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Effects of Pressure on Organic Reactions. VI.* The Acid-catalyzed Rearrangement of Benzopinacol in Acetic Acid

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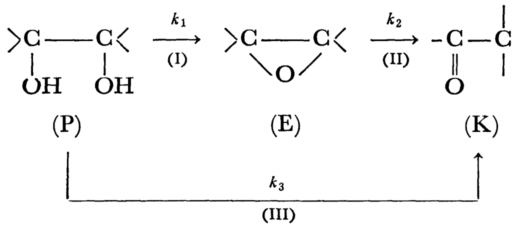
The rates of the acid-catalyzed rearrangements of benzopinacol and of tetraphenylethylene oxide in acetic acid have been measured in the range of 35—45 °C at pressures up to 983 kg/cm^2. It was proved under pressures that the rearrangement of pinacol proceeds through two routes, with three processes. The probable mechanism for each process has been discussed in the light of the activation parameters, particularly the volume parameters ($\Delta V^{\neq}$ and ΔV). Consequently, it may be probably inferred that the classical carbonium ion is an intermediate in the rearrangement of oxide, but not in the other two processes, *i.e.*, the conversion of pinacol to oxide and the direct rearrangement to pinacolone, and that the transition states in the two processes of rearrangement must be clearly distinguished.

The acid-catalyzed rearrangement of benzopinacol (P) to β-benzopinacolone (K) has already been studied kinetically by Gebhart and Adams[1] in acetic acid under atmospheric pressure. Their results indicate that P undergoes two concurrent reactions, consisting of three processes (I, II and III), as is shown in Scheme 1; one reaction is an indirect conversion to K through the intermediate formation of tetraphenylethylene oxide (E), and the other, a direct conversion. On the basis of the facts that correlations existed between the acidity function of the medium and the rate constant of each of the reactions involved, and that the entropies of activation ($\Delta S^{\neq}$) were found to be greatly positive, the authors suggested that any process of interest probably takes place by means of the A-1 mechanism, involving the formation of the classical carbonium ion.



Scheme 1

However, their reasoning seems not to be natural in giving the same transition state for different processes; further, the grounds stated by them are not necessarily helpful and decisive for determining the mechanism, as was pointed out by Whalley.[2] In order to find a more plausible explanation for the reaction mechanism, it is a useful tool to measure the volume changes of the reacting species attending the progress of the reaction.

In this paper, we will describe the effects of temperature and pressure on the acid-catalyzed rearrangements of P and E in acetic acid. Both the volume of activation ($\Delta V^{\neq}$) and the volume change of the complete reaction (ΔV) will be discussed together with the other parameters in order to understand the structures of the transition states for the processes under consideration.

Experimental

Materials. P prepared[3] was recrystallized from benzene and ligroin. E prepared[4,5] was recrystallized three times from a mixture of anhydrous ethanol and chloroform (10 : 1). K was prepared from P by boiling it with iodine in glacial acetic acid;[6] it was then recrystallized from benzene and ligroin. All the materials were identified by checking the mp and by elemental analyses. Commercial glacial acetic acid was distilled from potassium permanganate; the distillate was then dried over phosphorus pentoxide and redistilled. The stock solution of perchloric acid used as a catalyst was prepared by diluting commercial, analytical-grade 70% aqueous acid with the purified glacial acetic acid; it was titrated against a standard solution of sodium acetate in acetic acid by means of the potentiometric method. The other chemicals were of a reagent grade and were used without further purification.

Analytical Methods. Both P and K were analyzed by a small modification of the methods described by Gebhart and Adams.[1] The optical densities for the determination of K were measured with a Hitachi Model 139 UV-VIS spectrophotometer.

Kinetic Measurements. All the runs under atmospheric pressure and high pressures were carried out with a pressure apparatus described previously.[7] The reaction mixture was made up by adding the required amount of perchloric acid solution to a preheated acetic acid solution of P. The concentration of the reaction mixture was initially about 0.014 M in P and was 5.74×10^{-4} M in perchloric acid. The first sampling in the kinetic run was made after allowing one hour for thermal equilibrium to be attained; the sample removed was then analyzed for P and K. The same operation was repeated five times at intervals of one or two hours for each run. A similar procedure was also employed in the rearrangement of E at the same concentration of the catalyst as in the case of P. Six samples were taken during a kinetic run and were analyzed only for K. The initial concentration of E was determined from the amount of K produced at the completion of reaction after at least ten half-lives; it was approximately 5.6×10^{-3} M in all the runs.

Measurements of the Partial Molar Volumes. The partial molar volumes of the concerned substances in acetic acid were determined from density measurements according to the usual method. The pycnometers used were of the Ostwald-Sprengel type, with a capacity of about 20 ml.

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Results

The reaction manner shown in Scheme 1 can be expected to be true also at high pressures, as is illustrated in Fig. 1, which shows a typical plot of the concentration against the time for a run at 40 °C and 232 kg/cm^2.

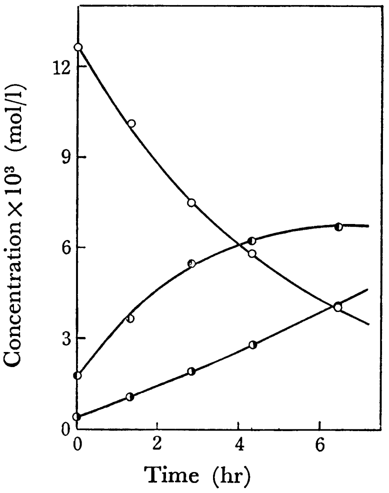


Fig. 1. Variation with time of the concentration at 40 °C and 232 kg/cm^2.
○: Benzopinacol, ◐: Tetraphenylethylene oxide, ◑: β-Benzopinacolone

Assuming that, in each of the three processes, the first-order rate law is obeyed exactly and that the reverse reaction from E to P does not occur, the concentration ratio, [E]/[P], at an arbitrary time, t, can be represented by the equation:

$$\frac{[E]}{[P]} = \left\{\frac{k_1}{k_p-k_2}+\frac{[E]_0}{[P]_0}\right\}\exp(k_p-k_2)t - \frac{k_1}{k_p-k_2}, \qquad (1)$$

where the k's are the rate constants for the processes shown in Scheme 1, k_p is the sum of k_1 and k_3, and $[E]_0$ and $[P]_0$ are the concentrations of E and P respectively at zero time in kinetics. Since k_p can be determined from the rate of the disappearance of P and k_2, from a separate run for the rearrangement of E to K under the same conditions, it is possible to evaluate k_1 from the slope or the intercept of a straight line obtained from a plot of [E]/[P] against $\exp(k_p-k_2)t$. Finally, k_3 can be calculated from this relation: $k_p = k_1+k_3$. As an example, the plot obtained from the results in Fig. 1 is illustrated in Fig. 2. From the fact that there is a satisfactory linear relationship between [E]/[P] and $\exp(k_p-k_2)t$, the validity of the above assumption is supported for the kinetics at high pressures; this is in agreement with the observations to be described below. The separation of k_p into two components, k_1 and k_3, was thus made from similar plots obtained under various conditions. The rate constants measured for the three processes are listed in Table 1. The mean error is within about a few per cent for k_p and k_2, and somewhat greater for k_1. However, it is apparent from the large difference in numerical value between k_1 and k_3 that the error for k_3 extracted from k_p is over ten times that for k_1. The second-order rate constants were obtained by dividing the first-order constants by the concentration of the catalyst, as corrected for the thermal expansion and compression of the solvent, taken by extrapolating the data in the literature.[8]

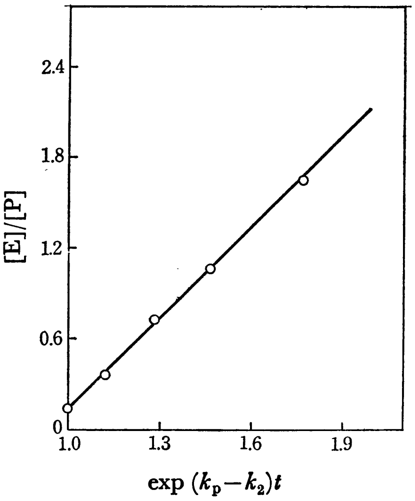


Fig. 2. A plot of [E]/[P] *vs.* $\exp(k_p-k_2)t$ at 40 °C and 232 kg/cm^2.

Table 1. Rate constants for each process, $k\times10^2$ (l·mol^{-1} s^{-1})

Temp. (°C)		Pressure (kg/cm^2) 1	232	489	735	983
35	k_p	4.23	4.25	4.38		
	k_1	4.02	3.93	3.92		
	k_2	2.11	2.41	2.70		
	k_3	0.21	0.32	0.46		
40	k_p	8.60	8.69	8.80		8.82
	k_1	8.02	7.90	7.71		6.76
	k_2	3.81	4.40	5.37	6.23	7.32
	k_3	0.58	0.79	1.09		2.06
45	k_p	17.5	17.7	18.0		18.1
	k_1	16.1	15.9	15.7		14.3
	k_2	6.92	8.11	9.71	11.5	13.6
	k_3	1.4	1.8	2.3		3.8

It may be also verified that, at high pressures, the rate observed cannot be explained in terms of a simplified reaction scheme neglecting the direct rearrangement of P. The concentration values at time t can be calculated from Eq. (1) and the over-all rate equation of P ($[P]=[P]_0e^{-k_pt}$), with the initial concentrations ($[P]_0$, $[E]_0$ and $[K]_0$) in kinetics. For example, in the reaction shown in Fig. 1, the values calculated by assuming that $k_3=0$ and $k_1=k_p$ in Eq. (1) are $[P]=5.83\times10^{-3}$ M, $[E]=6.67\times10^{-3}$ M, and $[K]=2.30\times10^{-3}$ M at $t=259$ min, while the corresponding values obtained from the values of the rate constants ($k_3\neq0$) given in Table 1 are $[P]=5.83\times10^{-3}$ M, $[E]=6.18\times10^{-3}$ M, and $[K]=2.79\times10^{-3}$ M. The experimental values are $[P]=5.81\times10^{-3}$ M, $[E]=6.19\times10^{-3}$ M, and $[K]=2.80\times10^{-3}$ M, in good agreement with the latter. The activation parameters evaluated in the usual way are summarized in Table 2. Our values of

TABLE 2. ACTIVATION PARAMETERS

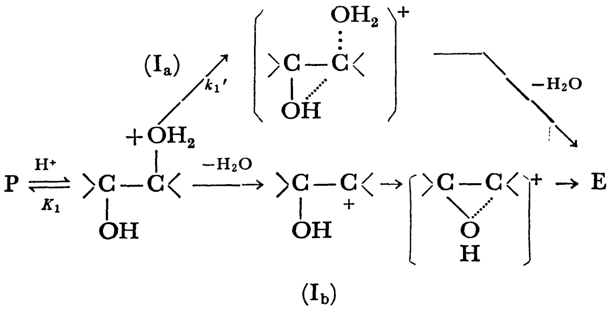
Parameter	Condition	Process I	Process II	Process III
$\Delta V^{\neq}$ (cm^3/mol)	35 °C	2.3	−15.5	−44
	40	2.1	−17.6	−34
	45	1.9	−18.6	−28
E_a (kcal/mol)	1 kg/cm^2	27.0	23.2	35
	232	27.1	23.8	32
	489	27.1	24.1	29
	735		24.1	
	983	27.5	24.4	24
$\Delta S^{\neq}$ [a] (cal/deg·mol)	1 kg/cm^2	20.6	7.0	41
	232	20.9	9.2	32
	489	20.9	10.5	23
	735		10.8	
	983	21.8	12.1	8

a) at 45 °C.

E_a and $\Delta S^{\neq}$ at 1 kg/cm^2 are somewhat different from those of Gebhart and Adams, but the difference seems to be due to the difference in reaction conditions, mainly in the temperature.

Discussion

Volume of Activation and Volume Change of the Reaction. Process I: Two mechanisms can be proposed for this process; they are shown in Scheme 2:



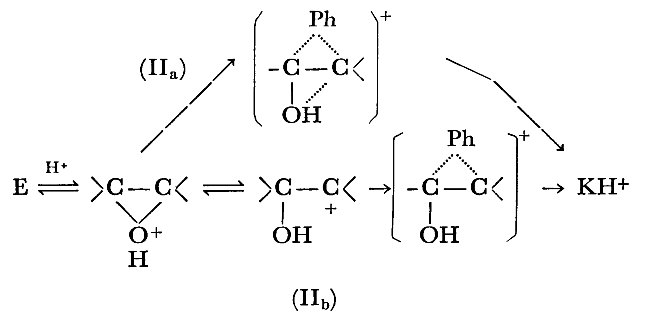
Scheme 2

where the molecules in square brackets denote the transition states. It is generally accepted that the volume of activation is negative in a simultaneous bond-forming and bond-breaking process. The $\Delta V^{\neq}$ in Mechanism (I$_a$) must be a small value near to zero, because the volume contraction described above offsets the increase in volume by the desolvation of solvent around an attacking hydroxyl group and by the dispersion of the electric charge arising from a ring structure formed partly in the transition state. Two possible rate-determining steps postulated in Mechanism (I$_b$), *i.e.*, the elimination of a water molecule and the formation of an oxide ring from a carbonium ion, will lead to a larger positive value of $\Delta V^{\neq}$ than the values observed, judging from the structural and electrostrictive contributions to the volume. The results for the hydrolysis of aliphatic epoxides reported by Koskikallio and Whalley,$^{9)}$ although different from the present case in the solvent used, give useful information which helps us to choose Mechanism (I$_a$). They concluded that the hydrolysis proceeds by the A-2 mechanism, in which a water molecule attacks the C$_\alpha$ atom from the back and synchronously the C$_\alpha$–O bond of the oxide ring stretches. The $\Delta V^{\neq}$ value for the reactions of the glycol to oxide becomes 2—3 cm^3/mol, calculating from the values of $\Delta V^{\neq}$ and of ΔV for the hydrolyses of ethylene and propylene oxides. The estimated values agree well with those for the present reaction, given in Table 2. This implies that Process I is similar to the reverse hydrolysis of epoxide and that it probably proceeds through Mechanism (I$_a$). The same conclusion may also be expected from the results for trimethylene oxide$^{10)}$ and epichlorohydrin.$^{10,11)}$

P probably consists of two conformers, the *trans*- and *gauche*-types being in equilibrium. The steric factor must largely participate in the reaction, so that in I$_a$ the *trans*-type is more favorable than the *gauche*-one. The results for the hydrolysis of 1,2-epoxy-1,2-dimethylcyclopentane$^{12)}$ support this theory.

Process III: This process is formally analogous to Process I except for the difference between the two attacking groups, hydroxyl and phenyl. As has been mentioned above, the precision of k_3 is very poor in comparison with that of the other constants, so that the activation parameters evaluated are not correct enough to permit an exact discussion. However, it is noteworthy that the values of $\Delta V^{\neq}$ are large and negative, while those of $\Delta S^{\neq}$ large and positive, as is shown in Table 2, in contrast to the results for aliphatic pinacol reported previously.$^{13)}$ Such anomalous findings, which have been also obtained for Process II with the same phenyl shift, suggest the participation of π-electrons of the shifting phenyl group besides the usual structural and electrostrictive contributions. This participation can be expected to result in much volume contraction despite the volume decrease being reduced by the charge delocalization, judging from the phenomena pointed out by le Noble *et al.*$^{14)}$ in solvolysis reactions. If it is permissible to make a further deduction, a random packing may be presumed to occur in the reorganization of the solvent environment due to the changing interaction between the reacting species and the solvent, accompanied by π-participation. These considerations, while leaving some logical doubt, suggest that a synchronous mechanism with a phenyl shift as the slow step, similar to I$_a$, is also probable in this process. Generally, the ring structure with an electric charge dispersed is stable in such a lower dielectric medium as acetic acid. In this mechanism, a *gauche*-conformer is suitable. The results of the rearrangements of 1,2-dimethylcyclopentane-1,2-diol$^{12)}$ and of *cis*- and *trans*-1,2-diphenylacenaphthene-1,2-diol$^{15)}$ support the above mechanism.

Process II: In the mechanism (II$_a$) shown in Scheme 3, in which the rate-determining cleavage of the C–O bond in the protonated oxide occurs simultaneously with the phenyl shift, there is necessarily a serious steric retardation and an additional energy is required for forming a bicyclic structure. A comparison of the activation parameters for this process with those for



Scheme 3

the others in Table 2 leads us to reject the mechanism as unacceptable. In an alternate mechanism (II_b), two slow steps, *i.e.*, the cleavage of the protonated oxide to the classical carbonium ion and the shift of the phenyl group in the resulting ion, may be postulated. In the mechanism with the former slow step, $\Delta V^{\neq}$ can be expected to be positive because of the stretching of the C–O bond in the oxide ring, accompanied by the dispersion of the ionic charge; this is evidently incompatible with the observed values, even if the volume change for the protonation step is permitted to be somewhat negative. The latter mechanism involves the formation of the carbonium ion besides the protonation in the pre-equilibrium step. The increase in volume by a cleavage of oxide ring is usually in the range from few to several cm^3/mol,[16)] but it is somewhat reduced if serious steric hindrance does not occur in the solvation of the resulting carbonium ion. The subsequent slow step can be thought to cause the fairly large contraction of the volume as a result of a ring closure, which is probably subject to such phenyl participation as has been described for Process III, although differing from that only in the absence of a leaving water molecule in the transition state. These considerations lead to the conclusion that this mechanism seems to explain the findings for $\Delta V^{\neq}$ more satisfactorily than the others discussed.

The schematic diagram in Fig. 3, which shows the volume changes along the reaction co-ordinate, provides strong evidence for the suggested structure of the transition state in Process II. In the curve illustrated for this process, the first small peak denotes the position of the carbonium ion as an intermediate. For simplification, there is no indication of any volume change for the proton-transfer step involved in each process. The volume change for that from H_3O^+ in an aqueous solution is usually small and negative,[17)] but in such a lower dielectric medium as acetic acid it becomes very negative as a result of the combination of ion-pair formation from dissolved acid and the action of $CH_3COOH_2^+$ as a proton-donor. The partial molar volumes of the concerned substances were determined in order to evaluate the volume change for the complete reaction for each process. The results are given in Tables 3 and 4. From this diagram, along with the values shown in Table 4, it is clear that there is an apparent difference in the volume of the transition state between Processes II and III. If Process II proceeds by way of II_b, as deduced, Process III cannot proceed by way of a mechanism forming a classical carbonium ion in agreement with the reasoning discussed above, because its transition state differs from that of II_b.

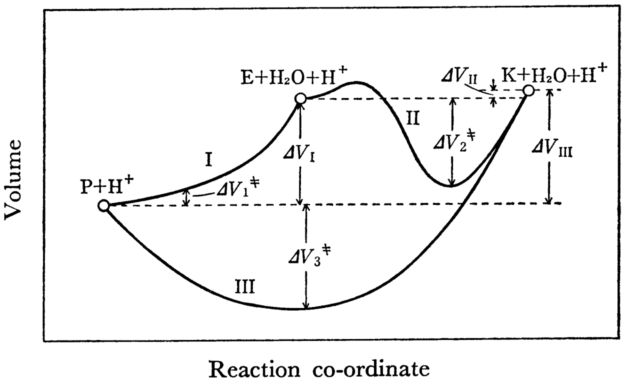


Fig. 3. Schematic diagram of the volume change along reaction co-ordinate at 40 °C.

Observed Volume of Activation and Its Constituent Terms. If one assumes that there is an equilibrium between the two conformers in P, of which the *trans*-type converts to E, and the *gauche*-one, to K, the over-all reaction rate for P can be expressed by the equation:

$$R = \frac{K_1 k_1' h_0}{1+K'}[\mathrm{P}] + \frac{K' K_3 k_3' h_0}{1+K'}[\mathrm{P}], \tag{2}$$

where K is the pre-equilibrium constant, and k', the rate constant for the slow step, and where the subscripts refer to the corresponding processes. K' is an equilibrium constant between the two conformers, and h_0, Hammett's acidity function ($H_0 = -\log h_0$). Therefore, the apparent second-order rate constants measured for the two processes may be given as follows:

$$k_1 = \frac{K_1 k_1'}{1+K'} \cdot \frac{h_0}{[\mathrm{HClO_4}]} \tag{3a}$$

and

$$k_3 = \frac{K' K_3 k_3'}{1+K'} \cdot \frac{h_0}{[\mathrm{HClO_4}]}, \tag{3b}$$

where $[HClO_4]$ is the concentration of the catalyst. From Eq. (3a), the observed volume of activation for Process I, $\Delta V_1^{\neq}$, is given as a composite quantity:

$$\Delta V_1^{\neq} = \Delta V_1 + \Delta V_1^{\neq\prime} + \frac{RT\partial \ln\{[\mathrm{HClO_4}]/h_0\}}{\partial P} + \frac{RT\partial \ln(1+K')}{\partial P}, \tag{4}$$

where ΔV_1 is the volume change for the pre-equilibrium step, and $\Delta V_1^{\neq\prime}$, the volume of activation for the step in which a hydroxyl group attacks the adjacent carbon atom, as is shown in Scheme 2. A similar equation can be also derived from Eq. (3b) for Process III. The fourth term on the right-hand side in Eq. (4) is likely to be negligible because the pressure dependence of K' is probably small; *i.e.*, there is no substantial difference in volume between the two conformers of P. The third term may be estimated approximately in the following way:[13,18)] if the change in h_0 with pressure can be assumed to be due to only the change in the concentration of the acid, then:

Table 3. Partial molar volumes at 40 °C

Substance	$\bar{V}$ (cm^3/mol)
P	310
E	317
K	318
H_2O	12.2

Table 4. Volume changes of complete reaction at 40 °C and 1 kg/cm^2

Process	ΔV (cm^3/mol)
I	19
II	1
III	20

$$\frac{RT\,\mathrm{d}\ln\{[\mathrm{HClO_4}]/h_0\}}{\mathrm{d}P} = RT\beta\left[1-\frac{\mathrm{d}\ln h_0}{\mathrm{d}\ln[\mathrm{HClO_4}]}\right], \qquad (5)$$

where β is the compressibility of the reaction mixture, assumed to be approximately that of the solvent. From the results of Ludwig and Adams,[19] $\mathrm{d}\ln h_0/\mathrm{d}\ln[\mathrm{HClO_4}]=1.05$ and so:

$$\frac{RT\,\mathrm{d}\ln\{[\mathrm{HClO_4}]/h_0\}}{\mathrm{d}P} = -0.12\ \mathrm{cm^3/mol}.$$

This value leads the third term apparently being insignificant under the present conditions, if the assumption for h_0 is actually valid. The dielectric constant of acetic acid increases with an increase in pressure, so the dissociation constant of perchloric acid in acetic acid will increase; this results in an increase in h_0. Hence, the assumption described above would not strictly hold for the present case. Since h_0 under high pressure has not yet, unfortunately, been measured, it is impossible to discuss this subject in detail. The value of $[\mathrm{HClO_4}]/h_0$ corrected for the compression and thermal expansion of the reaction mixture will decrease with an increase in pressure, judging from the fact that the concentration of the catalyst at 40 °C increases only 1.074 times[20] at 1000 kg/cm^2 compared with 1 kg/cm^2. This consideration brings about a larger negative value for the third term in Eq. (4) than -0.12 cm^3/mol; consequently, the net value of $(\Delta V_1+\Delta V_1^{\neq\prime})$ may be expected to have a larger value than that observed. Similar considerations must also be made for the volume of activation of Process III. Furthermore, since the acidity function term, Eq. (5), is present also in $\Delta V_2^{\neq}$ derived as a composite quantity for Process II, this term does not need to be considered when comparing the $\Delta V^{\neq}$ values of the processes.

Entropy of Activation. The results listed in Table 2 can be seen to satisfy roughly the pseudo-thermodynamic relationship:

$$(\partial\Delta V^{\neq}/\partial T)_P = -(\partial\Delta S^{\neq}/\partial P)_T. \qquad (6)$$

The partial derivatives of $\Delta V^{\neq}$ and $\Delta S^{\neq}$ for Process III are opposite in direction to those for the rearrangement of aliphatic pinacol.[13] The findings support the reasoning that the former proceeds through a mechanism different from that for the latter, described above. On the basis of the large positive values of $\Delta S^{\neq}$, Gebhart and Adams suggested that the classical carbonium ion is an intermediate in the processes under consideration. However, the problem concerning $\Delta S^{\neq}$ does not seem to be so simple because of the desolvation caused by the shift of the phenyl group.[21] It seems that the most significant part of the positive contribution to $\Delta S^{\neq}$ for Processes I and III is due to the desolvation in the step of the ring closure of the hydroxyl group or in that of the shift of the phenyl group, with the elimination of water. In addition, the phenyl participation proposed above seems likely to exert a more positive effect on $\Delta S^{\neq}$ for both processes, II and III. However, in the former the extent of the contribution must certainly be reduced because of the possible solvation of the carbonium ion; this is in qualitative agreement with the findings. Since the entropy change for the proton-transfer step is generally positive, but tends to have values over a relatively wide range dependent on the substrate,[17] those in the present cases are difficult to estimate.

From the results in Table 1, the proportion of the formation of K by the direct rearrangement (III) can be found to increase with the pressure, from 8 to 21% at 45°C between 1 and 983 kg/cm^2. Evidently, this increase results from the decrease in E_a with the pressure, as is shown in Table 2. Furthermore, a consideration according to the relationship given thermodynamically:

$$\Delta V^{\neq} = \left(\frac{\partial\Delta H^{\neq}}{\partial P}\right)_T - T\left(\frac{\partial\Delta S^{\neq}}{\partial P}\right)_T \qquad (7)$$

reveals that the effect of pressure on this process is not entropy-controlling, but enthalpy-controlling.

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