192 (97), 193 (26), 166 (37), 165 (100), 91 (18).

Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.62; H, 4.90; N, 4.03. Found: C, 72.45; H, 4.78; N, 4.02.

1-Chloro-2-(*N*-chloro-*p*-toluenesulfonamido)acenaphthene. To a well-stirred cold (0–2 °C) solution of 2.01 g of acenaphthylene in 15 mL of CH_2Cl_2 was added dropwise (10 min) a solution of 3.2 g of Cl_2NTs in 15 mL of CH_2Cl_2. Workup as described above followed except that CCl_4 at −30 °C was used in place of ether at 0–2 °C to triturate the crude solid. The insoluble portion (0.9 g, mp 149–152 °C) was identified as 1-chloro-2-*p*-toluenesulfonamidoacenaphthene (see below). The CCl_4 filtrate was evaporated and the residue was triturated with 15 mL of ether. Cooling to −30 °C (dry ice–acetone bath) gave a light-yellow solid, which was washed with two 3-mL portions of cold (−20 °C) ether to give 2.1 g (59.2%) of the *N*-chloro compound, mp 115–117 °C. The analytical sample had the following: mp 117–119 °C (ether); IR ($CHCl_3$) 1340, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3, CH_3), 5.50 (d, 1, ClCH), 6.37 (d, 1, CHN), 7.30–8.20 (m, 10, aryl).

Anal. Calcd for $C_{19}H_{15}Cl_2NO_2S$: C, 58.16; H, 3.83; N, 3.57. Found: C, 58.26; H, 3.86; N, 3.22.

1-Chloro-2-*p*-toluenesulfonamidoacenaphthene. The *N*-chloro sulfonamide (2.09 g) was reduced with $NaHSO_3$ (1.58 g) as described for the phenanthrene derivative. The crude product was recrystallized from CCl_4 to give 1.35 g (75.8%) of the title compound, mp 152–154 °C. The analytical sample had the following: mp 154.5–155.5 °C (CH_2Cl_2–ligroin, bp 67–71 °C); IR ($CHCl_3$) 3375 (NH), 1340, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3, CH_3), 5.10 (d, 1, NH), 5.35 (d, 1, CHN), 5.40 (s, 1, CHCl), 7.10–8.05 (m, 10, aryl).

***N*-(*p*-Tolylsulfonyl)acenaphthylenimine (6).** A solution of 1.79 g of 1-chloro-2-*p*-toluenesulfonamidoacenaphthene in 50 mL of CH_3OH was treated with 0.8 g of $NaOCH_3$ as described for the corresponding phenanthrene derivative. Recrystallization from ether–ligroin (bp 67–71 °C; 2/1, v/v) gave 1.5 g (94.7%) of the imine as a white solid: mp 140–142 °C; IR ($CHCl_3$) 1325, 1160 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.42 (s, 2, CH_3), 4.82 (s, 2, CHN), 7.27–7.95 (m, 10, aryl); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 47.5 (CHN); MS (80 eV), *m/e* 321 (M^+, 27), 167 (55), 166 (100), 144 (29), 139 (35), 91 (30).

Anal. Calcd for $C_{19}H_{15}NO_2S$: C, 71.00; H, 4.67; N, 4.36. Found: C, 71.05; H, 4.62; N, 4.35.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and in part by the National Science Foundation.

Registry No. 2, 60883-97-8; 3, 84195-16-4; 4, 84195-17-5; 6, 84195-18-6; Cl_2NTs, 473-34-7; phenanthrene, 85-01-8; 1-chloro-2-(*N*-chloro-*p*-toluenesulfonamido)acenaphthene, 84195-19-7; acenaphthylene, 208-96-8; 1-chloro-2-*p*-toluenesulfonamidoacenaphthene, 84195-20-0.

Activation Parameters and Location of the Transition State in the Retro-Diels–Alder Reaction of a 7-Oxabicyclo[2.2.1]hept-5-ene Derivative

G. Jenner,* M. Papadopoulos, and J. Rimmelin

Laboratoire de Chimie Organique Appliquêe, Ecole Nationale Supêrieure de Chimie, Universitê Louis Pasteur, 67008 Strasbourg, France

Received September 17, 1982

Retro-Diels–Alder thermolyses are thermally allowed ($_{\pi}4_s + {}_{\pi}2_s$) processes. The study of their mechanism cannot be dissociated from the corresponding one of the forward reaction for which the concerted pathway seems to be the most compatible with the experimental and theoretical results, at least for good donor–acceptor partners.[1]

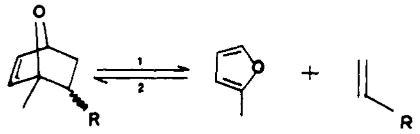
Table I. Temperature and Pressure Effect on the Rate Constant k in Thermolysis Reaction 1[a]

P, bar	T, K	10^4k,[b] s^{-1} cyclohexane[c]	dichloromethane	acetonitrile
1	342.9		1.13	0.97
	343.1	0.665		
	353.2	2.07	3.30	2.37
	363.0	5.20		
	364.1		10.40	7.76
	374.8		26.39	21.10
1	353.2	2.07	3.30	2.37
225		2.19		
260				2.53
290			3.43	
445			3.46	2.57
465		2.15		
750		2.22	3.46	2.50
930		2.23		
945			3.47	2.62
1930				3.01

[a] Adduct composition (endo/exo ratio of 2:3).
[b] Averaged value. Precision (5%); P, ±5 bar; T, ±0.1 K.
[c] The miscibility of adduct and cyclohexane is ensured with the addition of 500 mg of CH_2Cl_2 (standard) in each run.

Numerous (4 + 2) cycloadditions have been investigated in the light of activation volume $\Delta V^{\ddagger}$.[2] It was found invariably that for a given reaction $\Delta V^{\ddagger}$ is very close[3] to the reaction volume $\overline{\Delta V}$, suggesting a late transition state in terms of nuclear positions. To our knowledge, no $\Delta V^{\ddagger}$ value has been reported yet for the reverse reaction.[4]

We observed some time ago[5] that, in the condensation of furans, the retrodiene cleavage 1 regenerating the



starting materials occurs at moderate temperatures in contrast to common retro-Diels–Alder reactions which require much more drastic conditions.[6] The instability of the bridged bicyclic adducts was attributed to the aromatic character of the furan system[7] and the ring strain.[8]

The pressure effect was investigated in some condensations of 2-methylfuran and typical dienophiles. As an example, in the reaction (R = CN) it was found that for the forward reaction 2 $\Delta V^{\ddagger}_2 = -30.3$ cm^3/mol (at 37.2 °C).[5] The comparison of $\Delta V^{\ddagger}$ with the reaction volume ΔV (−28.7 cm^3/mol) suggests a quasicyclic and tight transition state.[9] According to the principle of microscopic reversibility, the mechanism of the reverse reaction should in-

---

(1) (a) Houk, K. N. *Top. Curr. Chem.* **1979**, *79*, 1. (b) Sauer, J.; Sustmann, R. *Agnew Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(2) (a) Grieger, R.; Eckert, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2918, 7149. (b) Brun, C.; Jenner, G. *Tetrahedron* **1972**, *28*, 3113. (c) Rimmelin, J.; Jenner, G. *Ibid.* **1974**, *30*, 3081. (d) Seguchi, K.; Sera, A.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2242. (e) Swieton, G.; Kelm, H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 519. (f) Papadopoulos, M.; Jenner, G. *Bull. Soc. Chim. Fr.* **1982**, 313.

(3) Some exceptions were recently found: (a) Jenner, G.; Rimmelin, J. *Tetrahedron Lett.* **1980**, *21*, 3039. (b) Jenner, G.; Papadopoulos, M.; le Noble, W. J., to be submitted for publication.

(4) An early investigation described the rearrangement of 1-hydroxydicyclopentadiene up to 7000 bar and considered it as a partial retrodiene reaction: Walling, C.; Shugar, H. *J. Am. Chem. Soc.* **1963**, *85*, 607.

(5) Rimmelin, J.; Jenner, G.; Rimmelin, P. *Bull. Soc. Chim. Fr.* **1978**, 461.

(6) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415.

(7) Albert, A. "Heterocyclic Chemistry", 2nd ed.; Oxford University Press: New York, 1968; p 257.

(8) Allinger, N.; Hickey, M. *J. Am. Chem. Soc.* **1975**, *97*, 5167.

(9) Jenner, G.; Rimmelin, J. *Tetrahedron* **1976**, *32*, 1107.

0022-3263/83/1948-0748$01.50/0

Table II. Activation Parameters of the Retro-Diene Reaction

	cyclohexane	dichloromethane	acetonitrile
$\Delta H^{\ddagger}$ (±5), kJ/mol	107.0	106.2	104.5
log A	12.13	12.24	11.87
$\Delta S^{\ddagger}$ (±5),[a] J mol^{-1} K^{-1}	−22.0	−20.0	−26.9
$\Delta G^{\ddagger}$,[a] kJ/mol	111.4	110.0	111.0
$\Delta V^{\ddagger}$ (±1.0), cm^3/mol	−2.0	−1.0	−3.4

[a] At 353 K.

volve the quasi-simultaneous breaking of two σ bonds.

Because the instability of the epimeric adduct mixture at temperatures well compatible with the usual high-pressure experimental conditions, we were prompted to study the temperature and the pressure effect on the rate of reaction 1.

At temperatures ≥70 °C, the thermolysis was found to be irreversible, at least within reaction periods not exceeding 3 days. The standard first-order rate law is obeyed within the examined temperature and pressure range. The kinetics was followed by ^{1}H NMR spectroscopy by taking into account the proton in α position of the formed 2-methylfuran (7.30 ppm) and the methylene protons in CH_2Cl_2, serving as an internal standard (5.25 ppm). Table I summarizes the thermolysis rate data.

Arrhenius plots afford $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, while $\Delta V^{\ddagger}$ is deduced from the initial slope of the graph reproducing the response to pressure of ln k according to Evans and Polanyi's equation (Table II).

While $\Delta H^{\ddagger}$ has rather low values, the magnitude of the present $\Delta S^{\ddagger}$ values lies at the lower limit of the usual reported literature values which are generally low, positive or negative.[10] It is concluded that there are no important modifications of rotational or vibrational degrees of freedom in the transition state. Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values may be in accordance with a process in which the transition state occurs early along the reaction coordinate. However, $\Delta V^{\ddagger}$ offers the most conclusive interpretation.

Since electrostriction effects are highly improbable in this type of reaction [only minor changes in rate constant are introduced by varying the polarity of the medium (Table I)], $\Delta V^{\ddagger}$ is a good measure of the progression of the reaction.[11] For the reverse reaction 1, we find a zero or a slightly negative value which is doubtless indicative of an early transition state so far as *the volume profile* is concerned, in contradiction with the hypothesis of a biradical or a biradicaloid intermediate, though the adduct is a rather unsymmetrical molecule for which it may be conceivable that the weaker C–C bond is cleaved first before attainment of the transition state. The present $\Delta V^{\ddagger}$ values give good evidence for the concerted breaking of the two bonds previously deduced by Seltzer[12] on the basis of secondary isotope effects.

It should be noted that bond cleavage is usually characterized by a large volume increase as examplified by the $\Delta V^{\ddagger}$ (10 cm^3/mol) for O–O breaking.[13] However, the present $\Delta V^{\ddagger}$ values are clearly related to the location of the transition state along the reaction coordinate.

The interesting observation is that the retro-Diels–Alder reaction seems to be slightly accelerated by pressure though the monitoring of procedure allows only a precision not better than 1 cm^3/mol. The result should not be surprising, since the former $\Delta V^{\ddagger}$ value we calculated for the forward reaction (conducted in CH_2Cl_2) was indicative of a minimum in the volume profile ($|\Delta V^{\ddagger} - \overline{\Delta V}| = 1.9$ cm^3/mol).[14] For reaction 1, we get $|\Delta V^{\ddagger} - \overline{\Delta V}| \simeq 1.0$ cm^3/mol. The agreement is satisfactory and could give support for the operation of secondary orbital interactions we invoked to rationalize the tighter transition state compared to the final state. However, the results can also support the possibility of a slight increase in polarity in the transition state, as suggested by le Noble.[15] This question needs further investigation, for the difference $|\Delta V^{\ddagger} - \Delta V|$ is too small here to enable a definitive discussion.

In conclusion, the present kinetic and thermodynamic date are doubtless in favor of an early transition state for the retro-Diels–Alder reaction of *endo*- and *exo*-1-methyl-2-cyano-7-oxabicyclo[2.2.1]hept-5-ene and are in excellent agreement with the concerted scheme postulated previously for the forward reaction.

Registry No. *endo*-1, 1727-98-6; *exo*-1, 56561-73-0.

---

(10) (a) Herndon, W. C.; Grayson, C. R.; Manion, J. M. *J. Org. Chem.* **1967**, *32*, 526. (b) Herndon, W. C.; Hall, L. H. *Tetrahedron Lett.* **1967**, 3095. (c) Mackenzie, K.; Lay, W. P. *Ibid.* **1970**, 3241. Walsh, R.; Wells, J. M. *Int. J. Chem. Kinet.* **1975**, *7*, 319. Snyder, J. P.; Harpp, D. N. *J. Am. Chem. Soc.* **1976**, *98*, 7821. Moll, K. K.; Ramhold, K.; Zimmermann, G.; Pohle, C. *J. Prakt. Chem.* **1980**, *322*, 1048.

(11) This may be not the case for some [2 + 2] cycloreversions which occur visibly via zwitterion intermediates: Osugi, J.; Sasaki, M.; Tsuzuki, H.; Uosaki, Y.; Nakahara, M. "Proceedings of the International Conference on High-Pressure Science and Technology"; Plenum Press: New York, 1978; Vol. 1, p 651.

(12) Seltzer, S. *J. Am. Chem. Soc.* **1965**, *87*, 1534. The argument was cited as inconclusive by Dewar: Dewar, M. J.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(13) Walling, C.; Metzger, G. *J. Am. Chem. Soc.* **1959**, *81*, 5365.

(14) This value arises from the difference $\Delta V^{\ddagger} - \overline{\Delta V}$ for the forward reaction calculated for $T = 353.0$ K. See: Elyanov, B. S.; Vasylvitskaya, E. M. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 169.

(15) le Noble, W. J. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 207.

Benzylic Oxidation with 2,3-Dichloro-5,6-dicyanobenzoquinone in Aqueous Media. A Convenient Synthesis of Aryl Ketones and Aldehydes

Hongmee Lee and Ronald G. Harvey*

Ben May Laboratory, University of Chicago, Chicago, Illinois 60637

Received July 26, 1982

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) has found extensive synthetic application as an oxidant in organic chemistry.[1–4] Oxidation of arylalkanes with DDQ proceeds via a mechanism thought to involve initial hydride abstraction from a benzylic or allylic site to generate a carbonium ion intermediate which can lose a proton to afford an olefinic product (Scheme I).[2,5] The method has important application in the preparation of dihydro aromatic compounds such as 7,8-dihydrobenzo[*a*]pyrene (**2**), re-

---

(1) Turner, A. B. In "Synthetic Reagents"; Pizey, J. S., Ed.; Halstead-Wiley: New York, 1977; Vol. 4, pp 193–225.

(2) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

(3) Becker, H. In "The Chemistry of Quinoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; Part 1, p 335.

(4) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153.

(5) Braude, E. A.; Jackman, L. M.; Linstead, R. P. *J. Chem. Soc.* **1954**, 3548.

0022-3263/83/1948-0749$01.50/0 © 1983 American Chemical Society