Electrochemical mechanistic criteria for the diagnosis and elucidation of cation radical mechanisms: the quantitative simulation of aminium salt catalysis by anodes of the same potential

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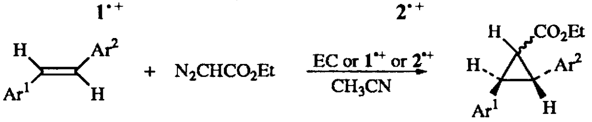
Intermolecular selectivities in the cyclopropanation of a series of *trans*-stilbenes by ethyl diazoacetate are essentially identical when an aminium salt catalyst or an anode of approximately the same potential is used.

Tris(4-bromophenyl)aminium hexachloroantimonate ($1^{\cdot+}$) has emerged as an effective catalyst for cation radical pericyclic chemistry.[1-4] Since the ionization of substrate molecules by $1^{\cdot+}$ is usually considered to be an outer sphere process, it is appealing to conjecture that the reactions of $1^{\cdot+}$ might be quantitatively simulated by an anode of the same electrochemical potential as $1^{\cdot+}$. The correspondence should presumably apply not only to the formation of identical products in identical diastereoisomeric ratios, but also to identical intermolecular selectivities in the competitive (pairwise) reactions of a series of substrate molecules (*i.e.* to identical Hammet–Brown ρ values). Selectivity correspondence could then be extended to higher potential aminium salts,[2] and anodes of higher oxidation potential resulting in an especially definitive mechanistic characterization. The present communication describes the fulfillment of these important mechanistic objectives and, in addition, provides the first general criterion for distinguishing chain from catalytic cation radical chemistry.

The reaction system studied in greatest detail is the cyclopropanation of *trans*-stilbenes by ethyl diazoacetate catalysed by $1^{\cdot+}$ at 0 °C in acetonitrile and the corresponding electrochemical (EC) cyclopropanation (Scheme 1). The mechanism proposed for these cyclopropanation reactions is given in Scheme 2.[5] When the relatively mild hole catalyst $1^{\cdot+}$ is used, the ionization of stilbene (**3**) is highly endergonic, and the exergonic back reduction of $3^{\cdot+}$ (by **1**) is found to be faster than cyclopropanation of $1^{\cdot+}$ by ethyl diazoacetate (**4**). Consequently, a ρ value close to the equlibrium ρ value for the (reversible) ionization of **3** is observed for stilbene and the substituted stilbenes which have electron withdrawing groups, and the reaction rate is linearly dependent upon the concentration of **4**. In contrast, back reduction of the cation radicals of the more readily oxidized stilbenes (**3a–c**) is slow in comparison to the cyclopropanation step. In these cases, the ionization step is rate limiting, and the reaction rate is independent of the concentration of **4**. The transition from a rate determining cyclopropanation step to a rate determining ionization step engenders a characteristic curved Hammett–Brown plot.[5]

$(4\text{-BrC}_6H_4)_3N^{\cdot+}\ SbCl_6^-$ **$1^{\cdot+}$** $(2,4\text{-Br}_2C_6H_3)_3N^{\cdot+}\ SbCl_6^-$ **$2^{\cdot+}$**



3a-h **4** **5a-h**

3a 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-Methylstilbene (3-MSB)
f *trans*-Stilbene (SB)
g 4-Chlorostilbene (4-CSB)
h 4,4′-Dichlorostilbene (4,4′-DCSB)

Scheme 1 Cyclopropanation of *trans*-stilbenes by ethyl diazoacetate under electrochemical (EC) and aminium salt conditions

$$\mathbf{3}\ \underset{\dashleftarrow}{\xrightarrow{-e\,(1^{\cdot+}\text{ or EC})}}\ \mathbf{3}^{\cdot+} \tag{1}$$

$$\mathbf{3}^{\cdot+} + \mathbf{4} \longrightarrow \mathbf{5}^{\cdot+} \tag{2}$$

$$\mathbf{5}^{\cdot+} \xrightarrow{+e\,(1\text{ or }3)} \mathbf{5} \tag{3}$$

Scheme 2 Transition from irreversible to reversible substrate ionization in the cyclopropanation of stilbenes by ethyl diazoacetate

The oxidation potential of the electrochemical cell (reticulated vitreous carbon anode) was fixed at 1.1 V to simulate the potential of $1^{\cdot+}$ [$E_{ox}(\mathbf{1}) = 1.06$ V]. An EC competition kinetic study for *trans*-stilbene and a series of mono- and di-substituted *trans*-stilbenes in acetonitrile (as described previously for the $1^{\cdot+}$ and $2^{\cdot+}$ catalysed reactions in dichloromethane[5]) yields the curve Hammett plot (the r^2 values for linear and quadratic correlations are 0.913 and 0.990, respectively).† A plot of the relative rate constants for cyclopropanation under EC conditions *vs.* those for aminium salt ($1^{\cdot+}$) conditions reveals that substituent effects are identical for these two reaction systems, including even the curvature of the plot. Note that the substituent effects are not merely parallel, but of identical magnitude (slope = 1.04; $r^2 = 0.997$). It is therefore evident that the 1.1 V EC conditions reproduce not only the magnitude of the charge development on the stilbene (*via* ρ) and its symmetrical distribution (substituent effects are multiplicative[5]) but also the mechanistic change observed in the cyclopropanations catalysed by $1^{\cdot+}$.

When the more reactive aminium salt tris(2,4-dibromophenyl)aminium hexachloroantimonate [$2^{\cdot+}$; $E_{ox}(\mathbf{2}) = 1.50$ V) was used as the catalyst, the previous study found that

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† The electrochemical experiments were carried out in a divided cell in acetonitrile solution at room temperature with lithium perchlorate as the electrolyte, using reticulated vitreous carbon working and counter electrodes and a Ag/Ag$^+$ reference electrode. The cell was calibrated *vs.* SCE using the ferrocene/ferrocenium ion couple. Equimolar amounts of two stilbene substrates (0.012 mol dm^{-3} each) were allowed to compete for a three-fold molar excess of ethyl diazoacetate. Reactions were carried out to no more than 10% conversion of the more reactive substrate and the products analysed by GC (corrected).[5]

stilbene ionization is kinetically controlled for all of the stilbene substrates ($\rho = -2.31$).[5] The corresponding EC reaction carried out at 1.5 V once again behaves analogously to the appropriate aminium salt reaction, and substituent effects are of similar but slightly greater magnitude in the EC reaction ($\rho = -2.64$). This suggests that, in the reactions involving $\mathbf{2}^{\bullet+}$ the stilbenes are not primarily ionized by $\mathbf{2}^{\bullet+}$ (in a classic catalytic mechanism), but by a cation radical of higher energy. In further support of this conclusion, EC studies at 1.8 V yield a value of ρ (-2.35) which closely approaches that observed for the $\mathbf{2}^{\bullet+}$ reactions. The data thus support the previously proposed chain mechanism for these latter reactions, in which ionization of the substrate is effected by product cation radicals of relatively high energy.

The close quantitative relationship between substrate selectivity in aminium salt catalysed cation radical reactions and the corresponding selectivity in reactions induced by anodes of the same potential is further confirmed for the Diels–Alder additions of a series of *trans*-β-methylstyrenes to 2,3-dimethylbuta-1,3-diene (Scheme 3). The plot of $\log k/k_0$(EC) *vs.* $\log k/k_0(\mathbf{1}^{\bullet+})$ in this case has a slope of 1.02, with $r^2 = 0.997$. Under the aminium salt conditions, $\rho = -4.99$ ($r^2 = 0.995$), and under EC conditions (1.1 V) $\rho = -4.85$ ($r^2 = 0.987$).

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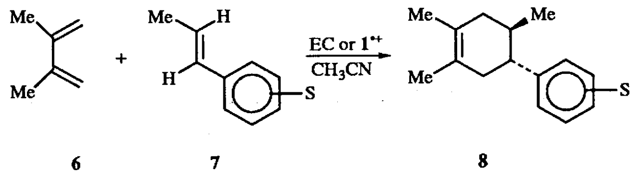

S = 3-Me, 4-Me, 4-PhO and 4-MeO

Scheme 3 Diels–Alder addition of *trans*-β-methylstyrenes to 2,3-dimethylbuta-1,3-diene under EC and aminium salt conditions

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