Evidence for Non-biradicaloid Transition States in Diels–Alder Reactions

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Linear free energy relationships and a measure of the degree of asynchronicity in Diels–Alder reactions of cyclopentadiene with some arylsulphonyl ethenes support a synchronous mechanism.

Dewar continues[1—3] to maintain that Diels–Alder (DA) reactions proceed *via* asymmetrical transition states with bond formation between the diene and each end of the dienophile being concerted and asynchronous. Using rate coefficients for DA reactions of cyclopentadiene with ethene $k(\mathbf{1})$, and with 1,2-disubstituted ethenes (RCH=CHR′) $k(\mathbf{3})$, he has predicted values of $k(\mathbf{2})$ [*viz.* $k'(\mathbf{2})$ and $k''(\mathbf{2})$] for monosubstituted ethenes ($RCH=CH_2$) based on the assumption of a purely concerted [equation (1)] and a purely two-step [equation (2)] process. Neither of these limiting behaviours has seemed to operate based on observed values of $k(\mathbf{2})$ (see Table 1), leading Dewar to postulate[1—3] rather that the reactions involved an intermittent two-stage process.[†] In this there is not a 'stable intermediate' as such but rather a 'biradicaloid' transition state.[1] A measure of the degree of asynchronicity (DASYN) could thence be determined [equation (3)].[3,4]

$$k'(\mathbf{2}) = [k(\mathbf{3}).k(\mathbf{1})]^{-\frac{1}{2}} \qquad (1)$$

$$k''(\mathbf{2}) = \tfrac{1}{2}[k(\mathbf{3}) + k(\mathbf{1})] \qquad (2)$$

$$\mathrm{DASYN} = \frac{k_{\mathrm{obs}}(\mathbf{2}) - k'(\mathbf{2})}{k''(\mathbf{2}) - k'(\mathbf{2})} \qquad (3)$$

Semiempirical Molecular Orbital calculations, based on UMNDO and UAM1 methods,[1] have been applied to the reactions of butadiene with ethene and its mono- and dicyano-derivatives and the results provide corroborating support by predicting unequal distances at the bonding sites in the transition states.

As part of a continuing study of transmission of electronic effects by $ArSO_2^-$ groups,[5] some DA reactions of arylsulphonyl ethenes and cyclopentadiene are currently under investigation. We report here some of our preliminary findings, *e.g.* rate coefficients, DASYN values (see Table 1), and linear free energy relationships (LFER) (see Figures 1 and 2), since all the data indicate that these reactions have greatly reduced asymmetry in their transition states.

Generally, the DASYN values shown in Table 1 increase as the reactivity of the dienophiles decrease. For the sequence (**1**) → (**2**) → *trans*-(**3**) involving the arylsulphonyl ethenes, the DASYN (*trans*) values are so small that it is difficult to invoke asymmetry arguments with these dienophiles. The slightly larger DASYN (*cis*) values for the sequence (**1**) → (**2**) → *cis*-(**3**) appears to reflect only a very modest increase in 'biradicaloid' character which may be associated with the rate retarding influences caused by steric effects in the *cis* isomers of (**3**) relative to those in the *trans* isomers.[6]

These kinetic results appear to be the first cases which convincingly meet the requirements[3] that the reactants (**1**)—(**3**) (i) must vary considerably in their reactivity and (ii)

[†] Definitions of synchronous, concerted, two-step, and two-stage processess in this work are the same as those described by Dewar. See, for example, ref. 1.

have rate coefficients [k(**2**) values] which agree well with predicted values as determined by equation (1) [k'(**2**)], and hence the process may be considered synchronous.

The implications of these findings are important. First, the reaction between ethene and cyclopentadiene ought to be considered as a concerted, synchronous process, since it has been suggested[3] that if equation (1) holds accurately, then the reactions with the arylsulphones (**2**) and *trans*-(**3**), and with ethene (**1**) all have to be synchronous. This conclusion has already been predicted from *ab initio* calculations[7] and refutes those based on MNDO[1] and MINDO/3 methods.[3] Secondly, the transmission of electronic effects by one arylsulphonyl group should be unaffected by the introduction of a second $ArSO_2^-$ group into the dienophile. Thirdly, the two arylsulphonyl groups in (**3**) should show simultaneous and equivalent electronic effects. The latter two hypotheses appear to be borne out fully by Hammett plots shown in Figures 1 and 2.

LFER plots of log k_{obs} *vs.* $\Sigma\sigma$ [where $\Sigma\sigma = \sigma_x$ for (**2**) (R = p-$XC_6H_4SO_2$) and $\Sigma\sigma = \sigma_x + \sigma_y$ for (**3**) (R = p-$XC_6H_4SO_2$ and R′ = p-$YC_6H_4SO_2$)] produce the three parallel linear curves shown in Figure 1. The ρ values of 0.94 ± 0.01 [for (**2**) r = 1.000)], 0.99 ± 0.02 [for *cis*-(**3**) r = 0.999], and 1.00 ± 0.05 [for

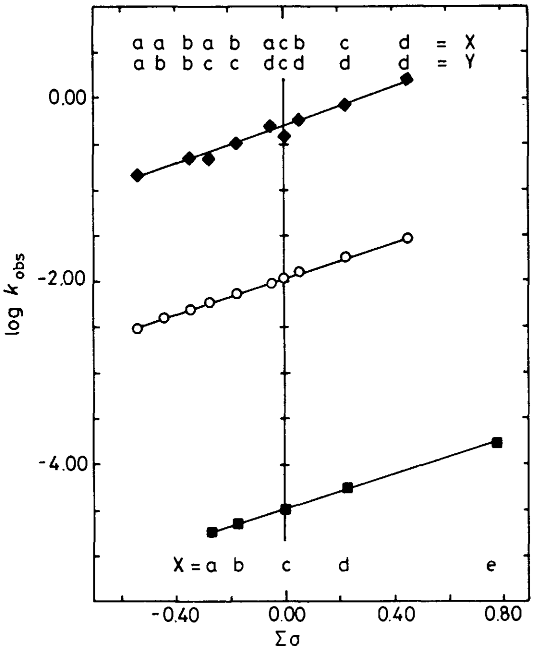

Figure 1. Relationships between log k_{obs} of aryl vinyl sulphones [(**2**) ■] and 1,2-bis(arylsulphonyl)ethenes [*cis*-(**3**) ○ and *trans*-(**3**) ◆] and Hammett $\Sigma\sigma$ values. Aryl = XC_6H_4 and YC_6H_4, where X and Y are (a) p-MeO, (b) p-Me, (c) H, (d) p-Cl, and (e) p-NO_2.

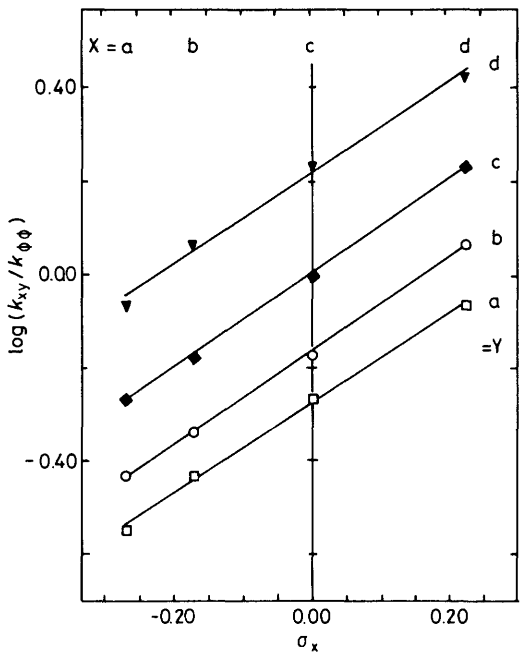

Figure 2. Relationship between log($k_{xy}/k_{\phi\phi}$) of *cis*-1,2-bis(arylsulphonyl)ethenes and Hammett σ_x-constants, where YC_6H_4 is held constant while XC_6H_4 is varied. X and Y = (a) p-MeO, (b) p-Me, (c) H, and (d) p-Cl.

Table 1. Second order rate coefficients[a] and DASYN values for Diels–Alder reactions of cyclopentadiene with monosubstituted ethenes (**2**; $RCH=CH_2$) and 1,2-disubstituted ethenes (**3**; RCH=CHR′).

R,R′	k(*trans*-**3**) /10^{-4}u[b]	k(**2**) /10^{-4}u	k'(**2**)[c] /10^{-4}u	k''(**2**)[c] /10^{-4}u	DASYN/10^{-3} (*trans*)	k(*cis*-**3**) /10^{-4}u	DASYN/10^{-3} (*cis*)
p-$ClC_6H_4SO_2$	15 894.2	0.550	0.2060	7 947.1	0.04	282.0	3.71
$C_6H_5SO_2$	3 761.1	0.322	0.1002	1 880.6	0.12	106.1	5.75
p-$MeC_6H_4SO_2$	2 236.4	0.225	0.0773	1 118.2	0.13	48.6	8.79
p-$MeOC_6H_4SO_2$	1 520.3	0.181	0.0637	760.2	0.15	30.0	11.48
COCl	50 000.0[e]	44.486[d]	0.3650	25 000.0	1.76	—	—
COMe	29.6[e]	0.269[d]	0.0089	15.0	17.35	—	—
CN	8.1[e]	0.104[e]	0.0046	4.1	24.27	9.1[c]	21.80
CO_2Me	7.4[e]	0.118[e]	0.0044	3.7	30.74	—	—

[a] Unless referenced, all determinations of rate coefficients were made for $CHCl_3$ solutions at 25 °C by measuring the disappearance in u.v. absorptions between 250 and 290 nm by *trans*-(**3**) and ν_{C-H} absorptions between 515 and 650 cm^{-1} or 970 and 985 cm^{-1} by (**2**) and *cis*-(**3**). The mean values of k (±3%) were derived from at least two kinetic runs with each dienophile, where the concentrations of dienophiles were varied within the ranges 0.1—0.3, 0.04—0.10, and 0.0001—0.004 mol dm^{-3} for (**2**), *cis*-(**3**), and *trans*-(**3**), respectively, and cyclopentadiene was always used in 1.2—4.0 fold excess. [b] u = dm^3 mol^{-1} s^{-1}. [c] Based on the rate coefficient [k(**1**)] equal to 2.67 × 10^{-10} dm^3 mol^{-1} s^{-1} for ethene (**1**). This value was calculated directly from relative reactivity data provided by Dewar[1] for the cycloadditions between cyanoethenes and cyclopentadiene (see Table, ref. 1) and it represents an estimate secured by him[3] from further data tor the ethene–butadiene reaction, see: D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, 1951, **10**, 198. Similar calculations based on k(**1**) values anywhere in the range 10^{-15} to 10^{-9} dm^3 mol^{-1} s^{-1} cause only minor variations in the DASYN values and do not alter the conclusions in the discussion. [d] Ref. 8. [e] Ref. 9.

trans-(**3**) $r = 0.987$] confirms within experimental expectations that the *para*-substituents in the aromatic rings influence reactivity identically.

Figure 2 is a similar type of plot which shows the individual transmission behaviours by each arylsulphonyl group in *cis*-(**3**). The gradients (ρ_x) of the parallel linear curves and the intercepts ($\rho_y\sigma_y$) indicate that $\rho_x = \rho_y = 0.98 \pm 0.02$ ($r = 0.996$) and that each $ArSO_2^-$ group in the bis-sulphones (**3**) participates equally in the transition states of these reactions.

One of us (B. F. W.) acknowledges the receipt of an O.R.S. Award.

Received, 27th October 1987; Com. 1563

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