given in our previous work [5]. All the calculations were carried out on a PDP 11/23 minicomputer using the Enraf-Nonius SDP-PLUS program set.

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EFFECT OF PRESSURE ON THE DIELS-ALDER REACTION

BETWEEN FURAN AND METHYL ACRYLATE

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A study was carried out on the effect of pressure up to 1400 MPa on the Diels-Alder reaction between furan and methyl acrylate at 20°C. At atmospheric pressure, the reaction proceeds with 20% yield after two months, while it proceeds at 1400 MPa with 70% yield after 2.5 h. The observed volumetric activation effect $(-\Delta V_p^{\neq})$ of this reaction decreases relatively slightly with increasing pressure and its value at 0.1 MPa (20 cm³/mole) is markedly less than the change in volume upon reaction $(-\Delta V_0 = 29 \text{ cm}^3/\text{mole})$. The ratio of the endo and exo isomers formed is 2.6 and is independent of the pressure.

In previous work [1,2], we studied the effect of high pressure (P) on the Diels-Alder reaction between furan and maleic anhydride in deuteroacetone at 20°C. The results obtained at atmospheric pressure and at high pressure did not confirm the rule of predominant endo addition. The rates of formation of the endo and exo isomers were identical for all the conditions studied [1]. The volumetric activation effect at atmospheric pressure $(\Delta V_0^{\neq} = -30.5 \text{ cm}^3/\text{mole})$ determined from the dependence of the logarithm of the reaction rate constant (K_p) on P proved virtually the same as the change in volume in the results of other studies of the Diels-Alder reaction involving maleic anhydride as the active dienophile, for which $-\Delta V_0^{\neq} \geq -\Delta V_0$ [3-5].

The pressure effect on the Diels-Alder reaction between furan (Φ) and methyl acrylate (MAC) has not been studied quantitatively. There have only been reports that this reaction was carried out at pressures up to 1500 MPa for the purpose of synthesizing the corresponding adducts [6,7].

MAC is a much less active dienophile than maleic anhydride. Furthermore, endo isomer (I) is formed in excess in its reaction with Φ at ~20°C in comparison with exo isomer (II) [7,8].



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TABLE 1. Mean Experimental and Calculated Rate Constants for Reaction (1) at $20\pm1^{\circ}$ C ([Φ] = 0.670 mole fraction and [MAC] = 0.330 mole fraction)

	mole fraction ⁻¹ .sec ⁻¹			$\frac{K \cdot 10^{\circ}}{\text{mole fraction}^{-1} \cdot \text{sec}^{-1}}$	
P. MPa	experiment	calculation	P. MPa	experiment	calculation
0,1	6,89	6,56	700	766	880
50	8,45	9,56	800	1.800	1 550
100	15,5	13,9	900	2.670	2 620
200	26,6	29,4	ј 1080	至(160	4 300
300	72,3	61,3	1100	5 920	6 860
400	104	125	1200	12/300	10 750
500	279	249	1300	17/260	16.670
600	489	477	1400	24 700	25 750



Fig. 1. Dependence of $-\Delta V_p^{\neq}$ on P in the Diels-Alder reaction between furan and methyl acrylate at 20°C: 1) calculation using the mean reaction rate constants K_p , 2) calculation using the minimal K_p value at 0.1 MPa and maximal K_p value at 50 MPa, 3) calculation for the reaction between furan and maleic anhydride in deuteroacetone at 20°C [2], 4) dependence of ln K_p on pressure in reaction (1).

In the present work, the effect of pressure P up to 1400 MPa on the rate and composition of the adducts of reaction (1) at $\sim 20^{\circ}$ C was studied.

EXPERIMENTAL

The experiments were carried out on a cylinder-piston system in 1-1.5-cm³ teflon ampuls as described in our previous work [1] at 20±1°C. The furan sample was distilled at 30.5°C and stored over sodium. PMR spectrum in CDCl₃: δ 6.45 and 7.52 ppm.

A sample of MAC was distilled taking the fraction obtained at about 80°C and stored over $CaCl_2$. PMR spectrum in $CDCl_3$ (δ , ppm): 3.68 (CO_2CH_3), 5.75, 6.05, and 6.32 ($CHCH_2$).

The starting reaction mixture contained 0.33 mole fraction MAC and 0.67 mole fraction Φ and 0.5 mass % stable 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl radical in order to prevent the possible polymerization of MAC.

The rate constants of the second-order reaction were calculated relative to the yields of (I) and (II) determined by PMR spectroscopy in CDCl_3 on a Bruker WM-250 spectrometer from the relative integral intensities of the signals corresponding to the hydrogen atoms of the carbomethoxy groups (δ , ppm): 3.63 (I), 3.72 (II), and 3.75 (MAC).

In order to determine the volumetric activation effects at any P in the range studied, we used the spline approximation method for the experimental dependence of the logarithm of the reaction rate constant ln K_p on P by a cubic spline in accord with Eq. (2) taken from the transition state theory.

$$\left(\frac{\partial \ln K_{P}}{\partial P}\right)_{T} = -\frac{\Delta V^{2}}{RT}$$
(2)

In contrast to our previous work [2,9], we used a simpler algorithm [10] in the present work. The calculations were carried out on an Élektronika 85 computer. This algorithm does not take account of the "weights" of the experimental data and does not include a "strained" spline subprogram, while the number of discontinuity points of the third derivative is given by the operator itself. The discontinuity points are uniformly distributed over the abscissa (P axis). Three discontinuity points were given in the calculations at from 0.1 to 1400 MPa, while a minimal number of discontinuity points (2) was given in a more narrow range of P values, i.e., the pressure range was divided into three regions.

The change in volume ΔV_0 in the reaction at 0.1 MPa was determined by measuring the densities of MAC and the adduct mixture ((I):(II) = 2.6:1). The density of furan was taken from the data of Rabinovich [11]; $\Delta V_0 = -30.0 \text{ cm}^3/\text{mole}$ at 30°C.

RESULTS AND DISCUSSION

Table 1 gives the mean experimental rate constants and the corresponding values obtained by the spline approximation method for reaction (1). From two to four experiments were carried out, as a rule, at each pressure value. The reaction rate is low at atmospheric pressure and the adduct yield is only 20% after two months. However, this yield is much less than the equilibrium value, which is about 60% at 0.1 MPa and 20°C. The result was calculated using the rate constant for adduct formation (Table 1) and the overall rate constant for the decomposition of both isomers, which was evaluated as follows. A 2.5:1 mixture of isomers (I) and (II) was obtained at 1000 MPa after 65 h in 95% yield. The mixture was maintained at 20°C and atmospheric pressure for 6 and 48 days. In this case, the overall decomposition of the isomers was 1 and 9.2%, which corresponds to an overall decomposition rate constant of $2.3 \cdot 10^{-6} \sec^{-1}$.

In regard to reaction (1), we note that five experiments were carried out at 1400 MPa (one of these was carried out with equimolar amounts of Φ and MAC in yields of 17% after 0.5 h and 69% after 2.5 h. In these experiments, the mean square deviation $(o_{\overline{x}})$ from the mean value of K_p was 2%. Four experiments were carried out at atmospheric pressure with yields from 7 to 20%, $\sigma_{\overline{x}} = 8$ %. The mean (I):(II) isomer ratio from 50 measurements for P was 2.6±0.1 and was independent of the reaction time. This indicates that the yields of (I) and (II) under the conditions studied are determined by kinetic parameters since, as shown by Quellette et al. [12], (I):(II) = 1 under equilibrium conditions (P = 0.1 MPa) at 75, 63, and 40°C.

Figure 1 gives the dependence of $-\Delta V_p^{\neq}$ on P calculated by the spline approximation method using the data in Table 1 (curve 1). The value of $-\Delta V_0^{\neq}$ is 18.8 cm³/mole and is less than $-\Delta V_0^{\neq}$ by 10 cm³/mole. For comparison, the corresponding dependence is given for the reaction between Φ and maleic anhydride (MA) (curve 3) calculated with our data [2] by the spline approximation method using the same algorithm [10]. We note that the value obtained for $-\Delta V_0^{\neq} = 30.4 \text{ cm}^3/\text{mole}$ (curve 3) is the same as $-\Delta V_0^{\neq} = 30.5 \text{ cm}^3/\text{mole}$ calculated by the spline approximation and a different algorithm [2]. The dependence of $-\Delta V_p^{\neq}$ on P is also identical.

The dependence of $-\Delta V_p^{\neq}$ on P was also calculated using the least of the rate constants obtained for reaction (1) at atmospheric pressure (K₀) and greatest value of K_p at 50 MPa from a parallel experiment carried out in a system with measurement of the pressure within the reactor by a spring manometer. For other pressure values, the mean values of K_p given in Table 1 were given. Presumably, this method would give $-\Delta V_0^{\neq}$ approaching its maximum possible value. Curve 4 in Fig. 1 gives the dependence of ln K_p on P, while curve 2 gives the corresponding dependence of $-\Delta V_p^{\neq}$ on P; $-\Delta V_0^{\neq} = 21 \text{ cm}^3/\text{mole}$. The latter value is 2 cm³/mole greater than the value calculated over all the mean K_p values. Thus, the value of $-\Delta V_0^{\neq}$ for reaction (1) is significantly less than $-\Delta V_0$ and similarly less than $-\Delta V_0^{\neq}$ for the reaction between furan and maleic anhydride [2]. However, since $-\Delta V_p^{\neq}$ for reaction (1) decreases relatively slightly with increasing P, the $-\Delta V_p^{\neq}$ values at 300-400 MPa of both reactions become identical and equal to 17-18 cm³/mole (Fig. 1).

The rate constants of many Diels-Alder reactions at 0.1 MPa depend relatively slightly on the nature of the solvent. Thus, the value of ΔV_0^{\neq} corresponds to the change in volume upon the formation of the activated complex (AC) from the starting reagents, i.e., the solvation effects of the solvent may be neglected. In this case, similarity of the values of ΔV_0^{\neq} and ΔV_0 of the Diels-Alder reaction indicates the formation of a cyclic activated complex, whose volume is equal to the volume of the reaction product. If, on the other hand, $-\Delta V_0^*$ is markedly less than $-\Delta V_0$, we conclude the existence of a linear activated complex or the possibility that the reaction proceeds through both cyclic and linear activated complexes [13].

At first glance, the latter concept is suitable for explaining our data. While the reaction proceeds through both linear and cyclic activated complexes at 0.1 MPa, the fraction of the reaction proceed through a cyclic activated complex increases with increasing pressure since the volume of the cyclic activated complex is less than the volume of the linear activated complex [14]. Upon reaching some pressure (300-400 MPa for reaction (1)), the reaction will proceed predominantly through a cyclic activated complex. The small decrease in $-\Delta V_p^{\neq}$ with increasing pressure may be explained from this viewpoint since there is a positive contribution to the change in $-\Delta V_p^{\neq}$ with this change in mechanism.

We should note that if this mechanism is obtained, we should expect only a relatively small increase in the activation entropy (ΔS^{\neq}) with increasing pressure to 400 MPa. However, ΔS^{\neq} increases significantly as indicated by our measurements, which will be reported later. Thus, it is not excluded that the marked difference in the values of ΔV_0^{\neq} and ΔV_0 for reaction (1) and the slight decrease in $-\Delta V_p^{\neq}$ with increasing pressure are a consequence of the effect of the dynamic properties of the solvent on the reaction rate constant [9] not taken into account by the standard transition state theory equation (2) [14].

Thus, the validity of the structure of the activated complexes, is usually made on the basis of the ΔV_0^{\neq} values and their comparison with ΔV_0 , is doubtful even for reactions, in which solvation effects of the solvent may be neglected.

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