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High-pressure Kinetic Analysis of [1,9] Sigmatropy of 2-(Benzyloxy)-3-bromotropone to 2-(Benzyloxy)-7-bromotropone$^{1)}$

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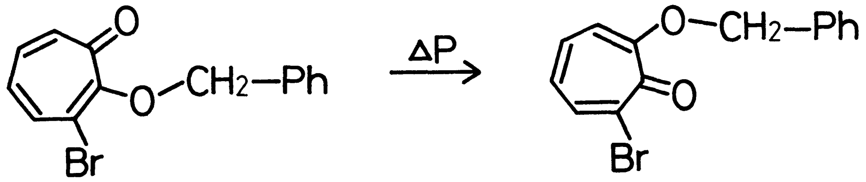
Thermal rearrangement of 2-(benzyloxy)-3-bromotropone to 2-(benzyloxy)-7-bromotropone, regarded to be the first [1,9] sigmatropic rearrangement, was analyzed by high-pressure kinetics. $\Delta V^{\neq}$ for the process were shown to be -11.1 and -10.1 cm^3 mol^{-1} in isopropylbenzene and 1-hexanol, respectively. The figures confirmed the concerted nature of the rearrangement, and were similar to various [1,5] sigmatropies of cyclopentadienes.

Recently, we have shown that,$^{2)}$ by the high-pressure kinetic analysis, the concerted [1,5] sigmatropy of the cycloheptatrienes does involve a loose transition state; reflecting a long-distance flight of the moving atom, the activation volume ($\Delta V^{\neq}$) was less negative than the typical [1,5] sigmatropies in cyclopentadienes$^{3)}$ and N-hydroxy-2-pyridone.$^{4)}$ In 1976, Harrison et al. discovered a benzyl group migration of 2-(benzyloxy)-3-bromotropone (**1**) to 2-(benzyloxy)-7-bromotropone (**2**), and proposed the [1,9] sigmatropy mechanism on the basis of activation energy criteria and no effect with the added radical trapping agent.$^{5)}$ Meanwhile, an important role of the [1,9] sigmatropy playing in the outstanding thermal reactions of troponoids$^{6-10)}$ has been noticed. For example, thermolysis of 4- and 6-isopropyl derivatives of 2-(2-furylmethoxy)tropones revealed the same product distributions to suggest a precedent [1,9] sigmatropy.$^{9)}$

In this paper, we will show the high-pressure experimental evidence for the concerted mechanism of the [1,9] sigmatropy in troponoids; reflecting a short-distance flight of the moving group, the $\Delta V^{\neq}$ are in the range of the [1,5] sigmatropies of cyclopentadienes, but not to that of cyloheptatrienes.



1 2

To us, **1** seems to be an appropriate substrate for the kinetic analysis. When isopropylbenzene (IP, ε=2.4) and 1-hexanol (HA, ε=13.3) solutions of **1** were heated at various temperatures (110—140 °C) under various pressures (1—1600 bar), the benzyl migration was taken place to form **2**, and the rates were measured by high-pressure liquid chromatography.

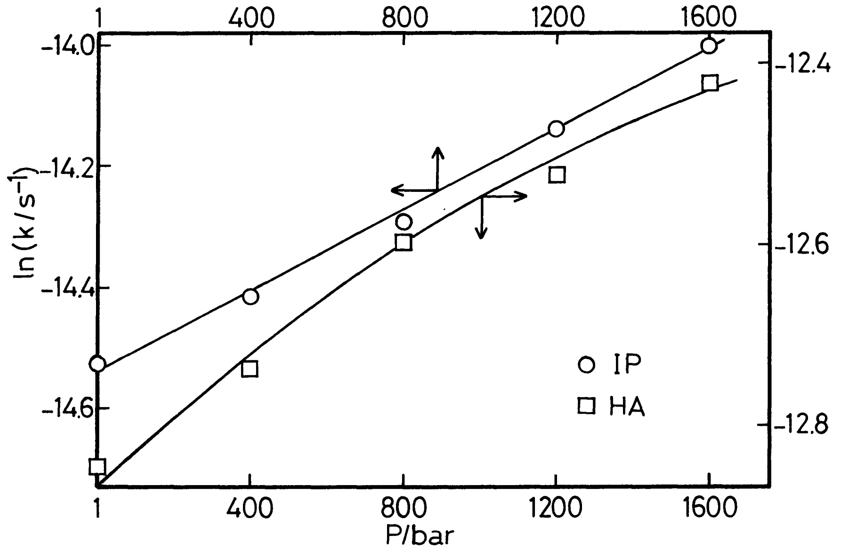


Fig.1. Pressure Dependence of lnk at 130 °C.

The results (Tables 1 and 2), show the rates in HA were about five times larger than those in IP. This magnitude of rate enhancement is just similar to that of the Diels-Alder reaction of isoprene to maleic anhydride, where the rates were about eight times larger in nitromethane (ε=38.6) than those in ethyl acetate (ε=6.03). This correlation shows that the [1,9] sigmatropy is little dependent on solvents, and can be interpreted as the concerted process. Furthermore, each activation parameter in both solvents shows a similar tendency to the typical [1,5] sigmatropy operating at the same temperature.[11] The activation entropies ($\Delta S^{\neq}$) obtained at 130 °C were -47 and -92 J mol^{-1} K^{-1} in IP and HA (Table 3), respectively; the stronger solvation, the larger negative $\Delta S^{\neq}$, being reasonable for the values expected as the concerted reactions. This indicated a weak, but not negligible contribution of polarized structure in the transition state. Again, the activation free energy ($\Delta G^{\neq}$) remained nearly constant in both solvents as the results of compensation effect between $\Delta S^{\neq}$ and $\Delta H^{\neq}$.12)

Table 1. The Rate Constants ($10^7k/s^{-1}$) at Various Pressures at 130 °C

P/bar		1	400	800	1200	1600
Solv	IP	4.91±0.16	5.48±0.01	6.19±0.18	7.24±0.08	8.28±0.03
	HA	26.6±0.4	29.3±0.8	33.8±2.0	36.2±0.5	40.4±2.2

Table 2. The Rate Constants ($10^7k/s^{-1}$) at Various Temperatures

Temp/°C		110	120	130	140
Solv	IP	1.17±0.02	2.94±0.16	4.91±0.16	25.1±0.1
	HA	4.22±0.07	10.0±0.3	26.6±0.4	49.2±0.3

The rates were accelerated by pressure; in IP, the logarithm of the rates were linear to the pressure (r=0.998), but in HA, the logarithm of the rates showed a curvature. One reason of this behavior must be a contribution of a somewhat polarized transition state, as could be seen in $\Delta S^{\neq}$, to alter the degree of solvation in HA under high pressures.

Table 3. Activation Parameters at 130 °C

	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
IP	128±4	-47±11	147±9
HA	106±3	-92±7	143±5

Thus, $\Delta V^{\neq}=-RT(\partial \ln k/\partial P)_T$ were evaluated by using a linear function in the case of IP and a quadratic function in the case of HA, respectively, to obtain $\Delta V^{\neq}$ being -11.1±0.7 in IP and -10.1±0.5 cm^3 mol^{-1} in HA. The solvent effect on $\Delta V^{\neq}$ was very little and the above-mentioned solvation effect to the transition state was very weak. However, $\Delta V^{\neq}$ obtained in this reaction were very close to those of [3,3] and typical [1,5] sigmatropies other than that of cycloheptatrienes, which should require a long-distance flight of the moving atom. Consequently, $\Delta V^{\neq}$ is indicating the tight-cyclic but not loose biradical-like transition state for this reaction.

Present results of the pressure effect support that the themal rearrangement of **1** to **2** must proceed via the concerted mechanism, that must be a symmetry-allowed [1,9] sigmatropy.

In conclusion, from the solvent, temperature, and pressure effects, the rearrangement of **1** to **2** is undoubtedly the concerted [1,9] sigmatropy. Moreover, since the activation volumes of the sigmatropies have shown to be dependent on the flight distance of the moving groups or atoms,2) the high-pressure kinetics can provide good informations to judge the concerted nature of the thermal processes in general.13)

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