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Aryl vinyl sulfides as probes for electrophilic *versus* electron transfer mechanisms

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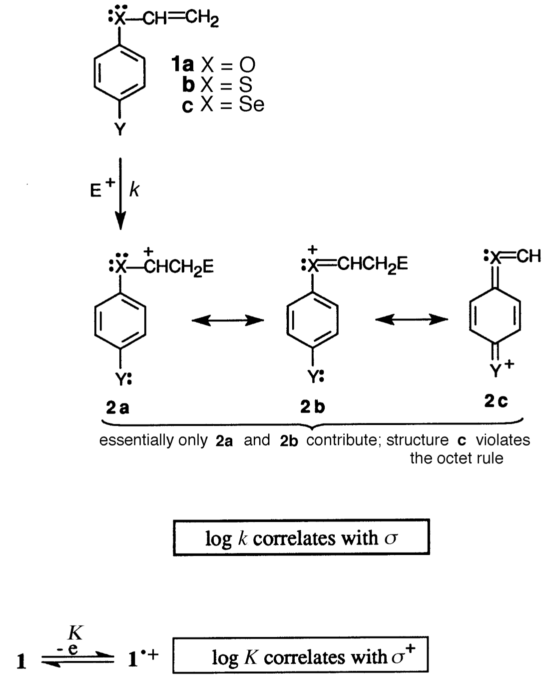
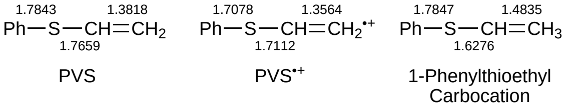
The distinction between electrophilic and electron transfer mechanisms of addition reactions to the vinyl double bond of aryl vinyl sulfides, ethers and selenides has been achieved by studying substituent effects. Specifically, the effects of *meta* and *para* substituents on the rates of electrophilic addition reactions correlate with Hammett σ values, while ionization of the substrates to the corresponding radical cations correlates with σ^+. The significance of the respective correlations are confirmed by statistical tests. The σ (electrophilic)/σ^+ (ET) dichotomy is in accord with the conventional paradigm for σ/σ^+ correlations and is further supported by *ab initio* SCF MO calculations. The application of this criterion to the reactions of aryl vinyl sulfides and ethers with tetracyanoethylene indicates that formation of cyclobutanes occur *via* direct electrophilic addition to the electron-rich alkene and not *via* an electron transfer mechanism. This conclusion is further supported by the results of previous radical cation probe studies.

Substituent effects in electrophilic additions to the alkene π bond of aryl vinyl ethers (AVEs, **1a**), aryl vinyl sulfides (AVSs, **1b**) and aryl vinyl selenides (AVSes, **1c**) are known to correlate with Hammett σ constants rather than Brown σ^+ constants.[1,2] This is in accord with the generally accepted paradigm which requires that for a σ^+ correlation, there must be a direct resonance interaction between a *para* resonance electron-donating substituent and a positively charged reaction site, as reflected in the familiar quinonoidal resonance structure.[3] In α-aryloxy-, α-arylthio- and α-arylselenylcarbocations (**2**; Scheme 1), the canonical structure **2c** required for a σ^+ correlation is unacceptable for oxygen (since it requires expansion of the valence shell) and is apparently also ineffective for sulfur and selenium (since it requires octet expansion). Evidently, the positioning of a heteroatom between an aryl ring and a homobenzylic carbocation site insulates these latter two moieties from each other in a resonance sense.



Scheme 1 The σ/σ^+ criterion for electrophilic *vs.* electron transfer mediated additions to electron rich alkenes

In the case of radical cations such as those of AVEs, AVSs and AVSes, the application of the simple paradigm is not straightforward, but it appeared to be a reasonable expectation that the 3p orbital of sulfur, for example, would be a major component of the SOMO of the AVS radical cation and that this SOMO would be delocalized over the entire conjugated system, including the aryl ring and a resonance electron-donating *para* substituent. This conjecture is supported by the results of MO calculations. In particular, a comparison of C–S bond lengths of phenyl vinyl sulfide (PVS), the corresponding radical cation ($PVS^{\cdot+}$) and the phenylthioethyl carbocation is especially compelling.[4] The bond lengths given in Scheme 2 were obtained from geometry optimized *ab initio* SCF MO calculations (6-31G*//6-31G*). The Ph–S bond length in the carbocation (1.7847 Å) is essentially identical to that in neutral PVS (1.7843 Å), which is consistent with the minimal importance of canonical structure **2c**, which should lead to the shortening of the Ar–S bond. However, the bond from sulfur to the carbocation site is greatly shortened (from 1.7659 to 1.6276 Å), as expected for a major contribution from **2b**. In contrast, the Ph–S bond of $PVS^{\cdot+}$ is substantially shortened (from 1.784 to 1.708 Å) and is virtually the same length as the vinyl–sulfur bond (1.711 Å).



Scheme 2 Selected bond lengths of the geometry optimized (6-31G*) structures of phenyl vinyl sulfide (PVS), its radical cation and the phenylthioethyl carbocation

The expectation that radical cation formation in a series of AVSs correlates with σ^+ rather than σ has been confirmed experimentally by measuring the peak oxidation potentials of a series of nine *m*- and *p*-substituted and disubstituted AVSs (Table 1).[5] The correlation with σ^+ is excellent (Fig. 1, $r^2 = 0.990$), while that with σ is very much inferior ($r^2 = 0.921$†). Statistical tests (*F* tests) verify that the preference for a σ^+ correlation is significant at the 95% confidence level (limiting *F* value required at the 95% confidence level, 3.79; observed, $F = 6.42$).[6]

In order to gain still further confidence in the reported correl-

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† Complementary figures, which allow comparison between σ and σ^+ values in Figs. 1–3, have been deposited at the British Library (SUPPL. No. 57235, 5 pp.). For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1997.

Table 1 Peak oxidation potentials (E_{ox}) for substituted aryl vinyl sulfides in acetonitrile by differential pulse voltammetry

Substrate	E_{ox}/V (*vs.* SCE)
4-Methoxyphenyl vinyl sulfide	1.097
4-Methylphenyl vinyl sulfide	1.267
Biphenyl-4-yl vinyl sulfide	1.249
3-Methylphenyl vinyl sulfide	1.314
Phenyl vinyl sulfide	1.346
4-Chlorophenyl vinyl sulfide	1.401
4-Bromophenyl vinyl sulfide	1.389
3-Chlorophenyl vinyl sulfide	1.475
4-(Trifluoromethyl)phenyl vinyl sulfide	1.594
3,5-Dichlorophenyl vinyl sulfide	1.603

Table 2 Relative rate constants for the formation of cyclobutane from substituted aryl vinyl sulfides and 2,5-dimethylhexa-2,4-diene **4**, catalysed by $\mathbf{3}^{\cdot+}$

Substrate	k_{rel}
4-Methoxyphenyl vinyl sulfide	4.19
4-Methylphenyl vinyl sulfide	2.34
3-Methylphenyl vinyl sulfide	1.58
Phenyl vinyl sulfide	1.0
4-Chlorophenyl vinyl sulfide	0.19
4-Bromophenyl vinyl sulfide	0.17
3-Chlorophenyl vinyl sulfide	0.11
3,5-Dichlorophenyl vinyl sulfide	0.012

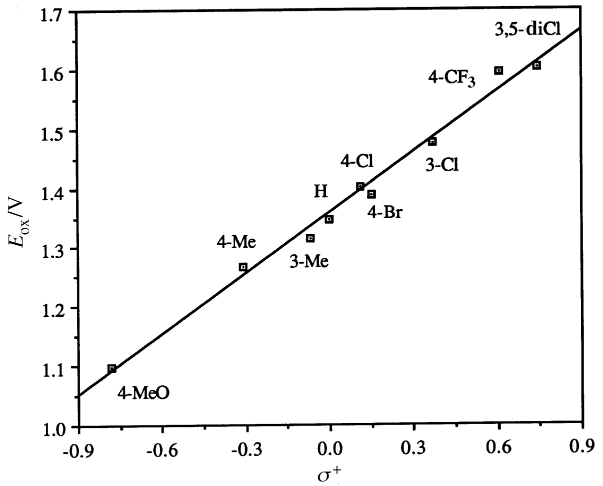
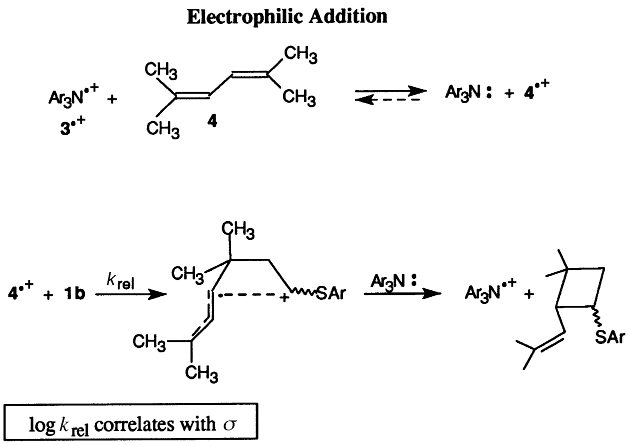


Fig. 1 Plot of the peak oxidation potentials of aryl vinyl sulfides *vs.* σ^+; slope = 0.341, r^2 = 0.990

ation of the rates of electrophilic additions to AVSs with σ rather than σ^+, the aminium salt ($\mathbf{3}^{\cdot+}$) catalysed reactions of the AVSs (**1b**) with 2,5-dimethylhexa-2,4-diene to form cyclobutanes (**4**; Table 2; Scheme 3) were studied by means of competition kinetics.[7] Since **4** has a much lower oxidation potential than the AVSs, the reaction mechanism involves the reaction of $\mathbf{4}^{\cdot+}$ with the neutral AVSs, *i.e.* electrophilic addition to the AVSs. The plot of log k/k_0 *vs.* σ for the data obtained using methylene chloride as the solvent is of excellent quality (Fig. 2, r^2 = 0.991), while log k/k_0 *versus* σ^+ is clearly much inferior (r^2 = 0.876†). The preference for the σ correlation is again statistically significant at the 95% confidence level (F = 32.8, limiting F value 4.28).



Scheme 3 Radical cation electrophilic addition to aryl vinyl sulfides

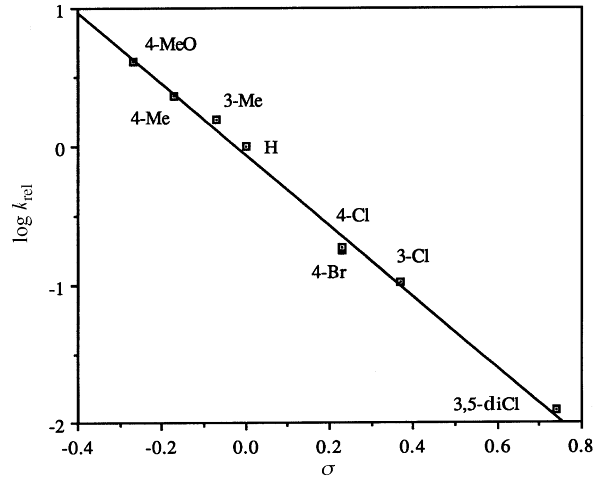
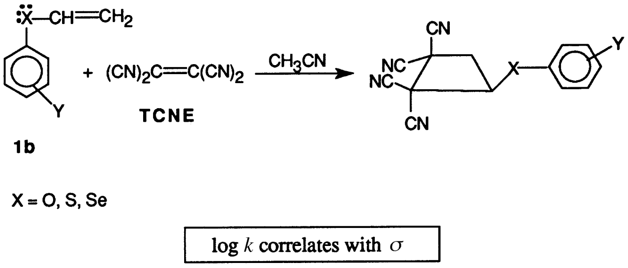


Fig. 2 Plot of log k/k_0 for the electrophilic additions of the 2,5-dimethylhexa-2,4-diene radical cation to aryl vinyl sulfides *vs.* σ; $\rho = -2.56$, r^2 = 0.994



Scheme 4 Cycloadditions of aryl vinyl esters, sulfides and selenides to tetracyanoethene

It is therefore proposed that the distinction between electron transfer and electrophilic reactions of AVSs, AVEs and AVSes can be diagnosed by means of the σ/σ^+ criterion. As an application of this criterion, we have considered the reaction to form cyclobutanes with tetracyanoethylene (TCNE) and electron-rich alkenes, including AVSs, AVEs and AVSes (Scheme 4). In all of these cases, the reported reaction rates correlate with σ much better than with σ^+† (Fig. 3).[8] We have carried out the appropriate statistical tests, and the correlations with σ are confirmed (and those with σ^+ rejected) at the 95% confidence level for both reaction series. For example, in the case of the AVSs, the limiting F value at 95% confidence level (9.28) is surpassed by the F value calculated from the experimental data (9.88). These reactions are clearly indicated to be of the electrophilic type, leading directly to a zwitterion intermediate, rather than involving electron transfer, which would generate radical ion pairs ($\mathbf{1b}^{\cdot+}$–TCNE$^{\cdot-}$). This conclusion receives strong support from conventional radical cation probe studies of related TCNE cycloadditions.[9] The combination of the σ/σ^+ criterion and classical radical cation probe studies would appear to be especially effective for rigorously excluding (or including) electron transfer mechanisms.

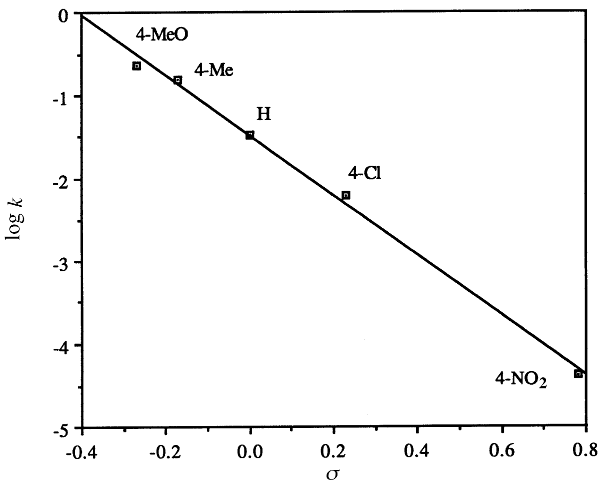


Fig. 3 Plot of log *k* for the electrophilic additions of the tetracyanoethene to aryl vinyl sulfides *vs.* σ; $p = -3.62$, $r^2 = 0.996$

Acknowledgements

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4 *Ab initio* molecular orbital calculations were carried out on a Cray YMP computer using Gaussian 92 software. Structures were fully optimized at the 6-31G* level.

5 Electrochemical measurements were performed using a Bioanalytical Systems 100 electrochemical analyser in the DPV mode scanning from 700 to 1500 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 0.5–1.0 mg ml^{-1}.

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