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Ion Radicals of Organometallic Compounds. III. Positional Effects on the Thermodynamics of Formation and the Kinetics of Decomposition of (Methyl-substituted Benzene)-tricarbonylchromium Cation Radicals

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Reversible oxidation potentials, rate constants, and activation parameters are reported for the formation and decomposition reactions of all isomers of (methyl-substituted benzene)tricarbonylchromium cation radicals. The reversible potentials were observed to depend both on the number and the positions of the methyl substituents. It was found that the effects on the reversible potentials of adding single methyl substituents to similar structures were additive. The activation energies and entropies for the decomposition reactions were found to be grouped into four different categories depending upon the numbers of adjacent unsubstituted positions on the methylarene ligands. Within each group the deviations from the averages were less than experimental error. The differences in activation parameters are explained in terms of how effective bonding is between the chromium atom and the arene ligands in the cation radicals.

In previous papers of this series we have examined the thermodynamics and kinetics of the formation and decomposition reactions of (arene)tricarbonylchromium cation radicals in acetonitrile.[1,2] The arene moieties were either methylbenzene[1] or benzenes substituted with heteroatom-containing substituents.[2] The (methyl-substituted benzene)tricarbonylchromium complexes show four main oxidation peaks during linear sweep voltammetry measurements at stationary platinum electrodes.[1] The cation radicals of the complexes are generated at the first reversible oxidation wave (wave I) and decompose by a first order chemical reaction (Eq. 1) followed by electron transfer reaction (Eq. 2),

$$\mathrm{MCr(CO)_3{}^+} \xrightarrow{k} \mathrm{M} + \mathrm{Cr(CO)}_n^+ + (3-n)\mathrm{CO} \qquad (1)$$

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

i.e. an $\mathrm{ECE_h}$ mechanism. Both the activation parameters and the oxidation potentials were observed to be related to the number of methyl substituents. The more highly substituted complexes show the higher activation energies for the decomposition reactions of the cation radicals, *i.e.* form the kinetically more stable cations. For the same cation radicals the more highly substituted ones are formed at the lower potentials, *i.e.* are the more thermodynamically stable. However, a number of discrepancies were observed for the parameters obtained for the 7 complexes studied, $(\mathrm{CH_3})_n\mathrm{C_6H_{6-n}Cr(CO)_3}$ with $n=0$ to 6, with one isomer for each value of n. For example, the difference in oxidation potentials of $1,4\text{-}(\mathrm{CH_3})_2\mathrm{C_6H_4Cr(CO)_3}$ and $1,3,5\text{-}(\mathrm{CH_3})_3\mathrm{C_6H_3Cr(CO)_3}$ was only 1 mV while the difference in activation energies for the decompositions of the corresponding cation radicals was 3.9 kcal mol^{-1}.[††] On the other hand the difference in activation energies for the decomposition reactions of the cation radicals of $1,3,5\text{-}(\mathrm{CH_3})_3\mathrm{C_6H_3Cr(CO)_3}$ and $1,2,4,5\text{-}(\mathrm{CH_3})_4\mathrm{C_6H_2Cr(CO)_3}$ was observed to be only 0.3 kcal mol^{-1}. This suggests that the effects of methyl substitution on the ease of the formation and the ease of the decomposition of the cation radicals differ.

In order to obtain more insight on the effects of methyl substitution on the formations and the decompositions, oxidation potentials and kinetic parameters were obtained for all of the remaining isomers of (methyl-substituted benzene)tricarbonylchromium complexes.

Experimental

All measurements were carried out in acetonitrile with 0.1 mol dm^{-3} n-$\mathrm{Bu_4NBF_4}$ and Ag/Ag$^+$ (0.01 mol dm^{-3} $\mathrm{AgNO_3}$ in acetonitrile with 0.1 mol dm^{-3} n-$\mathrm{Bu_4NBF_4}$) as reference electrode. The concentration of the substrate was 2.0 mmol dm^{-3}. The measurements of reversible oxidation potentials were performed at −10 °C in order to attain reversibility over a wide range of sweep rates. The kinetic measurements of rate constants were performed by derivative cyclic voltammetry (DCV) in the typical temperature range of −10 °C to 25 °C with an interval of 5 °C. Activation energies (E_a) and activation entropies ($\Delta S^{\neq}$) were obtained by Arrhenius correlations of rate constants. The details of the measurement procedure were reported in previous papers.[1,3,4]

In this paper the complexes are identified according to the number of the methyl substituents as follows:

(0)=$\mathrm{C_6H_6Cr(CO)_3}$,
(1)=$\mathrm{CH_3C_6H_5Cr(CO)_3}$,
(1,2), (1,3,), (1,4)=dimethyl-substituted complexes,
(1,2,3), (1,2,4), (1,3,5)=trimethyl-substituted complexes,
(1,2,3,4), (1,2,3,5), (1,2,4,5)—tetramethyl-substituted complexes,
(5)=$(\mathrm{CH_3})_5\mathrm{C_6HCr(CO)_3}$,
(6)=$(\mathrm{CH_3})_6\mathrm{C_6Cr(CO)_3}$.

Results

Reversible oxidation potentials of the complexes and kinetic parameters for the decomposition reactions of their cation radicals are shown in Table. 1. The reversibility was confirmed from the result that the potential differences of the oxidation and reduction peaks of cyclic voltammograms were close to *ca.*

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[††] 1 cal=4.184 J.

TABLE 1. REVERSIBLE OXIDATION POTENTIALS OF (METHYL SUBSTITUTED BENZENE)TRICARBONYLCHROMIUM COMPLEXES AND KINETIC PARAMETERS OF THE DECOMPOSITION REACTION OF THE COMPLEXES[a)]

Complex[b)]	E_{rev}[c)]/mV	k[d)]/s^{-1}	E_a[e)]/kcal mol^{-1}	$-\Delta S^{\neq}$[f)]/cal K^{-1} mol^{-1}
(1,2)	409	892(20)[g)]	8.6(0.2)[g)]	18.3(0.6)[g)]
(1,3)	417	569(6)	8.8(0.1)	18.5(0.3)
(1,2,3)	375	567(7)	8.9(0.1)	18.2(0.3)
(1,2,4)	374	117(3)	10.3(0.2)	16.6(0.4)
(1,2,3,4)	337	106(6)	10.4(0.4)	16.3(1.4)
(1,2,3,5)	358	7.8(0.4)	14.7(0.6)	7.2(1.6)

a) In acetonitrile containing n-Bu$_4$NBF$_4$ (0.1 mol/dm^3). b) See text for the structures. c) The reversible oxidation potential at -10 °C *vs.* Ag/Ag$^+$ of wave I. d) The rate constant at 25 °C calculated from the Arrhenius plots. e) The activation energy. f) The activation entropy. g) All errors are 95% confidence calculated according to the theory of least squares as described in Ref. 12.

60 mV at high scan rates where the two peaks were observed to have the same height. In this case these two peaks did not shift according to the chemical reaction (Eq. 1) of the ECE$_h$ mechanism.

Discussion

Reversible Oxidation Potentials of the Complexes. The reversible electrode potentials for the oxidation of all of the complexes in acetonitrile are plotted *vs.* the number of methyl substituents in Fig. 1. Linear regression anaiysis gives a slope of −33.6 mV/methyl group with a correlation coefficient of 0.985. There are differences in oxidation potentials within each group of isomers, *i.e.* those with 2, 3, and 4 methyl substituents. These differences affect the overall correlation. The points represented as black circles in Fig. 1 show the effect of additional methyl groups on two basic structural units, corresponding to 1,3-dimethyl- and 1,3,5-trimethylbenzene complexes. The linear regression line for the first case has a slope of −40.0 mV/(additional methyl group) and a correlation coefficient of 0.999. In these cases the effect of additional methyl groups on the reversible oxidation potentials is additive. This suggests that the scatter observed in Fig. 1 is due to the fact that the magnitude of the effect of a methyl substituent is dependent upon the total structure and that the reversible oxidation potentials cannot be considered independent of the substitution existing before the addition of the group.

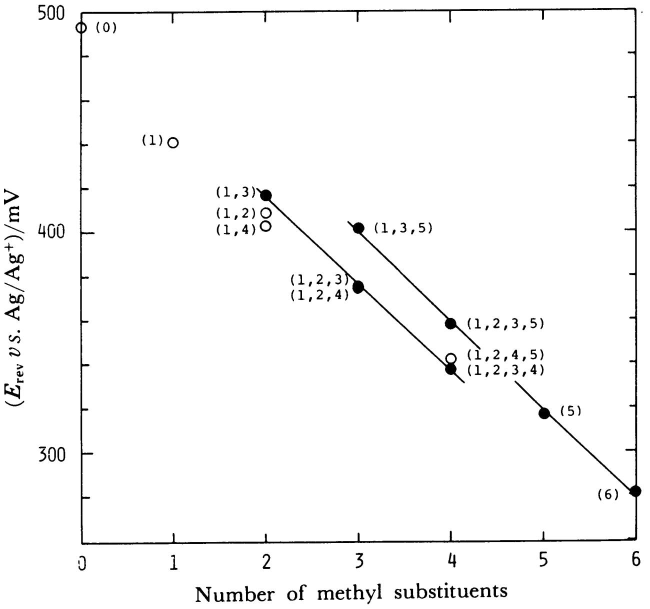
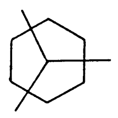


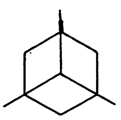
Fig. 1. Relation between reversible oxidation potentials and the structures of the complexes. See text for the structures.
(●) E_{rev} on lines.

Another interesting aspect of the correlations in Fig. 1 is that the line for 1,3-substituted complexes lies only 16 mV below the other line on the potential scale. This means that an additional meta methyl substituent has much smaller effect on the reversible oxidation potentials than the addition of substituents ortho to those in the basic structural unit.

Some of the effects of methyl substitution on the reversible oxidation potentials could be due to steric interactions between the methyl groups and the carbonyl groups. In complexes (0)[5–7)] and (6)[8)] the steric configuration of H and CH$_3$ of the arene in relation to CO is the staggered structure **1**, and in complex (1)[9)] it is the eclipsed form **2** due to electron donation from CH$_3$.[10)] It is possible that ortho substitution makes the staggered form energetically more favorable and meta substituents favor the eclipsed form. This effect could cause the difference in the potentials. With regard to conformation, it should be noted that the configuration around the chromium atom in the neutral complexes is tetrahedral, but there is a possibility that the change in oxidation state of chromium in going to the cation radical is accompanied by a change in configuration. Unfortunately the detailed structures of the cation radicals are not known, the rotational barriers in arene–Cr(CO)$_3$ are small,[10)] and thus further discussion of steric effects would be highly speculative.

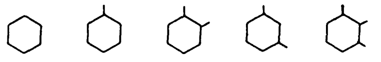
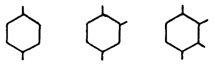
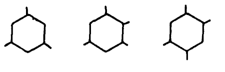
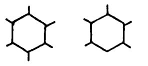


Staggered
1



Eclipsed
2

Table 2. Groups divided according to the activation energy and the structure of tricarbonylchromium complexes

Group	Designation	Structures of benzenes in complexes	E_a/kcal mol^{-1}	$-\Delta S^{\neq}$/cal K^{-1} mol^{-1}
1	3		8.6 (0.3)	18.2 (0.7)
2	2		10.3 (0.1)	16.2 (0.4)
3	1		14.4 (0.3)	8.1 (1.3)
4	0		17.0 (1.4)	5

Activation Parameters for the Decomposition Reactions of the Cation Radicals. The complexes can be divided into four groups according to the magnitudes of the activation parameters as shown in Table 2 and Fig. 2. These division also correspond to the substitution pattern of the methylarene ligand. Those complexes having three or more adjacent unsubstituted positions form the first group. The activation energies (E_a) for these compounds were found to be 8.6 ± 0.3 kcal mol^{-1} and the corresponding activation entropies ($\Delta S^{\neq}$) equal to -18.2 ± 0.7 cal K^{-1} mol^{-1}. The standard deviations are well within the experimental errors for the determination of any of the parameters. This fact implies that the parameters can be considered to be equal for all members of the group. The second group has two adjacent unsubstituted positions and in this case E_a are equal to 10.3 ± 0.1 kcal mol^{-1} and $\Delta S^{\neq}$ were estimated to be -16.2 ± 0.4 cal K^{-1} mol^{-1}. The complexes in the third group have only H substituents with adjacent methyl substituents and in all these cases there are two or three such H substituents. The activation parameters were estimated to be 14.4 ± 0.3 kcal mol^{-1} (E_a) and -8.1 cal K^{-1} mol^{-1} ($\Delta S^{\neq}$). The final group has only two members, the complexes of haxamethyl- and pentamethylbenzene, and the activation energies averaged 17.0 ± 1.4 kcal mol^{-1} and $\Delta S^{\neq}$ was evaluated as -5 cal K^{-1} mol^{-1} in both cases.

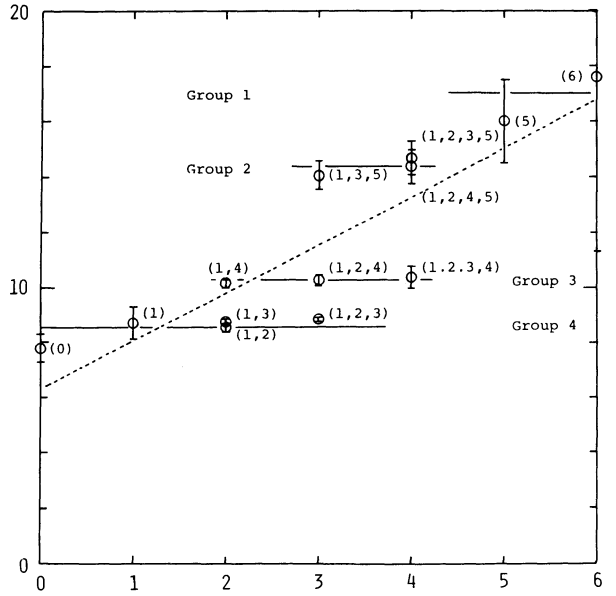


Fig. 2. Relation between activation energies of decomposition reactions of the cation radicals from the complexes and their structures. See text for the structures.
(——) Mean value of E_a in each group. (------) Linear regression line.

The data in Table 2 conform well to an isokinetic relationship.[11] The data are plotted in Fig. 3. The linear regression slope is equal to 601 K, *i.e.*, the isokinetic temperature, with a correlation coefficient of 0.995. The relationship implies an inversion of relative rate constant at temperatures above and below 601 K. However, the apparent isokinetic temperature is so far removed from the range in which the parameters were determined that we place little significance on it. On the other hand the linear relationship does exist and we point this out without becoming involved in a discussion of the possible significance of the relationship, which is in itself controversial.[11]

The most stable cation radical complex, both from a thermodynamic (E_{rev}) and a kinetic (k and E_a) points of view, is that derived from hexamethylbenzene. The least stable is that from benzene. This fact suggests that steric effects have little to do with the relative stability of the cation radicals. If we assume that the

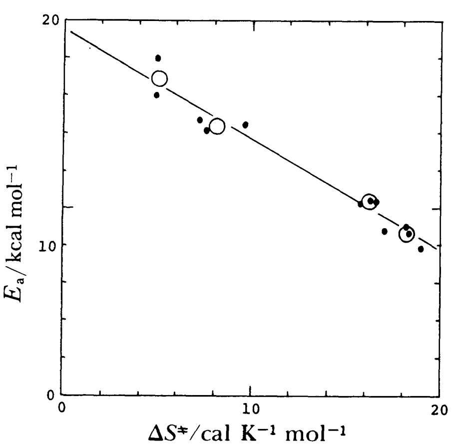


Fig. 3. Isokinetic relationship obtained from E_a and $\Delta S^{\neq}$ in Table 2.
(—O—) From Table 2. (●) Each isomer.

most important electronic effect of the methyl substituents is an inductive one, the positions where methyl is attached are the ones most affected by the substituent. All positions in the hexamethylbenzene complex cation radical are affected equally by the methyl groups. This would allow a maximum degree of transmission of the inductive effects of the methyl groups providing that Cr is located with the same relationship to all the C atoms of the benzene ring. Any unsubstituted position brings about a decrease in the donation of electrons from the methylarene ligand to the chromium atom. The complex of pentamethylbenzene forms a less stable cation radical than the corresponding hexamethylbenzene complex. The effect is amplified by having two or three unsubstituted positions as is the case for the group 3 complexes. The difference in stability becomes greater when adjacent positions are unsubstituted as in groups 2 and 1. In these cases the chromium atom could not be located equidistant from all of the ring carbon atoms except in (0) and have the maximum effect of the methyl groups at the substituted positions. There are most likely differences in the geometries of the cation radical complexes depending upon the substitution pattern.

In conclusion the linear relationship observed between the thermodydnamic and kinetic stabilities, with some scattering, can be considered to be due to different but similar aspects in three states. The thermodynamic stabilitites are related to two states of them, *i.e.* neutral complex and cation complex. On the other hand the kinetic stabilites are related to another set of two states, *i.e.* cation complex and transition state to decomposition.

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