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Original Scientific Paper

Kinetics and Mechanism of the Reaction between Mercury(II) and a Series of Macrocyclic Organochromium Cations*

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Kinetic data are presented for the reaction of alkylchromium complexes $(H_2O)([14]aneN_4)CrR^{2+}$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) with Hg^{2+} *via* electrophilic substitution. The rate constants decrease in the order CH_3 (1.1×10^6 mol^{-1} dm^3 s^{-1}) > C_2H_5 (7.7×10^2) > C_3H_7 (59) > 2-C_3H_7 (0.12) > $CH_2C(CH_3)_3$ (0.0086). A series of *meta* and *para* substituted benzyl complexes obey a Hammett relationship with the reaction constant $\rho = -1.66$, consistent with electrophilic substitution at α-carbon.

Key words: alkylchromium, electrophilic substitution, mercury(II), kinetics.

INTRODUCTION

Electrophilic cleavage of metal-carbon bonds is a well-studied area in organometallic chemistry.[1] Mercury(II) ion and other commonly studied electrophiles are believed to react by direct displacement (S_E2) of the alkyl group by a back-side attack at α-carbon to yield alkylmercury products. For Hg^{2+} as electrophile, this stereochemistry is strongly indicated in the case of

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

** Author to whom correspondence should be addressed. (butka@joker.irb.hr) alkylcobaloximes where the reaction results in the inversion of configuration at α-carbon.[2]

Two series of organochromium complexes, $(H_2O)_5CrR^{2+}$ and $([15]aneN_4)(H_2O)CrR^{2+}$ ($[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane), have been examined earlier[3,4] for their reactivity towards Hg^{2+}. For a given R group, especially a bulky one, the complex in the aquachromium series is more reactive than its macrocyclic counterpart. The ratio of the rate constants for the aqua and macrocyclic compounds, k_{aq} / k_{15ane}, increased from about 3 for R = methyl to over 300 for R = isopropyl, suggesting that electron donation from the macrocycle, which would be expected to push the rate constant in the opposite direction, is overridden by the steric crowding that it adds. This effect of the macrocycle is superimposed on the already strong steric effect exhibited by the alkyl group itself. Note that the electron donation (*i.e.* $CH_3 < C_2H_5 < 2\text{-}C_3H_7$) and the steric bulk run in opposite directions.

We have measured the kinetics of the reaction between Hg^{2+} and another series of organochromium complexes, $(H_2O)([14]aneN_4)CrR^{2+}$, ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) Eq. (1).

$$(H_2O)([14]aneN_4)CrR^{2+} + Hg^{2+} \xrightarrow{H_2O} RHg^{+} + ([14]aneN_4)Cr(H_2O)_2{}^{3+} \quad (1)$$

The complexes chosen differ in subtle ways from those in the [15]ane series. The macrocycle is now somewhat smaller, which may make the approach to the alkyl group even more sensitive to steric effects. Also, the stereochemistry around the nitrogens is probably different in the two macrocycles. The [14]ane complexes are almost certainly of the *R*, *R*, *S*, *S* (»two up, two down«) kind, the same as the starting $([14]aneN_4)Cr(H_2O)R^{2+}$ and the reaction product, $([14]aneN_4)Cr(H_2O)_2{}^{3+}$. The $([15]aneN_4)Cr$ complexes, on the other hand, have a tendency towards the less symmetrical »four up«[5,6] or »three up, one down« stereochemistries, as observed for R = $4\text{-}BrC_6H_4CH_2$.[7] It is not clear how this change in stereochemistry may affect the reaction rates, but one would expect the less symmetrical $[15]aneN_4$ complexes to allow a better approach to the reaction center. Our findings are presented below.

EXPERIMENTAL

The organochromium complexes were prepared in solution from $([14]aneN_4)Cr(H_2O)_2{}^{2+}$ and the desired organic bromide or iodide in weakly acidic solution under an atmosphere of purified argon as described previously.[4,8,9] The complexes were purified by ion-exchange on a column of Sephadex C-25 cation exchange resin and stored in a refrigerator. Stock solutions of mercury(II) perchlorate were prepared by boiling the oxide in a slight excess of perchloric acid. These solutions were standardized as described previously.[3]

(Caution. Solutions of metal perchlorates are potentially explosive and should be handled with care.)

Doubly distilled water, additionally purified by a passage through a Milli-Q system, was used throughout. All the experiments with air-sensitive complexes were carried out in an atmosphere of Cr^{2+}-scrubbed argon.

Spectral and kinetic data were obtained using a Cary 219 spectrophotometer and a Durrum D-110 stopped-flow instrument. The kinetics was monitored at an absorption maximum of organochromium complexes near 290 or 360 nm. All kinetic experiments were carried out at 25 °C in 0.25 mol dm^{-3} perchloric acid, at an ionic strength of 0.50 mol dm^{-3} ($HClO_4$ + $LiClO_4$).

RESULTS AND DISCUSSION

The kinetics was determined under pseudo-first order conditions using a large excess of Hg^{2+} over the concentration of organochromium complexes. The data obeyed the rate law of Eq. (2), as shown by the linearity of the first order plots and the linear dependence of the pseudo-first order rate constants on Hg^{2+} concentration, see Figure 1. The 1:1 stoichiometry and the formation of HgR^+, which were determined in earlier works[3,4] with $(H_2O)_5CrR^{2+}$

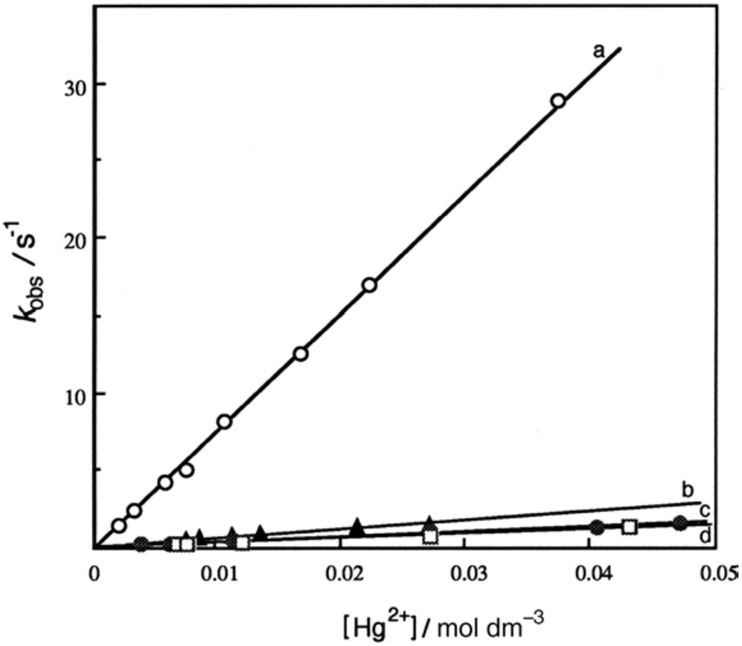


Figure 1. Plot of k_{obs} *vs.* the concentrations of Hg^{2+} ions for the reaction with (H_2O)-$([14]aneN_4)CrR^{2+}$ complexes, where R = (a) C_2H_5; (b) n-C_3H_7; (c) n-C_4H_9; (d) n-C_5H_{11}.

and $(H_2O)([15]aneN_4)CrR^{2+}$, are assumed to apply here as well. All the rate constants are shown in Table I, along with selected data for the other two series.

$$-d[(H_2O)([14]aneN_4)CrR^{2+}] / dt = k_{14ane}[(H_2O)([14]aneN_4)CrR^{2+}][Hg^{2+}] \quad (2)$$

As expected, the kinetics is not acid dependent. This was confirmed in several experiments for R = C_2H_5 at $[H^+] = 0.5$ mol dm^{-3}, which gave the same rate constant as that obtained in 0.25 mol dm^{-3} $HClO_4$. Similar observations were made earlier in analogous reactions of other organochromium complexes.

The reactivity order methyl > ethyl > n-propyl demonstrates the overwhelming importance of steric bulk at α-carbon and is typical of S_E2 reactions. The effect is stronger for the macrocycles, whose methyl complexes lag behind $(H_2O)_5CrCH_3^{2+}$ by less than an order of magnitude, but the difference increases for the larger alkyls – ethyl and propyl. Further increase in the chain length to butyl and pentyl has little additional effect on the values of the rate constants, Table I.

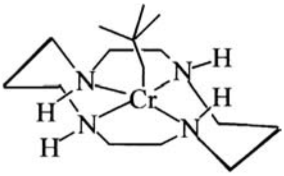
TABLE I

Kinetic data for the reaction of organochromium cations with Hg^{2+} [a]

	k / mol^{-1} dm^3 s^{-1}		
R	$(H_2O)([14]aneN_4)CrR^{2+}$	$(H_2O)([15]aneN_4)CrR^{2+}$ [b]	$(H_2O)_5CrR^{2+}$ [c]
CH_3	$(1.1 \pm 0.1) \times 10^6$	3.1×10^6	1.0×10^7
CH_3CH_2	$(7.7 \pm 0.2) \times 10^2$	2.53×10^3	1.40×10^5
$CH_3CH_2CH_2$	$(5.9 \pm 0.4) \times 10^1$	8.21×10^1	3.50×10^4
$CH_3CH_2CH_2CH_2$	$(3.1 \pm 0.1) \times 10^1$		
$CH_3CH_2CH_2CH_2CH_2$	$(2.7 \pm 0.3) \times 10^1$		
$(CH_3)_2CH$	$(1.15 \pm 0.08) \times 10^{-1}$	4.3×10^{-3}	1.56
$(CH_3)_3CCH_2$	$(8.6 \pm 0.4) \times 10^{-3}$		4.9×10^2
c-C_5H_9	$(1.49 \pm 0.09) \times 10^{-3}$		
c-C_6H_{11}	$(1.26 \pm 0.15) \times 10^{-2}$	1.6×10^{-3}	5.22×10^4
4-$CH_3C_6H_4CH_2$	$(2.29 \pm 0.11) \times 10^3$		
3-$CH_3C_6H_4CH_2$	$(1.66 \pm 0.15) \times 10^3$		
$C_6H_5CH_2$	$(1.43 \pm 0.05) \times 10^3$	1.14×10^3	4.87×10^4
3-$ClC_6H_4CH_2$	$(2.97 \pm 0.09) \times 10^2$		

[a] 25 °C, $[H^+] = 0.25$ mol dm^{-3}, $\mu = 0.5$ mol dm^{-3} ($HClO_4$ + $LiClO_4$). [b] Ref. 4. [c] Ref. 3.

The isopropyl group in the [14]ane series causes a further drop in reactivity, as expected. Surprisingly, however, the neopentyl complex is even slower by a factor of 13. This is different from the aqua series where the trend is reversed and the neopentyl complex reacts more than 300 times faster than the isopropyl complex. This reversal in reactivity seems to be caused by geometric constraints of the macrocycle. The increase in steric bulk at the β-position in the neopentyl complex severely impedes the entry of Hg^{2+} into the pocket defined by the rigid backbone of the macrocycle and secondary N–H bonds, as illustrated below.



Another surprising finding is the effect of the nature of the macrocycle on the reactivity of the isopropyl complex. Contrary to what one might expect on the basis of the larger size and possibly more favorable stereochemistry in the [15]ane complex, $(H_2O)([14]aneN_4)CrCH(CH_3)_2^{2+}$ is almost 30 times

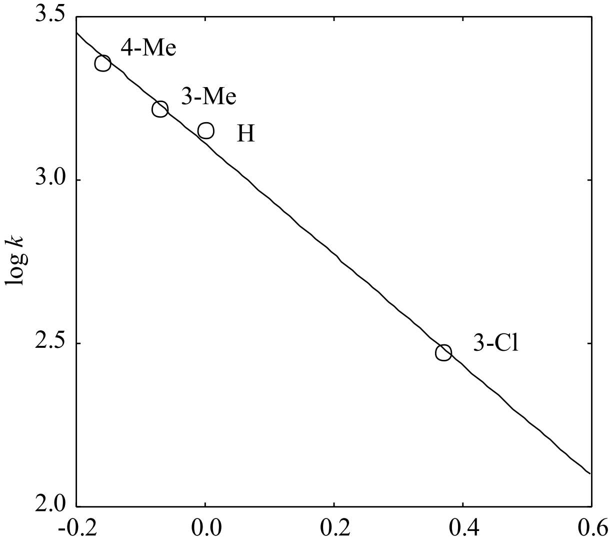


Figure 2. Plot of the logarithm of rate constants against the Hammett sigma values for the reaction of substituted benzyl complexes with Hg^{2+}. The slope gives the reaction constant $\rho = -1.66$.

more reactive. Similar results were observed in the reaction of another secondary alkyl, cyclohexyl. Thus, the fine differences in the geometry of the two macrocycles cause the [15]ane complexes to be more reactive for R = primary alkyl, but less reactive for R = secondary alkyl.

In the series of *m*- and *p*-substituted benzyl complexes, the rate increases as the electron donating properties of the substituents increase. The plot of log *k* *vs.* the Hammett σ value (Figure 2) is linear and yields a negative reaction constant, $\rho = -1.66$, consistent with the proposed electrophilic substitution at carbon. The absolute value is higher than that obtained in the aqua series, –0.62. The higher sensitivity to the substituent of the macrocycles is probably a result of the lower reactivity, which in turn may signal stronger Cr–C bonds. Thermodynamic bond dissociation energies (BDE) are not available, but the homolysis rates of $(H_2O)([15]aneN_4)Cr(CH_2C_6H_4R)^{2+}$,[10] and probably those of the analogous [14]ane complexes, are lower than the rates of the corresponding complexes in the aqua series,[11] as it would be expected if the BDEs were higher for the macrocycles.

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SAŽETAK

Kinetika i mehanizam reakcije između žive(II) i serije makrocikličkih organokromovih kationa

Vjera Butković, Andreja Bakač i James H. Espenson

Prikazani su kinetički podaci za reakciju organokromovih kompleksa $(H_2O)([14]\text{aneN}_4)CrR^{2+}$ s ionima Hg^{2+} ($[14]\text{aneN}_4$ = 1,4,8,11-tetraazaciklotetradekan), koja se odvija elektrofilnom supstitucijom. Konstante brzine reakcije smanjuju se u nizu CH_3 ($1{,}1 \times 10^6$ dm^3 mol^{-1} s^{-1}) > C_2H_5 ($7{,}7 \times 10^2$) > C_3H_7 (59) > 2-C_3H_7 (0,12) > $CH_2C(CH_3)_3$ (0,0086). Kompleksi sa supstituiranim *meta-* i *para-* benzil ligandima zadovoljavaju Hammett-ovu korelaciju s reakcijskom konstantom $\rho = -1{,}66$, što je u skladu s pretpostavkom o elektrofilnoj supstituciji na α-ugljikovu atomu.