In the case of p-chlorobenzyl chloride it is thought that the two lines arise from the two chemically different chlorines in the molecule. The higher frequency was assigned to the chlorine on the ring on the basis of the result obtained with benzyl chloride. σ-Values for the ortho substituents were calculated from the ionization constants of the corresponding benzoic acids,[4] for p-CH_2Cl from nuclear nitration data,[3,5] for p-OH from the ionization constant of p-hydroxybenzoic acid.[6] The work of Taft indicates that obtaining ortho σ-values in this fashion is a dubious procedure[7] although the fit is satisfactory. Further work with ortho substituted chlorobenzene compounds may help elucidate the polar effects of such substituents.

One might expect a relation to exist between the resonance frequency and sigma since the latter is a measure of the electron density at a given carbon atom in the ring[8] and the quadrupole frequency is closely related to the location of bonding electrons.[8] Solid state influences might upset this relation but these are apparently relatively constant in the present compounds. In iodine[8] and chloral hydrate[9] they cause larger deviations.

The σ-values assigned to the substituents p-CHO, p-COCH_3, p-COOH and p-CH=CHCOOH are probably too large as a result of resonance stabilization of the phenoxide ion in the experiments used to determine those values.[10] Hammett states that these values are probably only valid for phenol and aniline derivatives. There is a wider difference between the meta and para σ-values for these compounds than for compounds in which resonance is blocked. The same resonance effects in the chlorine substituted molecule might be expected to diminish the quadrupole frequency by increasing the double bond character of the C–Cl bond. The deviation of the p-OH substituent may arise from hydrogen bonding of the chlorine through the hydroxyl of an adjacent molecule as in chloral hydrate.[9] Also the σ-value assigned to the hydroxyl group is not well defined.[11] The deviation of the p-OCH_3 compound is unexplained.

The Cl^{36} quadruple frequency in p-deuterochlorobenzene has been observed to be equivalent, within experimental error (4 kc.), to that in chlorobenzene.

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Mallinckrodt Chemical Laboratory
Harvard University
Cambridge, Mass.

Preparation of Radiohypophosphate Ion

By Therald Moeller and Gladys H. Quinty

In conjunction with investigations on the hypophosphates of thorium and the rare earth elements,[1] hypophosphate ion ($P_2O_6{}^{-4}$) containing phosphorus-32 was required. This was best prepared as the disodium dihydrogen salt by the direct oxidation of elemental radiophosphorus with sodium chlorite by an adaptation of the procedure of Leininger and Chulski.[2] Attempted preparations involving exchange of inactive hypophosphate with radio-orthophosphate and with radiopyrophosphate gave negative results, in keeping with other observations[3–7] upon the general absence of exchange among the oxidation states of phosphorus.

Experimental

Chlorite Oxidation of Radiophosphorus.—One-gram samples of red phosphorus were sealed in evacuated quartz tubes and irradiated in the pile at the Oak Ridge National Laboratories. As received after irradiation, these samples had activities approaching 50 millicuries per gram of phosphorus. The tubes were opened in a dry-box in a carbon dioxide atmosphere by cutting grooves around the tips with a small emery wheel, continuing grinding until small holes developed to admit carbon dioxide, and then cracking off the tips. Each sample of active phosphorus was then mixed thoroughly with 25 g. of inactive red phosphorus.

The mixed solids were converted by chlorite oxidation to disodium dihydrogen hypophosphate 6-hydrate as described by Leininger and Chulski.[2] To obviate losses and reduce contamination hazards, the reaction vessel was of Pyrex with the central tube sealed in. Connection to the receiving flask was made with Tygon tubing. Both reaction vessel and receiving flask were surrounded by $1/_8$-in. lead sheeting, and all operations were conducted in well-ventilated hoods with ample precautions taken to prevent radiation hazards. The preparations proceeded as described,[2] yielding products of high purity and activity. The high-activity waste liquors which accumulated were stored in lead-shielded containers until activities had decreased to safe levels before disposal.

Attempted Orthophosphate–Hypophosphate Exchange.—Radiophosphoric acid, obtained from the Oak Ridge National Laboratories, was diluted with 0.1 M sodium dihydrogen orthophosphate solution to an activity of some 5000 counts per minute per milliliter. Equal aliquots of this solution and of a 0.1 M disodium hypophosphate solution were mixed, adjusted to pH 1, 5 and 10 and temperature equilibrated at 25, 60 and 90°. At various time intervals, 2-ml. samples were withdrawn, diluted with 2 ml. of 12 M hydrochloric acid, and treated with a few drops of concentrated thorium nitrate solution (7 g. of the salt in 50 ml.). Under these conditions, only thorium hypophosphate is precipitated,[1] and precipitation of thorium is quantitative.

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The precipitates were removed and washed five times by centrifuging with diluted hydrochloric acid containing sodium nitrate to prevent peptization. After being dried, the precipitates were counted, using a thin-wall beta counting tube. Inasmuch as activities in the precipitates (ca. 0–100 counts per minute) were negligible in comparison with the activity of the standards (4500–4600 counts per minute per milliliter) the absence of exchange is indicated. Extreme washing reduced activities in the precipitates still further, showing that observed activities were probably due only to adsorption and occlusion. Neither alteration of pH nor of temperature gave any evidences of exchange.

Attempted Pyrophosphate–Hypophosphate Exchange.—Radiophosphoric acid was converted to pyrophosphate by evaporating with disodium hydrogen orthophosphate solution and igniting the residue for 2 hr. at 600°. The active pyrophosphate was dissolved in water and diluted appropriately with tetrasodium pyrophosphate solution. The exchange procedure was identical with that described above except that concentrations were reduced to 0.01 M to avoid precipitation of thorium pyrophosphate.[8] Results exactly comparable with those mentioned above are again interpreted as indicating no exchange. Again some adsorption and occlusion effects were noted.

It should be pointed out that the counting rates noted for the solids were not absolutely correct because the weights of the precipitates used were not determined and because the layers counted were not of uniform thickness, but the values obtained were of the correct orders of magnitude and the interpretations logical.

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Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois

Radiometric Determination of the Solubilities of Thorium and Certain Rare Earth Metal Hypophosphates

By Therald Moeller and Gladys H. Quinty

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Although the extremely small acid solubility of thorium hypophosphate has been used to advantage for the efficient removal of thorium from its admixtures with the rare earth elements,[1-6] no quantitative comparisons of hypophosphate solubilities which might lend support to the method have appeared. The availability of radiohypophosphate[7] provided a tool for solubility determinations. Neodymium and yttrium were selected as representative members of the cerium and yttrium sub-groups, respectively, for comparison with thorium.

Data summarized in Table I indicate that thorium hypophosphate remains essentially quantitatively insoluble in at least 4 N hydrochloric acid, whereas under comparable conditions the rare earth metal hypophosphates are sufficiently soluble to permit separations. Thorium hypophosphate is markedly less soluble than the pyrophosphate.[8]

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TABLE I

SOLUBILITIES OF HYPOPHOSPHATES IN HYDROCHLORIC ACID SOLUTIONS

Sample	Hydrochloric acid concentration, N	Solubility, mole/liter $\times$ 10^4
ThP_2O_6	1.00	0.25
	2.00	.47
	4.00	1.65
	6.00	2.10
$Nd_4(P_2O_6)_3$	0.05	0.11
	.10	.48
	.20	1.60
	.30	2.00
	1.00	14.46
	2.00	34.70
$Y_4(P_2O_6)_3$	0.20	3.02
	0.30	5.52
	1.00	26.90

Experimental

Solubilities were determined by essentially the same procedure previously described for pyrophosphates.[8] Thorium, neodymium and yttrium hypophosphates were precipitated by adding suitable volumes of a standard sodium hypophosphate solution (26.4 mg. $P_2O_6^{-4}$ per ml.) of known radioactivity (ca. 4500 counts per minute per milliliter)[7] to excesses of the metal salt solutions. The precipitates were washed thoroughly, air-dried, and suspended in 50-ml. volumes of hydrochloric acid solutions of varying normalities. These suspensions were equilibrated for 5 days in a thermostat at 25 ± 0.1°, studies having shown that longer periods produced no significant changes. The suspensions were then filtered and the activities of the filtrates measured using an annular volume tube.[8] Comparisons of these activities with that of the standard indicated the solubilities. These are expressed in terms of anhydrous hypophosphates in Table I, the compositions of the precipitates having been determined by independent means.[9]

Although statistical errors at some of the low counting rates encountered and the probable presence of low activities of thorium decay products render these results not absolutely quantitative, the values are of the correct orders of magnitude and especially useful on comparative bases. The rare earth metal hypophosphates are too soluble at acidities above 1–2 N to permit accurate evaluations by this procedure.

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Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois

The Solid State Reaction between Magnesium and Chromium Oxides

By G. Parravano

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Chemical reactivity of inorganic materials is known to be structure-sensitive, being dependent on a variety of variables which are involved in the history and preparation of the reacting substances. Thus, ill-defined phase boundary effects are responsible for the empirical relations often deduced for the kinetics of solid state changes. These relations cannot be used for the direct establishment of a reaction mechanism.

It has been realized that in order to minimize the conditions under which phase boundary processes