomerizations.[12,16]

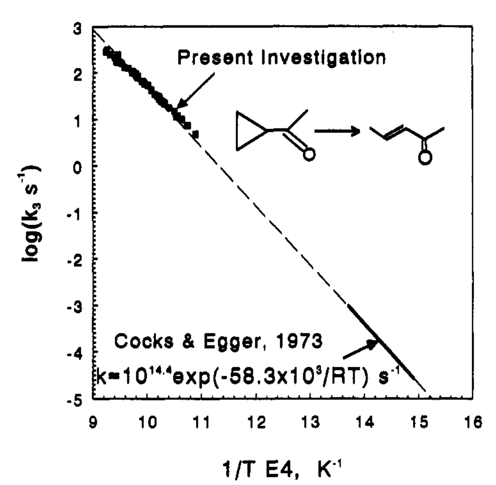


Figure 5. Arrhenius plot for the isomerization of acetylcyclopropane to 3-penten-2-one. The low-temperature data are shown for comparison.

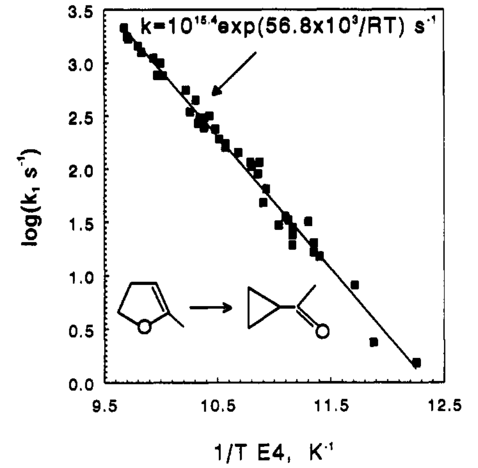


Figure 6. Arrhenius plot for the isomerization of 2-methyl-4,5-dihydrofuran to acetylcyclopropane.

The values of k_3 as deduced for each run in the second set of experiments and the values of $k_{\text{total}} = (k_1 + k_2)$ as obtained from the first set of experiments were plugged into eq V for β, and k_1 was calculated from the equation

$$k_1 = \frac{\beta[k_3 - (k_1 + k_2)]}{\exp[-(k_1 + k_2)t] - \exp[-k_3 t]} \qquad \text{(VII)}$$

k_2 was then obtained for each run from the relation $k_2 = k_{\text{total}} - k_1$.

Arrhenius plots of log k_1 vs $1/T$ and log k_2 vs $1/T$ are shown in Figures 6 and 7. The Arrhenius equation obtained for k_1 is $10^{15.4}$ exp($-56.8 \times 10^3/RT$) s^{-1}, and for k_2 $10^{15.7}$ exp($-63.6 \times 10^3/RT$) s^{-1}. As can be seen, k_2, which has a slightly higher preexponential factor, has a considerably higher activation energy and is therefore much smaller than k_1 and its contribution to k_{total} is not very large.

To summarize the observation so far:

If reaction 2 exists, then

$$k_1 = 10^{15.4} \exp(-56.8 \times 10^3/RT)\ \text{s}^{-1}$$

$$k_2 = 10^{15.7} \exp(-63.6 \times 10^3/RT)\ \text{s}^{-1}$$

$$k_3 = 10^{14.4} \exp(-58.3 \times 10^3/RT)\ \text{s}^{-1}$$

If reaction 2 does not exist and 3-penten-2-one is formed *only*

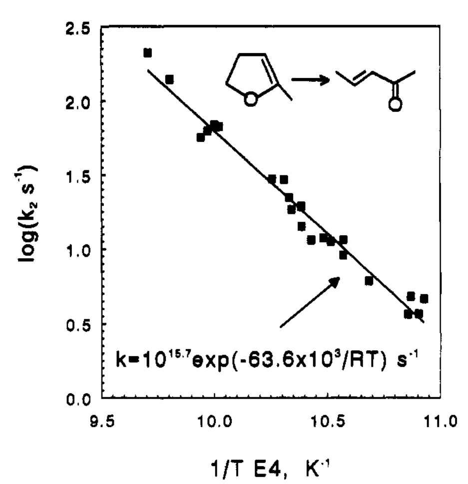


Figure 7. Arrhenius plot for the isomerization of 2-methyl-4,5-dihydrofuran to 3-penten-2-one.

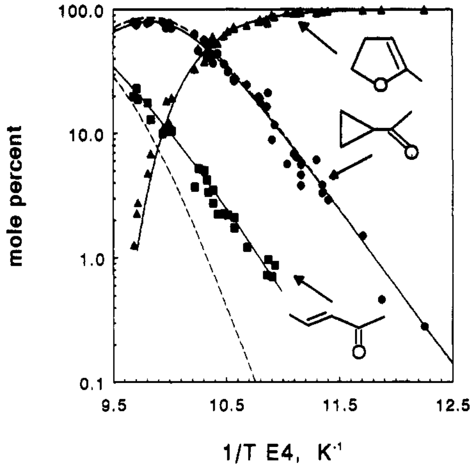


Figure 8. Comparison of calculated mole percent of 2-methyl-4,5-dihydrofuran, acetylcyclopropane, and 3-penten-2-one for the two- and three-reaction scheme. Solid lines, three-reaction scheme; broken lines, two-reaction scheme.

from acetylcyclopropane (reaction 3), then

$$k_1 = k_{\text{total}} = 10^{15.60} \exp(-57.6 \times 10^3/RT)\ \text{s}^{-1}$$

$$k_2 = 0$$

$$k_3 = 10^{14.4} \exp(-58.3 \times 10^3/RT)\ \text{s}^{-1}$$

Reaction Mechanism. To decide which one of these two possibilities is the correct one, we have calculated α, β, and γ using the two schemes and compared them to the experimental values obtained in the first series of experiments (Figure 2). Figure 8 shows such a comparison. This figure is similar to Figure 2 except that the decomposition products were removed from the figure and the calculated mole percents were added. The solid lines correspond to the three-reaction system, and the broken lines to the two-reaction system.

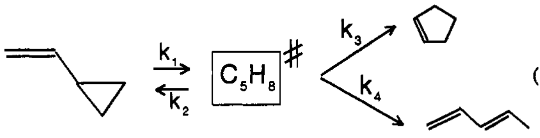
The mole percent of 2-methyl-4,5-dihydrofuran is identical in both schemes since $k_2 \ll k_1$. The mole percent of acetylcyclopropane is almost identical in both schemes, but there is a large difference in the mole percent of 3-penten-2-one. At low temperatures where the mole percent of acetylcyclopropane is still very low, the only contribution to the production of 3-penten-2-one comes from 2-methyl-4,5-dihydrofuran, which is at high concentration. At these temperatures the two-reaction scheme cannot reproduce the observed mole percent of 3-penten-2-one (Figure 8). At higher temperatures where the concentration of acetylcyclopropane begins to increase, it becomes the major source for 3-penten-2-one. At these temperatures the experimental and the calculated mole percents of 3-penten-2-one in both schemes become closer.

In conclusion, 3-penten-2-one is produced from both 2-methyl-4,5-dihydrofuran and acetylcyclopropane.

As has been mentioned before Cocks and Egger[5] tried to determine an equilibrium constant for acetylcyclopropane → 2-methyl-4,5-dihydrofuran conversion. The value that they reported for K_{eq} was $10^{0.96\pm0.25}\exp\{(-2294 \pm 3789)/RT\}$. This relation gives for K_{eq} at 1000 K a value of 2.88. Such a value could not be corroborated by the second set of experiments where the starting material was acetylcyclopropane as no traces of 2-methyl-4,5-dihydrofuran could be found in the analyses of the postshock mixtures. Unfortunately the thermochemistry of these compounds is not known well enough.

The preexponential factors obtained for k_1 and k_2 are high and indicate loose transition structures which are very close to a biradical mechanism. After the breaking (or very large extension) of the C(5)–O bond in 2-methyl-4,5-dihydrofuran and the formation of a keto group, two routes are possible. 1,2 hydrogen migration will result in the formation of the keto olefin, and 1,3 ring closure will produce the cyclopropane ring. The ratio of the rates for these two processes is 25–30 in favor of ring closure over the temperature range covered in this investigation.

A similar example for such a competition is the *cis–trans* isomerization vs propylene production in the isomerization of cyclopropane-*1,2-d*$_2$. The geometric isomerization namely, the ring closure was found experimentally to about 12 times faster than the structural isomerization.[17] Also, it has been found[18] that in the system vinyl-cyclopropane, 1,3-pentadiene and cyclopentene:



(VIII)

$k_2 > k_3 > k_4$.

The observations obtained in this investigation are therefore in very good agreement with the results obtained in other studies of similar processes.

Comparison with 2,3-Dihydrofuran. The general pattern in the isomerization of 2-methyl-4,5-dihydrofuran is almost identical to that of 2,3-dihydrofuran. In the latter the major isomerization product is cyclopropanecarboxaldehyde, rather than acetylcyclopropane, and it further isomerizes to crotonaldehyde.[3] The rate constant for the isomerization of 2,3-dihydrofuran to cyclopropanecarboxaldehyde was estimated as[13] $k_1 = 10^{13.30}\exp(-49.4 \times 10^3/RT)\ \mathrm{s}^{-1}$. Although there is not much difference in the magnitude of the isomerization rate constants of the two compounds, there is a big variation in the preexponential factors and the activation energies, being considerably lower in 2,3-dihydrofuran. This suggests that the presence of the methyl group on the ring in acetylcyclopropane, although not involved directly in the isomerization process, imposes a larger extension of the C(5)–O in order to form the transition state. This will require a higher activation energy but will make the transition state much looser.

Conclusion

The thermal reactions of 2-methyl-4,5-dihydrofuran and acetylcyclopropane can be summarized in the following statements:

The major reaction of 2-methyl-4,5-dihydrofuran over the temperature range 805–1030 K is an irreversible isomerization to acetylcyclopropane but is also directly isomerizes, although at a much lower rate, to 3-penten-2-one.

Acetylcyclopropane isomerizes only to 3-penten-2-one without a back reaction to 2-methyl-4,5-dihydrofuran.

Around 1000 K the decomposition products in 2-methyl-4,5-dihydrofuran constitutes approximately 1% of the post shock mixtures. They are produced from either acetylcyclopropane or 3-penten-2-one or both. We could not establish, in the present investigation, the exact mechanism of the decomposition process.

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