

Decomposition Reactions of the Electrogenerated Dications of Arenetricarbonylchromium Complexes

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We have previously reported studies on the decomposition reactions of the cation radicals of arenetricarbonylchromium complexes $[\text{MCr}(\text{CO})_3]$ in acetonitrile.¹⁻³ These reactions are of limited synthetic use, since the reaction products were invariably found to consist of the parent arenes (M) and decomposition products of the tricarbonylchromium moiety, as depicted in eqns. (1) and (2). This mode of decomposition is a reflection of the fact that



the charge of the cation radicals is localized on the metal rather than on the arene group. This suggests that, in order to obtain oxidation products of the parent arenes it would be necessary to convert the arenetricarbonylchromium complexes to a higher oxidation state, *i.e.* to the corresponding dications.

The reactions of the dication of 1,2,4,5- $(\text{CH}_3)_4\text{C}_6\text{H}_2\text{Cr}(\text{CO})_3$ (*I*) were studied by linear sweep voltammetry (LSV) along with potentiostatic electrolysis experiments. All the LSV measurements were carried out at either 25 °C or at -20 °C in acetonitrile containing Bu_4NBF_4 (0.1 M). The same platinum disk electrode ($\sim 0.5 \text{ mm}^2$) was used for the LSV and the potentiostatic experiments.

The LSV curves for the complexes such as *I* are complex with a number of peaks arising from *I* as well as from the parent molecule (*2*) formed in the decomposition of *I*. These curves have been discussed in Ref. 1. For the purpose of illustrating the reactions of the dication of *I* and for the sake of clarity, we represent the voltammograms with the peaks shown as lines, the height of which are proportional to the number of electrons transferred. The lines labelled S-1 and S-2 are due to the formation of the cation radical and dication, respectively, of the substrate (*I*). The line labelled P-1 is due to the oxidation of *2* and P-2 to P-4 are due to oxidation processes of products of *2*. The voltammetric behaviour of the polymethylbenzenes in acetonitrile has been discussed previously.⁴

At 25 °C and a voltage sweep rate (v) equal to 0.1 V/s, *I* undergoes $2e^-$ oxidation at S-1 to generate *2* which is oxidized at P-1 to give a product oxidized at P-2, and this cascading continues until the fourth methyl group is oxidized at P-4. This is confirmed by comparison of the voltammogram for the oxidation of *2* under the same conditions. The reason that the heights of P-1 to P-4 vary is that the processes involve kinetics and are not all complete under the time scale of the experiments. This is even more clear by considering the voltammogram for the oxidation of *2* at -20 °C and 10 V/s. In this case the peak heights for P-2 to P-4 are less. The peak heights represented in the Figure are approximate and are not meant to give a quantitative measure of the extent of the reactions.

At -20 °C and 10 V/s, *I* is oxidized to the cation radical at S-1 and under these conditions the further reactions of $I^{\cdot+}$ are slow. In this case, the formation of the dication can be observed at S-2. No decomposition of the dication to *2* can be detected in the voltammogram, but from the height of P-2 it can be concluded that I^{2+} decomposes directly to the oxidation product of *2*. From previous work^{4,5} on the oxidation methylbenzenes in acetonitrile it follows that the reaction of the dication can be represented as in eqn. (3). The

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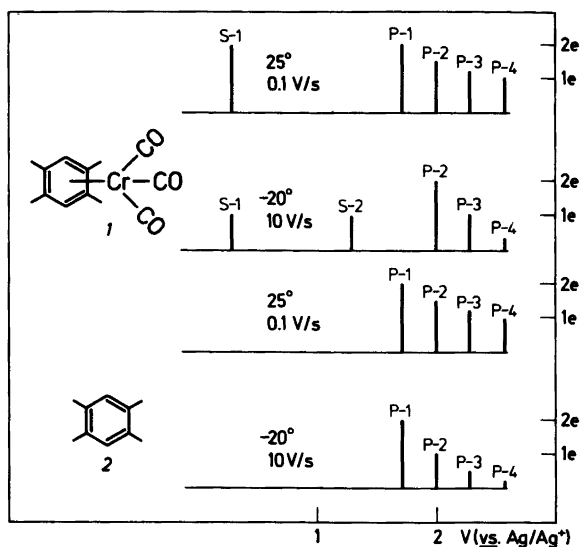
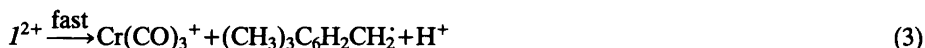


Fig. 1. Schematic linear sweep voltammograms for the oxidation of 1 and 2 in acetonitrile containing Bu_4NBF_4 (0.1 M).



final fate of $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2^+$, formed by oxidation of the radical, in this medium involves a Ritter type reaction to form the corresponding acetamide.⁵ As in previous work¹ the reaction pathways of $\text{Cr}(\text{CO})_3^+$ have not been established.

The same reaction pattern was also observed for the $\text{Cr}(\text{CO})_3$ complexes of 1,4- $(\text{CH}_3)_2\text{C}_6\text{H}_4$, 1,3,5- $(\text{CH}_3)_3\text{C}_6\text{H}_3$, and $(\text{CH}_3)_5\text{C}_6\text{H}$. Thus, it can be concluded that during the decomposition of all of the dications of $\text{MCr}(\text{CO})_3$ the arene-Cr bond is cleaved to produce the oxidation product of M.

Since the formation of $\text{MCr}(\text{CO})_3^{2+}$ takes place at a lower potential than the oxidation of M in the case of methylsubstituted benzene complexes,¹ it follows that the oxidation product of M can be formed from the complexes at potentials lower than the direct formation of M^{2+} occurs. This was confirmed from potentiostatic electrolysis of 1 in the same medium. At -20°C where the cation radical is sufficiently stable to be converted into the dication, exhaustive electro-oxidation of 1 resulted in the oxidation product of 2. The product was detected by LSV measurements after electrolysis. On the other hand, at 25°C where the cation radical is reactive, electro-oxidation of 1 resulted in the formation of 2. This conversion was followed by LSV measurements as well.

The direct conversion of $\text{MCr}(\text{CO})_3^+$ to M^{2+} suggests the possibility of electrocatalysis. In this particular instance it is not yet of practical value since the conversion of M to $\text{MCr}(\text{CO})_3$ has been carried out in separate experiments and there is no evidence to indicate that $\text{Cr}(\text{CO})_3^+$ formed in the decomposition of the dication can be made to react with M to complete the catalytic cycle. To determine whether or not these reactions can be carried out by electrocatalysis is the goal of work in progress.

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