

carbonyl anions have been isolated and structural studies are in progress.

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Supplementary Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2616.

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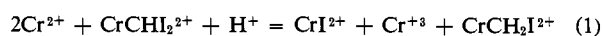
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Kinetics and Mechanism of the Reaction between Chromium(II) and Pentaquo(diodomethyl)chromium(III) Ion (Cr(OH)₂CHI₂²⁺). Evidence for a Carbon-Bridged Dinuclear Chromium Intermediate

Sir:

Pentaquo(diodomethyl)chromium(III) ion, abbreviated CrCHI₂²⁺, can be prepared by the reaction between excess iodoform and chromium(II); however, when excess chromium(II) is used, pentaquo(iodomethyl)chromium(III) ion, abbreviated CrCH₂I²⁺, is identified as a major product.¹ We wish to report results of our study of the reaction between CrCHI₂²⁺ and Cr²⁺, which provides evidence for a carbon-bridged dinuclear chromium intermediate.

The reduction of CrCHI₂²⁺ by Cr²⁺ produces CrCH₂I²⁺ quantitatively according to the equation



If excess Cr²⁺ is used, the CrCH₂I²⁺ will be further reduced to Cr³⁺ and CH₄, although at a much slower rate than (1).²

The kinetics of eq 1 were followed by a titrimetric analysis of unreacted chromium(II).³ Measured aliquots of the reaction mixture were injected into deoxygenated solutions of acidic Cr(VI); the resultant solution was then passed through a short column of cation-exchange resin. The negative Cr(VI) species were not retained in the resin and the decrease in absorbance

could then be determined without interfering absorbance by positive chromium complexes.

The disappearance of Cr²⁺ showed first-order dependence on CrCHI₂²⁺ and Cr²⁺ and was independent of H⁺. The rate constants were determined by a computer analysis based on the integrated rate law

$$\frac{1}{2A - B} \ln \frac{B(A - X)}{A(B - 2X)} = kt \quad (2)$$

where *A* = initial [CrCHI₂²⁺], *B* = initial [Cr²⁺], and 2*x* = [Cr²⁺] which has reacted. Plots of (2) were linear over 95% of the reaction and the rate constants are reported in Table I. The value of Δ*H*[‡] was cal-

Table I. Second-Order Rate Constants for the Reduction of CrCHI₂²⁺ by Cr²⁺ (−d[Cr²⁺]/dt = *k*₁[CrCHI₂²⁺][Cr²⁺])

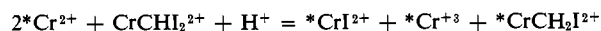
<i>T</i> , °C ^a	[H ⁺], <i>M</i> ^b	<i>k</i> ₁ , <i>M</i> ^{−1} sec ^{−1} ^c
0	0.1	2.66 ± 0.13
0	0.5	2.77 ± 0.16
0	1.0	2.72 ± 0.14
5	0.1	3.29 ± 0.18
5	0.5	3.31 ± 0.17
5	1.0	3.38 ± 0.18
10	0.1	4.15 ± 0.23
10	0.5	4.09 ± 0.17
10	1.0	4.11 ± 0.19
15	1.0	5.08 ± 0.22

^a Temperature error of ±0.05°. ^b Ionic strength maintained at 1.0 *M* by NaClO₄. ^c Determined by a linear least-squares computer analysis based on integrated second-order rate law.

culated to be 6.5 ± 0.5 kcal/mol and Δ*S*[‡] to be −32 ± 1 eu. The calculated value of *k* at 25° is 11.2 *M*^{−1} sec^{−1}.

The appearance of CrI²⁺ as a product and the first-order dependence on Cr²⁺ and CrCHI₂²⁺ is evidence that the rate-determining step of the reaction involves the abstraction of an iodine atom by Cr²⁺ by means of a bridged transition state [Cr–CHI–I–Cr]⁴⁺. This reaction would produce CrCHI²⁺ which could rapidly react with Cr²⁺ to form the final products. The low Δ*H*[‡] is consistent with breaking a relatively weak C–I bond, and the negative Δ*S*[‡] is consistent with the formation of a highly charged transition state involving the aggregation of two ions.⁴

Isotopic labeling experiments on (1) were also carried out. In one series, labeled Cr²⁺ (⁵¹Cr) was added to unlabeled CrCHI₂²⁺. The label appeared in all the products.



Similar results are obtained with labeling experiments involving CrCHCl₂²⁺ and Cr²⁺.⁵ The label in the organochromium product can be readily explained by postulating a carbon-bridged dinuclear chromium intermediate *[CrCHICr]⁴⁺ which can break either Cr–C bond to form the final products.⁶

In another series of experiments in which labeled CrCHI₂²⁺ was added to unlabeled Cr²⁺, a small amount

(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 129.

(5) J. H. Espenson, private communication.

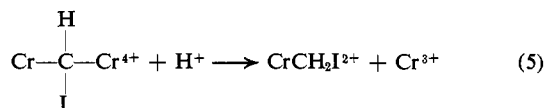
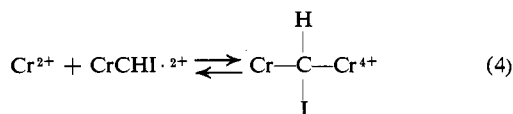
(6) When labeled Cr²⁺ is added to unlabeled CrCHI₂²⁺ and the reaction is quenched before completion, no label appears in unreacted CrCHI₂²⁺. Therefore the exchange CrCH₂I²⁺ + *Cr²⁺ = *CrCH₂I²⁺ + Cr²⁺ must be dismissed as an explanation for the labeling experiments with CrCHI₂²⁺ and Cr²⁺.

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(2) R. S. Nohr and L. O. Spreer, *Inorg. Chem.*, in press.

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of the label was found in the unreacted Cr^{2+} and in the CrI^{2+} product. In order to explain these observations a rapid equilibrium between $[\text{CrCHI}\text{Cr}]^{4+}$ and $\text{Cr}^{2+} + \text{CrCHI}\cdot^{2+}$ is suggested.⁸ The complete mechanism would then be



Step 4 involves a homolytic breakage of a carbon-Cr bond and this type of scission has been found in a number of organochromium compounds.^{10,11}

Further evidence for a rapid equilibrium (4) is provided by the specific activities (counts/minute/mole) of $\text{CrCH}_2\text{I}^{2+}$ compared to the total specific activities of all the products. (It was necessary to group together the specific activities of CrI^{2+} and Cr^{3+} due to the relatively rapid aquation of CrI^{2+} to Cr^{3+} .)¹² Starting with labeled CrCHI_2^{2+} and unlabeled Cr^{2+} , the specific activity ratio of $\text{CrCH}_2\text{I}^{2+}$ to total specific activity of all the products would be 0.50 if step 4 was not reversible. For experiments done at $[\text{H}^+] = 1.0 \text{ M}$, the ratio ranged from 0.38 to 0.45, depending upon the amounts of the reactants and the allowed reaction time. If step 4 is reversible part of the label will appear in Cr^{2+} and thus eventually in CrI^{2+} , and this will decrease the ratio of specific activity of $\text{CrCH}_2\text{I}^{2+}$ to total in products.

In the reaction between labeled Cr^{2+} and unlabeled CrCHI_2^{2+} , the expected specific activity ratio of $\text{CrCH}_2\text{I}^{2+}$ to total products would be 0.25 if no equilibrium steps were involved. The experimental values, ($[\text{H}^+] = 1.0 \text{ M}$), ranged from 0.28 to 0.32 depending on reaction conditions. This deviation can be explained by noting that part of the label will be transferred to $\text{CrCHI}\cdot^{2+}$ in step 4, thus resulting in the possibility of forming fully labeled $[\text{CrCHI}\text{Cr}]^{4+}$. The further reaction of this species would result in an increase in the specific activity ratio of $\text{CrCH}_2\text{I}^{2+}$.

Attempts were made to separate the species present in the reaction mixture using ion-exchange columns thermostatted at low temperatures and using a nitrogen atmosphere. No species of charge 4+ was detected so that if $[\text{CrCHI}\text{Cr}]^{4+}$ is formed it must rapidly dissociate to form the final products.

In labeling experiments which were identical except that the $[\text{H}^+]$ was 0.1 M instead of 1.0 M, the devia-

tion of the specific activity ratio of $\text{CrCH}_2\text{I}^{2+}$ to total products to that expected assuming step 4 was not reversible was greater for the lower acidity. This is qualitative evidence that the reaction of the intermediate to form the final products, step (5), is $[\text{H}^+]$ dependent. Further work to obtain more information about the intermediate is in progress.

The general form of the proposed mechanism (3-5) may be applicable to reduction of other polyhalo-organic compounds¹³⁻¹⁵ by Cr(II) . Castro¹³ has proposed a mechanism for the reduction of geminal halides by Cr(II) which does not involve carbon-bridged dinuclear chromium intermediates. However, his mechanism cannot accommodate the results of the labeling experiments in the present study.

Acknowledgment. Support by Grant No. C125 from The Research Corporation is gratefully acknowledged.

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[2.2]Paracyclophane System Optical Activity. III. Theory for Isotopic Substitution Chirality¹

Sir:

The circular dichroism (CD) due to ring substitution by deuterium in [2.2]paracyclophane has been reported recently.² This observation affords an opportunity to compare the effects of mass-induced perturbations through vibration to the earlier observed effects^{3,4} of substituents electronically different from hydrogen. The sign and approximate intensity of the long wavelength CD of such ring-substituted paracyclophanes can be predicted by a theory that accounts for the electronic perturbations of the benzene rings.⁵ Also, since variation of the substituent in the same absolute configuration can change the sign of CD, the twist of benzene rings around the interplanar axis which has been observed in crystalline [2.2]paracyclophane⁶ is not significantly operative by a substituent steric effect.

Therefore the CD observed for the deuterium substituent, which is only isotopically different from hydrogen, cannot be reasonably ascribed to either steric or electronic perturbations. We outline here a vibronic coupling theory for the source of rotatory strength.

The vibrational structure of the long wavelength

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(3) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4556 (1969).

(4) H. Falk, P. Reich-Rohrwig, and K. Schloegl, *Tetrahedron*, **26**, 511 (1969).

(5) O. E. Weigang, Jr., and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555 (1969).

(6) O. Schnepf, private communication.

(7) Recovered as the oxygen oxidation product, octaaquodi- μ -hydroxodichromium(III) ion.

(8) Another way of obtaining labeled Cr(II) would be through an exchange with labeled Cr(III) . However, this reaction has been discounted due to the relatively long half-life of the reaction ($t_{1/2} = 1.5$ days at 25°).⁹

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