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The Reactions of Metal Oxides with Aquated Chromium(II) Ion

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When aquated Cr^{+2} reacts with MnO_2 , PbO_2 , Ti_2O_3 , Mn_2O_3 , Co_2O_3 , or CeO_2 , $\text{Cr}(\text{OH})_2^{+3}$ is in each case the predominant form of the Cr(III) product. However, when the oxidizing agent has a higher ratio of O^{-2} :Pb(IV), as when Pb_3O_4 or $\text{Ca}_2\text{-PbO}_4$ reacts, the Cr(III) "dimer" (or a higher polymer) is formed. No oxygen transfer from PbO_2 to Cr occurs in the oxidation-reduction process, but some does occur when MnO_2 , Ti_2O_3 , or Mn_2O_3 react. The oxides containing metal ions which undergo $2e^-$ changes (MnO_2 , PbO_2 , Ti_2O_3) react much more rapidly than those having metal ions which undergo $1e^-$ changes. The effects are interpreted on the basis that the initial electron-transfer process is not necessarily localized at the metal ion of the oxide lattice which is in close proximity to the reducing ion and by taking into account the damage to the lattice that results when electrons are trapped at individual metal ion sites. When MnO_2 is the oxidizing agent, and when the concentration of Cr^{+2} is low, a remarkable deviation from the stoichiometry described above is observed. Under these conditions ClO_4^- is reduced by Cr^{+2} despite the fact that the reaction of MnO_2 with Cr^{+2} is rapid; as much as 90% of the Cr^{+2} may be oxidized by ClO_4^- rather than by MnO_2 .

Chromium(II) ion has been an especially useful reducing agent in the study of the mechanisms of oxidation-reduction reactions in homogeneous solutions.¹ The combination of properties which gives it such an important position in the field are (a) its capacity to capture ligands during the oxidation process (the ligands may be derived from the oxidizing agent or may be picked up from the solution) and (b) its capacity on being oxidized to assume two different forms of the same oxidation state (oxidation by a simple $1e^-$ process yields only mononuclear Cr(III) species; a number of $2e^-$ oxidizing agents are known to yield binuclear Cr(III)).² It seemed to us likely that these properties also would prove to be useful in studying the mechanisms of reduction of selected metallic oxides, and thus the reactions of the oxides with Cr^{+2} qualified for early attention in a program of investigating the mechanisms of reduction of these particular solid oxidizing agents.

Little has been done on the reactions of metal oxides with cationic reducing agents,³ and as a result our work to this point has been largely of a survey nature. However, a number of results have emerged from our work which seem to be of significance when they are compared with analogous results for reactions in homogeneous solution and, in addition, a number of new phenomena have been uncovered which seem of sufficient interest to merit further investigation. A report on our work at this stage thus appears to be worthwhile.

Experimental

Chromium(III) perchlorate was obtained either by recrystallization of a commercial product or by reduction with H_2O_2 of a solution of $\text{Na}_2\text{Cr}_2\text{O}_7$. The reduction of $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ in ClO_4^- medium was effected either by electrolysis or by using amalgamated zinc. Special experiments were done with MnO_2 to learn whether Zn^{+2} has an effect on the chemistry and kinetics of

the reduction process and none was detected. Analysis for total Cr in the solutions was done spectrophotometrically after oxidation to CrO_4^{-2} using hydrogen peroxide in alkaline solution.⁴ The Cr^{+2} content was determined by adding $\text{Co}(\text{NH}_3)_6\text{Cl}^{+2}$ in excess, then developing the Co^{+2} color either as the chloride or the thiocyanate complex.⁴ The reaction of Cr^{+2} with $\text{Co}(\text{NH}_3)_6\text{Cl}^{+2}$ is rapid and quantitative, and interference by excess Co(III) in the spectrophotometric analysis of the Co(II) produced is easily avoided. Neither Cr(III) nor Co(III) absorbs strongly at the wave length (λ 692 $m\mu$ for the chloro complex) used for analysis of the Co^{+2} complex.

Most of the oxides were commercial products used as obtained. For the kinetic studies the MnO_2 was ground and sorted. The results, except for effects arising from the slightly larger specific surface area of the treated sample, were unchanged by this treatment. The sources of the oxides were as follows: MnO_2 (pyrolusite) and Fe_2O_3 , J. T. Baker; Co_2O_3 , PbO_2 , Pb_3O_4 , Baker and Adamson; Ti_2O_3 , CeO_2 , Fisher Scientific Co.; Mn_2O_3 , Co_3O_4 , City Chemical Corp.; Mn_3O_4 , E. J. Lavino & Co. $\text{Ca}_2\text{-PbO}_4$ was prepared by heating $\text{Ca}(\text{OH})_2$ and PbO_2 , taken in a 2:1 molar ratio, at 300° for 6 hr. $\alpha\text{-PbO}_2$ was prepared by heating PbO_2 at 340° for 12 hr. CrO_2 was prepared by heating Cr_2O_3 at 350° for 12 hr. MnO_2 was also prepared by the decomposition of $\text{Mn}(\text{NO}_3)_2$ solution.⁷ In respect to the nature of the product formed and rate of reduction, this material did not differ from that obtained commercially. It must be admitted, however, that the rate comparisons which are implied are based only on qualitative observations for the material prepared by us.

Analyses were done on some of the oxides to determine the average oxidation state of the contained metal. The oxidizing capacity per unit weight was found using an iodometric method. Mn was determined spectrophotometrically⁴ as MnO_4^- ; Pb was determined by EDTA titration.⁸ The reaction of the metal oxide with Cr^{+2} also serves as an analytical method, if it is assumed that metal ion is removed from the oxides only as it is reduced and if the oxide alone oxidizes Cr^{+2} .

Three different kinds of experiments were done: (1) those bearing on questions of stoichiometry, (2) those dealing with the kinetics of the reactions, and (3) those tracing the path of the oxide oxygen in the reactions.

Of the problems arising in experiments in the first category, the only one requiring special mention is concerned with under-

(4) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Press, New York, N. Y., 1959.

(5) G. Butler and J. L. Copp, *J. Chem. Soc.*, 725 (1956).

(6) M. Domine-Berges, *Compt. Rend.*, 228, 1435 (1949).

(7) T. E. Moore, M. Ellis, and P. W. Selwood, *J. Am. Chem. Soc.*, 72, 856 (1950).

(8) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Princeton, N. J., 1958.

(1) H. Taube and H. Myers, *J. Am. Chem. Soc.*, 76, 2103 (1954).

(2) M. Ardon and R. A. Plane, *ibid.*, 81, 3197 (1959).

(3) But note work on the reduction of MnO_2 by Fe^{+2} : D. F. A. Koch, *Australian J. Chem.*, 10, 150 (1957).

standing the identity of the Cr(III) product. When ClO_4^- is the only anion, $\text{Cr}(\text{OH}_2)_6^{+3}$ and the so-called dimer or higher polymers are the only possible products. For most of the solids, $\text{Cr}(\text{OH}_2)_6^{+3}$ is rather clearly the product, as could be established by spectrophotometric examination. In a few instances little $\text{Cr}(\text{OH}_2)_6^{+3}$ is formed, and the spectrum of the product resembles that reported for the dimer.² But there is evidence that the substance (or substances) we denote as "dimer" in Table II is different from the genuine dimer³ produced by oxidizing Cr^{+2} with O_2 . The genuine dimer, but not our material, is precipitated by $\text{Fe}(\text{CN})_6^{-4}$. When Cl^- is present in the reaction mixture, CrCl^{+2} is also a product. This species was separated from other Cr(III) products by using a cation-exchange resin. The composition CrCl^{+2} for the fractions eluted with 1 *M* HClO_4 was established by determining the total chromium as described above and determining Cl^- gravimetrically as the silver salt.

For the kinetic experiments, aliquots of the reaction mixture were quenched by discharging them into solutions containing $\text{Co}(\text{NH}_3)_6\text{Cl}^{+2}$. The unreacted oxide in suspension was removed by filtration, and the Cr^{+2} was determined by developing the Co^{+2} formed in the reaction of Cr^{+2} with the $\text{Co}(\text{III})$ complex. The reaction mixtures in the kinetic experiments were stirred with a glass-enclosed bar which was actuated magnetically. Because the thickness of the diffusion layer is undefined, some of the rate measurements may have little absolute significance. Nevertheless, since the reaction conditions were similar for the various oxides, the rates are of interest on a comparative basis and will be used only in this way.

The oxygen tracer experiments were done using oxides of normal isotopic composition in O^{18} -enriched water, the oxide being in excess of the Cr^{+2} . After the reaction was complete, excess oxide was removed by filtration and the metal ions derived from the oxide were precipitated using potassium ferrocyanide. The procedure for determining the isotopic composition of the product $\text{Cr}(\text{OH}_2)_6^{+3}$ then was the same as that used by Plane and Hunt.⁹

Blank experiments were performed to learn if the oxides induce exchange between $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ and solvent and to measure any separation-induced exchange. For some experiments, $\text{Cr}(\text{OH}_2)_6^{+3}$ of normal isotopic composition was added to enriched water containing the oxide of normal isotopic composition. A small quantity of Cr^{+2} was also added, equivalent to 2% of the total Cr(III), as a check on the possibility that the oxide accelerates the Cr^{+2} -catalyzed¹⁰ exchange of $\text{Cr}(\text{H}_2\text{O})_6^{+2}$ with water. After leaving the mixture for a period of time approximately the same as that allowed for the transfer experiments, the solutions were worked up as described, and the isotopic composition of the $\text{Cr}(\text{OH}_2)_6^{+3}$ was determined. The results showed the product $\text{Cr}(\text{OH}_2)_6^{+3}$ to be contaminated with 0.5 ± 0.1 mole of enriched water when PbO_2 was used and 0.7 ± 0.1 mole when MnO_2 and Ti_2O_3 were used. In other blank experiments, the oxide and Cr^{+2} were omitted yet the results were much like those quoted above. Thus we believe that the apparent exchange occurs during precipitation. The effect is not caused by exchange between $\text{Cr}(\text{OH}_2)_6^{+3}$ (enriched) and PO_4^{+3} (normal) on heating the solid $\text{Cr}(\text{OH}_2)_6\text{PO}_4$. This was shown by doing isotopic analysis on $\text{Cr}(\text{OH}_2)_6^{+3}$ formed in enriched water by oxidizing Cr^{+2} with I_2 , precipitating $\text{Cr}(\text{H}_2\text{O})_6\text{PO}_4$ with phosphate of normal isotopic composition. The effect of the exchange in the actual runs was minimized by adjusting the isotopic composition of the solvent after the reaction so as to be close to the value established for the water contained in $\text{Cr}(\text{OH}_2)_6^{+3}$ determined in preliminary experiments, and corrections for the exchange were applied in accordance with the results of the blank experiments.

Results

The results of measurement of surface area and composition of the oxides are shown in Table I.

TABLE I
CHARACTERIZATION OF THE OXIDES

Nominal formula	Surface area, m^2/g^a	Formula by analysis
PbO_2	4.63	$\text{PbO}_{2.03}$
Ti_2O_3	2.06	...
MnO_2	0.43	$\text{MnO}_{2.02}$
Mn_2O_3	6.05	$\text{Mn}_2\text{O}_{3.00}$
Pb_3O_4	0.66	$\text{Pb}_3\text{O}_{3.91}$
$\alpha\text{-PbO}_2-x$	6.37	$\text{PbO}_{1.76}$
Co_2O_3	12.7	$\text{Co}_2\text{O}_{2.93}^b$
Mn_3O_4	2.80	$\text{Mn}_3\text{O}_{4.06}$

^a As measured with a Perkin-Elmer Shell Absorptometer.

^b This solid may actually be a hydrate; $\text{Co}_2\text{O}_{2.93}$ does not account for the entire weight of the material.

In Table II are summarized results on the nature of the Cr(III) product formed with the various oxidizing agents and measurements of the rate of reaction. Although these measurements are only approximate, and the conditions differ slightly from experiment to experiment, the rate comparisons which are made involve very large rate differences and will not be materially affected by the inaccuracies or slight variation in conditions.

The reaction volume in the experiments summarized in Table II was 50 ml. The rate in this table and elsewhere is expressed as the rate of change in concentration of Cr^{+2} (mole l^{-1} sec.⁻¹) for 1 l. of solution in contact with a surface of area of 1 m^2 .

An effort was made to study the kinetics of the reaction with MnO_2 as the oxidizing agent. We observed that when (Cr^{+2}) is in the range 6×10^{-2} to 9×10^{-3} and (H^+) is in the range 0.1 to 1.0 *M*, the rate of Cr^{+2} consumption at constant surface area of MnO_2 is almost independent of (Cr^{+2}), a result that was established both by varying the initial concentration of Cr^{+2} and by following the change in its concentration with time. In the same concentration range the rate increases slightly as (H^+) is increased at constant (ClO_4^-) using NaClO_4 to maintain the ionic strength constant. Table III lists the initial rates observed.

The system $\text{Cr}^{+2} + \text{MnO}_2$ displays a remarkable and unexpected complication which has a bearing on the kinetic results which have been summarized. It is found that Cr^{+2} is oxidized by ClO_4^- as well as by MnO_2 . The results presented in Table IV show that the proportion of the Cr^{+2} which reacts with ClO_4^- increases as (Cr^{+2}) decreases, and in an extreme case, such as is represented by experiment 3, 94% of the Cr^{+2} is oxidized by ClO_4^- rather than by MnO_2 . Even when the experiment is done by adding the total Cr^{+2} at once so that the initial ion concentration is high, 20% of it reacts with ClO_4^- . The contribution of the ClO_4^- reaction becomes largest toward the end of a "batch" experiment, and thus we feel that the data of Table III apply mainly to the oxidation of Cr^{+2} by MnO_2 .

For the effect demonstrated by the data of Table IV to be fully appreciated, it should be kept in mind that Cr^{+2} persists in 1 *M* HClO_4^- for months with little or

(9) R. A. Plane and J. B. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957).

(10) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

TABLE II
A SURVEY OF THE REACTIONS OF Cr⁺² WITH METAL OXIDES
(Temp. 25°; ClO₄⁻ medium; total volume 50 ml.)

Oxide	[H ⁺], M	[Cr ⁺²], M	Cr(III) product	Rate, M sec. ⁻¹ m. ⁻²	Metal ion/Cr ⁺²
PbO ₂	0.45	0.079	Cr(OH ₂) ₆ ⁺³ ^a	>8 × 10 ⁻⁶	0.55
Tl ₂ O ₃	0.89	0.080	Cr(OH ₂) ₆ ⁺³ ^a	>4 × 10 ⁻⁶	...
MnO ₂	0.95	0.022	Cr(OH ₂) ₆ ⁺³ ^a	~2 × 10 ⁻⁶	≤0.50
Mn ₂ O ₃	0.25	0.079	Cr(OH ₂) ₆ ⁺³ ^a	~3 × 10 ⁻⁷	...
Pb ₃ O ₄	0.45	0.079	Dimer ^b	>3 × 10 ⁻⁵	1.52
Ca ₂ PbO ₄	0.89	0.080	Dimer ^b	~4 × 10 ⁻⁶	1.52
PbO _{1.75}	0.45	0.079	Dimer ^b	>5 × 10 ⁻⁶	0.72
Fe ₂ O ₃	0.45	0.079	?	<8 × 10 ⁻⁹	...
Co ₂ O ₃	0.67	0.039	Cr(OH ₂) ₆ ⁺³ ^a	~4 × 10 ⁻⁸	1.00
CeO ₂	0.20	0.029	Cr(OH ₂) ₆ ⁺³ ^a	~2 × 10 ⁻⁸	1.0
Mn ₃ O ₄	0.45	0.079	?	~2 × 10 ⁻⁷	
V ₂ O ₅	0.10	0.016	Cr(OH ₂) ₆ ⁺³	~8 × 10 ⁻⁹	
SnO ₂	0.89	0.080	?	<i>c</i>	
TiO ₂	0.89	0.080	?	<i>c</i>	
CrO ₂	0.89	0.080	?	<i>c</i>	
Co ₃ O ₄	1.0	0.167	?	<i>c</i>	

^a Cr(OH₂)₆⁺³ constitutes more than 95% of the Cr(III) product. ^b Cr(OH₂)₆⁺³ constitutes less than 10%. ^c Less than 5% reaction during a time interval in which PbO₂ reacts completely. If surface area same as for Co₂O₃, rate < 2 × 10⁻⁷ M m.⁻².

TABLE III
KINETICS OF THE REACTION OF MnO₂ WITH Cr⁺² AT 25°

[Cr ⁺²] ₀ , M	[H ⁺], M	Ionic strength	Rate × 10 ³ , M sec. ⁻¹ m. ⁻²
5.55 × 10 ⁻²	1.33	1.33	2.5
2.72 × 10 ⁻²	1.33	1.33	2.1
9.15 × 10 ⁻³	1.33	1.33	2.5
4.85 × 10 ⁻²	1.33	1.33	2.0
2.40 × 10 ⁻²	1.33	1.33	2.0
2.15 × 10 ⁻²	0.95	1.00	2.0
2.23 × 10 ⁻³	0.64	1.00	2.5
2.77 × 10 ⁻²	0.31	1.00	1.5
2.68 × 10 ⁻²	0.11	1.00	1.3

TABLE IV
THE REDUCTION OF ClO₄⁻ BY Cr⁺² CATALYZED BY MnO₂
(Reaction volume 75 ml.; 25°)

(Cr ⁺²) ₀ ^a , M	(H ⁺) ₀ , M	Amt. of MnO ₂ , g.	Mode of addn. of aq. Cr ⁺²	(Cl ⁻) formed × 10 ³ , M	[2(Mn ⁺²) + 8(Cl ⁻)] ^b	% Cr ⁺² by ClO ₄ ⁻
0.0894	1.0	0.64	Rapid	2.64	0.0896	20
0.0602	1.0	0.43	Dropwise, over 40 min.	6.62	0.0624	84
0.0139	0.25	0.10	Dropwise, over 140 min.	1.64	0.0139	94

^a Represents what the initial concentration would be if the Cr⁺² solution were added all at once as in expt. 1. ^b An analysis of the product solution was made for [Mn⁺²] and [Cl⁻]. The exact correspondence between the entries in columns 1 and 6 shows that ClO₄⁻, rather than H⁺ or N₂, oxidized the Cr⁺² which escaped reaction with MnO₂.

no oxidation by ClO₄⁻. Reaction in an experiment such as 1 is 95% complete in 30 min.

When Mn₃O₄ or Mn₂O₃ was used as the oxidizing agent, no reduction of ClO₄⁻ was detected under conditions corresponding to those of experiment 1.

Whenever the effect was investigated, acceleration by Cl⁻ of the rate of reduction of the oxides by Cr⁺² was observed, and in every case CrCl⁺² is an important product of the reaction. The rate of reaction for a "slow" oxide such as Fe₂O₃ is more sensitive to (Cl⁻) than it is for an oxide such as MnO₂ which is much

more reactive. Chloride ion present at 0.45 M accelerates the rate of reaction of Fe₂O₃ with Cr⁺² by a factor of more than 100.

Sulfate ion has also been observed to increase the rate of reaction when MnO₂ is the oxidant. The rate of oxidation of Cr⁺² by Co₂O₃ in the presence of Cl⁻ is in a range which is convenient for the study of the kinetics of the process, and the results of measuring the rate of the reaction as a function of (H⁺), (Cr⁺²), and (Cl⁻) are summarized in Table V. The specific rate *k* in column 5 is defined by the equation

$$\text{rate} = (\text{moles of Cr}^{+2} \text{ consumed/l./sec.}) = k(\text{Cr}^{+2})(\text{H}^{+})(\text{Cl}^{-})A$$

where *A* is the surface area exposed per liter of solution expressed in meter².

An investigation was made of the distribution of Cr(III) in the products between CrCl⁺² and Cr(OH₂)₆⁺³ for an experiment comparable to the second

TABLE V
KINETICS OF THE REACTION OF Co₂O₃ WITH Cr⁺² IN THE PRESENCE OF Cl⁻

(25°; ionic strength = 1.0 except where otherwise noted)

(Cr ⁺²) × 10 ² , M	<i>A</i> , m. ²	(Cl ⁻) × 10 ² , M	(H ⁺) M	<i>k</i> × 10 ⁴ ^a
3.00	65.4	0	0.667	<i>b</i>
2.31	65.4	6.67	0.667	1.3
3.03	65.4	33.3	0.667	1.4
4.33	65.4	33.3	0.667	1.0
2.85	525	6.21	0.625	1.1
2.06	32.4	33.3	1.18	1.7 ^b
2.54	51.5	6.67	0.93	1.3
0.29	216	6.67	0.067	2.1
0.29	18.3	13.3	0.653	1.9
0.29	35.4	13.3	0.157	1.7
0.29	68.1	6.67	1.03	1.1

^a *k* is defined by the relation

$$-\frac{d(\text{Cr}^{+2})}{dt} = k(\text{Cr}^{+2})(\text{H}^{+})(\text{Cl}^{-})A$$

where time is in sec. and *A* is defined as the surface area (m.²) exposed per liter of solution. ^b In the absence of Cl⁻, the rate was less than 1% the rate observed in expt. 3.

experiment referred to in Table V. We found that CrCl^{+2} represents at least 95% of the Cr(III) product.

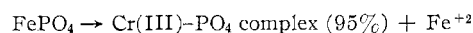
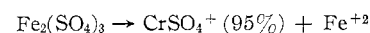
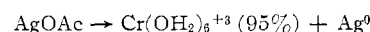
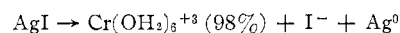
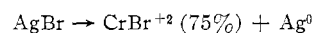
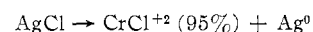
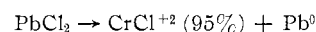
In the tracer experiments, the oxides were of normal isotopic composition and the solvent was *ca.* 6.4-fold enriched in O^{18} . The concentration of Cr^{+2} in each case was *ca.* 0.06 *M* and that of HClO_4 was *ca.* 0.6 *M*. With PbO_2 as oxidizing agent, it was found in two experiments that each product $\text{Cr(OH}_2)_6^{+3}$ derives 6.06 and 6.03 atoms of oxygen from the solvent; for MnO_2 , experiments in duplicate gave the results 5.50 and 5.59. The results obtained for PbO_2 show that little, if any, oxygen transfer from the solid to Cr^{+2} accompanies the electron-transfer process. If no transfer from oxide to Cr^{+2} takes place, 6.00 molecules of water per Cr(III) must originate in the solvent; the apparent pick-up by Cr(III) of solvent oxygen slightly exceeds this value, and the difference can be attributed to fractionation effects. Some oxygen transfer from MnO_2 to Cr^{+2} does take place, amounting to approximately one atom for every two Cr(III) ions formed, and corresponding perhaps to complete transfer in one of the steps of the two-step reduction of Mn(IV) to Mn^{+2} .

In addition to the experiments cited, both for PbO_2 and MnO_2 a number of experiments were done in which the results were incomplete because we failed to take into account the unreduced $\text{Cr(OH}_2)_6^{+3}$ in the Cr^{+2} solution. Since this $\text{Cr(OH}_2)_6^{+3}$ contains oxygen of normal isotopic composition, if a correction is not applied for this contribution, it will give results for pick-up by $\text{Cr(H}_2\text{O)}_6^{+3}$ of H_2O from the solvent which are too low. Even without correction, the results indicated that when PbO_2 is the oxidizing agent, substantially all of the oxygen in the $\text{Cr(OH}_2)_6^{+3}$ produced is derived from the solvent ($n = 5.84, 5.90, 5.88,$ and 5.78) and for MnO_2 an average value of $n = 5.6 \pm 0.2$ (eight determinations) was obtained. Although they are incomplete, these results are worth quoting since they do represent lower limits for the solvent oxygen contained in the $\text{Cr(OH}_2)_6^{+3}$; these lower limits are close to the value reported above and thus lend support to them. In experiments with Ti_2O_3 , the pickup of oxygen from the solvent was observed as 5.44 and 5.37; with Mn_2O_3 , 5.60 and 5.64. These are lower limits because we failed to take into account the $\text{Cr(OH}_2)_6^{+3}$ contained in the Cr^{+2} solution. However, the Cr^{+2} solutions were like those used in the early MnO_2 and PbO_2 experiments, and thus the values are probably little different from the true ones. It should be mentioned that bulk exchange of the oxides with solvent is very slow. The question of the rate of surface exchange compared to the rate of reduction is more directly pertinent to our experiments. Evidence bearing on this question is mentioned in the Discussion section; the results obtained here, namely that some oxygen is transferred to the reducing agent for some of the cases, show that surface exchange for MnO_2 , Mn_3O_4 , and Ti_2O_3 is at least not very much more rapid than the reaction of the surface layer with Cr^{+2} .

In the early phases of our work, we also explored the reactions of a number of nonoxidic solids with

Cr^{+2} . The experiments were done by adding a solution of Cr^{+2} (*ca.* 0.1 *M*) in HClO_4 (*ca.* 1.0 *M*) to the solid in question, then using ion-exchange or spectrophotometric techniques to learn the nature of the Cr(III) products. The results are summarized in Table VI. The numbers in parentheses after the formulas of the Cr(III) species represent lower limits on the fraction of Cr^{+2} which is converted to the form in question.

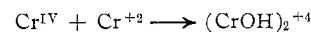
TABLE VI

THE REACTIONS OF Cr^{+2} WITH SOLIDS

In every case reaction is rapid; using about 2 equiv. of solid for every equiv. of Cr^{+2} solution, reaction was found to be over in 15 min. Some of the reactions referred to appear to be good methods of preparing the Cr(III) complexes in question. The results reported for the reaction of AgI with Cr^{+2} do not prove that $\text{Cr(H}_2\text{O)}_6^{+3}$ is the primary product of the reaction. Monoiodo Cr(III) may be the primary product, and its dissociation may be catalyzed by the elementary silver which is formed.

Discussion

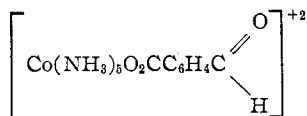
The mechanism of reduction of solid oxides by Cr^{+2} appears to be different from the reduction of oxidizing agents in homogeneous solution in some important respects. Thallium(III) ion is known to oxidize Cr^{+2} to form $(\text{CrOH})_2^{+4}$ as the major product,² but our results show that when Tl^{+3} is incorporated into the oxide, the product formed on oxidizing Cr^{+2} is $\text{Cr(OH}_2)_6^{+3}$. The formation of $(\text{CrOH})_2^{+4}$ may be taken to imply oxidation involving a $2e^-$ change



while the formation of $\text{Cr(OH}_2)_6^{+3}$ suggests that oxidation has occurred simply by extracting an electron from $\text{Cr(OH}_2)_6^{+2}$. It is to be noted that in respect to mechanism also the oxidizing agents MnO_2 and PbO_2 act as $1e^-$ oxidizing agents although each undergoes a $2e^-$ net reduction.

The observation that no oxygen transfer takes place when PbO_2 reacts with Cr^{+2} is quite unexpected in view of the experience gained on oxidizing Cr^{+2} in homogeneous solution. Almost without exception, when the oxidizing complex is homogeneously dispersed, it is found that a group derived from it is transferred

to Cr^{+2} in the oxidation process. The known exceptions are of two kinds and the reasons producing them in neither case apply to the solid oxide. Transfer fails to occur when the oxidizing agent does not have a suitable bridging group (as with $\text{Co}(\text{NH}_3)_6^{+3}$, for example) or when the product $\text{Cr}(\text{III})$ complex is substitution-labile¹¹ (as with



when Cr^{+2} attacks the remote carbonyl group). The nontransfer of oxygen from PbO_2 to chromium cannot be attributed to surface exchange being rapid compared to reduction, for extensive transfer is observed when U^{+4} reacts with PbO_2 ,¹² and this reaction is much slower than that of Cr^{+2} with PbO_2 . We must conclude, therefore, that a $\text{Cr}^{+2}\text{-O}^{-2}$ bond is not formed in the $\text{Cr}^{+2}\text{-PbO}_2$ reaction, or if it is formed, O^{-2} is not released from the lattice when the electron is transferred.

An obvious difference between the reduction of an isolated cation in homogeneous solution and the cation as part of a solid is that, in the former case, the electron which is absorbed is localized at the absorbing center, while in the latter case, the electron may be trapped at a point some distance removed from the absorbing center. Thus although Cr^{+2} may make a bond to O^{-2} in the reduction of the oxide, the damage¹³ that results to the lattice may occur at a point remote from the point of attack so that Cr^{+3} is unable to capture oxide from the lattice. The difference between PbO_2 , which shows no transfer, and Ti_2O_3 , which transfers one oxygen for each two Cr^{+2} ions oxidized, may reside in this: that O^{-2} is not so firmly bound by Ti_2O_3 as it is by PbO_2 , and Cr^{+3} is able to remove it from the lattice. But even in this case, we must stipulate that $2e^-$ reduction of Ti^{+3} is broken up into two $1e^-$ steps. The change in mechanism for the homogeneous compared to the heterogeneous process suggests that in the latter case, the primary electron transfer is to a level belonging to the lattice rather than directly to a trapped state on a particular ion. Also in the case of MnO_2 , the $2e^-$ net change is broken up into $1e^-$ steps; the oxygen transfer that occurs may in fact take place during the change $\text{Mn}^{+3} \rightarrow \text{Mn}^{+2}$ rather than $\text{Mn}^{+4} \rightarrow \text{Mn}^{+3}$.

The concept of lattice damage caused by the electron-transfer process is useful in explaining the fact that in the series of strongly oxidizing oxides PbO_2 , MnO_2 , Ti_2O_3 , CeO_2 , CrO_3 , Co_2O_3 , Co_3O_4 those in which the metal ions can undergo a $2e^-$ change are, as a class, reduced much more rapidly than those in which $1e^-$ changes take place. For each oxide, we may imagine

that the reducing agent attacks, transferring negative charge to the oxide and leaving excess positive charge on the surface. As the charge builds up, the rate at which Cr^{+2} can transfer charge diminishes. At the steady state, the loss of cations and O^{-2} from the solid is equal to the rate at which Cr^{+2} attacks. An oxide which resists reduction requires a larger build-up of negative charge relative to the positive charge at the surface than does one which reacts rapidly. The significant difference between the $2e^-$ and $1e^-$ case may be this: when a metal center is capable of absorbing two electrons, the product ion, differing by two units of charge, usually has steric requirements which differ markedly from those of the cation of the host lattice. Thus there will be a tendency for the damage attendant on electron absorption to concentrate at the surface. Here, release of O^{-2} (under the influence of H^+) and metal ion can readily take place and the process continues at a rapid rate. In the $1e^-$ case, the product ion fits into the host lattice better and the tendency for the damage to localize at the surface is not as great. Thus a large surface concentration of the reducing agent is needed to drive the reaction and it proceeds at a lower rate. Among the strongly oxidizing $1e^-$ oxides, Mn_2O_3 stands out as being especially reactive, and this case also fits the concept of damage coupled to electron transfer. The cation Mn^{+3} calls for a tetragonal distortion of its coordination sphere while Mn^{+2} , on the other hand, calls for a symmetrical coordination sphere. In this particular instance, even the $1e^-$ transfer to a metal center brings about a marked change in geometry and there will thus be a strong tendency for the electrons absorbed to be trapped at the surface where the defects are destroyed as H^+ removes O^{-2} .

The sensitivity to Cl^- of the rates of reduction of the oxides is very great, greater than in the reaction of Fe^{+3} or of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ with Cr^{+2} . The observations on the role of chloride ion require us to assume that $\text{Cr}^{+2}\text{-Cl}^-$ bonds are established, because CrCl^{+2} is known to be the product. But we cannot decide on the basis of the present evidence whether Cl^- acts as a bridging group or simply as a ligand. A possible mechanism for its mode of action is this: when it is associated with Cr^{+2} , by lowering the charge it lowers the energy necessary for the transfer of Cr^{+2} to the surface layer. Quantitative rate studies with ions of different charges and sizes, and with reducing agents having the first coordination sphere closed (such as $\text{Ru}(\text{NH}_3)_6^{+2}$, for example), are necessary to help define the role that the negative ion plays. In the single kinetic study which has been made, the rate law governing the reaction is very simple ($k(\text{H}^+)(\text{Cl}^-)(\text{Cr}^{+2})A$, where A is surface area), but the meaning of the rate law is by no means clear. Some of the questions which arise in formulating the activated complex have already been referred to. An additional one arising when the rate law is considered is this: does H^+ act at a point remote from Cr^{+2} or do the two cations act in concert on a particular center?

The change in chemistry which accompanies the

(11) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2242 (1961).

(12) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962). This work shows that surface exchange also for MnO_2 is slow compared to the reaction of U^{+4} with the oxide.

(13) The transfer of Cl from $\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$ to Cr^{+2} in the oxidation-reduction process can be understood as resulting from the fact that when $\text{Co}(\text{III})$ absorbs an electron, a ligand is labilized.

change from PbO_2 to Pb_3O_4 (Pb_2PbO_4) as the oxidizing agent is quite remarkable, with the former acting as a $1e^-$ oxidizing agent and the latter as a $2e^-$ oxidizing agent. In terms of the ideas that have been discussed, the change in chemistry would perhaps be expected when the solid changes from a situation as in PbO_2 where the Pb(IV) ions are close together and share O^{2-} ions to one in which each Pb(IV) is completely surrounded by O^{2-} , none of which is shared by adjacent Pb(IV) ions. But it is astonishing to find that only a slight increase in the ratio of $\text{O}^{2-}:\text{Pb(IV)}$, as when PbO_2 is converted to $\alpha\text{-PbO}_2$, suffices to change the mechanism of the oxidation process, and it is clear that the general explanation we have advanced will need to be refined to understand the great sensitivity of the process to the $\text{O}^{2-}:\text{Pb(IV)}$ ratio.

Many features of the interpretation of our observations are serviceable in explaining other dissolution reactions brought about by electron transfer, among them the Cr^{+2} -catalyzed dissolution of CrCl_3 in water.¹ It is significant that the process is catalyzed by reducing agents but not oxidizing agents such as Ce(IV) . Chromium(IV) appears to be substitution-labile, but this fact is not sufficient to ensure catalytic dissolution.

It is necessary in addition that there be lattice damage on electron transfer. When Cr^{+3} absorbs an electron, the electron enters a $d\gamma$ orbital and produces a strong tetragonal distortion of the coordination sphere; but when Cr(III) loses an electron, the resulting Cr(IV) ion ($d\epsilon^2$) still requires an almost perfectly octahedral coordination sphere, and so it presumably fits well into the lattice. The point made here is borne out also by observations which have been made with VCl_2 . This solid is very slow to dissolve, and it has been found¹⁴ that V^{+3} does not noticeably catalyze the dissolution of the solid, although V^{+3} is substitution-labile. It should be noted that the $\text{V}^{+2}\text{-V}^{+3}$ and $\text{Cr}^{+3}\text{-Cr}^{+4}$ systems are isoelectronic.

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(14) Observations made by T. E. Rogers in the course of trying to prepare methanolic solutions containing V^{+2} .

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Kinetics and Mechanism of the Aquation of Iodopentaquo chromium(III) Ion and of Oxidation of Coordinated Iodide Ion in Acidic Solution¹

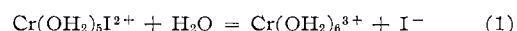
By JAMES H. ESPENSON

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The rates of aquation of iodochromium(III) ion have been determined in acidic solution as a function of reactant concentration, acidity, and temperature. The rate law is of the form $-\text{d}[\text{CrI}^{2+}]/\text{d}t = k_0 + k_{-1}/[\text{H}^+]$; values of the rate constants were determined for hydrogen ion concentrations 0.20–1.0 *M*, at 15–32° and unit ionic strength. Activation parameters associated with these paths are $\Delta H_0^* = 28.0$ kcal., $\Delta S_0^* = 16.4$ e.u.; $\Delta H_{-1}^* = 20.6$ kcal., $\Delta S_{-1}^* = -9.4$ e.u. Oxidation of bound iodide ion by iodate ion proceeds according to a rate law $-\text{d}[\text{CrI}^{2+}]/\text{d}t = k_{\text{ox}}[\text{CrI}^{2+}][\text{I}_2]$, independent of IO_3^- , a reactant, and accelerated by I_2 , a product. At 20.0° and unit ionic strength, $k_{\text{ox}} = 7.8 \text{ M}^{-1} \text{ sec}^{-1}$; alternative mechanisms are presented and discussed. Iodine does not catalyze aquation of CrI^{2+} . When either hydrogen peroxide or aquoiron(III) ion reacts with iodochromium(III) ion, oxidation proceeds no more rapidly than consistent with prior aquation of the complex, followed by oxidation of free iodide ion.

Iodochromium(III) ion² has been established as the dominant chromium(III) product, despite its very slight thermodynamic stability, of several reactions involving oxidations of substitution-labile chromium(II) ion. These include reaction with iodine,³ with iodopentaamminecobalt(III) ion,³ and with iron(III) in the presence of iodide ion.⁴ This complex, least stable of the monohalochromium(III) ions,^{5,6} is also the least stable of the series in the kinetic sense.^{7,8}

This work presents results on the kinetics of aquation of CrI^{2+} in acidic solution



Reaction of ligands coordinated to substitution-

(4) This reaction, analogous to that found for iron(III) and chromium(II) in the presence of chloride ion, must be carried out shortly after mixing to avoid reduction of iron(III) by iodide ion, although quantitative conversion to CrI^{2+} nonetheless results, since iodine is also effective. Qualitative observation that CrI^{2+} forms essentially instantly upon mixing establishes that this reaction occurs *via* an iodide-bridged transition state, rather than by formation of iron(II) and iodine followed by reaction of iodine with chromium(II), since the iron(III)–iodide ion reaction occurs at a rate substantially lower than those involved here.

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(7) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

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(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Iodopentaquo chromium(III); in general, the water molecules in the first coordination sphere of chromium(III) will not be indicated in the names or formulas of this and of similar ions.

(3) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).