Electrochemical Reduction of Group 6 Metal Hexacarbonyls in Aprotic Solvents

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The mechanism of the reduction of $[Cr(CO)_6]$ to $[Cr_2(CO)_{10}]^{2-}$ at a platinum electrode in acetonitrile has been investigated by cyclic voltammetry, and it is shown that $[Cr(CO)_5]^{\cdot-}$ is a species stable on the time scale of a few seconds. The mechanisms of reduction of $[Mo(CO)_6]$ and $[W(CO)_6]$ are apparently similar. Intermediates in the reductions of these Group 6 metal carbonyls react with alkyl halides and carbon dioxide.

SEVERAL years ago, Dessy *et al.*[1] reported that the carbonyls $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$ could be reduced electrochemically in aprotic solvents, and a recent publication [2] showed that the products of these reductions were the binuclear dianions $[Cr_2(CO)_{10}]^{2-}$, $[Mo_2(Co)_{10}]^{2-}$, and $[W_2(CO)_{10}]^{2-}$ respectively. In this paper, cyclic voltammetry is used to investigate the mechanisms of these reactions and in particular to seek evidence for stable anionic intermediates. The reduction of these metal carbonyls was also studied in the presence of alkyl halides and carbon dioxide, since it was thought that any anionic carbonyl intermediates would react with such electrophiles.

EXPERIMENTAL

The electrochemical instrumentation and cells, the spectrometers, and the sources and purification of the carbonyls and solvents [acetonitrile, *NN*-dimethylformamide (dmf), and tetrahydrofuran (thf)] have been described previously.[2] The alkyl halides and carbon dioxide were obtained from B.D.H. Ltd. and the Distillers Co. respectively and were used without purification.

G.l.c. analyses were made on a Pye 104 chromatograph.

RESULTS AND DISCUSSION

Mechanism of the Cathodic Reduction of $[Cr(CO)_6]$.—Figure 1 shows a set of cyclic-voltammetric experiments designed to elucidate the mechanism of the reduction of $[Cr(CO)_6]$ at a platinum cathode in MeCN containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$. The cyclic voltammograms were recorded at a potential scan rate of 0.3 V s^{-1} and each is a first cycle. Curve (*i*) shows the cyclic voltammogram for $[Cr(CO)_6]$ in MeCN over the potential range 1.2 to −2.7 V [relative to the standard calomel electrode (s.c.e.)]; the sweep was commenced at 0.0 V and went initially to negative potentials. The primary reduction process leads to peak (I) and the current function $I_p/v^{\frac{1}{2}}c$ for this process was independent of the potential scan rate, v, and the concentration, c, and was similar to that for a known one-electron reaction, the reduction of fluorenone. Hence it may be concluded that $[Cr(CO)_6]$ is reduced in a diffusion-controlled one-electron reaction. Indeed these conclusions may be confirmed by experiments with a rotating-disc electrode and by coulometry at a potential close to E_p. Investigation of the catholyte by i.r. spectroscopy at the end of the controlled-potential reduction [2] indicated that the product was $[Cr_2(CO)_{10}]^{2-}$. Even at −45 °C and fast potential scan rates, the reduction process (I) remained irreversible.

The oxidation peak (II) was, however, observed under all conditions and, indeed, the quotient of the peak currents I_p^{II}/I_p^{I} was independent of potential scan rate indicating that peak (II) is due to the reoxidation of a relatively stable intermediate. The value of the quotient I_p^{II}/I_p^{I} also shows that, when allowance is made for the effects of diffusion, peak (II) must be attributable to the oxidation of a major intermediate in the reduction of $[Cr(CO)_6]$.

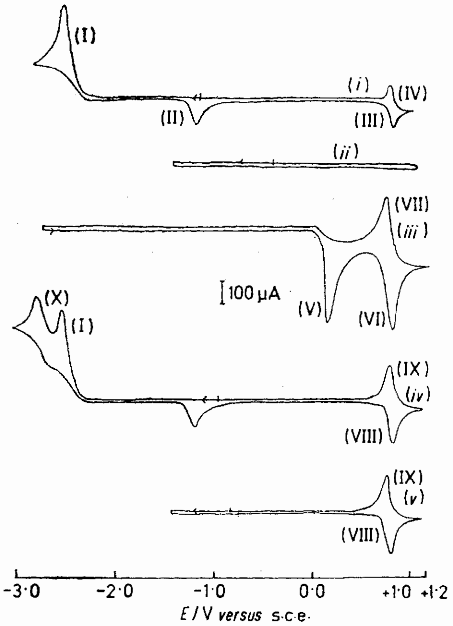

FIGURE 1 Cyclic voltammograms at a platinum electrode in MeCN +0.2 mol dm^{-3} $[NBu_4][BF_4]$. Sweep rate 0.3 V s^{-1}. (*i*) and (*ii*), 5 × 10^{-3} mol dm^{-3} $[Cr(CO)_6]$; (*iii*), after complete reduction of solution (*i*) at −2.6 V, *i.e.* solution was 2.5 × 10^{-3} mol dm^{-3} $[Cr_2(CO)_{10}]^{2-}$; (*iv*) and (*v*), solution (*i*) after u.v. irradiation, *i.e.* the solution contained some $[Cr(CO)_5(CNMe)]$

On continuing the anodic sweep to positive potentials, a pair of peaks (III) and (IV) with the properties for a reversible one-electron couple was also observed. Curve (*ii*), a cyclic voltammogram recorded between 0.0 and 1.2 V, confirms that peaks (III) and (IV) are not associated with a primary oxidation process of $[Cr(CO)_6]$, although were the sweep to be extended to more positive

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[1] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.* 1966 **88**, 471.

[2] C. J. Pickett and D. Pletcher, *J.C.S. Dalton*, 1975, 879.

potentials the reversible couple $[Cr(CO)_6]$–$[Cr(CO)_6]^+$, described in earlier publications, would be seen.[2,3]

A solution of $[Cr(CO)_6]$ was reduced at a controlled potential of −2.6 V to form a solution of $[Cr_2(CO)_{10}]^{2-}$, and curve (*iii*) of Figure 1 is a cyclic voltammogram of the catholyte after the electrolysis. The major features of the cyclic voltammogram are the irreversible process, peak (V), and at more positive potentials the reversible system (VI) and (VII). The current function for the first oxidation process of $[Cr_2(CO)_{10}]^{2-}$, peak (V), is independent of v and its magnitude suggests a two-electron reaction.

Finally a solution of $[Cr(CO)_6]$ in MeCN was irradiated with u.v. light of 356-nm wavelength to form a solution where part of the $[Cr(CO)_6]$ had been converted into $[Cr(CO)_5(NCMe)]$.[4] Curves (*iv*) and (*v*) of Figure 1 are cyclic voltammograms of this solution. Curve (*v*) shows that there is now a reversible couple, peaks (VIII) and (IX), which is a primary oxidation process for a species in the system; thus peaks (VIII) and (IX) can be attributed to the couple (1). Its properties as a function of potential scan rate exactly parallel those of the couples

$$[Cr(CO)_5(NCMe)] - e^- \underset{(IX)}{\overset{(VIII)}{\rightleftharpoons}} [Cr(CO)_5(NCMe)]^+ \quad (1)$$

(VI)–(VII) and (III)–(IV) and it may be concluded that these couples are due to the same processes. Curve (*iv*) shows that at negative potentials peaks (I) and (II) due to $[Cr(CO)_6]$ are again observed but in addition a new process, peak (X), was observed and it may be attributed to an irreversible reduction of $[Cr(CO)_5(NCMe)]$.

Comparison of this set of cyclic voltammograms allows the following conclusions to be drawn: (*a*) $[Cr(CO)_6]$ undergoes an irreversible one-electron reduction; (*b*) peak (II), although due to the oxidation of a stable species, is not due to the reoxidation of the final product $[Cr_2(CO)_{10}]^{2-}$; (*c*) $[Cr_2(CO)_{10}]^{2-}$ is not formed at all on the time scale of these cyclic voltammograms; and (*d*) $[Cr(CO)_5(NCMe)]$ is the product of the oxidation of $[Cr_2(CO)_{10}]^{2-}$ and is also formed during the cyclic voltammetry of $[Cr(CO)_6]$. The absence of peak (X) on curve (*i*) shows, however, that $[Cr(CO)_5(NCMe)]$ is not formed directly in the reduction of $[Cr(CO)_6]$ and hence must be the product of the process giving peak (II). These conclusions would appear to be compatible only with the mechanism in equations (2) and (3) for the reduction of $[Cr(CO)_6]$. Peak (II) would then be due to reaction (4).

$$[Cr(CO)_6] + e^- \longrightarrow [Cr(CO)_6]^{\overline{\cdot}} \xrightarrow[\text{fast}]{-CO} [Cr(CO)_5]^{\overline{\cdot}} \quad (2)$$

$$2[Cr(CO)_5]^{\overline{\cdot}} \xrightarrow{\text{slow}} [Cr_2(CO)_{10}]^{2-} \quad (3)$$

$$[Cr(CO)_5]^{\overline{\cdot}} - e^- \xrightarrow{\text{MeCN}} [Cr(CO)_5(NCMe)] \quad (4)$$

Hence it would appear that the carbonyl anion $[Cr(CO)_5]^-$ is stable for at least several seconds in MeCN. Although it has been proposed as an intermediate in the alkali-metal reduction of $[Cr(CO)_6]$,[5] this is the first occasion that evidence has been found for its existence as a metastable species in solution. Spectroscopic evidence for $[Cr(CO)_5]^{\overline{\cdot}}$ during low-temperature matrix-isolation experiments has, however, been reported.[6]

In the potential range 0 to −2.7 V, the pattern of the cyclic voltammetry for $[Cr(CO)_6]$ in thf and dmf is the same as that described above for MeCN. Likewise the cyclic voltammograms of $[Mo(CO)_6]$ and $[W(CO)_6]$ are very similar to those of $[Cr(CO)_6]$.[2] Hence it would seem that the anions $[Cr(CO)_5]^{\overline{\cdot}}$, $[Mo(CO)_5]^{\overline{\cdot}}$, and $[W(CO)_5]^{\overline{\cdot}}$ all have some stability in a range of aprotic solvents.

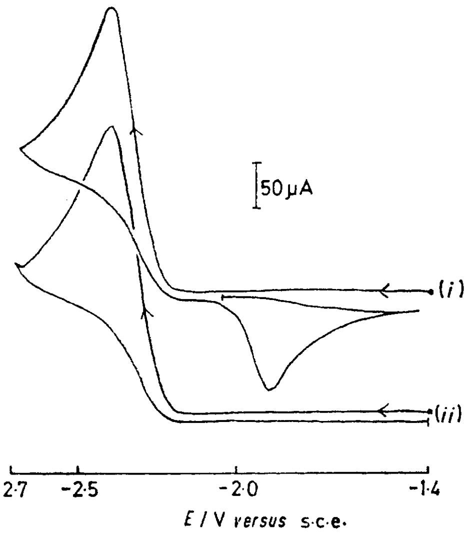

FIGURE 2 Cyclic voltammogram at a platinum electrode in MeCN + 0.2 mol dm^{-3} $[NBu_4][BF_4]$. Sweep rate 0.3 V s^{-1}. (*i*), 5 × 10^{-3} mol dm^{-3} $[Mo(CO)_6]$; (*ii*), 5 × 10^{-3} mol dm^{-3} $[Mo(CO)_6]$ + 2 × 10^{-2} mol dm^{-3} n-octyl bromide

Reduction of Group 6 *Metal Carbonyls in the Presence of Electrophiles*.—All the results described in this section involve the use of $[Mo(CO)_6]$ and thf as solvent. Cyclic-voltammetric experiments indicate, however, that the results would be similar if $[Cr(CO)_6]$ or $[W(CO)_6]$ were used or the solvent was MeCN.

Figure 2 shows a cyclic voltammogram for $[Mo(CO)_6]$ at a platinum electrode in the presence and absence of an excess of n-octyl bromide. It can be seen that the peak for the reduction of $[Mo(CO)_6]$ is unchanged, but that assigned above to the reoxidation of $[Mo(CO)_5]^{\overline{\cdot}}$ is removed by the addition of excess of n-octyl bromide. A similar pattern of behaviour was observed for a series of alkyl halides none of which themselves were reduced at the potential for the reduction of $[Mo(CO)_6]$: MeI; EtI; Pr^{n}Br; n-$C_5H_{11}I$; n-$C_5H_{11}Br$; n-$C_5H_{11}Cl$; n-$C_8H_{17}I$; n-$C_8H_{17}Br$; PhI; PhBr; and PhCl. By carrying out experiments with only low concentrations of alkyl halides

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[3] C. J. Pickett and D. Pletcher, *J.C.S. Chem. Comm.*, 1974, 660.

[4] G. R. Dobson, M. F. Amr E. Sayed, I. W. Stoltz, and R. K. Sheline, *Inorg. Chem.*, 1962, **1**, 526.

[5] W. L. Kaska, *J. Amer. Chem. Soc.*, 1968, **90**, 6340.

[6] P. A. Breeze and J. J. Turner, *J. Organometallic Chem.*, 1972, **44**, 67.

and observing the decrease in the height of the peak for the oxidation of $[Mo(CO)_5]^{\cdot-}$ it is possible to show that the rate at which the concentration of this species in solution decreases is (*a*) proportional to the concentration of RX and (*b*) decreases in the order RI > RBr > RCl.

A series of controlled-potential coulometric experiments were made with different alkyl halides present and with various ratios of $[Mo(CO)_6]/[RX]$. The current, the concentration of $[Mo(CO)_6]$ (monitored spectrophotometrically), and the concentration of RX (determined by g.l.c.) all decreased linearly with the charge passed during the electrolysis. Furthermore each of these sets of data could be extrapolated to show that the charge consumed during a complete electrolysis corresponded to 2*F* per mole of $[Mo(CO)_6]$ and 2*F* per mole of RX. A typical set of experimental results is shown in Figure 3 and the coulometric results are reported in the Table.

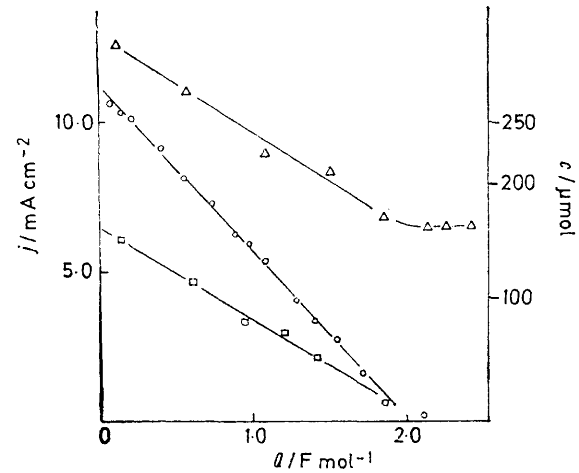

FIGURE 3 Controlled-potential electrolysis at platinum cathode of 5×10^{-3} mol dm^{-3} $[Mo(CO)_6]$ + 10^{-2} mol dm^{-3} octyl bromide in MeCN + $[NBu_4][BF_4]$. Plots of j and c against Q: (△), moles of octyl bromide; (□), moles of $[Mo(CO)_6]$; (○), current density

At the end of the electrolysis, the catholytes were analysed (*i*) by i.r. spectroscopy to determine the fate of the carbonyl entity. This showed that the major product was $[Mo(CO)_5X]^-$. For example when the alkyl halide was n-C_5H_{11}Br, peaks were observed at 1 915s and 1 875m cm^{-1}. A chemically prepared sample [7] of $[MoBr(CO)_5]^-$ gave peaks at 1 915s and 1 875m cm^{-1}. In some experiments a trace of $[Mo_2(CO)_{10}]^{2-}$ was also found. (*ii*) The organic products were determined by g.l.c.; these were generally RH with a trace of R–R. The current yields are reported in the Table. The overall reaction was, therefore, as in equation (5), where the source of proton is probably the $[NBu_4]^+$ cation. Further experiments showed that $[Mo_2(CO)_{10}]^{2-}$ did not react with alkyl halides and that $[Mo(CO)_5X]^-$ was electroinactive in thf.

					Current yields (%)	
RX	$\frac{[Mo(CO)_6]}{[RX]}$	n_1	n_2	n_3	RH	RR
n-C_3H_7Br	1.0	2.1	2.2	2.0	65	Trace
n-C_5H_{11}I	1.0	2.1	2.1	2.2	80	Trace
n-C_5H_{11}Br	1.0	2.0	2.0	2.1	70	4
	0.5	2.1	2.1	2.3	70	4
	0.1	2.1	2.0			
n-C_8H_{17}I	1.0	2.0	2.1	2.1	50	Trace
	0.1	2.1	2.0			

n_1, n_2 and n_3 are the n values estimated respectively from the extrapolation of plots of I against Q, $[Mo(CO)_6]$ against Q, and [RX] against Q.

$$[Mo(CO)_6] + RX + H^+ + 2e^- \longrightarrow RH + [Mo(CO)_5X]^- + CO \quad (5)$$

It is clear from the results presented above that the reduction of $[Mo(CO)_6]$ in the presence of RX is a one-electron process on the relatively short time scale of cyclic voltammetry, but is a two-electron process on the longer time scale of a preparative electrolysis. The species $[Mo(CO)_5]^{\cdot-}$ or a precurser to it is also clearly reacting completely on the time scale of cyclic voltammetry. This would suggest that the initial electron and following chemical reaction between RX and a molybdenum carbonyl anion is separated from the second electron transfer by a further slow chemical step. A possible mechanism would be as in equations (6)—(9). In reactions (7) and (8), the behaviour of $[Mo(CO)_5]^{\cdot-}$ is analogous to another 17-electron anion $[Co(CN)_5]^{3-}$ whose reactions have recently been reviewed.[8] The species $[MoR(CO)_5]^-$ has not previously been identified as a stable species but a half-life of 10 s would suffice for the proposed mechanism. It would also be possible to write mechanisms involving reaction between $[Mo(CO)_6]^{\cdot-}$ and RX but these have been ruled out since they would require the formation of a 20-electron seven-co-ordinate carbonyl.

$$[Mo(CO)_6] + e^- \longrightarrow [Mo(CO)_6]^{\cdot-} \xrightarrow[\text{fast}]{-CO} [Mo(CO)_5]^{\cdot-} \quad (6)$$

$$[Mo(CO)_5]^{\cdot-} + RX \xrightarrow{\text{fast}} [Mo(CO)_5X]^- + R^{\cdot} \quad (7)$$

$$R^{\cdot} + [Mo(CO)_5]^{\cdot-} \xrightarrow{\text{fast}} [MoR(CO)_5]^- \quad (8)$$

$$[MoR(CO)_5]^- + H^+ + e^- \xrightarrow{\text{slow}} [Mo(CO)_5]^{\cdot-} + RH \quad (9)$$

The behaviour of $[Mo(CO)_6]$ in the presence of CO_2 is somewhat different; Figure 4 shows cyclic voltammograms in the presence and absence of CO_2 for a solution containing CO_2 alone. It can be seen that the peak for the reduction of $[Mo(CO)_6]$ increases considerably in magnitude when CO_2 is present in solution. Indeed it may be shown that the peak current for this process is proportional to the concentration of CO_2 and that the total increase in the peak current may be by a factor of ten or more. The reverse peak for the oxidation of $[Mo(CO)_5]^{\cdot-}$ is again absent. Such cyclic voltammetry is characteristic of a catalytic mechanism where $[Mo(CO)_6]$ is regenerated by reaction of molybdenum anions with CO_2.

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[7] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 1964, 434; 1963, 2068.

[8] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

Such an interpretation is supported by coulometric experiments. Figure 5 shows a plot of current against charge passed during the electrolysis and it may be seen that (*i*) the current is independent of charge until late in the electrolysis, and (*ii*) while the charge for a complete electrolysis was dependent on the exact solution conditions, *n* values of 5—20 per molecule of $[Mo(CO)_6]$ were common. Towards the end of the electrolysis the concentration of $[Mo(CO)_6]$, determined by cyclic voltammetry, decreased rapidly and it may be that a product of the electrolysis can act as a ligand and compete with CO for co-ordination to the molybdenum. At the end of these electrolyses, the catholytes were treated with methyl iodide or n-butyl bromide and the resulting solution was examined by g.l.c. and g.l.c.–mass spectroscopy. The major products were esters of oxalic acid, current yields 50—70%. The simplest mechanism for this reaction would be as in equations (10)—(12),

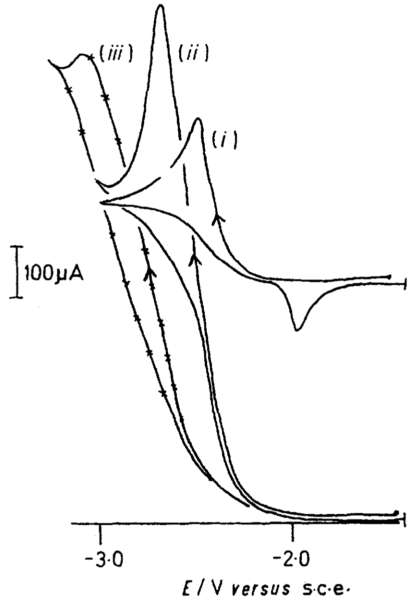


FIGURE 4 Cyclic voltammograms at a platinum electrode in MeCN +0.2 mol dm^{-3} $[NBu_4][BF_4]$. Sweep rate 0.3 V s^{-1}. (*i*), $[Mo(CO)_6]$ alone; (*ii*), $[Mo(CO)_6]$ + CO_2; (*iii*), CO_2 alone

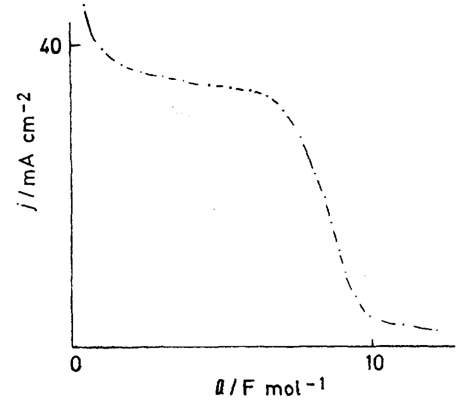
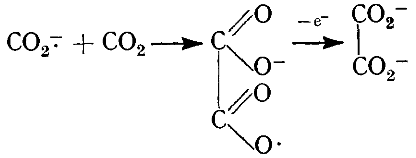


FIGURE 5 Controlled-potential electrolysis at a platinum cathode of a solution of 5 × 10^{-3} mol dm^{-3} $[Mo(CO)_6]$ in the presence of excess of CO_2

$$[Mo(CO)_6] + e^- \longrightarrow [Mo(CO)_6]^{\cdot-} \qquad (10)$$

$$[Mo(CO)_6]^{\cdot-} + CO_2 \longrightarrow [Mo(CO)_6] + CO_2^{\cdot-} \qquad (11)$$



$$CO_2^{\cdot-} + CO_2 \longrightarrow \begin{matrix} C(=O)O^- \\ | \\ C(=O)O^{\cdot} \end{matrix} \xrightarrow{-e^-} \begin{matrix} CO_2^- \\ | \\ CO_2^- \end{matrix} \qquad (12)$$

although mechanisms involving formation of a Mo–(CO_2) bond cannot be ruled out. The formation of oxalate *via* $CO_2^{\cdot-}$, reaction (12), has been shown to occur by attack of the radical anion on the neutral molecule.[9]

The reduction of $[Mo(CO)_6]$ in the presence of both CO_2 and an alkyl halide, n-C_4H_9Br, was also investigated. The cyclic voltammetry and coulometry paralleled that in the presence of CO_2 alone and hence was substantially different from that in the presence of n-C_4H_9Br alone. The major product of these electrolyses were, however, di-n-butyl carbonate, current yield 40—60%, and no RCO_2R was identified. The behaviour can be rationalised by a mechanism involving reactions (10) and (11) followed by (13)—(15). The isolation of the carbonate rather than the oxalate requires reaction (13) to be fast compared to (12).

$$CO_2^{\cdot-} + C_4H_9Br \longrightarrow \dot{C}O_2C_4H_9 + Br^- \qquad (13)$$

$$\dot{C}O_2C_4H_9 + e^- \longrightarrow {}^-CO_2C_4H_9 \longrightarrow CO + OC_4H_9^- \qquad (14)$$

$$CO_2 + OC_4H_9^- \longrightarrow C_4H_9\text{-}O\text{-}CO_2^- \xrightarrow{C_4H_9Br} C_4H_9\text{-}O\text{-}CO_2C_4H_9 \qquad (15)$$

We thank the Monsanto Company for support.

[5/1705 *Received, 4th September*, 1975]

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[9] A. W. B. Aylmer Kelly, A. Bewick, P. R. Cantrill, and A. M. Tuxford, *Faraday Discuss. Chem. Soc.*, 1973, **56**, 96.