with acetic anhydride and sodium acetate gave a mixture of acetates, which was fractionated in a high vacuum (0.5 mm.). The pentaerythritol tetraacetate fraction collected between 150 and 170° and the dipentaerythritol hexaacetate at 257–262°. The latter was refluxed with dilute hydrochloric acid and the solution thus formed was concentrated. From 100 g. of the double compound, 8.5 g. of the pure dipentaerythritol, m. p. 221° (from water), was obtained.

**Dibenzaldipentaerythritol.**—A mixture of 2.5 g. of dipentaerythritol, 3.2 cc. of benzaldehyde, some crystals of *p*-toluenesulfonic acid and 100 ml. of benzene was heated azeotropically. When water ceased to separate, the benzene solution was treated with calcium carbonate and filtered, the benzene distilled off and the residue triturated with methanol and recrystallized from butanol; long, lancet-shaped crystals of m. p. 166° were thus obtained which decompose rapidly on exposure to humid air; yield 60%.

*Anal.* Calcd. for $C_{24}H_{30}O_7$: C, 67.0; H, 7.0. Found: C, 66.6; H, 7.1.

**Di-(*p*-methoxybenzal)-dipentaerythritol** was obtained analogously from dipentaerythritol (2.5 g.) and anisaldehyde (3.7 ml.). The crude product was triturated with dry ether and recrystallized from pyridine; m. p. 167.5°; yield 3 g. (60%).

*Anal.* Calcd. for $C_{26}H_{34}O_9$: C, 63.6; H, 7.0. Found: C, 63.9; H, 7.1.

**Di-(*p*-nitrobenzal)-dipentaerythritol**, obtained from dipentaerythritol (2.5 g.) and *p*-nitrobenzaldehyde (4.6 g.), formed an oily layer which did not dissolve in benzene. The solvent was decanted, and the product triturated with glycol monoethyl ether and washed with ether; m. p. 112° after sintering at 100°; soluble in pyridine; yield 2 g. (40%).

*Anal.* Calcd. for $C_{24}H_{28}O_{11}N_2$: C, 55.4; H, 5.4; N, 5.4. Found: C, 55.1; H, 5.5; N, 5.7.

Benzoylation with benzoyl chloride in pyridine gave a dibenzoate which melted at 126° (after sintering); soluble in acetone and chloroform, insoluble in ether.

*Anal.* Calcd. for $C_{38}H_{36}O_{13}N_2$: N, 3.9. Found: N, 4.1.

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REHOVOTH, ISRAEL
RECEIVED OCTOBER 22, 1949

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## Ultraviolet Absorption Study of the Ionization of Substituted Phenols in Ethanol

BY NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR.

In a private communication Brother Columba Curran and Professor J. L. Magee of Notre Dame University have recently pointed out improved interpretations of certain of the data previously reported under the above title.[1] The weak acidity of the hindered phenols is now to be attributed to the small difference in energy of solvation between the ions and the un-ionized molecules. This is due to the reduction of interaction energy between the ion and the solvent as a result of steric hindrance offered by the large ortho substituents. The large $\Delta(1/\lambda)$ values observed for the hindered phenols may be now regarded as a consequence of the reduction of interaction energy between the ion and solvent. This weaker interacting energy would allow the oxygen electrons to migrate more freely into the phenyl ring with a consequent increase of $\Delta(1/\lambda)$. The same considerations apply in a comparison of the $\Delta(1/\lambda)$ values for the unhindered and partially hindered phenols.

GULF RESEARCH AND DEVELOPMENT COMPANY
PITTSBURGH, PENNSYLVANIA
RECEIVED NOVEMBER 18, 1949

[1] N. D. Coggeshall and A. S. Glessner, Jr., THIS JOURNAL, **71**, 3150 (1949).

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## The Preparation and Polymerization of Diallyl Cyclohexanephosphonate

BY A. J. CASTRO[1] AND W. E. ELWELL

The interest in allyl resins and the use of esters of phosphoric acid as plasticizers because of the flame resistance thereby imparted[2] prompted an investigation of the possibility of preparing a fire resistant resin from diallyl cyclohexanephosphonate. The synthesis of this ester and its polymerization are described in this report.

### Experimental

**Diallyl Cyclohexanephosphonate.**—Thirty-seven and eight-tenths grams of cyclohexanephosphonyl chloride[3] and 59.5 g. of pyridine were mixed in a flask equipped with a short condenser having a calcium chloride tube attached at the top. During mixing, the solution warmed and became yellow in color. The calcium chloride tube was removed periodically and 43.7 g. of allyl alcohol was added portionwise through the condenser during a period of ten minutes. The first addition of alcohol was accompanied by the evolution of considerable heat and the reaction flask was immersed in an ice-bath while the remainder was added. A white solid precipitated from solution during this period. The reaction mixture was allowed to stand overnight while the ice melted and the system came to room temperature. The mixture was stirred with 400 ml. of water and the oil that separated was removed. The cloudy aqueous layer was extracted with ether and the combined ether–oil mixture was washed with water and dried over anhydrous sodium sulfate. The addition of a small amount of salt was found to be a convenient aid in destroying the emulsion that formed during the water washing. The ether was evaporated from the dried and filtered solution and the remaining oil distilled. Twenty-five and six-tenths grams (55.7%) of diallyl cyclohexanephosphonate was collected at 117–134° (1.8–3.0 mm.). This product was redistilled for analysis and substantially the entire volume boiled at 119.5–119.7° (1.95–2.2 mm.). Unsaturation in this product was demonstrated by the decoloration of a carbon tetrachloride solution of bromine.[4]

The ester is a colorless liquid possessing a faint garlic-like odor; $n^{20}D$ 1.4760; $d^{20}_4$ 1.0548.

*Anal.* Calcd. for $C_{12}H_{21}PO_3$: P, 12.68. Found: P, 12.40, 12.45.

On the basis of the observed refractive index and density and the calculated molecular weight, the molecular refraction (*M*D) for this compound is found to be 65.32. Using the values for the group refractivities[5] for carbon, hydrogen and the double bond, reported[6] refractive in-

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[1] Present address: Chemistry Department, University of Santa Clara, Santa Clara, California.

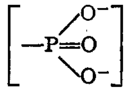
[2] Simonds and Ellis, "Handbook of Plastics," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 101.

[3] Kindly furnished by J. O. Clayton and W. L. Jensen, THIS JOURNAL, **70**, 3880 (1948).

[4] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 36.

[5] Lange, "Handbook of Chemistry," 3rd ed., Handbook Publishers, Inc., Sandusky, Ohio, 1939, p. 855.

[6] Kosolapoff, THIS JOURNAL, **67**, 1180 (1945).

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  $\left[-\mathrm{P}{=}\mathrm{O}\,(\mathrm{O}^-)_2\right]$ 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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RECEIVED OCTOBER 21, 1949

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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 $(n, \gamma)$ 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.