

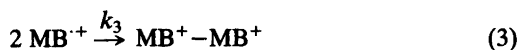
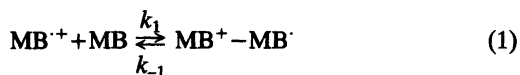
Short Communication

The Second Order Coupling Mechanism of 4-Methoxybiphenyl Cation Radical

BJØRG AALSTAD,^a ALVIN RONLÁN^b and VERNON D. PARKER^a

^a Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and ^b Division of Organic Chemistry 2, Lund Institute of Technology, S-220 07 Lund, Sweden

We recently observed that the overall reaction order $R_{A/B}$ during the dimer-forming reactions of 4-methoxybiphenyl (MB) cation radical changed from 3 at low substrate concentration (C_A) to 2 at C_A greater than about 2 mM.¹ We suggested that the reaction involves competing mechanisms, cation radical–substrate coupling (1–2) and cation radical dimerization (3) with rate laws (4) and (5), respectively. Our data were re-examined by Savéant² and found to be consistent with a single mechanism (1–2) with a change in rate-determining step with increasing C_A so that the rate law changed from (4) to (6). We neglected to consider this possibility although we were well aware that the reaction order analysis³ does not distinguish between the two second order rate laws, (4) and (6). The theoretical data necessary to distinguish between the latter is available for the derivative cyclic voltammetry (DCV) analysis used.⁴ The slopes,



$$\text{Rate} = k_2 K_1 [\text{MB}^{\cdot+}]^2 [\text{MB}] \quad (4)$$

$$\text{Rate} = k_3 [\text{MB}^{\cdot+}]^2 \quad (5)$$

$$\text{Rate} = k_1 [\text{MB}^{\cdot+}] [\text{MB}] \quad (6)$$

$d \ln R'_1 / d \ln v^{-1}$ where R'_1 is the derivative peak current ratio and v the voltage sweep rate, are significantly different for processes obeying rate laws (5) and (6). Under the conditions of our measurements¹ the theoretical values of the slopes are -0.307 (rate law (5)) and -0.373 (rate law (6)).

The data in Table 1 were obtained in the same experiments as the data reported in Table 1 of Ref. 1. The value of $d \ln R'_1 / d \ln v^{-1}$ varied from -0.485 to -0.127 while C_A varied from 8.0 to 0.125 mM. The data of most interest are those at C_A greater than 2 mM. The theoretical value for rate law (6) was only slightly greater than the observed slope at C_A equal to 4.0 mM but significantly smaller than the value observed at C_A equal to 8.0 mM. It is not unexpected that experimental voltammetric data deviate from theoretical values when substrate concentrations are much larger than about 1 mM. We can conclude that the data are more consistent with rate law (6) than with rate law (5) at the high end of the C_A range. Thus, it seems likely that the suggestion² that only mechanism (1–2) is in-

Table 1. Derivative cyclic voltammetry analysis of the coupling reactions of 4-methoxybiphenyl cation radical in acetonitrile.^a

C_A/mM^b	$-d \ln R'_1 / d \ln v^{-1}^c$
8.0	0.485
4.0	0.352
2.0	0.267
1.0	0.242
0.5	0.215
0.25	0.175
0.125	0.127

^a Logarithmic analysis according to Ref. 4. ^b Substrate concentration. ^c Slope defined in the text.

volved in the dimer forming reactions of $MB^{\cdot+}$ is correct. However, since some problems were encountered with electrode filming and attributed to adsorption,¹ the data are not ideal.

Linear sweep voltammetry (LSV) analysis would be the least ambiguous way to distinguish between rate laws (5) and (6). This follows from the fact that the reaction orders in substrate (A) and primary intermediate (B) are separable by LSV.⁵ However, because of the electrode filming problems, electrode potential measurements were not reliable and it was not possible to make the LSV analysis.

An Arrhenius activation energy of 10.6 kcal/mol was observed at high C_A and this was attributed to the activation energy for reaction (3). In view of the discussion in the previous paragraphs it appears more likely that the observed activation energy reflects that for forward reaction (1). The transition states for reaction (2) and forward reaction (1) differ only by charge and thus many of the factors contributing to the entropy of activation for the two processes will be of similar magnitude. This suggests that the activation energy for reaction (3) could be even greater than 11 kcal/mol if this reaction does not compete with (1) under the reaction conditions.

Our primary interest at the outset of this study¹ was to determine whether or not the cation radical-substrate coupling mechanism which we had observed in a related study on the coupling reactions of 4,4'-dimethoxystilbene cation radical⁶ was of general importance in contradiction to the belief that ion radical dimerization is the most likely reaction pathway for the dimer-forming reactions of anion radicals⁷ as well as cation radicals.⁸ The importance of ion radical-substrate coupling has now been amply demonstrated for both cation radicals^{1,6} and anion radicals.⁹⁻¹¹

Although we agree with Savéant² that our data are most consistent with rate-determining forward reaction (1) at the higher concentrations, we challenge his statements that this represents a failure in the reaction order approach.³ In fact, the further calculations on this system² used the reaction orders that we derived using the reaction order approach. The data, especially at the higher concentrations (Table 1) do not fit the theoretical working curve⁵ for reaction (1). The data cannot be expected to fit any theoretical working curve that does not take into account the electrode filming which was reported as a severe problem.¹ Taking the latter into account would appear to be a very complex theoretical problem which would require very much more experimental data as well. As far as we are aware,

Savéant² has done no experiments on this system. The criticism of the reaction order approach in this case is surely not justified since without it the rate data could not have been obtained. It was because of such problems as we encountered in this case that the reaction order analysis was developed in the first place.³

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