oxygen concentration is of the type described by Schwarz[21] for diffusion controlled radiation processes. It is seen in the present work that the effect of increasing the oxygen concentration is small for the (n,α) recoils from boron although considerably larger for the lithium recoil triton ($\sim$8%). Yields of ferrous ion oxidation are increased by 0.08 and 0.6, respectively, for the 1–2 Mev. α-radiation and 2.7 Mev. triton in going from air- to oxygen-saturated solutions.[24]

The increase of the oxidation yield with increased ferrous sulfate concentration, though small, appears to be quite real. A mechanism by which the ferrous ion might increase the yield is not immediately obvious. Scavenging of the hydrogen atoms within the radiation track by the ferrous ion does not appear to be significant because of the low rate of this reaction. Reaction of ferrous ion with hydroxyl radicals does not directly increase the yield since one ferrous ion is oxidized for each hydroxyl equivalent whether or not peroxide is formed as an intermediate. Reaction of ferrous ion with hydroxyl radicals within the track can, however, indirectly influence the yield by decreasing the back reaction of ·OH with H· thereby freeing hydrogen atoms with an ultimate increase in the oxidation yield.

Acknowledgment.—We wish to acknowledge the coöperation of the Brookhaven Biology Department in making available the neutron irradiation facility used in these measurements. We are indebted to Dr. J. B. Cumming for assistance with the absolute counting of the gold monitors and to Drs. A. O. Allen and H. A. Schwarz for many discussions on the effect of ionization density on radiation chemical yields.

UPTON, LONG ISLAND, N. Y.

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[24] J. A. Ghormley and C. J. Hochanadel, *Radiation Research*, **3**, 227 (1955), have shown that for γ-rays the yield of hydrogen from oxygen-saturated KBr solutions is 13% less than for degassed solutions. However, because of the low contribution of the molecular yield to the over-all decomposition, $G\gamma(\mathrm{Fe}^{+++})$ is increased by only a negligible amount.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Activity Coefficients of Electrolytes of High Charge: Potassium Octacyanomolybdate (IV) and Tris-(ethylenediamine)-Platinum(IV) Chloride

BY CARL H. BRUBAKER, JR.

RECEIVED JUNE 14, 1956

The mean activity coefficients of potassium octacyanomolybdate(IV) and tris-(ethylenediamine)-platinum(IV) chloride in fairly concentrated aqueous solutions have been determined by isopiestic comparison with potassium chloride solutions. It appears to be possible to predict the activity coefficients of these salts in solutions up to about 0.1 *m* by the Debye–Hückel equation, using $\mathring{a}$ = 4.33 and 3.61, respectively.

In this Laboratory, we have been studying various equilibria involving complex ions of high charge and have found interpretation of these equilibria complicated by a notable lack of information on the activity coefficients for fairly concentrated solutions of such electrolytes. Prompted by these considerations, we have undertaken a program of measuring the activity coefficients of very stable complex salts with the view of using them as models for the estimation of activity coefficients of other complexes of similar type and configuration.

There is a paucity of information concerning the activity coefficients of electrolytes of the 1–4 and 4–1 types. Robinson has studied potassium hexacyanoferrate(II)[1] and thorium(IV) chloride,[2] but certainly the latter cannot qualify as a strong electrolyte and hydrolysis appears to disqualify it as a 4–1 electrolyte.

According to the work of Kolthoff and Tomsicek,[3] potassium octacyanomolybdate(IV) and the acid $[\mathrm{HMo(CN)_8}^{\equiv}]$ appear to be strong electrolytes and stable toward oxidation or reduction in aqueous medium. Tris-(ethylenediamine)-platinum(IV) chloride represents a somewhat less satisfactory example, as we shall see, but it is very stable and we have not been able to detect much hydrolysis.

Experimental

Potassium octacyanomolybdate(IV) was prepared and purified according to the directions of Furman and Miller.[4] The product, $\mathrm{K_4Mo(CN)_8 \cdot 2H_2O}$, was recrystallized three additional times by the recrystallization method of Furman and Miller. The salt was weighed as the air-dried dihydrate.[3]

Basolo, Bailar and Tarr have previously prepared tris-(ethylenediamine)-platinum(IV) chloride,[5] but we found that the product contained a small amount of dichlorobis-(ethylenediamine)-platinum (IV) chloride. We, therefore, put the mixture through a four step fractional crystallization (the tris-(ethylenediamine) compound was concentrated in the least soluble fraction) and thus obtained, after drying the product over barium oxide or at 75° in an oven, the compound in good purity. (*Anal.* Calcd. for $\mathrm{Pt(en)_3Cl_4}$ (en = ethylenediamine): Pt, 37.73; Cl, 27.41. Found for oven-dried material: Pt, 37.81; Cl, 27.29. Found for desiccated material: Pt, 37.85; Cl, 27.30. It appears that the compound originally precipitated from water at room temperature is the dihydrate, but water is quickly lost in the air and can be completely removed by drying over barium oxide. Once water is removed, the material does not absorb it rapidly and the anhydrous material can be weighed conveniently in the air.

The apparatus we have used for determining isopiestic molalities of the two salts and potassium chloride is a modified version of the one used by Scatchard, Hamer and Wood[6]

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[1] A. Robinson, THIS JOURNAL, **59**, 84 (1937).

[2] R. A. Robinson, *ibid.*, **77**, 6200 (1955).

[3] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **40**, 247 (1936).

[4] N. H. Furman and C. O. Miller, "Inorganic Syntheses," Vol. 3, ed. by L. F. Audrieth, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 160.

[5] F. Basolo, J. C. Bailar and B. R. Tarr, THIS JOURNAL, **72**, 2438 (1950).

[6] G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).

and has been described previously.[7] Potassium chloride was used as the reference electrolyte.

The more concentrated solutions were prepared by weighing the salts directly into the crucibles and the more dilute solutions were prepared in larger volumes and portions of the solutions were weighed into the crucibles. The times required for the various solutions to reach equilibrium ranged from one day for the most concentrated solutions to three for the least concentrated.

For the studies on potassium octacyanomolybdate(IV) the temperature was 24.945 ± 0.003° and for the tris-(ethylenediamine)-platinum(IV) chloride it was 24.990 ± 0.005°.

Duplicate samples agreed to within three parts per thousand in equilibrium concentrations.

Results and Discussion

The results are given as molalities of isopiestic solutions in Table I and the osmotic coefficients of the potassium octacyanomolybdate(IV) and tris-(ethylenediamine)-platinum(IV) chloride, calculated from the known osmotic coefficients of the potassium chloride solutions, are also recorded.

The highest concentration employed for the $K_4Mo(CN)_8$ was determined, not by the solubility of the salt, but by the limitation on the amount of the fairly bulky material which could be weighed conveniently in one of the crucibles and then dissolved.

Solubility did dictate the upper concentration limit of the $Pt(en)_3Cl_4$; however, the precise solubility of the compound could not be determined by the isopiestic method. In every case the salt weighed was the anhydrous one, but it appears that the dihydrate is the form in equilibrium with aqueous solutions at 25°. Conversion of undissolved anhydrous salt to the dihydrate is slow and equilibrium was not reached in seven days. The solubility is estimated to be about 0.35 *m*.

The calculation of activity coefficients from data of this type has been discussed in detail by Harned and Owen[8] and others. In the case of the present data, activity coefficients were determined by graphical integration of the equation[8]

$$\ln \gamma_\pm = -(1-\phi) - 2\int_0^m \frac{(1-\phi)}{m^{1/2}}\,dm^{1/2} \quad (1)$$

Extension of the function $(1 - \phi)/m^{1/2}$ *vs.* $m^{1/2}$ to infinite dilution by means of the Debye–Hückel equation required that the distance of closest approach, $\mathring{a}$, be 4.33 ± 0.10 for $K_4Mo(CN)_8$ and 3.61 ±0.10 (Å.) for $Pt(en)_3Cl_4$, in order that the values of the function calculated from the Debye–Hückel equation coincide with the smoothed experimental curve in the region around 0.1 *m* and below.

These values of $\mathring{a}$ are smaller than we should expect if the electrolytes are indeed strong. Larger $\mathring{a}$ could be obtained if the extrapolation made use of the Debye–Hückel equation extended by a term, linear in concentration, but such a procedure involves adjusting two arbitrary parameters. Measurements of conductance and transference numbers of $K_4Mo(CN)_8$ solutions, being made at this Laboratory,[9] suggest that the salt behaves as a strong electrolyte in dilute solutions.

TABLE I

ISOPIESTIC MOLALITIES AND OSMOTIC COEFFICIENTS OF SOLUTIONS OF $K_4Mo(CN)_8$ AND $Pt(en)_3Cl_4$ AT 25°

$m_{av.}$	$\phi_{obsd.}$	$m_{av.}$	$\phi_{obsd.}$
	$K_4Mo(CN)_8$		
0.05105	0.6337	0.8093	0.4831
.06562	.6157	.8338	.4826
.2031	.5524	.8988	.4824
.2504	.5447	.9299	.4804
.2615	.5354	.9609	.4841
.3539	.5225	.9989	.4853
.4258	.5183	1.048	.4862
.5733	.4900	1.135	.4899
.6485	.4867	1.246	.4902
.7093	.4843	1.429	.5094
.7591	.4835		
	$Pt(en)_3Cl_4$		
0.05582	0.5797	0.2355	0.4848
.08505	.5408	.2705	.4802
.1203	.5184	.3034	.4833
.1811	.4991	.3073	.4814
.2231	.4882	.3281	.4774

TABLE II

MEAN ACTIVITY COEFFICIENTS AND SMOOTHED OSMOTIC COEFFICIENTS OF $K_4Mo(CN)_8$ AND $Pt(en)_3Cl_4$ AT VARIOUS MOLALITIES

	$K_4Mo(CN)_8$		$Pt(en)_3Cl_4$	
m	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ
0.01	0.362	0.7221	0.342	0.6982
.02	.280	.6740	.256	.6379
.03	.238	.6552	.213	.6051
.05	.194	.6271	.167	.5724
.07	.169	.6168	.141	.5553
.10	.145	.6027	.117	.5356
.20	.104	.5596	.0806	.4912
.30	.0831	.5293	.0652	.4781
.33	...	...	.0641	.4757
.50	.0632	.4972		
.70	.0521	.4846		
1.00	.0436	.4848		
1.20	.0400	.4936		
1.40	.0376	.5061		
1.50[a]	.0365[a]	.5151[a]		

[a] Obtained by a short extrapolation.

Table II (and Fig. 1) gives the values of the mean activity coefficients and osmotic coefficients for the two salts. It is interesting to note that the activity coefficients for $K_4Mo(CN)_8$ are higher than

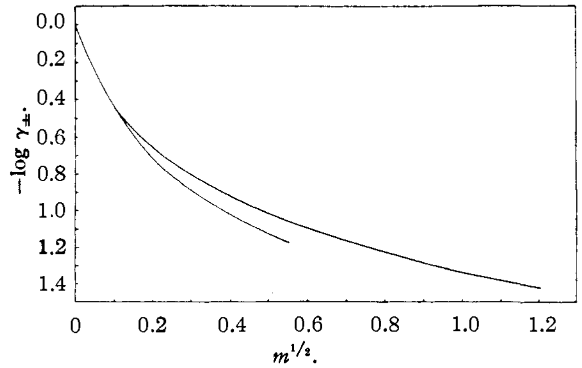

Fig. 1.—log $\gamma_\pm$ *vs.* $m^{1/2}$ for $K_4Mo(CN)_8$ (upper curve) and $Pt(en)_3Cl_4$ (lower curve).

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[7] C. H. Brubaker, Jr., C. E. Johnson, C. P. Knop and F. Betts, Paper No. 5, Division of Chemical Education, 129th Meeting, American Chemical Society, Dallas, Texas, April 8, 1956.

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Ch. 9, 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[9] J. L. Dye, private communication.

those for $K_4Fe(CN)_6$[1] at corresponding molalities, but the shape of the curves $-\log \gamma_{\pm}$ *vs.* $m^{1/2}$ are similar. The activity coefficients for $Pt(en)_3Cl_4$ are lower than those for the two 1–4 salts.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Reactions of 2-Iodobutane with Iodine. Evidence for a Radical Reaction with Inversion of Carbon

BY RAYMOND A. HERRMANN[1] AND RICHARD M. NOYES

RECEIVED JUNE 7, 1956

Optically active 2-iodobutane undergoes iodine-catalyzed racemization and also exchanges with isotopically labeled elementary iodine. The two simultaneous thermal reactions have been studied between 130 and 170° in hexachlorobutadiene-1,3. If iodine atoms caused exchange only by direct substitution involving inversion of carbon, the ratio of rates of racemization to exchange would be 2.0; if they reacted only by abstracting iodine to form racemic butyl radicals, the ratio would be 1.0. The observed ratio is 1.54 ± 0.06 independent of temperature and of concentration of either species. The results provide strong evidence for an inversion of a carbon atom caused by a radical reagent, but we cannot completely exclude the less plausible interpretation that a large fraction of racemic *sec*-butyl radicals react with the identical iodine molecules formed at their own geneses. Experiments are suggested which might more firmly establish the presence or absence of a radical inversion reaction in this system.

Introduction

Nucleophilic reagents containing a free pair of electrons usually react with organic compounds either by substitution with inversion of a carbon atom or by abstraction of a species (most frequently but by no means invariably a proton) attached to carbon, nitrogen or oxygen. Radical reagents usually react either by addition to a multiple bond or by abstraction of a species. The possibility has been recognized that radicals might cause substitution with inversion of a carbon atom, but until very recently no examples had been clearly demonstrated.

Theoretical calculations[2] could not make a clear prediction whether an iodine atom would react with an alkyl iodide by abstraction of iodine or by substitution with inversion of carbon.

Most attempts to obtain experimental evidence for inversion by halogen radicals have yielded results that were negative or inconclusive. Thus Brown, Kharasch and Chao[3] showed that the chlorination of optically active 1-chloro-2-methylbutane yielded inactive 1,2-dichloro-2-methylbutane. This result demonstrates only that if the reaction involved displacement of hydrogen by a chlorine atom, then the product was racemized as fast as it was formed. Yuster and Reyerson[4] failed to find evidence for hydrogen atoms during the chlorination of propane, and Franklin and Shepherd[5] similarly failed to detect iodine atoms from the reaction of methyl radicals with isopropyl iodide, but it is not certain that the analytical methods in the first study were sufficiently sensitive.

The elegant work of Davidson and Sullivan gave more clearly negative results. These authors studied the exchange of labeled bromine with bromotrichloromethane and also measured the rate of the bromine atom initiated reaction

$$Cl_3CBr + HBr \longrightarrow Cl_3CH + Br_2$$

The rate of exchange could be equated quantitatively to the rate of the process

$$Cl_3CBr + Br \longrightarrow Cl_3C\cdot + Br_2$$

and the direct displacement of one bromine atom by another was clearly too slow to detect under these conditions.

The kinetic study of Ogg and Polanyi[7] provides the most positive evidence for a halogen radical inversion reaction. These authors studied the gas phase racemization of 2-iodobutane caused by the iodine produced in its own decomposition at 240–280°. The kinetics clearly indicated that racemization involved reaction of an iodine atom with 2-iodobutane. It was argued that this reaction was an inversion reaction and could not involve abstraction of iodine to form a racemic *sec*-butyl radical because a significant reaction of these radicals with iodine would cause iodine inhibition of the decomposition of 2-iodobutane. This decomposition would presumably involve the same radicals, and no inhibition by iodine was observed. The results are certainly suggestive, but they hardly seem conclusive because the data were complicated by heterogeneous effects and because the authors failed to consider that racemization might also occur through abstraction of iodine from 2-iodobutane by a *sec*-butyl radical.

While our work was in process, Steacie and coworkers failed to find evidence for the reaction[8]

$$H + CH_3C_6H_5 \longrightarrow CH_4 + C_6H_5$$

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[1] Based on the Ph.D. Dissertation of Raymond A. Herrmann. The original dissertation and microfilms thereof are available from the Library of Columbia University.

[2] E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

[3] H. C. Brown, M. S. Kharasch and T. N. Chao, THIS JOURNAL, **62**, 3435 (1940).

[4] S. Yuster and L. H. Reyerson, *J. Phys. Chem.*, **39**, 859 (1935).

[5] J. L. Franklin and G. R. L. Shepherd, THIS JOURNAL, **76**, 609 1954).

[6] N. Davidson and J. H. Sullivan, *J. Chem. Phys.*, **17**, 176 (1949); J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).

[7] R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

[8] A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).