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EFFECT OF PRESSURE ON THE RATE OF [3,3]-SIGMATROPIC REARRANGEMENTS

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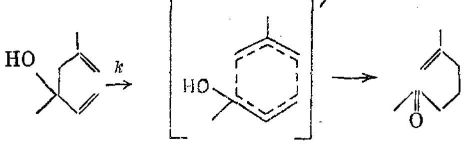
It is well known that with rare exceptions [1-3] a thermal [3,3]-sigmatropic shift takes place by a concerted mechanism through a transition state (TS) in which cleavage of the old and formation of the new σ bond take place place simultaneously. This mechanism is favored by the stereospecificity of the process, by the retention of optical activity during the reaction, by the negative entropy of activation, and also by the data from quantum-chemical calculations [4]. The effect of pressure on the rate of the Claisen [5, 6] and Cope [6] rearrangement has been investigated before; the negative values of the volume effect of activation $\Delta V_0^{\neq}$ represent an important argument in favor of a concerted mechanism for these reactions, since for the alternative biradical mechanism $\Delta V_0^{\neq} > 0$ [6, 7]. It is interesting to note that change in the sign of $\Delta V_0^{\neq}$ was observed in [7] with variation in the mechanism of the 1,4-shift from concerted to biradical. The aim of the present work was, first, to study the effect of pressure on the rate of the oxy-Cope rearrangement and, second, to describe quantitatively the effect of pressure on the rate constants of the [3, 3]-sigmatropic rearrangement.

DISCUSSION OF RESULTS

As subject for investigation we chose the thermal rearrangement of 3,5-dimethyl-1,5-hexadien-3-ol (I) to 6-methyl-6-hepten-2-one (II).



(I) (II)

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TABLE 1. Rearrangement of (I) to (II) (Yield, %) in N-Methylpyrrolidone $[(I)]_0$ = 0.54 M, 453°K, 5 h

Ratio of concentrations	p, MPa							
	10	100	250	400	500	600	750	1000
$[(I)]/[(I)]_0$	64,5	54,9	44,6	43,1	42,8	31,7	30,0	26,5
$[(II)]/[(I)]_0$	34,6	41,4	53,2	–	51,6	–	–	63,7
$([(I)]+[(II)])/[(I)]_0$	99,1	96,3	97,8	–	94,4	–	–	90,2

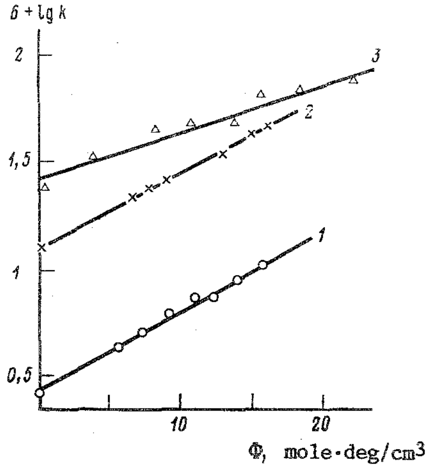

Fig. 1. The dependence of the logarithm of the rate constants on the parameter Φ: 1) Reaction I-1, good accuracy; 2) reaction II-2, good accuracy; 3) reaction III-1, satisfactory accuracy.

The reaction was realized in N-methylpyrrolidone, which makes it possible to reduce the fragmentation reaction to a minimum [8]. The results given in Table 1 show that the process is fairly selective at all pressures; the sum of (I) + (II) after the experiments amounts to not less than 90%, calculated on the initial compound (I). The existing tendency for this sum to decrease with increase in the pressure is due to the acceleration of the further transformations of the ketone (II). In a control test at a pressure of 1000 MPa and 453°K the concentration of (I) in the N-methylpyrrolidone solution decreased from 0.49 to 0.13 M in 5 h. Since the disbalance between the amounts of the unreacted (1) and formed (2) compounds under the reaction conditions is small and is due to the subsequent transformations of (II), the reaction rate constants were calculated from the initial and final concentrations of (I) (Table 1) by means of a first-order equation [4].

In order to calculate the $\Delta V_0^{\neq}$ values we obtained an equation which describes the effect of pressure on the rate of the Claisen and Cope rearrangements. Earlier [9] it was shown that the effect of pressure on the rate constants of nonionic liquid-phase reactions can be described by an equation of the general type:

$$\lg (k_p/k_0) = -\Delta V_0^{\neq}\Phi/T \tag{1}$$

in which

$$\Phi = \left[(1+\alpha)p - \frac{\alpha}{\beta}(1+\beta p)\ln(1+\beta p)\right]\Big/ R\ln 10 \tag{2}$$

where k is the rate constant and the subscripts p and 0 relate to pressures p and atmospheric pressure; α can be taken as equal to 0.170 [10]; β is parameter which has a constant value for related reactions.

In order to determine the parameter β we used the kinetic data which we obtained and also published experimental data for 12 [3,3]-sigmatropic shift reactions with more than three

TABLE 2. Calculation of the Volume Effects of Activation for the Three Versions of the [3,3]-Sigmatropic Rearrangement

Initial compound, solvent	No. of points	T., °C	$\Delta V_0^{\neq}$, calc. by Eq. (4)	Reference
I. Claisen rearrangement :				
1) Allyl phenyl ether, octan-1-ol	8	160	−16,6±0,5 *	[6]
2) The same, ethylene glycol	8	160	−14,4±0,5	[6]
3) The same, butylcellosolve	8	160	−12,2±0,7	[6]
4) The same without a solvent	5	160	−18,2±0,6	[6]
5) The same, decalin	8	160	−15,0±0,9	[6]
6) m-methoxyphenyl allyl ether, 65 percent ethanol—35 percent water	4	155,9	−19,8±1,7	[5]
7) Vinyl allyl ether, without solvent	5	130,4	−18,3±2,5	[5]
II. Cope rearrangement :				
1) 4-cyano-4-ethoxycarbonyl-5-ethyl-1,5-heptadiene, octan-1-ol	8	119	−14,1±0,8	[6]
2) The same, butyl cellosolve	7	119	−13,7±0,3	[6]
3) The same, decalin	7	119	−13,1±0,5	[6]
4) The same, propylene glycol	10	119	−13,2±0,4	[6]
5) The same, 1,4-dibromobutane	7	119	−14,1±0,5	[6]
III. Oxy-Cope rearrangement				
3,5-Dimethyl-1,5-hexadien-3-ol, N-methylpyrrolidone	8	180	−9,7±1,0	

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*The mean-square deviation is given as error.

†During the calculation the points for 450 and 690 MPa, which deviate greatly from the straight line, were omitted; it is not impossible that this is due to the freezing of the system (in the absence of the solvent).

experimental points (Table 2). The statistical treatment was realized according to [10] by minimization of the function M with respect to the parameter β:

$$M = \sum_{i=1}^{n} (g_i - 2.5) \ln S_{0_i} \tag{3}$$

Here i is the number of the reaction, g_i is the number of experimental points in reaction i, S_{0_i} is the standard deviation for Eq. (1), calculated by the method of least squares with fixed β. The obtained value of β was $7.12 \cdot 10^{-2}$ mPa^{-1}. Thus, the effect of pressure on the rate constant of the reactions is described by the following equation (with the p values expressed in MPa):

$$\lg (k_p/k_0) = -(\Delta V_0^{\neq}/T)[0.0611p - 0.125 (1 + 0.0712p) \ln (1 + 0.0712p)] \tag{4}$$

A check of the applicability of Eq. (4) by means of the tests proposed in [9] and the quality parameters of the calculation gave the following results. The linearity criterion was observed for all 13 reactions, and good accuracy was obtained in nine cases and satisfactory accuracy in four (on the accuracy scale adopted in [9]). A test was also made for random errors, i.e., for the values of B calculated by the method of least squares according to the equation:

$$\lg k_p = \lg k_0 - (\Delta V_0^{\neq}/T)\, \Phi + B\Phi^2 \tag{5}$$

The inequality B > 0 is observed in six cases out of 13, i.e., the frequency of its observance does not differ significantly from 0.5. The Abbe test (see [11]) is also observed; the value $\gamma = 0.9244$ was obtained, which is more than $\gamma^{\min} = 0.8028$. Consequently, Eq. (4) can be used to describe the effect of pressure on the rate constants of the [3,3]-sigmatropic shift reactions. For illustration Fig. 1 shows curves for the three dependences of the logarithms of the rate constants for the Claisen, Cope, and oxy-Cope rearrangements on the values of Φ calculated by means of Eq. (2) with the obtained value of β.

TABLE 3. Volume Effects of the Model Reactions

Initial compound	Model of TS	T., °C	ΔV_{mod}	Reference
I. Claisen rearrangement				
1) Vinyl allyl ether	Δ-2-Dihydropyran	160	−21,3	[12, 13]
2) Allyl phenyl ether	Chroman	160	−18,0	[12]
II. Cope rearrangement				
1) 4-Methyl-1,4-heptadiene	1,3-Dimethylcyclohex-1-ene	119	−19,8	[14]
2) 4,5-Dimethyl-1,5-heptadiene	1,2,4-Trimethylcyclohex-1-ene	119	−21,0	[14]
III. Oxy-Cope rearrangement				
1) 1,5-Hexadien-3-ol	1-Cyclohexen-3-ol	180	−21,9	[12]
2) 3,5-Dimethyl-1,5-hexadien-3-ol	1,3-Dimethyl-2-cyclohexen-1-ol	180	−19,3	[15, 16]

In [6] it was proposed to estimate the minimum value of $\Delta V_0^{\neq}$ for reactions of this type, by calculating the difference in volumes between the initial reagents and the cyclic compounds which model the transition state (ΔV_{mod}). The true TS must be looser compared with the cyclic model on account of the large bond lengths and must therefore have a larger volume. However, the choice of cyclic compounds as models of the TS in [6] was incorrect, since they contain two hydrogen atoms less than the initial reagents and, consequently, have a demonstrably smaller molecular volume. As models of the TS we chose the cyclic isomers of the initial compounds. From the available values of the density for the compounds at 20°C [12-16] we calculated their molar volumes and ΔV_{mod}. For the transition from 20°C to the higher temperatures we used the equation [9]

$$\Delta V_t = \Delta V_{20}\left[1 + \varkappa_{20}(t - 20)\right] \qquad (6)$$

where $\kappa_{20} = 4.4 \cdot 10^{-3}$ deg^{-1}. The obtained ΔV_{mod} values were given in Table 3.

We will compare the values of the volume effect of activation with ΔV_{mod}. For most of the Cope and Claisen rearrangements the $\Delta V_0^{\neq}$ values lie in the range between −12 and −18 cm^3/mole. (The exceptions are reactions I-6 and I-7, for which the accuracy of the calculation is low and the error in the calculation of $\Delta V_0^{\neq}$ is more than 1.5 cm^3/mole.) These $\Delta V_0^{\neq}$ values agree well with the minimum values (ΔV_{mod} = −18 to −21 cm^3/mole). However, for our investigated oxy-Cope rearrangement the difference between ΔV_{mod} and $\Delta V_0^{\neq}$ is relatively large; the $\Delta V_0^{\neq}$ value lies between $\Delta V_0^{\neq}$ and Δ_{mod}. In all probability, this result indicates significant looseness in the transition state of the reaction.

The value $\beta = 7.12 \cdot 10^{-2}$ MPa^{-1} obtained for the [3, 3]-sigmatropic rearrangements was almost 20 times larger than for the previously examined [17] processes of homolytic cleavage of the bonds, where $\beta = 0.36 \cdot 10^{-2}$ MPa^{-1}. This is an additional argument against the biradical and in favor of the concerted mechanism for the rearrangement.

Earlier [17 it was shown that the compressibility $\Delta V_0^{\neq}$ $(b = -(\partial \Delta V^{\neq}/\partial p)_{p=0}/\Delta V_0^{\neq})$ reflects the relative contributions from the free and natural volumes to $\Delta V_0^{\neq}$. The larger values of b must be characteristic of reactions which are characterized by a larger contribution from the free term to $\Delta V_0^{\neq}$. Since $b = \alpha\beta$ while the values were taken as identical for the various types of reactions [10], the differences in the b values lead to similar differences in the β values [12].

We will analyze the value $\beta = 7.12 \cdot 10^{-2}$ MPa^{-1}, obtained for the [3, 3]-sigmatropic shift, from this standpoint. This value is appreciably larger than $\beta = 4.94 \cdot 10^{-2}$ MPa^{-1} for the Diels–Alder reaction [9], the transition state of which is also cyclic. Consequently, the reactions are characterized by a larger contribution from the free volume to $\Delta V_0^{\neq}$. This result can be explained in the following way. Unlike the Diels–Alder reactions, which take place without cleavage of the σ bonds, in the transition state of the investigated reactions one σ bond is formed while another is broken. Bond cleavage is accompanied by an increase mainly of the natural volume; the contribution from the free volume during homolytic cleavage of the bond is small [17]. On the other hand, the formation of the new bond is characterized by a decrease both in the natural volume and in the free volume, the proportion of which is extremely significant. In all probability the contributions from the natural volume to $\Delta V_0^{\neq}$ during the formation and cleavage of the bonds are noticeably compensated by each other. This is consistent with synchronous cleavage and formation of the bonds in the transition state.

EXPERIMENTAL

The initial 3,5-dimethyl-1,5-hexadien-3-ol was obtained according to [18]. A solution of the alcohol (I) in N-methylpyrrolidone (0.54 M) was loaded into thin-walled Teflon tubes, which were placed in the cylinder of a high-pressure unit with heater [19].

The reaction mixture was analyzed by chromatography on a Biokhrom-1 instrument (100 × 0.3 cm glass columns with 5% of XE-60 on Chromaton N-AW-HMDS, nitrogen, 40 ml/min, flame-ionization detector, 85°C, internal standard dodecane). The calculations were made on a BÉSM-6 computer.

CONCLUSIONS

1. It was found that pressure has an accelerating effect on the rearrangement of 3,5-dimethyl-1,5-hexadien-3-ol to 6-methyl-6-hepten-2-one; the volume effect of the activation of this reaction at 180°C, equal to −10 cm^3/mole, indicates a concerted reaction mechanism and looseness in the transition state.

2. An equation is proposed which describes the effect of pressure on the rate constants of the Claisen and Cope rearrangements, the parameters of which are consistent with the fact that the cleavage and formation of the bonds takes place simultaneously in the reaction.

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