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KINETIC STUDIES ON THE HIGH-PRESSURE DIELS-ALDER REACTION OF TROPONE WITH MALEIC ANHYDRIDE

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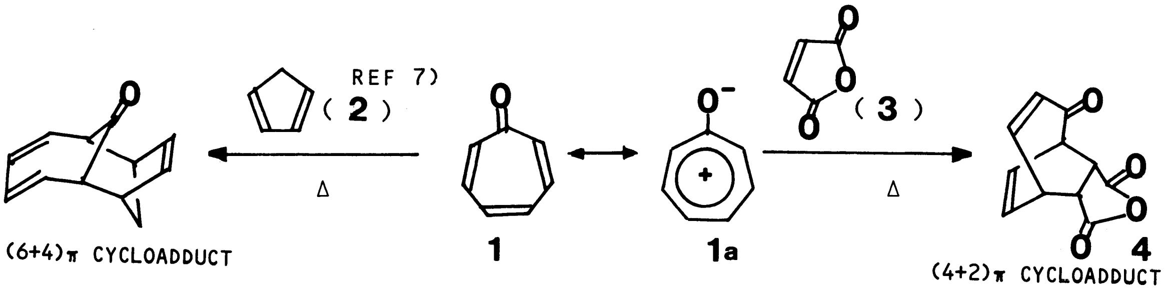
The rates and activation parameters of the (4+2)π cycloaddition of tropone with maleic anhydride were measured in the range of 105–135 °C at pressures up to 2000 bar in cumene and in DMF. The values of activation volume and the volume change of reaction revealed a deviation to a great extent from those of (6+4)π process of tropone with cyclopentadiene, but to a small extent from the other (4+2)π process.

Up to date, there are many papers on the high-pressure analysis of the electrocyclic reactions, *e.g.*, Diels-Alder reaction is known to show large negative activation volumes ($\Delta V^{\ddagger}$, *ca.* -33–38 cm^3/mol) and the volume changes (ΔV).[1] In the same time, tropone (1),[2] a parent compound of representative family of the non-benzenoid aromatics, has attracted attentions to the pericyclic reactions as it is capable of forming (2+4)-,[3] (4+2)-,[4] (6+4)-,[5] and (8+2)π cycloadducts[6] *via* concerted thermal reactions. However, there has been only one paper on the high-pressure analysis of the electrocyclic reactions of troponoids, *i.e.*, the (6+4)π cycloaddition of 1 with cyclopentadiene (2) in dioxane by le Noble and his colleague,[7] who have given extraordinary values for $\Delta V^{\ddagger}$ and ΔV of the reaction, -7.5 and -4.3 cm^3/mol, respectively. These exceptionally small negative figures, compared to those of typical Diels-Alder reactions, have been explained on the basis of the polar structure of tropone (1a) in the initial state; *i.e.*, an electrostriction due to 1a is responsible to reduce the partial molar volume of 1 ($\bar{V}_1$) to such small $|\Delta V^{\ddagger}|$ and $|\Delta V|$. If it is the case, the concerted cycloaddition of 1 must be strongly pressure- and solvent-dependent.



Herein we wish to present our study of the high-pressure (4+2)π cycloaddition reaction of 1 with maleic anhydride (3), and to discuss the electrostriction in the initial state of 1 in connection with le Noble's results. The reaction of 1 with **3** is known to produce the single adduct (**4**),[4a,8,9] and is suitable for the kinetic analysis.

All the kinetic runs, including under the atmospheric pressure, were carried out with the pressure vessel having an outlet valve for sampling. The concentrations in the reaction mixture were initially *ca.* 0.007 mol/kg for **1** and 0.14 mol/kg for **3**. The reaction was gas-liquid-chromatographically monitored by measuring the consumption of **1**. The temperature was controlled within 0.5 K, and the pressure was measured with a Heise Burdon gauge.

The measurements of $\overline{V}_1$, $\overline{V}_3$, and $\overline{V}_4$ were performed in *N,N*-dimethylformamide (DMF) and in cumene with the Ostwald's pycnometer. The temperature was controlled at 333.15±0.01 K, the same to the le Noble's condition for the data of **1** in dioxane.

Table 1. Second-order Rate Constants for Diels-Alder Reaction of **1** with **3** at Various Temperatures ($10^5 \times k$/kg·mol^{-1}·s^{-1})

	Temperature/K			
Solv.	378.2	388.2	398.2	408.2
Cumene	2.32±0.02	3.66±0.08	5.50±0.18	7.36±0.15
DMF	1.56±0.09	2.51±0.01	3.96±0.16	5.54±0.12

The reaction rate was analyzed as a pseudo-first-order reaction of **1**. Second-order rate constants at various temperatures in cumene and in DMF are summarized in Table 1, and the Arrhenius plots are shown in Fig. 1. Table 2 shows activation energy (*Ea*), activation entropy ($\Delta S^\ddagger$), and activation free energy ($\Delta G^\ddagger$) in two solvents at 378.2 K.

Table 2. Activation Parameters for Diels-Alder Reaction of **1** with **3** at 378.2 K

Solv.	*Ea*/kJ·mol^{-1}	$\Delta S^\ddagger$/J·mol^{-1}·K^{-1}	$\Delta G^\ddagger$/kJ·mol^{-1}
Cumene	49.7±3.3	-220±9	130±7
DMF	54.8±2.5	-219±7	134±5

Indeed, the rate constants in DMF (dielectric constant: ε=36.7) are smaller than those in cumene (ε=2.4), and a polarity of **1** has affected on the rate of the reaction as mentioned by le Noble. However, the difference of the rate was as small as $k_{\mathrm{DMF}}/k_{\mathrm{cumene}}$=0.7. The *Ea* and $\Delta G^\ddagger$ also indicated the stabilized initial state in DMF, but the $\Delta S^\ddagger$ showed little difference in both solvents.

In order to understand the solvent effect more precisely, $\overline{V}_1$, $\overline{V}_3$,and $\overline{V}_4$ must be determined. The $\overline{V}_1$, $\overline{V}_3$,and $\overline{V}_4$ at 333.15 K, which can be find in Table 3, were determined by the extrapolation to infinite dilution of the apparent molar volumes, almost constant for each substrate throughout this experiment: $\overline{V}_4$ in cumene was not obtained due to its insolubility, $\overline{V}_3$ was in accord with the Eckert's values at 308.2 K,[10] and $\overline{V}_1$ and $\overline{V}_3$ in cumene were larger than those in DMF. Therefore, **1** and **3** are more tightly solvated in DMF than in cumene, and it is consistent with the expected from the dipole moments of **1** (μ=4.17 D;[11a] 4.30 D[11b]) and **3** (μ=

3.95 D).[10)]

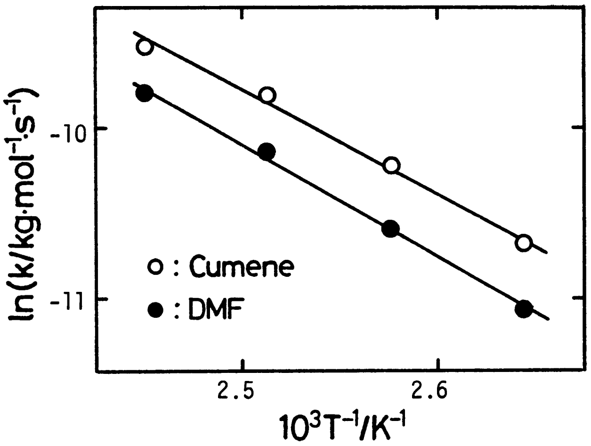


Fig. 1. Arrhenius plots of the reaction of **1** with **3**.

The rate constants at various pressures in cumene and DMF are listed in Table 4. A good linear correlation of ln k with the pressure, 1 to 2000 bar, was exhibited in Fig. 2. From the following equation, $\Delta V^{\ddagger}$ can be obtained:

$$\Delta V^{\ddagger}=-RT(\partial \ln k/\partial P)_T$$

Thus, the negative figure of $\Delta V^{\ddagger}$ of the reaction in cumene, -21.4 cm^3/mol, is larger than in DMF, -16.8 cm^3/mol. This means that the initial state of **1** is less tightly solvated in cumene than in DMF, and these $|\Delta V^{\ddagger}|$ are considerably smaller than those obtained from the other Diels-Alder reactions, but rather similar to those from the concerted 1,3-dipolar cycloadditions.[12,13)] However, this reaction was affected little with the solvents, and the volume profile in DMF, $\Delta V^{\ddagger}/\Delta V$=0.66, was in a range of the ordinary Diels-Alder reaction.

Table 3. The Partial Molar Volumes ($\overline{V}$), Volume Changes (ΔV), and Activation Volumes ($\Delta V^{\ddagger}$) for the Reaction of **1** with **3** to **4**

Solv.	$\overline{V}_1$ [a)] $cm^3 \cdot mol^{-1}$	$\overline{V}_3$ [a)] $cm^3 \cdot mol^{-1}$	$\overline{V}_4$ [a)] $cm^3 \cdot mol^{-1}$	ΔV $cm^3 \cdot mol^{-1}$	$\Delta V^{\ddagger}$ [b)] $cm^3 \cdot mol^{-1}$
Cumene	99.8	75.0	—[c)]	—	-21.4
DMF	97.0	72.6	144.1	-25.5	-16.8

a) Measured at 333.15±0.01 K. b) Values at 378.2 K. c) Insoluble.

Table 4. Second-order Rate Constants for the Reaction of **1** with **3** under Various Pressures at 378.2 K ($10^5 \times k/kg \cdot mol^{-1} \cdot s^{-1}$)

	Pressure/bar				
Solv.	1	500	1000	1500	2000
Cumene	2.32±0.02	3.03±0.11	4.29±0.29	5.99±0.26	9.02±0.21
DMF	1.56±0.09	2.31±0.02	3.02±0.06	3.69±0.31	4.71±0.25

As a whole, the Diels-Alder reaction of **1** with **3** revealed relatively small negative $\Delta V^{\ddagger}$ and ΔV, which were, however, inconsistent with the extremely small values of the $\Delta V^{\ddagger}$ and ΔV in the previously reported (6+4)π cycloaddition of **1** and **2**, -7.5 and -4.3 cm^3/mol, by le Noble and his colleague. The results have been interpreted in terms of the polar nature of **1**. Namely, $\overline{V}_1$ in dioxane (85.6 cm^3/mol at 333.2 K) is some 20 cm^3/mol smaller than the predicted volume based on the parachor listings. Since a polar effect of **1** in the concerted reactions should not differ by the mode of pericyclic nature, (6+4)π or (4+2)π, this would be attributable to the other factors; at present stage, these may be: i) different polarity between the second cycloaddends, **2** and **3**, and ii) a very special role of dioxane, other than simple solvation. Certainly, it would be desirable to carry out further investigations to clarify the point.

Currently, intensive studies along the related lines are in progress, and the results will be published in near future.

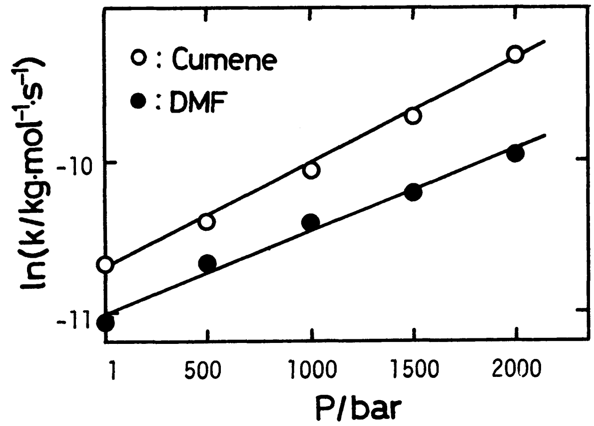


Fig. 2. Pressure dependence of ln *k* for addition reaction of **1** with **3** at 378.2 K.

References

1) T. Asano and W. J. le Noble, *Chem. Rev.*, 78, 407(1978); G. Swieton, J. von Jouanne, H. Kelm, and R. Huisgen, *J. Chem. Soc., Perkin Trans. 2*, 1983, 37.

2) Tropone was prepared after Nozoe's procedure (T. Ikemi, T. Nozoe, and H. Sugiyama, *Chem. Ind.(London)*, 1960, 932), and was purified by a silica-gel column chromatography and distillation. Purity of the sample was at least 99.1%.

3) In this paper, (m+n)π denotes the cycloadditions of mπ-component of tropones with nπ-component of other cycloaddends. For (2+4)π process, see H. Takeshita, Y. Wada, A. Mori, and T. Hatsui, *Chem. Lett.*, 1973, 335.

4) a) T. Nozoe, T. Mukai, T. Nagase, and Y. Toyooka, *Bull. Chem. Soc. Jpn.*, 33, 1247 (1960); b) S. Itô, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, 1969, 1815.

5) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 1966, 15; S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, 39, 1351 (1966).

6) M. Oda, M. Funamizu, and Y. Kitahara, *J. Chem. Soc., Chem. Commun.*, 1969, 737; M. E. Garst, V. A. Roberts, and C. Prussin, *Tetrahedron*, 39, 581(1983).

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

8) The Diels-Alder adduct (4) was purified by recrystallizations from acetone.

9) H. R. Pfaendler, H. Tanida, and E. Haselbach, *Helv. Chim. Acta*, 57, 383 (1974).

10) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, 66, 2579(1970).

11) a) T. Nozoe, T. Mukai, and K. Takase, *Proc. Jpn. Acad.*, 28, 477(1952); b) D. J. J. Bertelli and T. G. Andrews, Jr., *J. Am. Chem. Soc.*, 91, 5280(1969).

12) Y. Yoshimura, J. Osugi, and M. Nakahara, *J. Am. Chem. Soc.*, 105, 5414(1983).

13) G. Swieton, J. von Jouanne, H. Kelm, and R. Huisgen, *J. Org. Chem.*, 48, 1035 (1983).

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