ON THE COMPARISON OF THE THEORETICAL AND EXPERIMENTAL DATA FOR THE KINETICS OF THE COPE REARRANGEMENT OF 1,5-HEXADIENE*

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The Cope rearrangement of 1,5-hexadiene is treated as a process passing through an intermediate; this feature was verified by recent quantum-chemical studies. Relationships are derived between the characteristics of the both partial activation processes involved and the experimental data (which characterize the overall process). It is shown that proper consideration of the kinetic consequences of the existence of the intermediate might help to eliminate the recently reported large difference between the MINDO/3 activation entropy and the experimental entropy for the boat pathway for the Cope rearrangement.

Recently, considerable work has been done on the theoretical study[1-4] of the mechanism of the Cope rearrangement[5] (for a general discussion of contemporary knowledge on the Cope rearrangement, see[6,7]). MINDO/2 and MINDO/3 results[3,4] have verified the existence of two[8] distinct paths, each with an intermediate[9]. In terms of stationary points on a potential energy hypersurface, this implies the existence of two different ways interconnecting superimposable energy minima (I, I′), each passing through a pair of superimposable transition states (II, II′), and one local minimum (III) separating them (Fig. 1). The transition states are conventionally called chair and boat, the first being of lower energy. The overall experimental kinetic parameters of the (I) → (I′) rearrangements of a partially deuterated biallyl for the chair[9] and the boat[10] pathways were obtained using the kinetic scheme of forward-reverse reactions[9] (FRR) and of a single forward reaction[10] (FR), respectively. The formation of an intermediate (III) was not considered explicitly. However, quantum-chemical calculations[3,4] yielded only the activation parameters $\Delta X_1^{\ddagger}$ ($X = H, S$) for the simple rate process (I) → (III). The object of this report is to note that mere conventional comparison of theoretical $\Delta X_1^{\ddagger}$ values with the overall experimental activation parameters may generally be quite misleading for processes of this type.

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Formulae

The kinetic problem corresponding to Fig. 1 is described by a system of differential equations which are solvable in closed form[11] without introduction of simplifying assumptions on the system itself. However, here the following presumptions were introduced for the whole kinetic problem: (*i*) zero concentration of species (III) and (I′) at time $t = 0$, (*ii*) mutual independency of the two reaction pathways, (*iii*) neglect of tunnelling, (*iv*) neglect of an isotope effect when comparing with the experiment, and (*v*) full separability of the motions of the individual (rigid) stationary points involved (this assumption cannot be, however, fulfilled for an intermediate of very low stability). Comparison of the results[11] with the form of the integrated rate equations used in the evaluation of the experimental data[9,10] leads to the following relationships between the effective values (*i.e.* theoretical analogues) of the rate constants measured in the experiment and rate constants k_1 and k_2 corresponding to the simple rate processes (I) → (III) and (III) → (I), respectively (within our study, possible consequences caused by use of absorbances instead of concentrations in an experiment are ignored):

$$k_{\mathrm{eff}}^{2} = \frac{k_1}{2} - \frac{1}{2t} \ln \left[1 + \frac{k_1}{2k_2} \left(1 - \mathrm{e}^{-2k_2 t} \right) \right] \qquad (1)$$

$$k_{\mathrm{eff}}^{1} = k_1 - \frac{1}{t} \ln \left[\frac{1}{2} + \frac{k_1 + k_2}{k_1 + 2k_2} \mathrm{e}^{k_1 t} - \frac{k_1}{2(k_1 + 2k_2)} \mathrm{e}^{-2k_2 t} \right]. \qquad (2)$$

Here, k_{eff}^{2} denotes the effective rate constant for (I) → (I′) obtained when the FRR scheme was applied[9] to the observables, while k_{eff}^{1} is obtained[10] using the FR scheme. Both effective rate constants generally depend on time t. In the limiting case, $k_2 \gg k_1$, the value of k_{eff}^{2} reduces to time independent $k_1/2$ while k_{eff}^{1} remains time-dependent.

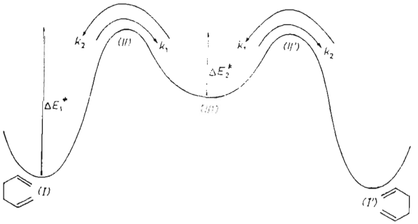

FIG. 1

Reaction profile diagram for the chair and boat Cope rearrangements of 1,5-hexadiene

CHART I

Analytic formulae for time dependences of effective values of activation enthalpies $\Delta H^{\neq 2}_{\mathrm{eff}}$ and $\Delta H^{\neq 1}_{\mathrm{eff}}$ and activation entropies $\Delta S^{\neq 2}_{\mathrm{eff}}$ and $\Delta S^{\neq 1}_{\mathrm{eff}}$

$$\Delta H^{\neq 2}_{\mathrm{eff}} = -RT + \frac{k_1}{k^2_{\mathrm{eff}}}\left(\frac{1}{2} - \frac{1 - \mathrm{e}^{-2k_2t}}{P_1}\right)(RT + \Delta H_1^{\neq}) -$$

$$- \frac{k_1}{k^2_{\mathrm{eff}} P_1}\left((2k_2t + 1)\,\mathrm{e}^{-2k_2t} - 1\right)(RT + \Delta H_2^{\neq}),$$

where $P_1 = 4k_2t + 2k_1t(1 - \mathrm{e}^{-2k_2t})$

$$\Delta H^{\neq 1}_{\mathrm{eff}} = -RT + \frac{k_1}{k^1_{\mathrm{eff}}}\left[1 - \frac{1}{tP_2}\left((k_2 + (k_1^2 + 3k_1k_2 + 2k_2^2)\,t\right) .\right.$$

$$\left. .\,\mathrm{e}^{k_1t} - k_2\mathrm{e}^{-2k_2t}\right)\bigg](RT + \Delta H_1^{\neq}) +$$

$$+ \frac{k_2}{k^1_{\mathrm{eff}} t P_2}\left[k_1\mathrm{e}^{k_1t} - (k_1 + (k_1 + 2k_2)\,k_1t)\,\mathrm{e}^{-2k_2t}\right](RT + \Delta H_2^{\neq}),$$

where $P_2 = (k_1 + 2k_2)^2/2 + (k_1 + 2k_2)(k_1 + k_2)\,\mathrm{e}^{k_1t} - (k_1/2)(k_1 + 2k_2)\,\mathrm{e}^{-2k_2t}$

$$\Delta S^{\neq 2}_{\mathrm{eff}} = \frac{1}{T}\,\Delta H^{\neq 2}_{\mathrm{eff}} + R\ln\left(\frac{h}{kT}\,k^2_{\mathrm{eff}}\right)$$

$$\Delta S^{\neq 1}_{\mathrm{eff}} = \frac{1}{T}\,\Delta H^{\neq 1}_{\mathrm{eff}} + R\ln\left(\frac{h}{kT}\,k^1_{\mathrm{eff}}\right)$$

$$k_1 = \frac{kT}{h}\,\mathrm{e}^{\Delta S_1^{\neq}/R}\,\mathrm{e}^{-\Delta H_1^{\neq}/R/T}$$

$$k_2 = \frac{kT}{h}\,\mathrm{e}^{\Delta S_2^{\neq}/R}\,\mathrm{e}^{-\Delta H_2^{\neq}/R/T},$$

where T denotes temperature and h, k, and R are the fundamental constants.

Starting from Eqs (*1*) and (*2*), somewhat complicated but still analytic formulae for the time dependences of the effective values of the activation enthalpy ($\Delta H^{\ddagger 2}_{\text{eff}}$ or $\Delta H^{\ddagger 1}_{\text{eff}}$) and entropy ($\Delta S^{\ddagger 2}_{\text{eff}}$ or $\Delta S^{\ddagger 1}_{\text{eff}}$) can be derived (Chart I).

DISCUSSION AND CONCLUSIONS

Five variable parameters appear in our formulae (for a given temperature): $\Delta X^{\ddagger}_{1}$, $\Delta X^{\ddagger}_{2}$ (the latter corresponding to rate process (III) → (I)), and the time of observation. Of all these parameters, the $\Delta H^{\ddagger}_{2}$ term represents a key indefinite value. The MINDO/3 values[4] of $\Delta X^{\ddagger}_{1}$ at a temperature of 523 K (a value representing the experimental temperature intervals[9,10] well) can be considered reliable enough[12,13]. However, there is a vagueness in the $\Delta H^{\ddagger}_{2}$ terms due to orbital degeneracy[3,4]. Three MINDO/3 estimations of the $\Delta H^{\ddagger}_{2}$ values can be found[4] (*cf.*[12-14]) in the literature (11·3, 53·1, 115·9 and 6·7, 79.5, 142·3 kJ mol^{-1} for the chair and the boat pathway, respectively). In addition, the values of $\Delta H^{\ddagger}_{2}$ taken from the interval between the highest estimation of $\Delta H^{\ddagger}_{2}$ and the value of $\Delta H^{\ddagger}_{1}$ were also treated. No data on $\Delta S^{\ddagger}_{2}$ have been reported, but the region of its values is supposed to be rather narrow (*cf.*[15]). Considering symmetry, $\Delta S^{\ddagger}_{2}$ was set equal to 0·0 and $-9{\cdot}6$ J mol^{-1} K^{-1} for the boat and the chair pathway, respectively. Results of the $\Delta H^{\ddagger}_{2}$ parameter variation are sketched in Figs 2 and 3 for the chair and boat pathways, respectively.

In the $\Delta H^{\ddagger}_{2}$ region studied, intermediate (III) manifests itself in the $\Delta X^{\ddagger 2}_{\text{eff}}$ values rather insignificantly for the chair pathway, especially for the $\Delta H^{\ddagger 2}_{\text{eff}}$ term. The $\Delta S^{\ddagger 2}_{\text{eff}}$ term (in the relevant time interval[9]) is somewhat lower than $\Delta S^{\ddagger}_{1}$ by a value close to $R \ln 2$. Nervetheless, the agreement[4] between the MINDO/3 and experimental data[9] does not change substantially if intermediate (III) is considered.

On the other hand, for the boat pathway the differences between the $\Delta X^{\ddagger 1}_{\text{eff}}$ and $\Delta X^{\ddagger}_{1}$ values are considerable (except for the lowest estimates of $\Delta H^{\ddagger}_{2}$). For the sake of unification, the time interval in Fig. 3 was chosen the same as that in Fig. 2, *i.e.* close to the region given in ref.[9] No information concerning the time region was given in ref.[10] Although (according to ref.[16]) the interval chosen in fact differs from the region used in ref.[10], the qulitative features of Fig. 3 are not influenced by this fact. Clerly, values of $\Delta H^{\ddagger}_{2}$ can be chosen that lead to satisfactory agreement between the theoretical $\Delta X^{\ddagger 1}_{\text{eff}}$ terms and experimental data[10]. Thus, the only case of serious disagreement between the MINDO/3 and experimental activation entropies for processes studied so far[12,13] might be explained in this way. The required $\Delta H^{\ddagger}_{2}$ values would however exceed the above-mentioned estimates, that would essentially be connected with an increase in the stability of intermediate (III) and with a deepenning of the time dependency of the effective rate constant (*2*). Nevertheless, even in the case of the highest $\Delta H^{\ddagger}_{2}$ term used in our study, the equilibrium constant $K = k_1/k_2$ is still sufficiently low (about 10^{-4}). It can be concluded that our analysis supports the existence of intermediate (III) indicating, however, a need of a more precise quantum-chemical evaluation of the $\Delta H^{\ddagger}_{2}$ term itself.

Finally, there may still be one important feature of the Cope rearrangement to consider: the proposed fact[3,4] that intermediate (III) might be common to both pathways (and even to the rearrangement of bicyclo[2.2.0]hexane). The study of an extension of the presented kinetic scheme to one generalized in this way is in progress.

Even if our approach were only partly helpful as far as the specific discrepancy between the MINDO/3 and experimental data for the boat pathway is concerned, there remains a clear warning in relation to meaningful comparisons of experimental

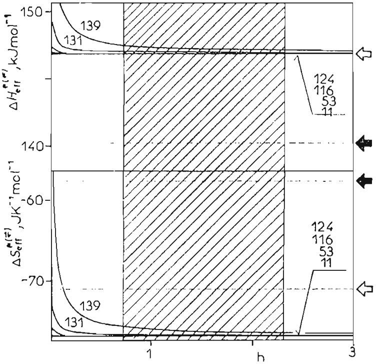

FIG. 2

Time dependences of the effective activation enthalpy $\Delta H^{\ddagger 2}_{\text{eff}}$ and entropy $\Delta S^{\ddagger 2}_{\text{eff}}$ for the chair pathway of the Cope rearrangement of 1,5-hexadiene at 523 K; the indices on the curves denote the $\Delta H^{\ddagger}_{2}$ values in kJ mol^{-1}; the bold arrow indicates the experimental value[9], the vacant arrow the $\Delta X^{\ddagger}_{1}$ value[4], and the hatching the experimental time region[9] (in the Figure, $\Delta H^{\ddagger 2}_{\text{eff}}$ and $\Delta S^{\ddagger 2}_{\text{eff}}$ is labelled as $\Delta H^{\ddagger(\rightleftarrows)}_{\text{eff}}$ and $\Delta S^{\ddagger(\rightleftarrows)}_{\text{eff}}$, resp.).

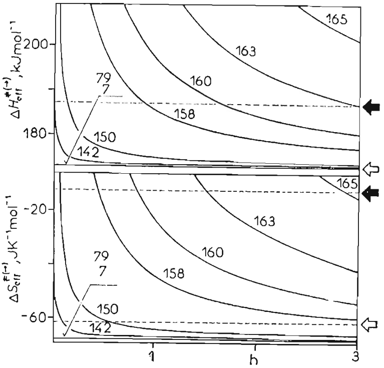

FIG. 3

Time dependences of the effective activation enthalpy $\Delta H^{\ddagger 1}_{\text{eff}}$ and entropy $\Delta S^{\ddagger 1}_{\text{eff}}$ for the boat pathway of the Cope rearrangement of 1,5-hexadiene at 523 K; the indices on the curves denote the $\Delta H^{\ddagger}_{2}$ values in kJ mol^{-1}; the bold arrow indicates the experimental value[10], the vacant arrow the $\Delta X^{\ddagger}_{1}$ value[4] (in the Figure, $\Delta H^{\ddagger 1}_{\text{eff}}$ and $\Delta S^{\ddagger 1}_{\text{eff}}$ is labelled as $\Delta H^{\ddagger(\rightarrow)}_{\text{eff}}$ and $\Delta S^{\ddagger(\rightarrow)}_{\text{eff}}$, resp.).

and theoretical values in similar situations. Recent quantum-chemical studies have disclosed[17-21] a number of rate processes which are relized through an (relatively stable) intermediate (or even intermediates). According to the results presented, due respect should be paid to this fact when comparing such theoretical data with experimental values. However, the procedure suggested is useful for an intermediate of non-negligible stability; its behaviour for $k_2 \to \infty$ needs a further investigation[22].

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Note added in proof: Since the time when this work was completed (Sept. 1980) further progress appeared in the field[23]. A two-step generalization of reaction scheme was suggested[24,25] and corresponding overall $\Delta H^{\ddagger}_{eff}$ and $\Delta S^{\ddagger}_{eff}$ terms derived. Moreover, a difference in treating the situations, where either the concentration of absorbance data are available was pointed out[24,26]. Finally, a combination of the existing experimental and theoretical information on Cope rearrangement of 1,5-hexadiene (*via* the boat pathway) has shown[26] that this reaction should involve an intermediate of very low stability.