several possibilities. For example, the following scheme is eliminated

$$R_2NH + TiF_4 \longrightarrow [TiF_4{\cdot}R_2NH] \qquad (1)$$

$$TiF_4R_2NH + R_2NH \longrightarrow R_2NH_2^+ + TiF_4NR_2^- \qquad (2)$$

$$TiF_4NR_2^- + 2TiF_4 \longrightarrow R_2NTiF_3 + Ti_2F_9^- \qquad (3)$$

Continued reaction of $Ti_2F_9^-$ as
in the proposed mechanism (4)

This scheme can be eliminated, for completion of steps 1, 2, and 3 would produce the maxima in the conductance curve and would require 0.66 mole of base per mole of TiF_4 instead of the 0.33 mole found experimentally. Appreciable quantities of alkylammonium ion at low mole ratios also are required and this species is found to be absent.

Many other schemes can be eliminated by similar reasoning.

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CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO
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Oxygen Tracer Experiments on the Oxidation of Aqueous Uranium(IV) with Oxygen-Containing Oxidizing Agents[1]

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Oxygen^{18} tracer studies have been made on the oxidation of aqueous uranium(IV) with various oxygen-containing oxidizing agents. The reactions studied were the oxidation of U_{aq}^{+4} by solutions of MnO_4^-, $CrO_4^=$, H_2O_2, and some halogenates; solid samples of PbO_2, MnO_2, and $NaBiO_3$; and gaseous samples of O_2 and O_3. With oxygen or ozone only one of the oxygens in the UO_2^{++} product derives from the oxidizing agent. In the case of PbO_2 or MnO_2 both (very nearly) oxygens in the UO_2^{++} derive from the oxidizing agent. These results are interpreted in terms of oxygen atom transfer accompanied either by hydrolysis with solvent or by oxide ion transfer from the oxidizing agent.

This paper presents the results we have obtained measuring the extent of oxygen transferred when oxy-oxidizing agents react with U^{+4}. The results are of some special interest since they are the first of this kind to be obtained for an oxycation of the actinide series. The work[3-5] which has been done on the exchange between UO_2^{++} and water has prepared the way for the present study. UO_2^{++}, at least when the UO_2^+ concentration is kept low,[5] exchanges oxygen with the solvent only slowly, so that with the oxidizing agents suitably chosen meaningful tracer experiments can be done.

Experimental

The steps involved in carrying out a tracer experiment on the oxidation of uranium(IV) were: preparation of uranium(IV) and of the 'normal' oxidizing agent in oxygen^{18}-enriched water; mixing of the reagents to bring about reaction; removal of excess oxidizing or reducing agent or of substances which may interfere in the step following; precipitation of the UO_2^{++} as $(UO_2)_2Fe(CN)_6$; conversion of oxygen in the UO_2^{++} to CO_2; mass spectrometric analysis of the carbon dioxide.

Preparation of Materials.—All of the chemicals used in this work were reagent grade. Uranyl perchlorate pentahydrate was prepared from uranyl nitrate.[4] Uranium(IV) solutions were prepared by electrolytic reduction of UO_2^{++} in $HClO_4$, using a Hg cathode and Pt anode in a compartmented cell. Providing the solution was kept cold (0°), the reduction of U(VI) to U(IV) went to completion. Any U(III) formed was removed by a stream of oxygen. Oxygen only slowly oxidizes acidic solutions of uranium(IV).[6] Uranium(IV) concentrations were determined by ceric sulfate titration at 50° using ferroin as the indicator.[4] The absence of U(III) and U(VI) peaks in the spectrum of the U(IV) solution constituted the criterion for purity of the preparation.[7] The hydrogen ion concentration was determined by titration with standard NaOH after the uranium was removed with an ion-exchange resin column. Cor-

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(2) Department of Chemistry, University of Maryland, College Park, Maryland.

(3) H. W Crandall, *J. Chem. Phys.*, **17**, 602 (1949).

(4) G. Gordon and H. Taube, *J. Inorg. & Nuclear Chem.*, **16**, 272 (1961).

(5) G. Gordon and H. Taube, *ibid.*, **19**, 189 (1961).

(6) J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).

(7) D. Cohen and W. T. Carnall, *J. Phys. Chem.*, **64**, 1933 (1960).

rection was made for the hydrogen ion released by the column.

The $HClO_4$ solutions were prepared by diluting concentrated acid and were standardized by titration. The concentrated acid was analytical reagent 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; the second distillation was from alkaline $KMnO_4$ in an all Pyrex still, the third distillation was at atmospheric pressure from an all Pyrex still.

Chlorine dioxide was prepared using $H_2C_2O_4$ and $KClO_3$ as recommended by Bray.[8] The ClO_2–CO_2 gaseous product was bubbled through 2 M Na_2CO_3 solution to remove Cl_2 and HCl. Dilute solutions of chlorine dioxide were prepared by passing the gaseous mixture through cold distilled water.

Sodium chlorite, obtained from the Matheson Company, was 98% by weight $NaClO_2$ (1.2% NaCl) and was used without further purification. Chlorite solutions were prepared in very dilute acid immediately prior to use.

Hypochlorous acid solutions were prepared by acidifying cold solutions of NaOCl which had been prepared from Cl_2O. The NaOCl solution was stirred at 0° and contained small amounts of ClO_3^-. The chlorine dioxide, chlorite, and hypochlorite solutions were analyzed iodometrically.

Procedure in Bringing about Reaction.—In most cases, reaction was carried out by slowly adding one solution to another, with rapid stirring using a magnetic stirrer. In some of the systems the reaction was very rapid, and by reversing the order of mixing a considerable variation in the concentration ratio of reactants during reaction was achieved.

With the oxidizing agents used as solids, the reactions were carried out in several ways. Small amounts of oxidizing agent were added to the rapidly stirred uranium(IV) solution until, as judged by the color, the U(IV) had disappeared, excess oxidizing agent was removed by centrifugation, and the uranyl solution was treated as described below. An alternative procedure was to place an excess of solid oxidizing agent into the dry reaction vessel. Then slightly less than stoichiometric quantities of uranium(IV) solution were added with rapid stirring and the solution next was treated as above. In a few cases excess U(IV) was used and, after all the oxidizing agent was consumed, the excess U(IV) was removed by the precipitation of UF_4 with HF. The UF_4 was removed by centrifugation and UO_2^{++} precipitated as the ferrocyanide.

Experiments in which gases (oxygen, ozone, and chlorine dioxide) were used as oxidizing agents were carried out by passing a steady stream of oxidizing gas through the uranium(IV) solution of the desired acidity. With ClO_2 the reaction was complete in about 10–12 seconds. Molecular oxygen and ozone required reaction times of about 20 to 80 min., depending on the H^+ concentration, to obtain UO_2^{++} samples large enough for isotope analysis. Excess gaseous oxidizing agent was swept out of the reaction flask with a stream of N_2 before precipitating uranyl ferrocyanide.

Isotope Analysis.—The metal ions formed on the reduction of MnO_2, PbO_2, or $NaBiO_3$ interfere with the isotopic analysis for UO_2^{++} since hydrous ferrocyanides apparently are precipitated with the uranyl ferrocyanide. This interference is not so severe as to completely vitiate the ordinary procedure and some results were obtained with it which agree fairly well with those obtained using the modification of the method to be described. The modification consisted of pouring the product solution rapidly through an ion-exchange column (Dowex 50-X resin was used). Conditions were found under which the interfering metal ions were removed completely with only partial loss of UO_2^{++}. This procedure, which exploits a difference in rate of equilibration rather than equilibrium affinities, gave reasonable and consistent results (see Table IV).

The product uranyl ion was separated from the solution by precipitation of uranyl ferrocyanide using a procedure described previously.[4] It needs to be pointed out that an excess of ferrocyanide must be avoided if the precipitate is to be uncontaminated by solvent water. The dried samples of $(UO_2)_2Fe(CN)_6$ were heated to 400° with $HgCl_2$ and the carbon dioxide formed was purified for analysis over Zn–Hg at 200°. The isotopic composition of the CO_2 thus prepared was read directly on the mass spectrometer. Duplicate samples usually were precipitated from the same solution.

To test the precision of the method, separate precipitations and isotopic analyses were made on UO_2^{++} of normal isotopic composition contained in water 8-fold enriched in O^{18}. The average deviation from the mean in the series was less than 0.1%, the value of isotopic composition measured differed from that expected for the normal sample by less than 0.2%. Since the mass spectrometer readings can be made to a precision of better than 0.025%, the imprecision observed probably is caused by fractionation effects or by a small amount of contamination by the solvent oxygen. To test whether isotopic dilution takes place in the treatment to which the $(UO_2)_2Fe(CN)_6$ is subjected, $U_{aq.}^{+4}$ in 4-fold enriched water was oxidized by Cl_2 so that the oxygen contained in UO_2^{++} was of necessity derived from the solvent. The O^{18} content of the uranyl ion following the usual procedure was found to be only 1% less than that of the water used as solvent. The difference in isotopic composition may well be the result of a fractionation effect in forming UO_2^{++} in water. In another series of experiments $Cr_2O_7^=$ in isotopic equilibrium with 5-fold enriched water was used to oxidize U^{+4}, thus again forming UO_2^{++} of known isotopic enrichment. $R_{H_2O}/R_{UO_2^{++}}$ for experiments in triplicate came out as 1.032, 1.031, and 1.034 (*vide infra* for definition of R). Here again a large part of the deviation from 1.00 can be ascribed to isotopic fractionation. The blank experiments show that the procedure leads to dependable isotopic analyses, and that contamination of the precipitate by acetone (in the washing procedure) or by exchange with glass during the heating procedure is slight. These are the only sources of oxygen of normal isotopic composition with which the uranyl ion comes into contact after its formation.

With the exception of the MnO_2 used in some of the experiments, all of the oxidizing agents were of normal O^{18} content and were analyzed for isotope ratio by standard procedures. Only the solvent water was enriched in O^{18}. Except where otherwise indicated the $Fe(CN)_6^{-4}$ used to precipitate the UO_2^{++} also was contained in O^{18}-enriched water. With the exceptions noted in the preceding paragraph, the only source of 'normal' oxygen for UO_2^{++} was the oxidizing agent so that in all cases reported the values

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(8) W. C. Bray, *Z. physik. Chem.*, **54**, 575 (1906).

for n_t and n_a (see below) would seem to be minimum values.

Treatment of the Data.—The calculation of oxygen transfer will be outlined with reference to reaction 1, which is typical of those studied.

$$2MnO_4^- + 5U(IV) + 2H_2O \rightleftharpoons 2Mn^{++} + 5UO_2^{++} + 4H^+ \quad (1)$$

The symbol U(IV) denotes total uranium(IV) concentration.[9]

The following symbols have been used in this paper.

n_t is the number of oxygen atoms per uranyl ion which derive from oxidizing agent and is determined experimentally. If both oxygens on the product uranyl were derived from oxidizing agent, n_t would be 2.

R_x represents the experimentally determined ratio of O^{18} to O^{16} in the species X. Values of n_t can be calculated from R_x where

$$n_t = \left[\frac{R_{solv.} - R_{UO_2^{++}}}{R_{solv.} - R_{oxid.}}\right] \quad (2.00)$$

From the form of the above equation, it can be seen that as $R_{solv.}$ is approached by $R_{UO_2^{++}}$ or $R_{oxid.}$ an error in any of the values of R is greatly magnified as a fractional error in n_t. In general, $R_{UO_2^{++}}$ or $R_{oxid.}$ differed from $R_{solv.}$ by 50% or more, so that the precision of the value of n_t is about ±0.03. Effects due to isotope fractionation which arise from the fact that the oxidizing agent may have been used in slight excess are not great enough to affect n_t by more than the precision of the experiments.

n_a is the number of oxygen atoms derived from one molecule of the oxidizing agent which appears in the product uranyl ion.

Results

Some Blank Experiments.—A condition for the success of the tracer experiments is that UO_2^{++} must not exchange oxygen with the oxidizing agent, and the oxidizing agent must not induce exchange with the solvent. The exchange of UO_2^{++} with H_2O is sufficiently sensitive to catalysis that it was considered necessary to test for induced exchange using at least some of the oxidizing agents. In experiments with enriched 1.0 M UO_2^{++}, 1.0 M $HClO_4$ in normal water, and with the oxidizing agent of normal isotopic composition at 1.0 M, less than 1.5% exchange was observed in UO_2^{++} when the oxidizing agents used were MnO_4^-, $Cr_2O_7^=$, H_2O_2, ClO_2, PbO_2, O_2, or O_3. The time of contact was of the order of 1 minute. With BrO_3^- and ClO_2^- present some exchange in UO_2^{++} is observed: *ca.* 4% and 2%, respectively. Also, when $NaBiO_3$ is the oxidizing agent decrease in the enrichment of the UO_2^{++} is observed. This may, however, not be real, and may be the result of contamination of uranyl ferrocyanide by a hydrous bismuth ferrocyanide (Bi(III) may be leached from the solid by the acidic solution). When H_2O_2 is present and uranyl peroxide is precipitated, the contained uranyl ion has undergone considerable exchange with the solvent. HF (used as a precipitant for U^{+4} in some experiments) does not bring about appreciable exchange in UO_2^{++} in the time of separation of UF_4. A slight exchange is noticed when UO_2^{++} in acid is left in contact with Dowex 50X cation exchange resin. With (H^+) at 0.8 M, (UO_2^{++}) at 1.00 M, the percentages of exchange after 0.5, 1–1.3, 3, and 6 min. of contact are 0.5, 3.1, 9.2, and 22.2%, respectively. In the actual separation of Mn^{++}, Pb^{++}, and Bi^{+++} from UO_2^{++}, the time of contact of UO_2^{++} and resin is only 15–20 sec., and no correction has been applied to the data obtained in experiments in which the resin was used. When UO_2^{++} solution is made sufficiently alkaline so that a precipitate of uranyl hydroxide just begins to appear, and then is acidified immediately, the uranyl ion is found to have undergone 70% exchange with the solvent.

$U^{+4}{}_{aq}$ is known from earlier work to bring about a slow exchange of UO_2^{++} with solvent, and this was confirmed in the course of the present study. U^{+4} presumably catalyzes the exchange by producing UO_2^+ from UO_2^{++}. UO_2^+ however will react rapidly with most of the oxidizing agents used and we believe therefore that no serious error from this source is introduced into the present series of experiments.

The Reaction $4H^+ + 3U^{+4} + 2CrO_4^= \rightleftharpoons 3UO_2^{++} + 2Cr^{+++} + 2H_2O$.—Chromate exchanges oxygen with the solvent quite rapidly in acid solution. Only if the reaction of $CrO_4^=$ with U^{+4} is rapid compared to the exchange, can any of the $CrO_4^=$-oxygen be expected to appear in UO_2^{++}. The results in Table I in which substantial transfer is recorded show that the system apparently

TABLE I

OXYGEN TRANSFER IN THE REACTION OF U(IV) AND CHROMATE

[(U^{+4}), 0.25–0.40 M, mixed with $CrO_4^=$ in stoichiometric amounts]

$(H^+)^a$	n_t	n_a
2.5	1.17	1.76
2.5	1.17	1.76
2.1	1.22	1.83
2.1	1.24	1.86
0.47	0.89	1.34
.47	0.87	1.31
.15	1.07	1.61
.15	1.23	1.85

[a] Concentration of acid contained in the U^{+4} solution.

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(9) The work of K. A. Kraus and F. Nelson (*J. Am. Chem. Soc.*, **72**, 3901 (1950), and **77**, 3721 (1955)) indicates that in 0.5 M $HClO_4$ about 10% of the U(IV) is present in the form UOH^{+++}.

satisfies the condition on the relative rates. In all cases, the chromate was dissolved in unacidified water of normal isotopic composition, and a small volume of this was added to a much larger volume of an acid solution of U^{+4} in enriched water.

The amount of acid in the last two experiments was not sufficient for complete reaction and the U(IV) left at the end of the experiment was removed as UF_4 before the uranyl ferrocyanide was precipitated.

The Reaction of Permanganate and U(IV).—The tracer results on this reaction (see equation 1) are shown in Table II.

TABLE II

OXYGEN TRANSFER IN THE REACTION OF U(IV) AND MnO_4^-

[$(MnO_4^-)_0$, 0.4–0.5 *M;* temp., 25°; MnO_4^- added to U(IV), reagents used in ratios corresponding to stoichiometry of equation 1]

(H^+)	$[U(IV)]_0$	n_t	n_a
2.14	0.50	1.46	3.65
2.14	0.50	1.40	3.50
1.42	1.00	1.45	3.63
1.38	0.33	1.56	3.90
1.38	.33	1.73	4.33[a]
1.03	.45	1.61	4.03
1.03	.45	1.49	3.73
0.34	1.00	1.20	3.00
.34	1.00	1.23	3.08
.17	0.50	1.15	2.88
.17	0.50	1.13	2.83

[a] This is the only experiment of the series in which a precipitate of MnO_2 was observed to form.

It has been shown by Zimmerman[10] and McDonald[11] that the exchange of MnO_4^- with water is slow under conditions similar to those used in our experiments. The extensive transfer observed (see entries under n_a) shows that in any case, the oxidation–reduction reaction is rapid compared to MnO_4^-–H_2O exchange.

The Reaction $H_2O_2 + U^{+4} \rightleftharpoons UO_2^{++} + 2H^+$.—The tracer results obtained in the study of this reaction are summarized in Table III.

The reaction of U^{+4} and H_2O_2 is rapid, so that changing the order of mixing brings about a wide variation in the ratio of $(U^{+4})/(H_2O_2)$ during reaction. It is remarkable that n_t is so little sensitive to the variation in this ratio as it appears to be from the data of Table III.

TABLE III

OXYGEN TRANSFER IN THE REACTION OF U(IV) WITH H_2O_2

$(H_2O_2)_0$ = 0.50 *M;* $(U^{+4})_0$, 0.8 to 1.0 *M;* temp., 25°

(H^+)	Conditions	Number of experiments	$n_t = n_a$
0.39	H_2O_2 added slowly to U(IV), stoichiometric ratios	1	1.00
0.85		3	1.05
1.50		2	0.98
0.39	U(IV) added rapidly to H_2O_2, stoichiometric ratios[a]	1	1.31
0.85		2	1.19
1.4–1.5		2	1.14
0.03	H_2O_2 added slowly to excess U(IV)[b]	5	1.06
0.39		2	1.04
0.85–0.92		6	1.18
1.4–1.5		3	1.19

[a] Slow addition of U^{+4} resulted in the formation of a precipitate, presumably $UO_2O_2 \cdot 2H_2O$. [b] Excess U^{+4} removed as UF_4.

The Reaction $2U^{+4} + O_2 + 2H_2O \rightleftharpoons 2UO_2^{++} + 4H^+$.—To get enough reaction of U^{+4} with O_2 in a reasonable time, it is necessary to keep (H^+) fairly low.[6] Over the range of (H^+) from 0.012 to 0.126 *M*, the average value of n_t observed was 0.99 ± 0.017 (mean of 9 determinations), with no observable trend in the values with (H^+). This value of n_t corresponds to n_a = 1.98, and therefore to essentially complete transfer of oxygen from O_2 to U^{+4}.

The Reaction $O_3 + U^{+4} + H_2O \rightleftharpoons O_2 + UO_2^{++} + 2H^+$.—The reaction of O_3 with U^{+4} is by no means rapid, and in this system as in that using O_2 as oxidizing agent it was necessary to keep the concentration of H^+ low. In the range of (H^+) from 0.02 to 0.4 *M*, the rate of reaction appears to be inverse in (H^+), and in the same range of acid concentration n_t = 1.00 ± 0.0016 (average of 11 determinations). The exchange of O_3 with H_2O is known to be very slow,[12] so that no difficulty from this source is expected in spite of the slow rate of reaction.

It needs to be pointed out that the stoichiometry represented by the equation in the heading of this section has not been established, but it does correspond to a reasonable course for the reaction.

The Reaction of U(IV) with MnO_2, PbO_2, and Sodium Bismuthate.—For solid oxidizing agents, a slow rate of oxygen exchange with the solvent compared to the rate at which they react with the reducing agents by no means ensures the success of the tracer experiments. The exchange of oxygen between insoluble oxides and water may be limited by the rate of diffusion in the solid, whereas the feature which is important for tracer experiments is the rate of reduction of the surface layer compared to the rate at which it exchanges oxy-

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(10) G. Zimmerman, Ph.D. Thesis, University of Chicago, 1949.

(11) H. O. McDonald, Ph.D. Thesis, University of Arkansas, 1960.

(12) O. L. Forchheimer and H. Taube, *J. Am. Chem. Soc.*, **76**, 2099 (1954).

gen. The tracer studies performed with the solids MnO_2, PbO_2, and sodium bismuthate show that in every case reduction of the surface layer competes favorably with the exchange.

Only the results obtained using the cation exchange method of separating the metal ion reduction product from UO_2^{++} are reported in detail. A large number of experiments were done precipitating uranyl ferrocyanide directly from the product solution. The results agree in general with those which are reported in detail, but the values of n_t are much more variable, ranging from some as high as those reported to some which are perhaps 20% lower, for MnO_2 and PbO_2, and as much as 50% lower for sodium bismuthate. These deviations can without doubt be ascribed to the incorporation of some hydrated Mn(II), Pb(II), or Bi(III) ferrocyanides into the uranyl ferrocyanide precipitate.

Table IV shows the results of the tracer experiments with MnO_2, PbO_2, and sodium bismuthate.

TABLE IV

REACTION OF SOLID OXIDIZING AGENTS WITH U^{+4}_{aq}.

(H^+)	Oxidizing agent	n_t
1.5	PbO_2	1.79
1.5	PbO_2	1.83
0.8	PbO_2	1.76
0.8	PbO_2	1.80
0.4	PbO_2	1.86
0.4	PbO_2	1.86
1.8	MnO_2	1.74
0.8	MnO_2	1.81
0.8	MnO_2	1.79
0.8	MnO_2[a]	1.68
1.8	Sodium bismuthate	1.70
1.8	Sodium bismuthate	1.70
0.8	Sodium bismuthate	1.82
0.8	Sodium bismuthate	1.80

[a] Average of 3 experiments using enriched MnO_2 in normal water.

Miscellaneous Experiments.—The tracer results with BrO_3^-, ClO_2^-, and ClO_2 are not reported in detail because the stoichiometry of the reactions has not yet been established. The reactions with ClO_2^- and ClO_2 are certainly complex, with disproportionation of the oxidizing agent accompanying the oxidation of U^{+4}. Cl_2 (and even HOCl) reacts only slowly with U^{+4} so that Cl^- is by no means the only reduction product which can be expected. It is interesting in this connection that HOCl reacts much less rapidly with U^{+4} than do ClO_2 and ClO_2^-—usually HOCl is a more reactive oxidizing agent than are the higher oxidation states. In the BrO_3^- system also, elementary halogen as well as halide ion can be the reduction product. The reactions are being investigated in detail, and the tracer results will be published in detail[13] when the stoichiometry is better understood. For the present purpose it is sufficient to note that extensive oxygen transfer to uranium takes place with each of the three oxidizing agents, and for each under some conditions it exceeds one atom of oxygen per UO_2^{++}. With BrO_3^- as oxidizing agent at lower acid concentrations (0.40 *M* and less), all of the bromate oxygen appears in the product uranyl ion.

Exchange of oxygen between HOCl and solvent is much too rapid compared to the rate at which HOCl oxidizes U^{+4} to make a tracer study possible. But before it was appreciated that the U^{+4}–HOCl reaction is really quite slow some tracer experiments were done which, while not contributing to the main theme of this paper, revealed an interesting effect which seems worth describing. Although the reaction of HOCl with U^{+4} was carried out in H_2O highly enriched in O^{18}, it was found that the uranyl ion which precipitated as the ferrocyanide was almost normal in isotopic composition. The source of the oxygen of normal isotopic composition was traced back to the small amount of water used to carry the precipitant, ferrocyanide ion. In a typical experiment, a few drops of ferrocyanide solution are added to several ml. of UO_2^{++} solution, yet despite the preponderance of other water, the uranyl ferrocyanide gathers its oxygen almost exclusively from the water contained in the ferrocyanide solution. To lead to this result, two conditions must be satisfied: a catalyst for the UO_2^{++}–H_2O exchange needs to be generated and uranyl ferrocyanide must be formed by diffusion of UO_2^{++} into the ferrocyanide solution. The catalyst for the exchange probably is UO_2^+ formed by the reaction of U^{+4} with HOCl (small amounts of both reagents were left in solution). Direct experiments showed that U^{+4} and HOCl do produce a catalyst for UO_2^{++}–H_2O exchange. As to the second condition, it can be realized if, as seems possible, a skin of uranyl ferrocyanide surrounds the droplets of ferrocyanide solution, thus preventing diffusion of $[Fe(CN)_6]^{-4}$ out but permitting that of UO_2^{++} into the droplets.

Discussion

The oxidizing agents studied in detail fall into two classes: in one class which contains O_2 and

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(13) G. Gordon and D. M. H. Kern, to be published.

O_3, the maximum number of oxygen atoms the oxidizing agent can supply is equivalent to the change in oxidation number, each O atom being equivalent to a $2e^-$ change; in the other, containing MnO_4^-, $CrO_4^=$, H_2O_2, PbO_2, and MnO_2, the oxygen supply exceeds that called for as equivalent to the change in oxidation number so that in effect, oxide ions as well as oxygen atoms are available for transfer.

For oxidizing agents of the first class, it would be remarkable[14] indeed if more than one oxygen atom per UO_2^{++} formed were derived from the oxidizing agent, but it is interesting nevertheless that the maximum transfer which can reasonably be expected is observed, corresponding almost exactly to one oxygen atom per UO_2^{++}. The reaction of U^{+4} with O_3 has not been studied in detail kinetically, and in the absence of kinetic or other evidence to the contrary, it seems reasonable to regard the reaction as involving direct oxygen atom transfer from O_3 to U^{+4}, a water molecule attached to U^{+4} losing two protons to make up the "yl" ion

$$O_3 + U^{+4}(H_2O)_n \longrightarrow O_2 + OUO^{++}(H_2O)_m + 2H^+ + (n-m-1)\,H_2O$$

When O_2 is the oxidizing agent, the final products cannot be formed by a simple process first-order in each reactant of the oxidation–reduction pair. From the observations of Halpern and Smith[6] the reaction is nevertheless first-order in U^{4+} and in O_2. While it would not be difficult to devise a mechanism that is compatible with the Halpern and Smith rate law, and with our tracer results, it is difficult to devise a chain mechanism that satisfactorily accounts for both sets of observations. Of the evidence cited by Halpern and Smith for the conclusion that a chain reaction is involved, only that dealing with the strong inhibition in the rate by low concentrations of Cl^- or Ag^+ is convincing. Thus although catalysis by various of the metal ions may mean only that new reaction paths are provided, there seems to be no alternative explanation for the inhibition effects. The chain mechanism proposed by Halpern and Smith is

$$U(IV) + O_2 \longrightarrow U(V) + HO_2 \qquad (2)$$

$$O_2 + U(V) \longrightarrow U(VI) + HO_2 \qquad (3)$$

$$HO_2 + U(IV) \longrightarrow U(V) + H_2O_2 \qquad (4)$$

$$U(V) + HO_2 \longrightarrow U(VI) + H_2O_2 \qquad (5)$$

$$U(IV) + H_2O_2 \longrightarrow U(VI) \qquad (6)$$

By this mechanism, for every molecule of UO_2^{++} formed by oxidizing U(IV) with H_2O_2 at least one is formed by an alternative route. It is unlikely that oxidation by the alternate routes proposed (reactions 2 and 3, 4 and 5) involves oxygen atom transfer, and it seems much more likely that the reactions take place by electron flow to the oxidizing agents O_2 or H_2O_2 with concomitant addition to them of H^+. Now in the reaction of H_2O_2 with U^{+4} only slightly more than one oxygen atom is transferred from each H_2O_2 to uranium, and thus by the Halpern–Smith mechanism only 0.5 to 0.6 O atoms for each UO_2^{++} would be derived from the oxidizing agent.

The Halpern–Smith mechanism is unsatisfactory in an important detail, that is, in accounting for inhibition by Cl^-. The most potent intermediate present is HO_2, and it is doubtful in the extreme that it is reactive enough to be destroyed by Cl^-. Using the free energy data given by Latimer,[15] the values of $\Delta F°$ for the reactions

$$HO_2 + H^+ + Cl^- \longrightarrow H_2O_2 + Cl$$

and

$$HO_2 + H^+ + Cl^- \longrightarrow HOCl + HO$$

are 26 and 18 kcal., respectively, and the values of $\Delta H°$ are probably even greater ($\Delta S°$ is likely positive for the reaction[6]). This argument by no means invalidates all features of the mechanism, since it may be possible to account for inhibition by Cl^- short of oxidizing it to $Cl\cdot$, and it must be admitted that the disagreement with our tracer results may not be real. The tracer experiments on transfer of oxygen from H_2O_2 to $U^{+4}{}_{aq.}$ were not done under the conditions which obtain in the O_2 reaction (O_2 present, and H_2O_2 at very low steady-state concentrations), so it is possible that the chain path for the H_2O_2–U^{+4} reaction (see below) is eliminated under the conditions of the O_2–U^{+4} reaction, and that two atoms of oxygen do transfer to uranium for each molecule of the intermediate which reacts.

Of the reagents of the second class, the most interesting results are those obtained with the solid oxidizing agents. For these, substantially all of the oxygen in UO_2^{++} is derived from the solid. This result hardly would have been predicted, but having been observed it points up the feature that the solid contains oxide ion ready-formed and made available by the reduction of the metal ion. To get the oxide required to complete the "yl" ion structure from the solvent, protons must be removed from the water molecules, and it is not too surprising

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[14] But it is possible to find more than one oxygen atom transferred for each UO_2^{++}. This can take place if excess oxidizing agent is used, and this exchanges oxygen with UO_2^+ or UO_2^{++}.

[15] W. M. Latimer, "Oxidation Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1953.

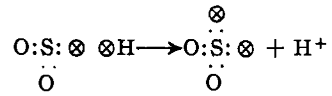
that this process does not compete favorably against the alternative one provided by the solid.

With $CrO_4^=$ and MnO_4^- as oxidizing agents, there is the additional complication that the net change in oxidation state for the oxidizing agent does not match that for U^{+4}, and the reactions must occur in stages, involving at least intermediate oxidation states of the oxidizing agents. It is all the more remarkable therefore that in the case of MnO_4^- under some conditions (see Table II) all of the contained oxygen appears in the UO_2^{++} formed. This may involve successive stages, Mn(VII) → Mn(V), Mn(V) → Mn(III), with efficient oxide transfer accompanying oxygen atom transfer in each of these stages, or, as seems more likely, reduction to Mn(VI) in the first step without transfer followed by efficient transfer of oxygen in the succeeding two electron stages. When $CrO_4^=$ is the oxidizing agent, despite the higher ratio of contained oxygen to change in oxidation state, less efficient transfer is observed. But it also should be noted that exchange of chromate with water in acid solution is much more rapid than for MnO_4^-, and for the intermediate oxidation states the reduction may compete even less favorably with exchange.

H_2O_2 reacting with $U^{+4}_{aq.}$ has the capacity to provide all the oxygen in UO_2^{++}, just as MnO_2 for example does, and in certain systems it is known to transfer oxide as well as oxygen atoms.[16] In the present system, the extent of transfer is only slightly in excess of 1.0. This is consistent with the conclusion reached by Baker and Newton[17] that a chain mechanism operates. For a simple bimolecular process, the transfer of two oxygen atoms for each molecule of H_2O_2 might well be expected, but it is difficult to see how this can occur by a chain reaction involving intermediates such as HO, HO_2, and UO_2^+. The fact that the extent of transfer is slightly in excess of one oxygen for each H_2O_2 suggests that simple bimolecular reaction may accompany the principal chain reaction process.

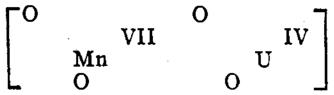
The transfer of two atoms of oxygen for each $2e^-$ act of oxidation until now has been observed only for H_2O_2 acting as oxidant,[18,19] and in every such case it can be regarded as involving a peroxy intermediate which rearranges. This kind of mechanism is herewith illustrated for sulfite as the reducing agent

$$H_2\otimes_2 + HOSO_2^- \longrightarrow H_2O + H\otimes\otimes SO_2^-$$



$$O{:}\underset{\overset{\cdot\cdot}{O}}{S}{:}\otimes\ \otimes H \longrightarrow O{:}\overset{\otimes}{\underset{\overset{\cdot\cdot}{O}}{S}}{:}\otimes + H^+$$

A similar explanation cannot, however, be offered for the reaction, for example, of MnO_4^- or MnO_2 with U^{+4}. One possibility is that a doubly bridged transition state is formed



On electron flow from U(IV) to Mn(VII), the oxygen bridging groups move from equilibrium positions near Mn to positions nearer U. Reaction is complete when the Mn–O bonds are severed by hydration or hydrolysis. It should be mentioned that there is no evidence for a doubly bridged structure in the transition state for the reaction of *cis*-CrF_2^+[20] with Cr^{++} or of *cis*-$en_2Co(H_2O)_2^{+++}$[21] with Cr^{++}, but such structures have been postulated[22] for reactions involving $2e^-$ changes.

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(16) J. Halpern and H. Taube, *J. Am. Chem. Soc.*, **74**, 380 (1952).

(17) F. B. Baker and T. W. Newton, *J. Phys. Chem.*, in press.

(18) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6243 (1954).

(19) R. M. Milburn and H. Taube, *ibid.*, **81**, 3515 (1959).

(20) Y. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

(21) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).

(22) See H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, New York, N. Y., 1959, chap. I.