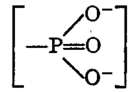
dices and densities for the dibutyl esters of ethane-, *n*-butane-, *n*-heptane-, and *n*-decanephosphonic acids, and the corresponding calculated molecular weights, the refractivity for the group  $\left[-\mathrm{P}(=\mathrm{O})(\mathrm{O}^-)(\mathrm{O}^-)\right]$ in esters of this class is calculated to be equal to 9.82. Employing this value and the aforementioned data for carbon, hydrogen and the double bond, the calculated molecular refractivity for diallyl cyclohexanephosphonate is 65.32.

Polymerization Experiments.—Three-gram samples of the ester were placed in several small test-tubes containing 0.0, 1.0, 2.0 and 5.0%, respectively, of benzoyl peroxide. The tubes were stoppered and heated in an oil-bath for seven and one-half hours while the temperature of the bath was raised from 70° to 115° as follows: 70–75° (one hour), 75–80° (one hour), 80–85° (one hour), 85–90° (one hour), 90–95° (one-half hour), 95–100° (one-half hour), 100–105° (one-half hour), 105–110° (one hour), and 110–115° (one hour). The mixture containing the highest concentration of benzoyl peroxide became solid at the end of four hours. The samples were allowed to stand overnight in the oil-bath without further heating and were then observed. The results are tabulated:

%$(C_6H_5CO_2)_2$	Product
0.0	No noticeable change
1.0	Viscous liquid
2.0	Clear, stiff gel
5.0	Clear, colorless, moderately hard solid

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The Electron Transfer Exchange Reaction of Ferricyanide and Ferrocyanide Ions

BY JAMES W. COBBLE[1] AND ARTHUR W. ADAMSON

The exchange reaction of ferricyanide–ferrocyanide ions in water solution is of considerable interest because it presents a case of a one-electron exchange involving negative ions. The slow exchange observed for such positive ion systems as ferrous–ferric,[2] and the cobaltous and cobaltic hexammine complexes[3] would lead one to believe, *a priori*, that the electron exchange between highly charged negative ions would also be measurable. The results reported to date do not substantiate this expectation. It is true that Seaborg, *et al.*,[4] have reported no electron exchange for ferri- and ferrocyanide ions, but both Lewis[3] and Thompson[5] have reported complete and rapid exchange,[6] even on duplicating the procedures of Seaborg and co-workers. The problem is further complicated by the fact that these authors have all used chemical precipitation methods of separating the two chemical species. It is known that such a procedure may induce exchange,[7] and the amount of such induced exchange can only be measured when it is less than complete.

Because of these reasons, it was felt that it would be of interest to investigate the exchange of the system using the various physical methods of separation which are now known. In addition, we have found a new and rapid method of separation involving the use of ion-exchange resins which may be of further applicability in the study of exchange reactions.

We have investigated this exchange system with the use of electrophoresis in order to obtain results less suspected of error due to catalysis. A diffusional separation was first employed, then, to eliminate the large glass diaphragm surface, the moving boundary transference type separation was tested. Since both of these methods require several hours, a very rapid method employing an anion exchanger was also desired. The results in all cases indicated complete exchange.

Experimental Procedure

Materials.—The initial stock solutions of potassium ferricyanide and potassium ferrocyanide were made up from C. P. J. T. Baker Analyzed Reagent grade materials and distilled water. These solutions were tested for the presence of ferricyanide in ferrocyanide and *vice versa* by the addition of ferric ion and benzidine acetate, respectively. The radioactive iron was obtained by (n, γ) reaction on iron metal and supplied as an iron (III) chloride solution by the Oak Ridge National Laboratory on allocation by the Atomic Energy Commission. It consisted of a mixture of Fe^{55-59}. The solution was converted to ferrocyanide by treatment of the tracer plus carrier iron in the form of iron(II) chloride solution with satd. potassium cyanide solution, with subsequent filtration to remove any ferric hydroxide present. An equal volume of ethanol was then added to the filtrate, and the product was allowed to crystallize out. The crystals were recrystallized once more from ethanol–water mixtures. These crystals were then mixed with the required amount of inactive potassium ferrocyanide and the system diluted to the proper concentration. A copper sulfide test of the solution for the presence of cyanide ion proved negative.

The stock solutions used were made $0.468\,f$ in potassium ferricyanide and $0.096\,f$ in potassium radio-ferrocyanide. Equal volumes of these stock solutions were mixed to form the exchange solution used.

A subsequent diffusion study of the potassium radio-ferrocyanide into water established the fact that the radioactive and inactive forms of iron were the same chemical species.

Diffusion Separation.—The procedure first developed by Van Alten and Rice[2] was used in this separation. The diffusion cells were of the McBain sintered-glass double-ended type having various porosities. The exchange solution was placed in the upper compartment[8] of these cells, and distilled water in the lower compartment. They were then suspended vertically in a thermostat at 25°. The diffusion times ranged from four to seventeen hours.

The solutions were analyzed by titration of the ferrocyanide by standard permanganate, and for ferricyanide by titration of the liberated iodine by standard thiosulfate after potassium iodide and zinc sulfate (to precipitate the ferrocyanide) had been added.[9]

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(1) Oak Ridge National Laboratory, P. O. Box P, Oak Ridge, Tennessee.

(2) L. Van Alten and C. N. Rice, THIS JOURNAL, **70**, 884 (1948).

(3) W. Burton Lewis, Tech. Report #19, ONR Task Contract N5-ori-07806, "Isotopic Exchange by Electron Transfer between Complex Ions," Mass. Institute of Tech., Jan. 1949.

(4) G. T. Seaborg, J. W. Kennedy and S. Ruben, unpublished work mentioned by G. T. Seaborg, *Chem. Revs.*, **27**, 199 (1940).

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

(6) In addition, W. Burton Lewis, ref. 3, has reported that C. H. Haenny has found slow exchange between these ions; it is not known what separation procedure was used.

(7) R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949).

(8) With some of the more porous diaphragms, the exchange solution was placed in the lower compartment to prevent streaming which would lower the enrichment.

(9) E. H. Swift, "A System of Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1939, p. 440.

The radioactive analysis was made by using a glass-jacketed glass-walled alcohol–argon filled Geiger tube as a solution counter for the radiation from the Fe^{59} ($T^{1/2}$ 45 days) and a suitable scaling circuit. Corrections were made for coincidence and background. No correction was made for adsorption as the ratio of the adsorption coefficients of all of the solutions was assumed to be essentially unity.

From the chemical and radioactive analysis, the per cent. exchange was calculated from (7) and is listed in Table I.

Electrophoretic Separation.—The procedure mentioned by Linnenbom and Wahl[10] was adopted for this separation. The apparatus consisted of a series of three U-tubes with a stopcock located at the middle of the central U-tube. The side arms of this central U-tube were connected by rubber tubing to the side arms of the other two U-tubes. One side of the system was filled with a dilute potassium chloride solution up to the central stopcock; the other side was filled with the exchange mixture. Two platinum electrodes were inserted in the end arms of each of the end U-tubes. One hundred and fifty volts (about 1.5 volts $cm.^{-1}$) were applied at these terminal electrodes and migration allowed to proceed for five hours. This arrangement ensured that none of the exchange solution to be later analyzed would come into contact directly with either electrode, since only the solutions in the central U-tube were used in the analysis. The chemical and radioactive analysis and the calculation of exchange were made as before, and the results are listed in Table I.

Ion-Exchange Resin Separation.—It has been found that the anion exchange resin Amberlite IR-4 in the carbonate form will preferentially adsorb ferricyanide ion in a water solution of ferrocyanide and ferricyanide ions. The enrichments are about 10–20-fold larger than in either of the above mentioned methods, and separation can be effected in times comparable to chemical precipitation procedures (about three to four minutes.)

The exchange mixture was allowed to trickle through a column 30 cm. long and 1 cm. in diameter filled with 20–30-mesh resin at a rate of about 25 cc. $min.^{-1}$. Two 30-cc. portions of the eluent solution were collected and analyzed by the procedures given above, and the per cent. exchange calculated as before. The resin had previously been tested to see if it would undergo or induce a decomposition or oxidation–reduction reaction with each of the original stock solutions in thirty minutes. No detectable chemical effect of the resin on the solutions could be noted under the exchange conditions. The results are summarized in Table I.

Considering the variety of exchange resins available, this method should prove valuable in studying exchange with ionic or non-ionic groups, limited only by the chemical stability of the system under the conditions of the exchange study.

Calculations and Discussion

If the activity is initially present in the ferrocyanide, then the exchange reaction can be represented as

$$\mathrm{Fe^*(CN)_6^{-4} + Fe(CN)_{.}^{-3} = Fe(CN)_6^{-4} + Fe^*(CN)^{-3}} \qquad (1)$$

We shall schematically represent the partial separation methods used as

$$\left.\begin{matrix}a_0\\ b_0\\ x_0\end{matrix}\right\}\xrightarrow[\text{solution}]{\text{original}}\ \vdots\begin{matrix}\text{separation}\\ \text{mechanism}\end{matrix}\vdots\ \xrightarrow[\text{solution}]{\text{enriched}}\left\{\begin{matrix}a_1\\ b_1\\ x_1\end{matrix}\right.$$

Let

F_1 = fraction of ferrocyanide in enriched solution = a_1/a_0
F_2 = fraction of ferricyanide in enriched solution = b_1/b_0
F_3 = fraction of total activity in enriched solution = x_1/x_0
y = activity as ferrocyanide after exchange
z = activity as ferricyanide after exchange

We shall assume that the exchange is either very rapid or very slow as compared to the separation time. We can then write for the total activity in the enriched solution

$$yF_1 + zF_2 = x_1 \qquad (2)$$

or

$$y = \frac{a_0b_0x_1 - a_0b_1x_0}{a_1b_0 - a_0b_1}. \qquad (3)$$

Therefore

$$z = x_0 - y = \frac{a_1b_0x_0 - a_0b_0x_1}{a_1b_0 - a_0b_1} \qquad (4)$$

If we define the per cent. exchange, E, as

$$E = 100\left(\frac{\text{activity as Fe(CN)}_6^{-3}}{\text{equilibrium act. as Fe(CN)}_6^{-3}}\right) \qquad (5)$$

then

$$E = 100\left\{\frac{z}{x_0\left(\dfrac{b_0}{a_0 + b_0}\right)}\right\} \qquad (6)$$

which can be rewritten as

$$E = 100\left\{\left(\frac{F_1 - F_3}{F_1 - F_2}\right)\left(\frac{a_0 + b_0}{b_0}\right)\right\}^{11} \qquad (7)$$

When there is 0% exchange, the ferrocyanide ratio, F_1, will equal the activity ratio, F_3. When there is complete exchange, the activity ratio will be the same as the total iron ratio $(a_1 + b_1)/(a_0 + b_0)$.

Representative data collected for the various separation procedures used are given in Table I. The deviations were estimated from known errors in the chemical and radioactive analysis.

TABLE I

EXCHANGE OF FERRO AND FERRICYANIDE IONS AT 25°

$a_0 = 0.048 f$; $b_0 = 0.234 f$

Run type	F_1	F_2	$(a_1 + b_1)/(a_0 + b_0)$	F_3	Sep. time, hr.	E, %	$E_{av.}$, %
	0.0375	0.0498	0.0477	0.0499	8	119	
Diff.	.0424	.0591	.0560	.0588	8	118	
	.102	.133	.131	.132	4	116	118 ± 20
Diff.	.0379	.0598	.0560	.0615	17	130	
acid[a]	.0500	.0653	.0627	.0662	17	129	129 ± 20
Elect.	.0780	.116	.110	.116	5	120	
	.162	.188	.183	.184	5	102	111 ± 9
Ion-	.577	.270	.321	.355	4 min.	87	
exchg.	.938	.483	.557	.517	4 min.	101	94 ± 7

[a] In these runs, the exchange solution and the lower compartment were made $10^{-3} f$ in hydrochloric acid.

It can be seen that all of the methods used indicate that there is complete exchange in agreement with the previous results. Runs made in the absence of light were similar to those in Table I. The large positive errors are in part due to the sensitivity of equation (7) to the excess of ferricyanide, and also to considerable experimental difficulties in analysis in the diffusion separation method because of the small differences in the rates of diffusion of the two ions. However, even

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(10) V. J. Linnenbom and A. C. Wahl, THIS JOURNAL, **71**, 2589 (1940).

(11) This equation is similar to one derived by Van Alten and Rice[3] for their diffusional separation procedure.

with the large errors involved, this method unmistakenly indicates complete exchange in water and slightly acid solutions. It is possible, of course, that the sintered glass membrane, with its large amount of surface, might have catalyzed the exchange. However, the mobility experiments and the results of the ion-exchange separations also show complete exchange. It is interesting to note that the ferricyanide ions diffuse faster and also have the higher mobility.

Electron exchange between like-charged ions frequently has been found to be a slow process.[12] This can in part be attributed to the fact that the exchange path involves direct collision between highly charged species. The activation energy for such a process can be estimated to be at least 15 kcal./mole.[13]

It is interesting to note that all of the known examples of slow exchange involve positive ions so that the apparent inconsistency of our results with the ferrocyanide–ferricyanide system with the general pattern of behavior may be in some manner due to the fact that negative charges are involved. Thus the positive ion presumably would be present as aquo-complexes or at least as highly hydrated species and would present an external sheath mainly of hydrogen atoms, since the oxygen atoms in the water molecules should be oriented toward the metal ions. These peripheral hydrogens would be expected to bear a positive formal charge and this electron deficiency would reduce the chance of electron exchange on collision between two such ions.

On the other hand, the external nitrogen atoms in the cyanide complexes bear a negative formal charge and the central ion is thus surrounded by a sheath of electron rich atoms and this higher electron density may be responsible for the "anomalous" rapid exchange.

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[12] For a listing of many such reactions, see J. W. Gryder, *Trans. N. Y. Acad. Sci.*, II **12**, 18 (1949).

[13] M. H. Gorin, THIS JOURNAL, **58**, 1794 (1936).

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The Reaction of Acrolein with Ethanol and Ethyl Orthosilicate[1]

BY CHARLES E. FEAZEL AND WALTER G. BERL

The reaction of acrolein with ethyl orthoformate and ethanol leads to the formation of acrolein diethyl acetal in 73% yield when ammonium nitrate is used as catalyst[2] or β-ethoxypropionaldehyde diethyl acetal (45% yield) if hydrogen chloride is the catalyst used.[3]

We have investigated the analogous reaction of acrolein with ethyl orthosilicate and ethanol, using the procedure reported for the preparation of β-ethoxybutyraldehyde diethyl acetal from crotonaldehyde.[4] Catalysis by either ammonium nitrate or hydrogen chloride gave β-ethoxypropionaldehyde diethyl acetal as the only identifiable acetal. The hydrogen chloride-catalyzed reaction was clean cut, resulting in a 76% yield. The use of ammonium nitrate as catalyst led to considerable tar formation, with a reduction in yield to 40%. The hydrogen chloride-catalyzed reaction of acrolein with ethanol alone gives a mixture of β-ethoxypropionaldehyde diethyl acetal (26% yield) and acrolein diethyl acetal (30% yield).[5]

Experimental

The ethyl orthosilicate (Carbide and Carbon technical grade) was distilled before use (b. p. 155–157° at 760 mm.). Eastman Kodak Co. acrolein was used.

Acetal Formation (Hydrogen Chloride Catalysis).—A mixture of 208 g. (1 mole) of ethyl orthosilicate, 56 g. (1 mole) of acrolein, 150 ml. (2.5 moles) of absolute ethanol and 5 ml. of a 4% solution of anhydrous hydrogen chloride in absolute ethanol was allowed to stand at room temperature for two weeks.

The mixture was then added with stirring to a solution of 100 g. (2.5 moles) of sodium hydroxide in 500 ml. of water at room temperature, and the resulting emulsion stirred for one hour. Then the organic material was extracted with ether and water salted out of the extract with anhydrous potassium carbonate. After drying over anhydrous potassium carbonate, the mixture was distilled through a short Vigreux column. Following the distillation of the ether and alcohol at atmospheric pressure, a yield of 133 g. (76%) of β-ethoxypropionaldehyde diethyl acetal, b. p. 71–73° at 13 mm., was obtained. No evidence of the presence of the lower boiling acrolein diethyl acetal was obtained. After redistillation at reduced pressure through a 60-cm. Fenske column, the acetal had the following physical properties: $n^{25}\text{D}$ 1.4035, d^{25}_{4} 0.880.

Acetal Formation (Ammonium Nitrate Catalysis).—The above proportions of reactants were used, except that the catalyst was 3 g. of U. S. P. ammonium nitrate. One month at room temperature was required for the odor of acrolein to disappear from the reaction mixture; workup of the mixture yielded 70 g. (40%) of β-ethoxypropionaldehyde diethyl acetal, together with a large amount of tar which precipitated when the alcohol was distilled from the mixture. When conducted at reflux temperature for ten to fifteen minutes, the reaction yielded a very small amount of acetal, and correspondingly more tar.

β-Ethoxypropionaldehyde 2,4-Dinitrophenylhydrazone (Not Previously Reported).—The acetal was hydrolyzed by warming with an equal volume of water containing a few drops of concentrated hydrochloric acid. One gram of the resulting aldehyde in this solution was added to a solution of 1 g. of 2,4-dinitrophenylhydrazine in 1 l. of 2 *N* hydrochloric acid. A precipitate was formed immediately. It was recrystallized twice from alcohol–water, giving shining yellow plates, m. p. 84.5–85.0° (cor.).

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.85. Found[6]: C, 46.61, 46.93; H, 4.86, 4.96; N, 20.64, 20.94.

Attempts to form the dinitrophenylhydrazone in the

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[1] This investigation was supported by the U. S. Navy Bureau of Ordnance under Contract NOrd 7386.

[2] Fischer and Baer, *Helv. Chim. Acta*, **18**, 514 (1935).

[3] Claisen, *Ber.*, **31**, 1014 (1898).

[4] Helferich and Hausen, *ibid.*, **57**, 759 (1924).

[5] Pingert, "Org. Syntheses," Vol. 25, p. 1 (1945).

[6] Analyses by Oakwold Laboratories, Alexandria, Va.