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Mechanistic Studies on the Electrohydrodimerization of Benzylidenemalononitriles

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Rate constants and activation parameters for the reductive dimerization of substituted benzylidenemalononitriles were obtained from derivate cyclic voltammetry measurements in dimethylformamide as solvent. Benzylidene-, *p*-methyl- and *p*-methoxybenzylidenemalononitrile react exclusively via dimerization of their anion radicals (radical-radical coupling) while for *p*-fluorobenzylidenemalononitrile 25% of the dimerization proceeds by coupling of the anion radical with the substrate.

(Keywords: Electrohydrodimerization; Benzylidenemalononitriles; Kinetics)

Untersuchungen zum Mechanismus der Electrohydrodimerisierung von Benzylidenmalonnitril

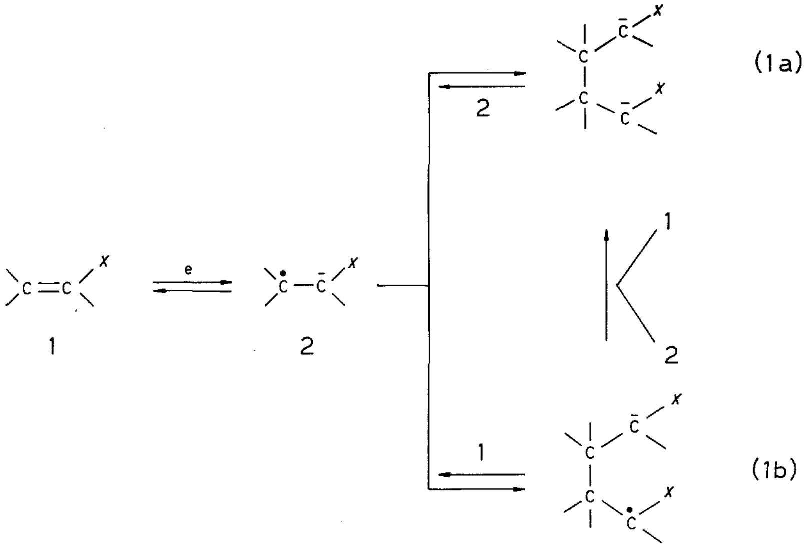
Mittels derivativer cyclischer Voltammetrie wurden für die Titelreaktion Geschwindigkeitskonstanten und Aktivierungsparameter erhalten (Dimethylformamid als Lösungsmittel). Benzyliden-, *p*-Methyl- und *p*-Methoxybenzylidenmalonnitril reagieren ausschließlich über die Dimerisierung ihrer Anionenradikale (Radikal-Radikal-Kopplung), währenddessen die Dimerisierung von *p*-Fluorbenzylidenmalonnitril zu 25% über die Kopplung des Anionenradikals mit dem Substrat erfolgt.

(Keywords: Electrohydrodimerization; Benzylidenemalononitriles; Kinetics)

Introduction

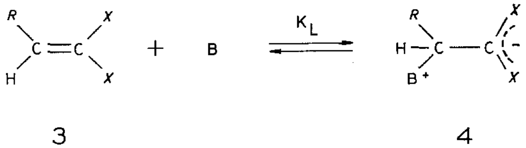
The mechanisms of the electrohydrodimerization of activated olefins (**1**) have been studied intensively over the years[2,3]. Much of the interest in these reactions stems from commercial development of the acrylonitrile reduction to adiponitrile[4]. Primary mechanistic questions are centered around the order of events, i.e. whether the initially formed anion radical **2** undergoes dimerization [radical-radical coupling (1 a)] or reacts with substrate **1** [radical-substrate coupling (1 b)] (Scheme 1).

Scheme 1



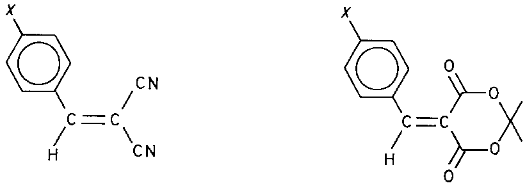
In this context it can be expected that the radical-substrate coupling will became more important for molecules where the substrate itself is a good *Michael*-type acceptor. Some time ago this quality had been correlated with the ability of adding bases reversibly to the β-carbon atom of the C=C double bond for a variety of activated olefins (Scheme 2). These compounds (**3**) were classified as electrically neutral organic *Lewis* acids and the pK_L values for such reactions $\mathbf{3} \rightleftharpoons \mathbf{4}$ have been determined[5].

Scheme 2



In preliminary studies we have investigated the mechanisms of the electrohydrodimerization of *p*-methylbenzylidenemalononitrile (**5 b**)[6] and *p*-fluorobenzylidene *Meldrum*'s acid (**6 d**)[7]. A recent report on polarographic data of benzylidenemalononitriles[8] prompts us to report the results obtained in kinetic studies of the electrohydrodimerization of the benzylidenemalononitriles **5 a**–**5 e** in dimethylformamide in the presence of varying amounts of water (Scheme 3).

Scheme 3



5 6

a $X = H$
b CH_3
c OCH_3
d F
e CN

Results

The kinetics of the dimerization reactions of the anion radicals of **5 a**–**5 e** were studied by derivate cyclic voltammetry (DCV)[9] in *DMF*. The data were treated by the reaction order approach discussed earlier[10]. The essential feature of the method is comprised in eqns. (2) and (3). The reaction order $R_{A/B}$ refers to the sum of the order in substrate (A) and intermediate (B) reacting in process (4). The quantity z is the power to which C_A must be raised in order for relationship (3) to hold, where $v_{1/2}$ is the voltage sweep rate necessary for the derivative peak ratio to equal 0.500.

$$R_{A/B} = 1 + z \tag{2}$$

$$v_{1/2}/C_A = \text{constant} \tag{3}$$

$$A + e \rightleftharpoons B \rightarrow \text{products} \tag{4}$$

For the simple dimerization mechanism (1 a) the reaction order in substrate **1** is zero and that in the intermediate anion radical **2** is 2 which results in $R_{A/B} = 2$ and $z = 1$. On the other hand the radical-substrate coupling mechanism (1 b) follows the rate law rate $= k[\mathbf{2}]^2[\mathbf{1}]$ which corresponds to $R_{A/B} = 3$ and $z = 2$.

Table 1. *Reaction order analysis of reactions of the anion radicals of* **5a–5e** *in DMF*[a]

Substrate	C_A [mM]	$v_{1/2}$ [V s^{-1}]	$v_{1/2}/C_A$	$v_{1/2}/C_A{}^{1.25}$
5a	0.2	31.25	156.26	—
	0.4	60.16	150.41	—
	0.6	88.99	148.32	
5b	0.2	22.35	111.74	
	0.4	46.17	115.42	—
	0.6	64.61	107.68	
5c	0.2	25.89	129.47	
	0.4	53.56	133.89	—
	0.6	78.79	131.32	
5d	0.2	75.09	375.46	561.43
	0.4	189.31	473.27	595.11
	0.6	302.48	504.13	572.81
5e	b			

[a] Measurements by DCV in solvent containing Bu_4NBF_4 (0.1 M) and H_2O (50 mM) at a mercury electrode with $E_{sw} - E_{rev} = 300$ mV.

[b] Too fast to be measured under these conditions.

Table 2. *Rate constants for the dimerization of benzylidene malononitrile in DMF*[a]

C_A/mM	[H_2O]/mM		$10^{-5} k/M^{-1}\,s^{-1}$
0.20	50		7.38
0.40	50		7.10
0.60	50		7.00
0.60	100		7.26
0.60	200		7.75
0.60	400		7.52
		mean	7.34 ± 0.28

[a] Measurements by derivative cyclic voltammetry in solvent containing Bu_4NBF_4 (0.10 M) with a mercury electrode at 21.7 °C.

In Table 1 the reaction order analysis of the reaction of the anion radicals of **5a–5e** in *DMF* is summarized. Several series of experiments were carried out at constant C_A while the concentration of water was varied from 0–400 mM. No dependence of the apparent rate constant on the water concentration could be observed. The rate constants for the dimerization of the anion radicals of **5a–5d** summarized in Tables 2–5 were calculated from eqn. (5) which holds for the simple dimerization

Table 3. *Rate constants for the dimerization of p-methylbenzylidene malononitrile in DMF*[a]

C_A/mM	[H_2O]/mM		$10^{-5}k/M^{-1}\,s^{-1}$
0.20	50		5.59
0.40	50		5.77
0.60	50		5.38
0.60	100		5.49
0.60	400		5.51
		mean	5.55 ± 0.15

[a] Conditions as in Table 2 with $T = 5.6\,°C$.

Table 4. *Rate constants for the dimerization of p-methoxybenzylidene malononitrile in DMF*[a]

C_A/mM	[H_2O]/mM		$10^{-5}k/M^{-1}\,s^{-1}$
0.20	50		6.45
0.30	50		6.93
0.40	50		6.67
0.60	50		6.54
0.80	50		6.22
0.80	100		6.84
0.80	200		6.61
0.80	400		6.80
		mean	6.63 ± 0.23

[a] Conditions as in Table 2 with $T = 6.5\,°C$.

Table 5. *Rate constants for the dimerization of p-fluorobenzylidene malononitrile in DMF*[a]

C_A/mM	[H_2O]/mM		$10^{-6}k/M^{-1}\,s^{-1}$
0.20	50		1.80
0.40	50		2.26
0.60	50		2.41
0.60	50		2.11
0.60	100		2.07
0.60	200		2.28
0.60	400		2.16
		mean	2.16 ± 0.19

[a] Conditions as in Table 2 with $T = 17.5\,°C$.

mechanism (1 a) with a difference of the switching and reversible potentials $E_{sw} - E_{rev} = 300\,\mathrm{mV}$ and the derivative peak ratio $R'_i = 0.500$[11].

$$k = 1\,362 \cdot v_{1/2}/C_A \cdot T \qquad (5)$$

In Table 6 the kinetic and activation parameters for the dimerization of the anion radicals of **5 a**–**5 d** obtained from *Arrhenius* correlations are summarized.

Discussion

It is evident from the data in Table 1 that the predominant mode for the dimerization of substituted benzylidenemalononitrile anion radicals is of the radical-radical coupling type (1 a). Only in the case of **5 d** there is any evidence for the deviation from this pattern. In that case it appears that as much as about 25% of the reaction can take place by a higher order mechanism, presumably involving radical-substrate coupling (1 b). This is in sharp contrast to the results we have obtained in our study of the dimerization of *p*-fluorobenylidene *Meldrum*'s acid (**6 d**)[7] in which case (1 b) becomes a major reaction pathway. The latter appears to confirm the assumption that **6 d** is a better *Michael*-type acceptor. As a matter of fact, electron withdrawing substituents in the *para* position of the phenyl group increase the pK_L value for the acid-base reaction (Scheme 2) in a given series of compounds (e.g. $X = \mathrm{CN}$), and for a common substituent R (e.g. *p*-fluorophenyl) the *Meldrum*'s acid derivative **6** is a much stronger *Lewis* acid than the corresponding malononitrile derivative **5**[5].

The data in Tables 2–5 clearly show that water in concentrations up to 400 m*M* has no effect on the rates of dimerization of the anion radicals. This is to be expected from previous work[3,6] and our interpretation of these results is that the substituted benzylidenemalononitrile anion radicals are not involved in equilibrium (6) to any significant extent. Had (6) been of some

$$\mathbf{5}^{\cdot-} + H_2O \rightleftharpoons \mathbf{5}^{\cdot-}/H_2O \qquad (6)$$

consequence, as it is in the case of the dimerization of diethylfumarate anion radical[2,12], the mechanism would have been expected to involve the pre-equilibrium (6) followed by the rate determining coupling reaction (7). A further indication

$$\mathbf{5}^{\cdot-}/H_2O + \mathbf{5}^{\cdot-} \xrightarrow{k_7} \text{products} \qquad (7)$$

that reaction (6) need not be considered is that in the case of **5 b** the reversible reduction potential in *DMF* was observed to be independent of $[H_2O]$[6].

Table 6. *Kinetic and activation parameters for the dimerizations of substituted benzylidene malononitrile anion radicals*[a]

Substituent	$k_{273.2}{}^{b}/M^{-1}\,s^{-1}$	E_a/(kcal/mol)	ΔS^{+}/(cal/K mol)
*Me*O	$5.70 \cdot 10^5$	2.85	28.2
Me	$6.18 \cdot 10^5$	2.75	22.5
H	$6.08 \cdot 10^5$	1.63	19.3
F	$16.9 \cdot 10^5$	2.83	25.6

[a] *Arrhenius* correlation data for reactions carried out in *DMF* by derivative cyclic voltammetry at 5–6 different T ranging from 250 to 295 K.

[b] The rate constant obtained from the correlation.

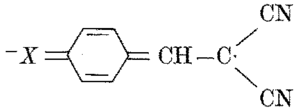
The activation energies for the dimerization reactions (Table 6) are somewhat lower than expected for a simple coupling of anion radicals. In a related case the dimerization of diethylfumarate anion radical has been proposed to have an energy of activation approaching 12 kcal/mol and no evidence could be found for the simple coupling[2]. The dimerization of 9-cyanoanthracene anion radical does have rate and activation parameters in the same range as those in Table 6[13]. Arguments have been presented that this is incompatible with a simple mechanism and that the reaction must pass through a two step mechanism involving pre-equilibrium (8) followed by rate determining bond formation (9) where $A^{\overline{\cdot}}$ is 9-cyanoanthracene anion radical. It seems likely that a similar mechanism is

$$2\,A^{\overline{\cdot}} \overset{K_8}{\rightleftharpoons} A^{\overline{\cdot}}/A^{\overline{\cdot}} \tag{8}$$

$$A^{\overline{\cdot}}/A^{\overline{\cdot}} \xrightarrow{k_9} A^{-} - A^{-} \tag{9}$$

involved during the dimerization of $\mathbf{5}^{\overline{\cdot}}$.

It is interesting to note that there appears to be either a very small effect, or no effect at all, on the rate constants for dimerization as the *para* substituent is changed from *Me*O to *Me* to H. On the other hand, the rate is dramatically increased by electron-withdrawing substituents. When X is F (**5 d**) the observed rate constant was nearly a factor of 3 greater than when X is H (**5 a**). When X is strongly electron withdrawing CN (**5 e**) the reaction is so rapid that the rate could not be measured by DCV. This puts a lower limit of about $10^7\,M^{-1}\,s^{-1}$ on the rate constant at 273.2 K. The substituent effect can be attributed to polarization of the anion radical by the electron withdrawing substituents in such a way that the negative charge is localized on the substituent as in the electron configuration **7**. Configuration **7** contributes



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to the electronic structure and is meant to account for the kinetic effect of the electron withdrawing substituents.

Experimental Part

The cells, electrodes, instruments and data handling procedures have been described in detail[14]. The benzylidenemalononitriles **5a–5e** were prepared according to literature procedures[15].

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