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Ion Radicals of Organometallic Compounds. I. The Products and the Mechanism of the Decomposition of Methylbenzene Tricarbonylchromium Cation Radicals

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The electrochemically derived cation radicals of methylbenzene tricarbonylchromium complexes decompose by mechanisms of the ECE_h type to generate the methylbenzenes and carbon monoxide. First order rate constants ranging from 2500 to 0.046 s^{-1} at 298 K with corresponding activation energies of 7.8 to 17.6 kcal/mol were observed for complexes prepared from compounds with varying numbers of methyl groups ranging from benzene to hexamethylbenzene. The corresponding activation entropies ranged from -19 to -5 cal/K mol. The reversible oxidation potentials of the complexes were observed to be dependent upon the number of methyl groups but to a much lesser extent than the parent methylbenzenes. The potentials ranged from 493 to 281 mV *vs.* Ag/Ag^+ in the same order as above. All of the cation radicals are further oxidized to the dications irreversibly at about 1280 mV independent of structure.

There has been interest in the electrochemistry of organometallic compounds for a number of years.[1,2] Recently, modern techniques have been applied to study some of the redox processes in more detail.[3] The importance of the nature of the ligands on both the ease of formation and decomposition of cation radicals of some transition metal carbonyl complexes has been demonstrated.[4]

In general, organometallic compounds are readily oxidized and reduced electrochemically. Some of them, like ferrocene, are converted into stable ion radicals while others form ion radicals of limited stability which decompose to final products. The knowledge of the properties of these species is limited and it would be desirable to have a better understanding of their behaviour in solution. For example, what are the factors that govern the stability of the ion radicals? Are the reactivities related to the thermodynamic stability, *i.e.* the reversible potentials for formation either by oxidation or reduction? By what mechanisms do the ion radicals decompose? Are the kinetics of decomposition amenable to study by voltammetric techniques? What are the magnitudes of the rate constants, activation parameters, and reaction orders for the decomposition reactions? In order to obtain answers to some of these questions we have undertaken a systematic investigation of the formation and reactions of ion radicals of organometallic compounds. In this, the first stage of the investigation, we describe results obtained during the oxidation of tricarbonylchromium complexes of benzene and methyl substituted benzenes.

Some tricarbonylchromium complexes of arenes have been observed to be oxidized reversibly.[5,6] On the other hand, many of the corresponding cation radicals have been found to be highly unstable and form products which disturb electrochemical measurements by electrode filming.[5] It has recently been shown that tin

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complexes of arenetricarbonylchromium compounds can be oxidized to very stable cation radicals.[7]

Up until now, the stability of cation radicals of tricarbonylchromium complexes has only been estimated qualitatively. Thus, the mechanisms of decomposition and the related kinetic parameters have not been evaluated. The cation radicals of a number of *p*-substituted phenyltricarbonylchromium complexes have recently been reported to decompose so rapidly that it was not possible to detect the intermediates by cyclic voltammetry.[8] Our preliminary results indicated that the lifetimes of the cation radicals of a number of methylarenes complexes are sufficiently long in acetonitrile to permit the study of the formations and the decompositions by derivative cyclic voltammetry (DCV).[9]

We applied the DCV method to measure kinetic parameters for the decomposition reactions of the cation radicals of benzene and methylbenzene tricarbonylchromium complexes. In this paper we first report the general aspects of the electro-oxidation of these complexes and then the DCV measurement results. The complexes which were studied are listed below with the number in parentheses indicating the number of methyl groups which will be used later for identification. The compounds studied were tricarbonylchromium complexes of benzene (*0*), toluene (*1*), 1,4-dimethylbenzene (*2*), 1,3,5-trimethylbenzene (*3*), 1,2,4,5-tetramethylbenzene (*4*), pentamethylbenzene (*5*) and hexamethylbenzene (*6*).

EXPERIMENTAL

The solvent, acetonitrile, containing the supporting electrolyte (Bu_4NBF_4, 0.1 M) was passed through a column of activated alumina before use. The concentration of complex used was generally 2.0 mM for DCV and linear sweep voltammetry (LSV) and 10–20 mM for product studies. Highly purified nitrogen was bubbled through the solution before use.

All measurements were made at stationary platinum electrodes and the potentials refer to Ag/Ag^+ (0.01 M in acetonitrile). The DCV peak current ratios and zero current crossing potentials were the average of 5 scans which were processed after an initial scan before which the working electrode was pulsed to +3 V. The pulse was necessary to clean the surface and without it the data were not reproducible. The switching potential during DCV was set at the reversible potential +(300±2) mV. Other details of the instrumentation, cells, electrodes and data handling procedures were similar to those reported earlier.[9,10]

The temperature was controlled to ±0.1 °C from −20 to 40 °C during DCV analysis. Activation parameters were obtained by Arrhenius correlations of rate constants evaluated at 7–8 temperatures for *2, 3* and *4* and 4–6 temperatures for *0, 1* and *6*. Errors were estimated by the theory of least squares using standard procedures. Preparative electrolyses were carried out at ambient temperature and LSV analyses were made at 25.0(±0.2) °C.

The gas chromatographic conditions[11] were as follows: column, 10 % SE-30, carrier gas, N_2, temperature control, 80 °C for 8 min, programmed from 80 to 200 °C at 8 °C/min. Electrolysis solutions were injected without any treatment.

During the measurement of the volume of gas evolved, the solution was pre-saturated with carbon monoxide.

For mass spectroscopic detection, the evolved gas was removed using helium as a carrier.

The complexes were prepared from the parent molecules and hexacarbonylchromium by refluxing in 1,2-dimethoxyethane or with the parent molecule as solvent under an atmosphere of nitrogen.[12] The complexes were recrystallized twice from diisopropyl ether.

RESULTS

Assignment of LSV peaks. Typical LSV curves, measured for (*4*), at several scan rates ranging from 0.1 to 100 V/s are shown in Fig. 1. There are four main waves (I–IV) and several peaks following IV. Although the relative shapes of the LSV curves were similar for all complexes, the effect of changing the scan rate (v) varied. In each case v was varied over a factor of 10^3.

At high scan rates the first oxidation wave (I) was reversible and wave III was observed, while at low v wave I was irreversible and waves II and IV were observed. The fewer methyl substituents in the complexes, the higher v was required to be in order to observe reversibility. The disappearance of peak III accompanied by the appearance of peaks II and IV is a convenient measure of the reversibility. Waves II–IV were irreversible at all scan rates.

The peak current at I, normalized by dividing by $v^{1/2}$, increased in the low scan rate region to

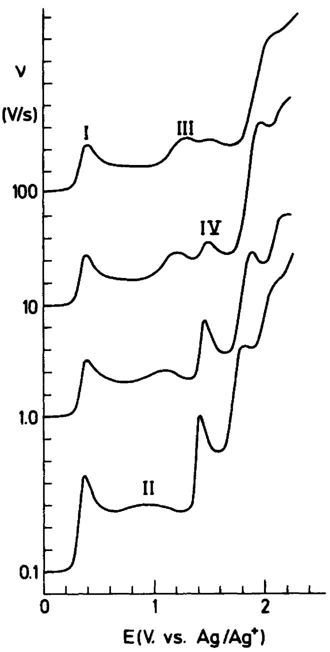

Fig. 1. Linear sweep voltammograms for the oxidation of 1,2,4,5-tetramethylbenzene tricarbonylchromium (2.0 mM) in acetonitrile containing Bu_4NBF_4 (0.1 M) at 25 °C.

about twice the diffusion current in the high *v* region during oxidation of (*2*)–(*5*). The latter indicates that I involves the transfer of 2 e^- under conditions where the wave is irreversible.[13] For complexes *0* and *1*, the scan rate necessary to observe the diffusion current was too high. Conversely, for (*6*), the current didn't reach twice the diffusion current even at the lowest sweep rate practical to make the measurement. The diffusion current was 11.2(±0.3) μA/ $(V/s)^{1/2}$ for *3*–*6* at a concentration of 2.0 mM. Under the same conditions, that for ferrocene was 13.4 μA (1 V/s) which is a reversible one-electron oxidation wave. From the above results we conclude that oxidation wave I involves two one-electron transfers with a chemical reaction occurring before the second electron transfer, *i.e.* the ECE_h mechanism (the subscript h indicates that the second electron transfer takes place in homogeneous solution rather than at the electrode).

The oxidation waves (II) were broad with peak currents and peak potentials nearly the same for all of the complexes. The broad peak (II) was observed to shift from about 910 mV at 0.1 V/s to about 1250 mV at 100 V/s. This wave is most likely due to the oxidation of a substance which is produced at the ECE_h wave (I), since it is not observed under conditions where wave I was reversible.

The peak current for wave III increased with increasing reversibility of I. This indicates that III is due to the oxidation of the primary intermediate at I, *i.e.* the cation radical. The peak potential separation between waves I and III, 800–940 mV at 100 V/s, is also in accord with what would be expected if peak III involves the oxidation of the cation radical to the dication of the complex.

The peak potentials for III measured at 100 V/s were very nearly the same, 1279(±16) mV, for complexes *2, 6*. The cation radicals of *0* and *1* were so reactive that it was not possible to measure potentials for wave III. In any event, waves III were irreversible and the peak potentials were observed to shift about 80 mV per decade change in *v*.

On the other hand, the peak potentials of wave IV were observed to be dependent upon the structure of the complexes and were within −70 to 40 mV of the oxidation peaks for the corresponding parent compounds under the same experimental conditions. The current at this peak increased as the reversibility of wave I decreased as would be expected if peak IV is due to a product of the ECE_h reaction at I. We conclude that wave IV is due to the oxidation of the parent molecule produced during the decomposition of the cation radical of the complex. Several peaks following IV can also be assigned to oxidation products of the parent molecules.

Reversible oxidation potentials of wave I. Measurements were carried out at −10 °C in order to reach reversibility at optimum scan rates. The reversible potentials were obtained by measurement of the zero crossing points on the DCV curve.[14] Results for measurements on all of the complexes are shown in column 2 of Table 1. The difference in reversible potential for the oxidation of *6* measured at −10 and 25 °C was 0 ± 1 mV. Under the same experimental conditions a difference of −18.6 mV was observed for the oxidation of ferrocene. No attempt was made to control the reference electrode temperature.

The oxidation potentials measured in this work differed from those in the literature[5] by 251(±24) mV. The previous values were obtained by polarographic measurements in CH_2Cl_2 and were with a different reference electrode (S.C.E.).[5] There is an approximate linear relationship between the reversible oxidation potentials of the complexes and the irreversible peak potentials for the oxidation of the parent molecules. The slope of the linear regression line was observed to be 0.20 with a correlation coefficient of 0.991. The peak potentials for the oxidation of the parent molecules were measured at 0.1 V/s.

Kinetic parameters for the decomposition of the cation radicals. The cation radicals decompose by an ECE_h mechanism at wave I. The first order rate constants (k) for these reactions were measured by DCV at temperatures ranging typically from −10 to 25 °C and were evaluated according to eqn. (1) derived from theoretical

$$k=1284(\nu_{1/2}/T) \qquad (1)$$

data.[15] In (1) $\nu_{1/2}$ refers to the sweep rate necessary for the derivative peak ratio to equal 0.500. Activation energies (E_a) were determined directly from $\nu_{1/2}$ eqn. (2)[16] and activation entropies (ΔS^+) were evaluated using eqn. (3).[17] The results are listed in Table 1.

$$\log(\nu_{1/2}/T)=-E_a/(4.576\,T)+\text{constant} \qquad (2)$$

$$\Delta S^+=4.576\log(k/T)+E_a/T-49.21 \qquad (3)$$

The reaction orders in cation radical were determined from the dependence of $\nu_{1/2}$ on substrate concentration. For a first order reaction in the primary intermediate $\nu_{1/2}$ is expected to be a constant independent of concentration.[18] With concentrations ranging from 0.5 to 2.0 mM the reaction orders were observed to range from 0.8–1.0 indicating some deviation from theory.

Double potential step chronoamperometry (DPSC) was also applied for the measurement of the kinetic parameters for the reactions of (*2*). The DPSC measurements gave; $E_a=10.3(\pm0.1)$ kcal/mol, $\Delta S^+=-15.2(\pm0.4)$ cal/K mol, and $k_{298}=240(\pm4)\ s^{-1}$. The values of the parameters obtained by DCV and DPSC agreed within experimental error with the exception that k_{298}, evaluated from the Arrhenius plots, differed by slightly more than expected. The value of $\tau_{1/2}$, the pulse width which corresponds to $\nu_{1/2}$ was only 1.14 ms at 298 K and this is near the limit for DPSC under the conditions of the measurements. The good agreement between the DCV and DPSC results indicates that the results in Table 1 are reliable.

Products of decomposition of the cation radicals. It has already been indicated that the parent molecules were identified as the principal products of the decomposition by the LSV analyses. This was also confirmed by gas chromatographic analysis of the solution in which complex *2* was oxidized at 400 mV, which corresponds to peak I. Coulometric results using gas chromatography to analyze for the formation of the parent substance indicate that 1.2–1.9 Faradays were consumed for the formation of 1 mol of product. Only peaks due to the complex *2*, 1,4-dimethylbenzene, and acetonitrile were observed. A peak due to hexacarbonylchromium, which was used in the

Table 1. Oxidation potentials for tricarbonylchromium complexes and kinetic parameters for the decomposition of the cation radicals.[2]

Complex[b]	E_{rev}[c]	k_{298}[d]/s^{-1}	E_a/kcal mol^{-1}	$-\Delta S^+$/cal $K^{-1}mol^{-1}$
(*0*)	493	2500(400)	7.8(0.5)	19(3)
(*1*)	441	1280(140)	8.7(0.6)	17(3)
(*2*)	403	212(4)	10.2(0.2)	15.8(0.6)
(*3*)	402	17.2(1.1)	14.1(0.5)	7.6(1.7)
(*4*)	342	6.5(0.3)	14.4(0.6)	9.6(2.0)
(*5*)	317	0.46(0.04)	16.0(1.5)	5(5)
(*6*)	281	0.046(0.019)	17.6(6.3)	5(20)

[a] In acetonitrile containing Bu_4NBF_4 (0.1 M). [b] See text for the structures. [c] The reversible peak potential *vs.* Ag/Ag^+ of wave I. [d] All errors are 95 % confidence calculated according to the theory of least squares as described in Ref. 16. The rate constants were calculated from the Arrhenius correlations.

preparation of the complex, was not observed.

Gas evolution from the anode was observed during the electrolysis of *2* at 400 mV. The gas was confirmed to be carbon monoxide by mass spectroscopy. The coulometric *n* value based on the analysis assuming the formation of 3 CO/mol was 2.6 Faradays/mol, which was associated with a high degree of error due to the small quantity of gas evolved.

Tests for the influence of other substances on the decomposition reactions. the reactions of ion radicals are often influenced by the presence of other reactants in solution, often as impurities in the solvent–electrolyte. In order to test for the influence of other reactants, kinetic experiments were carried out in the presence of water, parent substance, and carbon monoxide.

Only minor changes in rate constant for the decomposition of the cation radical of *5* were observed on changing the water concentration from nearly zero, in the presence of neutral alumina, to 200 mM. Over this range of water concentration *k* decreased by about 10 %.

In order to test for reversibility of the overall decomposition reaction, measurements were made in the presence of 1,4-dimethylbenzene and carbon monoxide during the oxidation of *2*. No change was observed in *k* with 1,4-dimethylbenzene concentrations up to about 50 mM. At higher concentrations the DCV data were not reproducible. No effect on the kinetics were observed either at −10 or 25 °C when the kinetics were carried out on solutions saturated with carbon monoxide. The experiment at −10 °C was carried out since the concentration of carbon monoxide should be higher at lower temperatures. Likewise, 1,4-dimethylbenzene (50 mM) had no effect in the CO saturated solutions.

From these experiments we conclude that the decompositions are not effected by water, present in concentrations up to 200 mM, and that the decomposition is irreversible.

DISCUSSION

Under conditions where wave I is reversible, either at high sweep rates or with the highly substituted complexes at lower sweep rates as well, the reactions can be described by eqns. (4)–(6) (Scheme 1) where M is the parent molecule.

$$\mathrm{MCr(CO)_3} - e^- \rightleftharpoons \mathrm{MCr(CO)_3^{+}} \quad \text{wave I} \qquad (4)$$

$$\mathrm{MCr(CO)_3^{+}} - e^- \rightleftharpoons \mathrm{MCr(CO)_3^{2+}} \quad \text{wave III} \qquad (5)$$

$$\mathrm{MCr(CO)_3^{2+}} \longrightarrow \text{products} \qquad (6)$$

Scheme 1.

The products of reaction (6) are not known but the parent molecule could not be detected during LSV under conditions where the cation radicals are stable. It is possible that the decomposition of the dication gives an oxidation product of the parent molecule. Further work on the reactions of the dications are necessary.

At low sweep rates, under conditions where wave I is irreversible, the cation radicals decompose into carbon monoxide, the parent molecule and unidentified chromium compounds. The kinetic studies are indicative of an $\mathrm{ECE_h}$ mechanism and the product studies along with the LSV results indicate that the cation radicals completely decompose to parent molecule at wave I. The latter is evident from the voltammogram measured at 0.1 V/s (Fig. 1) where the peak heights of waves I and IV, both involving the transfer of $2e^-$, are very nearly identical. The peak height of wave IV was about 80 % of that observed for the parent substance at the same concentration as the complex. On the other hand, the gas evolution studies indicate that less than 3 CO per cation radical are evolved at wave I. This suggests that the chromium containing species after decomposition of the cation radical still contails CO. The $\mathrm{ECE_h}$ reaction scheme (Scheme 2) accounts for all of the results.

$$\mathrm{MCr(CO)_3} - e^- \rightleftharpoons \mathrm{MCr(CO)_3^{+}} \qquad \mathrm{E} \qquad (7)$$

$$\mathrm{MCr(CO)_3^{+}} \longrightarrow \mathrm{M} + \mathrm{Cr(CO)_n^{+}} + (3\text{-}n)\mathrm{CO} \qquad \mathrm{C} \qquad (8)$$

$$\mathrm{Cr(CO)_n^{+}} + \mathrm{MCr(CO)_3^{+}} \rightleftharpoons \mathrm{Cr(CO)_m^{2+}} + \mathrm{MCr(CO)_3} + (n\text{-}m)\mathrm{CO} \qquad \mathrm{E_h} \qquad (9)$$

Scheme 2. $\mathrm{ECE_h}$ reaction scheme.

There is no evidence for the nature of the chromium containing cations written as $Cr(CO)_n^+$ and $Cr(CO)_m^{2+}$ but it is likely that they exist, probably with BF_4^- and CH_3CN as ligands. The irreversible LSV wave II is most likely due to oxidation of the chromium containing product.

The cation radicals of some arenetricarbonylchromium complexes have been generated by treatment with strong acids. The tricarbonyl chromium complex of benzyl alcohol is converted to the cation of benzyl tricarbonylchromium, by sulfuric or perchloric acid and decomposes with the release of carbon monoxide.[19,20] The electronic structure of this cation differs substantially from the cation radicals that we have studied. The positive charge is localized on the odd alternant hydrocarbon (benzyl) ligand while the cation radicals that we have been concerned with have the charge distributed mainly on the chromium atom. Since the benzyl cation complex also releases CO it is likely that a similar decomposition mechanism is involved in this case as well.

It is interesting to note that the reversible oxidation potentials of the complexes shift about 40 mV to less positive potentials for each additional methyl group. This potential shift is only about 20 % that observed for the LSV peak potentials of the parent hydrocarbons. This would seem to indicate that the highest occupied molecular orbital from which the electron is lost during oxidation is mainly associated with the chromium atom even though the orbital arises from an interaction between a chromium atom orbital with a ligand orbital. Since the reversible potentials for the oxidation of the complexes correlate well with the peak potentials for the oxidation of the parent hydrocarbons, it is most likely that the substituent effect is due to electron donation by the methyl groups. The attenuated effect then is due to the fact that the inductive donation of electrons must be transmitted to the chromium atoms.

Lloyd and co-workers[5] observed that the potential for the oxidation of the cation radicals depends more strongly on the number of methyl substituents than does the potential for the oxidation of the substrates. They report oxidation potentials ranging from 1300 to 1110 mV vs. S.C.E. for wave III. However, we cannot substantiate these observations. We find that the potential of wave III is very nearly the same for all of the complexes. Since there are three peaks (II, III and IV) after the first oxidation peak (I), one or more of these waves may have merged due to electrode filming during the longer measurement times involved in rotating disc electrode studies.[5] This then could have resulted in confusion as to the location of the wave for the oxidation of the cation radicals.

Since there is considerable error associated with the activation entropies, we do not attempt to give a detailed treatment of the effect of structure on ΔS^+. On the other hand, there are definite trends in the activation parameters. The magnitude of E_a increases with increasing substitution while ΔS^+ becomes increasingly less negative. It is most likely that the origin of the entropy effects lies in solvation differences in the reactants and transition states.

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