The Kinetics and Mechanism of Cation Radical Coupling Reactions. Second and Higher Order Reactions 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

The coupling reactions of 4-methoxybiphenyl cation radical in acetonitrile were investigated by derivative cyclic voltammetry. At substrate concentrations lower than about 0.25 mM, the reaction appears to take place almost exclusively by the cation radical-substrate coupling mechanism. At higher substrate concentrations, the cation radical dimerization begins to compete and is the predominant coupling mechanism at concentrations greater than 2 mM. Deuterium kinetic isotope effects were observed for both mechanisms when substrate deuterated in the ring positions was used. The magnitude of k_H/k_D was observed to be of the order of 0.7 in all cases. The reaction rate was observed to be nearly temperature independent at low substrate concentration and an apparent activation energy of 10.6 kcal/mol was observed at 8.0 mM. The kinetic isotope effects were interpreted to be due to non-bonded interactions indicating that proton loss does not occur before or as the rate determining step. The apparent activation energy at high substrate concentration is thus that for the dimerization of the cation radicals.

We have recently found that the anodic coupling of 4,4'-dimethoxystilbene takes place by a complicated mechanism involving coupling of the cation radical with substrate in a key step.[1] Subsequent investigations of the mechanism of the electrohydrodimerization of activated olefins[2-4] have indicated that these reactions are more complex than previously believed as well and that anion radical-substrate coupling takes place in the absence of proton donors. Thus, contrary to common belief, the ion radical dimerization mechanism is not the exclusive coupling pathway and in many cases appears to be the minor one.

The coupling reactions described above all involve olefinic substrates. The ion radicals of these compounds differ considerably in charge distribution from the ion radicals of benzenoid substrates and the coupling mechanisms may therefore differ considerably. We chose the coupling of 4-methoxybiphenyl cation radical in acetonitrile as a model process to obtain mechanistic information of the coupling reactions of ion radicals of this class of substances. The reasons for the choice are that the dimer is formed in high yield during anodic oxidation[5] and the reactivity of the cation radical was expected to be moderated and hence easier to study than that of the corresponding benzene derivatives.

RESULTS

Kinetic measurements. The measurements employed derivative cyclic voltammetry[6] and the method of handling the data was based on eqn. (1) in the manner recently described.[7,8] In (1) R'_I is the ratio of the derivative peaks on the reverse and

$$R'_I = f(k_{app} v C_A^{-x}) \qquad (1)$$

forward scans of a cyclic voltammogram (the observable), v is the voltage sweep rate and x is a number, usually an integer, related to the reaction

order defined below. In practice, $v_{\ddagger}$, the value of the voltage sweep rate necessary for R_1' to equal 0.500,[8] can be determined from the linear equation (2) and kinetic data obtained by varying v in the appropriate range.[9]

$$\ln R_1' = m(\ln 1/v) + c \qquad (2)$$

range.[9] The overall reaction order, $R_{A/B}$, which takes into account the possible participation of not only B but also A in the reaction following charge transfer (3) has been defined by (4).[8] It follows that $R_{A/B}$ can be determined directly from (5), i.e. $v_{\ddagger}$ is

$$A \pm e^- \rightleftarrows B \rightarrow \text{products} \qquad (3)$$

$$R_{A/B} = 1 + x \qquad (4)$$

$$v_{\ddagger} C_A^{-x} = \text{constant} \qquad (5)$$

independent of C_A for a first order reaction of B, is directly dependent on the latter for a second order reaction, etc. The units of k_{app} are evident from (5). The unit of $v_{\ddagger}$ is s^{-1} after multiplication with F/RT. When $v_{\ddagger}$ is expressed in these units it can be used directly for the determination of apparent activation energies without the need to evaluate rate constants.[7] In this case, the quantity is determined from (6) by finding $v_{\ddagger}$ in a series

$$\ln(v_{\ddagger}) = -(E_a)_{app}/RT + c \qquad (6)$$

of experiments in which only the temperature is changed.

*Table 1.* Kinetic analysis of the coupling of 4-methoxybiphenyl cation radical.[a]

(C_A/mM)[b]	$(v_{\ddagger}/Vs^{-1})$[c]	$(v_{\ddagger}/C_A)/V$ $M^{-1}s^{-1}$	$(v_{\ddagger}/C_A^2)/V$ $M^{-2}s^{-1}$
8.0	48.3	6.04	0.755
4.0	23.6	5.90	1.48
2.0	9.63	4.82	2.41
1.0	3.40	3.40	3.40
0.5	1.34	2.68	5.36
0.25	0.49	1.96	7.84
0.125	0.11	0.88	7.04

[a] Measurements by derivative cyclic voltammetry in acetonitrile containing Bu_4NBF_4 (0.1 M) at 22 °C. [b] Substrate concentration. [c] The voltage sweep rate necessary for the ratio of the derivative peaks on the backward and forward scans of the cyclic voltammogram (R_1') to equal 0.500 according to Ref. 8.

The effect of substrate concentration. Measurements were made on solutions containing 4-methoxybiphenyl ranging in concentration from 0.125 to 8.0 mM. The value of $v_{\ddagger}$ varied from 0.11 to 48.3 Vs^{-1} (Table 1). The simple dimerization mechanism (7), according to (5) predicts that $v_{\ddagger}/C_A$

$$2 R^{\cdot+} \overset{k_7}{\rightarrow} R^+ - R^+ \qquad (7)$$

should be constant. The data in Table 1 suggest this situation to be approached at the high end of the concentration range but large deviations are evident at the lower concentrations. The cation radical-substrate coupling mechanism described by eqns. (8) and (9), according to (5), should give rise to

$$R^{\cdot+} + R \rightleftarrows R^{\cdot} - R^+ \qquad (8)$$

$$R^{\cdot} - R^+ + R^{\cdot+} \rightarrow R^+ - R^+ + R \qquad (9)$$
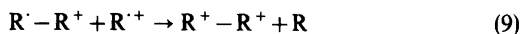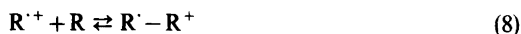
constant $v_{\ddagger}/C_A^2$ providing conditions are such that rate law (10) applies. Test for this behaviour

$$\text{Rate} = k_{app}[R^{\cdot+}]^2[R] \qquad (10)$$

indicates the relationship very nearly holds at the low concentrations of substrate. The data strongly indicate that the mechanism of coupling of 4-methoxybiphenyl cation radical is concentration dependent, going from nearly purely cation radical dimerization at 8.0 mM to purely cation radical-substrate coupling at 0.125 mM.

The effect of temperature on the reaction rate. Measurements of $v_{\ddagger}$ over a range of temperature were made on solutions at both extremes of substrate concentration. Arrhenius plots of the data are illustrated in Fig. 1. At a substrate concentration of 0.125 mM, $v_{\ddagger}$ was nearly temperature independent and the Arrhenius plot was not linear. This type of behaviour has recently been discussed and attributed to complex reaction mechanisms involving equilibria.[10] This, again is consistent with predominance of mechanism (8) and (9) at the low concentration. On the other hand, the data obtained at a concentration of 8.0 mM gave an excellent Arrhenius plot. The data are summarized in Table 2. Correlation gave an activation energy of 10.6 kcal/mol with a correlation coefficient of 0.9997 and log A equal to 12.3.

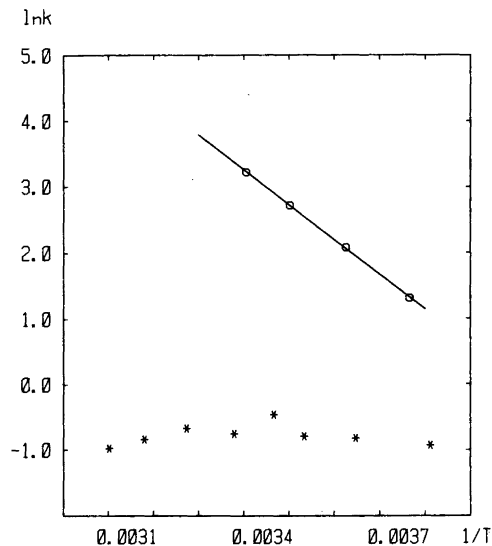*Deuterium kinetic isotope effects.* Kinetic studies were carried out on 4-methoxybiphenyl (d_9) in

Fig. 1. Arrhenius plots for the coupling reactions of 4,4'-dimethoxybiphenyl cation radical in acetonitrile. Circles ($C_A = 8.0$ mM) and stars ($C_A = 0.125$ mM).

which the aromatic hydrogens had been exchanged with deuterium. Several determinations of $v_{\frac{1}{2}}$ were made for both the isotopic isomers at three different concentrations. The data are summarized in Table 3. The numbers in parentheses following the $v_{\frac{1}{2}}$ values are the standard deviations for all of the measurements. The last column gives the range of isotope effects calculated by using the extreme values of the data obtained. The data clearly show that the overall reaction rate is enhanced by deuterium substitution with k_H/k_D in all cases being significantly less than 1.0.

Table 2. The effect of temperature on the rate of dimerization of 4-methoxybiphenyl cation radical in acetonitrile.[a]

$t/°C$	$(v_{\frac{1}{2}}/V\ s^{-1})$	$10^{-3}(k/M^{-1}\ s^{-1})$[b]
−7.6	5.77	3.70
2.6	13.0	8.03
12.4	25.6	15.3
20.5	43.7	25.3

[a] Measurements in solvent containing Bu_4NBF_4 (0.1 M) by derivative cyclic voltammetry according to Ref. 6. [b] Calculated from, $k = 1362\ v_{\frac{1}{2}}/TC_A$, according to Ref. 8. Correlation gives $E_a = 10.6$ kcal/mol and log $A = 12.3$.

Table 3. Deuterium kinetic isotope effect during the coupling of 4,4'-dimethoxybiphenyl cation radical.[a]

| C_A[b]/mM	$(v_{\frac{1}{2}})_H/V\ s^{-1}$	$(v_{\frac{1}{2}})_D/$ $(V\ s^{-1}/V\ s^{-1})$	k_H/k_D[c]
8.00	44.7(3.2)	67.4(4.7)	(0.60−0.75)
0.25	0.46(0.03)	0.63	(0.69−0.78)
0.125	0.104(0.01)	0.124(0.002)	(0.76−0.93)

[a] Measurements by derivative cyclic voltammetry in solvent containing Bu_4NBF_4 (0.1 M) at 22 °C. [b] The range of the isotope effect using all data.

DISCUSSION

The observed reaction order $R_{A/B} = 3$ at low concentrations during the oxidative coupling of 4-methoxybiphenyl is a strong indication that the cation radical-substrate coupling mechanism predominates under these conditions. The non-linear Arrhenius plot with only small changes in the reaction rate with temperature does not give any quantitative information in this case but it is consistent with the complex nature of this reaction scheme. Similar behaviour was observed in a related case, the electrohydrodimerization of diethyl fumarate in water free acetonitrile under which conditions both linear sweep voltammetry and derivative cyclic voltammetry kinetic analyses are most consistent with the ion radical-substrate coupling scheme.[4]

The data at the higher end of the substrate concentration range are of special interest since the Arrhenius plot is linear and the reaction order $R_{A/B} = 2$ indicates a possible simple dimerization mechanism. No activation energy data are available for ion radical coupling reactions and if we can establish the dimerization mechanism in this case this will serve as a reference point. An activation energy of about 4 kcal/mol has been proposed for the dimerization of the anion radical of diethyl fumarate.[11,12] However, it has been pointed out that the very low activation energy is inconsistent with the low rate constants observed and the mechanism has been shown to be more complex.[2]

It is not possible to distinguish between the simple dimerization reaction (7) and a more complex scheme involving reversible dimerization followed by rate determining proton loss (eqns. 11 and 12) from the form of the rate law. Both mechanisms result in rate law (13) where k_{app} is k_7 in the first

$$2\,Ar-H^{\cdot+} \xrightleftharpoons{K_{11}} H-Ar^+-Ar^+-H \qquad (11)$$

$$H-Ar^+-Ar^+-H \xrightarrow{k_{12}} Ar-Ar+2\,H^+ \qquad (12)$$
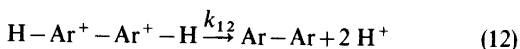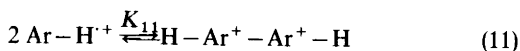
$$\text{Rate} = k_{app}C_B^2 \quad (B = \text{cation radical}) \qquad (13)$$

case and $k_{12}K_{11}$ in the second. The mechanisms do predict different kinetic isotope effects. The simple dimerization mechanism (7) would not be accompanied by any more than a secondary kinetic isotope effect if the carbons at which bond formation takes place were isotopically substituted with hydrogen and deuterium. On the other hand, a primary kinetic isotope effect, in addition to the secondary one is predicted for mechanism (11) and (12). The fact that only a secondary deuterium kinetic isotope effect is observed, the magnitude of which depends only slightly on whether cation radical-substrate or cation radical dimerization is taking place, appears to rule out the reversible dimerization followed by rate determining proton loss (11 and 12).

It appears to be safe to conclude that the mechanism of coupling at high substrate concentrations is the simple cation radical dimerization. The latter being the case, the apparent activation energy of 10.6 kcal/mol can be attributed to the barrier to the coupling of the cation radicals. Charge repulsion must contribute significantly to the activation energy since the free aryl radicals would be expected to dimerize at a nearly diffusion controlled rate. In order to use the data obtained here for comparison with other systems, it is of interest to consider the structure of 4-methoxybiphenyl cation radical. The charge is expected to be distributed over both rings but the center of charge will be in the ring substituted by the methoxy group as indicated by the extreme structure below.
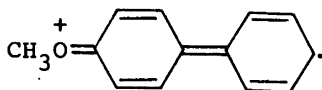
Thus, the charge repulsion in this case would be expected to contribute less to the activation energy than to coupling of either mono-nuclear ion radicals or of activated olefins. On this basis, we can suggest that the observed activation energy, 10.6 kcal/mol, can be regarded as a minimum value when predicting reaction rates of smaller ion

Table 4. Rate constant-activation energy relationship for ion radical dimerization reactions.[a]

$E_a/(\text{kcal/mol})$	$k/\text{M}^{-1}\,\text{s}^{-1}$
14.0	10^2
11.3	10^4
8.6	10^6
5.9	10^8
3.1	10^{10}

[a] Calculated from the Arrhenius equation assuming that $\log A = 12.3$ and a temperature of 298 K.

radicals. The data in Table 4 can then be used as a guide to predict the second order rate constant-activation energy relationship for the dimerization of ion radicals. It is interesting to note that a rate constant of 10^{10} M^{-1} s^{-1} at 298 K for a dimerization reaction with an activation energy of 3.1 kcal/mol is predicted. This further supports the earlier suggestion[2] that an activation energy of 4 kcal/mol with a second order rate constant less than 10^2 as proposed by Bard, Maloy, and co-workers[11,12] is inconsistent with a simple dimerization mechanism.

The observed values of k_H/k_D (0.74 ± 0.09) requires some discussion. The magnitude of the effect is very similar to that observed by Cordes and co-workers,[13] $k_H/k_D = 0.73$, during the reaction of p-methoxybenzaldehyde with phenylhydrazine or semicarbazide. The explanation of the phenomenon is that when an sp^2 hybridized carbon atom is converted to an sp^3 hybridized carbon in the transition state, a hydrogen bonded to that carbon will experience an increased resistance to $C-H$ bending.

Ion radical coupling with neutral aromatics has been inferred from product distributions during the oxidation of aromatic hydrocarbons by Nyberg and co-workers.[14] The kinetics of the coupling between relatively stable cation radicals, those from thianthrene and 9-phenylanthracene, and neutral aromatics such as anisole have been studied by Svanholm and Parker.[15,16] The latter studies provide ample precedent for the cation radical-substrate coupling mechanism. It is especially interesting to note that the homogeneous kinetic studies[15,16] resulted in rate laws similar to (10).

The question arises as to why the partitioning of the 4-methoxybiphenyl cation radical between the dimerization and the cation radical-substrate cou-

pling mechanisms depends upon substrate concentration in the manner observed. If the reaction were conducted in homogeneous solution, the relative rates of the two reactions would be given by eqn. (14) which predicts that the proportion of reaction going by the cation radical-substrate route

(cation radical-substrate rate)/(dimerization rate) $= k_9 K_8 [\mathrm{R}]/k_7$ $\qquad$ (14)

should increase with increasing substrate concentration, i.e. opposite to the observed trend. Reaction in the vicinity of the electrode is more complicated. At high substrate concentration, the cation radical concentration is high near the surface where the substrate concentration is very low. Dimerization is rapid under these conditions and the reaction layer is relatively thin. At lower substrate concentrations the dimerization close to the electrode is slower and the reaction layer is thicker. Since the substrate concentration increases nearly exponentially with distance from the electrode the slower reaction makes the cation radical-substrate coupling mechanism more favorable.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification were the same as recently described.[17] 4-Methoxybiphenyl was prepared as before.[5] Deuteration was achieved by dissolving 4-methoxybiphenyl (0.5 g) in trifluoroacetic acid (d) (20 ml) containing trifluoromethane sulfonic acid (50 mg) and allowing to stand at room temperature for 72 h. The mixture was diluted with water (100 ml) and extracted with dichloromethane (3 × 10 ml). The combined dichloromethane extracts were washed with aqueous sodium bicarbonate before drying over sodium sulfate and isolation of the product. After two repetitions of the procedure NMR and MS analyses indicated 97 % exchange of D for H. After the final equilibration, the product was recrystallized twice from ethanol.

The measurements were made at a platinum electrode in the presence of active alumina.[18] Alumina (∼1 g) was added to 10 ml of the electrolyte solution before starting the measurements. Due to problems with product adsorption, the electrode was removed and wiped with tissue between each series of replicate measurements. After replacing the electrode, six scans were recorded and data from the first was discarded. Each data point consists of three such sets. The value of $v_{\frac{1}{2}}$ was obtained from a minimum of three data points with $R'_1 = 0.500$ in about the middle of the range.

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