

EFFECT OF HIGH PRESSURE ON THE RATE CONSTANT OF THE DIELS-ALDER  
REACTION BETWEEN FURAN AND MALEIC ANHYDRIDE

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The effect of high pressure (up to 700 MPa) on the rate of the Diels-Alder reaction between furan and maleic anhydride has been investigated in deuterated acetone at 20°C. The volume effect of the reaction at atmospheric pressure is found to be  $\Delta V_0 = -28.0 \text{ cm}^3/\text{mole}$ . The rate constants for the formation, decomposition and isomerization of the products have been found by numerical integration. The volume of activation  $\Delta V^\ddagger$  in the pressure range studied has been determined from the observed dependence of  $\log k$  upon  $P$  by spline approximation and was found to be  $-30.5 \text{ cm}^3/\text{mole}$  at atmospheric pressure, close to the volume change in the reaction, which is consistent with the assumption of a conjugated cyclic transition state.

Results obtained previously [1] show that at atmospheric and high pressures the exo- and endo isomers [(I) and (II), respectively] are formed at approximately equal rates in the reaction between furan (F) and maleic anhydride (MA) in deuterioacetone or deuterioacetonitrile. The kinetic results at atmospheric pressure satisfy the scheme (1), which includes the isomerization of (II) into (I)

$$\frac{d[(I)]}{dt} = K_1 C^2 + K_3 [(II)] - K_{-1} [(I)] \quad (1a)$$

$$\frac{d[(II)]}{dt} = K_2 C^2 - K_3 [(II)] - K_{-2} [(II)] \quad (1b)$$

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

$$K_1 + K_2 = K_{\text{sum}}$$

where  $K_1$  and  $K_2$  are the rate constants for the formation of (I) and (II),  $K_{-1}$  and  $K_{-2}$  are the rate constants for the decomposition of (I) and (II) into the initial substances,  $K_3$  is the rate constant for the isomerization of (II) into (I), and  $C = [F] = [MA]$ .

If  $K_{-1} [(I)] + K_{-2} [(II)]$  is considerably smaller than  $(K_1 + K_2) C^2$ , Eq. (1c) becomes the equation for a second-order reaction with respect to the concentrations of the reactants F and MA and can be used in the usual way to calculate  $K_{\text{sum}}$ .

In the present paper, the results of a kinetic study of the reaction at pressures up to 700 MPa have been treated by the numerical integration of Eqs. (1a) and (1b) as described in [1]. The results of experiments at pressures above 700 MPa could not be treated in this way because the reaction rates are too high.

#### EXPERIMENTAL

The experimental procedure and the analysis of the reaction mixtures have been described [1]. In addition, measurements of the densities of approximately 10% solutions of F and MA in deuterioacetone at 20°C were used to determine the molar volumes of F and MA, giving  $\bar{V}_F = 70.87 \text{ cm}^3/\text{mole}$ ,  $\bar{V}_{MA} = 68.17 \text{ cm}^3/\text{mole}$ . In order to determine the molar volume of (I) a solution containing 0.050 mole fractions of F and MA in 0.90 mole fraction of deuterated acetone was kept at 20°C for 263 h to attain equilibrium, when (II) had practically disappeared and the content of (I) was 64.6 mole %. After measuring the density of this mixture  $\bar{V}_{(I)}$  was calculated

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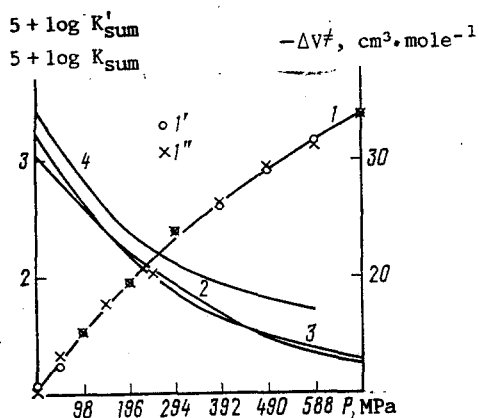


Fig. 1

Fig. 1. Diels-Alder reaction between furan and maleic anhydride in deuterioacetone at 20°C. Curve 1 has been drawn through the experimental points for  $\log K_{\text{sum}}'$  and  $P$  by the spline approximation method [1')  $\log K_{\text{sum}}' - P$ ; 1'')  $\log K_{\text{sum}}' - P$ ]; curves 2 and 3 represent the dependence of  $\Delta V^\ddagger$  upon  $P$  obtained by spline approximation for the experimental values (1') and (1''); curve 4 is the same dependence for the reaction of isoprene with maleic anhydride [3].

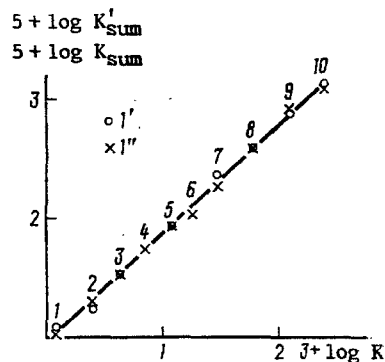


Fig. 2

Fig. 2. Dependence of  $\log K_{\text{sum}}'$  (1') and  $\log K_{\text{sum}}$  (1'') for the reaction between furan and maleic anhydride in deuterioacetone at 20°C on  $\log K_{\text{sum}}$  for the reaction between isoprene and maleic anhydride in ethyl acetate at 35°C [3].  $P$  in MPa: 1) 0.1, 2) 49, 3) 98, 4) 147, 5) 196, 6) 245, 7) 294, 8) 392, 9) 490, 10) 588.

Table 2 shows that in general  $K_1$  and  $K_2$  have similar values, except at atmospheric pressure ( $P = 0.1$  MPa) where  $K_2 = 1.8 K_1$  and at a pressure of 294 MPa, where  $K_1 = 1.7 K_2$ . These exceptions are probably within the maximum experimental errors. For example, at  $P = 0.1$  MPa the values of  $K_1$  and  $K_2$  are practically identical for  $[F]_0 = [MA]_0 = 0.150$  mole fraction in deuterioacetone and for  $[F]_0 = [MA]_0 = 0.050$  or 0.150 mole fraction in deuterioacetonitrile. Therefore, in determining the volume of activation (VA) at atmospheric pressure ( $\Delta V_0^\ddagger$ ) we have used not  $K_1$  and  $K_2$  separately but the sum  $K_1 + K_2$ , which as might be anticipated gives more reliable results. Moreover, in published investigations of Diels-Alder reactions  $\Delta V_0^\ddagger$  is usually calculated from the rate constant for the formation of all the isomers.

We shall write  $K_1 + K_2 \equiv K_{\text{sum}}'$ , as distinct from  $K_{\text{sum}}$ , determined from the second-order kinetic equation (see text and Table 1).

According to transition state theory (TST) the pressure dependence of the rate constant of a reaction is expressed by the equation

$$\left(\frac{d \ln K}{dP}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (2)$$

where  $R$  is the gas constant and  $T$ , the absolute temperature. The form of the relation  $\ln K = f(P)$  is not theoretically determined and the value of  $\Delta V^\ddagger$  is usually obtained by graphical or analytical differentiation of the observed dependence of  $\ln K$  upon  $P$ .

In the present study we have used the method of spline approximation (SA) for this purpose, first applied by Zhulin et al., [2] to the observed dependence of  $\log K$  upon  $P$ . A fourth-order approximating spline function was passed through the experimental points so as to minimize the sum of the squares of the deviations and at the same time to ensure the continuity of the first and second derivatives of the function  $\log K = f(P)$ . In other words, the SA method determines  $\Delta V^\ddagger$  and  $\partial(\Delta V^\ddagger)/\partial P$  for any value of  $P$  in the range investigated.

In Fig. 1, curve 1 has been drawn through the experimental points for  $\log K_{\text{sum}}'$  and  $P$  by the SA method and curve 2 shows the dependence of  $\Delta V^\ddagger$  upon  $P$ . Curve 2 corresponds to  $\Delta V_0^\ddagger = -30.5$  cm<sup>3</sup>/mole which is almost the same as the volume change for this reaction ( $\Delta V_0 = -28.0$  cm<sup>3</sup>/mole). The other curve 3 shows the dependence of  $\Delta V^\ddagger$  upon  $P$  obtained by spline approximation from the results for the dependence of  $\log K_{\text{sum}}$  upon  $P$ ; here  $\Delta V_0^\ddagger = -32.3$  cm<sup>3</sup>/mole.

From the point of view of the traditional application of TST to Diels–Alder reactions, the rates of which depend only slightly on the polarity of the solvent, the approximate equality of  $\Delta V_0^\ddagger$  and  $\Delta V_0$  indicates that the volume of the transition state is equal to the volume of the reaction products, i.e., the reaction takes place by a concerted mechanism.

In a study of another Diels–Alder reaction, between oxazole derivatives and acrylonitrile in various solvents at 20°C [2], it was found that  $-\Delta V_0^\ddagger$  was as a rule less than  $-\Delta V_0$ . For example, for reactions in  $\text{CH}_2\text{Cl}_2$  calculations for the range 1–700 MPa gave  $\Delta V_0^\ddagger = -21.3$  and  $\Delta V_0 = -29.0$   $\text{cm}^3/\text{mole}$ . However, this result may be due not to a change in the structure of the activated complex, but rather to the fact that at 20°C and comparatively low pressures the reaction rate may be limited by the stage in which the molecules are excited up to energies which exceed the energy barrier to reaction: an increase in pressure then raises the collision frequency and hence the rate at which the molecules acquire the necessary energy. With increasing pressure (and hence increasing collision frequency) the reaction may pass into the region in which Eq. (2) is applicable, so that the value of  $\Delta V^\ddagger$  determined experimentally in this region will correspond to the volume change on forming the activated complex. If the absolute value of this quantity exceeds the absolute value of the VA corresponding to the increase in collision number with increase in pressure, then the VA determined experimentally should change more slowly on increasing the pressure. A different type of variation of  $-\Delta V^\ddagger$  with P is in fact observed for the Diels–Alder reactions just mentioned [2].

For the reaction between F and MA the decrease in  $-\Delta V^\ddagger$  with increasing pressure is very considerable, as is shown by curves 2 and 3 in Fig. 1. Curve 4 shows for comparison the dependence of  $-\Delta V^\ddagger$  on P calculated from experimental data [3] by the SA method. These data refer to the Diels–Alder reaction between isoprene and maleic anhydride at 35°C at pressures up to 600 MPa and are among the most accurate of this kind. As can be seen from Fig. 1, the values of  $-\Delta V^\ddagger$  for the two reactions vary approximately in parallel, which is also confirmed by subsequent treatment of the results [4].

If we write Eq. (2) for both reactions (i = isoprene, f = furan) and divide one equation by the other we obtain

$$\frac{d \ln K_f}{d \ln K_i} = \frac{d \lg K_f}{d \lg K_i} = \frac{\Delta V_f^\ddagger T_i}{T_f \Delta V_i^\ddagger} \quad (3)$$

The linearity of the plot of  $\log K_f$  vs.  $\log K_i$  (Fig. 2) shows that  $\Delta V_f^\ddagger$  and  $\Delta V_i^\ddagger$  must change identically with P within experimental error. If we take  $\Delta V_i^\ddagger$  at atmospheric pressure as  $-34.3$   $\text{cm}^3/\text{mole}$  (curve 4, Fig. 1), then we find from the slope of the line in Fig. 2, taking Eq. (3) into account, that  $-\Delta V_f^\ddagger$  at atmospheric pressure is 31  $\text{cm}^3/\text{mole}$  which is 10% greater than  $-\Delta V_0$ .

On the basis of these results we may conclude that the reactions studied appear to be in the kinetic region, in which the VA reflects the change in volume in forming the activated complex, the volume of which is close to the volume of the reaction products.

According to the data in Table 2, the rate constant for the decomposition of the exo isomer ( $K_{-1}$ ) and the sum of the rate constants for the decomposition of the endo isomer and for its conversion into the exo isomer ( $K_{-2} + K_3$ ) are in general little affected by an increase in pressure which is consistent with the assumption of equal volumes for the activated complex and for the reaction products.

From the data given in Table 2, it is difficult to account for the fact that at pressures of 300 MPa and above the value of  $K_3$  remains small compared with  $K_{-2}$ , i.e., that at these pressures the endo isomer is transformed into the exo isomer only by first dissociating into the initial substances.

#### LITERATURE CITED

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