Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Reactions of the Difunctional Organochromium Cation 3,3′-Oxybis[(chromiomethyl)benzene](4+), $(CrCH_2C_6H_4)_2O^{4+}$

WERNER MARTY[1] and JAMES H. ESPENSON*

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The title compound, I, was prepared from bis[*m*-(bromomethyl)phenyl] ether and excess chromium(II) in aqueous acetone. The product was purified by ion-exchange chromatography, and its composition was verified from its spectrum and from the products obtained on base hydrolysis and on reaction with mercury(II) and mild oxidants. Reaction of the dibromide with limiting quantities of chromium(II) produces the complex $[CrCH_2C_6H_4OC_6H_4CH_2Br]^{2+}$ (II) which was similarly characterized. Kinetic data were obtained on the reactions forming I and II and on the reactions of I and II with mercury(II) ion. The data are interpreted to show that the difunctional materials react at about twice the rate of their monofunctional analogues, suggesting little important neighboring group assistance. Reactions known to occur in (at least) two stages having comparable rates occasionally give evidence of but a single kinetic step; some general statements relating to statistically related biphasic kinetic schemes are given.

Introduction

From the time organochromium(III) cations of the general formula $(H_2O)_5CrR^{2+}$ were first prepared,[2,3] it was recognized that some of their reactions are novel and interesting. Radical processes, both unimolecular[4] and bimolecular,[5] and bimolecular electrophilic substitution[6,7] processes at the chromium-substituted carbon atoms are now recognized.

The study of difunctional analogues, apart from being an obvious extension to this previous work, can serve to answer specific questions of general interest in this area: Can the presence of a second group significantly alter the reactivity of the first? Are there preferred pathways for intramolecular reaction of such species having difunctionality?

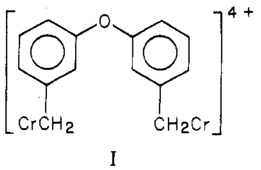
Reaction of benzyl bromide with Cr(II) ions results in the formation of the benzylchromium(III) cation via a two-step radical mechanism (eq 1–3).[2,3]

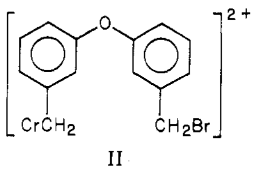
$$PhCH_2Br + Cr^{2+} \rightarrow CrBr^{2+} + PhCH_2\cdot \qquad (1)$$

$$PhCH_2\cdot + Cr^{2+} \xrightarrow{\text{fast}} CrCH_2Ph^{2+} \qquad (2)$$

$$\text{net:}\ PhCH_2Br + 2Cr^{2+} = CrBr^{2+} + CrCH_2Ph^{2+} \qquad (3)$$

An analogous method has been used to obtain good yields of the dichromium cation I and the monochromium cation II


I


II

starting with m,m'-$(BrCH_2C_6H_4)_2O$. We describe here the preparation, characterization, and reactions of these organochromium species, with particular emphasis on mechanistic questions relating to interactive effects between the metal centers.

Results

Preparation and Characterization of I and II. The reaction of m,m'-$(BrCH_2C_6H_4)_2O$ with Cr^{2+} either was carried out to produce I, by using a 20–30% stoichiometric excess of Cr^{2+}, or, alternatively, was used to produce mainly II along with some I, by using 2 mol of Cr^{2+}, allowing the reaction to proceed for approximately 1 half-life. The dibromide is insoluble in water and the reaction was thus carried out in aqueous acetone containing 0.1 M $HClO_4$. Aqueous solutions of the products were obtained by ion-exchange chromatography on Sephadex SP-C25 (H^+ form) at 0 °C. Since I and II, like the benzylchromium cation, react readily with dioxygen, the reaction solution, column, and eluting solutions were maintained under nitrogen. In all cases, the first band to be eluted was excess or unreacted Cr^{2+}, indicating the absence of major oxygen contamination. This was followed by a green Cr(III) complex judged by its elution position to be a dipositive complex, which is probably[8] $CrCl^{2+}$. For the experiments set up to produce II, this brownish yellow dipositive organochromium cation followed next. Some Cr^{3+} was eluted slowly after the 2+ species, by using 0.1 M $HClO_4$. Following Cr^{3+} is the organodichromium cation I, also brownish yellow, which was eluted by using 1 M electrolyte (generally 0.1 M $HClO_4$, 0.9 M $NaClO_4$).

Freshly eluted solutions of the dichromium cation I and the monochromium cation II have the following characteristic absorption spectra,[9] given as λ/nm (ϵ/dm^3 mol^{-1} cm^{-1}): I 420 (1840 ± 100, sh), 359 (4200 ± 200, max), 335 (3440 ± 140, min), 300 (14540 ± 700, sh), 282 (16 000 ± 800, max); II 420 (1022 ± 50, sh), 356 (2270 ± 110, max), 336 (1960 ± 100, min), 300 (8250 ± 400, sh), 278 (10 000 ± 500, max).

The chromium content of I and II was determined in two ways, the total chromium being determined spectrophotometrically as chromate after oxidation by peroxide in base[10] and the Co(II) being determined spectrophotometrically as $Co(NCS)_4^{2-}$ in aqueous acetone, produced by homolysis of I in the presence of $(NH_3)_5CoCl^{2+}$ ion.[4] The latter typically gave 90–93% of the former and, while probably subject to a larger error than the former (5 vs. 1%), indicates not only that the separations of I and II are reasonably efficient but also that their chemistry is not unlike that of the benzylchromium cation which reacts with this Co(III) complex in a reaction of 1:1 stoichiometry.[4]

As further confirmation of their identity, complexes I and II were subjected to mild base hydrolysis with carbonate ion in water, followed by dissolution of the precipitated $Cr(OH)_3\cdot H_2O$ with perchloric acid. ^1H NMR and mass spectra of the organic material thereby produced showed the presence of m,m'-ditolyl ether (from I) and of m-(bromomethyl)-m'-methyldiphenyl ether (from II) as the only detectable organic products.

$$\text{I} \xrightarrow[H_2O]{CO_3^{2-}/OH^-} 2Cr(OH)_3\cdot H_2O + (m\text{-}CH_3C_6H_4)_2O \qquad (4)$$

$$\text{II} \xrightarrow[H_2O]{CO_3^{2-}/OH^-} Cr(OH)_3\cdot H_2O + m\text{-}BrCH_2C_6H_4OC_6H_4CH_3\text{-}m' \qquad (5)$$

Kinetics of the Formation of I. The kinetics of the following two processes were studied in acetone–water (1:1).

$$m,m'\text{-}(BrCH_2C_6H_4)_2O \xrightarrow{4Cr^{2+}} \underset{\text{I}}{m,m'\text{-}(CrCH_2C_6H_4)_2O^{4+}} \qquad (6)$$

$$m\text{-}BrCH_2C_6H_4OC_6H_4CH_2Cr^{2+}\text{-}m' \xrightarrow{2Cr^{2+}} \text{I} \qquad (7)$$

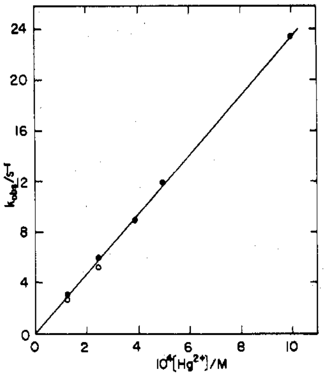


Figure 1. Plots showing the linear dependence of the pseudo-first-order rate constants on $[Cr^{2+}]$ in its reaction with *m,m′*-$(BrCH_2C_6H_4)_2O$ (open circles) and with II (filled circles).

Table I. Kinetic Data[a] for the Cr^{2+} Reaction with $(m\text{-}BrCH_2C_6H_4)_2O$ and II

$[Cr^{2+}]/M$	$10^3k_{obsd}/s^{-1}$ (no. of runs)	$k_{Cr}/dm^3\ mol^{-1}\ s^{-1}$
	Part A: $Cr^{2+} + (m\text{-}BrCH_2C_6H_4)_2O$	
0.030	2.88 (1)	0.096
0.052	5.27 ± 0.52 (3)	0.101
0.075	8.00 (1)	0.107
0.095	9.90 (1)	0.104
0.104	10.7 ± 1.0 (4)	0.103
		av 0.102 ± 0.004
	Part B: Cr^{2+} + II	
0.008	0.81[b] (1)	0.102
0.016	1.66 (1)	0.106
0.031	3.15 (1)	0.100
0.055	5.21 ± 0.23 (3)	0.085
0.079	7.23 (1)	0.092
		av 0.099 ± 0.006

[a] At 25.0 ± 0.1 °C, $[H^+] = 0.05$ M, $\mu = 0.38$ ($NaClO_4$) followed at λ 440 nm. [b] λ 410 nm.

The bromides were used as the limiting reagents under pseudo-first-order conditions and both reactions followed the same monophasic, first-order rate law

$$-\mathrm{d}\ \ln\ [\text{limiting reagent}]/\mathrm{d}t = k_{obsd} \qquad (8)$$

with linear plots of log $(D_t - D_\infty)$ vs. time for at least 80% of the reaction. The observed rate constant is directly proportional to $[Cr^{2+}]$

$$k_{obsd} = k_{Cr}[Cr^{2+}] \qquad (9)$$

(Figure 1, Table I). For reaction 7, the spectrum was recorded before and at completion of the reaction with excess Cr^{2+}. The increase of the optical density in the range 500–325 nm was observed and it constituted 92% of the expected increase of the original value. The reasonably small deficit may most likely be accounted for by decay of I during the time needed for completion of the reaction, although contamination by another organochromium species such as *m,m′*-$CrCH_2C_6H_4OC_6H_4CH_3^{2+}$, possibly resulting from decomposition of I during the synthesis and separation of II, may contribute.

Reactions of the Organochromium Ions I and II. With exclusion of oxygen, solutions of I and II can be kept for 2–3 days at <0 °C with only slight decrease in absorbance. When they are kept for longer periods or at room temperature, the decay is accompanied by appearance of turbidity. Eventually, a white, noncrystalline solid precipitates leaving a faint greenish aqueous phase. Its IR spectrum (ν_{C-H} at 3030, 2920, and 2856 cm^{-1}, $\nu_{C=C}$(aromatic) at 1605, 1580, and 1485 cm^{-1}, δ_{C-H} at 1445 cm^{-1}, and ν_{C-O-C} at 1255 cm^{-1}) is in some aspects similar to that of the parent hydrocarbon *m,m′*-ditolyl ether[11] and also to that of poly[*p,p′*-oxidobis(phenylmethylene)].[12] The ^1H NMR spectrum, with signals at δ 7.6–7.9 ppm (m, ~8 H) and δ 2.8 ppm (s, broad, ~4 H) is also consistent with the formation of poly(*m,m′*-ditolyl ether).

The same material also appears to be formed copiously by the reactions with O_2, Cu^{2+}, $(NH_3)_5CoCl^{2+}$, and $(NH_3)_5CoBr^{2+}$. The reaction with Br_2 apparently also produces this material, in contrast to the reactions of benzylic monochromium species such as $(H_2O)_5CrCH_2Ph^{2+}$ with Br_2(aq), which give the organic bromides via an S_E2 pathway in good yields.[6] The reaction products of dichromium species I with Br_2(aq) were also examined by TLC and checked against the authentic 3,3′-bis(bromomethyl)diphenyl ether; a detectable quantity of the latter was not found.

Kinetics of Homolysis. As with the benzylic organochromium species,[4] addition of excess Cu^{2+} to solutions of I leads to rapid loss of the spectral bands associated with the chromium–carbon bonds and formation of $Cr(OH_2)_6^{3+}$. Owing to the turbidity which develops, many runs were not suitable for kinetics. A few acceptable kinetic determinations were made at $\mu = 1.0$ M ($HClO_4$, $NaClO_4$), 0.1 M $[H^+]$, 25.0 ± 0.1 °C. The reaction followed pseudo-first-order kinetics with $k = 8.2 \times 10^{-4}\ s^{-1}$ (0.10 M Cu^{2+}) and $8.4 \times 10^{-4}\ s^{-1}$ (0.05 M Cu^{2+}). This is taken to represent the rate constant for homolysis of a chromium–carbon bond in I, first because the value is independent of $[Cu^{2+}]$ and second because the value is comparable to that for homolysis of *p*-$BrC_6H_4CH_2Cr^{2+}$ ($k = 1.56 \times 10^{-3}\ s^{-1}$)[4] which has a Hammett substituent constant ($\sigma^p_{Br} = +0.23$) similar to the one applying here ($\sigma^m_{OC_6H_5} = +0.252$). Precipitate formation completely precluded the determination of the rate corresponding to homolysis of II in water.

Table II. Kinetic Data[a] for the Reaction of I and II with Excess Hg^{2+}

$10^4[Hg^{2+}]/M$	k_{obsd}/s^{-1} (no. of runs)	$10^{-4}k_{Hg}/dm^3\ mol^{-1}\ s^{-1}$
	Part A: Hg^{2+} + I, $\mu = 1.00$	
4.98	15.6 ± 0.5 (7)	3.13
7.46	22.8 ± 0.5 (5)	3.05
9.95	35.0 ± 2.8 (10)	3.52
		av 2.32 ± 0.25
	Hg^{2+} + I, $\mu = 0.500$	
1.24	2.92 ± 0.39 (29)	2.35
2.49	5.93 ± 0.33 (19)	2.38
3.73	8.85 ± 0.34 (15)	2.37
4.98	11.8 ± 0.4 (19)	2.38
9.95	23.4 ± 0.8 (21)	2.36
		av 2.37 ± 0.01
	Part B: Hg^{2+} + II, $\mu = 0.500$	
1.24	2.67 ± 0.12 (19)	2.15
2.49	5.03 ± 0.08 (10)	2.02
		av 2.09 ± 0.09

[a] At 25.0 ± 0.1 °C, $[H^+] = 0.500$; monitoring wavelength λ 365 nm.

Kinetics with Hg^{2+}. Reaction of I with excess Hg^{2+} occurs rapidly to cleave both chromium–carbon bonds. The kinetics were evaluated by stopped-flow techniques (Table II, Figure 2) at 365 nm. In the presence of excess Hg^{2+} the reaction followed pseudo-first-order kinetics. No evidence for consecutive reactions was obtained. In these runs $[I]_0$ was varied by a factor of about 5 without significant effect. Aging of the organochromium solutions at room temperature beyond a certain time did, however, lead to a significant (10%) increase in the rate constants; concurrently the final absorbance increased in successive runs using the same aged solutions. Such

Table III. Summary of Kinetic Equations and Rate Constant Values

reaction	rate law	k/dm^3 mol^{-1} s^{-1}
$(BrCH_2C_6H_4)_2O \xrightarrow{4Cr^{2+}} I$	$-d \ln [(BrCH_2C_6H_4)_2O]/dt = k_1[Cr^{2+}]$	$0.204^{a,b}$
$II \xrightarrow{2Cr^{2+}} I$	$-d \ln [II]/dt = k_2[Cr^{2+}]$	0.099^{a}
$I \xrightarrow{2Hg^{2+}} (HgCH_2C_6H_4)_2O^{2+}$	$-d \ln [I]/dt = k_A[Hg^{2+}]$	$4.74 \times 10^{4\,c}$
$II \xrightarrow{Hg^{2+}} BrCH_2C_6H_4OC_6H_4CH_2Hg^+$	$-d \ln [II]/dt = k_B[Hg^{2+}]$	$2.09 \times 10^{4\,c}$

[a] 25.0 °C, $[H^+] = 0.050$ M, $\mu = 0.38$ M, in 1:1 acetone/water. [b] The values of k_1 and k_A are calculated from the experimental rate constants of Tables I and II based on the relationships of eq 16 and 17 which contain certain assumptions about the relative values of sequential rate constants. [c] 25.0 °C, $[H^+] = 0.500$ M, $\mu = 0.500$ M.

problems were thus easily recognized, and these runs were neglected.

The reaction of II with excess mercury(II) ion was examined cursorily under the same conditions ($\mu = 0.5$ M only), and it followed the same pattern as I with a very similar second-order rate constant (Table II).

The product of the reaction of I with excess Hg^{2+} was isolated and characterized as its chloro derivative. From moderately concentrated perchlorate solutions a white precipitate formed, presumably *m,m'*-$[(HgCH_2C_6H_4)_2O](ClO_4)_2$. This material proved rather unstable, however, and it was converted into the stable insoluble dichloro derivative which was characterized by elemental analysis and IR spectra (ν_{C-H} at 3050–3000, 2960, 2920 cm^{-1} (vw); $\nu_{C=C}$ at 1590, 1560, 1470 cm^{-1}; δ_{C-H} at 1430 cm^{-1}; ν_{C-O-C} at 1255 cm^{-1}). The dibromo derivative is also insoluble.

The reaction of 1 equiv of Hg^{2+} with the dichromium species I, carried out on a micro scale in water, gave an amorphous, flocculent precipitate. Only a small fraction of this was extracted with acetone, leaving an insoluble residue which is presumably the polymeric poly[*m,m'*-oxybis(phenylmethylene)mercury(II)]. Its elemental analysis is consistent with a 1:1 organomercurial (1 Hg:1 $(CH_2C_6H_4)_2O$) and its IR spectrum is very similar to that of $(ClHgCH_2C_6H_4)_2O$ and is consistent with the absence of ClO_4. The mass spectrum of this material as well as that of the acetone-soluble fraction showed no peaks of a cyclic monomer or dimer, $Hg(CH_2C_6H_4)_2O$ or $[Hg(CH_2C_6H_4)_2O]_2$.

Attempts to measure the kinetics of the (poly-)diorganomercurial formation were made in a series of solvent mixtures, with Hg^{2+} as the limiting reagent. Injection of a small volume containing 1 equiv of Hg^{2+}/dichromium ion in the original solution is expected to give a very rapid decrease (~50%) in optical density, followed by a slower rate process to give $D_\infty \sim 0$ (at a wavelength where the absorption is essentially due to the organochromium species), according to the reactions

$$I + Hg^{2+} \rightarrow m\text{-}HgCH_2C_6H_4OC_6H_4CH_2Cr\text{-}m^{3+} \quad (10)$$
$$k = 4.74 \times 10^4\ M^{-1}\ s^{-1}$$

$$2m\text{-}HgCH_2C_6H_4OC_6H_4CH_2Cr\text{-}m^{3+} \rightarrow [CrCH_2C_6H_4OC_6H_4CH_2HgCH_2C_6H_4OC_6H_4CH_2Hg]^{3+} + Cr^{3+} \quad (11)$$

For the latter reaction, a rate constant in the order of 10^1–10^2 M^{-1} s^{-1} is expected from analogous reactions[7] of RHg^+ with $C_6H_5CH_2Cr^{2+}$ in mixed solvents. The initial drop of absorption was always observed, but any slow second reaction (11) was obscured by the turbid suspensions of the products formed or by the competing Hg^{2+}-independent decay of the organochromium species at the low Hg^{2+} concentrations used.

Discussion

The organochromium species I and II were obtained by reaction of the dihalide *m,m'*-$(BrCH_2C_6H_4)_2O$ with ≥4 mol and 2 mol of Cr^{2+}, respectively, in analogy to the original method[2,3] of producing $(H_2O)_5CrCH_2C_6H_5^{2+}$. The formulas assigned to I and II follow not only from their relative elution patterns during their chromatographic separations but also from their reactions. The known parent hydrocarbon *m,m'*-$(CH_3C_6H_4)_2O$ is formed by hydrolysis of I in carbonate solution, and the faster eluting species II produces the corresponding compound, *m*-$BrCH_2C_6H_4OCH_2C_6H_4CH_3$-*m'*. Another experiment supporting the structural assignments is the isolation of *m,m'*-$(ClHgC_6H_4)_2O$ from the reaction of Hg^{2+} with I.

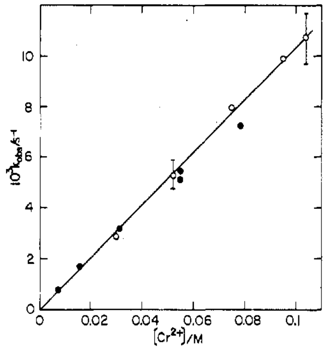


Figure 2. Linear dependence of the pseudo-first-order rate constants on $[Hg^{2+}]$ for its reaction with I (filled circles) and with II (open circles).

Although the formation of I is expected to occur in two consecutive steps, and indeed the present work has shown II is formed first, the reaction of Cr^{2+} with the dibromide follows exact pseudo-first-order kinetics within experimental error. Since I is a byproduct in the synthesis of II, an obvious explanation of the single stage kinetics—that either $k_2 \gg k_1$ or $k_1 \ll k_2$ in the following scheme—is thus ruled out.

$$m,m'\text{-}(BrCH_2C_6H_4)_2O \xrightarrow[k_1]{2Cr^{2+}} II \xrightarrow[k_2]{2Cr^{2+}} I \quad (12)$$

We note rather that the rate constants for the two reactions, $k_1/2 = 0.102$ and $k_2 = 0.099$ M^{-1} s^{-1} (Table III), are very nearly the same. Further comment on this point is given later.

The rate of reaction of I with Hg^{2+} is first order in $[Hg^{2+}]$ and is comparable to that of the Hg^{2+} reaction with $C_6H_5CH_2Cr^{2+}$ ($k = 4.9 \times 10^4$).[7] Again, uniphasic kinetics is observed for this reaction which may be expected to occur in two consecutive stages (this will be discussed later).

The reaction of *m*-$BrCH_2C_6H_4OC_6H_4CH_2Cr$-*m*$^{2+}$ with Hg^{2+} has nearly the same rate constant, although this possibly fortuitous agreement[13] is not necessarily relevant to this discussion, because this compound differs significantly from the supposed intermediate of the reaction, *m*-$HgCH_2C_6H_4OC_6H_4CH_2Cr$-*m*$^{2+}$. The latter appears to be difficult to prepare because of its fast polymerization (eq 10 and 11).

We believe that formation of I and its reaction with excess Hg^{2+} occur with little interaction between the metal centers through the oxybis(*m*-tolyl) moiety in I and in radical or other intermediates of the reactions discussed. Clearly, for the meta isomers less interaction is expected than for the para or ortho isomers for which electronic and steric factors, respectively, may enter. We presume, therefore, that the reactions studied will occur in a nearly statistical fashion and that deviations will be caused mainly by solvent-mediated electrostatic interaction between the centers.

We note, furthermore, that the molar absorptivities of I and II are nearly additive, and presumably this also extends to $m\text{-}HgCH_2C_6H_4OC_6H_4CH_2Cr\text{-}m^{3+}$. If these relationships hold, then the reaction schemes for the two processes can be expressed as

$$\underset{\epsilon_1 \simeq 0}{\text{Br–R–Br}} \xrightarrow[k_1 \simeq 2k_2]{2\text{Cr}^{2+}} \underset{\epsilon_2}{\text{Br–R–Cr}^{2+}} \xrightarrow[k_2]{2\text{Cr}^{2+}} \underset{\epsilon_3 \simeq 2\epsilon_2}{\text{Cr–R–Cr}^{4+}} \quad (13)$$

$$\underset{\epsilon_A \simeq 2\epsilon_B}{\text{Cr–R–Cr}^{4+}} \xrightarrow[k_A \simeq 2k_B]{\text{Hg}^{2+}} \underset{\epsilon_B}{\text{Cr–R–Hg}^{3+}} \xrightarrow[k_B]{\text{Hg}^{2+}} \underset{\epsilon_C \simeq 0}{\text{Hg–R–Hg}^{2+}} \quad (14)$$

where ϵ values are molar extinction coefficients. ϵ_1 and ϵ_C are known to be $\simeq 0$ at the monitoring wavelength. Substitution of the individual *k*'s and ϵ's into the general equation[14] for biphasic kinetics

$$\text{I} \xrightarrow{1} \text{II} \xrightarrow{2} \text{III}$$

$$D_t = \epsilon_{\text{III}}[\text{I}]_0 + (\epsilon_{\text{I}} - \epsilon_{\text{III}})[\text{I}]_0 e^{-k_1 t} + (\epsilon_{\text{II}} - \epsilon_{\text{III}})[k_1[\text{I}]_0/(k_2 - k_1)]\{e^{-k_1 t} - e^{-k_2 t}\} \quad (15)$$

provides these relations for eq 13 and 14 respectively:

$$D_\infty - D_t = 2\epsilon_2[\text{Br–R–Br}]_0 e^{-k_2 t} \quad (16)$$

$$D_t = 2\epsilon_B[\text{Cr–R–Cr}]_0 e^{-k_B t} \quad (17)$$

The phenomenological rate constants of eq 8 are therefore identical with the true rate constants for disappearance of the *monofunctional* species, irrespective of the circumstance that a colorless starting material is involved in one case and a colorless product in the other.

The equations apply to the case of a strictly statistical relationship between the consecutive rate constants and extinction coefficients. Our data show that these do not hold exactly, although the deviations are small. This raises the general question: Which is the maximum deviation from the statistical ratio which is not detectable by the appearance of biphasic kinetics? This question has practical importance and has been examined by analog computer simulation; these results will be reported later.[13]

In light of the complicated form of the kinetic equations a summary giving carefully defined rate laws seems called for. Such a summary is given in Table III.

It is useful to compare the rate constants determined here for the Hg^{2+} reactions with values found for related complexes. The values of $k_A/2$ (statistical correction) and k_B from Table III, both $(2.3 \pm 0.1) \times 10^4$ dm^3 mol^{-1} s^{-1}, compare favorably with an estimated value[15] of 3.1×10^4 for the reaction of $(H_2O)_5CrCH_2C_6H_4OC_6H_5\text{-}m^{2+}$ and Hg^{2+}.

Experimental Part

Materials. 3,3′-Bis(bromomethyl)diphenyl ether was prepared from 3,3′-ditolyl ether[11] similarly to the described procedure for the 2,2′ and 4,4′ isomers.[16,17] It had mp 78–78.5 °C (from benzene–petroleum ether) and ^1H NMR signals at δ 7.3–6.5 (m, 8 H) and δ 2.27 (s, 4 H) in $CDCl_3$ relative to internal Me_4Si.[18]

Typical procedures for generating and isolating (in aqueous solution) I and II were as follows.

I. A deaerated acetone solution (20 cm^3) of 3,3′-bis(bromomethyl)diphenyl ether (100 mg, 0.28 mmol) was treated with aqueous Cr^{2+} ($\sim$1.5 mmol, prepared by zinc amalgam reduction of hydrated chromium(III) chloride in 0.1 M $HClO_4$) for 20 min at room temperature. A color change from light blue to greenish olive occurred in that time. The reaction mixture was then transferred to the top of a deaerated column of Sephadex SP-C25 (H^+ form), where 20–40 cm^3 of 10^{-2} M $HClO_4$ served to dilute the acetone solution initially (Sephadex is attacked by pure acetone). Elution with deoxygenated 0.1 M $HClO_4$ first removed excess Cr^{2+} (the excess was used to ensure complete removal of oxygen from the column), then a green Cr(III) species[8] of charge 2+, and, finally, Cr^{3+}. I was then eluted with 0.9 M $NaClO_4$/0.1 M $HClO_4$. The yield was typically ≥75%, based on dibromide. On the column there remained some polymeric Cr(III) species arising from oxidation of Cr(II) by traces of oxygen. These were eluted with 2 M $NaClO_4$.

II. Species II was formed along with I when the dibromide (100 mg, 0.28 mmol) was treated (20 min) with Cr^{2+} ($\sim$ 0.6 mmol) as described above. The reaction solution ($\sim$20 cm^3) was then added to 0.1 M $HClO_4$ (40 cm^3) on the top of the column. Adsorption was accompanied by separation of the bands at this electrolyte concentration. The bands appeared in the following order: (a) unreacted Cr^{2+}, (b) a green dipositive Cr(III) species,[8] (c) II, (d) Cr^{3+} (slightly overlapping with II), (e) I, (f) Cr(III) polymers. The bands (a)–(d) were eluted in this order by 0.1 M $HClO_4$. For a typical experiment, II constituted 30% and I 16% of the total dibromide; precipitated dibromide largely made up the material balance. Doubling the reaction time significantly reduced the yield of II and more I was produced. Typically, solutions of II off the column were $(2\text{–}3) \times 10^{-4}$ M.

Poly[*m,m*′-oxybis(phenylmethylene)]. When a solution of I was kept in a refrigerator in a sealed bottle for longer than ca. 1 week, its decomposition became apparent from the color change to faint green and a white, flocculent precipitate appeared. This was collected by centrifugation and washed with water. The material was completely soluble in acetone and most of it was separated as an oil by the addition of water and dried in vacuo. ^1H NMR (CCl_4): δ 7.5–6.6 (m, 8 H), 2.8 (s, broad, 4 H). The IR spectrum showed the presence of acetone in the sample (1705 cm^{-1}, $\nu_{C=O}$). Anal. Calcd for $(C_{14}H_{12}O)_n \cdot 0.2n(CH_3)_2CO$: C, 84.36; H, 6.40. Found: C, 84.17; H, 6.37.

Poly[*m,m*′-oxybis(phenylmethylene)mercury(II)]. To a solution of I (9.9×10^{-3} M, 21 cm^3), a solution of $Hg(ClO_4)_2$ (9.95×10^{-2} M, 2.0 cm^3) was added. Upon addition of a first portion, a voluminous, gellike precipitate formed immediately, and adding the final portion caused the yellow color of I to disappear. The precipitate was collected by centrifugation, washed with water, and extracted with acetone. The acetone extract gave a very small soluble fraction. The insoluble fraction decomposed readily on heating or light exposure or drying in vacuo at 25 °C, turning gray. It was therefore dried gently over H_2SO_4 at atmospheric pressure, but its IR spectrum indicated the presence of some acetone and water. Anal. Calcd for $(C_{14}H_{12}OHg)_n$: C, 42.37; H, 3.05. Found: C, 41.26; H, 2.98.

3,3′-Oxybis(chloromercurimethylbenzene). Solutions of I were treated with an excess of Hg^{2+} solution, to give an instantaneous decoloration. With more concentrated solutions of I, a white precipitate formed, presumably $[O(C_6H_4CH_2Hg\text{-}m)_2](ClO_4)_2$. This compound turned black on drying but its more stable chloride salt was prepared by adding excess HCl to the suspension and allowing it to stand for 2 weeks. Alternatively, the dichloro compound was precipitated by HCl from a homogeneous diperchlorate solution. Anal. Calcd for $C_{14}H_{12}OCl_2Hg_2$: C, 25.16; H, 1.81. Found: C, 25.05; H, 1.82.

Characterization of Base Hydrolysis Reaction Products of I and II. Solutions of I and II were treated with an excess of saturated sodium carbonate.[19] The solutions were immediately reacidified and the blue homogeneous solutions extracted with benzene or CH_2Cl_2. The extracts were dried over molecular sieves and the solvent evaporated at room temperature in vacuo. ^1H NMR spectra were run on the residues. The spectrum of the reaction product of I matched that of authentic $O(C_6H_4CH_3\text{-}m)_2$, and that from II was consistent with that expected for $CH_3C_6H_4OC_6H_4CH_2Br$. In addition, the latter product was analyzed by combined GC–MS. The major GC peak ($\sim$95% of total peak area) showed the M^+ ion $^+CH_2C_6H_4OC_6H_4CH_2Br$, *m/e* 279 (13.3%) and 277 (13.6%), and the fragment $CH_3C_6H_4OC_6H_4CH_2$, *m/e* 197 (100%).

Physical Measurements. UV–vis spectra and the slower kinetics runs were recorded on a Cary 14 or 219 spectrophotometer. IR spectra were run in KBr pellets on a Beckman 4820 instrument; frequencies given are accurate to ±5 cm^{-1}. ^1H NMR spectra were run at 35 °C on a Varian A-60 instrument, using Me_4Si as the internal standard. Mass spectra were recorded on a Finnigan 4000 GC–MS data system using a subambient, programmable direct insertion probe. The fast reactions with Hg^{2+} were followed on a Durrum stopped-flow spectrophotometer. The absorbance vs. time data were either photographed and treated graphically or digitized and stored in a Biomation Transient Recorder for subsequent least-squares computer fitting.

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Registry No. I, 69493-83-0; II, 69493-84-1; 3,3′-bis(bromomethyl)diphenyl ether, 69484-03-3; poly[*m*,*m*′-oxybis(phenylmethylene)], 69484-06-6; poly[*m*,*m*′-oxybis(phenylmethylene)mercury(II)], 69484-07-7; 3,3′-oxybis(chloromercurimethylbenzene), 69484-04-4; $CH_3C_6H_4OC_6H_4CH_2Br$, 69484-05-5; Cr^{2+}, 22541-79-3; Hg^{2+}, 14302-87-5.

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(8) The green dipositive species has not been definitely identified although it appears to be $(H_2O)_5CrCl^{2+}$. The material can be rechromatographed and purified on Dowex 50W-X2 resin, 100–200 mesh, and has reproducible characteristics. Its absorption spectrum resembles that of a $(H_2O)_5CrX^{2+}$ complex with maxima at 608 nm (ϵ 16.7) and 427 (20.8), which agrees well with that reported for $CrCl^{2+}$: 607 (16.4), 428 (20.7) [Espenson, J. H.; Birk, J. P. *Inorg. Chem.* **1965**, *4*, 528]. Boiling slowly produces $Cr(H_2O)_6{}^{3+}$, as does base hydrolysis with carbonate ion followed by reacidification. The complex reacts *slowly* with mercury(II) ion forming $Cr(H_2O)_6{}^{3+}$ (the half-time is $\sim 7 \times 10^2$ s at 0.008 M Hg^{2+}, 0.25 M H^+), compared to 5.4×10^2 s for $CrCl^{2+}$. The chloro complex presumably arises from the small quantity of $CrCl^+$ in the solution of chromium(II) chloride.
(9) Compare the spectrum[4] of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ which shows very similar maxima: 356 (2200), 295 (6970), 273 (7670).
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Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

Organometallic Nitrosyl Chemistry. 8.[1] Preparation and Characteristic Chemistry of $(\eta^5\text{-}C_5H_5)W(NO)_2H$ and Its Group 6B Congeners

PETER LEGZDINS* and DAVID T. MARTIN

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The chloro compounds $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Mo, W, or Cr) react with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in toluene to form either the new hydrido complexes $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) or the known $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ complex. The hydridomolybdenum complex slowly decomposes at ambient temperature, but the thermally stable tungsten analogue can be isolated and fully characterized. $(\eta^5\text{-}C_5H_5)W(NO)_2H$ exhibits a ν_{M-H} at 1900 cm^{-1} in its infrared spectrum and a low-field hydride resonance at δ 2.27 in its ^1H NMR spectrum. Its characteristic chemistry is dominated by its tendency to function as a source of H^-. Hence, $(\eta^5\text{-}C_5H_5)W(NO)_2H$ is inert to $CHCl_3$, CCl_4, and $(C_2H_5)_3N$, but it reacts readily with anhydrous *p*-toluenesulfonic acid and trityl tetrafluoroborate (in CH_3CN) to yield $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$ and $[(\eta^5\text{-}C_5H_5)W(NO)_2(CH_3CN)]BF_4$, respectively. However, the hydridotungsten complex is not sufficiently hydridic to attack $Fe(CO)_5$, and it reacts with acidic hydridocarbonyls such as $HCo(CO)_4$ or $(\eta^5\text{-}C_5H_5)W(CO)_3H$ to afford products resulting from the scrambling of CO and NO ligands rather than bimetallic carbonyl nitrosyls.

Introduction

Organometallic carbonyl hydrides have received, and continue to receive, considerable attention by virtue of their utility in organic and organometallic syntheses.[2] In contrast, analogous nitrosyl complexes, even though being capable of existence in principle, remain virtually unknown. Indeed, the only such complex that has been isolated to date is $(\eta^5\text{-}C_5H_5)Re(CO)(NO)H$.[3] During our earlier work,[4,5] we developed preparative methods leading to chloronitrosyl compounds which are logical precursors of hydridonitrosyl species. In this paper we report the results of our attempts to convert some of these precursors, specifically the complexes $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, or W),[6] to the desired hydridonitrosyls.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T60 spectrometer with tetramethylsilane being employed as an internal standard. Mass spectra were recorded at 70 eV on Atlas CH4B or AEI MS902 spectrometers by using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$. To a green solution of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$[6] (3.00 g, 8.71 mmol) in toluene (75 mL) at −78 °C was added dropwise with stirring a solution of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$[7] (2.49 mL, 8.71 mmol) diluted to 20 mL with toluene. The reaction mixture changed immediately to

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