EFFECT OF HIGH PRESSURE ON THE COMPOSITION OF STEREOISOMERS OF THE DIELS–ALDER REACTION BETWEEN FURAN AND MALEIC ANHYDRIDE

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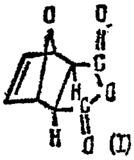
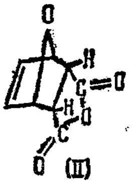
The kinetic data on the Diels–Alder reaction between furan and maleic anhydride at atmospheric pressure and 20 and 40°C correspond to a scheme of the process which includes transformation of an endo-isomer into an exo-isomer without preliminary decomposition into the starting substances. The reaction is significantly accelerated by an increase in the pressure, and the rate of formation of the exo-isomer is close to the rate of formation of the endo-isomer both at atmospheric and at high pressure. The endo-isomer is obtained with a high yield (up to 45%) at a high pressure, and this permitted determining the rate constant of its decomposition at atmospheric pressure.

It was shown for the first time in [1] that the product of the reaction of furan (F) with maleic anhydride (MA) has an exo configuration (I)


(I)


(II)

It was shown by PMR in [2] that both isomers are initially obtained, and (I) is formed two times faster than endo-isomer (II). After one day (at room temperature in acetonitrile), (II) almost totally disappears, and (I) and small amounts of F and MA remain in the reaction mixture.

A very brief communication [3] was published much later in which it was noted that the result obtained in [2] contradicts the rule of dominant endo-addition which should be obeyed by the reaction between F and MA, and for this reason, this reaction was studied repeatedly by NMR. It was found that only (II) is formed from the very beginning in acetonitrile ([F] = [MA] = 1.5 M; 40°C), the concentrations of (I) and (II) are equalized after 24 min, and virtually (I) alone remains after 24 h. As a result of calculations of the kinetic curves with the scheme of parallel equilibrium reactions (the basic experimental data are not reported), it was concluded in [3] that the rate constant of endo-addition (K_2) is 500 times higher than the rate constant of exo-addition (K_1).

The results of the last two studies thus converge into only one: (I) is thermodynamically much more stable than (II), and (II) is converted into (I) in time by decomposition into the starting substances. Since the equilibrium constant for the reaction of formation of the endo-isomer is low, the relative rates of formation of (I) and (II) can be judged by only considering the brief initial period of the reaction (low degree of conversion); as noted, the conclusions in [2, 3] are diametrically opposed with respect to the relative rates.

The reaction between F and MA was investigated in the present study both at atmospheric and at high pressures (up to 1400 MPa).

It was possible with all certainty to predict that the equilibrium of formation of (II), like (I), will be shifted toward adducts with an increase in the pressure, since the reaction in this direction takes place with a decrease in the volume ($\Delta V_0 \sim -30$ cm^3/mole). This means that the range of the degree of conversion in which the ratio of isomers is determined by

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kinetic and not by thermodynamic factors will increase significantly with an increase in the pressure. As a consequence, if K_2 is actually 500 times greater than K_1 [3], then at a high enough pressure, only (II) will be obtained with a high yield.

EXPERIMENTAL

The experiments were conducted in standard deuteroacetone and deuteroacetonitrile basically at room temperature (20 ± 1°C). A setup of the "cylinder—piston" type was used to create a high pressure in the Teflon ampul containing the reaction mixture (1-1.5 cm^3) [4]. The pressure was determined with the readings of a pressure gauge connected to a low-pressure chamber, with consideration of a multiplication factor equal to the ratio of the areas of the large and small pistons. The pressures of crystallization (P_{cr}) and melting (P_m) of pure deuteroacetone and a mixture of deuteroacetone with F (5 mole % F) were determined on this setup with a display of the clock type which records the magnitude of movement of the small piston when the pressure changes. For pure deuteroacetone, P_{cr} = 920 and P_m = 720 MPa; for the mixture of deuteroacetone with F, P_{cr} = 1100, and P_m = 900 MPa. For pure deuteroacetone, these values were also determined with a setup in which the pressure was measured directly in the reaction zone with a manganin pressure gauge: P_{cr} = 920, P_m = 800 MPa. According to the data in [5], nondeuterated acetone freezes at 20°C at approximately 830 MPa.

The P_{cr} = 600 MPa of the mixture with 5 mole % F and MA in deuteroacetonitrile was also determined on the "cylinder—piston" setup; P_{cr} of nondeuterated acetonitrile is ~350 MPa at 20°C. The separation of deuteroacetone in the solid phase from the liquid reaction mixture (0.05 mole fraction of F and MA) should thus be predicted above 1000 MPa at 20°C, and separation of deuteroacetonitrile should be predicted for P > 500 MPa. The pressure in the basic experiments was increased to 1400 MPa over 1.5-2 min.

The furan was previously distilled, sampling the fraction which boils near 30.5°C, and stored over Na: n_D^{26} 1.4190, n_D^{20} 1.4214 [6]; PMR spectrum: in deuteroacetone, δ 6.43 and 7.55 ppm; in deuteroacetonitrile, δ 6.44 and 7.52 ppm.

Pure maleic anhydride was crystallized twice from benzene and dried in air. The PMR spectrum in deuteroacetone: δ 7.32 ppm, contains an impurity ~1%, 6.39 ppm; in deuteroacetonitrile, δ 7.12 ppm (for MA).

In agreement with the data in [2, 3], the PMR spectrum of the mixture after the experiment contained peaks corresponding to the exo- and endo-adduct. In deuteroacetone, the following (ppm) correspond to the exo-isomer: $\delta_{2,3}$ 3.37 s (2H), $\delta_{1,4}$ 5.37 t (2H), and $\delta_{5,6}$ 6.63 t (2H); in deuteracetonitrile: $\delta_{2,3}$ 3.25, $\delta_{1,4}$ 5.34, and $\delta_{5,6}$ 6.55. For the endo-isomer in deuteroacetone: $\delta_{2,3}$ 3.96 m (2H), corresponding to the AA' part of the spectrum of the AA'BB' spin system, $\delta_{1,4}$ 5.44 m (2H), corresponding to the BB' part of the spectrum, additionally split by the reaction with vinyl protons H^5 and H^6 and δ 6.63.

In deuteroacetonitrile: $\delta_{2,3}$ 3.87, $\delta_{1,4}$ 5.39, and $\delta_{5,6}$ 6.60. The composition of the mixture after the experiment was determined with the relative integral intensities of the signals corresponding to MA and the exo- and endo-isomer.

RESULTS AND DISCUSSION

The following conclusions can be drawn from an examination of the data reported in Tables 1-3.

The rate of formation of the endo-isomer at atmospheric pressure and for low degrees of conversion is less than the rate of formation of the exo-isomer. The fraction of exo-isomer increases with an increase in the degree of conversion, approaching the limiting value at which the concentration of (II) in a mixture of (I) + (II) becomes low (<1%).

As should have been expected, the reaction is significantly accelerated with an increase in the pressure, and the concentration of the endo-isomer remains at the level of 40-45% of the mixture of (I) + (II) up to deeper degrees of conversion the higher the pressure is (Table 2). For P = 800 MPa, the mixture of isomers contains 41% (II) for a total yield of 82% after 1 h, and at P = 1400 MPa, the reaction takes place quantitatively after 5 min, and the mixture contains 47% (II). In the conditions studied, the dependence of the concentration of (II) on the time has a maximum. When the temperature is increased from 20 to 40°C, the fraction of (II) in the mixture decreases, and in going from deuteroacetone to deuteracetonitrile, the rate of formation of the isomers increases by ~2 times for all the pressures up to 500 MPa (Table 3).

TABLE 1. Reaction between Furan and Maleic Anhydride in Deuteroacetone (1 atm, $[F]_0 = [MA]_0 = 0.05$ mole fraction)

Time, h	Yield of (I) + (II), mole %	$\frac{[I]}{[I]+[II]}$	$\frac{[II]}{[F][MA]}$ mole·fraction^{-1}	$[II]\cdot 10^3$ mole fraction	$K_{over}\cdot 10^5$* mole fraction^{-1}·sec^{-1}
			20°		
1	2,0	0,54	0,19	0,46	11,3
2	3,6	0,57	0,33	0,77	10,4
3	5,1	0,61	0,44	1,00	10,0
4	7,3	0,64	0,61	1,31	10,9
5	8,2	0,68	0,62	1,30	9,9
5,15	8,7	0,76	0,50	1,05	10,3
9	15,6	0,89	0,47	0,84	11,4
15	24,8	0,91	0,79	1,11	12,3
20	25,4	0,94	0,51	0,71	9,5
31,2	32,7	0,96	0,58	0,65	8,6
66,3	49,7	0,98	0,56	0,36	10,2
119	63,3	0,98	1,87	0,63	8,0
263	64,9	0,99	0,53	0,16	3,9
282	60,3	0,99	0,38	0,15	2,9
			40°		
0,25	0,9	0,70	$5,4\cdot 10^{-2}$	0,13	20
0,50	2,5	0,70	0,16	0,37	28
0,75	2,7	0,71	0,16	0,39	20
1	3,2	0,73	0,18	0,43	18
2	11,8	0,92	0,23	0,45	37
3	12,0	0,92	0,25	0,50	25
4,38	18,7	0,95	0,27	0,45	29
10	36,0	0,99	0,18	0,18	31
15	45,2	0,99	0,30	0,22	30
31	53,4	0,99	0,39	0,21	20

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*K was calculated with the equation for the rate of the second order reaction of formation of both isomers.

TABLE 2. Reaction between Furan and Maleic Anhydride at High Pressures in Deuteroacetone (20°C, $[F]_0 = [MA]_0 = 0.05$ mole fraction)

P, MPa	Time	Yield of (I) + (II), mole %	$[I]\cdot 10^3$	$[II]$*$\cdot 10^3$	$\frac{[I]}{[I]+[II]}$
			mole fraction		
100	1 h	8,7	2,64	1,73	0,60
100	6 h	28,5	11,2	3,07	0,78
100	71 h	74,4	36,4	0,82	0,98
400	10 min	13,0	3,68	2,80	0,57
400	5 h	78,3	29,6	9,5	0,76
400	66.5 h	92,7	45,9	0,51	0,99
800	1 min	40,1	11,1	9,0	0,55
800	1 h	82,0	24,1	16,9	0,59
800	62.5 h	97,2	48,6	0	>0,99
1000	5 sec	36,8	10,1	8,3	0,55
1000	1 h	91,6	26,8	19,0	0,59
1000	22.5 h	99,3	45,5	4,2	0,92
1400 **	5 sec	73,8	19,9	17,0	0,54
1400	5 min	100	26,5	23,5	0,53
1400	24 h	100	34,9	14,9	0,70

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*With a correction for decomposition of (II) while unloading the reactor (10-15 min) at atmospheric pressure.

**The reaction mixture solidifies at 1400 MPa.

The results obtained are thus more in agreement with the data in [2] but not with the data in [3].

Let us now examine these results from the point of view of Scheme (1) concerning the parallel equilibrium reactions

$$(II) \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} F + MA \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} (I) \tag{1}$$

TABLE 3. Reaction Between Furan and Maleic Anhydride in Deuteroacetone and in Deuteroacetonitrile at Different Pressures* (20°C, $[F]_0 = [MA]_0 = 0.05$ mole fraction)

P, MPa	Time	Deuteroacetone		Deuteroacetonitrile	
		yield of (I)+(II), mole %	$\frac{[I]}{[I]+[II]}$	yield of (I)+(II), mole %	$\frac{[I]}{[I]+[II]}$
0,1	15 h	24,9	0,91	35,8	0,95
50	2 h	6,0	0,60	14,6	0,68
300	0,5 h	10,2	0,56	22,3	0,59
400	15 min	16,2	0,63	25,7	0,60
500	5 min	16,6	0,58	29,1	0,57

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*The experiments were conducted by simultaneously placing two ampuls in the reactor: one with the solution in deuteroacetonitrile, and the other with the solution in deuteroacetone.

The following differential equations correspond to Scheme (1)

$$\frac{d[I]}{dt} = K_1[MA][F] - K_{-1}[I] \tag{2}$$

$$\frac{d[II]}{dt} = K_2[MA][F] - K_{-2}[II] \tag{3}$$

for [MA] = [F] = C

$$-\frac{dC}{dt} = \frac{d[I]}{dt} + \frac{d[II]}{dt} = (K_1 + K_2)C^2 - K_{-1}[I] - K_{-2}[II] \tag{4}$$

$$-\frac{1}{C^2}\frac{dC}{dt} = (K_1 + K_2) - K_{-1}\frac{[I]}{C^2} - K_{-2}\frac{[II]}{C^2} = K_{\text{over}} - \frac{K_{-1}[I] + K_{-2}[II]}{C^2} \tag{5}$$

As the data in Table 1 show, the value of K_{over}, calculated from the equation for a second-order reaction rate, changes little up to a yield of (I) + (II) ~ 50%, which is the consequence of the approximate constancy of the ratio $\frac{[II]}{C^2}$ and the smallness of $\frac{K_{-1}[I]}{C^2}$ in comparison to $(K_1 + K_2)$.

According to Scheme (1), the ratio of [I]/[II] in different stages of the reaction should be determined by the ratio K_1/K_2.

As the data in Table 1 show, up to the yield of 8.2%, the value of [I]/([I]+[II]) is 0.61 on average. Then $K_1 \approx K_{\text{over}} \times 0.61 = 9.9 \cdot 10^{-5} \cdot 0.61 = 6.0 \cdot 10^{-5}$. In the period from 5 to 15 h (Table 1), the value of [II] virtually does not change, while [I] increases from $2.8 \cdot 10^{-3}$ to $11.3 \cdot 10^{-3}$ mole fraction. Let us set the point of 5 h at zero with the corresponding concentration C and calculate the value of K_1 in the indicated range with the same second-order reaction equation; we obtain $13.7 \cdot 10^{-5}$. Similar calculations for the reactions in deuteroacetone ([F] = [MA] = 0.15 mole fraction) and in deuteroacetonitrile ([F] = [MA] = 0.05 mole fraction) result in the same conclusion: in the time periods in which [II] does not change, $K_1 \approx K_{\text{over}}$. This permits hypothesizing that (II) can be converted into (I) without preliminary decomposition into the starting substances

$$\begin{tikzcd}
F + MA \arrow[r, shift left, "K_1"] & (I) \arrow[l, shift left, "K_{-1}"] \\
F + MA \arrow[r, shift left, "K_2"] & (II) \arrow[l, shift left, "K_{-2}"] \arrow[u, "K_3"']
\end{tikzcd} \tag{6}$$

In this case, Eqs. (2) and (3) are replaced by (7) and (8), and Eq. (5) remains unchanged

$$\frac{d[I]}{dt} = K_1C^2 + K_3[II] - K_{-1}[I] \tag{7}$$

$$\frac{d[II]}{dt} = K_2C^2 - K_3[II] - K_{-2}[II] \tag{8}$$

where K_3 is the rate constant of the reaction of transformation of (II) into (I).

TABLE 4. Reaction between Furan and Maleic Anhydride in Deuteroacetone ($[F]_0$ = $[MA]_0$ = 0.05 mole fraction, 1 atm, 20°C)

Time, h	$[I]\cdot 10^3$	$[II]\cdot 10^3$	$[I]\cdot 10^3$	$[II]\cdot 10^3$	Time, h	$[I]\cdot 10^3$	$[II]\cdot 10^3$	$[I]\cdot 10^3$	$[II]\cdot 10^3$
	experimental		modeling			experimental		modeling	
1	0,55	0,46	0,49	0,54	15	11,3	1,11	9,92	0,94
2	1,03	0,77	1,11	0,85	20	12,0	0,71	12,5	0,82
3	1,55	1,00	1,82	1,02	31,2	15,7	0,65	17,0	0,63
4	2,34	1,31	2,56	1,11	66,3	24,5	0,36	24,8	0,37
5	2,80	1,30	3,31	1,15	119	31,0	0,63	29,2	0,25
5,15	3,30	1,05	3,42	1,16	263	32,3	0,16	31,5	0,19
9	6.96	0.84	6,20	1,11	282	30,0	0,15	31,6	0,19

TABLE 5. Rate Constants of the Reaction between Furan and Maleic Anhydride, 1 atm, 20°C

$K\cdot 10^5$ *	$[F]_0$ = $[MA]_0$ = 0.05 mole fraction		$[F]_0$=$[MA]_0$=0.15 mole fraction		$K\cdot 10^5$ *	$[F]_0$ = $[MA]_0$ = 0.05 mole fraction		$[F]_0$ = $[MA]_0$ = 0.15 mole fraction	
	deuteroacetone	deuteroacetonitrile	deuteroacetone	deuteroacetonitrile		deutero acetone	deuteroacetonitrile	deuteroacetone	deuteroacetonitrile
K_1	4,2	16,1	9,5	22,0	K_{-2}	2,5	0,22	0,86	8,3
K_2	7,7	14,7	9,0	15,9	K_3	10,7	9,6	10,0	4,4
K_{-1}	0,11	0,11	0,25	0,06	K_{over}^{av}	10,4	30,3	17,8	31,8

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*K_1, K_2, K_{over}^{av}, mole fraction$^{-1}\cdot$sec^{-1}; K_{-1}, K_{-2}, K_3, sec^{-1}.

The rate constants of the reactions in Eqs. (7) and (8) were found with the algorithm for a deformed simplex proposed in [7]. This algorithm was previously used successfully in solving optimization problems encountered in chemical studies in practice. The comparatively simple, but reliable Runge–Kutta–Feldberg algorithm of fourth–fifth order of precision was used for the numerical integration of the system of differential equations [8]. The experimental dependences of the concentrations of (I) and (II) on the reaction time were processed on an ES 1022 computer, and the calculations were performed with a doubled length of the machine word (8 bytes).

The minimum of the value of ln $(S_1 \cdot S_2)$, where S_1 and S_2 are the standard deviations of the curves of the solution for (I) and (II) from the corresponding experimental values, was selected as the criterion of the simultaneous optimization of two curves of the solution in searching for the rate constants. This criterion was selected for the following reasons.

The errors of the experimental data are normally distributed and consequently are characterized by the estimation of the standard deviations S_1 and S_2.

The entropy H_i of the normal distribution with an average value of zero and a dispersion of S_i^2, i = 1, 2, serves as a measure of the uncertainty of this distribution and is represented by Eq. (9)

$$H_i = -\int_{-\infty}^{+\infty} P_i(x) \ln P_i(x)\, dx = \ln (S_i \sqrt{2\pi e}) \tag{9}$$

where $P_i = \frac{1}{S_i \sqrt{2\pi}} e^{-\frac{x^2}{2S_i^2}}$ is the density function of the corresponding normal distribution.

Due to the additivity of the entropy, the overall indefiniteness of the approximation of the curves can be assumed to be equal to the sum of ln S_1 + ln S_2 = ln $(S_1 S_2)$ with a precision of up to the constant ln $(2\pi e)$ = 1 + ln (2π). The maximum of the amount of experimental information used in the kinetic model examined corresponds to the minimum of this "maximum information" criterion.

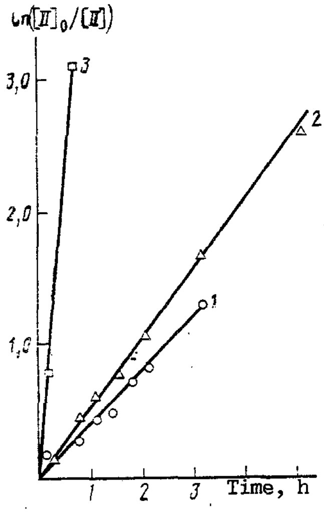

Fig. 1. Semilogarithmic anamorphoses of the decomposition of the endo-isomer, 20°C: 1) in deuteroacetone, $K_d = 11.3 \cdot 10^{-5}\ sec^{-1}$; 2) in deuteroacetonitrile, $K_d = 14.5 \cdot 10^{-5}\ sec^{-1}$; 3) in deuteroacetone, 40°C, $K_d = 129 \cdot 10^{-5}\ sec^{-1}$.

The data are reported in Table 4 and show that the calculated values of [I] and [II] in general totally satisfactorily coincide with the experimental values. The rate constants of the reactions determined by numerical integration and the average values of the overall reaction rate (K_{over}^{av}) calculated with the experimental data as in Table 1 are reported in Table 5.

As Table 5 shows, in all cases except for one, the values of K_3 are significantly higher than the values of K_{-2}, and $K_{over}^{av} \simeq K_1 + K_2$. It was found that K_3 is two times smaller than K_{-2} only for the reaction in deuteroacetonitrile with [F] = [MA] = 0.15 mole fraction. In three cases, K_1 is slightly higher than K_2, and $K_2 > K_1$ in only one case. The difference in rate constants K_1 and K_2 is apparently within the limits of the experimental error and K_2 and K_1 can be considered the same in all cases.

Since (II) is obtained at high pressures in amounts which are many times higher than its equilibrium concentration at atmospheric pressure, it is possible to directly determine the rate of decomposition of (II) at atmospheric pressure. Experiments were conducted in deuteroacetone (1400 MPa, 0.05 mole fraction of F and MA, 10 min, ~95% yield of isomers) and in deuteroacetonitrile (1000 MPa, 0.05 mole fraction of F and MA, 10 min, ~95% yield) for this purpose, and decomposition of (II) was then followed in an NMR spectrometer at 20 and 40°C. In both experiments at high pressures, the yields of (I) were close to the equilibrium yields at atmospheric pressure, and the concentration of (I) virtually does not change during decomposition of (II).

The dependence of $\ln \frac{[II]_0}{[II]}$ on time is shown in Fig. 1, and the rate constants of decomposition of (II) (K_d) were calculated with the slope of the lines. For 40°C, the value of K_d was only estimated with three points (including the zero point) due to the rapid decomposition of (II). The values of K_d obtained at 20°C differ little from the sum of $K_{-2} + K_3$ (see Fig. 1 and Table 5).

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