3360 Inorg. Chem. 1986, 25, 3360-3367

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

Oxidative and Electrophilic Pathways in the Reactions of Pentaaquo(organo)chromium(2+) Ions with Nitrous Acid[1]

Jon D. Melton, Andreja Bakac,* and James H. Espenson*

Received April 7, 1986

The reactions of HONO with $(H_2O)_5CrR^{2+}$ complexes occur with a 1:1 stoichiometry at rates given by $k[CrR^{2+}][HONO][H^+]$. Values of k range from 0.12 ($R = CH_2Br$) to 1010 $M^{-2}\ s^{-1}$ ($R = p\text{-}CH_2C_6H_4CH_3$). The chromium product is $Cr(H_2O)_6^{3+}$ for R = alkyl, haloalkyl, and aralkyl but the kinetically stable nitrosyl complex $(H_2O)_5CrNO^{2+}$ for R = α-hydroxy- and α-alkoxyalkyl. All of the reactions are believed to proceed by a bimolecular reaction between the nitrosyl cation NO^+ and CrR^{2+}. In the case of the aralkyl complexes, the data are consistent with an electrophilic process; correlations with data in the literature support the assignment of an S_E2 mechanism. The other reactions are best interpreted in terms of electron transfer to form CrR^{3+}. The fate of the latter depends on the nature of the group R. Intramolecular electron transfer for $R = CH_2OH$, CH_2OCH_3, and $CH(CH_3)OC_2H_5$ results in Cr^{2+}, which is scavenged by NO to give $CrNO^{2+}$. The rate constant for the reaction between Cr^{2+} and NO has been independently evaluated as $2.2 \times 10^6\ M^{-1}\ s^{-1}$ by competition methods. All the other CrR^{3+} complexes decompose by homolysis. The free radical so formed reacts with NO to yield RNO.

Introduction

The cleavage of a metal–carbon bond during the reaction of an organometallic complex with an electrophile represents an area of reactivity that has been reviewed recently.[2-5] The characterization of the mechanism is made more difficult by the diverse reaction pathways open to electrophilic reagents, in that electrophiles are also oxidizing agents and Lewis acids.[3,5] Metal–carbon bond cleavage is the rate-limiting step if an electrophilic mechanism operates, whereas bond cleavage will probably occur only at a later stage if the mechanism is defined by another process, such as electron transfer.

An interesting situation is posed by HONO, a reagent that quite often reacts via the nitrosyl cation, NO^+. Because NO^+ can function as both an electrophile and a potent one-electron acceptor, both mechanisms, at least in principle, are open to it. With the resolution of this potential dichotomy as one of our objectives, we thus undertook an investigation of the reactions between $(H_2O)_5CrR^{2+}$ complexes and nitrous acid.

The organochromium cations offer two advantages as substrates: first, they contain but a single metal–carbon bond; second, these paramagnetic cations differ considerably from coordinatively and electronically saturated organometallic reagents. The former feature is advantageous in that kinetic data are free of the complications and ambiguities that can arise from sequential reactions of identical or similar alkyl groups in, e.g., MR_n complexes. The latter feature tends to broaden and rectify the established picture that disfavors unimolecular reactions for the decomposition of stable species; indeed, these organochromium complexes are distinctive in that both heterolytic and homolytic pathways for unimolecular decomposition have been noted.[4]

Certain reactions of the $(H_2O)_5CrR^{2+}$ complexes, such as those with Hg^{2+}[6] and Br_2,[7] have been formulated as electrophilic rather than electron-transfer processes, compatible with their products, kinetics, and stereochemistry. We present here results on reactions between NO^+ and aliphatic CrR^{2+} complexes that cannot be accommodated by an electrophilic mechanism; prior to this, no example of an outer-sphere electron-transfer mechanism for CrR^{2+} complexes was known. The implied reluctance of CrR^{2+} complexes to undergo oxidation does not extend, for example, to organocobaloximes, $RCo(dmgH)_2$. These complexes adopt an electrophilic pathway for Hg(II) reactions,[8-10] whereas their reactions with halogens compete between electrophilic and oxidative processes.[11-14]

Table I. Products of the Reaction of HNO_2 with CrR^{2+}

R	Cr product[a]	organic product
CH_2OH	$CrNO^{2+}$	CH_2O[b]
CH_2OCH_3	$CrNO^{2+}$	CH_2O,[b] CH_3OH[c]
$CH(CH_3)OCH_2CH_3$	$CrNO^{2+}$	$[CH_3CHO, CH_3CH_2OH]$[d]
CH_3	Cr^{3+}	$[CH_2O]$[d]
CH_2CH_3	Cr^{3+}	CH_3CHO[c]
$CH(CH_3)_2$	Cr^{3+}	CH_3COCH_3[c]
$CH_2C_6H_5$	Cr^{3+}	$[HON{=}CHPh]$[d]
$4\text{-}CH_2C_5H_4NH^+$	Cr^{3+}	$HON{=}CHpyH^+$[a]

[a] Determined by UV-visible spectroscopy. [b] Determined by the chromotropic acid method. [c] Determined by GC. [d] The organic product was not determined for this reaction, but the presumed product is given in brackets.

The difficulty of providing a general distinction between electrophilic and oxidative pathways has been noted.[5,15,16] Aside from one early report concerning (4-pyridylmethyl)chromium(2+) ion,[17] to our knowledge, no reports on these reactions have appeared. We also note the recent report[18] of NO^+ insertion into the chromium–methyl bond of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$, a reaction that shares certain features with this chemistry.

Results

Stoichiometry and Products. Except for one instance where O_2 was deliberately added, the reactions were examined under rigorously anaerobic conditions. In every case the organochromium cations reacted completely with nitrous acid. The reactions are complete typically in a few minutes or less, except

---

(1) Based in part on the Ph.D. thesis of J.D.M., Iowa State University, 1986.
(2) Johnson, M. D. *Rec. Chem. Prog.* **1970**, *31*, 143.
(3) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57.
(4) Espenson, J. H. *Adv. Inorg. Bioinorg. React. Mech.* **1982**, *1*, 1.
(5) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapters 17–18.
(6) Leslie, J. P., II; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839.
(7) (a) Espenson, J. H.; Williams, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 1008. (b) Espenson, J. H.; Chang, J. C. *J. Chem. Soc., Chem. Commun.* **1974**, 233. (c) Espenson, J. H.; Samuels, B. J. *J. Organomet. Chem.* **1976**, *113*, 143.
(8) Adin, A.; Espenson, J. H. *J. Chem. Soc. D* **1971**, 653.
(9) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166.
(10) Fritz, H. L.; Espenson, J. H.; Williams, D. A.; Molander, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 2378.
(11) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S.; Topich, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1606.
(12) Magnuson, R. H.; Halpern, J.; Levitin, I. Ya.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1978**, 44.
(13) Anderson, S. N.; Ballard, D. H.; Chrzastowski, J. Z.; Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1972**, 685.
(14) Dreos, R.; Tauzher, G.; Marsich, N.; Costa, G. *J. Organomet. Chem.* **1975**, *92*, 227.
(15) Halpern, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 274.
(16) Vol'pin, M. E.; Levitin, I. Ya.; Sigan, A. L.; Nikitaev, A. T. *J. Organomet. Chem.* **1985**, *279*, 263.
(17) Bartlett, E. H.; Johnson, M. D. *J. Chem. Soc. A* **1970**, 523.
(18) Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 317.

0020-1669/86/1325-3360$01.50/0

for those of the haloalkyl complexes, $CrCH_2X^{2+}$, which occur very slowly. The stoichiometry of the reaction between $(H_2O)_5CrCH_2OCH_3^{2+}$ and HONO was determined by a spectrophotometric titration. A plot of the absorbance at 386 nm (λ_{max} for this complex; ϵ 404 M^{-1} cm^{-1}) vs. the concentration ratio is shown in Figure 1. The end point break defining $\Delta[CrR^{2+}]:\Delta[HONO]$ occurs at a ratio of (1.05 ± 0.02):1.

The inorganic products were separated by cation-exchange chromatography on Sephadex SP-C25 resin. The product was exclusively the well-known[19-21] nitrosyl complex $(H_2O)_5CrNO^{2+}$ in some reactions and exclusively $Cr(H_2O)_6^{3+}$ in others. Those organochromium complexes with α-OH and α-OR groups produce $CrNO^{2+}$ quantitatively and only traces of Cr^{3+}. This set of reactants consists of the $(H_2O)_5CrR^{2+}$ complexes with R = CH_2OH, CH_2OCH_3, and $CH(CH_3)OC_2H_5$. The other organochromium complexes—alkyls, haloalkyls, and benzyls—formed exclusively $Cr(H_2O)_6^{3+}$. The $CrNO^{2+}$ complex is *completely* stable under the reaction conditions, decomposing <5% in 5 h.[20] It is not formed from any known reaction of $Cr(H_2O)_6^{3+}$ with HONO or NO.

The report[17] that 4-pyridylmethyl complex formed 4-pyridecarbaldoxime was confirmed. The alkyl complexes with R = ethyl and 2-propyl gave acetaldehyde and acetone, respectively, as the major organic products. The methoxymethyl complex produced methanol (GC) and formaldehyde (chromotropic acid analysis,[22] 87% yield). These results are summarized in Table I. The three reaction types are illustrated in eq 1–3 for typical members of each family.

$$(H_2O)_5CrCH_2OH^{2+} + HONO = (H_2O)_5CrNO^{2+} + HCHO + H_2O \quad (1)$$

$$(H_2O)_5CrC_2H_5^{2+} + HONO + 2H^+ + H_2O = Cr(H_2O)_6^{3+} + CH_3CHO + NH_3OH^+ \quad (2)$$

$$(H_2O)_5CrCH_2C_5H_4NH^{3+} + HONO + H^+ = Cr(H_2O)_6^{3+} + HON{=}CHC_5H_4NH^+ \quad (3)$$

Kinetics. Rate constants were evaluated with nitrous acid and hydrogen ions in considerable excess over the organochromium complex. Typical concentrations were $[CrR^{2+}]$ = 0.03–0.9 mM, [HONO] = 0.3–20 mM, and $[H^+]$ = 0.01–0.10 M. The data were collected at constant temperature (23.4 °C) and a constant ionic strength of 0.10 M, maintained with perchloric acid and lithium perchlorate.

The reactions with nitrous acid occur much more rapidly than the "spontaneous" decay reactions of CrR^{2+}. The latter consist of the parallel and competing unimolecular acidolysis and homolysis reactions,[4,23] eq 4 and 5. The pseudo-first-order rate

$$(H_2O)_5CrR^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + RH \quad (k_A) \quad (4)$$

$$(H_2O)_5CrR^{2+} + H_2O \rightarrow Cr(H_2O)_6^{2+} + R^\bullet \quad (k_H) \quad (5)$$

constants[24] for the nitrous acid reactions were corrected for these side reactions by use of the known rate constants; $k_{cor} = k_\psi - k_A - k_H$. These corrections, necessary for precise evaluation of the data, were for the most part quite minor, often 1–10% of k_ψ or even less.

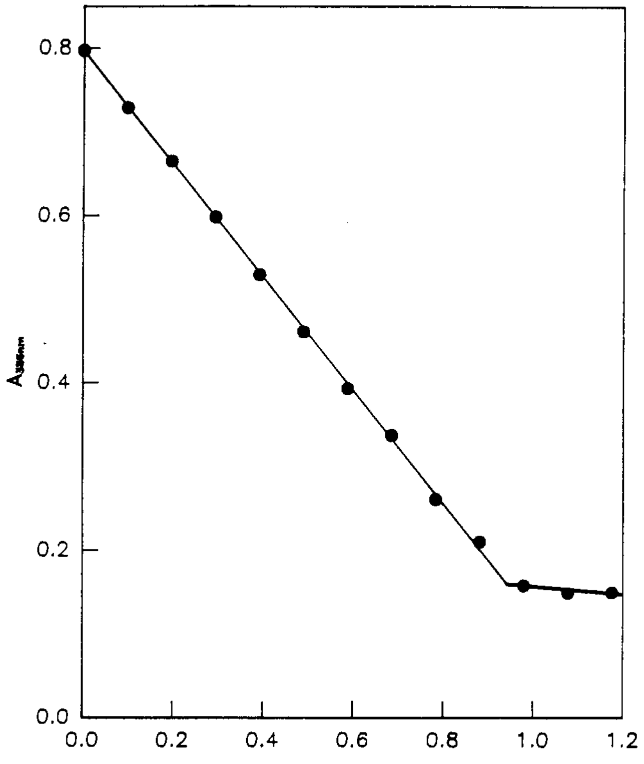

Figure 1. Absorbance at 386 nm (measured in a cell with a 2-cm optical path) decreasing after each incremental addition of a solution of nitrous acid to a solution of $CrCH_2OCH_3^{2+}$, initially 9.88 × 10^{-4} M, at $[H^+]$ = 1.0 M under anaerobic conditions. The reaction was allowed to proceed to stable absorbance reading (for about 30–60 s) after each increment before the absorbance measurement was taken. The end point defines the (nearly) 1:1 stoichiometric consumption of the reactants.

Table II. Rate Constants for the Reactions of Nitrous Acid with Organochromium(III) Complexes[a,b]

R	$k/(M^{-2}\ s^{-1})$	$k'/(M^{-1}\ s^{-1})$
CH_2OH	745 ± 26	5.1 ± 1.8
CH_2OCH_3	330 ± 6	1.1 ± 0.4
$CH(CH_3)OCH_2CH_3$	45 ± 2	2.5 ± 0.1
CH_3	38.8 ± 0.8	0
CH_2CH_3	87 ± 5	0.6 ± 0.4
$CH_2CH_2CH_3$	15.1 ± 0.8	0
$CH(CH_3)_2$	17.9 ± 0.5	0.076 ± 0.027
CH_2Cl	0.46 ± 0.02	0
CH_2Br	0.12 ± 0.01	0.005 ± 0.001
CH_2I	0.247 ± 0.006	0
p-$CH_2C_6H_4CH_3$	1010 ± 31	0
$CH_2C_6H_5$	956 ± 56	13 ± 4
p-$CH_2C_6H_4CF_3$	241 ± 2	0
p-$CH_2C_6H_4CN$	92 ± 3	0
4-$CH_2C_5H_4NH^+$	0.561 ± 0.005	0

[a] T = (23.4 ± 0.1) °C; I = 0.10 M. [b] Rate constants k and k' defined by eq 6.

Values of the (corrected) pseudo-first-order rate constants[24] increase with both [HONO] and $[H^+]$. At constant $[H^+]$, k_{cor} is directly proportional to [HONO] for every complex. This is illustrated in Figure 2 for the reaction of $CrCH_2OH^{2+}$. To establish the algebraic form of the dependence on $[H^+]$, it is convenient to examine the function $k_{cor}/[HONO]$, which is constant at a given $[H^+]$. Plots of $k_{cor}/[HONO]$ vs. $[H^+]$ are linear. The extrapolated line usually passes through the origin within experimental error; in several cases, however, a small but statistically significant intercept was evaluated. Typical plots are shown in Figure 3. The rate law that will accommodate all of the kinetic data is given by eq 6. The least-squares rate constants k (and,

$$-d[CrR^{2+}]/dt = \{k[H^+] + k'\}[HONO][CrR^{2+}] \quad (6)$$

where required, k') are summarized in Table II. The satisfactory fit of the kinetic data to this expression is evident from the graphs depicted.

The third-order term in the rate law represents the path that carries the bulk of the reaction of all of the compounds. Even in the case of $CrCH(CH_3)OC_2H_5^{2+}$, in which the contribution of the $[H^+]$-independent term represented by k' is the greatest, at 0.1 M H^+ <36% of the reaction proceeded along the k' pathway. For all the other complexes the contribution of the k' pathway

---

(19) Ardon, M.; Herman, J. *J. Chem. Soc.* **1962**, 507.
(20) Armor, J. N.; Buchbinder, M. *Inorg. Chem.* **1973**, *12*, 1086.
(21) Moore, P.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1966**, *5*, 223.
(22) Bricker, C. E.; Johnson, H. R. *Anal. Chem.* **1945**, *17*, 40.
(23) Espenson, J. H. *Prog. Inorg. Chem.* **1983**, *30*, 189.
(24) The thesis cited[1] gives the rate constant and concentrations from each experiment.

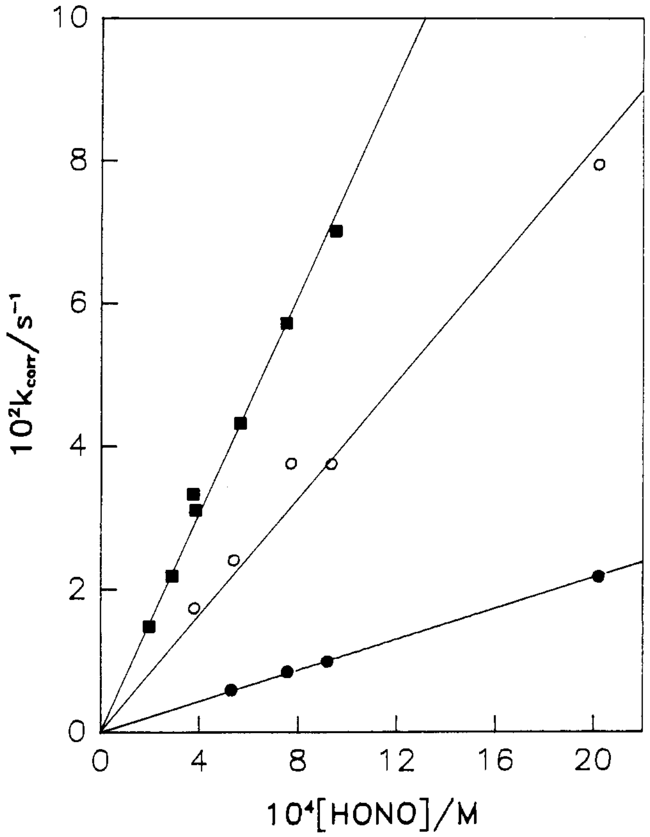

Figure 2. Pseudo-first-order rate constant (after correction for the relatively minor contributions from the acidolysis and homolysis reactions of the CrR^{2+} complexes) varying linearly with [HONO] at constant [H^+]. Data at 23.4 °C and $\mu = 0.10$ M are shown for $CrCH_2OH^{2+}$ at different [H^+]: 0.01 M (filled circles), 0.05 M (open circles), 0.10 M (squares).

was much less, typically <10%. This also means that values k' are relatively imprecise even for complexes in which the second-order term may be a "real" pathway (those, for example, in which the value of k' exceeds zero by at least three standard deviations). Furthermore, it is always possible that k' may be only an artifact, as might arise from a small systematic error in one concentration or from a minor deviation from ideal solution relationship between activity and concentration. For those reasons we shall focus our attention on the chemistry of third-order pathway: it is common to all of the reactants, it is the major if not sole pathway, and accurate rate constants for it have been determined.

Is Cr^{2+} an Intermediate? This possibility was tested by conducting the reaction between $CrCH_2OCH_3^{2+}$ and HONO in the presence of either $(NH_3)_5CoBr^{2+}$ or O_2. These reagents react with neither of the starting materials, but both react rapidly with $Cr(H_2O)_6^{2+}$.[25-28] When the cobalt complex was present, Co^{2+} was formed in a yield that corresponded to 58% of the possible quantity of Cr^{2+}. Kinetic determinations in the presence of $(NH_3)_5CoBr^{2+}$ showed that it had no effect on the rate constant, which confirms its role of a scavenger for Cr^{2+} in a reaction that occurs after the rate-limiting step.

When the same reaction was carried out in an oxygen-saturated solution, no $CrNO^{2+}$ could be detected by using the same ion-exchange method as before. The major product seen on Sephadex column was $Cr(H_2O)_6^{3+}$. Very little, if any, Cr^{III} dimer[29] was observed, which is understandable since $[O_2] = 1.05 \times 10^{-3}$ M whereas Cr^{2+} is at steady-state concentration. Some of the Cr^{3+} formed may have resulted from CrO_2^{2+} being reduced by the resin.

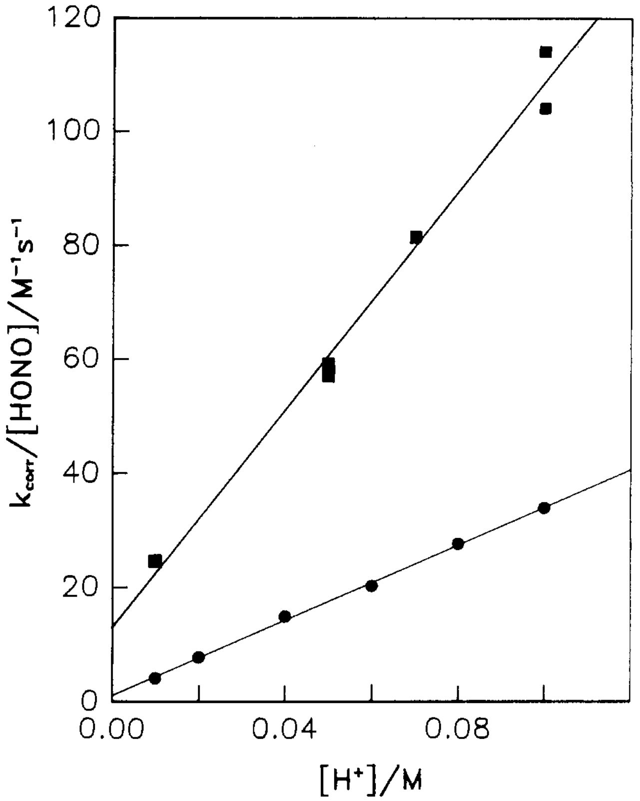

Figure 3. Apparent second-order rate constants for reactions between organochromium ions and nitrous acid vary linearly with [H^+], showing an [H^+]-independent intercept that is either very small or zero. Data are shown for $CrCH_2OCH_3^{2+}$ (circles) and $CrCH_2C_6H_5^{2+}$ (squares). The lines drawn throught the data correspond to the least-squares parameters according to eq 6.

These experimental results thus provided an *affirmative* answer to the question used to introduce this section. This finding applies, of course, only to those reactions that, if unperturbed, yield $CrNO^{2+}$. The possibility that Cr^{2+} might be formed during the reaction of this group of complexes was considered for the following reasons: (a) If $Cr(H_2O)_6^{3+}$ were formed directly, it would not be converted to the nitrosyl product under the reaction conditions. (b) The nitrosyl product was obtained only in those cases where the free radical is itself strongly reducing; these are the radicals derived from alcohols or ethers, which have an OH or OR group on the α-carbon. (c) $Cr(H_2O)_6^{2+}$ is known to react with both HONO[30] and NO[19-21] to yield $CrNO^{2+}$.

Kinetics of the Reaction between $Cr(H_2O)_6^{2+}$ and NO. The clear implication of the results in the preceding section is that NO as well as Cr^{2+} is formed as an intermediate in the reactions of a certain subset of the organochromium complexes with nitrous acid. If so, the stable nitrosyl product would result from a reaction between the two intermediate species (eq 7). Quantitative formation of $CrNO^{2+}$ indicates that this is a rapid and efficient reaction. Indeed, the literature suggests that it is, although no kinetic data are given.[19,20] The reason for the lack of quantitative data is very probably the high rate and the relatively small absorbance changes that accompany it. The latter is a problem especially at the low concentrations that would be required to lower the rate into the range accessible by the stopped-flow method.

$$Cr(H_2O)_6^{2+} + NO \rightarrow (H_2O)_5CrNO^{2+} + H_2O \qquad (7)$$

Indeed, we confirmed that this reaction is very rapid, but were unable to measure its rate directly. We determined k_7 indirectly

---

(25) Taube, H.; Rich, R. L. *J. Am. Chem. Soc.* **1954**, *76*, 2103.

(26) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766.

(27) Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15.

(28) Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145.

(29) (a) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. (b) Kolaczkowski, R.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322. [The μ-$(OH)_2$ species characterized from this reaction is now recognized as being distinct from the μ-oxo ion of the same charge, $(H_2O)_5CrOCr(H_2O)_5^{4+}$: Holwerda, R. A.; Peterson, J. S. *Inorg. Chem.* **1980**, *19*, 1775. Johnson, R. F.; Holwerda, R. A. *Inorg. Chem.* **1981**, *22*, 2942.]

(30) Ogino, H.; Tsukahara, K.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 308.

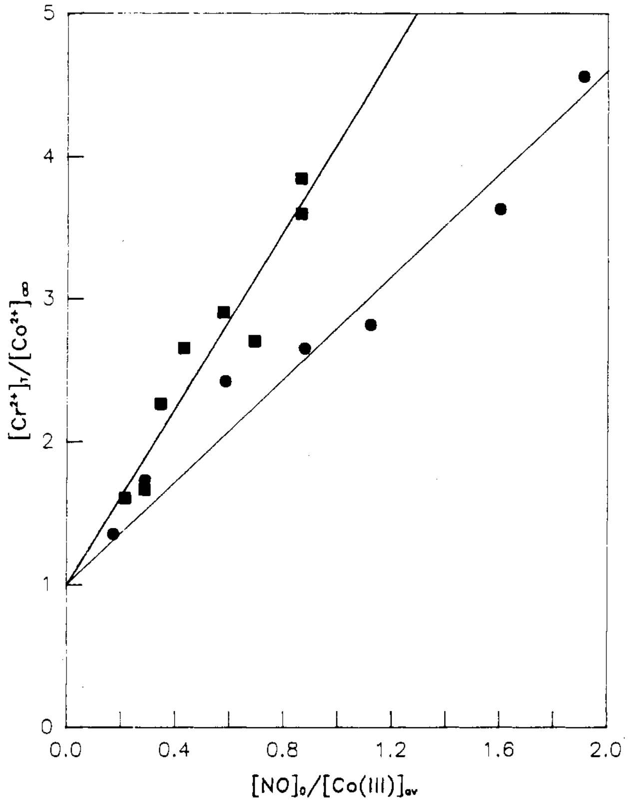

Figure 4. Analysis of the results from competition experiments designed to measure the rate of formation of $CrNO^{2+}$ from Cr^{2+} and NO (eq 7) in competition with the known reactions of Cr^{2+} with $(NH_3)_5CoBr^{2+}$ (k_{Br}, circles) and $(NH_3)_5CoCl^{2+}$ (k_{Cl}, squares). The data are plotted as in eq 8.

by using $(NH_3)_5CoBr^{2+}$ and $(NH_3)_5CoCl^{2+}$ (whose rate constants for reaction with Cr^{2+}, k_X, are known[26]) to compete with NO for Cr^{2+}. The data[24] are shown in Figure 4, which depicts an analysis of the results according to eq 8, where $[Cr^{2+}]_T$ represents the total concentration of Cr^{2+} added in a given experiment.

$$\frac{[Cr^{2+}]_T}{[Co^{2+}]_\infty} = 1 + \frac{k_7}{k_X}\frac{[NO]_0}{[Co(NH_3)_5X^{2+}]_{av}} \tag{8}$$

The least-squares slopes of the lines give the ratios k_7/k_{Br} = 1.8 ± 0.1 and k_7/k_{Cl} = 3.0 ± 0.2. Thus, the values of k_7 are (2.5 ± 0.7) × 10^6 and (1.8 ± 0.3) × 10^6 M^{-1} s^{-1} or an average value of 2.2 × 10^6 M^{-1} s^{-1}. Although the two sets of data yielded somewhat different values for k_7, one cannot conclude from that that the values are significantly different or that the model implicit in the design of the experiments is faulty. It should be noted that the ratio of the slopes yields a value for the ratio of the rate constants for the cobalt complexes with chromium(II), k_{Br}/k_{Cl}. The value so obtained, 1.67 ± 0.14, agrees with the value of 1.44 ± 0.22 reported from competition experiments involving various cobalt(III) complexes,[31] whereas it is a little smaller than the ratio of the independently determined[26] values, 2.3 ± 0.8.

Discussion

The diversity of products found for the different groups of organochromium cations is one argument for a change in mechanism for the different groups. Further support for this comes from an analysis of steric and electronic effects, as described subsequently. On the other hand, the common rate law for all of the reactions does suggest that in some respects, at least, the reactions proceed along a common pathway. The discussion centers on both issues.

Common Intermediate and Reactant: The Nitrosyl Cation. In every instance the rate law term that represents the sole or major pathway shows a first-order $[H^+]$ dependence. This points to a protonation prior to the rate-limiting step or in the transition state. No protonation reaction of the organochromium cations is known, and no other reaction of CrR^{2+} aside from direct protonolysis[4] is accelerated by $[H^+]$. On the other hand, an analogous acid-catalyzed kinetic term is often encountered in nitrous acid reactions.[32-34] One interpretation is that the reaction might proceed by way of the protonated species H_2ONO^+ (the "nitrous acidium ion"). Although it is a proposed intermediate in nitrosation reactions, spectroscopic evidence in support of it has not been obtained.[33] There is good reason, on the other hand, to account for the findings in terms of a nitrosonium cation that is formed in the equilibrium reaction of eq 9.

Table III. Bimolecular Rate Constants (M^{-1} s^{-1}) for Reactions of $(H_2O)_5CrR^{2+}$ Complexes with NO^+ and with the Electrophiles Hg^{2+}, Br_2, and I_2

complex	$10^{-8}k_{NO^+}$[a]	$k_{Hg^{2+}}$[b,c]	k_{Br_2}[b,d]	k_{I_2}[b,d]
CH_2OH	25	2.28 × 10^2		
CH_2CH_3	11	9.05 × 10		
$CH(CH_3)OC_2H_5$	1.5	0.535/$[H^+]$[e]		
CH_3	1.2	1.0 × 10^7	2.1 × 10^6	8.5 × 10^4
CH_2CH_3	2.9	1.40 × 10^5	4.9 × 10^5	
$CH_2CH_2CH_3$	5.0	3.50 × 10^4	6.2 × 10^5	
$CH(CH_3)_2$	0.60	1.56	1.7 × 10^4	
CH_2Cl	0.015	5.90 × 10^{-1}	1.06	6.3 × 10^{-1}
CH_2Br	0.004	4.68 × 10^{-1}	3.5 × 10^{-1}	
CH_2I	0.0082		7.13	
p-$CH_2C_6H_4CH_3$	33.6	5.22 × 10^4		4.76 × 10^3
$CH_2C_6H_5$	31.8	4.87 × 10^4	8.3 × 10^5	4.2 × 10^3
p-$CH_2C_6H_4CF_3$	8.0	2.10 × 10^4	1.55 × 10^5	1.39 × 10^3
p-$CH_2C_6H_4CN$	3.1	1.64 × 10^4	9.6 × 10^4	1.06 × 10^3
4-CH_2pyH^+	0.019	5.0 × 10^2	1.1 × 10^3	

[a] At 23.4 °C, μ = 0.10 M, calculated from values of *k* (Table II) according to eq 9. [b] At 25.0 °C, μ = 0.50 M, ref 6. [c] References 4, 6, 41. [d] References 4, 7. [e] $CrCH(CH_3)OC_2H_5^{2+}$ reacts with Hg^{2+} by an electron-transfer mechanism. All other organochromium complexes listed in this table react with Hg^{2+} by an S_E2 mechanism. (See ref 41.)

$$HONO + H^+ \rightleftarrows H_2O + NO^+ \tag{9}$$

The equilibrium constant for this reaction, K_9, has the value 3 × 10^{-7} M^{-1}.[35] Clearly, this very unfavorable reaction produces a minute proportion of NO^+ as compared to HONO even at the highest $[H^+]$ concentration. Nonetheless, we suggest that NO^+ is the species that reacts with CrR^{2+} complexes. In that event, the rate constant for the bimolecular reaction between CrR^{2+} and NO^+ will, whatever its mechanism, be related to the third-order rate constant *k* of eq 6 according to

$$k_{NO^+} = k/K_9 \tag{10}$$

The values of k_{NO^+} are given in Table III. Many of the bimolecular rate constants, but not all, are at or near the diffusion-controlled limit. Under the circumstances of the experiments, the reaction between CrR^{2+} and NO^+ is always the rate-limiting step, not the formation of NO^+ in eq 9. This is so (a) because the reactions show a first-order dependence on $[CrR^{2+}]$ and (b) because with k_9 = 6.2 × 10^2 M^{-1} s^{-1} [36] (and, therefore, k_{-9} = 2 × 10^9 s^{-1}) it will always be true that $k_{-9} \gg k_{NO^+}[CrR^{2+}]$.

The nitrosyl cation is both a better oxidant[37,38] and a better electrophile[33] than HONO itself. This explains why the NO^+ reactivity predominates despite the unfavorable equilibrium

---

(31) Moore, M. C.; Keller, R. N. *Inorg. Chem.* **1971**, *10*, 747.

(32) Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1.

(33) Stedman, G. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 143.

(34) Beck, M. T.; Dozsa, L.; Szilassy, I. *J. Ind. Chem. Soc.* **1974**, *51*, 6.

(35) Bayliss, N. S.; Dingle, R.; Watts, D. W.; Wilkie, R. J. *Aust. J. Chem.* **1963**, *16*, 933.

(36) Benton, D. J.; Moore, P. *J. Chem. Soc. A* **1970**, 3179.

(37) A standard reduction potential of $E°$ = 1.21 V is estimated for the NO^+/NO couple on the basis of the value[32-35] of the equilibrium constant K_9 and the value[38] of $E°$ = 0.842 V for the half-reaction HONO + H^+ + e^- = NO + H_2O.

(38) Ram, M. S.; Stanbury, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 8136.

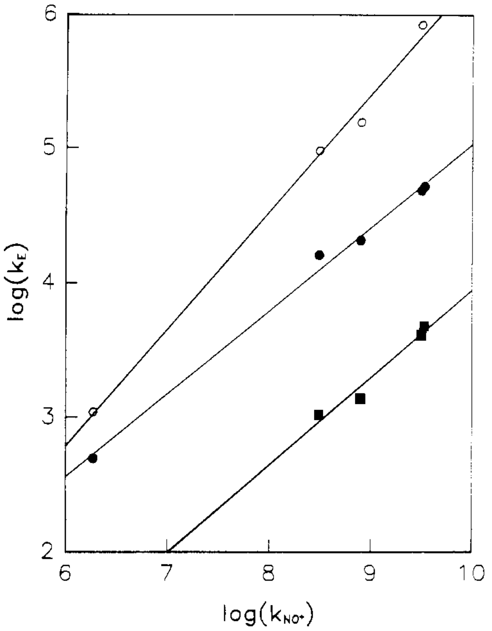

Figure 5. Correlations of the rate constants k_{NO^+} for reactions of organochromium cations containing aralkyl groups with data for reactions known to proceed by bimolecular electrophilic substitution. Data are shown for Hg^{2+}[6] (filled circles), Br_2[7] (open circles), and I_2[7b] (squares).

producing it. Since NO^+ can react both as oxidizing agent and as an electrophile, it is able to adopt the path most favored for a given complex.

Aralkylchromium Complexes: An S_E2 Mechanism. The first case we consider is the (4-pyridylmethyl)chromium(2+) ion. The product originally observed and confirmed again in this work is the aldoxime, the more stable tautomer of the RNO product that would arise from direct electrophilic attack of NO^+ at the α-carbon atom. The benzylchromium(2+) ion and all of the ring-substituted derivatives appear to react analogously. Our standard in these cases consists of kinetic comparisons with other reactions of organochromium(2+) cations where evidence points to an S_E2 mechanism. The electrophiles (E) used for comparison are Hg^{2+},[6] Br_2,[7] and I_2.[7b]

One correlation the data for the reactions with HONO show is seen from plots of log (k_{NO^+}) vs. log (k_E). Figure 5 shows these plots for the three series of reactions. There is a reasonable correlation in every case, consistent with a common mechanism.

The values of k_{NO^+} can also be examined by the linear free-energy correlation found for reactions that follow an S_E2 mechanism. The Hammett equation has proved useful in such circumstances.[7b,9] The data are shown in Figure 6 as a plot of log (k_{NO^+}) vs. the Hammett substituent constant σ. The correlation of the data with this relation is satisfactory although not as good as in some other cases, as represented by the correlation coefficient $r = 0.96$. The slope of the line gives a reaction constant ρ of -1.26. This compares with similarly negative values for other electrophiles: Hg^{2+}, -0.62 (also illustrated in the figure); Br_2, -1.29; I_2, -0.81; CH_3Hg^+, -0.85. The negative sign and the magnitude of ρ are, indeed, consistent with the mechanism being analogous to the others.

As discussed subsequently, the kinetic evidence supports a change to an electron-transfer mechanism for the simple alkyl complexes. If so, one asks why the methyl complex, with a rate constant found to lie *below* the diffusion-controlled limit, does not adopt the S_E2 mechanism: After all, the methyl complex does react with the other electrophiles (Hg^{2+}, etc.) *more rapidly* than the aralkyl complexes do. Because it does not, we suggest that the electrophilic pathway for the reactions of NO^+ with the aralkyl complexes is favored by a further interaction. It is likely that NO^+, a π-acid, interacts with the phenyl ring of the benzylchromium ion.

This type of interaction has been proposed to account for the rates of N-nitrosation of aromatic amines being larger than for aliphatic amines and to account for certain substituent effects.[39a,b] A π complex between NO^+ and benzene has been detected[39c] in the gas phase. The π-bound NO^+ could then attack the α-carbon of the organochromium ion, displacing Cr^{3+}, in an electrophilic process. This interaction would lower the energy of the activated complex, favoring the electrophilic pathway for the benzyl derivatives.

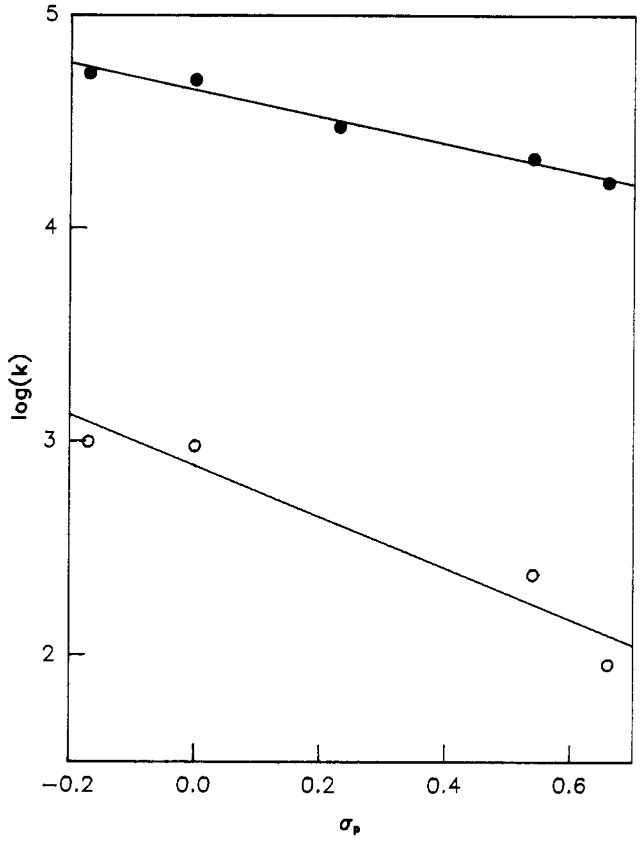

Figure 6. Hammett correlations of kinetic data for the reactions of aralkylchromium(2+) ions with nitrous acid (open circles), as compared with a similar treatment for the mercury(II) ion reactions (filled circles).

Alkyl and Substituted-Alkyl Complexes: Evidence for an Electron-Transfer Mechanism. The correlation between k_{NO^+} and k_E illustrated in Figure 5 for the aralkyl complexes fails if one attempts to extend it to the alkylchromium(2+) ions. This argues for a different mechanism.

A striking decrease in reactivity is noted for electrophilic reactions along a series of alkyl groups—methyl, ethyl, and 2-propyl—in which the extent of steric hindrance increases dramatically. For example, the rate constants for Hg^{2+} are 1×10^7, 1.4×10^5, and $1.6\ M^{-1}\ s^{-1}$, respectively. The rate constants for NO^+, on the other hand, vary but little in this series (the third-order rate constants k of eq 6 are 38.8, 87, and $17.9\ M^{-2}\ s^{-1}$). The lack of a parallel suggests a different mechanism. The insensitivity of the values for the NO^+ reactions implies a transition state lacking a strong interaction between the reactants. An electron-transfer process satisfies these criteria.[2-7]

An additional approach to validating an electron-transfer mechanism for the alkyl complexes was sought. The group of alkyl and haloalkyl complexes constitutes a series in which steric and electronic effects vary markedly. To consider a correlation of all the members would be to intermingle kinetic effects arising from both factors. On the other hand, the lack of strong and regular steric effect among the alkyl complexes has already been noted. Assuming the same insensitivity to steric influences applies to other complexes, it does appear that an informative correlation can be attempted by considering the electronic factors alone. To minimize

---

(39) (a) Challis, B. C.; Ridd, J. H. *J. Chem. Soc.* **1962**, 5208. (b) de Fabrizio, E. c. R.; Kalatzis, E.; Ridd, J. H. *J. Chem. Soc. B* **1966**, 533. (c) Reents, W. D., Jr.; Freiser, R. S. *J. Am. Chem. Soc.* **1980**, *102*, 271.

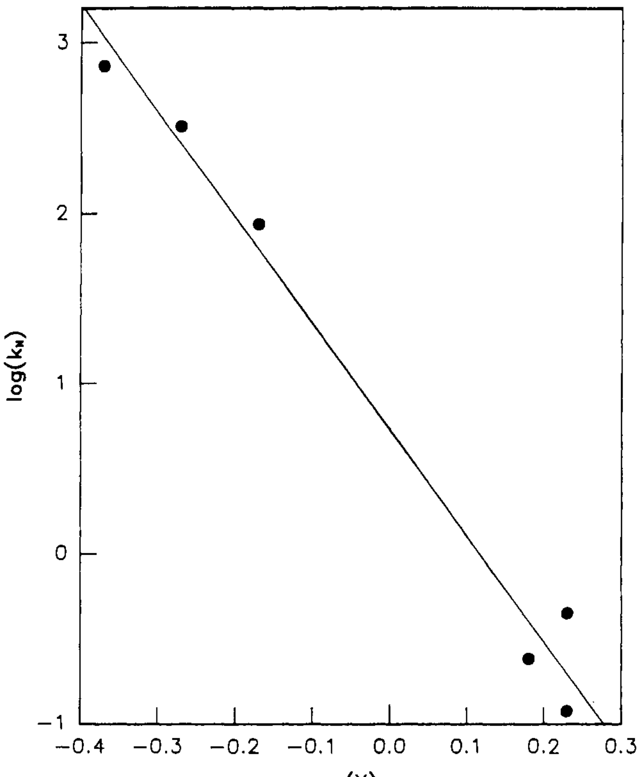

Figure 7. Attempted LFER correlation for $(H_2O)_5CrCH_2Y^{2+}$ complexes, in a plot of log *k* vs. the Hammett substituent parameter. The complexes with Y = CH_3, OH, OCH_3, Cl, Br, and I are included.

whatever influence steric factors may have, however, we consider just the complexes in the series $(H_2O)_5Cr{-}CH_2Y^{2+}$, where Y consists of groups of roughly the same size. This correlation thus employs the complexes with Y = Me, OH, OMe, Cl, Br, and I. As a measure of the inductive effect of each substituent, we use simply the same Hammett σ parameter that applies to para-substituted phenyl rings. These complexes differ by some 4 orders of magnitude in reactivity; an adequate but not superb correlation is noted, as depicted in Figure 7 in a plot of log *k* vs. $\sigma_p(Y)$. The fact that the rate changes so sharply and so regularly along this series in which Y groups of appreciably different electron-attracting ability are employed lends credence to the notion that the reaction rate is controlled by a process in which electron transfer is a critical aspect.

Other Aliphatic Organochromium Ions: Detection of Intermediates. The organochromium complexes with the reducing alkyl groups to some extent constitute a class apart from the others. These are the complexes with R = CH_2OH, CH_2OCH_3, and $CH(CH_3)OC_2H_5$. These are the only complexes whose reactions with HONO lead to the nitrosylchromium complex. The formation of $CrNO^{2+}$ would be difficult to explain in terms of electrophilic attack at the site of greatest electron density, i.e., the α-carbon atom, since that mechanism would result in the substitutionally inert complex $Cr(H_2O)_6^{3+}$. Other options are to suggest that NO^+ attacks at the metal center, despite the constitution of the complex, or that the reaction proceeds by outer-sphere electron transfer. Indeed, the latter is supported by the LFER correlation of these rates along with others in the series of substituted-alkyl complexes.

As a further test, we note that if electron transfer does provide the reaction mechanism, it must occur in a way that leads to $CrNO^{2+}$, which is formed quantitatively. Moreover, there must be something special about this group of complexes or their mechanism, since they are the only ones yielding $CrNO^{2+}$. Experimental results cited earlier were obtained to show that addition of $(NH_3)_5CoBr^{2+}$ or O_2—reagents known to react rapidly with $Cr(H_2O)_6^{2+}$—reduced or eliminated $CrNO^{2+}$ production. In such instances other products were obtained that are consistent with Cr_{aq}^{2+} being formed as a reaction intermediate. One suggestion, illustrated for the methoxymethyl complex, is shown in Scheme I.

Scheme I

$$HONO + H^+ \rightleftarrows H_2O + NO^+ \qquad \text{(I-1)}$$

$$NO^+ + CrCH_2OCH_3^{2+} \rightarrow NO + (H_2O)_5CrCH_2OCH_3^{3+} \qquad \text{(I-2)}$$

$$(H_2O)_5CrCH_2OCH_3^{3+} \xrightarrow{H_2O} Cr_{aq}^{2+} + HOCH_2OCH_3 + H^+ \qquad \text{(I-3)}$$

$$Cr^{2+} + NO \rightarrow CrNO^{2+} \qquad \text{(I-4)}$$

$$HOCH_2OCH_3 \rightarrow HCHO + CH_3OH \qquad \text{(I-5)}$$

Although written for the one complex indicated, the mechanism shown in Scheme I can be made directly applicable to the other two cases. The formation of the nitrosyl chromium product is, according to this scheme, a result of the independenty known reaction between Cr^{2+} and NO. The kinetics of that step, I-4, have been investigated independently. The reaction between Cr^{2+} and NO, with a rate constant of 2.2×10^6 M^{-1} s^{-1}, occurs sufficiently rapidly to be a suitable step for inclusion in this proposal.

The oxidation of the organochromium complex is precisely analogous to the mechanism proposed for the oxidation of organocobalt complexes by the outer-sphere reagent $IrCl_6^{2-}$.[15] The tendency of this particular group of organochromium cations to adopt electron transfer over electrophilic mechanisms has been noted previously. Their reactions with Cu^{2+} and Fe^{3+} proceed by electron transfer.[40] The same is true also of their reactions with Hg^{2+}, although in that case the transition from an S_E2 mechanism in the case of the less sterically crowded complexes $CrCH_2OH^{2+}$ and $CrCH_2OCH_3^{2+}$ to an electron-transfer process for the others should also be noted.[41] Indeed, the parallel situation occurs here to some extent, since it is necessary to postulate two different mechanisms—electrophilic substitution (aralkyl complexes) and electron transfer (substituted alkyls)—to account for the full range of results obtained. Note that *free* Cr_{aq}^{2+} and NO are released in the electron-transfer reaction, since it is their *subsequent* combination to form $CrNO^{2+}$ in eq 7 that can be interfered with by the reagents added to trap Cr^{2+}.

Unified Reaction Mechanism. The data point to an electron-transfer process for all of the substituted alkyls, despite the different products obtained (Cr_{aq}^{3+} vs. $CrNO^{2+}$) and despite the evidence for Cr^{2+} and NO intermediates in only some of the reactions. These facts can be reconciled by a mechanism in which the product of the single electron-transfer reaction, $(H_2O)_5CrR^{3+}$, reacts along different pathways, depending on the nature of the group R. Consider that the reaction between NO^+ and $(H_2O)_5CrR^{2+}$ yields, within the solvent cage, [NO + $(H_2O)_5CrR^{3+}$]. Depending on the nature of the alkyl group, the oxidized organochromium complex can undergo either intramolecular electron transfer (eq I-3) or dissociation to Cr^{3+} and R. The former process dominates with strongly reducing alkyl groups (CH_2OH, CH_2OCH_3, $CH(CH_3)OC_2H_5$). The sequence is completed by the reaction of NO with the Cr^{2+} generated by reaction I-3.

Intramolecular electron transfer is inaccessible to CrR^{3+} complexes, where R = alkyl and haloalkyl. The oxidized complex thus dissociates (eq 11). Numerous precedents for oxidative homolysis

$$(H_2O)_5CrR^{3+} \rightarrow (H_2O)_5Cr^{3+} + R^{\bullet} \qquad (11)$$

can be cited, especially in main-group chemistry.[42] Oxidative homolysis has also been established for the outer-sphere oxidation of certain CrR^{2+} complexes[43] by $Ru(bpy)_3^{3+}$, a process that also

---

(40) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.

(41) Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1981**, *103*, 2728.

(42) (a) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1855. (b) Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 571.

(43) Melton, J. D.; Bakac, A.; Espenson, J. H., unpublished results.

leads to a transient $(H_2O)_5CrR^{3+}$ species.[1,43]

The radical produced in reaction 11 reacts with NO (eq 12). This reaction is known in the gas phase,[44] where it occurs so rapidly that it is likely to be diffusion-controlled in solution. This may occur in the initial solvent cage or as a discrete bimolecular event.

$$\mathrm{R^{\bullet} + NO \rightarrow RNO} \tag{12}$$

According to these proposals, only in the case of the electrophilic reactions are the organic products formed directly. In the electron-transfer reactions, they are actually secondary products. The alcohols formed in the reactions of the alkoxy and hydroxyalkyl complexes arise from the decomposition of hemiacetals (or, for $CrCH_2OH^{2+}$, a hydrate) to the constituent alcohols and aldehydes or ketones, as in eq I-5. The nitrosoalkanes formed by the radical capture process (eq 12) are unstable with respect to tautomerization to oximes in acidic solutions.[45] The latter then hydrolyze with release of hydroxylamine. No attempt was made to detect the latter, but the observed aldehydes or ketones are consistent with the reactions indicated. For $CrCH_2CH_3^{2+}$, for example, the sequence is as shown in Scheme II.

Scheme II

$$\mathrm{HONO + H^+ \rightleftarrows H_2O + NO^+} \tag{II-1}$$

$$\mathrm{NO^+ + CrCH_2CH_3^{2+} \rightarrow \{NO + (H_2O)_5Cr^{3+} + {}^{\bullet}CH_2CH_3\}} \tag{II-2}$$

$$\mathrm{NO + {}^{\bullet}CH_2CH_3 \rightarrow CH_3CH_2NO} \tag{II-3}$$

$$\mathrm{CH_3CH_2NO \rightarrow CH_3CHNOH} \tag{II-4}$$

$$\mathrm{CH_3CHNOH + H_2O \rightarrow CH_3CHO + NH_2OH} \tag{II-5}$$

Outer-Sphere Electron Transfer. The evidence concerning the reactions of HONO with the aliphatic complexes thus points to an electron-transfer step occurring between NO^+ and CrR^{2+}. The nitrosyl cation is known to act as a one-electron oxidant in several reactions.[32-34,46-48] In most of these it probably adopts an inner-sphere mechanism.[38] In the present instance, however, an inner-sphere mechanism is unlikely, considering the ligand substitution rates[49] of the organochromium(2+) ions. Although they undergo substitution considerably more rapidly than do related inorganic complexes $(H_2O)_5CrX^{2+}$, they nonetheless appear to react too slowly to accommodate the nearly diffusion-controlled values of k_{NO^+}.

Two reactions of NO^+ that are, however, believed to occur by an outer-sphere mechanism and thus might serve as comparison reactions are those of HONO with $Fe(phen)_2(CN)_2$[50] and $IrCl_6^{3-}$.[48] Both complexes are substitutionally inert and generally react by outer-sphere electron transfer. The kinetic data for the latter reaction have been analyzed in terms of Marcus theory.[51] On that basis the self-exchange rate constant for the NO^+/NO couple has been estimated as 4×10^6 M^{-1} s^{-1}, a value that agrees very poorly with the theoretical estimate,[46] $\sim 10^{-2}$ M^{-1} s^{-1}, obtained by using a classical valence force field model. This comparison has been taken to suggest[48] a strong overlap of the orbitals of NO^+ with those of a chloride ligand on $IrCl_6^{3-}$. That is, chloride provides the bridging ligand needed to enhance the rate over the value expected for outer-sphere electron transfer.

A similar situation arises for $Fe(phen)_2(CN)_2$,[50] with $k = 6.7 \times 10^9$ M^{-1} s^{-1}. By estimating the self-exchange rate for the iron complex as 10^5 M^{-1} s^{-1} from known values for $Fe(CN)_6^{3-/4-}$ (1.9×10^4) and $Fe(phen)_3^{2+/3+}$ (1×10^6), we calculate $k_{NO^+/NO} = 1.7 \times 10^8$ M^{-1} s^{-1}. Here again, it is possible that the activated complex may be stabilized by interaction of the NO^+ orbitals with those on the cyanide ligand, in effect opening an inner-sphere mechanism for the reaction.

The analysis of both of these reactions in Marcus theory terms assumes that the self-exchange rate constant $k_{NO^+/NO}$ is a parameter reliably determined from the rates of cross-reactions. Perhaps an additional consideration enters for this couple, as it does for O_2/O_2^-.[52] Because the latter couple yields a large range of calculated[52] exchange rates (10^{-6}–10^7 M^{-1} s^{-1}), it is argued that the two constituent species differ greatly in their interactions with the solvent. Thus, each transition state may occur at a very different location along the reaction coordinates; these large differences in reorganization energy are not adequately accounted for by Marcus theory, which is usually applied to charged coordination complexes in which the changes in the degree of solvation between the partners are not nearly so great.

That point aside, one might use one value or another of the self-exchange rate constants for NO^+/NO to consider the data for the CrR^{2+} complexes. The self-exchange rates of the $CrR^{3+/2+}$ couples and their reduction potentials have not been reported, however, and so any further consideration on such a basis will necessarily await additional data.

Experimental Section

Reagents. The organochromium complexes were prepared by the methods described in earlier publications.[4,6,53-56] In most cases the complex was separated and purified by ion-exchange chromatography on an ice-jacketed column of Sephadex SP C-25 ressin. A few of the more rapidly decomposing complexes (e.g., $CrCH_2OH^{2+}$) were used without this step. All of these complexes are ones that have been characterized previously; their identity and purity were confirmed by the agreement of the UV–visible spectra with reported values.[4,6,40,49,53,56]

Solutions of $CrNO^{2+}$ were prepared by bubbling alkali-scrubbed NO into a solution of Cr_{aq}^{2+}. The nitrosyl complex was separated and purified by ion-exchange chromatography and identified by the characteristic peak at 449 nm (ϵ 117 M^{-1} cm^{-1}, as compared to the literature value, 121 M^{-1} cm^{-1}) in its UV–visible spectrum.[19-21] Reagent grade solutions of sodium nitrate served as the source of the nitrous acid solutions. Since nitrous acid solutions decompose upon standing, the nitrite solutions were not acidified until the initiation of the reaction. Other reagents were prepared and purified by standard methods or were commercially available compounds.

Kinetics. The kinetics experiments were carried out under conditions chosen such that the concentrations of nitrous acid and hydrogen ion were in large excess over that of CrR^{2+}. All of the runs were carried out in an oxygen-free environment, under Cr^{2+}-scrubbed nitrogen, at 23.4 °C and an ionic strength of 0.10 M, maintained by lithium perchlorate. The kinetic data were measured spectrophotometrically by monitoring the absorbance arising primarily from the given CrR^{2+} complex at the most intense peak in its spectrum, which lies between 260 and 290 nm. The procedure used consisted of the addition of a solution of sodium nitrite to a spectrophotometer cell containing the other reagents. The latter include the organochromium(2+) complex, perchloric acid, and lithium perchlorate.

Data collected by this method invariably followed excellent pseudo-first-order kinetics to >90% completion. The pseudo-first-order rate constant, k_ψ, was evaluated by standard methods. The only exceptions to this treatment were the slow reactions of the complexes $CrCH_2X^{2+}$ (X = Cl, Br, I). Only the data from the first half-life were used, since significant decomposition of the nitrous acid would occur over longer periods at the higher nitrous acid concentrations employed.

Competition experiments were used to evaluate k_7, the rate constant for the reaction of Cr^{2+} with NO. A solution of $Co(NH_3)_5X^{2+}$ (X = Cl,

---

(44) The gas-phase reaction of ethyl radical with nitric oxide has $k \geq 10^8$ M^{-1} s^{-1}: Heicklen, J.; Cohen, N. *Adv. Photochem.* **1968**, *5*, 157. Pratt, G.; Veltman, I. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2477.

(45) Meuller, E.; Metzger, H.; Fries, D.; Heuschkel, U.; Witte, K.; Waidelich, E.; Schmid, G. *Angew. Chem.* **1959**, *71*, 1959.

(46) Eberson, L.; Radner, F. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 861.

(47) Bates, J. C.; Reveco, P.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1487.

(48) Ram, M. S.; Stanbury, D. M. *Inorg. Chem.* **1985**, *24*, 2954.

(49) Bakac, A.; Espenson, J. H.; Miller, L. P. *Inorg. Chem.* **1982**, *21*, 1557.

(50) Reveco, P.; Stedman, G. *Z. Anal. Chem.* **1979**, *295*, 252.

(51) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (c) Newton, T. W. *J. Chem. Educ.* **1968**, *45*, 571. (d) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980. (e) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(52) McDowell, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 2232.

(53) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(54) Dodd, D.; Johnson, M. D. *J. Chem. Soc. A* **1968**, 34.

(55) Kochi, J. K.; Davis, D. D. *J. Am. Chem. Soc.* **1964**, *86*, 5264.

(56) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.

Br), prepared anaerobically in perchloric acid at 0.10 M ionic strength, was saturated with alkali-scrubbed nitric oxide. A solution of chromium(II) perchlorate was then slowly added while the solution was efficiently stirred and continuously saturated with NO. After addition of Cr^{2+} was complete, the NO was removed with a vigorous stream of argon. Samples were taken for the analysis of the cobalt(II) produced by the thiocyanate method[57] in 1:1 aqueous acetone. This measurement was made by incorporating an appropriate reagent blank, which was critical given the small concentrations involved, and was based on a molar absorptivity of 1.84×10^3 M^{-1} cm^{-1} at 623 nm. These measurements provided the values of $[Co^{2+}]_\infty$ necessary for the calculation of the data according to eq 8.

Product Analysis. The inorganic products, $Cr(H_2O)_6^{3+}$ and $(H_2O)_5CrNO^{2+}$, were readily recognized by their elution times from a column of Sephadex SP C-25 ion-exchange resin. Their identities were confirmed and yields determined on the basis of their known UV–visible spectra and, in the case of $(H_2O)_5CrNO^{2+}$, analysis for total chromium.

The organic products, with the exception of CH_2O, were identified and determined by gas chromatography. The experiments with $CrCH_2CH_3^{2+}$ and $CrCH(CH_3)_2^{2+}$ used as blanks solutions of the same organochromium complex, which had been allowed to undergo acidolysis to give $Cr(H_2O)_6^{3+}$ and RH. No sodium nitrite was added to the blanks. The purity of $CrCH_2OCH_3^{2+}$, which undergoes acidolysis very slowly, was checked by gas chromatography of the eluent during purification on the ion-exchange resin. This analysis showed that no methanol (a product of the reaction with HNO_2) was present in the original stock solution of $CrCH_2OCH_3^{2+}$. The compounds sought were compared with the known materials calibrated in concurrent experiments. All of the experiments used a 10% FFAP column.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $(H_2O)_5Cr(CH_2OH)^{2+}$, 103533-92-2; $(H_2O)_5Cr(CH_2OCH_3)^{2+}$, 103533-93-3; $(H_2O)_5Cr(CH(CH_3)OCH_2CH_3)^{2+}$, 103562-45-4; $(H_2O)_5Cr(CH_3)^{2+}$, 103533-94-4; $(H_2O)_5Cr(CH_2CH_3)^{2+}$, 103533-95-5; $(H_2O)_5Cr(CH(CH_3)_2)^{2+}$, 103533-96-6; $(H_2O)_5Cr(CH_2C_6H_5)^{2+}$, 103562-46-5; $(H_2O)_5Cr(4\text{-}CH_2pyH)^{3+}$, 103533-97-7; $(H_2O)_5Cr(CH_2CH_2CH_3)^{2+}$, 103533-98-8; $(H_2O)_5Cr(CH_2Cl)^{2+}$, 103533-99-9; $(H_2O)_5Cr(CH_2Br)^{2+}$, 103534-00-5; $(H_2O)_5Cr(CH_2I)^{2+}$, 103534-01-6; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CH_3)^{2+}$, 103534-02-7; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CF_3)^{2+}$, 103534-03-8; $(H_2O)_5Cr(p\text{-}CH_2C_6H_4CN)^{2+}$, 103534-04-9; $(NH_3)_5CoBr^{2+}$, 14970-15-1; $(NH_3)_5CoCl^{2+}$, 14970-14-0; $Cr(H_2O)_6^{2+}$, 20574-26-9; O_2, 7782-44-7; NO, 10102-43-9; HNO_2, 7782-77-6.

---

(57) Kitson, R. F. *Anal. Chem.* **1950**, *22*, 664.

Contribution from the Departments of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, and Rosary College, River Forest, Illinois 60305, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Electron-Transfer Reactions of Technetium Complexes. 1. Rate of the Self-Exchange Reaction of the Tc(I)/Tc(II) Couple $[Tc(DMPE)_3]^{+/2+}$, Where DMPE = 1,2-Bis(dimethylphosphino)ethane[1]

Mary Noon Doyle,[2] Karen Libson,[2] Mary Woods,[3] James C. Sullivan,[4] and Edward Deutsch*[2]

Received October 7, 1985

The rate of the self-exchange electron-transfer reaction between $[Tc(DMPE)_3]^+$ and $[Tc(DMPE)_3]^{2+}$ has been determined by two independent applications of the Marcus theory. (1) The rates and equilibrium constants governing the cross-reactions between $[Tc(DMPE)_3]^{+/2+}$ and $[(NH_3)_5RuL]^{2+/3+}$ (L = isonicotinamide, pyridine, 4-picoline) were measured in aqueous LiCl/HCl solutions. The known self-exchange rate of $[(NH_3)_5Ru(py)]^{2+/3+}$ was then used within the Marcus cross relationship to calculate three values of k_{ex} for $[Tc(DMPE)_3]^{+/2+}$. These values fall within the range $(0.8\text{–}4.0) \times 10^6$ M^{-1} s^{-1} (25 °C, $\mu = 0.10$ M). Estimated activation parameters for this reaction are $\Delta H_{ex}{}^* = 7 \pm 3$ kcal/mol and $\Delta S_{ex}{}^* = -8 \pm 4$ eu. (2) Available bond length data show that, because of extensive π-back-bonding from Tc to P, the Tc–P bond *expands* by about 0.068 Å upon oxidation of the technetium center. This information, combined with estimates for the radius of the complex (4.8 Å) and for the force constant of the Tc–P bond (1.64×10^5 dyn/cm), can be used within the Marcus formalism to calculate k_{ex}. The resulting calculated value is 3×10^6 M^{-1} s^{-1} (25 °C), in excellent agreement with the median value determined kinetically. This agreement between kinetically and structurally determined values of k_{ex} demonstrates that the self-exchange reaction of the extensively π-back-bonded $[Tc(DMPE)_3]^{+/2+}$ system is adequately described within the Marcus formalism. Moreover, the value of k_{ex} for this d^6/d^5 couple is in good agreement with the value of k_{ex} (2.2×10^6 M^{-1} s^{-1}; 25 °C, $\mu = 0.10$ M) observed for $[(NH_3)_4Ru(bpy)]^{2+/3+}$, a predominantly σ-bonded d^6/d^5 couple of similar radius (4.4 Å). Thus, the success of the Marcus formalism does not depend on the intimate nature of metal–ligand bonding within the complex, and it appears that it is the overall size of low-spin d^6/d^5 couples that is the predominant factor in determining the self-exchange rate.

Introduction

For many years the study of outer-sphere electron-transfer reactions and the concomitant determination of self-exchange rates have been a major focus of the field of inorganic kinetics and mechanism. Much of this research has been aimed at testing the theories of adiabatic electron transfer that were developed by Marcus[5,6] and Hush[7,8] and that have been promulgated by Sutin.[9–12] In early studies most of the experimentally accessible redox couples suitable for evaluating outer-sphere self-exchange rates were either (a) first-row transition metals containing six identical, "hard", O- or N-donating ligands or (b) tris(bipyridine) and tris(phenanthroline) complexes of Fe, Ru, Os, and some other metals. In the late 1960s Taube and co-workers introduced the ammine Ru(III)/Ru(II) complexes, which greatly expanded the number and type of suitable redox couples.[13] These systems are characterized by transfer of a t_{2g} electron (as opposed to the e_g

---

(1) Abstracted in part from: Noon, M. Ph.D. Thesis, University of Cincinnati, 1984.

(2) University of Cincinnati.

(3) Rosary College.

(4) Argonne National Laboratory.

(5) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(6) Marcus, R. A.; Siders, P. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; Chapter 10.

(7) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

(8) Hush, N. S. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; Chapter 13.

(9) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(10) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(11) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

(12) Herbert, J. W.; Macartney, D. H. *Inorg. Chem.* **1985**, *24*, 4398.

(13) Taube, H. *Science (Washington, D.C.)* **1984**, *226*, 1028.

0020-1669/86/1325-3367$01.50/0