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

The Exchange Reaction between Octacyanotungstate(IV) and Octacyanotungstate(V) Ions[1]

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Exchange of radiotungsten between $W(CN)_8^{-4}$ and $W(CN)_8^{-3}$ ions in aqueous solution at complex ion concentrations of 0.001 and 0.0001 *f* and at *p*H 2.4–3.0, 5.8–6.6, and 11.3–11.8 has been found to be apparently complete in an exchange time of 0.2 second at 1–2° in the dark. The possibility of an induced exchange was not excluded. Heterogeneous exchange between $W(CN)_8^{-4}$ in the aqueous phase and $[(C_6H_5)_4As]_3W(CN)_8$ in the solid phase is approximately one-third complete under the same conditions and with a reaction time of one minute. If it be assumed that the homogeneous exchange is not separation-induced and that the rate law is first order in each of the reactant tungsten complexes, the specific rate at 1–2° is greater than 4×10^4 liter mole^{-1} sec.$^{-1}$. Solubility product constants for $[(C_6H_5)_4As]_3W(CN)_8$ and $[(C_6H_5)_4As]_4W(CN)_8$ at 0° were found to be $\sim 10^{-15}$ and $\sim 10^{-6}$, respectively. The absorption spectra of $K_3W(CN)_8$ and $K_4W(CN)_8$ in aqueous solution are presented.

Relatively few anion–anion systems have been investigated for isotopic exchange *via* a possible electron-transfer mechanism. Complete exchange in the times required for mixing and separating the reactants has been reported for the hexacyanomanganate(II)–hexacyanomanganate(III),[2] octacyanomolybdate(IV)–octacyanomolybdate(V)[3] and hexachloroiridate(III)–hexachloroiridate(IV)[4] systems.

Two other systems, reported earlier as immeasurably rapid, have recently been found measurable by rapid-mixing techniques, namely, permanganate–manganate(VI), for which a half-time of several seconds at 1° and reactant concentrations of *ca.* 0.0001 *f* were reported,[5] and hexacyanoferrate(II)–hexacyanoferrate(III), for which a half-time of *ca.* 0.3 second at 4° and reactant concentrations of 0.002 *f* was found.[6]

In this paper we report our examination of another anion–anion system, octacyanotungstate(IV)–octacyanotungstate(V), for possible measurable rates of radiotungsten exchange.

Experimental

Radiotungsten Tracer.—Radiochemically purified 73-day W^{185}, produced by (n,γ) reaction on tungsten(VI) oxide, was obtained as an alkaline solution of potassium tungstate(VI) from the Oak Ridge National Laboratory. The purity was checked by a half-life determination and by determining the energy of the γ-radiation with a γ-ray spectrometer; the values found were in good agreement with those reported.[7]

W^{185}-Labeled Potassium Octacyanotungstate(IV).—This compound was prepared and analyzed in the same manner as the inactive compound described in the preceding paper[8] except that the above radiotungsten tracer was added to the disodium tungstate(VI) at the start of the preparation. The synthesis was carried out by Dr. Bernard Finkle.

Anal. Calcd. for $K_4W(CN)_8 \cdot 2H_2O$: W, 31.5; N, 19.2; H_2O, 6.2. Found: W, 31.4; N, 19.7; H_2O, 6.2; 97.3% pure by $KMnO_4$ titration.

Potassium Octacyanotungstate(V).—The method of preparing and analyzing this compound was given in the preceding paper.[8] The substance was dried to a composition corresponding to $K_3W(CN)_8 \cdot 0.87H_2O$.

Anal. Calcd. for $K_3W(CN)_8 \cdot 0.87H_2O$: W, 35.0; N, 21.3; H_2O, 3.0. Found: W, 34.6; N, 22.3; H_2O, 3.0.

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

Exchange Runs.—Separate aqueous solutions of the octacyanotungstate(V) and labeled octacyanotungstate(IV) were prepared from weighed portions of the potassium complex salts immediately before carrying out each exchange run. If other than the natural *p*H was desired, the *p*H was adjusted with potassium hydroxide or hydrochloric acid. These reactant solutions were cooled in an ice-bath, then loaded into an apparatus at 1–2° where the reactants were mixed in a 3-way stopcock[9] and the resultant 4 ml. of exchange mixture injected directly into an equal volume of 0.05 *f* tetraphenylarsonium chloride contained in a 15-ml. centrifuge cone. Independent experiments showed that the mixing was at least 95% complete and the effective exchange time was 0.2 second. For the "infinite-time" samples the reactants were mixed in the same way and delivered into an empty centrifuge cone and kept at 1–2° for 5 minutes, then the tetraphenylarsonium chloride added and the separation made as before. The precipitate of tris-(tetraphenylarsonium)-octacyanotungstate(V), which forms immediately, was centrifuged out for 5 minutes, washed with two 1-ml. portions of 0.025 *f* tetraphenylarsonium chloride, and the washings added to the supernatant solution for radioassay. Experiments indicated that the separation is essentially quantitative at 0.001 *f* complex concentrations. At 0.0001 *f* complex concentrations some mechanical difficulties were occasionally experienced in the separations due to the small amount of solid phase.

Heterogeneous exchange runs were carried out in the same way, except that the labeled octacyanotungstate(IV) solution was injected into a suspension of the tris-(tetraphenylarsonium)-octacyanotungstate(V), agitated for 1 or 5 minutes, then the mixture centrifuged for 5 minutes. The effective exchange time was considered to be the time during which the mixture was agitated, namely, 1 or 5 minutes.

All handling of the octacyanotungstate(V) and of the exchange runs was performed under a red dark-room light inasmuch as the octacyanotungstate(V) is decomposed by the action of ordinary light.

Specific Activity Determinations.—The combined supernatant solution and washings, *i.e.*, the octacyanotungstate(IV) fraction, was made up to volume with water in a 10-ml. volumetric flask. A 2-ml. aliquot was pipetted into a 1-dram screw-cap glass vial which was then inserted into the well of a Nuclear-Chicago Model DS-3 well-type scintillation counter connected to a scale-of-64 and recorder circuit. The 0.13-Mev. γ-rays were counted. Background corrections (*ca.* 470 c.p.m. with extra lead shielding) were applied. Decay corrections were unnecessary because samples, including standards, for a given run were all counted on the same day.

Determination of Solubility Product Constants and Spectra.—The spectra of various solutions of the potassium complex compounds and of tetraphenylarsonium chloride were determined in the visible and ultraviolet at *ca.* 25° with a Model 11 PMS Cary recording spectrophotometer, using quartz cells of 1-cm. path length, immediately after prepara-

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[3] R. L. Wolfgang, THIS JOURNAL, **74**, 6144 (1952).

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[5] J. C. Sheppard and A. C. Wahl, *ibid.*, **75**, 5133 (1953).

[6] A. C. Wahl and C. F. Deck, *ibid.*, **76**, 4054 (1954).

[7] See W^{185} bibliography in paper of J. M. Hollander, I. Perlman and G. T. Seaborg, *Revs. Mod. Phys.*, **25**, 469 (1953).

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TABLE I

EXCHANGE OF W^{185} BETWEEN $W(CN)_8^{-3}$ AND $W(CN)_8^{-4}$ IONS IN AQUEOUS SOLUTION AT 1–2° IN THE DARK

System	Exchange mixture, *f* $K_3W(CN)_8$	$K_4W(CN)_8$	*p*H of exch. mixture	Exchange time, sec.	W(IV) fr., net c.p.m.[a]	Total net c.p.m.[a]	Exch., %
Homogeneous	0.00106	0.00103	2.4	0.2	5857 ± 57	11825 ± 79	100
			5.8		5787 ± 56		101
			11.8		5772 ± 56		102
				∞	5857 ± 57		
	.000100	.000099	3.0	0.2	527 ± 7	985 + 9	106
			6.6		586 ± 7		92
			11.3		606 ± 7		88
				∞	552 ± 7		
Heterogeneous	.00053	.00078	Nat.	~ 60	5767 ± 57	6516 ± 60	28
				~300	5779 ± 57	6458 ± 59	28
	.000050	.000050		~ 60	822 ± 9	964 ± 9	29

[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.

tion of the solutions. These spectral data were employed to analyze the complex ion concentration of a solution equilibrated at 0° with tris-(tetraphenylarsonium)-octacyanotungstate(V) at a known concentration of tetraphenylarsonium chloride, and thus to obtain a rough value of the corresponding solubility product constant. A rough value of the solubility product constant of tetrakis-(tetraphenylarsonium)-octacyanotungstate(IV) was found by determining the specific activity of the solution having a known tetraphenylarsonium chloride concentration and equilibrated at 0° with the W^{185}-labeled solid.

Results

The exchange results are exhibited in Table I. The counting rates given are averages of duplicate runs, the agreement of duplicates with each other being *ca.* 2 and 10% for the homogeneous runs at 0.001 and 0.0001 *f*, respectively, and *ca.* 5% for the heterogeneous runs. The per cent. exchange was calculated from the equation

$$\%\ \text{exchange} = 100S_{(V)}/S_\infty = 100(y_0 - y)/(y_0 - y_\infty) \quad (1)$$

where $S_{(V)}$ and S_∞ are the specific activities of the W(V) fraction at time t and at infinite time, respectively, and y_0, y and y_∞ are the net activity (c.p.m.), respectively, of the initially active W(IV) fraction at $t = 0$, $t = t$ and $t = \infty$. Isotopic fractionation has been assumed to be negligible. Values of y_∞ were calculated from the relationship

$$y_\infty = y_0b/(a + b) \quad (2)$$

where a and b are the volume formal concentrations of octacyanotungstate(V) and octacyanotungstate(IV), respectively. These values were used in equation 1 for the heterogeneous runs and served as a check on the experimental values of y_∞ for the homogeneous runs. The over-all standard error in the per cent. exchange is estimated to be 5 and 10% for the homogeneous runs at 0.001 and 0.0001 *f*, respectively, and 10 and 30% for the heterogeneous runs at 0.0005 and 0.00005 *f*, respectively. There were some indications of incomplete separations in the lower concentration runs.

Approximate values for the solubility product constants of $[(C_6H_5)_4As]_3W(CN)_8$ and $[(C_6H_5)_4As]_4W(CN)_8$, in terms of volume formalities, *f*, were found to be $\sim 10^{-15}$ and $\sim 10^{-6}$, respectively, at 0°. Equilibrium was approached from one side only, the solid phases were not analyzed, and activity effects were not considered. These rough values were obtained primarily as an aid in selecting conditions for the exchange separations.

The visible and ultraviolet spectra of the potassium salts of octacyanotungstate(IV) and octacyanotungstate(V) in aqueous solution (natural *p*H) are presented in Fig. 1. At the concentrations shown there is essentially no absorption in the range 525–700 mμ for the former and 400–700 mμ for the latter. Beer's law is obeyed by the former within the experimental error of 10% over the range 0.001–0.008 *f* for the peaks at 429 and 368 mμ and over the range 0.00001–0.00010 *f* for the 249-mμ peak. For the octacyanotungstate(V) Beer's law is valid within the experimental error of 15% over the range 0.0001–0.0010 *f* for the 356, 255 and 242-mμ peaks. In the *ca.* 4-minute interval required to scan the spectrum, there appeared to be no significant photolysis of the light-sensitive octacyanotungstate(V) ion, as was shown by getting the same spectrum on rescanning. However, exposure of a scanned 0.0005 *f* $K_3W(CN)_8$ solution to the laboratory fluorescent lighting for several successive 10-minute intervals, with rescanning of the spectrum in between exposures, showed that the 356-mμ peak decreased in intensity slowly, while the twin peaks at 255 and 242 mμ grew more intense and changed over to a single peak at 249 mμ. As can be seen from Fig. 1, this behavior is in accord with the known decomposition of the octacyanotungstate(V) ion to octacyanotungstate(IV) ion in the presence of light.

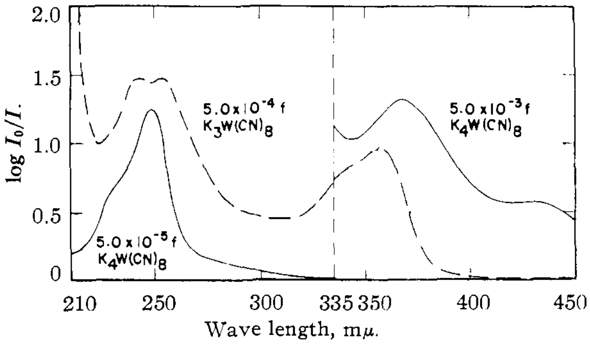

Fig. 1.—Absorption spectra of $K_4W(CN)_8$ and $K_3W(CN)_8$ in water solution at 25°; 1-cm. light path.

Discussion

The apparent extent of the heterogeneous exchange of radiotungsten between $W(CN)_8^{-4}$ and preformed solid $[(C_6H_5)_4As]_3W(CN)_8$ is essentially constant at ~30% under the experimental conditions tried. Such an initial relatively rapid exchange is characteristic of many solid–fluid heterogeneous exchange reactions,[10] representing rapid exchange between the reactant on the surface of the solid and the reactant in the fluid. Subsequent exchange may be much slower, occurring by slow self-diffusion and/or recrystallization. Although the accuracy of the heterogeneous run measurements was poor, these experiments indicate that the rapid exchange found for the homogeneous systems is probably an exchange actually occurring predominantly in the solution phase and not on the precipitate surface introduced in the chemical separation.

Within the experimental error, complete exchange of radiotungsten between $W(CN)_8^{-4}$ and $W(CN)_8^{-3}$ in aqueous solution was found for all concentrations and *p*H values noted in Table I. Although within the experimental error, the apparent trend toward incomplete exchange with rising *p*H for the homogeneous exchange at 0.0001 *f* complex ion concentration may possibly indicate that the experiments at *p*H 11.3 are approaching measurable rates. Inasmuch as our mixing apparatus was not designed for shorter reaction times and the separation method was already giving some troubles at this low concentration, we were unable to check this possibility experimentally.

Because kinetic measurements could not be made, the possibility of rapid exchange arising during the separations could not be excluded. If the observed exchange be not separation-induced, and if we assume that the rate law is first order in each of the tungsten reactants and that the homogeneous exchange at 0.0001 *f* reactant concentrations may have been incomplete by as much as 20%, then the specific rate at 1–2° is greater than 4×10^4 liter mole^{-1} sec.$^{-1}$. This lower limit on the specific rate is roughly an order of magnitude larger than that estimated by Wolfgang[3] for the $Mo(CN)_8^{-4}$–$Mo(CN)_8^{-3}$ radiomolybdenum exchange at 2° (estimated 5-second exchange time) and than the specific rates measured by Sheppard and Wahl[5] and by Wahl and Deck[6] for the MnO_4^-–$MnO_4^=$ radiomanganese exchange at 1° and the $Fe(CN)_6^{-4}$–$Fe(CN)_6^{-3}$ radioiron exchange at 4°, respectively.

The very slow exchange of radiocarbon between CN^- and either $W(CN)_8^{-4}$ or $W(CN)_8^{-3}$ reported by us in the preceding paper[8] and the large coördination number of the tungsten in these complexes suggest that the apparent rapid charge-transfer reaction does not occur through a bridged activated complex of the kind demonstrated by Taube[11,12] as valid for many charge-transfer exchange reactions. Theoretical considerations made by Libby[13] and by Marcus, Zwolinski and Eyring[14] suggest that electron transfer between anions may be very rapid. However, Sheppard and Wahl[5] have remarked that electron transfer between MnO_4^- and $MnO_4^=$ in aqueous solution is relatively improbable, since the exchange rate was observed to be smaller than the collision frequency in spite of presumably small Franck–Condon restrictions.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORIES, HARVARD UNVIVERSITY]

The Reduction of Cupric Chloride by Carbonyl Compounds

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Cupric chloride is easily reduced to cuprous chloride by organic carbonyl compounds which are oxidized to the chloro compounds. With acetone the reaction is: $2CuCl_2 + CH_3COCH_3 \longrightarrow 2CuCl + ClCH_2COCH_3 + HCl$. The kinetics of this reaction have been studied.

The first indications that solutions of cupric chloride in acetone are abnormal were reported by Jones and Veazey[1] and Kohlschütter,[2] who were unable to get reproducible results in electrical conductivity experiments with this system. Kohlschütter noted the formation of cuprous chloride, acid and chlorinated products.

We find that the reaction between cupric chloride and acetone proceeds readily at room temperature according to the following stoichiometry

$$2CuCl_2 + CH_3COCH_3 \longrightarrow 2CuCl + ClCH_2COCH_3 + HCl$$

The rate of the reaction is increased by increasing acetone concentration (in aqueous solutions) and by chloride ion, decreased by neutral salt and is inhibited by the products, hydrogen chloride (or acid) and cuprous chloride. The dependence on copper concentration is half-order in gross copper. The variation in half-order rate constant at constant copper concentrations shows a first-order dependence on chloride ion.

Experimental

Materials. Acetone.—Mallinckrodt analytical reagent grade acetone was refluxed with chromic anhydride overnight, decanted and distilled from more chromic anhydride and then from sodium hydroxide pellets. The foreruns were discarded; b.p. 56.6°.

Cupric Chloride.—Mallinckrodt analytical reagent grade material was recrystallized from dilute hydrochloric acid and desiccated by heating on a steam-bath *in vacuo*. The brown crystals analyzed correctly for $CuCl_2$.

Lithium Chloride.—J. T. Baker analyzed reagent grade crystals were dissolved in water, filtered, and the solution standardized with silver nitrate potentiometrically.

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