

Ion Radicals of Organometallic Compounds. II. Heteroatom Substituent Effects on the Rates of Decomposition of the Cation Radicals of Arenetricarbonylchromium Complexes

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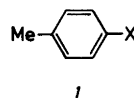
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The kinetics of the decomposition of a number of cation radicals derived by electrochemical oxidation of substituted arenetricarbonylchromium complexes were studied in acetonitrile. The reversible potentials for the formation of cation radicals of complexes derived from 1,4-substituted benzenes, where one substituent was methyl and the other contained a heteroatom, were observed to be linearly related to the logarithm of the rate constant for decomposition measured at 253 K. The best Hammett correlation was observed using σ_m (correlation coefficient=0.95). First order rate constants for the decomposition reactions ranged from 3.5 to 2000 s^{-1} at 253 K. The complex substituted with dimethylamino was the least reactive while that substituted with electron withdrawing acetyl was most reactive. Activation energies for the decomposition reactions were nearly independent of structure (9.6 ± 0.4 kcal/mol) while the corresponding activation entropies varied from 14 to 20 cal/K mol. The reversible potentials for the formation of the cation radicals ranged from 175 to 515 mV vs. Ag/Ag⁺ and all the cation radicals were oxidized to the dications irreversibly at 1000-1500 mV.

mechanism of the decomposition of some of the cation radicals in acetonitrile and found the overall mechanism to be of the ECE_h type accompanied by the formation of the parent molecules and carbon monoxide.³ The effect of methyl substitution on the ease of formation and the reactivity of the cation radicals was examined. It was found that the reversible potentials were lower for the formation of cation radicals of complexes from more heavily substituted methylbenzenes (for example, hexamethylbenzene) and the rate constants for the decompositions were lower. This suggested a substituent effect in which the electron donating methyl groups stabilize the cation radicals.³

In this paper we present the results of an investigation designed to study the substituent effect in more detail. Complexes derived from 1,4-disubstituted benzenes (*I*) in which X was Me₂N, H₂N, CH₃O, and CH₃CO, along with those derived from 1,4-dimethoxy- and 1,2-dimethoxybenzene were studied. Reversible potentials for the formation of the cation radicals along with kinetic and activation parameters for the decomposition reactions are reported.

A number of arenetricarbonylchromium complexes have been observed to undergo reversible electrooxidation to the corresponding cation radicals.¹⁻³ We have recently studied the



- 1a* X=NMe₂ *1c* X=OMe
1b X=NH₂ *1d* X=OCCH₃
1e X=Me

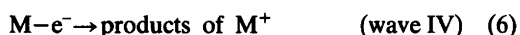
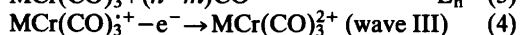
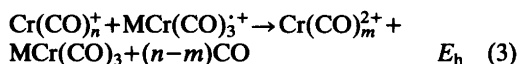
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EXPERIMENTAL

All measurements were carried out at a platinum electrode in acetonitrile containing Bu_4NBF_4 (0.1 M) and the electrode potentials refer to Ag/Ag^+ (0.1 M in acetonitrile). The concentration of the substrates was 1.0 mM in all cases. The kinetics were studied at temperatures ranging from 253 to 298 K at 5 K intervals. Reversible potentials (E_{rev}) were measured at 253 K under conditions where all of the cation radicals were of sufficient lifetime for the measurements. Details of the measurement procedures have been reported previously.³⁻⁵

RESULTS AND DISCUSSION

The linear sweep voltammetry (LSV) curves for the oxidation of the complexes consisted of four main waves corresponding to the same type of processes involved in the oxidation of the methyl substituted complexes.³ The latter was established by the effect of the sweep rate (v) on the relative currents at the various peaks. That is, wave III was observed only when wave I was reversible and wave IV was observed when wave I was irreversible. The reaction scheme previously proposed is summarized by eqns. (1)–(6) (Scheme 1).³ In this scheme M refers to the arene substrate.



Scheme 1.

The reversible oxidation potentials of the complexes to the corresponding cation radicals (wave I) at 253 K and the peak potentials for the oxidation of the cation radicals to the dications (wave III) measured at 100 V/s are listed in Table 1. The voltammograms from complexes derived from *Ia*, *Ib*, *Ic*, and 1,4-dimethoxybenzene had oxidation waves IV interposed between waves I and III and in some cases overlapped with wave

II. Wave II was broad and is most likely due to Cr oxidation products formed in reaction (3).³

The first order rate constants (k) for the decomposition reactions of the cation radicals (wave I, ECE_h mechanism) were obtained by derivative cyclic voltammetry (DCV) and evaluated using eqn. (7) derived from theoretical data.⁶ In (7) $v_{1/2}$ refers

$$k = 1284(v_{1/2}/T) \quad (7)$$

to the sweep rate necessary for the derivative peak ratio to equal 0.500. Activation energies and entropies were derived from the Arrhenius plots.^{7,8} The kinetic and activation parameters along with $v_{1/2}$ and oxidation potentials of the parent molecules under the same conditions are summarized in Table 1.

If we take $v_{1/2}$ as a measure of the stability of the complexes we see (Table 1) variations of the order of 10^4 in this series. A plot of $\log k$ vs. Hammett σ_m for the complexes derived from parent molecules I and 1,4-dimethoxybenzene resulted in ρ equal to 4.2 with a correlation coefficient of 0.93. From this we conclude that the apparent stabilization effect of electron donating groups arises from inductive and field effects rather than from mesomeric effects. This is accentuated by the fact that methoxy appears to be less stabilizing than methyl while the converse is expected on the basis of the mesomeric effects. In considering the effect of substituents it must be kept in mind that factors other than the electronic effects are of importance. This is obvious from the fact that benzenetricarbonylchromium cation radical undergoes decomposition at rates much greater than any of those on which the Hammett analysis was made. In this regard it is of interest to note that the cation radical of the complex derived from 1,2-dimethoxybenzene is the most reactive one that we have studied so far and decomposes with a rate constant more than 10^2 than that for the 1,4-substituted isomer. This rate difference could be due to a steric effect. The rate constant for the decomposition of the cation radical of the complex derived from 1,2-dimethylbenzene has been observed to be about 5 times as great as that obtained when the arene ligand was 1,4-dimethylbenzene.

Although the first order rate constants for the decomposition of the 4 complexes derived from I

Table 1. Oxidation potentials for substituted benzenetricarbonylchromium complexes and kinetic parameters for the decomposition of the cation radicals and those of the parent molecule.^a

Substitution	E_{rev}/mV	k_{253}/s^{-1}	k_{298}/s^{-1}	$E_a/kcal$ mol^{-1}	$-A\Delta S^\ddagger/cal$ $K^{-1} mol^{-1}$	E_{III}^d/mV	E_{IV}^e/mV	$v_{1/2}^f/Vs^{-1}$
		^g	^g	^g	^g			
1,4-(N(CH ₃) ₂)(CH ₃)	175	3.5(0.2)	7.1(0.3)	10.1(0.3)	18(1)	990 ^{d1}	395 ^{e1}	0.1
1,4-(NH ₂)(CH ₃)	206	5.1(0.4)	85(6)	9.4(0.4)	20(2)	1150 ^{d1}	550 ^{e2}	>1000
1,4-(OCH ₃)(CH ₃)	353	65(3)	1070(40)	9.3(0.2)	15(1)	1360 ^{d2}	1390 ^{e2}	>1000
1,4-(OCH ₃) ₂	325	106(3)	1790(80)	9.4(0.2)	14(1)	1290 ^{d2}	974 ^{e1}	0.02
1,4-(COCH ₃)(CH ₃)	615	1920(80)				1440 ^{d3}	ca. 1100 ^{e1}	100
1,2-(OCH ₃) ₂	ca. 390	>10000					2280 ^{e2}	>1000

^a In acetonitrile containing Bu₄NBF₄(0.1 M). ^b Reversible oxidation potential vs. Ag/Ag⁺ of wave I. ^c Activation entropy. ^d Oxidation peak potential vs. Ag/Ag⁺ of wave III. (d₁: 100 V/s, 25 °C, d₂: 100 V/s, -20 °C, d₃: 200 V/s, -20 °C) ^e Oxidation potential vs. Ag/Ag⁺ of parent molecule at 25 °C. (e₁: reversible potential, e₂: peak potential at 10 V/s). ^f Approximate value for parent molecule. ^g All errors are 95 % confidence calculated according to the theory of least squares as described in Ref. 11. The rate constants were calculated from the Arrhenius correlations.

ranged from 3.5 to 106 s⁻¹, the corresponding activation energies were identical within experimental error at 9.6(0.4) kcal/mol. This value is very close to that observed for the decomposition of the cation radical of 1,4-dimethylbenzenetricarbonylchromium equal to 10.9(0.4) kcal/mol.³ This result should be compared to the effect of the number and the position of the methyl groups in methylbenzenetricarbonylchromium cation radical decompositions.³ In that case the activation energies ranged from 7.8 to 17.6 kcal/mol with the extreme values observed for the complexes of benzene and hexamethylbenzene, respectively. Thus, it may be concluded that as long as only cation radicals of complexes having the same substitution pattern are considered, that the substituent effect does not show up significantly in the activation energies but is manifested mainly in the entropies of activation.

It is also of interest to note that there does not appear to be any relationship between the reactivities of the cation radicals of the complexes and the corresponding cation radicals of the parent substances. For example, the cation radical of 1,4-dimethoxybenzene is stable ($v_{1/2}=0.02$ V/s) under the conditions of the measurements while that from 1-amino-4-methylbenzene is very reactive ($v_{1/2}>1000$ V/s) under the same conditions. The opposite order of reactivity was observed for the corresponding cation radicals with that for the complex derived from 1,4-dimethoxybenzenetricarbonylchromium being 20 times more reactive at 253 K than the corresponding 1-

amino-4-methyl substituted cation radical. The apparent reason for the differences in the order of reactivity is that the reactivities of the cation radicals of the complexes depends primarily on the strength of the bonding between the benzene rings and chromium and there is little charge distribution onto the arene ligand. This is accentuated by the stability of the cation radical of 1-amino-4-methylbenzenetricarbonylchromium. The amino protons become decidedly acidic in the cation radical of the parent compound.

There does appear to be a relationship between reactivity and ease of formation of the cation radicals. A correlation of k_{253} with E_{rev} for the cation radicals of complexes derived from I was linear with a correlation coefficient of 0.98. This correlation does not hold for cation radicals of complexes derived from parent molecules with different substitution patterns. There is also a relationship between E_{rev} of the complexes and the oxidation potentials of the parent molecule. Excluding the data for 1,2-dimethoxybenzene and the corresponding complex, a slope of 0.25 was observed in the correlation. This value is similar to the corresponding slope for the correlation of the same quantities for the methylbenzenes and their complexes in which case the slope was 0.20. Thus, it appears that the attenuation of the transmittance of electron donation to the Cr atom from the arene does not differ greatly for the various substituents, but E_{rev} is not independent of the substituent pattern, the Taft factors (σ_I and σ_R).¹⁰ Our reversible potential measure-

ments support this. The values found for the oxidation of the complexes of 1,4-dimethylbenzene, 1-methoxy-4-methylbenzene and 1,4-dimethoxybenzene were 403, 353 and 325 mV, respectively.

On the other hand, a reasonably good Hammett plot for the cation radical decompositions was only found when σ_m values were used. The Hammett ρ value was observed to be equal to +4.2 which indicates a strong rate enhancement by electron withdrawing substituents. Thus, the effect of methoxy on the decomposition kinetics appears to fit that of a polar electron withdrawing substituent. As mentioned earlier, effects other than the electronic one could play a dominant role in the decomposition reactions. Thus, we will not attempt to explain the apparent anomaly between the relative thermodynamic and kinetic stabilities of the cation radicals.

Acknowledgement. We thank the Royal Norwegian Council for Scientific and Industrial Research for a postdoctoral fellowship for T. I.

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Received April 25, 1983.