CHEMISTRY LETTERS, pp. 681 - 684, 1984. © The Chemical Society of Japan 1984

KINETIC CHARACTERIZATION OF AN ANION RADICAL-SUBSTRATE DIMERIZATION MECHANISM

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The anion radical of isobutylidene Meldrum's acid undergoes dimerization by coupling with substrate to give an intermediate which is converted to dimer by electron transfer reduction from the anion radical.

The mechanisms of the electrohydrodimerization of activated olefins have been studied intensely over the years.1) For a long time it was believed that the exclusive mechanism involves the simple dimerization of anion radicals. However, it has been observed that if water is excluded from aprotic solvents that in some cases the predominant mechanism involves the socalled radical-substrate mechanism (1-2).2)

$$R^{\bar{\cdot}} + R \underset{}{\overset{K_1}{\rightleftharpoons}} R^{\cdot}\text{-}R^{-} \qquad (1)$$

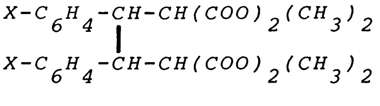
$$\text{rate} = k_2K_1[R^{\bar{\cdot}}]^2[R]$$

$$R^{\cdot}\text{-}R^{-} + R^{\bar{\cdot}} \xrightarrow{k_2} R^{-}\text{-}R^{-} + R \qquad (2)$$

We have found this to be the case for the dimer forming reactions of the anion radicals of substituted benzylidene Meldrum's acids (1→2),3) but even under the most favorable conditions no more than about 50% of the dimerization goes by that mechanism.

$$X\text{-}C_6H_4CH = C(COO)_2C(CH_3)_2$$

1



$$\begin{array}{l} X\text{-}C_6H_4\text{-}CH\text{-}CH(COO)_2(CH_3)_2 \\ \qquad\qquad\quad | \\ X\text{-}C_6H_4\text{-}CH\text{-}CH(COO)_2(CH_3)_2 \end{array}$$

2

We now report preliminary results of our studies on the dimerization of the anion radical of the alkylidene compound 3.4) A linear sweep voltammetry study of the reaction of $3^{\bar{\cdot}}$ is summarized in Table 1. The theoretical values of $\Delta E^p/\Delta \log \nu$ and $\Delta E^p/\Delta \log C_A$, where E^p is the peak potential, ν the sweep rate and C_A the substrate concentration, are given by eqns. (3) and (4), respectively.[5)]

$$\Delta E^p/\Delta \log \nu = \ln 10\,(RT/F)/(b+1) \qquad (3)$$

$$\Delta E^p/\Delta \log C_A = (a+b-1)\ln 10\,(RT/F)/(b+1) \qquad (4)$$

In (3) and (4) a and b are the reaction orders in substrate (R in this case) and primary intermediate ($R^{\overline{\cdot}}$ in this case). Equations (3) and (4) allow the rate laws for electrode mechanisms to be derived directly from experimental data. At 298K, ln 10 (RT/F) is equal to 58.5 mV and thus the theoretical slopes for mechanisms (1) and (2) are 19.5 and 39.0 mV/decade, respectively. The values found for experiments with substrate concentration ranging from 0.25 to 4.00 mM and ν from 0.1 to 1.0 V/s were 20.1 ± 0.3 mV/decade for $\Delta E^p/\Delta \log \nu$, 39.4 ± 0.9 (at 0.1 V/s) and 39.8 ± 1.6 (at 1.0 V/s) mV/decade for $\Delta E^p/\Delta \log C_A$. The theoretical values for the simple dimerization of anion radicals are 19.5 mV/decade for both slopes. Thus, the data correspond very well with the expected values for the anion radical-substrate coupling mechanism (1)+(2) with rate determining electron tranfer (2).

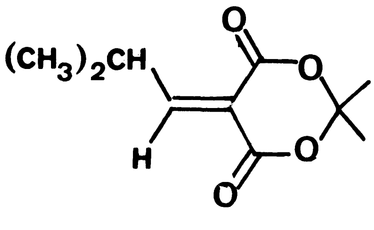


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Table 1. Linear sweep voltammetry data for dimerization of isobutylidene Meldrum's acid anion radical[a)]

Slope	Conditions	Value/(mV/decade)
$\Delta E^p/\Delta \log \nu$	ν = 0.10 - 1.0 V/s C_A = 0.25 - 4.0 mM	20.1 ± 0.3
$\Delta E^p/\Delta \log C_A$	C_A = 0.25 - 4.0 mM ν = 0.1 V/s	39.4 ± 0.9

a) Measurements by linear sweep voltammetry with a mercury electrode at 295 K in DMF containing water (0.28 M) and Bu_4NBF_4 (0.10 M).

The kinetics were also studied by derivative cyclic voltammetry (DCV)[6)] and were observed to conform to the same mechanism with rate law (5).

$$\text{rate} = k_1k_2[R^{\overline{\cdot}}]^2[R]/(k_{-1} + k_2[R^{\overline{\cdot}}]) \qquad (5)$$

It was possible to make measurements with C_A *ranging from 0.05 to 0.5 mM. A reaction order plot of rate-concentration data is illustrated in Fig.1. The line beginning at the low concentration limit has a slope of 1.78 with a correlation coefficient of 0.98 for the three data points while the other line corresponds to a slope of 1.05 with a correlation coefficient of 0.999. The theoretical values of the two slopes if they correspond to the two limiting cases of rate law (5) are 2 at the low concentration in which case* $k_{-1} >> k_2[R^{\bar{\cdot}}]$ *and 1 at the other extreme where* $k_{-1} << k_2[R^{\bar{\cdot}}]$ *(for a discussion of the reaction order approach and the relation between* C_A*, i.e. the substrate concentration [R], and the anion radical concentration* $[R^{\bar{\cdot}}]$ *, cf. ref.* 7)*). The data obviously do not correspond to these two limits but do indicate that the measurements were made in a concentration range where there is a transition from one limiting case to the other. A much broader concentration range, which was not experimentally possible, is necessary to observe the complete transition.*

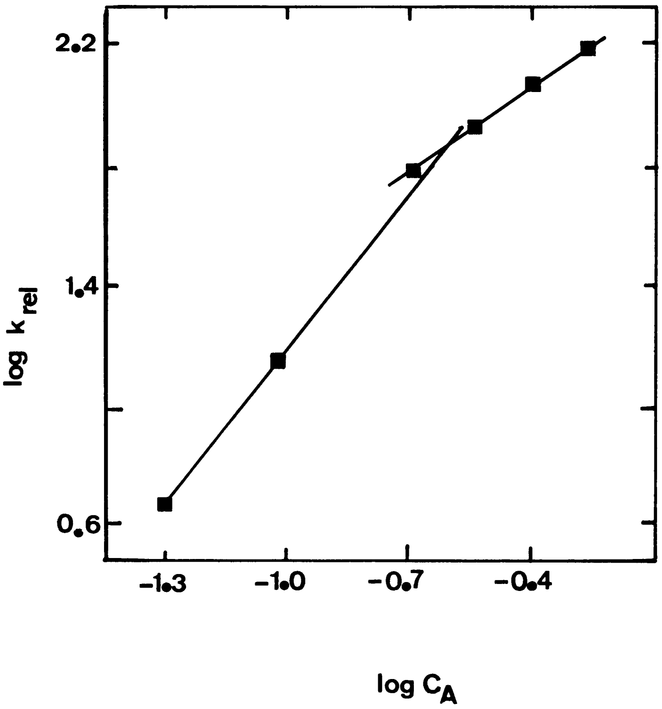

Fig.1. Reaction order data for the dimerization of isobutylidene Meldrum's acid anion radical in DMF (linear regression for $\log C_A$ *ranging from -1.3 to -0.7 and -0.7 to -0.3*

It is clear that the two independent kinetic methods provide evidence for the anion radical-substrate coupling mechanism (1)+(2). For anion radical dimerization competing with mechanism (1)+(2) the low concentration limit in Fig.1 would have a limiting slope of 1 while that at high C_A *is predicted to equal 2.* 7)

Much of the interest in electrohydrodimerization reactions stem from commercial development of the acrylonitrile reduction to adiponitrile.[8)] All of the activated olefins that have previously been used in mechanism studies[1)] were either diactivated olefins, e.g. **fumarodinitrile** or diethylmaleate, or styrene type molecules, e.g. ethylcinnamate or benzylidenemalononitriles. These substances have been studied as models for acrylonitrile, the anion radical of which is too active to study. Since most of these mechanism studies have led to the conclusion that anion radical dimerization is involved, it has been infered that this is also the case with acrylonitrile anion radical. But, we see now that if we have an alkyl group as substituent on the C-C double bond that the favored mechanism involves coupling between the anion radical and the substrate, even when working in a medium containing water as we have done here. It thus becomes apparent that replacing R = phenyl by R = alkyl in anion radicals of the type $R\dot{C}H-\bar{C}(X)_2$ leads to an increased radical-substrate vs. dimerization reactivity of these species, although the reasons for it are not quite obvious. Further work on more simply substituted activated olefin anion radicals will be necessary before making definitive conclusions about the mechanism of the hydrodimerization of acrylonitrile.

References

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(Received February 7, 1984)