  Bull. Chem. Soc. Jpn., 60, 977—980 (1987)

High-Pressure Kinetics of the (6+4)π Cycloaddition of Tropone with 2,3-Dimethyl-1,3-butadiene, an Acyclic Diene. The Temperature and Solvent Effects

Shigeru SUGIYAMA and Hitoshi TAKESHITA*
Research Institute of Industrial Science, 86, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816
(Received July 30, 1986)

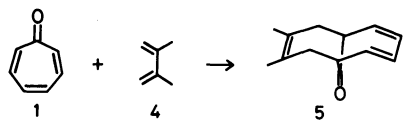
By a high-pressure kinetic analysis in isopropylbenzene, 1,4-dioxane and *N,N*-dimethylformamide, the activation parameters for the (6+4)π cycloaddition reaction of tropone with 2,3-dimethyl-1,3-butadiene were determined. The findings support the concerted nature for the Woodward-Hoffmann rule-allowed thermal addition reaction of tropone. A secondary orbital interaction, which was used to predict the correct stereochemistry of the adducts, exerted no effect on the volume profile.

Previously, we confirmed the concerted nature of the (6+4)π cycloaddition of tropone (**1**) to 1,3-cyclohexadiene (**2**) by a kinetic analysis regarding pressure and temperature effects.[1] The activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$), showing no anomaly, were consistent with those obtained by Tanida and Pfaendler in a reaction of **1** with cyclopentadiene (**3**) under ordinary pressure.[2] Moreover, the activation volume ($\Delta V^{\neq}$) and the volume profile ($\Delta V^{\neq}/\Delta V$, where ΔV represents reaction volume) were also in accord with the concerted cycloadditions.

Herein, we wish to describe the pressure and temperature effects on the cycloaddition of **1** with 2,3-dimethyl-1,3-butadiene (**4**), an acyclic diene, which is conformationally mobile in solutions.[3] The volume profile of the (6+4)π cycloaddition with such a combination has not been investigated; the rate constant showed a little different pressure dependence from our previous combinations.[1,4,5]

Experimental

The purity of **1**[6] was more than 99.0% in respect to a gas-liquid chromatographic analysis. A commercial sample of **4**, from Aldrich Japan Co. Ltd., Tokyo, was purified by distillation over $NaBH_4$ under an N_2 atmosphere. The solvents, isopropylbenzene (cumene), 1,4-dioxane (dioxane) and *N,N*-dimethylformamide (DMF), were purified as stated previously.[1] The adduct (**5**), a pale yellow oil, was purified by repeated silica-gel column chromatography, and showed pertinent figures of elemental analysis. Its IR, NMR, and mass spectra were also consistent with the structure.



Scheme 1.

The same instruments were used for a density measurement and kinetic experiment as those in previous studies.[1,5] The progress of the reaction was monitored by observing an increase of product (**5**) by means of high-pressure liquid chromatography (Nippon Waters' Model 244 Apparatus).

Results and Discussion

Activation Parameters. Although extensive studies have been carried out concerning both theoretical and synthetic aspects of the (6+4)π cycloaddition of **1**, there have been few kinetic studies, even under atmospheric pressure on the subject (e.g., those by Tanida et al.[2] and ours[1]). This could be due to an instability of the popular cycloaddend, **3**, toward spontaneous dimerization. In this respect, **4** is thermally stable and the present combination is appropriate for a kinetic analysis.

Table 1 shows the second order rate constants (k) in three solvents of different polarities at various temperatures (T) under atmospheric pressure. Within the temperature range studied, there is a good linear relationship between ln k and $1/T$ in each solvent (correlation coefficient: $r>0.999$), as predicted by the Arrhenius equation. The $\Delta H^{\neq}$, $\Delta S^{\neq}$ and the activation free energy ($\Delta G^{\neq}$) at 100 °C are listed in Table 2. There

Table 1. Rate Constants for the Reaction of **1** with **4** at Various Temperatures ($10^6 k$/kg mol^{-1} s^{-1})

Solvent	Temperature/°C			
	80	90 (85) [a]	100 (90) [a]	110 (95) [a]
Cumene	2.16±0.05	3.67±0.02	7.47±0.07	13.6 ±0.1
Dioxane	1.58±0.02	2.22±0.04	3.16±0.08	4.28±0.06
DMF	0.99±0.01	1.81±0.02	3.32±0.04	5.41±0.08

a) Rates in dioxane were measured at the temperatures indicated in parentheses.

were very little solvent effects, and the values of $\Delta S^{\neq}$ were similar to those of a typical Diels–Alder reaction[4,5,7,8] and those of other (6+4)π cycloadditions of **1** with **3**[2] and with **2**.[1] Therefore, this reaction could be interpreted as a concerted electrocyclic reaction. The considerably large negative $\Delta S^{\neq}$ indicates that the pressure effect on the reaction is as large as that on a Diels–Alder reaction, because $\Delta S^{\neq}$ is generally known to be related to $\Delta V^{\neq}$.[9]

The rate constants at various pressures are listed in Table 3. The pressure dependence of the rate constants is expressed by

$$(\partial \ln k/\partial P)_T = -\Delta V^{*}/RT. \quad (1)$$

As illustrated in Fig. 1, in each solvent plots of ln k vs. P showed a more pronounced curvature than those obtained in our previous Diels–Alder reactions and the (6+4)π cycloaddition of **1**,[1,4,5] indicating that $\Delta V^{\neq}$ become less negative with increasing pressure. In this respect, there have been very few theoretical studies; however, it has been stated that the differences in the compression between the ground and the transition states may influence the pressure effect on $\Delta V^{\neq}$. In the present case, one reason for this phenomenon might be the conformational mobility of acyclic diene, **4**. Under the atmospheric pressure, **4** may be sufficiently mobile, but its mobility might be restricted with increasing pressure. This means, the ground state may be less rigid reflecting the flexibility of the cycloaddend, **4**, than the transition state, for which, there would be no objection to conceive a rigidity from the cyclic and product-like structure (see below). On the other hand, under high-pressure conditions, the freedom of the ground state is restricted, but the degree of freedom of the transition state is not appreciably altered. Thus, with increasing pressure, the difference in the degree of freedom between the ground state and the transition state ($\Delta S^{\neq}$) might become less negative. Since $\Delta S^{\neq}$ is known to be related to $\Delta V^{\neq}$, the $\Delta V^{\neq}$ would become less negative at higher pressures and the plot of ln k vs. P would show a curvature. This interpretation might be justified by the observation that an almost linear plot was obtained using a conformationally-rigid, cyclic cycloaddends for **1** in the Diels–Alder and the (6+4)π cycloaddition reactions.[1,4,5] To express the present dependence of ln k, we used the following equation because of its established wide usage:

$$\ln k = a + bP + cP^2. \quad (2)$$

Table 4 shows the partial molar volume of each substance (Vi), given by the density measurement, ΔV at 60 °C, $\Delta V^{\neq}$ at 80 °C under atmospheric pressure, and the volume profile ($\Delta V^{\neq}/\Delta V$). As shown, the $\Delta V^{\neq}$ and $\Delta V^{\neq}/\Delta V$ are in the range of those for the typical Diels–Alder reactions.[10] Moreover, the other reliable data from the (6+4)π cycloaddition of **1** with **2**[1] was similar.

With respect to the solvent effect, $\Delta V^{\neq}$ became slightly less negative upon increasing the polarity of the solvent. This behavior resembled our results regarding the concerted cycloaddition of **1** measured in cumene and DMF.[1,5] Also, this solvent effect was

Table 2. Activation Parameters for the Reaction of **1** with **4** at 100 °C.

Solvent	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J mol^{-1} K^{-1}	ΔG^{*}/kJ mol^{-1}
Cumene	67±3	−166±9	129±7
Dioxane	69±2	−162±5	130±4
DMF	61±2	−188±5	131±3

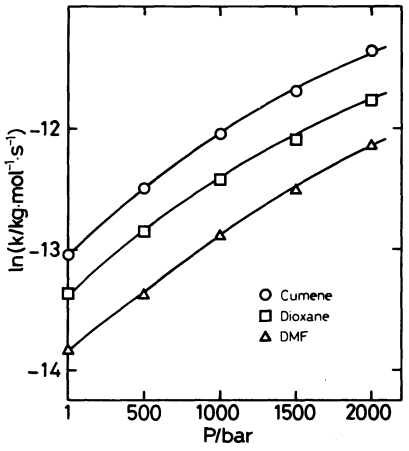


Fig. 1. Pressure dependence of ln k for the reaction of tropone with dimethylbutadiene at 80 °C.

Table 3. Rate Constants for the Reaction of **1** with **4** at Various Pressures at 80 °C ($10^6 k$/kg mol^{-1} s^{-1})

Solvent	Pressure/bar				
	1	500	1000	1500	2000
Cumene	2.16±0.05	3.70±0.04	5.83±0.01	8.29±0.07	11.6 ±0.1
Dioxane	1.58±0.02	2.59±0.06	4.01±0.09	5.57±0.06	7.79±0.05
DMF	0.99±0.01	1.55±0.01	2.57±0.03	3.80±0.01	5.48±0.05

very small and in accord with typical concerted reactions.

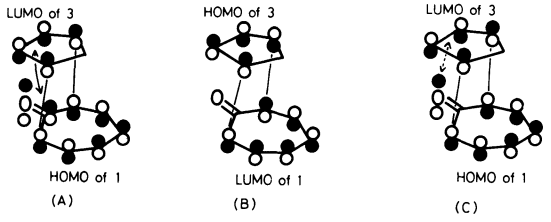
Consequently, an effect resulting from the dipolar character of **1** on the volume, pointed out by le Noble and Ojosipe,[11] is insignificant.

Volume Profile. From our previous and the present results, the transition state of the (6+4)π cycloaddition of **1** was found to be very product-like as far as the reaction volume is concerned: that is, $0.87<\Delta V^{\neq}/\Delta V<1.04$.[1] This phenomenon has often been observed in Diels–Alder reactions; in a special case, $\Delta V^{\neq}$ was more negative than ΔV.[12] In view of the secondary orbital interaction by the Woodward–Hoffmann rule for the Diels–Alder reaction,[13] the attractive force between the HOMO of dienes and the LUMO of dienophiles should yield the endo-adducts under kinetically controlled conditions. Accordingly, the transition state could be explained as becoming very product-like, or smaller than the product. On the same grounds, the exemplified exo-orientation for the (6+4)π cycloadducts of **1** has been explained in terms of a repulsive secondary orbital interaction in the endo-transition state.[14]

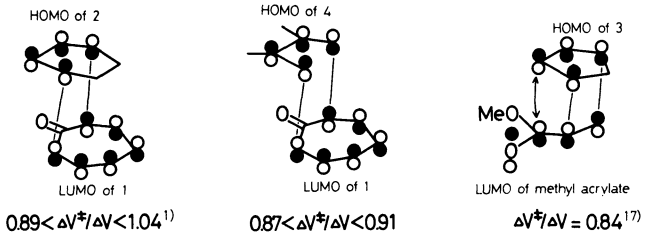
According to le Noble and Ojosipe,[11] a much larger $\Delta V^{\neq}/\Delta V=1.74$ in the (6+4)π cycloaddition of **1** with **3**, which was invalidated though,[1] was explainable in terms of an attractive, secondary interaction between the HOMO of **1** and the LUMO of **3** in the exo-transition state to make the transition state compressed (Scheme 2: **A**, unfortunately, the illustration contained a false figure).[11] However, an ab initio calculation showed the difference in energy level between the HOMO of **1** and the LUMO of **3** to be ca. 10 eV, and that between the LUMO of **1** and the HOMO of **3** to be ca. 8 eV.[15] Consequently, the former combination is not appropriate; in fact, the (6+4)π cycloaddition of **1** has often been explained[16] on the basis of the latter combination, in which the coefficient of the carbonyl group of **1** in the LUMO is 0 (Scheme 2: **B**).

In such a circumstance, the secondary orbital interaction can not be significant in the exo-(6+4)π cycloaddition of **1**. Moreover, if one considers the contribution of HOMO of **1** and the LUMO of dienes on volume profile, it should at least be discussed on the basis of the correct figure drawn as Scheme 2: **C**.[15] That is, the coefficient of carbon in carbonyl group is 0, and the attractive secondary orbital interaction can not be so strong as mentioned by le Noble. Furthermore, this combination is minor one. Taking these points into accounts, the secondary orbital interaction is concluded to contribute insignificantly to the volume profile of the exo-(6+4)π cycloaddition of **1**. In addition, the comparison on volume profile between (6+4)π cycloaddition of **1** and the Diels–Alder reactions disclosed a remarkable feature; Scheme 3 shows, although (6+4)π cycloaddition and Diels–Alder reaction suffer differently from secondary orbital interaction, very similar volume profiles with illustrations of the HOMO-LUMO combinations for a (6+4)π cycladdition of **1** observed by us[1] and one of the typical Diels–Alder reaction, **3** with methyl acrylate.[17] Therefore, the secondary orbital interaction does not play a significant role on the volume profile, and the often observed $\Delta V^{\neq}/\Delta V>1$ in the Diels–Alder reaction must be explained in terms of another factor, such as a transannular attractive force.[18]

In conclusion, contributions of the dipolar character of **1** and the secondary orbital interaction to the volume profile of the Woodward–Hoffmann rule-allowed thermal (6+4)π electrocyclic reaction of **1** should not be overestimated. Also, the high-pressure cycloadditions of troponoids in organic syntheses are certainly profitable.[19]



Scheme 2.



Scheme 3.

Table 4. The Volume Parameters for the Reaction of **1** with **4** ($cm^3\ mol^{-1}$)

Solvent	ΔV_1[a]	ΔV_4[a]	ΔV_5[a]	ΔV[a]	ΔV^{*}[b]	$\Delta V^{*}/\Delta V$
Cumene	99.8	118.5	183.4	−34.9	−33.1	0.91
Dioxane	99.1	119.4	183.5	−35.0	−30.5	0.87
DMF	97.0	115.8	178.8	−34.0	−30.1	0.89

a) Measured at 60±0.01 °C. b) Measured at 80±0.5 °C.

The authors thank the Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research to S. S. (No. 61740294).

References

1) H. Takeshita, S. Sugiyama, and T. Hatsui, *J. Chem. Soc., Perkin Trans. 2.*, **1986**, 1491.

2) H. Tanida and H. R. Pfaendler, *Helv. Chim. Acta*, **55**, 3062 (1972).

3) M. E. Gorst, V. A. Roberts, and C. Prussin, *Tetrahedron*, **39**, 581 (1983).

4) H. Takeshita, S. Sugiyama, and T. Hatsui, *Chem. Lett.*, **1984**, 1855.

5) H. Takeshita, S. Sugiyama, and T. Hatsui, *Bull. Chem. Soc. Jpn.*, **58**, 2490 (1985).

6) T. Ikemi, H. Sugiyama, and T. Nozoe, *Chem. Ind. (London)*, **1960**, 932.

7) J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

8) S. Itô, A. Mori, Y. Shoji, and H. Takeshita, *Tetrahedron Lett.*, **1972**, 2685.

9) D. Chen, and K. J. Laider, *Trans. Faraday Soc.*, **354**, 1026 (1958); K. J. Laider and D. Chen, *Can. J. Chem.*, **37**, 599 (1959).

10) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978).

11) W. J. le Noble and B. A. Ojosipe, *J. Am. Chem. Soc.*, **97**, 5939 (1975).

12) R. A. Grieger and G. A. Echert, *J. Am. Chem. Soc.*, **92**, 2918 (1970).

13) R. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim/ Bergstr., 1970, pp. 83—84.

14) The (6+4)π cycloaddition of isobenzofuran with 6,6-dimethylfulvene and 6,6-diphenylfulvene gave stereospecifically the endo-adducts. The results have been explained in terms of the cross-conjugated geometry for the 6π system of the fulvenes where the secondary effect is not strong enough to control the stereochemistry. See H. Takeshita, A. Mori, S. Sano, and Y. Fujise, *Bull. Chem. Soc. Jpn.*, **48**, 1661 (1975).

15) D. Mukherjee, C. R. Watts, and K. N. Houk, *J. Org. Chem.*, **43**, 817 (1978).

16) I. Fleming, "Frontier Orbital and Organic Chemical Reactions," John Wiley & Sons, Ltd., New York (1976), Chap. 4; and the references cited therein.

17) K. Seguchi, A. Sera, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **47**, 2242 (1974).

18) This has been pointed out in the pressure accelerated retro-Diels–Alder reaction. See A. V. George and N. S. Isaacs, *J. Chem. Soc., Perkin Trans., 2*, **1985**, 1845.

19) K. Matsumoto and A. Sera, *Synthesis*, **1985**, 999; S. Sugiyama, T. Tsuda, A. Mori, H. Takeshita, and M. Kodama, *Chem. Lett.*, **1986**, 1315.