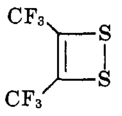
$Fe(CO)_2(NO)_2$ similar to previously reported compounds.[10] The tendency for $Hg[Fe(CO)_3NO]_2$ to produce $Fe(CO)_2(NO)_2$ on heating alone[1] makes the formation of a derivative of $Fe(CO)_2(NO)_2$ on heating with tris-(dimethylamino)-phosphine not at all surprising.

The proton n.m.r. spectrum of $(Tdp)_2Fe(NO)_2$, like that of the isoelectronic $(Tdp)_2Ni(CO)_2$,[6] exhibits a doublet rather than a triplet due to the 36 equivalent methyl protons. This indicates that the phosphorus–phosphorus coupling in $(Tdp)_2Fe(NO)_2$ is so small that each methyl proton is split by only one of the phosphorus atoms. This further confirms the observation that the coupling between the two phosphorus atoms in a tetrahedral system is much smaller than the coupling between the two phosphorus atoms in the *trans* positions of a trigonal bipyramidal or octahedral system.[6]

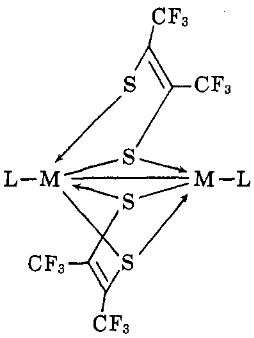
When $Hg[Fe(CO)_3NO]_2$ was allowed to react for 7 hr. in boiling benzene with bis-(trifluoromethyl)-dithietene (I), complete displacement of carbon monoxide occurred to produce a black derivative of stoichiometry $C_4F_6S_2FeNO$, apparently according to the equation

$$Hg[Fe(CO)_3NO]_2 + 2C_4F_6S_2 \longrightarrow 2C_4F_6S_2FeNO + Hg + 6CO$$

This iron nitrosyl derivative $C_4F_6S_2FeNO$ appears to be related to the isoelectronic black compound of stoichiometry $C_4F_6S_2CoCO$ isolated from the reaction between bis-(trifluoromethyl)-dithietene and dicobalt octacarbonyl.[11] Unfortunately, $C_4F_6S_2FeNO$ like $C_4F_6S_2CoCO$ was too sparingly soluble in benzene for a molecular weight determination by the vapor pressure osmometer. The F^{19} n.m.r. spectrum of this nitrosyl derivative indicated it to be diamagnetic. The volatility and diamagnetism of these compounds suggest them to be dimeric and a consideration of related derivatives of bis-(trifluoromethyl)-dithietene (I)[11] suggests structures with four sulfur bridges for $[C_4F_6S_2CoCO]_2$ (II) and $[C_4F_6S_2FeNO]_2$ (III).



I



II, M = Co, L = CO
III, M = Fe, L = NO

No iron nitrosyl derivatives of interest were isolated from the reactions between $Hg[Fe(CO)_3NO]_2$ and certain olefinic hydrocarbons such as cyclopentadiene, cyclooctatetraene, and cycloheptatriene. No evidence for the formation of derivatives of the type $(RC{\equiv}CR)Fe_2(CO)_4(NO)_2$ isoelectronic with the known compounds $(RC{\equiv}CR)Co_2(CO)_6$[12] was obtained in the reactions of $Hg[Fe(CO)_3NO]_2$ with diphenylacetylene and with hexafluorobutyne-2. Reaction between $Hg[Fe(CO)_3NO]_2$ and *p*-anisyl isonitrile gave a green reaction mixture from which nothing of interest was isolated.

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance.

[10] M. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957); W. Hieber, W. Beck, and H. Tengler, *Z. Naturforsch.*, **15b**, 411 (1960); D. W. McBride, S. L. Stafford, and F. G. A. Stone, *Inorg. Chem.*, **1**, 386 (1962).

[11] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[12] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *ibid.*, **78**, 120 (1956); M. R. Tirpak, C. A. Hollingworth, and J. W. Wotiz, *J. Org. Chem.*, **25**, 687 (1960); J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

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Oxygen-18 Tracer Studies on the Reduction of Uranyl Ion by Chromium(II)[1]

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Oxygen-18 tracer experiments have been carried out on the reaction between UO_2^{+2} and Cr(II) in aqueous perchloric acid. Evidence is presented suggesting efficient transfer of oxygen from UO_2^{+2} to Cr(II) under conditions where the reaction between the excess Cr(II) and intermediate is rapid. The results of oxygen-transfer experiments are given at 0 and 25°. The results at 25° and low H^+ are interpreted in terms of an activated complex containing Cr–O–U–O–Cr bonds.

Introduction

Newton and Baker[2] have studied the reaction between U(VI) and Cr(II) in perchloric acid and have found that the reaction is complicated in that the reactants disappear much faster than final products appear. When the reactants are mixed in acid solution a rapid reaction occurs, followed by a slower reaction which yields the final products U(IV) and Cr(III). The stoichiometry of the net reaction is

[1] A preliminary account of this work was presented at the 7th International Conference on Coordination Chemistry, Stockholm, June, 1962.

[2] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

$$2Cr(II) + UO_2^{+2} + 4H^+ = 2Cr(III) + U(IV) + 2H_2O$$

Newton and Baker have postulated that the initial rapid reaction results in the formation of at least one intermediate

$$Cr(II) + U(VI) = [Cr^{III} \cdot U^{V}]$$

This paper presents the results of oxygen-18 tracer studies on the transfer of oxygen from UO_2^{+2} to Cr^{+2} in the formation of $[Cr(OH_2)_6]^{+3}$. The system chosen is ideal because it provides an oxidizing agent which is inert to substitution reactions and an oxidized product which is also inert to substitution.

TABLE I

NUMBER OF OXYGEN ATOMS TRANSFERRED TO Cr(II) IN THE REDUCTION OF UO_2^{+2}; INITIAL CHROMIUM–URANIUM RATIO OF 2.00

$HClO_4$, *M*	Temp., °C.	Time elapsed during addn. of Cr(II), sec.	Oxygen atoms transferred from UO_2^{+2} to Cr^{+2}, n_t
0.10	25	3	1.0
.30	25	4	0.91
.44	25	4	.86
.50	25	3	.84
.81	25	3	.79
1.04	25	4	.75
1.44	25	4	.70
0.26	0	4	.08
0.50	0	4	.08
1.09	0	12	.06

Experimental

Chromium(III) perchlorate was prepared by the reduction of chromium trioxide with a slight excess of formic acid in the presence of excess perchloric acid. The salt was recrystallized two times from perchloric acid solution. The chromium(II) perchlorate stock solution was prepared by the reduction of Cr(III) solutions with amalgamated zinc. The Cr(II) solutions were stored under Matheson prepurified nitrogen (99.996%) in a nitrogen-filled reservoir. All solutions were swept with prepurified nitrogen before use.

Solutions of uranyl perchlorate were prepared from uranyl nitrate.[3] Concentrations of the uranyl solutions were determined by reduction of an aliquot to U(IV) followed by titration of the U(IV) with ceric sulfate at 50° using ferroin as the indicator.[4]

The $HClO_4$ solutions were prepared by diluting concentrated acid and were standardized by titration. The concentrated acid was A.R. grade and was further purified by boiling at atmospheric pressure and again under reduced pressure. The water used in the preparation of all the solutions was triply distilled at atmospheric pressure from an all-Pyrex still.

The solutions were rapidly stirred with Teflon-covered magnetic stirring bars and the reactions were carried out in thermostated vessels at 0 or 25°. The reaction vessels were flushed with nitrogen before filling and an atmosphere of nitrogen was kept above the reaction mixture during the course of the reaction.

The steps involved in carrying out a tracer experiment on the reduction of UO_2^{+2} by Cr^{+2} were: preparation of a solution containing oxygen-18 enriched UO_2^{+2} dissolved in normal water; preparation of a solution of Cr(II) in normal water; rapid mixing of the reagents with Teflon-covered magnetic stirring bars to bring about reaction; removal of product U(IV) by precipitation with cupferron; precipitation of $[Cr(OH_2)_6]PO_4$ by Hunt and Plane's method[5]; partial thermal decomposition of $[Cr(OH_2)_6]PO_4$ to remove H_2O for isotopic analysis; conversion of H_2O to CO_2 by Anbar and Guttman's method[6]; and mass spectrometric analysis of the carbon dioxide.

A typical experiment was carried out by the addition, with rapid stirring, of *ca.* 0.16 *M* Cr(II) to an acidic solution of UO_2^{+2} using amounts which resulted in an initial concentration of Cr(II) and UO_2^{+2} of 4×10^{-2} and 2×10^{-2} *M*, respectively. In other experiments the initial Cr(II) and UO_2^{-2} concentrations varied by a factor of two and the final volumes ranged between 4 and 10 ml. In all of the solutions the final ratio of chromium to uranium was two. The actual mixing time is directly reflected by the length of time elapsed during the addition of one of the reactants.

After the initial rapid mixing, the stirred solutions were stored at constant temperature under an inert atmosphere for 5 min. and then the reaction products were separated by the addition of sufficient 4% cupferron solution to result in the complete precipitation of both the product U(IV) from the reaction and the Zn(II) present in the initial Cr(II). The metal cupferrate precipitate was removed by filtration and the resulting chromium(III) perchlorate solution was treated with sodium phosphate to precipitate $[Cr(OH_2)_6]PO_4$.[5] The 0° reactions were warmed to 25° prior to the addition of the cupferron to assure complete reaction. All of the experiments reported in Tables I–IV are the results of duplicate or triplicate experiments. Each set of experiments was reproducible to better than 2%, which is indicative of the reliability of the individual values of n_t.

To test the precision of the isotopic analysis, separate precipitation and isotopic analyses were made on $[Cr(OH_2)_6]^{+3}$ in isotopic equilibrium with water 8-fold enriched in O^{18}. The partial decomposition of $[Cr(OH_2)_6]PO_4$ was carried out at 140° *in vacuo* after the sample had been outgassed for 10 min. at 10^{-5} mm. and 35.° The water was trapped and redistilled into a vessel suitable for direct conversion to CO_2 by the method of Anbar and Guttman[6] using anhydrous $Hg(CN)_2$ and $HgCl_2$. These preliminary tracer studies showed that less than 1% contamination occurred during precipitation and conversion of the water contained in $[Cr(OH_2)_6]^{+3}$ to CO_2. Additional blank experiments were carried out using mixtures of $[Cr(OH_2)_6]^{+3}$ of known O^{18} content and U(IV) under conditions similar to those obtained in an actual tracer experiment. Oxygen-18 analysis of the $[Cr(OH_2)_6]^{+3}$ after removal of U(IV) by precipitation with cupferron showed that the method was subject to errors of less than 1%.

The stoichiometry of the reaction of UO_2^{+2} with Cr^{+2} indicates that 2 Cr(II) ions are oxidized per UO_2^{+2} ion reduced. Thus on the average each of the two $[Cr(OH_2)_6]^{+3}$ ions formed could obtain no more than one oxygen per UO_2^{+2} reduced. If the quantity n_t is the fraction of one oxygen transferred to *each* of the two $[Cr(OH_2)_6]^{+3}$ per UO_2^{+2}, the values of n_t can be calculated from the measured ratios where

$$n_t = \frac{\Delta R_{obsd}}{\Delta R_{max}} = \left\{ \frac{6(R_p - R_{H_2O})}{R_{UO_2^{+2}} - R_{H_2O}} \right\}$$

R_p represents the experimentally observed O^{18} to O^{16} ratio of the product $[Cr(OH_2)_6]^{+3}$, R_{H_2O} represents the ratio of the solvent water, and $R_{UO_2^{+2}}$ represents the ratio of the oxygen-18 enriched UO_2^{+2}. Thus, n_t can have values between 0 and 1. A value of zero indicates that none of the uranyl oxygen appears in the product $[Cr(OH_2)_6]^{+3}$. A value of 1.00 indicates that all of the uranyl oxygen has been transferred and appears in the product $[Cr(OH_2)_6]^{+3}$.

Results and Discussion

It is postulated that the addition of Cr(II) to UO_2^{+2} in acid solution results in the immediate capture of UO_2^{+2} to form an intermediate[2]

$$Cr(II) + UO_2^{+2} = [Cr^{III}\text{–}O\text{–}U^{V}\text{–}O]^{+4} \qquad (1)$$

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(3) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961).

(4) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).

(5) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

(6) M. Anbar and S. Guttman, *J. Appl. Rad. Isotopes*, **5**, 233 (1959).

TABLE II

OXYGEN-18 TRACER RESULTS WITH UO_2^{+2} ADDED TO Cr^{+2} AT 25°; FINAL CHROMIUM–URANIUM RATIO OF 2.00

$HClO_4$, *M*	Time elapsed during addn. of UO_2^{+2}, sec.	n_t
0.26	6	0.72
0.55	4	1.01
1.04	4	0.65
0.26	30	.72
0.55	35	.89
1.04	35	.52

which concurrently reacts with excess Cr(II) to form products

$$[Cr^{III}\text{–}O\text{–}U^{V}\text{–}O]^{+4} + Cr(II) = 2Cr(III) + U(IV) \quad (2)$$

During the process shown in eq. 1 and 2 very efficient transfer of oxygen from UO_2^+ to Cr(II) takes place at 25°. The data supporting these conclusions are shown in Table I. At 25° the observed value of n_t is always greater than 0.70, which implies that Cr–O–U bonds must be formed.

It has been suggested[2] that the intermediate is indeed a U(V)–Cr(III) species rather than a U(VI)–Cr(II) species since its spectrum is similar to those of other Cr(III) complexes. Thus the species is probably $[(H_2O)_5\text{–}Cr^{III}\text{–}O\text{–}U^{V}\text{–}O]^{+4}$. Since complete oxygen transfer can be observed, we conclude that the intermediate is capable of reactions with excess Cr(II) before disproportionating or dissociating. If dissociation did occur before reaction with a second Cr(II), a maximum value for n_t of 0.75 would be observed; if disproportionation to Cr(III), U(IV), and U(VI) took place, the maximum value of n_t would be even less.

Additional experiments have been carried out in which UO_2^{+2} is added to Cr(II) at 25°. These results are summarized in Table II. The principal reactions which occur are (1) and (2) and substantial transfer of oxygen from the UO_2^{+2} to the initially excess chromium does occur. Even when the UO_2^{+2} is added very slowly, the intermediate is capable of reacting immediately with Cr(II) so that large values of n_t are observed and in some cases they are close to the theoretical maximum. An unusual dependence of n_t on the H^+ ion is observed and this is interpreted in terms of various competing rates for the decomposition of intermediates and the oxygen exchange of intermediates with solvent.

Experiments also have been carried out by mixing chromium with uranium in a 1:1 ratio. These conditions should result in a maximum amount of intermediate. The data are shown in Table III. At 25° the intermediate is very reactive and almost all of the intermediate disproportionates before the second aliquot of Cr(II) is added some 30 to 300 sec. later (the final chromium–uranium ratio is 2.00). This is substantiated by the fact that the final values of n_t shown in Table III do not change appreciably when the delay time between addition of aliquots ranges from 30 to 300 sec.

TABLE III

OXYGEN-18 TRACER RESULTS WITH Cr(II) ADDED IN TWO ALIQUOTS; FINAL CHROMIUM–URANIUM RATIO OF 2.00

$HClO_4$, *M*	Temp., °C.	Time between addn. of 2 aliquots of Cr(II), sec.	n_t
0.26	25	30	0.28
0.55	25	30	.48
1.04	25	30	.64
0.26	25	300	.33
0.55	25	300	.55
1.04	25	300	.70
0.26	0	30	.35
0.50	0	30	.38
1.09	0	30	.47
0.26	0	300	.28
0.50	0	300	.26
1.09	0	300	.28

Assuming that Newton and Baker's mechanistic arguments based on data at 0° will also apply at 25° under conditions of high intermediate concentration, there exist at least two intermediates

$$[Cr^{III}\text{–}O\text{–}U^{V}\text{–}O]^{+4} = Cr\cdot U^* \quad (3)$$

The exact composition of the species designated by $Cr\cdot U^*$ is unknown. However, the detailed oxygen-18 tracer experiments can be used to elucidate its composition. Then under the conditions of the tracer experiments the principal path for loss of intermediate is

$$Cr\cdot U^* + [Cr^{III}\text{–}O\text{–}U^{V}\text{–}O]^{+4} = UO_2^{+2} + U(IV) + 2Cr(III) \quad (4)$$

and

$$Cr\cdot U^* = Cr(III) + UO_2^{+} \quad (5)$$

followed by

$$UO_2^{+} + Cr\cdot U^* = Cr(III) + UO_2^{+2} + U(IV) \quad (6)$$

or

$$2UO_2^{+} = UO_2^{+2} + U(IV) \quad (7)$$

Since $Cr\cdot U^*$, which is taken to be the more reactive intermediate, could be as much as 10% of the original intermediate, the disappearance of intermediates is certainly complex.

It has been suggested that $Cr\cdot U^*$ cannot be a mixture of UO_2^+ and Cr(III). If the intermediate were dissociated, the UO_2^+ would catalyze the UO_2^{+2}–H_2O exchange as shown by Gordon and Taube.[7] Their results indicate that the rates of oxygen exchange between UO_2^+ and H_2O proceeds 10^7 times faster than that for UO_2^{+2} in dilute acid, and in 1 *M* $HClO_4$ the rates differ by more than 10^{10}. The dominant path for the exchange of UO_2^{+2} with water presumably takes place through the ion UO_2OH^+. Gordon and Taube also cite evidence that the rate of exchange of UO_2^+ with water is linear in H^+.[3]

Masters and Schwartz[8] and others[9,10] have shown that UO_2^+ disproportionates more rapidly at high acid appropriate to the rate law

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[7] G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **19**, 189 (1961).

[8] B. J. Masters and L. L. Schwartz, *J. Am. Chem. Soc.*, **83**, 2620 (1961).

[9] H. Imai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957).

[10] D. M. H. Kern and E. F. Orlemann, *J. Am. Chem. Soc.*, **71**, 2102 (1949).

$$-\frac{d}{dt}[UO_2^+] = k_D[UO_2^+]^2[H^+] \qquad (8)$$

The rate constant k_D has the value 436 M^{-2} sec.$^{-1}$ for solutions of ionic strenght 2 at 25°.

TABLE IV
OXYGEN-18 TRACER RESULTS WITH SLOW ADDITION OF Cr(II); FINAL CHROMIUM-URANIUM RATIO OF 2.00

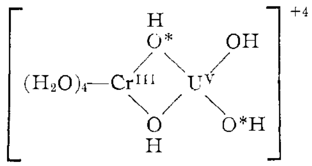
$HClO_4$, M	Temp., °C.	Time elapsed during addn. of Cr(II), sec.	n_t
0.26	25	30	0.39
0.55	25	35	.41
1.04	25	60	.25
0.26	0	50	.26
0.50	0	50	.27
1.09	0	40	.26

Therefore if the more reactive intermediate were dissociated, UO_2^+ and Cr(III), the UO_2^+ would be at isotopic equilibrium with solvent and would catalyze the UO_2^+-H_2O exchange. However, the concentration of catalyst would decrease with increasing acidity and the value of n_t should increase to a maximum of 0.5 if UO_2^+ were the reactive intermediate. Therefore the steady-state concentration of UO_2^+ must be very small.

At 0° with an initial chromium-uranium ratio of two, rapid addition of Cr(II) results in very low values of n_t (see Table I). When the Cr(II) is added more slowly the value of n_t is increased more than threefold. Newton and Baker have shown that, with an initial chromium–uranium ratio of two, at the end of 30 sec. less than 0.07 intermediate per UO_2^{+2} is left in solution. If (4) is the dominant path for the destruction of intermediate, even if UO_2^{+2} exchanges completely before addition of the second aliquot of Cr(II), n_t must be at least 0.5. This is also true if (5) is the dominant decomposition reaction. Since n_t is as little as 0.06 at 0°, the transfer is not efficient in at least one form of the intermediate or exchange can occur at 0° between the intermediate and the solvent.

Taube[11] has suggested that two forms of the intermediate might only differ in degree of hydration and bridging. A more detailed representation of eq. 3 is shown in eq. 9.

$H_2O + [(H_2O)_5\text{–}Cr^{III}\text{–}O^*\text{–}U^V\text{–}O^*]^{+4} =$



(9)

The double-bridged intermediate would be the more reactive one and this species could also account for the oxygen exchange of the intermediate with solvent if at 25° eq. 9 represented a rapid equilibrium. However, the double-bridged intermediate is not uniquely necessary for the exchange.

The increasing of n_t with increasing H^+ under conditions of high intermediate concentration shown in Table III is not in disagreement with this proposal; however, it does not preclude the possibility that simply less efficient transfer of uranyl oxygen takes place at higher acidities.

Table IV shows the results of slow addition of Cr(II) to UO_2^{+2} with a final chromium–uranium ratio of two. The slow addition of Cr(II) results in combinations of reactions 2–6. The amount of transfer at 25° is substantially smaller than when the Cr(II) is added rapidly and smaller differences are observed in the values of n_t.

The slow addition of Cr(II) and the experiments with an initial chromium to uranium ratio of one at 0° are in substantial agreement with the results at 25°, although the trends are somewhat less pronounced.

In conclusion, the results of the oxygen-18 tracer experiments show that at 25° the predominant intermediate in the reduction of UO_2^{+2} by Cr^{+2} is a species which contains U–O–Cr bonds and that this species in the presence of excess Cr^{+2} forms an activated complex containing Cr–O–U–O–Cr bonds which under conditions of low H^+ results in the complete transfer of uranyl oxygen to the Cr(II).

Additional tracer experiments in the presence of complexing ligands Cl^-, Br^-, and NCS^- are currently under investigation in an attempt to find evidence for a double-bridged intermediate with the anion acting as one of the bridging ligands.

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[11] H. Taube, private communication, 1962.