

Electron Transfer Reactions. XV.* On the Mechanism of the Radical Cation Catalyzed Diels-Alder Dimerization of 1,3-Cyclohexadiene

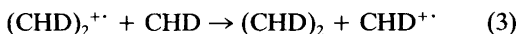
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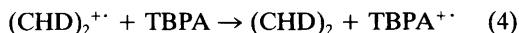
We have for some time studied the dual reactivity – electrophilic or electron transfer – of tris(4-bromophenyl)ammoniumyl^{1,2} (TBPA⁺), a radical cation often used to catalyze reactions which are believed to occur via an initial outer-sphere electron transfer (ET) step. In this context we became intrigued by its seemingly unique capability to strongly catalyze Diels-Alder reactions, an area where both electrophilic and ET-mediated mechanisms have been proposed.[§] We have therefore initiated kinetic studies of the TBPA⁺-catalyzed dimerization of 1,3-cyclohexadiene (CHD), previously studied by Bauld *et al.*^{3,4} Our results and interpretation differ on significant points.

The TBPA⁺-catalyzed dimerization of CHD has been formulated[§] as a radical chain mechanism [eqns. (1)–(3)] in which CHD^{•+} is formed in



a first ET step and then reacts with another CHD to give the radical cation of the Diels-Alder dimer, (CHD)₂^{•+}. Chain transfer then occurs by

ET between (CHD)₂^{•+} and a new molecule of CHD. We are sceptical concerning this interpretation, since CHD is oxidized at 1.65 V (vs. SCE), i.e. 0.60 V higher than the reversible oxidation potential of TBPA, viz. 1.05 V. In kinetic terms, this corresponds to a ratio between the ET rate constants[†] of 10⁶–10⁷, indicating that the TBPA inevitably formed according to eqn.(1) or in other reactions (see below) or present initially in the radical cation salt^{1,2} might compete favourably with CHD. In such a case, eqn. (3) should be replaced by (4), and a conventional catalytic



mechanism should be operative. Such a reaction would in principle not consume any TBPA⁺.

However, it is a characteristic of the reaction between TBPA⁺ and CHD that the radical cation disappears relatively slowly in a dichloromethane solution of the two components (this process being denoted “the background reaction” in the following). We have measured the kinetics

[†]As calculated by the Marcus theory. See Ref. 5. *E*(dimer^{•+}/dimer) was determined to be 2.17 V vs. SCE in dichloromethane (5% in trifluoroacetic anhydride)/0.1 M tetrabutylammonium tetrafluoroborate, and the reorganisation energies of the self-exchange reactions TBPA⁺/TBPA, CHD^{•+}/CHD and dimer^{•+}/dimer were taken to be 10, 60 and 60 kcal mol⁻¹, respectively.

*Part XIV, see Ref. 10.

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[§]For a review, see Ref. 3.

Table 1. Representative k_{obs} for the background reaction between CHD and TBPA⁺ SbCl₆⁻ in dichloromethane,^a as calculated by the computational method outlined in Ref. 6. Temperature: 20 °C.

[TBPA ⁺] ₀ /mM	Added [TBPA]/mM	[CHD] ₀ /mM	[Base] ₀ /mM	k_{obs} /min ⁻¹
0.60	0	6.0	0	0.072 ^b
0.60	0	6.0	0	0.058 ^c
0.60	0.30	6.0	0	0.045
0.60	0.90	6.0	0	0.030
0.60	1.50	6.0	0	0.014
0.40	0.40	4.0	0	0.029
0.40	0.60	4.0	0	0.025
0.40	1.20	4.0	0	0.014
0.40	0	4.0	0	0.047
0.40	0	10.0	0	0.33
0.40	0	40.0	0	6.7
0.40	0	75	0	27
0.40	0	4.0	0.44 ^d	10
0.40	0	4.0	2.0 ^d	10
0.40	0	8.0	0.44 ^d	19
0.40	0	8.0	2.0 ^d	19
0.40	0	8.0	0.84 ^e	17

^aMonitored by UV/Vis spectrophotometry (conventional or stopped-flow technique^{1,2}) at 728 nm. ^bFresh sample from previously unopened bottle; all experiments except the one commented upon in note *c* were performed with this batch. ^cSample from used bottle (opened intermittently over a period of 2–3 months). ^d2,6-Di-*tert*-butylpyridine. ^e2,6-Lutidine.

of this reaction and found it to be second-order (2.2 ± 0.2) in [CHD] and inverse first-order (-1.2 ± 0.4) in added [TBPA]. The treatment of the kinetic data assumed a reversible ET step followed by rate-determining follow-up steps, treated mathematically according to an approximate method developed earlier.⁶ Table 1 gives representative rate constants for the background reaction, with half-lives typically in the range of 10–50 min under conditions giving high yields (up to 95 %) of dimers ([TBPA⁺] = 0.4–0.6 mM, [CHD] = 4.0–6.0 mM).

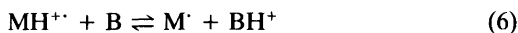
When a relatively strong, hindered base was added (2,6-di-*tert*-butylpyridine or 2,6-lutidine), the nature of the reaction changed, in that it now was first-order in [CHD] and 100–200 times faster (representative rate constants are given in the lower part of Table 1). This is the result of a synergistic effect between CHD and the base, since check experiments established that TBPA⁺ (0.8 mM) and 2,6-di-*tert*-butylpyridine (16 mM) or 2,6-lutidine (16 mM) reacted slowly in a pseudo first-order process, with rate constants equal to 0.030 and 0.027 min⁻¹, respectively.

The slow background reaction between

TPBA⁺ and CHD was found to have little relevance to the Diels-Alder dimerization process with respect to kinetics. In the absence of added TBPA, the latter proceeded very rapidly (82 % yield of dimer within 2 min when a 0.8 mM solution of TBPA⁺ was made 8 mM in [CHD]). The second-order rate constant was $6.8 \text{ M}^{-1} \text{ s}^{-1}$. The same experiment, but with 0.8 mM TBPA added, gave 74 % dimer within 3 min, rate constant $3.5 \text{ M}^{-1} \text{ s}^{-1}$. Thus, the reaction is approximately inverse first-order in [TBPA]. The ratios between the rate constants of the Diels-Alder and background reaction were calculated to be 60 and 45, respectively. These experiments could be combined into one showing the persistent catalytic activity of a reacted solution: a solution, 0.8 mM in TBPA⁺, was made 8.0 mM in CHD and then gave 82 % dimer after 2 min. At this stage, when the background reaction had proceeded to an extent of ca. 50 % (UV), the solution was again made 8.0 mM in CHD, whereupon rapid Diels-Alder dimerization took place (71 % yield after 3 min).

The background reaction most likely consists of an ET/proton transfer/ET (ECE in electro-

chemical nomenclature) sequence, leading to the 1,3-cyclohexadienyl cation and, ultimately, to oligomers⁷ derived from reactions of this carbocation. With added strong base, proton abstraction from the radical cation becomes prominent, leading to benzene (20–40% yield, depending upon the reaction conditions) after a second ET/deprotonation sequence. Both these reactions consume TBPA^{•+}. The oligomerization process should be approximately second-order in [CHD] and inverse first-order in [TBPA], provided the initial ET step and the proton transfer step are reversible [eqns. (5)–(8), where CHD has been denoted MH and B is a base]. These requirements seem to be fulfilled when no external base is added and CHD itself and/or TBPA must act as very weak base(s) in the reaction of eqn. (6), as appears feasible on the basis of a steady-state treatment of the kinetic scheme of eqns. (5)–(8)



(assuming that [CHD^{•+}] and [M[•]] are constant and the oxidation of the latter very fast). With added strong base, the reaction of eqn. (6) becomes irreversible and the kinetic expression changes so that the reaction becomes first-order in [CHD].

Thus, the TBPA^{•+}-catalyzed Diels-Alder dimerization of CHD is presumably not a radical chain reaction, as indicated by its kinetics and the fact that TBPA must be present in appreciable concentration during the reaction, formed via the unavoidable background reaction and also likely to be present as a non-trivial impurity in the radical cation salt. The dual mechanism also nicely explains why anodic initiation of the Diels-Alder dimerization reaction is so inefficient (for

CHD itself, yields of the dimer are at best of the order of 15%, with oligomers as the products;⁷ cross Diels-Alder reactions gave yields of 30–35% under optimized anodic conditions⁸). A radical chain reaction would not be disfavoured by the mere fact that the radical cation is generated at an anode, as exemplified by the high yields of products from the anodically initiated oxygenation of certain olefins,⁹ but the follow-up reaction is favoured under electrochemical conditions (base attack upon the radical cation by the anion of the supporting electrolyte and/or water, inevitably present in relatively high concentration at the electrode/solution interface).

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References

1. Ebersson, L. and Larsson, B. *Acta Chem. Scand., Ser. B* **40** (1986) 210.
2. Ebersson, L. and Larsson, B. *Acta Chem. Scand., Ser. B* **41** (1987) 367.
3. Bauld, N. L., Bellville, D. J., Harirchian, B., Lorenz, K. T., Pabon, R. A. Jr., Reynolds, D. W., Wirth, D. D., Chiou, H.-S. and Marsh, B. K. *Acc. Chem. Res.* **20** (1987) 371.
4. Lorenz, K. T. and Bauld, N. L. *J. Am. Chem. Soc.* **109** (1987) 1157.
5. Ebersson, L. *J. Mol. Catal.* **20** (1983) 27; Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer, Heidelberg 1987.
6. Ebersson, L. *J. Am. Chem. Soc.* **105** (1983) 3192.
7. Nigenda, S. E., Schleich, D. M., Narang, S. C. and Keumi, T. *J. Electrochem. Soc.* **134** (1987) 2465.
8. Mlcoch, J. and Steckhan, E. *Tetrahedron Lett.* **28** (1987) 1081.
9. Nelsen, S. F. *Acc. Chem. Res.* **20** (1987) 269.
10. Ebersson, L. and Ekström, M. *Acta Chem. Scand., Ser. B* **42** (1988) 113.

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