Acta Chemica Scandinavica B 34 (1980) 187–193

Oxidative Dehalogenation of Aryl Halides. The Mechanism of the Dehalodimerization of 4-Halo-*N*,*N*-dimethylanilines

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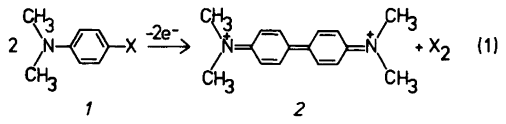
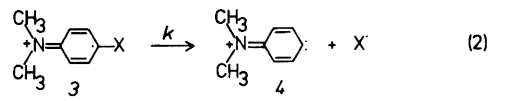
The oxidative dehalodimerizations of 4-iodo- and 4-bromo-*N*,*N*-dimethylaniline were observed to take place by a second order dimerization of the initially formed cation radicals contrary to a previous report. The rate constant for the reaction of the iodo derivative was almost ten times that for the bromo compound and the rates of the reactions were found to be nearly independent of the temperature. The data were found to be consistent with a mechanism involving a reversible dimerization followed by rate determining loss of halogen. Kinetic analysis was complicated by the homogeneous electron transfer oxidation of the substrates by the product dimeric dications. Digital simulation was used to calculate working curves for double step chronoamperometry which gave excellent correspondence with the experimental data when the complication was taken into account.

Oxidative cleavage of aryl halide bonds at electrodes has been observed in several instances. Nucleophilic displacements of halogen by water,[1] pyridine bases[2,3] and acetate[4] have been reported. The details of the mechanisms of these reactions are not known and in this connection the mechanistic study of the dehalodimerization of halo-*N*,*N*-dimethylanilines reported by Nelson and coworkers[5] is of particular interest. The overall reaction involved is that shown in eqn. (1). Coulometry showed that one electron per molecule of substrate was consumed during the electrode reaction. Product studies indicated that the dication (*2*) and molecular halogen are formed in good yield. A kinetic study was carried out which led to the conclusion that the reaction is first order in cation



radical (*3*) and it was proposed that the rate limiting step is loss of halogen to form the cationic carbene (*4*).[5]



The suggestion of intermediate *4* warrants further study in the light of recent reports indicating the intermediacy of carbene anion radicals in the reduction of diazo compounds.[6] McDonald and coworkers[6] have presented cyclic voltammetric data which they interpret to indicate the direct voltammetric observation of fluorenylidene anion radical.

RESULTS

The primary evidence leading to the conclusion that the cation radicals *3* undergo unimolecular decomposition to *4* consisted of the failure to observe the expected concentration dependence of I_b/I_f, the ratio of peak currents for the backward and forward scans during cyclic voltammetry, for a second order mechanism. Little change was reported in the peak current ratio while the substrate concentration was varied by a factor of 8. In our experiments, we find that there is indeed a concentration dependence on the lifetime of the cation

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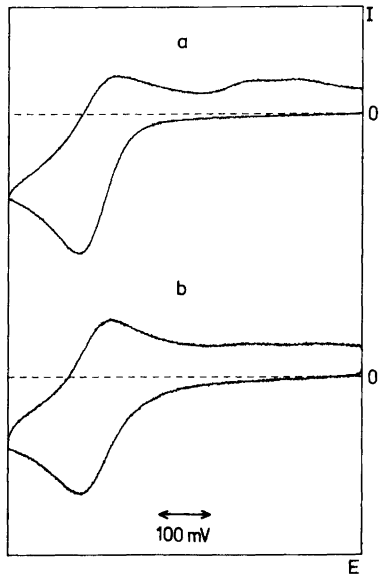


Fig. 1. Cyclic voltammograms of 4-bromo-*N*,*N*-dimethylaniline measured in acetonitrile containing Bu_4NBF_4 (0.1 M). Substrate concentration 10.0 mM (a) and 1.0 mM (b). Voltage sweep rate was 5 V s^{-1} and the reference electrode was Ag^+ (0.01 M), Bu_4NBF_4 (0.1 M)/Ag in acetonitrile. The electrode was a platinum disk (0.8 mm diam.). Oxidation peak potential = 0.55 V.

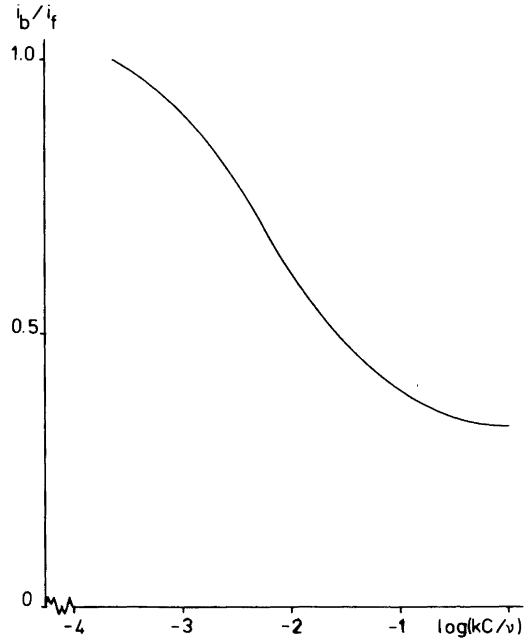


Fig. 2. Working curve for the EC dimerization mechanism during cyclic voltammetry. Calculated by digital simulation.

radicals *3* generated in acetonitrile containing Bu_4NBF_4 (0.1 M). This is illustrated by the cyclic voltammograms shown in Fig. 1 for 4-bromo-*N*,*N*-dimethylaniline (BDMA). At a concentration of 1.0 mM (Fig. 1b) the ratio of the peak currents at R_1 and O_1 approaches 1.0 and very little current due to reduction of further reaction products was observed at 5 V s^{-1}. Under the same conditions with a concentration of 10 mM, the peak current ratio was significantly lower and reduction peaks due to reaction products were observed at less anodic potentials.

Cyclic voltammetric kinetic study. In order to obtain more quantitative data on the concentration dependence of the rate of decomposition of *3* generated from BDMA and 4-iodo-*N*,*N*-dimethylanile (IDMA), peak current ratios obtained in the manner described by Nicholson[7] were compared with a theoretical working curve calculated by digital simulation[8] for a second order dimerization mechanism as in eqns. (3) and (4). The calculated curve (Fig. 2) shows that for a given rate constant,

$$A \pm e^- \rightleftarrows B \quad (3)$$

$$2B \xrightarrow{k} C \quad (4)$$

k, at voltage sweep rate, v, the peak current ratio, $R_1(I_b/I_f)$, varies with the substrate concentration, C, and if the value of v is chosen to obtain the maximum effect, a factor of about 2 is expected for a tenfold change in C. Peak current ratio data and rate constants obtained using the working curve for the reactions of BDMA and IDMA are summarized in Tables 1 and 2, respectively. The second order rate constants measured at 20 °C were found to be equal to $3.6 (\pm 1.5) \times 10^3$ and $1.9 (\pm 0.7) \times 10^4$ M^{-1} s^{-1} for BDMA and IDMA, respectively, where the values in parentheses are the standard deviations. The relatively high uncertainty in the rate constants is inherent in the method and is due to the uncertainty in the baseline estimated during the measurement.

Double step chronoamperometric kinetic study. This method[9] is more precise and was thus used for more detailed mechanism studies. Briefly, the method involves a potential step from an initial

Table 1. Kinetic data for the dehalodimerization of 4-bromo-*N*,*N*-dimethylaniline in acetonitrile at 20 °C.[a]

I_b/I_f [b]	log (k C/v)[c]	v[d]/V s^{-1}	C/mM	k/M^{-1} s^{-1}/10^3
0.72	−2.35	0.5	1.0	2.2
0.76	−2.46	1.0	1.0	3.5
0.96	−3.32	5.0	1.0	2.4
0.57	−1.86	0.5	2.5	2.8
0.65	−2.09	1.0	2.5	3.3
0.81	−2.60	5.0	2.5	5.0
0.50	−1.60	0.5	5.0	2.5
0.59	−1.90	1.0	5.0	2.5
0.71	−2.26	5.0	5.0	5.5
0.81	−2.60	10.0	5.0	5.0
0.45	−1.36	0.5	10.0	2.2
0.50	−1.58	1.0	10.0	2.6
0.62	−2.03	5.0	10.0	4.7
0.69	−2.23	10.0	10.0	5.9

[a] Measured by cyclic voltammetry at a platinum electrode, supporting electrolyte was Bu_4NBF_4 (0.1 M). [b] Ratio of cathodic to anodic peak currents. [c] Parameters taken from the working curve. [d] Voltage sweep rate.

Table 2. Kinetic data for the dehalodimerization of 4-iodo-*N*,*N*-dimethylaniline in acetonitrile at 20 °C.[a]

I_b/I_f [d]	log (k C/v)[c]	v[d]/V s^{-1}	C/mM	k/M^{-1} s^{-1}/10^4
0.50	−1.60	0.5	1.0	1.3
0.61	−1.98	1.0	1.0	1.1
0.88	−2.85	5.0	1.0	0.71
0.43	−1.20	0.5	2.5	1.3
0.45	−1.35	1.0	2.5	1.8
0.63	−2.06	5.0	2.5	1.7
0.72	−2.35	10.0	2.5	1.5
0.85	−2.74	20.0	2.5	1.5
0.51	−1.62	5.0	5.0	2.4
0.58	−1.85	10.0	5.0	2.8
0.68	−2.18	20.0	5.0	2.6
0.84	−2.70	50.0	5.0	2.0
0.45	−1.32	5.0	10.0	2.4
0.50	−1.61	10.0	10.0	2.5
0.58	−1.90	20.0	10.0	2.5
0.70	−2.25	50.0	10.0	2.8

[a] Measured at a platinum electrode by cyclic voltammetry, supporting electrolyte was Bu_4NBF_4 (0.1 M). [b] Ratio of anodic to cathodic peak currents. [c] Parameters from working curve. [d] Voltage sweep rate.

potential where no reaction occurs to a potential where the reaction of interest is diffusion controlled. At time τ, the potential is stepped back to the initial value where substrate is regenerated. The analysis involves measuring the current at τ (I_f) and at 2τ (I_b). The normalized current ratio, R_I is obtained by dividing I_b/I_f by $1-2^{-\frac{1}{2}}$ which is the theoretical value for the no reaction case. A convenient method for treating the data has been devised by Bard.[10] This procedure involves plotting R_I *vs.* the appropriate parameter, kCt for the second dimerization, and finding the time ($t_{\frac{1}{2}}$) when R_I is equal to 0.5. Another working curve is then constructed with R_I as a function of time in units of $t_{\frac{1}{2}}$. Working curves for all mechanisms pass through a common point at R_I equal 0.5, but maximum devia-

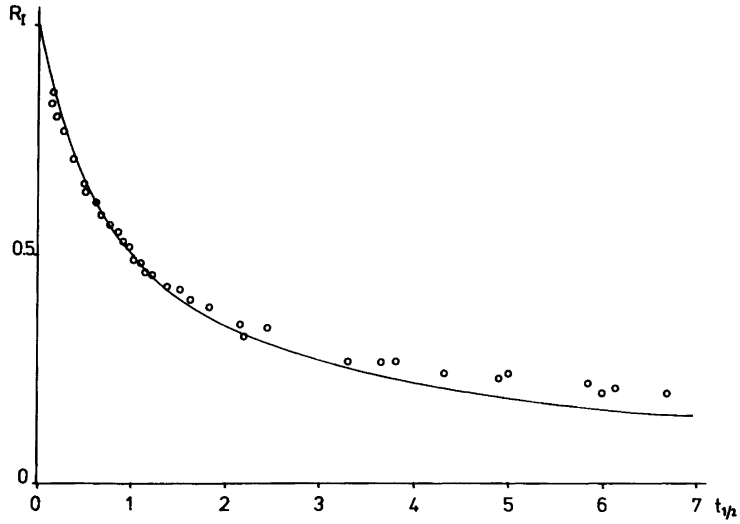


Fig. 3. Double step chronoamperometric data for the oxidation of 4-bromo-*N*,*N*-dimethylaniline and the working curve for the EC dimerization mechanism.

tions are found at long times. Thus, this method of data presentation is very useful in distinguishing between mechanistic possibilities.

Experimental values of R_I for BDMA and IDMA along with the theoretical working curve for the simple EC dimerization mechanism are shown in Figs. 3 and 4, respectively. The experiments were conducted under the same conditions as those used for the cyclic voltammetric studies and the concentrations of the substrates were varied over a tenfold range. It is noteworthy that a good fit is not observed between the data and the theoretical curve in either case.

Simulation of a more complex mechanism. The

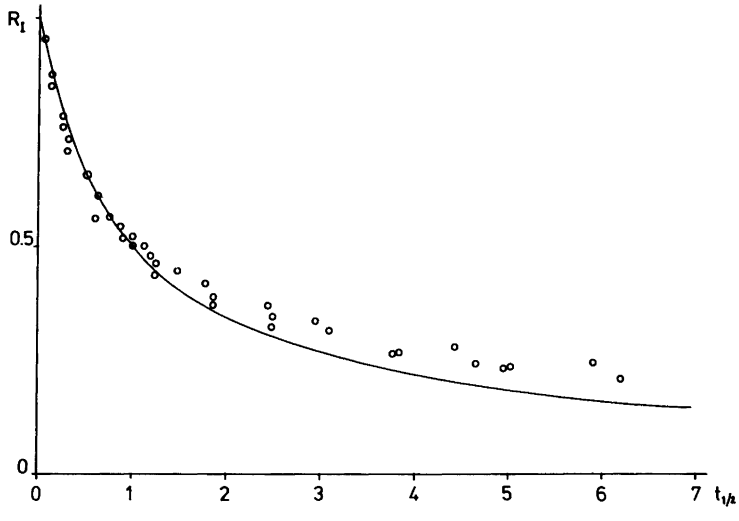


Fig. 4. Double step chronoamperometric data for the oxidation of 4-iodo-*N*,*N*-dimethylaniline and the working curve for the EC dimerization mechanism.

relatively poor fit of the experimental data to the double step chronoamperometric working curve for the EC dimerization mechanism led to the consideration of possible complications. An obvious one is that the products *2* are in oxidized states. The difference in redox potentials for the dimeric dications and the substrates are of the order of 250 mV.[5] Assuming that k_{-5} is a diffusion controlled rate constant which is reasonable for this potential difference,[11] leads to an estimate of 10^6 M^{-1} s^{-1}

$$Ar-X + (X-Ar-Ar-X)^{2+} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Ar-X^{\cdot+} + (X-Ar-Ar-X)^{\cdot+} \quad (5)$$

for the value of k_5 for the 4-halo-*N*,*N*-dimethylaniline cation systems. Thus, reaction (5) is expected to play a role in the overall mechanism.

The mechanism used in the simulation is described by eqns. (6)–(8). Working curves of R_I *vs.* k_7tC were calculated for several values of the rate constant ratio, k_7/k_8 and the data are summarized in Table 3.

$$A-e^- \rightleftarrows B \quad (6)$$

$$2B \xrightarrow{k_7} BB \quad (7)$$

$$BB + A \xrightarrow{k_8} C + B \quad (8)$$

The rate constant ratio equal to zero corresponds to the simple EC dimerization mechanism. R_I values are listed at times of $7t_{\frac{1}{2}}$, a value which we have found most convenient for experimental comparisons.

Table 3. Simulated kinetic parameters showing the effect of substrate oxidation by product on the normalized current ratio at long times during double step chronoamperometry.[a]

k_7/k_8 [b]	R_I (at $7t_{\frac{1}{2}}$) [c]	ktC (at $R_I=0.5$) [d]
0	0.144	0.864
0.001	0.147	0.864
0.01	0.180	0.879
0.05	0.310	0.947

[a] Obtained using digital simulation. [b] Rate constants for the dimerization (7) and electron transfer (8) reactions as described in the text. [c] The normalized current ratio at a time equal to $7t_{\frac{1}{2}}$ where $t_{\frac{1}{2}}$ is as defined in the text. [d] The parameter used to calculate the rate constant from the experimental data.

The numbers in the third column are those which can be used to calculate the rate constant from the value of $t_{\frac{1}{2}}$. The important feature of the data in Table 3 is that the value of R_I at $7t_{\frac{1}{2}}$ is greater when reaction (8) is taken into account. Furthermore, for small deviations in R_I at $7t_{\frac{1}{2}}$ from the simple EC dimerization case, the value of k_7tC used to calculate the rate constant does not deviate significantly.

Second order rate constants obtained by double step chronoamperometry. The values of R_I at $7t_{\frac{1}{2}}$ during the dehalodimerization of BDMA and IDMA were observed to be equal to 0.19 and 0.20, respectively. The simulation results discussed in the previous paragraphs indicate that no serious error will come from using the value of $kt_{\frac{1}{2}}C$, 0.864, for the simple EC dimerization reaction in order to calculate k. The reason for not attempting to calculate the exact value from the data in Table 3 is that the real mechanism is probably more complex than the simulated one and thus the simulated values are not expected to be exact for the experimental data. This is discussed in more detail later. Rate constants for the two reactions are summarized in Table 4. The average values were found to be equal to 2.23 ($\pm$0.20)$\times 10^4$ and 4.47 ($\pm$1.02)$\times 10^3$ M^{-1} s^{-1} corresponding to precision of $\pm$9 and $\pm$23 % for the reactions of IDMA and BDMA, respectively. These values are more precise than those obtained by cyclic voltammetry. However, the agreement between values obtained by the two techniques is excellent.

The effect of temperature on the second order rate constants. In order to obtain further detailed mechanistic information on the dimerization reactions, kinetic studies were carried out under the

Table 4. Summary of second order rate constants for the dehalodimerization of 4-halo-*N*,*N*-dimethylanilines in acetonitrile at 20 °C measured by double step chronoamperometry.[a]

Conc./mM	4-Iodo-*N*,*N*-dimethylaniline $k/M^{-1}s^{-1}/10^4$	4-Bromo-*N*,*N*-dimethylaniline $k/M^{-1}s^{-1}/10^3$
1.0	2.15	5.79
2.5	2.12	4.71
5.0	2.12	3.91
10.0	2.52	3.47

[a] Measured at a platinum electrode, supporting electrolyte was Bu_4NBF_4 (0.1 M). All the data are represented in Figs. 3 and 4.

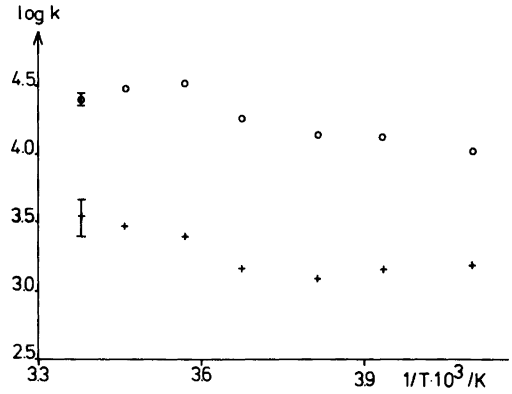


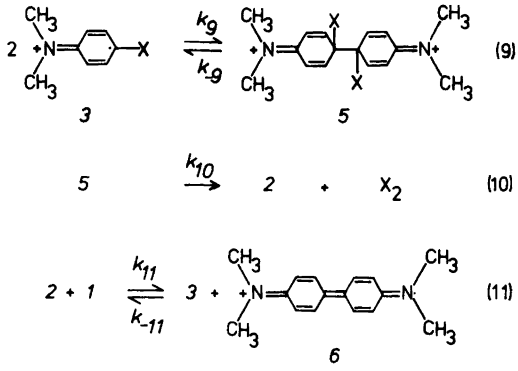
Fig. 5. Arrhenius plots for the reactions of 4-halo-*N*,*N*-dimethylanilines. The circles refer to the iodo compound and the crosses to the bromo compound. The error limits for each experiment set are shown on the first data point and is the same for the others.

same conditions as those described above but over about a fifty degree range in temperature. The Arrhenius plots for the two cation radical reactions are shown in Fig. 5. Neither plot is linear and the shapes of the two curves are similar. The most striking feature of the data is the very small effect of temperature on the rate constants. Rate constants for both reactions were observed to vary by only a factor of about 2 over the fifty degree temperature range.

DISCUSSION

The very good fit of our data to second order working curves for both the cyclic voltammetric and double step chronoamperometric response clearly rules out the previously proposed[5] first order decomposition of the 4-halo-*N*,*N*-dimethylaniline cation radicals.

The fact that IDMA$^{\cdot+}$ reacts about 5 times as fast as BDMA$^{\cdot+}$ strongly suggests that the dimerization of the cation radicals is not the rate determining step in the reactions. This is also indicated by the fact that the reaction was not observed at all with the cation radical of 4-fluoro-*N*,*N*-dimethylaniline.[5] The dimerization step would be expected to be subject to steric effects and the rate should be inversely related to the size of the halogen atom. The relative reactivities appear to be dependent upon the carbon–halogen bond energies which suggests that the bond cleavage takes part in the



rate determining steps. A mechanism which is consistent with these observations is shown in eqns. (9)–(11). This mechanism also accounts for the near independence of the observed rate constants upon the temperature. One would predict a characteristic linear Arrhenius plot with the rate decreasing with decreasing temperature for the dimerization step (9). However, if (9) is reversible and at equilibrium, a decrease in the temperature would be expected to favor the dimer and contribute to an increase in the reaction rate. On the other hand, the halogen cleavage reaction (10) would be expected to be retarded with decreasing temperature. Thus, the two opposite temperature effects counteract one another and are consistent with the results observed.

Reactions (9) through (11) involve five different rate constants. The rate constants that we measure are obviously complex functions of the rate constants for the various steps and we cannot possibly assign values to those for the individual steps from our data. In order to simulate the voltammetric response for this mechanism, it would be necessary to make a number of assumptions relating to the relative values of the rate constants. We found that if (9) is considered to be at equilibrium, our simulation rate constant is equivalent to $k_{10}K_9$. In the simulation, the homogeneous electron transfer reaction (8) was considered to be irreversible. Including a reversible step as in (11) requires assumptions regarding the relative values of k_{10} and k_{-11}. We regard making estimates of the various rate constants to be somewhat pointless. Our results strongly support the reversible dimerization mechanism and meaningful discussion of the relative values of the rates of the various steps can only come after independently obtaining values for some of the rate constants. For example, it would be possible to study the electron transfer reaction

(11) as a catalytic reaction; voltammetric measurements could be made on the reduced form of *2* in the presence of the 4-halo-*N*,*N*-dimethylanilines. Detailed analysis of data from such a kinetic study could possibly provide values for k_{11}, k_{-11} and K_{11}. Further work is planned along these lines. The details of reaction (10) also warrant further study. It is not clear whether the reaction is a concerted loss of halogen or if the halogens leave in stepwise fashion.

EXPERIMENTAL

The instrumentation, cells, electrodes, reference electrodes and solvent purification procedures were identical to those used previously..[11] The 4-halo-*N*,*N*-dimethylanilines were prepared by standard literature procedures.

Acknowledgement. We thank the Norwegian Research Council for Science and the Humanities for support of E. A.

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Received September 13, 1979.