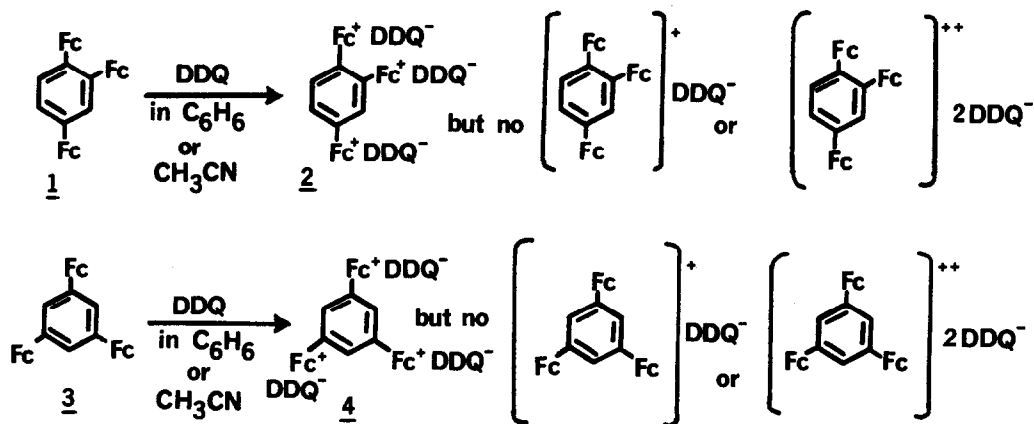


## THE SELECTIVE TRIOXIDATION OF 1,2,4- AND 1,3,5-TRIFERROCENYL BENZENE

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It is well known, from voltammetric studies, that ferrocene and its substituted derivatives show a reversible one electron oxidation wave.<sup>3</sup> Ferrocenium salts are stable, isolable species.<sup>4</sup> Biferrocene [Fe(II)Fe(III)] picrate and tetrafluoroborate salts have been readily prepared and isolated, as have their corresponding [Fe(III)Fe(III)] salts.<sup>5</sup> The electrochemical oxidation of biferrocene proceeds in two one-electron steps, the second step requiring a significantly higher potential (0.635V) than the first step (0.286V).<sup>6</sup> When compared to ferrocene (0.385V), it can be seen, clearly, that a ferrocenyl substituent acts as an electron donating group, but a ferrocenium moiety is distinctly electron withdrawing thereby raising the potential of the second oxidation step in biferrocene. Thus, we were surprised upon discovering that upon chemical oxidation of both 1,2,4- and 1,3,5-triferrocenylbenzene with 2,3-dichloro-5,6-dicyanoquinone (DDQ) only the trioxidized salts, 2 or 4 were obtained.

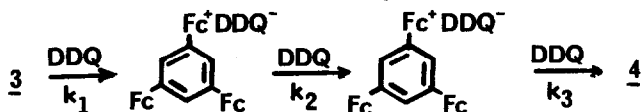


In an effort to prepare mixed-valence state ferrocene salts for conductivity studies,<sup>7,8</sup> we undertook the mono- and dioxidation of cyclotrimers 1 and 3 with DDQ.<sup>9</sup> The reaction of both 1 and 3 with DDQ, in ratios ranging from 1:3 to 3:1 (cyclotrimer:DDQ), gave only trisalts 2 or 3 and recovered cyclotrimer. Even when a 3 molar excess of cyclotrimer was used (thus a 9 molar excess of Fc:DDQ), only trisalts and unreacted cyclotrimer could be isolated. In none of these reactions were any mono- or disalts ever found. Thus, there is a distinct propensity for the

mono- and disalts to further oxidize to the trisalt at a rate greater than the first oxidation step. Some representative reactions are summarized in Table 1.

The reactions were carried out under nitrogen in thoroughly deoxygenated solutions. The cyclotrimer and DDQ were dissolved in separate portions of solvent, and the DDQ solutions were then rapidly added to the cyclotrimer solutions. The resulting solution became dark, and a black precipitate of the trisalt formed very rapidly. The salts were filtered and thoroughly extracted with benzene, acetonitrile, and pet-ether (30-60°). They were vacuum dried at 60° for 24 hrs. and analyzed for C, H, Fe, N, and Cl. All analyses were within 0.4% of that calculated for 2 or 4. The IR spectra of both 2 and 4 exhibited a CN str. band at 2205 to 2215 cm<sup>-1</sup> (this band should be from 15 to 25 cm<sup>-1</sup> lower than that of neutral DDQ<sup>9</sup>), CO str. from 1580 to 1600<sup>10</sup> (verses 1680 in DDQ), and the cyclopentadienyl C-H out-of-plane bending frequency was found at 845-860 cm<sup>-1</sup> as expected for ferrocenium groups.<sup>9,11</sup> This bending mode occurs at 810-830 cm<sup>-1</sup> in ferrocene and its derivatives<sup>12</sup> and specifically at 818 cm<sup>-1</sup> in 1 and 822 cm<sup>-1</sup> in 3.

What can cause preferential trioxidation? Recently, Nakashima and Kunitake<sup>13</sup> observed that cyclotrimers 1 and 3 underwent a three electron one-step oxidation electrochemically. They argued that this could be explained if there is no appreciable interaction among the ferrocene nuclei in the cyclotrimers. Since, the intensity of the 450 nm band in the cyclotrimers is about three times that of phenylferrocene and since the electron removed in the oxidation is largely isolated on the metal, this explanation, at first, appeared reasonable. However, in a chemical oxidation the field effect would still operate to slow down the second and third oxidation steps. Furthermore, if the second and third oxidation steps occurred at the same rate as the first step, one should then get a statistical mixture of the mono-, di- and trisalts on chemical oxidation with DDQ. Thus, we feel that an "internal solvation effect" is taking place that enhances the rates of the second and third oxidation steps relative to the first in the DDQ reaction.



The first molecule of DDQ encounters a neutral molecule of 1 or 3. Charge must be generated going to the transition state in the first oxidation step. There is only solvent to solvate this charge separation. However, in the second step the molecule already has an internal salt site which can be viewed as internally solvating the transition state of this oxidation. Another way to view this process is to picture the first salt site increasing the effective dielectric constant of the medium in the vicinity of the second oxidation. In the third oxidation step,

TABLE 1. EXAMPLE of DDQ with 1,2,4- and 1,3,5-TRIFERROCENYLBENZENE

Cyclotrimer (mmol. charged)	Mole Ratio Charged Cyclotrimer/DDQ	Solvent (ml)	Temp. °C	Time hr.	Trisalt Isolated (mmol.)	Cyclotrimer recovered (mmol.)	Yield of Trisalt <sup>b</sup> %
<u>2</u> (.476)	1:1	benzene (150)	22	1	1.46	2.71	92
<u>2</u> (.476)	3:1	benzene (50)	40	1	.038	.424	72
<u>2</u> (.476)	1:1	CH <sub>3</sub> CN (100)	60	1	.136	.182	85
<u>2</u> (.476)	1:3	CH <sub>3</sub> CN (130)	22	24	.198	.209	42
<u>2</u> (.476)	1:1	benzene (80)	22	24	.101	.373	64
<u>3</u> (.476)	1:1	CH <sub>3</sub> CN (80)	22	24	.098	.375	62
<u>3</u> (1.00)	2:1	CH <sub>3</sub> CN (85)	40	24	.137	.788	81

a. In no case were any mono- or disalts isolated, despite specific attempts to isolate them.

b. Based on conversion of DDQ to trisalt

c. 5% H<sub>2</sub>O in the CH<sub>3</sub>CN

two such internal salts act to facilitate the rate. Thus, it is reasonable that  $k_3 > k_2 > k_1$ . After first discovering this reaction in benzene, we felt the propensity toward trioxidation would be reduced in a more polar solvent, because the ratios  $k_3/k_2$  and  $k_2/k_1$ , should be reduced as the dielectric constant of the medium is increased. That is, any internal solvation effect could eventually be swamped out as the solvents'  $\epsilon$  enlarged. However, going from benzene ( $\epsilon=2.3$ ) to acetonitrile ( $\epsilon=36.2$ ) and even to 5% H<sub>2</sub>O in acetonitrile ( $\epsilon > 36.2$ ) did not suppress the production of 2 or 4.

This phenomenon might be more general than previously suspected. Already, we have observed that reaction of polyvinylferrocene, polyferrocenylene, or polyethynylferrocene with a deficiency of DDQ gives polysalt precipitates in which the amount of oxidation is greater than the starting ferrocene:DDQ ratio. Furthermore, unoxidized (or very slightly oxidized) polymer remains dissolved. Apparently, once oxidation occurs on a polymer chain it facilitates neighboring oxidations, and these oxidized sites coil away from the organic solvent. More DDQ then reacts in the salt-like regions until the polymer precipitates.

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