to dissolve metallic hydroxides, noble metals whose diffusion currents are low in *p*H 5 buffer also show low diffusion currents in 0.1 *N* acid.

The formation of a precipitate in the palladium solution may be prevented by the addition of chloride. The diffusion current increases with the chloride ion concentration (Table I). Uncontrolled factors apparently also have an effect, for we obtained somewhat different diffusion coefficients for several palladium solutions with the same chloride ion concentration.

The addition of chloride to iridium or ruthenium solutions does not prevent precipitation, and therefore the diffusion current remains small.

On standing without added salt, solutions of rhodium(III) chloride show a slow change in color from red to yellow accompanied by an increase in diffusion current (Table I). Evidently the yellow complex, in which the chlorines have been replaced by hydroxyls or water,[15,16] is more easily reducible than the red complex.

When rhodium chloride is allowed to stand in acetate buffer, still another complex is formed, for the slope of the wave in such solutions decreases, *i.e.*, the reduction becomes more irreversible.

Laitinen and Onstott[4] investigated the polarographic reduction of chloroplatinite and showed that the current measured at −0.7 volt obeys the Ilkovic equation. Nevertheless, they interpreted the wave between 0 and −0.8 volt as an "adsorption wave," and their work has been cited in a review[17] as "a very convincing demonstration of the part which adsorption may play in polarographic reductions."

Except for the dip at −0.8 v., platinum waves exhibit the characteristics of a normal diffusion controlled wave, including the voltage at which they appear. We therefore think that the cause for the dip would bear further investigation. We have noted that the dip is less pronounced in an old solution than in a freshly dissolved one. Measurement of the current through the same voltage range using a rotating platinum electrode would be of interest to see whether the dip in current occurs with a different polarographic method.

BETHESDA, MD.

---

(15) Reference 9, p. 112.

(16) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 2, Univ. Press, Oxford, 1951, p. 1518.

(17) C. Tanford and S. Wawzonek, "Annual Review of Physical Chemistry," Vol. 3, Annual Reviews, Inc., Stanford, Calif., 1952, p. 255.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Exchange of Radioiridium between Hexachloroiridate(III) and Hexachloroiridate(IV) Ions[1a]

BY ERIC N. SLOTH[1b] AND CLIFFORD S. GARNER

RECEIVED OCTOBER 8, 1954

Exchange of radioiridium between $IrCl_6^{-2}$ and $IrCl_6^{-3}$ ions in 1 *f* hydrochloric acid at complex ion concentrations ranging from 0.1 to 0.0001 *f* has been found to be complete in exchange times of the order of one minute at 1 and 50° in the dark. Although the same results were obtained with three different chemical separation methods, the possibility of an induced exchange cannot be excluded. If it be assumed that the exchange is not separation-induced and that a rate law first order in each of the reactant iridium complexes is followed, the specific rate at 1° is greater than 290 liter mole^{-1} sec.$^{-1}$. Precautions in the isotopic labeling of substitution-inert complexes are discussed.

At the time when this investigation was started only two anion–anion systems had been examined for isotopic exchange *via* a possible electron-transfer mechanism, namely, the permanganate–manganate[2–5] and hexacyanoferrate(II)-hexacyanoferrate(III)[6–11] systems. Complete exchange in the time required for mixing and separating the reactants was reported[12] in both cases. More recently both systems have been shown to have measurable exchange rates, the former[13] with half-times of several seconds at 1° and reactant concentrations of $\sim 10^{-4}$ *m*, and the latter[14] with a half-time of ~ 0.3 second at 4° and reactant concentrations of 0.002 *m*. In addition, the octacyanomolybdate(IV)–octacyanomolybdate(V) system was later reported[15] to exhibit complete exchange at similar low concentrations and exchange times of the order of several seconds at 2°, and the hexacyanomanganate(II)–hexacyanomanganate(III) exchange has been tentatively reported[16] as immeasurably rapid.

The hexachloro complexes of iridium(IV) and iridium(III) in acid solution offer another opportunity to examine an anion–anion system for pos-

---

(1) (a) This work was supported in part under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California. (b) Chemistry Division, Argonne National Laboratory, Lemont, Illinois.

(2) W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

(3) H. C. Hornig, G. L. Zimmerman and W. F. Libby, *ibid.*, **72**, 3808 (1950).

(4) N. A. Bonner and H. A. Potratz, *ibid.*, **73**, 1845 (1951).

(5) A. W. Adamson, *J. Phys. Colloid Chem.*, **55**, 293 (1951).

(6) S. Ruben, G. T. Seaborg and J. W. Kennedy, *J. Applied Phys.*, **12**, 308 (1941).

(7) R. C. Thompson, THIS JOURNAL, **70**, 1045 (1948).

(8) W. B. Lewis, Tech. Report No. 19, O.N.R. Task Contract N5-ori-07806, M.I.T., Jan., 1949.

(9) C. Haenny and E. Wikler, *Helv. Chim. Acta*, **32**, 2444 (1949).

(10) J. W. Cobble and A. W. Adamson, THIS JOURNAL, **72**, 2276 (1950).

(11) L. Eimer and R. W. Dodson, Brookhaven National Laboratory Quarterly Progress Report, BNL 93 (S-8), 1950, p. 69.

(12) Ref. 6 reported incomplete exchange, but this was apparently an error arising from a faulty separation method; see ref. 7.

(13) J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **75**, 5133 (1953).

(14) A. C. Wahl and C. F. Deck, *ibid.*, **76**, 4054 (1954).

(15) R. L. Wolfgang, *ibid.*, **74**, 6144 (1952).

(16) A. W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).

sible measurable exchange rates, and this paper reports our studies of exchange in this system.

Experimental

Radioiridium Tracers.—Six separate tracer preparations were made, as follows, in an effort to obtain unambiguously labeled Na_2IrCl_6 and Na_3IrCl_6. All except tracer F were prepared from 74-day Ir^{192} produced by (n,γ) reaction on iridium metal and radiochemically purified by the Oak Ridge National Laboratory.

Tracer A was an Oak Ridge shipment, stated to be "$IrCl_3$ in HCl" and initially assumed by us to be H_3IrCl_6 in HCl. Later experiments indicated that the preparation was probably H_2IrCl_6 in HCl.

Tracer B was prepared by reduction of A with SO_2, followed by aeration to remove excess SO_2. This was initially assumed by us to be H_3IrCl_6 in HCl, but experiments later suggested B was Ir(III) in some aquated form such as $Ir(H_2O)Cl_5^{=}$.

Tracer C was made from B by oxidation to Ir(IV) with Cl_2, followed by aeration, then reduction to Ir(III) with SO_2, followed by aeration. Experiments subsequently implied that this tracer was Ir(III) in at least two different forms, probably both as aquochloro complexes with different ratios of water to chlorine.

Tracer D was a second Oak Ridge shipment, stated to be Na_2IrCl_6 in HCl. Inactive carrier Na_2IrCl_6 was added to raise the concentration 20-fold, then SO_2 was passed through to reduce all Ir(IV) to Ir(III), followed by aeration and treatment with Cl_2 to reoxidize back to Ir(IV), followed by aeration, giving solution C′. Part of C′ was added to inactive Na_2IrCl_6 and reduced to Na_3IrCl_6 with sodium oxalate, and solid $Na_3IrCl_6 \cdot 2H_2O$ isolated by the method indicated below. Although we were not certain that the tracer iridium present in this compound was in the $IrCl_6^{-3}$ form, the exchange results were consistent with that assumption.

Tracer E was the remainder of C′ added to inactive Na_2IrCl_6 which was then reduced to metallic iridium by refluxing with ethanol. This metal was mixed with sodium chloride and treated with Cl_2 at 600° to convert it to labeled Na_2IrCl_6, which was purified by the method given below. It appears highly probable that the radioactivity was also in the form of solid Na_2IrCl_6.

Tracer F was prepared as a completely unambiguously labeled Na_2IrCl_6 by irradiating high purity iridium metal sealed in helium inside a quartz ampoule with the slow neutron flux of the North American Aviation, Inc., water boiler neutron source[17,18] for a length of time calculated to give the proper specific activity of 74-day Ir^{192} for using in the exchange experiments without isotopic dilution. The activated metal was converted to solid Na_2IrCl_6 by treatment with sodium chloride and Cl_2 as for tracer E.

The half-life and radiation characteristics of these tracers were determined by decay measurements and in some cases by range measurements of the negatrons in aluminum absorbers; the values agreed well with those reported[19] for 74.4-day Ir^{192}. *E.g.*, our value for the half-life of tracer F was 74.3 days. In addition, the specific activity of the 74-day radiations remained essentially constant through the preparation of a series of pure compounds, after correction for decay.

Sodium Hexachloroiridate(IV).—C.P. ammonium hexachloroiridate(IV) was dissolved in aqua regia and taken to dryness on a steam-bath to remove ammonium ion. Nitrate ion was destroyed by dissolving the solid in 12 *f* HCl and taking to dryness; this step was repeated. The solid was next dissolved in 2 *f* HCl, a slight excess of sodium chloride added, then purified chlorine was passed through the solution for several hours to ensure the oxidation of any Ir(III) to Ir(IV). This solution was evaporated to dryness and the solid treated with purified acetone at 0° to extract the Na_2IrCl_6. Insoluble material was removed by filtration, the filtrate concentrated by evaporation and purified chloroform added to the filtrate until precipitation began. The solution was heated to the boiling temperature, filtered, then more chloroform added. Cooling gave crystals of $Na_2IrCl_6 \cdot 6H_2O$ which were washed with cold acetone–chloroform mixture. Fractional recrystallization was repeated, and the final crop of washed crystals dried in an oven at 100°, ground in an agate mortar, then dehydrated at 100° in an Abderhalden drier with P_2O_5 present, first in a chlorine atmosphere, then *in vacuo*. The product was deep black-red in color, and because of its hygroscopic nature, it was always stored and handled under a dry inert atmosphere. Several such products were prepared.

Analyses of the products were made by reduction of weighed portions to metallic iridium in a stream of hydrogen at 750°, the hydrogen chloride formed being absorbed in an excess of standardized silver nitrate solution which was later back-titrated with standardized potassium thiocyanate solution by the Volhard method. The residues were weighed, the sodium chloride leached away from the metallic iridium with water and the iridium metal dried and weighed.

Typical Anal. Calcd.[20] for Na_2IrCl_6: Na, 10.20; Ir, 42.63; Cl, 47.17. Found: Na, 10.2; Ir, 42.6; Cl, 47.2.

Tracers E and F were similarly analyzed and gave correct analyses for Na_2IrCl_6.

Sodium Hexachloroiridate(III) Dihydrate.—This substance was synthesized essentially by the methods of Delépine[21] and Ogawa.[22] Sodium hexachloroiridate(IV), prepared as above, was dissolved in distilled water with an equivalent amount of C.P. sodium oxalate, and this solution was evaporated on a steam-bath nearly to dryness. Cooling gave a crop of crystals which were repeatedly washed with absolute ethanol, then dried in an oven. The solid was ground in an agate mortar, then dried for several hours at 100° in an evacuated Abderhalden drier with P_2O_5 present. The olive-green product was analyzed by the procedure given for Na_2IrCl_6. Water was determined from the loss in weight on treatment with hydrogen at 750°, taking into account the removal of half the chlorine as hydrogen chloride.

Typical Anal. Calcd. for $Na_3IrCl_6 \cdot 2H_2O$: Na, 13.54; Ir, 37.69; Cl, 41.71; H_2O, 7.06. Found: Na, 13.5; Ir, 37.9; Cl, 41.7; H_2O, 6.9.

Tracer D was analyzed likewise and gave essentially the same analysis.

Other Reagents.—C.P. acetone was further purified by shaking with aqueous silver nitrate solution and sodium hydroxide, filtering and fractionally distilling in the presence of calcium sulfate. C.P. 2-butanone was similarly purified, except that it was dried by shaking with anhydrous magnesium sulfate, followed by distillation. C.P. chloroform was shaken with concentrated sulfuric acid, washed repeatedly with water, then fractionally distilled in the presence of calcium sulfate. All other reagents were C.P. or reagent quality used without further purification.

Exchange Runs.—Runs made with tracers A, B, and C were carried out by dissolving weighed portions of the inactive reactants in standardized acid solution, bringing to the desired temperature, then initiating exchange by addition of the tracer solution. In runs made with tracers D, E and F, weighed portions of the solid reactants, one of which was a labeled reactant, were separately dissolved in the solvent acid solution, quickly brought to temperature, then exchange initiated by mixing equal volumes and shaking. Exchange mixtures generally had volumes of 20–25 ml., with 2-ml. aliquots taken at known times for separation of reactants. Larger volumes were used when the separation was made by solvent extraction. Exchange mixtures run at 50° were in a bath thermostated to ±0.2°; mixtures at 1° were kept in an ice-bath the temperature of which was 1 ± 1°. All runs, including separations, were carried out in the dark (red safe light when visibility was required) except some of the early runs specifically stated as carried out in ordinary laboratory lighting.

Separation Methods.—Three distinct chemical methods were devised for the separation of $IrCl_6^{-2}$ from $IrCl_6^{-3}$.

(1) **Precipitation of Ir(IV) as Ammonium Hexachloroiridate(IV).**—Aliquots of the exchange mixture were added to centrifuge cones containing solid ammonium chloride

---

[17] R. Chalker, *Science*, **119**, 9 (1954).

[18] M. E. Remley, *ibid.*, **119**, 21 (1954).

[19] See Ir^{192} bibliography in paper of J. M. Hollander, I. Perlman and G. T. Seaborg, *Revs. Mod. Phys.*, **25**, 469 (1953); see also R. W. Pringle, W. Turchinetz and H. W. Taylor, *Phys. Rev.*, **95**, 115 (1954).

[20] In all the work the new 1953 international value of the atomic weight of Ir was taken, namely, 192.2; see E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

[21] M. Delépine, *Bull. soc. chim.*, [4] **3**, 901 (1908); *ibid.*, [4] **9**, 771 (1911).

[22] E. Ogawa, *J. Chem. Soc. Japan*, **50**, 248 (1929).

(at room temperature for the 50° runs, and at 1° for the 1° runs) and stirred quickly. Black-red $(NH_4)_2IrCl_6$ precipitated at once and was centrifuged down, the supernatant liquid removed by a capillary draw-off pipet, and the precipitate washed once with 0.5–1 ml. of iced 2 *f* ammonium chloride (washings added to supernatant liquid). In method 1a 2-ml. aliquots were added to 110 mg. NH_4Cl, the separation being from a solution 1.0 *f* in NH_4Cl. In method 1b the procedure was the same except that the separation mixture was 5.6 *f* in NH_4Cl, obtained by adding 2-ml. aliquots to 600 mg. of NH_4Cl for the 0.01 *f* runs and 10-ml. aliquots to 3 g. of NH_4Cl for the 0.001 *f* runs. The exchange time was taken as the interval between mixing of labeled reactants and stirring of the separation mixture with the ammonium chloride. The $(NH_4)_2IrCl_6$ precipitates were dissolved in 5 ml. of water and Ir(IV) determined by addition of excess potassium iodide, acidification with hydrochloric acid and titration of the liberated iodine with standard sodium thiosulfate. Precipitation of Ir(IV) was generally 95–100% complete, and corrections were applied to the counting data for incomplete precipitation. In some cases an aliquot of the $(NH_4)_2IrCl_6$ solution was chlorinated, then titrated for Ir(III) + Ir(IV), as a check on possible coprecipitation of Ir(III); such coprecipitation was essentially negligible. This precipitation method was not well suited for use with the 0.0001 *f* runs.

(2) **Extraction of Ir(IV) into Acetone–Chloroform Mixtures.**—Experiments with several ratios of acetone to chloroform indicated that a partial separation of $IrCl_6^{-2}$ from $IrCl_6^{-3}$ could be obtained by adding 100 ml. of the exchange mixture at 1° to 300 ml. of purified acetone at 1°, shaking, then adding 100 ml. of purified chloroform at 1° to form a second (chloroform–acetone) phase, shaking, then drawing off the chloroform–acetone layer. A second extraction of the water–acetone layer with fresh chloroform was made, and like layers combined from the two extractions. Tests with labeled Na_3IrCl_6 alone, as well as spectrophotometric analyses, showed that less than 0.2% of the Ir(III) was extracted into the chloroform–acetone layer, whereas radioassay and spectrophotometric analyses indicated that 16% of the Ir(IV) was extracted into this layer. Because of the large volumes necessitated by the dilute exchange solutions and the low specific activity of the Ir^{192} the separation times were rather long: 9 minutes for the first extraction and a total of 15 minutes for the two extractions. The exchange time was considered to be the period between mixing of the reactants and the end of the first extraction.

(3) **Extraction of Ir(IV) into 2-Butanone.**—Spectrophotometric studies, as well as extractions with labeled Na_2IrCl_6 or labeled Na_3IrCl_6 alone showed that extraction from a 1 *f* HCl solution, 0.0001 *f* in each complex, with twice the volume of 2-butanone at 1° gave a 2-butanone layer containing 56% of the Ir(IV) and less than 3% of the Ir(III). In using this method, 10 ml. of 0.0002 *f* Na_3IrCl_6, 1.0 *f* in HCl, was rapidly ejected from a pipet at 1° into a separatory funnel containing 10 ml. of 0.0002 *f* labeled Na_2IrCl_6, 1.0 *f* in HCl, also at 1°, shaken for 10 seconds, 40 ml. of 2-butanone at 1° quickly added and the mixture shaken for 20 seconds. The layers were allowed to separate for 60 seconds before the bottom (aqueous) layer was drawn off. Exchange time was taken as the interval between mixing the reactants and the end of the shaking with 2-butanone.

Separations were also attempted with several anion-exchange resins, including Dowex-1, Dowex-2, Amberlite IR-4B and Amberlite IR-400. Separations, although possible, were too slow under all conditions tried.

Specific Activity Determinations.—The $(NH_4)_2IrCl_6$ precipitates from separation method 1 were dissolved in water, transferred to a cell used for radioassay with a dip-type Geiger–Mueller tube and associated scale-of-64 circuit, and made up to 20-ml. volume with water for the counting. In many cases, these dissolved precipitates were first titrated by the thiosulfate method for Ir(IV), then transferred to the cell for dip counting, the additional salts present being shown to have only a small effect on the counting rate, which arises mainly from the 0.66-Mev. negatrons associated with the disintegration of 74-day Ir^{192}. The supernatant liquids were often similarly dip counted as a check. The total activity was obtained from dip counting unseparated aliquots of the exchange mixture.

The acetone–chloroform layers from separation method 2 were evaporated on a steam-bath to remove the acetone and chloroform, then taken up in water and transferred to a cell for dip count as above. Total activity was obtained as above.

Water layers and 2-butanone layers from separation method 3 were each separately collected in 50-ml. beakers, evaporated to dryness under heat lamps, treated with concentrated nitric acid to destroy small organic residues, then taken up in 1 *f* HCl and transferred quantitatively to 1-dram screw-cap vials and made up to a volume of 2 ml. with 1 *f* HCl for gamma counting in a Nuclear-Chicago Model DS-3 well-type scintillation counter with associated scale-of-64 circuit. Total activity was obtained as above.

Background corrections (*ca.* 25 c./min. for the Geiger–Mueller counter and *ca.* 295 c./min. for the scintillation counter, the latter having been lowered by a factor of two from the original background by the use of additional lead shielding over that supplied with the counter) were applied, and the background of dip tube and cell determined prior to each radioassay to check their decontamination. Coincidence corrections were made for the more active samples. Decay corrections were unnecessary because samples, including total activity samples, for a given run were all counted within one or two days at most.

Results

The first exchange runs, carried out with tracer A, gave apparent complete exchange at room temperature in 2 to 150 minutes under laboratory lighting (exchange mixtures 0.005 *f* in Na_2IrCl_6 and Na_3IrCl_6 and 0.01 *f* in $HClO_4$). The color of tracer A was noted to be more like that of $IrCl_6^{-2}$, and treatment with sulfur dioxide changed the color to a pale yellow-green similar to that of $IrCl_6^{-3}$ and $Ir(H_2O)Cl_5^{-2}$. Thus, tracer A was apparently mainly Ir(IV), perhaps as $IrCl_6^{-2}$; this conclusion is consistent with the exchange results obtained later.

In an attempt to put the tracer into a known form, A was reduced with sulfur dioxide to give tracer B which was then used to label Na_3IrCl_6. Exchange runs with complexes at 0.001 *f* in 1 *f* HCl were run at room temperature in the light, giving apparent exchanges up to 7% in one hour. Increasing the reactant complex concentrations to 0.01 *f* gave apparent exchanges up to 15% in 11 hours. Examination of the literature suggested that B could well be an aquochloro complex of Ir(III), such as $Ir(H_2O)Cl_5^{-2}$, which is known to undergo substitution reactions slowly, as does $IrCl_6^{-2}$. Exchange by a relatively rapid charge-transfer mechanism would then be blocked until slow substitution reactions brought one or both of these species into forms differing only in charge.

Slow exchange was also observed in runs made at 50° in laboratory lighting at reactant concentrations of 0.01 *f* in HCl, using tracer C. The latter was obtained from B by oxidation with chlorine, followed by reduction back to Ir(III) in an effort to get the radioiridium into the form of $IrCl_6^{-3}$. Exchange varied from *ca.* 6% in 2 minutes to *ca.* 28% in 39 days; an exponential exchange plot of the data showed an initial rapid drop in the first 2 days, changing to an essentially linear decrease having a half-time of *ca.* 200 days. The cause of the initial fast decline was not studied. The linear decrease of long half-time is again characteristic of slow aquation reactions of Ir(III) and Ir(IV), so that it appears probable that the tracer was not initially in the $IrCl_6^{-3}$ form.

At this point it became clear that more reliable

TABLE I

EXCHANGE OF Ir* BETWEEN $IrCl_6^{-2}$ AND $IrCl_6^{-3}$ IONS IN 1.0 *f* HCl IN THE DARK

Sepn. method[a]	Tracer	Exchange mixture, *f*[b] Na_3IrCl_6	Na_2IrCl_6	Temp., °C.	Exchange time, min.	$IrCl_6^{-2}$ fr., c./min.[c]	Total c./min.[c]	Exch., %
1a	D	0.106	0.092*	50	9	1929 ± 14	3583 ± 30	100
					82	1936 ± 10		101
					520	1890 ± 10		99
1a	E	.085*	.070		4	937 ± 8	1835 ± 11	108
1b	F	.0099*	.0097	1	2	166 ± 4	308 ± 5	93
					1170	165 ± 4		94
1b	F	.00106*	.00115		4	77 ± 2	145 ± 3	98
					34	79 ± 2		95
2	D	.000100	.000111*		9	120 ± 5	259 ± 3	98
					42	123 ± 5		100
3	F	.000098*	.000100		0.7	61 ± 4	123 ± 2	100

[a] 1a, precipitation of $(NH_4)_2IrCl_6$ from solution 1.0 *f* in NH_4Cl; 1b same as 1a, except 5.6 *f* in NH_4Cl; 2, extraction of Ir(IV) into acetone–chloroform mixture; 3, extraction of Ir(IV) into 2-butanone. [b] The asterisk denotes which reactant was initially labeled. [c] Error given is statistical counting error, taken as the square root of the sum of the squares of the standard deviations of sample and of background.

results could be obtained by isolating and characterizing solid Na_3IrCl_6 and Na_2IrCl_6 in which the radioiridium was definitely put into the same chemical state as the isotopic carrier at an early stage in the preparation. Tracers D, E and F were synthesized accordingly (see Experimental section), and it appears probable that these tracers were satisfactory. In particular, F is unequivocally correctly labeled Na_2IrCl_6, inasmuch as the radioiridium was produced in the form of metallic iridium in a matrix of 1.2 g. of the metal and converted without admixture with inactive iridium at any step to solid Na_2IrCl_6, the identity of which was then established by chemical analyses.

Results obtained with these three tracers, and with the three separation methods developed, are exhibited in Table I. The percentage exchange was calculated from the equation

$$\% \text{ exchange} = 100(x/y_0)[1 + (b/a)] \qquad (1)$$

where x is the net activity (c./min.) of the initially inactive fraction and y_0 is the total net activity, both measured under the same conditions and corrected for decay, and a and b are, respectively, the molar concentrations of the initially inactive and initially active iridium complexes; x is obtained from the net activity of the initially inactive fraction actually isolated by multiplication by an experimentally determined factor to take into account any incomplete separation of the iridium reactants. The activities reported in Table I for the $IrCl_6^{-2}$ fraction have already been multiplied by the appropriate factor, which nearly always ranged from 1.00 to 1.05, except for the extraction separations where the factors were 6.25 and 1.79. The over-all standard error in the percentage exchange is estimated to be 5–10%.

Discussion

Within the experimental error, complete exchange of radioiridium between $IrCl_6^{-2}$ and $IrCl_6^{-3}$ was observed in every case studied with the better characterized tracers (D, E, F). Inasmuch as kinetic measurements could not be made, the possibility of rapid exchange arising during the chemical separations cannot be ruled out in spite of the use of three different separation methods. If it be assumed that the observed exchange was not separation-induced, that the rate law is first order in each of the iridium reactants, and that the exchange may have been incomplete by as much as 10%, then the specific rate at 1° is greater than 290 liter mole^{-1} sec.$^{-1}$ based upon the run made with 0.0001 *f* reactant concentrations and the shortest exchange time, 0.7 minute. This lower limit on the specific rate is of the same order of magnitude as the known[13] specific rate for the $MnO_4^{=}$–MnO_4^- exchange at 1°.

The principal iridium species present in the exchange mixtures are the $IrCl_6^{-2}$ and $IrCl_6^{-3}$ ions, the acids of the salts being strong acids.[23,24] Magnetic measurements[25] on Na_2IrCl_6 and $Na_3IrCl_6 \cdot 2H_2O$ as solids and in 1 *f* HCl solution have indicated that there is no measurable shift in the d^2sp^3 covalent bond type in the dissolution in 1 *f* HCl. Thus, the close structural similarity and bond type of the dissolved ions would imply that the Franck-Condon principle should not impose a high potential barrier to electron transfer between $IrCl_6^{-2}$ and $IrCl_6^{-3}$ in solution, and the exchange might be expected to be rapid.[26] Marcus, Zwolinski and Eyring[27] have proposed an electron-tunnelling hypothesis for electron-exchange reactions, and have concluded that electron transfer between anions will be very rapid because of the small hydration shell for anions and the consequent low values of the activation free energy for rearrangement of the hydration shells. However, Sheppard and Wahl[13] have stated that the probability of electron transfer between $MnO_4^{=}$ and MnO_4^- in aqueous solution is small, since the exchange rate was found smaller than the collision frequency, even though the Franck–Condon restrictions are small.

The apparent rapid exchange between $IrCl_6^{-2}$ and $IrCl_6^{-3}$ ions may well occur by an electron-transfer mechanism, inasmuch as both these ions are substitution-inert[28] and the coördination spheres are blocked, so that exchange is not possible through

---

(23) S. Nagami, *J. Chem. Soc. Japan*, **48**, 501 (1927).

(24) E. Ogawa, *ibid.*, **51**, 1 (1930).

(25) E. N. Sloth and C. S. Garner, *J. Chem. Phys.*, **22**, 2064 (1954).

(26) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

(27) R. J. Marcus, B. J. Zwolinski and H. Eyring, *ibid.*, **58**, 432 (1954).

(28) Unpublished experiments in this Laboratory have demonstrated that the exchange of radiochlorine between Cl^- ion and either $IrCl_6^{-2}$ or $IrCl_6^{-3}$ in aqueous solutions is slow.

a bridged activated complex of the kind which has been so successfully applied[29,30] to many charge-transfer exchange reactions.

Our experiences in preparing Na_2IrCl_6 and Na_3IrCl_6 unequivocally isotopically labeled with radioiridium suggest that care is necessary in preparing labeled complexes which undergo substitution reactions slowly. It does not appear safe to assume that a labeled complex at tracer concentrations will necessarily be in the same chemical form as the isotopic carrier with which it may be mixed, even though both have been through the same chemical treatment. Aquation and other reactions may take place at different rates and even to different equilibrium states for the tracer and carrier. Where certainty of labeling is to be ensured, the direct production of the desired radioactivity in a matrix of the metal (or elemental form where possible) at the appropriate specific activity has much to recommend it. Conversion of the labeled substance to the desired form without admixture with inactive isotopic substances and on a scale large enough to permit analytical characterization of the final product then results in a clearly labeled product.

Acknowledgment.—The authors wish to thank Dr. M. E. Remley and the operating staff of the North American Aviation, Inc., water boiler neutron source for irradiating the metallic iridium used for tracer F.

LOS ANGELES, CALIFORNIA

---

[29] H. Taube, H. Myers and R. L. Rich, THIS JOURNAL, **75**, 4118 (1953).

[30] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heat of Combustion of Gadolinium[1,2]

BY ELMER J. HUBER, JR., AND CHARLES E. HOLLEY, JR.

RECEIVED SEPTEMBER 30, 1954

Calorimetric combustions of gadolinium metal were performed at an initial temperature of 24.6° under an oxygen pressure of 25 atm. The energy of combustion under these conditions was found to be 5773 ± 12 joules/g. The corresponding standard heat of formation of the sesquioxide (B-type) from the elements is calculated to be -1815.6 ± 3.6 kjoules/mole. No literature values are available for comparison.

Introduction.—Only recently have some of the rare earth metals become available in a sufficiently pure state for the determination of their chemical and physical properties. This paper reports the results of the combustion of analyzed gadolinium metal to determine the heat of formation of its oxide. No literature values are available for comparison.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in a bomb calorimeter at a known initial pressure of oxygen. The energy equivalent of the calorimeter was determined from the heat of combustion of benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 8 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the standard deviations.

The units of energy used are the absolute joule and the defined calorie; 1 defined calorie = 4.1840 absolute joules.

The unit of mass is the gram mass *in vacuo*. The gadolinium metal was weighed to the nearest 0.0001 g. The water for the calorimeter was weighed to the nearest 0.01 g.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[3] The bomb used in this work is the same as there described. Its volume is approximately 360 ml. The two methods of calibration gave substantial agreement. By the electrical method, carried out in 1950, the energy equivalent of the calorimeter filled with oxygen to 25 atm., based on 15 runs, was 10,092.4 ± 5.3 absolute joules/° where the uncertainty includes the uncertainty in the measuring instruments as well as the uncertainty due to random errors. Since that time the calorimeter has been calibrated periodically with benzoic acid (NBS standard samples 39f and 39g). There has been some slight variation in the values obtained although they are in agreement when the uncertainties attached to them are taken into consideration. The latest value, based on 20 runs using NBS sample 39g, is 10,099.8 ± 3.4 joules/° and is the value used in the work reported here.

Gadolinium Metal.—The gadolinium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the A.E.C. This metal was analyzed at the Los Alamos Scientific Laboratory with the following results: Ca, 0.008%; C, 0.020%; N, 0.018%; O, 0.245%; and H, 0.021%. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. No other rare earths were found on examination of an aqueous solution by absorption spectra, the limits of detection being: Nd, 0.01%; Pr, 0.03%; Sm, 1.0%; Dy, 0.4%; Er, 0.04%. Excluding other rare earths the gadolinium thus contained about 0.31% impurities. The chemical state of the impurities is unknown. If it is assumed that the oxygen, nitrogen, hydrogen and carbon are combined with gadolinium as Gd_2O_3, GdN, GdH_2 and GdC_2, respectively, and not combined with the calcium, then the material is 97.05 mole per cent. gadolinium metal. A Debye X-ray pattern of the metal showed only lines of the metal in the hexagonal form.

Combustion of Gadolinium.—The gadolinium was burned as chunks on sintered discs of 90% gadolinium oxide supported on a platinum platform weighing 103.8 g. A piece of the metal showed no increase in weight after 1½ hours in oxygen at 25 atm. The impurities in the discs consisted mainly of dysprosium and samarium oxides. New discs were used for each run. The discs were made by mixing 0.5% dextrin in water with the powder and pressing in a steel die at 10,000 p.s.i. They were fired in air for eight hours at 1150°. The oxygen used analyzed better than 99.5% O_2 with no detectable nitrogen. Pure magnesium was used for the fuse wire. Its heat of combustion was taken as 24,667 joules/g.[3] The amount varied from 0.0048 to 0.0054 g. The amount of magnesium is believed to be too small to account for any significant heat change, assuming that a double oxide was formed from magnesium and gadolinium oxides. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the discs, the platinum and the difference in energy

---

[1] This work was performed under the auspices of the A.E.C.

[2] Presented before the Section on Physical and Inorganic Chemistry, 126th Meeting, A.C.S., New York, N. Y., September 16, 1954.

[3] C. E. Holley, Jr., and E. J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).