Characterization of cation radical reactions. Aminium salt-catalysed Diels–Alder reactions

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Kinetic studies of the Diels–Alder cycloadditions of a series of *trans*-stilbenes (2) to 2,3-dimethylbuta-1,3-diene (3), catalysed by tris(4-bromophenyl)aminium hexachloroantimonate ($1^{\bullet+}$), reveal a curved Hammett–Brown plot, consistent with a mechanistic transition from reversible to rate determining ionization of 2 to $2^{\bullet+}$ as the substituents become progressively more electron donating. Further, substituent effects in mono- and di-substituted stilbenes are essentially multiplicative, describing a distribution of positive charge which is symmetrical with respect to both aryl rings. The symmetry of the charge development is inconsistent with an electrophilic addition to the substrates, proceeding *via* a carbocation. The combination of the magnitude and symmetry of the positive charge distribution provides strong evidence for a cation radical mechanism.

The discovery of the triarylaminium salt catalysed Diels–Alder reaction has stimulated interest in cation radical chemistry and facilitated the development of a wide range of cation radical pericyclic chemistry.[1] The ability to generate cation radicals of a variety of substrates using catalytic quantities of the commercially available and shelf-stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate ($1^{\bullet+}$)[2] is an especially attractive feature of the method. The reactions are often stereospecific and surprisingly selective, as well as extraordinarily fast and efficient. The scope and limitations of aminium salt catalysed pericyclic chemistry have already been discussed.[3,4] In a few interesting cases, $1^{\bullet+}$ has been found to induce Brønsted acid-catalysed, carbocation-mediated chemistry, rather than the expected cation radical chemistry.[5] Fortunately, a simple diagnostic test for distinguishing these two mechanistic types has been developed.[6,7] Specifically, inclusion of a hindered base such as 2,6-di(*tert*-butyl)pyridine in the reaction medium completely suppresses Brønsted acid catalysed processes but allows most cation radical processes to proceed. Recently, the possibility that $1^{\bullet+}$ could act as an electrophile *via* one of its electron deficient aryl positions has been suggested as an alternative mechanism for generating carbocations, which would not necessarily be suppressed by hindered bases. Such an electrophile-catalysed, carbocation mediated mechanism was, in fact, proposed for the Diels–Alder cyclodimerization of cyclohexa-1,3-diene, a reaction which is widely considered to be a prototypical cation radical reaction.[8] While it is important to realize that the assignment of a cation radical mechanism for this and other aminium salt-catalysed Diels–Alder reactions rests upon a far broader platform than the hindered base criterion,[3,4] it nevertheless appeared important to develop definitive mechanistic criteria which would decisively rule out (or rule in) the hypothetical electrophilic mechanism. Beyond this, the ultimate goal of this research was to develop criteria which would point positively and uniquely to a cation radical mechanism for these reactions.

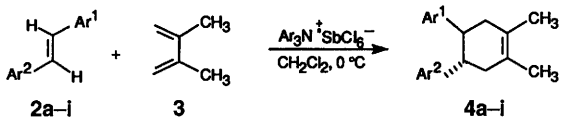
Results and discussion

It is proposed that for a symmetrical π system (such as *trans*-stilbene), the development of a full unit of positive charge distributed symmetrically over the system is a unique and positive indication of cation radical formation. In contrast, electrophilic addition yielding a carbocation intermediate generates a highly unsymmetrical positive charge distribution. Symmetrical bridging by the electrophile could result in a symmetrical charge distribution, but in that case a substantial portion of the charge would be borne by the bridging electrophile, rather than the substrate. In any case, symmetrical bridging would not appear to be a viable possibility for the triarylaminium electrophile.[9] The stilbene system appeared especially appropriate because the peak oxidation potentials of a very long series of symmetrically *p,p'*-disubstituted stilbenes had been obtained and found to correlate nicely with the σ^+ parameter.[10] The $E_{\frac{1}{2}}$ *vs.* σ^+ equation quoted in this latter study affords a ρ value of -10.8. A subsequent study found the oxidations of the 4,4'-dimethyl- and 4,4'-dimethoxystilbenes to be essentially reversible.[11] The oxidation potentials found in this second study for these reversibly oxidized stilbenes are also consistent with $\rho = -10.8$. Other studies have demonstrated that ρ values for electrochemical oxidations are not very sensitive to solvent polarity.[12] The value $\rho = -10.8$ would therefore appear to be a valid approximate indication for the generation of a full unit of positive charge (as the cation radical) in the stilbene system. This ρ value, however, is based upon a symmetrically disubstituted stilbene system wherein the σ^+ value of a single substituent is used. For example, in the case of 4,4'-dimethylstilbene, the σ^+ value of a single *p*-methyl substituent (-0.31) was used.[10] To assess the *symmetry* of the charge distribution, it was essential to include monosubstituted stilbenes in our experimental study. Consequently, the more general form of the Hammett–Brown equation, $\log k/k_0 = \rho\Sigma\sigma^+$, was used. In this context, 4,4'-dimethylstilbene has two *p*-methyl substituents and $\Sigma\sigma^+ = -0.62$. The effect of recasting the Hammett–Brown equation in the more general form is simply to divide the ρ value by a factor of two (*i.e.* $\rho = -5.4$).

The Diels–Alder addition of stilbene, and of a series of mono- and di-substituted stilbenes (**2**) to 2,3-dimethylbuta-1,3-diene (**3**) was selected as an appropriate reaction system (Scheme 1). The competition kinetics of the Diels–Alder reactions of a series of nine stilbenes with a five-fold excess of **3** were studied at 0 °C in dichloromethane in the presence of $1^{\bullet+}$. Each relative rate constant (Table 1) was cross-checked by matching a specific substrate with at least two different partners. The kinetic runs were always carried out to less than 10% conversion, and mass balances were *ca.* 98%. No products other than the Diels–Alder adducts (**4**) were detectable. The Hammett–Brown plot is very nicely linear ($r^2 = 0.998$; Fig. 1) for all but the three most easily ionizable substrates (**2a–2c**) and has $\rho = -5.45$. The full plot

Table 1 Relative rate constants for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene (**3**), catalysed by $\mathbf{1}^{\bullet+}$

Substrates	$k_{rel}(CH_2Cl_2)$	k_{rel}(MeCN)
4,4′-Dimethylstilbene (**2a**)	44.0	20.8
3,4-Dimethylstilbene (**2b**)	34.0	11.7
4-Methylstilbene (**2c**)	10.0	6.5
3,3′-Dimethylstilbene (**2d**)	5.8	3.1
3,5-Dimethylstilbene (**2e**)	5.9	3.0
3-Methylstilbene (**2f**)	2.5	1.8
Stilbene (**2g**)	1.0	1.0
4-Chlorostilbene (**2h**)	0.22	0.39
4,4′-Dichlorostilbene (**2i**)	0.07	0.09



2a–i **3** **4a–i**

2a 4,4′-Dimethylstilbene = 4,4′-DMSB
b 3,4′-Dimethylstilbene = 3,4-DMSB
c 4-Methylstilbene = 4-MSB
d 3,3′-Dimethylstilbene = 3,3′-DMSB
e 3,5-Dimethylstilbene = 3,5-DMSB
f 3-Methylstilbene = 3-MSB
g Stilbene = SB
h 4-Chlorostilbene = 4-CSB
i 4,4′-Dichlorostilbene = 4,4′-DCSB

Scheme 1

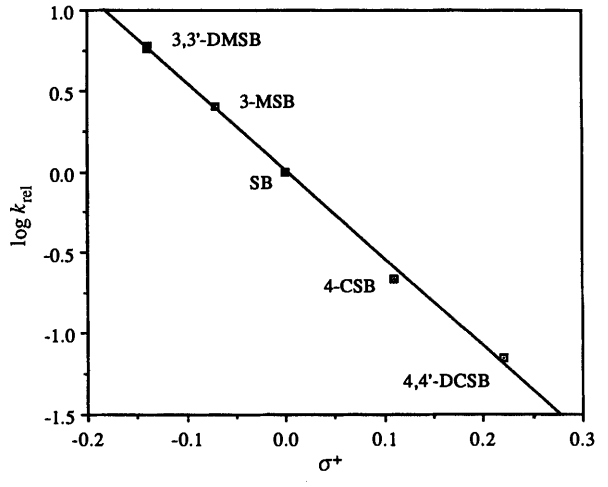
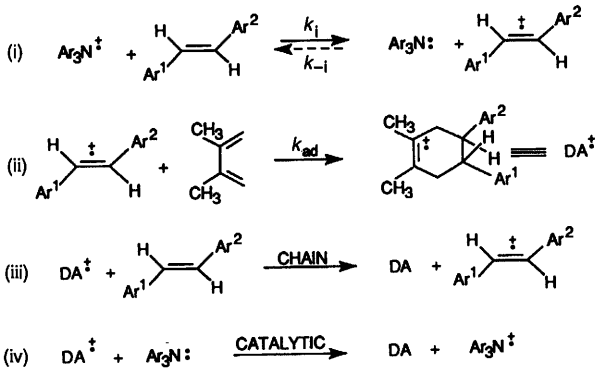


Fig. 1 Partial Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene, catalysed by $\mathbf{1}^{\bullet+}$ in dichloromethane at 0 °C; SB = stilbene, MSB = methylstilbene, DMSB = dimethylstilbene, C = chlorostilbene, DC = dichlorostilbene; $\rho = -5.45$, $r^2 = 0.998$

(Fig. 2) shows marked curvature for the three noted substrates, suggesting a mechanistic change. The effective ρ value in this region sharply diminishes to ρ = *ca.* −2.7. These observations are consistent with a mechanistic change from equilibrium controlled ionization ($\rho = -5.4$) to a kinetically controlled ionization step (Scheme 2). According to the Marcus equation, a kinetically controlled electron transfer having no thermodynamic driving force would have a ρ value exactly one-half that for the equilibrium electron transfer.[13] A mildly endergonic electron transfer (ET) such as that involved in the ionization of stilbene by $\mathbf{1}^{\bullet+}$ is predicted to have a slightly larger (negative) ρ value.

Further support for the proposed cation radical mechanism is available from a plot of log k_{rel} for these Diels–Alder reactions *vs.* the corresponding log k_{rel} values for aminium salt-catalysed cyclopropanation by ethyl diazoacetate, a reaction for which a cation radical mechanism has already been strongly supported (Fig. 3).[14] Not only are substituent effects nicely parallel, they are quantitatively virtually identical, in a



Scheme 2 (*a*) If $k_{ad}[\text{diene}] \gg k_{-i}[Ar_3N:]$, ionization is kinetically controlled. If $k_{-i}[Ar_3N:] \gg k_{ad}[\text{diene}]$, ionization is equilibrium controlled. (*b*) Steps (i), (ii) and (iii) constitute a cation radical chain mechanism, with step (i) as the initiation and steps (ii) and (iii) as propagation. A mechanism involving steps (i), (ii) and (iv) is a classic catalytic mechanism. In the chain mechanism, the substrate is ionized by product cation radicals ($DA^{\bullet+}$). In the catalytic mechanism, the aminium salt ionizes the substrate.

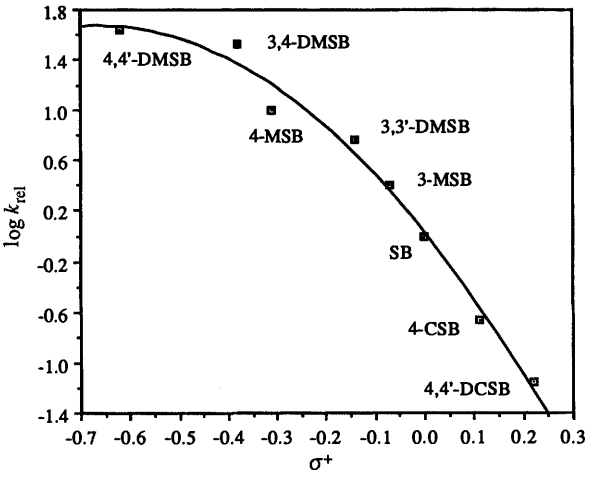


Fig. 2 Full Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene, catalysed by $\mathbf{1}^{\bullet+}$ in dichloromethane at 0 °C

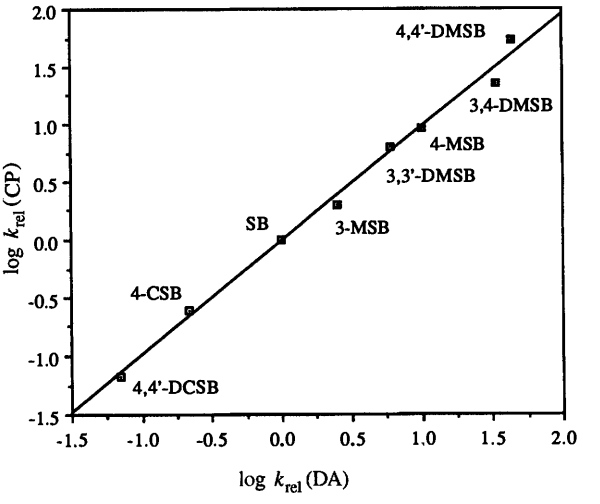


Fig. 3 Plot of log k_{rel}(CP) for the cyclopropanation of substituted *trans*-stilbenes by ethyl diazoacetate *vs.* log k_{rel}(DA) for the Diels–Alder additions of the same stilbenes to 2,3-dimethylbuta-1,3-diene, both reactions catalysed by $\mathbf{1}^{\bullet+}$ in dichloromethane at 0 °C; slope = 0.982, $r^2 = 0.993$

statistical sense (slope = 0.98). This correlation strongly indicates that substituent effects are primarily determined in a step which does not involve the neutral components and that the two reactions have essentially identical mechanisms,

Table 2 Effect of the concentration of 2,3-dimethylbuta-1,3-diene (**3**) upon the absolute reaction rate of Diels–Alder cycloadditions

Substrates	[3]/mol dm^{-3}	t/min	Conversion (%)
4-Methylstilbene (**2c**)	0.082	10	7.3
	0.170	10	7.4
	0.082	20	8.7
	0.170	20	8.9
	0.082	30	10.1
	0.170	30	10.7
	0.082	40	11.9
	0.170	40	12.5
4-Chlorostilbene (**2h**)	0.100	30	0.3
	0.200	30	0.6
	0.100	60	0.4
	0.200	60	0.8
	0.100	90	0.5
	0.200	90	0.9
	0.100	120	0.6
	0.200	120	1.1
3,3′-Dimethylstilbene (**2d**)[a]	0.081	180	0.7
	0.162	180	1.9

[a] In the presence of 11 mol% of neutral **1**.

Table 3 Peak oxidation potentials (E_{ox}/V *vs.* SCE) for substituted *trans*-stilbenes in acetonitrile, by differential pulse voltammetry

Substrates	E_{ox}/V (25 °C)	E_{ox}/V (0 °C)
4,4′-Dimethylstilbene (**3a**)	1.236	1.229
3,4-Dimethylstilbene (**3b**)	1.275	1.269
4-Methylstilbene (**3c**)	1.322	1.302
3,3′-Dimethylstilbene (**3d**)	1.359	1.334
3-Methylstilbene (**3f**)	1.386	1.366
Stilbene (**3g**)	1.420	1.389
4-Chlorostilbene (**3h**)	1.458	1.417
4,4′-Dichlorostilbene (**3i**)	1.476	1.455
3-Chlorostilbene (**3j**)	1.516	1.483

including the transition from thermodynamically controlled to kinetically controlled ionization.

Mechanistic transition

The proposed transition from reversible to rate determining ionization (Scheme 2) closely parallels that found for the cyclopropanation of these same stilbene substrates.[14] The reversibility of the ionization step for the substrates on the linear portion of the Hammett–Brown plot (**2d–2i**) is indicated by the magnitude of ρ which, as noted previously, approaches the equilibrium ρ value for the ionization of these substrates and is much larger than expected for kinetically controlled ionization. Further, the absolute rate of reaction of 4-chlorostilbene (**2h**) with **3** is linearly dependent upon the concentration of the diene **3** (Table 2), as would be expected for a rate determining cycloaddition step. In sharp contrast, the absolute rate of reaction of 4-methylstilbene (**2c**) is independent of the concentration of **3**, as would be expected for rate determining ionization. Analogous observations have previously been made for the cyclopropanation of these same substrates (**2c** and **2h**).[14] Further corroboration of these mechanistic assignment was sought *via* experiments using 3,3′-dimethylstilbene (**2d**), which appears to be at the borderline of the mechanistic transition. Using added **1** (the neutral triarylamine; 10 mmol%) to enhance the rate of reversal of ionization, the dependence of the absolute rate of reaction of **2d** with **3** was investigated. The rate (Table 3) is essentially linearly dependent upon the concentration of **3**.

While it is reasonable to propose that electron-donating groups such as *p*-methyl substantially diminish the rate of reversal of ionization, it is also expected that they will retard the rate of cycloaddition. Is it reasonable to expect that the reversal of ionization is more strongly affected than is the cycloaddition rate? The present kinetic studies appear to provide an affirmative response. Since the kinetic ρ value for the substrates for which cycloaddition is rate determining rather closely approaches the equilibrium ρ value, it is clear that the (positive) ρ value for the rate determining step itself is much smaller than the equilibrium ρ value. Thus, there is apparently relatively little charge transfer from $\mathbf{2}^{\bullet+}$ to **3** in the transition state for cycloaddition. Consequently, it is plausible that substituent electronic effects on the ionization step (and its reversal) are dominant over substituent effects on the cycloaddition step.

The observation that, in both the Diels–Alder additions and in cyclopropanation, the amount of charge transfer to the neutral reactant in the cycloaddition transition state is relatively small is of fundamental interest. The extent of this charge transfer will be assessed more quantitatively in a subsequent section. However, qualitatively, the much lower oxidation potential of the stilbenes than either of the relevant neutral reactants (**3** and ethyl diazoacetate) is consistent with this observation.[15]

Symmetry of the charge distribution

The symmetrical disposition of the charge essentially follows from the inclusion of both mono- and di-substituted stilbenes on the plot, but is more critically evaluated from a comparison of the rate constants themselves. For example, the first *m*-methyl substituent accelerates the rate by a factor of 2.5 relative to stilbene, while the second *m*-methyl substituent (3,3′-dimethylstilbene) accelerates the rate by a factor of 2.3 relative to 3-methylstilbene. Similarly, the relative rate constants for 3,3′-dimethylstilbene (5.80) and 3,5-dimethylstilbene (6.00) are very nearly equal. Further, the first *p*-chloro substituent retards the rate by a factor of 0.22, while the second retards by a further 0.32. In the case of the more strongly electron donating *p*-methyl substituent, the effect of the second *p*-methyl group (4.4) is noticeably less than that of the first such substituent (10.0), but is still far greater than expected for a carbocation forming process. In the rate determining protonation of *cis*-stilbenes (leading to geometric isomerization), for example, the effect of the first *p*-methyl substituent is virtually the same as found in the present work (10.5), but the second *p*-methyl accelerates the rate by only a factor of 1.4.[16] It is, of course, not unlikely that more strongly perturbing substituents will induce some asymmetry in the charge distributions of monosubstituted stilbene cation radicals, so that appreciable deviations from the ideal of multiplicative substituent effects are plausible even for a cation radical forming process.

Kinetic studies in acetonitrile

In order to define more quantitatively the extent of positive charge accumulation on the stilbene moiety, it appeared necessary to study the reaction kinetics in the same solvent and at the same temperature used to measure the oxidation potentials which provide the value of ρ corresponding to the development of a unit positive charge on the stilbene system. To fulfill this requirement, the kinetics were studied in acetonitrile at 0 °C (Table 1), and the oxidation potentials of the present series of stilbenes were measured under the same conditions of solvent and temperature by differential pulse voltammetry (DPV, Table 3). The latter correlate nicely with σ^+ (Fig. 4), and the resulting slope (0.272) corresponds to $\rho = -5.02$. The Hammett–Brown plot for the kinetic data is curvilinear, just as in the case of the dichloromethane system (Fig. 5). The datasets in the two solvents correlate very well (Fig. 6), providing additional confidence in the data. The linear portion of the Hammett–Brown plot (Fig. 7) yields a ρ value of -4.16. Comparing this with the equilibrium ρ value (-5.02), it emerges that substituent electronic effects on the free energy of activation — which are engendered by the positive charge development — are approximately 83% as large as in the full-

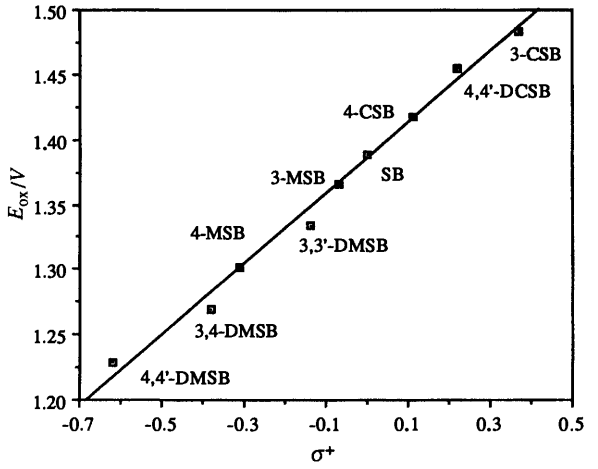


Fig. 4 Plot of oxidation potentials (E_{ox}) of substituted *trans*-stilbenes in acetonitrile at 0 °C *vs.* σ^+; slope = 0.272, r^2 = 0.989

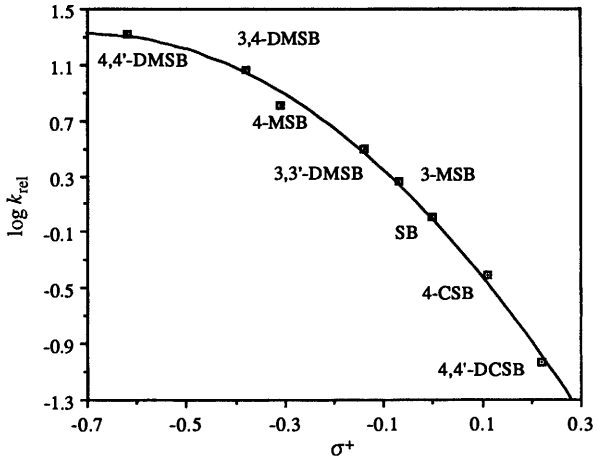


Fig. 5 Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene, catalysed by $\mathbf{1}^{\bullet+}$ in acetonitrile at 0 °C

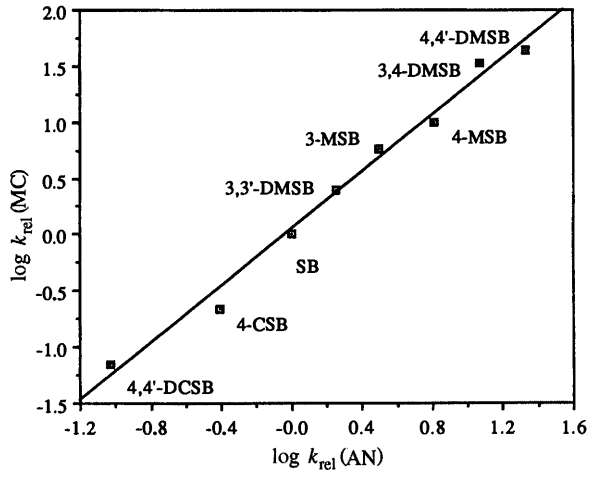


Fig. 6 Plot of $\log k_{rel}$ for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene in dichloromethane (MC) *vs.* $\log k_{rel}$ in acetonitrile (AN), catalysed by $\mathbf{1}^{\bullet+}$ at 0 °C; slope = 1.27, r^2 = 0.988

fledged stilbene cation radical. The ρ value for cyclopropanation of these same stilbene substrates (−4.56) indicates that substituent free energy effects are approximately 91% of the value for stilbene cation radicals.[14] These data suggest that approximately 17% and 9%, respectively, of the positive charge is transferred to the neutral component (**3** or ethyl diazoacetate)

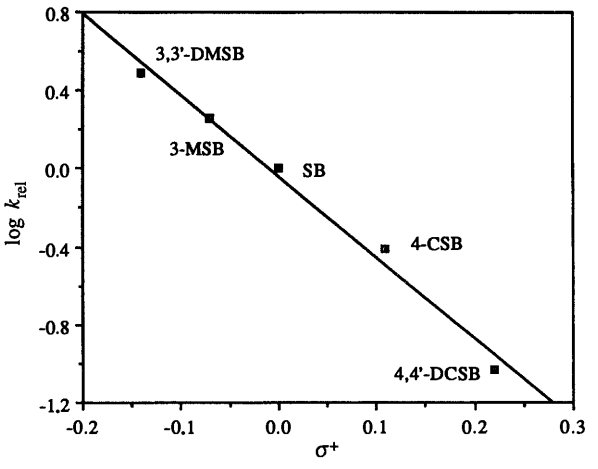


Fig. 7 Linear portion of the Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-stilbenes to 2,3-dimethylbuta-1,3-diene, catalysed by $\mathbf{1}^{\bullet+}$ in acetonitrile at 0 °C; ρ = −4.16, r^2 = 0.988

in the transition state of the relevant rate determining cycloaddition. The relative extents of charge transfer to these neutrals is, in fact, in accord with their relative oxidation potentials.[15]

While these substituent effects yield quantitative insights into the amount of positive charge development on **2**, they yield no quantitative information concerning the amount of unpaired spin density developed or even whether unpaired spin density is developed at all. The crucial factor which links the positive charge development to the development of cation radical character (as opposed to carbocation character) is the symmetry of the charge development, which has already been established.

In the most rigorous sense, it is the development of unit positive charge in a symmetrical distribution which characterizes cation radical formation.[14] In the context of cation radical *reactions*, unit positive charge development appears to be attainable only in two hypothetical situations: (i) in a rate determining substrate ionization which is so highly endergonic that there is complete charge transfer to the substrate in the transition state, and (ii) in a reaction wherein cation radical formation is reversible, and there is no charge transfer to the reaction partner in the subsequent rate determining step. Neither of these hypothetical situations appear realistic, but the present results represent a rough approximation of the second scenario. Nevertheless, it would appear that the development of cation radical character in the overwhelming amounts estimated in this work and in the previous work on cyclopropanation can be confidently interpreted as evidence for a cation radical intermediate (specifically $\mathbf{2}^{\bullet+}$).

Rate retardation by added triarylamine 1

The kinetic data already presented exclude a hypothetical electrophilic mechanism proceeding *via* a carbocation intermediate and provide positive evidence for a cation radical mechanism. The possible formation of a charge transfer complex between $\mathbf{1}^{\bullet+}$ and **2** and its Diels–Alder addition to **3** is also excluded by the size of the charge development on **2**. Further evidence for complete electron transfer (affording **1** and $\mathbf{2}^{\bullet+}$), as opposed to partial electron transfer (as in a complex) is the pronounced rate retardation observed upon addition of the neutral triarylamine **1**. When **1** (100 mol% relative to the substrate) is added to solutions of the most reactive substrate included in this study, 4,4'-dimethylstilbene (**2a**), the rate of Diels–Alder addition to **3** is slowed to an unobservable rate. A very conservative estimate of the rate retardation is a factor of 100. Rate retardation by **1** is expected for the proposed cation radical mechanism based upon the

exergonic reversal of the ionization step, but is not anticipated for a reaction involving the hypothetical charge transfer complex. It was also previously noted that the addition of 10 mol% of **1** changes the rate law for the reaction of 3,3′-dimethylstilbene, an observation nicely consistent with the proposed cation radical mechanism, but not readily interpreted in terms of a charge transfer complex mechanism. Further, rate retardation by added **1** would not be expected for a carbocation mechanism, since the only plausible mechanism for the trapping of a carbocation intermediate by **1**, *viz.* reduction to the corresponding radical by electron transfer from **1**, is substantially endergonic for the relevant benzylic carbocations.[12]

Reactivity of *cis*- *vs.* *trans*-stilbenes

In the stilbene series, electrophilic additions to the *cis*-isomer are typically about five times as fast as to the *trans*-isomer.[17] In contrast, the oxidation of *trans*-stilbene ($E_{\frac{1}{2}}$ = 1.59 V *vs.* SCE) is significantly more facile than the oxidation of *cis*-stilbene ($E_{\frac{1}{2}}$ = 1.70 V).[11] In fact, the aminium salt ($\mathbf{1}^{\bullet+}$) catalysed Diels–Alder addition of *cis*-stilbenes to 2,3-dimethylbuta-1,3-diene is too slow to be observed. The estimated minimum value of the reactivity ratio for *trans*/*cis*-stilbene is at least a factor of 100, in qualitative accord with the cation radical mechanism. At 0 °C, the 0.11 V (2.54 kcal mol^{-1}†) difference in oxidation potentials of *cis*- and *trans*-stilbene could account for a relative rate ratio of 107.

Summary

Kinetic studies of the Diels–Alder cycloadditions of a series of *trans*-stilbenes (**2**) to 2,3-dimethylbuta-1,3-diene (**3**), catalysed by tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{\bullet+}$), reveal a curved Hammett–Brown plot, consistent with a mechanistic transition from reversible to rate determining ionization of **2** to $\mathbf{2}^{\bullet+}$ as the substituents become progressively more electron donating. In the former case (reversible ionization followed by rate determining cycloaddition), the reaction rates depend linearly upon the concentration of **3**, and in the latter case (rate determining ionization) the rates are independent of the concentration of **3**. For the substrates for which ionization is reversible, the Hammett–Brown plot is linear and the magnitude of ρ (−4.16) is rather close to the ρ value for the reversible conversion of these substrates to the corresponding cation radicals in the same solvent and at the same temperature (ρ = −5.02). The magnitude of the kinetic ρ value reflects the fact that substituent effects in the transition state of the rate determining cycloaddition are 83% of those for the conversion to the full-fledged cation radical. Further, substituent effects in mono- and di-substituted stilbenes are essentially multiplicative, describing a distribution of positive charge which is symmetrical with respect to both aryl rings. The symmetry of the charge development is inconsistent with an electrophilic addition to the substrates, proceeding *via* a carbocation. The combination of the magnitude and symmetry of the positive charge distribution provides strong evidence for a cation radical mechanism. The transfer of only a relatively small amount of positive charge (*ca.* 17%) to **3** in the cycloaddition transition state is of fundamental interest, and is consistent with the much lower ionization potential of **2** than **3**. For the more readily oxidizable stilbenes (**2a**–**2c**), the effective ρ value drops sharply to a value roughly one-half of the equilibrium ρ value, as would be expected for a rate determining electron transfer. The suppression of these Diels–Alder reactions by added neutral **1** is construed as supporting the proposed cation radical mechanism, as opposed to a hypothetical mechanism involving a charge transfer complex of $\mathbf{1}^{\bullet+}$/**2** or a carbocation mechanism.

† 1 cal = 4.184 J.

Experimental

Analysis

^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from the reference, tetramethylsilane (TMS). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; m, multiplet. Analytic gas chromatographic (GC) analyses were performed on a Perkin-Elmer model 8500 using a PE Nelson model 1020 reporting integrator for data collection. The instrument was equipped with flame ionization detectors and DB-1 (J & W Scientific, 30 m × 0.25 mm, 1 μm film thickness) capillary column using helium as the carrier gas. Naphthalene was used as internal standard for all the quantitative analyses, and detector response factors were calculated for all the products. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5971A GC-MS spectrometer equipped with a DB-1 (15 m × 0.25 mm, 1 μm film thickness) capillary column. Electrochemical measurements were performed using a Bioanalytical Systems 100 electrochemical analyser in the differential pulse voltametry (DPV) mode scanning in the range of 500 to 1900 mV at a scan rate of 4 mV s^{-1} with a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 1000 ms and a sensitivity of 1 × 10^{-6}. The DPV measurements were carried out using a divided cell equipped with a platinum disk working electrode (anode), a reticulated vitreous carbon counter electrode and a Ag/Ag$^+$ reference electrode (calibrated against ferrocene/ferrocene$^+$) in 0.1 M $LiClO_4$ in acetonitrile. The analyte concentration was 1 to 10 mg ml^{-1}.

Solvents and reagents

Methylene chloride (CH_2Cl_2) and acetronitrile (AN) were dried over phosphorus pentoxide (P_2O_5), hexane was dried over CaH_2 and tetrahydrofuran (THF) was dried over Na–benzophenone. All other reagents were commercially available and used as received unless otherwise specified. The stilbenes in this study were synthesized *via* a Grignard procedure (*vide infra*). All of the stilbenes[18] had been synthesized and characterized previously.

General procedure for the preparation of the Diels–Alder products of *trans*-stilbenes, catalysed by $Ar_3N^{\bullet+}$ ($\mathbf{1}^{\bullet+}$)

Approximately 5 mol% of $\mathbf{1}^{\bullet+}$ was weighed into a 25 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath and purged with nitrogen. Methylene chloride (15 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing 0.5 mmol of appropriate stilbenes and an excess (10 fold) of 2,3-dimethylbuta-1,3-diene in methylene chloride (5 ml). After an appropriate interval (30 min, or after the colour of the aminium salts disappeared), the reaction mixtures were quenched with 3 ml of saturated methanolic potassium carbonate. Water (20 ml) and methylene chloride (10 ml) were added and the organic layer was separated and dried ($MgSO_4$). After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the Diels–Alder adducts were purified by TLC (hexane–ethyl acetate, 9:1, v/v) and characterized (NMR, LRMS).

(±)-(4*S*,5*S*)-4,5-Bis(4′-methylphenyl)-1,2-dimethylcyclohexene (4a). GC yield 50%; $\delta_H(CDCl_3)$ 7.40–7.31 (m, 4 H), 6.95–6.86 (m, 4 H), 2.30–2.16 (m, 4 H), 2.20 (s, 6 H) 2.05–1.97 (m, 1 H), 1.94–1.85 (m, 1 H), 1.65 (s, 6 H); *m*/*z* 290 (M^+), 209, 208 (base), 207, 194, 193, 178, 172, 115, 105, 91, 67.

(±)-(4*S*,5*S*)-4-(3′-Methylphenyl)-5-(4′-methylphenyl)-1,2-dimethylcyclohexene (4b). GC yield 42%; *m*/*z* 290 (M^+), 209, 208 (base), 194, 193, 192, 179, 178, 174, 173, 172, 157, 105, 91.

(±)-(4*S*,5*S*)-4-(4′-Methylphenyl)-5-phenyl-1,2-dimethyl-

cyclohexene (4c). GC yield 35%; *m/z* 276 (M^+), 195, 194 (base), 193, 180, 179, 178, 158, 157, 129, 115, 91, 67.

General procedure for the preparation of the cycloaddition products of *trans*-stilbenes catalysed by $Ar'_3N^{\bullet+}$ ($5^{\bullet+}$)

Approximately 10–15 mol% of $5^{\bullet+}$ was weighed into a 25 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath and purged with nitrogen. Methylene chloride (15 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing 0.5 mmol of appropriate stilbenes and an excess (5 fold) of 2,3-dimethylbuta-1,3-diene in methylene chloride (10 ml). After an appropriate interval (3 min, or after the colour of the aminium salts disappeared), the reaction mixtures were quenched with 3 ml of saturated methanolic potassium carbonate. Water (20 ml) and methylene chloride (10 ml) were added and the organic layer was separated and dried ($MgSO_4$). After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the Diels–Alder adducts were purified by TLC (hexane–ethyl acetate, 9 : 1, v/v) and characterized (NMR, LRMS).

General procedure for the competitive cycloadditions of *trans*-stilbenes with 2,3-dimethylbuta-1,3-diene, catalysed by aminium salts

Approximately 5–10 mol% of $1^{\bullet+}$ or 0.1–0.5 mol% of $5^{\bullet+}$ was weighed into a 10 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath, and purged with nitrogen. Methylene chloride (5 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing equimolar amounts (*ca.* 0.12 mmol) of stilbenes and an excess (10 fold) of 2,3-dimethylbuta-1,3-diene in methylene chloride (5 ml). After an appropriate interval (timed so that the conversion was less than 10%), a 0.5 ml aliquot of the reaction mixture was quenched with 1 ml of saturated methanolic potassium carbonate. Water (5 ml) and methylene chloride (2 ml) were added, and the organic layer was separated and dried ($MgSO_4$). After removal of $MgSO_4$, the competition ratios were determined and corrected for varying response factors. In all cases, the results of at least three runs were averaged. The resulting relative rate ratios were cross-checked by pairing each substrate with at least two other reaction partners. At the 10% conversion to product level, the mass balances were 97–99%. Competitive experiments in acetonitrile (AN) were performed in exactly the same manner as indicated above but using AN as the solvent.

(±)-(4*S*,5*S*)-4,5-Bis(3′-methylphenyl)-1,2-dimethylcyclohexene (4d). GC yield 40%; *m/z* 290 (M^+), 210, 209, 208 (base), 195, 194, 193, 192, 179, 178, 174, 173, 172, 157, 105.

(±)-(4*S*,5*S*)-4-(3′,5′-Dimethylphenyl)-5-phenyl-1,2-dimethylcyclohexene (4e). GC yield 33%; *m/z* 290 (M^+), 210, 209, 208 (base), 195, 194, 193, 192, 179, 178, 174, 173, 172, 157, 105.

(±)-(4*S*,5*S*)-4-(3′-Methylphenyl)-5-phenyl-1,2-dimethylcyclohexene (4f). GC yield 33%; *m/z* 276 (M^+), 195, 194 (base), 193, 180, 179, 178, 158, 157, 129, 115, 91.

(±)-(4*S*,5*S*)-4,5-Diphenyl-1,2-dimethylcyclohexene (4g). GC yield 30%; *m/z* 262 (M^+, trace), 207, 180 (base), 179, 178, 165, 158, 143, 141, 128, 115, 97, 95, 91.

(±)-(4*S*,5*S*)-4-(4′-Chlorophenyl)-5-phenyl-1,2-dimethylcyclohexene (4h). GC yield 25%; *m/z* 298, 296 (M^+), 216, 214 (base), 179, 178, 165, 143, 141, 115, 97, 91.

(±)-(4*S*,5*S*)-4,5-Bis(4′-chlorophenyl)-1,2-dimethylcyclohexene (4i). GC yield 22%; *m/z* 236, 234, 232 (M^+), 254, 252, 250 (base), 179, 178, 165, 143, 141, 115, 97, 71.

Effect of the concentration of 2,3-dimethylbuta-1,3-diene upon the absolute reaction rates of cycloaddition

The conversions to Diels–Alder products were measured for samples which were of identical composition except for the concentration of 2,3-dimethylbuta-1,3-diene, run in parallel and for identical reaction times (see Table 2).

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References

1 D. J. Bellville, D. D. Wirth and N. L. Bauld, *J. Am. Chem. Soc.*, 1981, **103**, 718.
2 R. I. Walter, *J. Am. Chem. Soc.*, 1955, **77**, 5999.
3 N. L. Bauld, *Tetrahedron*, 1989, **45**, 5307.
4 N. L. Bauld, *Advances in Electron Transfer Chemistry*, ed. Patrick S. Mariano, JAI Press, Greenwich, 1992, **2**, 1.
5 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 6085.
6 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 7993.
7 D. W. Reynolds, K. T. Lorenz, H.-S. Chiou, D. J. Bellville, R. A. Pabon and N. L. Bauld, *J. Am. Chem. Soc.*, 1987, **109**, 4960.
8 L. Eberson, B. Olofsson and J.-O. Svensson, *Acta Chem. Scand.*, 1992, **46**, 1005.
9 Especially since the highly hindered nitrogen is non-basic and non-nucleophilic.
10 T. Kubota, B. Uno, Y. Matsuhisa, H. Miyazaki and K. Kano, *Chem. Pharm. Bull.* 1983, **31**, 373.
11 F. D. Lewis, A. M. Bedell, R. E. Dykstra, J. E. Elbert, I. R. Gould and S. Farid, *J. Am. Chem. Soc.*, 1990, **112**, 8055.
12 B. A. Sim, P. H. Milne, D. Griller and A. D. M. Wayner, *J. Am. Chem. Soc.*, 1990, **112**, 6635.
13 R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.
14 N. L. Bauld and W. Yueh, *J. Am. Chem. Soc.*, 1994, **116**, 8845.
15 The oxidation potentials of **2,3** and ethyl diazoacetate are, respectively, 1.59, 1.90 and > 2.1 V *vs.* SCE.
16 D. S. Noyce, D. R. Hartter and F. B. Miles, *J. Am. Chem. Soc.*, 1968, **90**, 6333.
17 G. Bellucci, R. Bianchini, R. S. Brown and H. Slovocka-Tilk, *J. Am. Chem. Soc.*, 1991, **113**, 8012.
18 W. Yueh and N. L. Bauld, *J. Am. Chem. Soc.*, 1995, **117**, 5671.

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