we determine the equilibrium constant to be 5.0×10^{-2}. A similar graph of the data obtained at 18° (graph not shown) gives a value of 2.8×10^{-2} for the equilibrium constant. Only two significant figures are retained because of the number of significant figures in γ_{22} and uncertainties involved in making the corrections of γ_{22}.

Conclusions

It appears then that when hydrous stannic oxide is dissolved in dilute sulfuric acid a partially complexed species, $(SnSO_4)^{++}$, is formed and that further complexing occurs only at considerably higher sulfuric acid concentrations.[1]

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

Exchange of Radiocyanide Ion with Tungsten Octacyanide Complexes[1]

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Essentially no exchange of radiocyanide with $W(CN)_8^{-3}$ and $W(CN)_8^{-4}$ ions in aqueous solution of natural *p*H occurs in the dark at 25° even after 100 days. At 25° the corresponding respective unimolecular specific rates are $k_1 < 5.9 \times 10^{-8}$ and $k_1 < 5.3 \times 10^{-8}$ sec.$^{-1}$, and the respective bimolecular specific rates are $k_2 < 3.5 \times 10^{-7}$ and $k_2 < 3.1 \times 10^{-7}$ liter mole^{-1} sec.$^{-1}$. The rate law is not known. These exchanges are strongly light-accelerated and the rates under the illumination conditions used are approximately independent of the concentration of free cyanide ion or complex ion. These slow exchanges are consistent with Taube's postulate regarding "inert inner orbital" complexes. The effect of light on the *p*H of aqueous solutions of these two complex ions was investigated.

Some qualitative rate investigations and several detailed kinetic studies have been made of the isotopic exchange between free cyanide ion and metal cyanide complex ions in aqueous solutions. Previous work in this field has been reviewed by MacDiarmid and Hall[2] in their recent paper on complex cyanide–simple cyanide exchange systems.

In this paper we report our investigation of the rate of exchange of radiocyanide ion with octacyanotungstate(IV) ion and octacyanotungstate(V) ion in aqueous solution, undertaken in order to provide further information on the substitution process in octacoördinated complex ions and to give additional insight into the charge-transfer exchange of radiotungsten between these two tungsten octacyanide complex ions which we report in the succeeding paper.[3] Apparently only one octacoördinated complex, $Mo(CN)_8^{-4}$, has been investigated previously for exchange lability.[4]

Experimental

Radiocyanide Tracer.—A stock tracer solution 0.04 *f* in NaCN labeled with C^{14} and 0.04 *f* in NaOH was synthesized by the method of MacDiarmid and Hall[5] from C^{14}-labeled barium carbonate obtained from the Oak Ridge National Laboratory. Labeled potassium cyanide was prepared by addition of aliquots of this tracer solution to portions of reagent grade potassium cyanide solution.

Potassium Octacyanotungstate(IV) 2-Hydrate.—This compound was made from potassium enneachloroditungstate(III), $K_3W_2Cl_9$, as follows by a modification of the methods of Collenberg (*alias* Olsson).[6–8] Twenty grams of C.P. disodium tungstate(VI) 2-hydrate and 2.2 g. of sodium carbonate were dissolved in 27 ml. of warm distilled water, heated to 65° and added at a rate of *ca.* 10 ml. per min. with swirling to 450 ml. of C.P. concd. hydrochloric acid which had been saturated with hydrogen chloride gas and heated to 65°. Resaturation of the resulting mixture with hydrogen chloride dissolved the small amount of yellow tungsten(VI) acid which had precipitated, leaving a white precipitate of sodium chloride which was filtered out. The filtrate was reduced electrolytically at a mercury cathode in a cell equipped with a graphite anode immersed in a porous cup filled with hydrochloric acid. Electrolysis with a cathode current density of 0.06 amp./sq. cm. was continued until the originally colorless solution became blue, then deep purple, after which the cathode current density was increased to 0.08 amp./sq. cm. and the temperature to 42°. At intervals 1-ml. aliquots of the catholyte were removed and titrated for W(III) with standardized potassium permanganate, electrolysis being stopped when the titer became constant. The stoichiometric amount of reagent grade potassium chloride was added to the catholyte to precipitate potassium enneachloroditungstate(III). The mixture was cooled to −10° and saturated with hydrogen chloride. After 4 hours at −10° the mixture was filtered and the crystals washed with ethanol and then with diethyl ether and finally sucked dry on the filter. A 48% yield of raw product, shown by permanganate titration to have a purity of 92% or less, was obtained. Other preparations were made in essentially the same way.

The crude product was converted to potassium octacyanotungstate(IV) 2-hydrate as follows. Fifty grams of the impure product was dissolved in 380 ml. of distilled water, and 158 g. of C.P. potassium cyanide was added slowly to the solution with vigorous agitation. The solution was evaporated on a steam-bath to *ca.* 80% of the original volume, a stream of nitrogen being used to facilitate evaporation and prevent air-oxidation of the enneachloroditungstate(III) ion. The precipitate which formed, mainly potassium chloride, was removed by centrifugation, and an equal volume of ethanol added to the supernatant solution, which was cooled to −20° and kept there for 2 hours. The impure potassium octacyanotungstate(IV) 2-hydrate precipitate was filtered off, dissolved in distilled water, boiled for several minutes with decolorizing charcoal (Nuchar), filtered hot, and the filtrate retreated similarly with Nuchar until a clear orange-yellow color was obtained. Ethanol was added to form a saturated solution at 90°, then the flask was wrapped in a towel to allow crystallization to proceed slowly. Ultimately the mixture was cooled to −10° and the crystals filtered off. This recrystallization was repeated twice, the final crop of crystals being washed with ethanol,

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(1) This work was partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

(2) A. G. MacDiarmid and N. F. Hall, THIS JOURNAL, **76**, 4222 (1954).

(3) E. L. Goodenow and C. S. Garner, *ibid.*, **77**, 5272 (1955).

(4) A. W. Adamson, J. P. Welker and M. Volpe, *ibid.*, **72**, 4030 (1950).

(5) A. G. MacDiarmid and N. F. Hall, *ibid.*, **75**, 4850 (1953).

(6) O. Olsson, *Z. anorg. Chem.*, **88**, 49 (1914).

(7) O. Collenberg and A. Gutbe, *Z. anorg. allgem. Chem.*, **134**, 317 (1924).

(8) O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924).

then with diethyl ether, and dried in a vacuum desiccator. The yield of yellow product was *ca.* 44% based on the enneachloroditungstate(III). Several lots were prepared in like manner.

Analyses of the products for tungsten and potassium were made by heating weighed portions for *ca.* 40 hours with concd. nitric acid on a steam-bath to break up the complex and oxidize the tungsten to W(VI), then diluting the solution and precipitating tungsten(VI) acid with the acid of cinchonine, finally igniting the washed precipitate to tungsten(VI) oxide for weighing; potassium was determined gravimetrically as the sulfate in the filtrate. The departmental Microanalytical Laboratory determined the nitrogen content by a micro Dumas method. Water was determined by heating weighed samples to constant weight at 115°. Over-all purity was checked by titrating weighed samples for W(IV) with standardized potassium permanganate.

Typical anal. Calcd. for $K_4W(CN)_8{\cdot}2H_2O$: K, 26.8; W, 31.5; N, 19.2; H_2O, 6.2. Found: K, 26.4; W, 30.8; N, 19.2; H_2O, 6.2; 99.7% pure by $KMnO_4$ titration.

Potassium Octacyanotungstate(V).—This substance was prepared from the octacyanotungstate(IV), in a manner similar to that of Collenberg-Olsson,[9] by dissolving the latter potassium salt in distilled water, acidifying with sulfuric acid and titrating with potassium permanganate to give the octacyanotungstate(V) in solution. Under a photographic red light a slight excess of silver nitrate was added to precipitate silver octacyanotungstate(V), which was centrifuged down and washed with water until free of silver ion and sulfate ion as shown by tests made with chloride ion and barium ion, respectively. Slightly less than the stoichiometric amount of C.P. potassium chloride in water was added to the silver salt to metathesize it to the potassium salt, the silver chloride and slight excess of silver octacyanotungstate(V) being removed afterwards by centrifugation. The supernatant solution was evaporated on a steam-bath and a crop of reddish-yellow crystals of potassium octacyanotungstate(V) formed by cooling. These crystals were dried over magnesium perchlorate in a vacuum desiccator, then stored in an opaque bottle (the compound is light sensitive).

Analyses were performed as for the octacyanotungstate(IV), omitting analysis for potassium and titration with permanganate. According to Collenberg-Olsson[9] the composition of the solid under ordinary conditions of temperature and humidity is $K_3W(CN)_8{\cdot}2.5H_2O$. At the time of analysis our preparation had been dried to an average composition corresponding to $K_3W(CN)_8{\cdot}0.55H_2O$.

Anal. Calcd. for $K_3W(CN)_8{\cdot}0.55H_2O$: W, 35.4; N, 21.6; H_2O, 1.9. Found: W, 34.7; N, 21.5; H_2O, 1.9.

All other reagents were C.P. or reagent grade.

Exchange Runs.—Separate aqueous solutions of potassium cyanide and the potassium complex compound were prepared gravimetrically immediately prior to each exchange run, mixed in the proper proportions and exchange initiated by addition of 100–200 µl. of stock $NaC^{14}N$ tracer solution. For the photochemical exchange runs the exchange mixtures were placed in 100-ml. glass volumetric flasks having tightly fitting glass stoppers. A 100-watt incandescent light bulb at 30 cm. from the centers of the flasks, which were suspended in the top half of a 25° thermostated water-bath, served to illuminate the mixtures. Mixtures for the "dark" runs were placed in polyethylene bottles painted black on the outside and fitted with sponge rubber serum-vial caps. Perchloric acid used to lower the *p*H of the "low-*p*H" mixtures was added through the rubber cap by means of a hypodermic syringe, and all aliquots of the exchange mixture were removed by the same technique to avoid loss of hydrogen cyanide, the plastic bottle collapsing gradually with successive removals of aliquots. All solutions of the octacyanotungstate(V) and all exchange mixtures were synthesized and handled in the dark or under a dim photographic red light. All exchange mixtures were thermostated at 25.0 ± 0.2°.

At known intervals aliquots of each exchange mixture were removed for determination of the extent of exchange. Neither tungsten octacyanide complex is appreciably decomposed by cold dilute acid over a 10-hour period. Accordingly, free cyanide was separated from the complex by placing the exchange-mixture aliquot in an opaque still, making the solution 0.2 *f* in sulfuric acid and sweeping the liberated hydrogen cyanide with a slow stream of nitrogen into a deficiency of aqueous sodium hydroxide over a period of about a half a day. Zinc nitrate was added to each such sodium cyanide solution to precipitate zinc cyanide for radioassay. Standard aliquots of the C^{14}-labeled potassium cyanide solution were run through the same procedure to serve as total activity samples.

Specific Activity Determinations.—Each zinc cyanide precipitate was washed twice with distilled water made barely acid with nitric acid, then twice with 95% ethanol, and finally dried for 2 days in an oven at 110°. The dried precipitate was crushed and the powder pressed into a uniform compact flat disc in a polished steel die fitted with a polished steel plunger. Sample and die were then weighed to be sure the amount of sample was slightly greater than the "infinite-thickness" amount. Each die was then fitted with an accurately machined brass collar of 1.59-cm. inside diameter which served to define the area of sample exposed for beta counting. The samples were dried in the dies for 2 days over magnesium perchlorate in a desiccator prior to counting them in the dies at close geometry under an end-window Geiger counter having a 1.4 mg./sq. cm. mica window and connected to a scale-of-64 circuit. Background corrections (*ca.* 15 c.p.m.) were applied. All counting rates were normalized to that of a standard counted before and after each set of samples. Inasmuch as all samples were thicker than the range of the C^{14} beta particles, the specific activity is proportional to the determined net activity.

Determination of Effect of Light on *p*H.—The *p*H of freshly prepared aqueous solutions of each complex, 0.05 *f* in complex and having the natural *p*H, was determined with a Beckman Model G *p*H meter equipped with a one-drop glass electrode and calibrated against standard *p*H buffers. Each solution was arranged so that it could be illuminated for a known time with light from a 100-watt incandescent lamp 30 cm. from the solution.

Results

The results of the exchange runs are given in Table I. Counting rates given are averages of those for duplicate samples, which agreed with each other to *ca.* 3%. The per cent. exchange was calculated from the relationships

$$\%\ \text{exchange} = 100F = 100S_0/S_\infty = 100(8a + b)(y_0 - y)/(8ay_0) \quad (1)$$

where F is the fraction exchange, S_0 and S_∞ are the specific activities of the tungsten-complex fraction at time t and at infinite time, respectively, a and b are, respectively, the volume formal concentrations of the initially inactive complex ion and free cyanide ion, and y_0 and y are the net activities (c.p.m.) of the "infinitely-thick" zinc cyanide precipitates from the free cyanide fraction at $t = 0$ and $t = t$, respectively. The estimated standard error of the per cent. exchange is *ca.* 10%. The large negative zero-time per cent. exchange values for $K_3W(CN)_8$ at 0.0200 *f* are known to arise from total activity standards prepared under conditions somewhat different than those under which the other samples and standards were prepared; the values are significant, however, for the purpose of estimating exchange half-times.

The results of the experiments on the effect of light on the *p*H of 0.05 *f* aqueous solutions of $K_4W(CN)_8$ and $K_3W(CN)_8$ are shown in Fig. 1.

Discussion

Within experimental error there is little or no exchange of radiocyanide with either tungsten octacyanide complex in the dark even for the relatively long exchange times involved, excluding the longest time in the two low *p*H runs, for which partial decomposition of the complex was noted. If

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[9] O. Collenberg-Olsson, *Ber.*, **47**, 917 (1914).

TABLE I

EXCHANGE OF RADIOCYANIDE ION WITH TUNGSTEN OCTACYANIDE COMPLEXES AT 25°

Complex and concn.	KC*N, f	pH	Illum.	Exch. time days	CN^- fr., net c.p.m.[a]	Total net c.p.m.[a]	Exch., %
$K_4W(CN)_8$, 0.0100 f	0.17	11.1	Dark	0	2441 ± 13	2460 ± 14	2
				7	2432 ± 13		4
				34	2442 ± 13		2
				123	2416 ± 13		6
		9.5		0	2450 ± 14	2491 ± 14	5
				14	2427 ± 13		8
				73	2321 ± 13		21[b]
	0.16	11.1	Light	0	2420 ± 13		8
				0.2	2427 ± 13		8
				1	2363 ± 13		15
				3	2273 ± 13		26
				12	2027 ± 12		56
0.0200 f		10.9		0	2214 ± 13	2235 ± 13	2
				3	2173 ± 12		6
				8	1809 ± 11		38
	0.32	11.2		0	2221 ± 13	2211 ± 13	−1
				3	2110 ± 12		14
				8	1980 ± 12		31
$K_3W(CN)_8$, 0.0100 f	0.17	10.4	Dark	0	2382 ± 13	2460 ± 14	10
				7	2426 ± 13		4
				28	2466 ± 14		−1
				111	2395 ± 13		8
		9.5		0	2472 ± 14	2491 ± 14	2
				15	2474 ± 14		2
				69	2217 ± 13		32[b]
	0.16	10.4	Light	0	2474 ± 14		2
				0.2	2425 ± 13		8
				1	2407 ± 13		10
				6	2221 ± 13		32
0.0200 f	0.15	10.0		0	2307 ± 13	2235 ± 13	−6[c]
				3	2112 ± 12		11[c]
	0.32	10.3		0	2288 ± 13	2211 ± 13	−11[c]
				3	2144 ± 12		9[c]

[a] Error given is statistical counting error, taken as the square root of the sum of the squares of the standard deviations of sample and background. [b] Decomposition of complex indicated by brown suspension. [c] Large absolute error associated with total activity standard prepared under abnormal conditions.

we assume for the natural pH runs as much as 10% exchange in 111 days and 123 days for the octacyanotungstate(V) and octacyanotungstate(IV), respectively, and assume the exponential exchange law with all eight cyanide ligands equivalent, the respective unimolecular rate constants are $k_1 < 5.9 \times 10^{-8}$ and $k_1 < 5.3 \times 10^{-8}$ sec.$^{-1}$ (k_1 defined by the rate law $R = k_1$[complex]) and the respective bimolecular rate constants are $k_2 < 3.5 \times 10^{-7}$ and $k_2 < 3.1 \times 10^{-7}$ liter mole^{-1} sec.$^{-1}$ (k_2 defined by the rate law $R = k_2$[complex][CN^-]) at 25° in the dark. Inasmuch as kinetic studies could not be made for these dark exchanges, we do not know the rate law. A zero-order dependence on [CN^-] of the rate of exchange of radiocyanide ion with $Mn(CN)_6^{-3}$ in the dark and photocatalytically with $Fe(CN)_6^{-4}$, $Cr(CN)_6^{-3}$ and $Co(CN)_6^{-3}$ has been observed.[2,10]

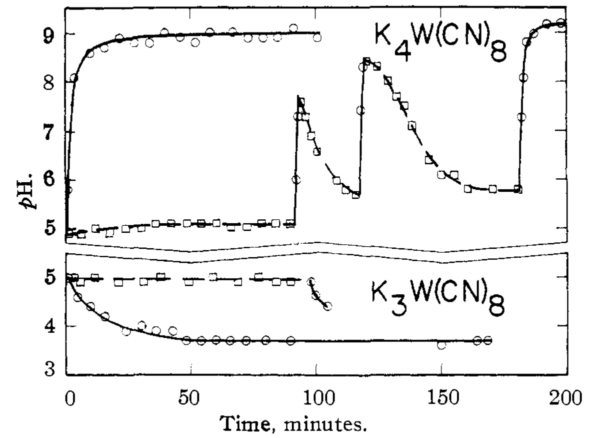

Fig. 1.—Effect of light on pH of 0.05 f $K_4W(CN)_8$ and 0.05 f $K_3W(CN)_8$ at 25°: pH in dark, □; pH in light from 100 w. incandescent lamp at 30 cm., ○.

As was found[4] for $Mo(CN)_8^{-4}$, the cyanide exchange with $W(CN)_8^{-3}$ and with $W(CN)_8^{-4}$ is strongly light-accelerated. The McKay plots[11] constructed from the light-run data of Table I correspond to exchange half-times at 25° in the range from 250 to 290 hours, except for the $W(CN)_8^{-4}$ run at 0.32 f KCN, which gave the value 350 hours. The latter value is known to be too large because the incandescent lamp used in the photoexchange studies burned out immediately after this

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(10) A. W. Adamson, J. P. Welker and W. B. Wright, THIS JOURNAL, **73**, 4786 (1951).

(11) H. A. C. McKay, *Nature*, **142**, 997 (1938).

run and the intensity of light in this run was somewhat less than in the earlier runs. Excepting this latter value, and within the rather large experimental error, the exchange half-time is approximately constant on doubling either the free cyanide ion concentration or complex ion concentration. This implies that under the illumination conditions involved the rate-determining step in the reaction which provides the path for cyanide exchange is a photoactivation step. Presumably the extinction coefficient for the complex ion is such that all of the incident light in the region of the absorption peaks is absorbed at the concentrations used in the exchange studies, and the amount of exchange then becomes proportional to the intensity of the incident light and independent of concentration of either complex ion or free cyanide ion. All of the cyanide exchange rates investigated by MacDiarmid and Hall[2] may be zero order in the complex as well as in free cyanide because of the rate being controlled by the light intensity, inasmuch as the concentration of the complex was not varied and the effect of such variation on the rate is not known. Some possible tungsten species formed in the photochemical exchange runs are indicated in the discussion below on the effect of light on the *p*H of the solutions.

The non-exchanges or slow exchanges of W-$(CN)_8^{-3}$ and $W(CN)_8^{-4}$ reported above are consistent with the slow substitution reactions of "inner orbital" complex ions of the "inert" type, to which W(V) and W(IV) octacoördinated complexes belong, in accordance with the postulation of Taube.[12] In the nomenclature of Taube, the probable electronic structures of tungsten in $W(CN)_8^{-3}$ and $W(CN)_8^{-4}$ are $d^1D^4SP^3$ and $d^2D^4SP^3$, respectively.[13] Inasmuch as the inner stable orbitals are occupied, slow substitution is expected.

The effect of light on the *p*H of $K_4W(CN)_8$ in aqueous solution, shown in Fig. 1, is similar to the behavior of $K_4Mo(CN)_8$ reported by MacDiarmid and Hall.[14] They proposed that the rise in *p*H on illumination arises from a photocatalyzed aquation of the octacyano complex with the consequent formation of the aquoheptacyano complex and free cyanide ion which instantly hydrolyzes and produces the *p*H rise. The decrease in *p*H on extinction of the light was regarded as due to a reversal of the aquation reaction. The drop in *p*H which we find on illumination of $K_3W(CN)_8$ in aqueous solution may be accounted for by reduction of the $W(CN)_8^{-3}$ ion by water according to the over-all reaction

$$4W(CN)_8^{-3} + 2H_2O = 4W(CN)_8^{-4} + 4H^+ + O_2$$

According to the oxidation potentials at 25°, namely, $W(CN)_8^{-4} = W(CN)_8^{-3} + e^-$, E^0 estimated[15] to be −0.57 volt, and $2H_2O = O_2 + 4H^+ + 4e^-$, $E^0 = -1.23$ volt,[16] this reduction of W-$(CN)_8^{-3}$ is thermodynamically possible at a *p*H near 5 and at low partial pressures of oxygen. The observed drop of *ca.* 1 *p*H unit would correspond to the formation of only 10 μmoles of $W(CN)_8^{-4}$ in a 10-ml. volume, which is too low a concentration to find by $KMnO_4$ titration or spectrophotometrically in the presence of 0.05 *f* $K_3W(CN)_8$. The leveling off of the *p*H shown in Fig. 1 could be explained as aquation of the $W(CN)_8^{-4}$ formed, which would release free cyanide ion and remove hydrogen ion produced by the photocatalyzed reduction of W-$(CN)_8^{-3}$. This is compatible with the known effect of light in decomposing aqueous $K_3W(CN)_8$ with the formation of $W(CN)_8^{-4}$, and with our observations on the effect of light on the visible and ultraviolet absorption spectrum of aqueous K_3W-$(CN)_8$ reported elsewhere.[3] Our *p*H observations are in accord with a preliminary empirical classification of MacDiarmid and Hall,[14] namely, that those cyanocomplexes which are relatively inert toward acids show a photodissociation effect and those which are easily decomposed by acids do not show the photo effect.

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(12) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(13) J. L. Hoard and H. H. Nordsieck, THIS JOURNAL, **61**, 2853 (1939), have shown by X-ray study of crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ that the $Mo(CN)_8^{-4}$ ion is dodecahedral, implying D^4SP^3 hybridization in this ion. The $W(CN)_8^{-4}$ ion probably has the same structure and bonding.

(14) A. G. MacDiarmid and N. F. Hall, *ibid.*, **75**, 5204 (1953).

(15) O. Collenberg, *Z. physik. Chem.*, **109**, 353 (1924).

(16) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1952, p. 39.