from ethanol. If the substance remained liquid (generally a heavy oil), it was extracted with ether, the extract dried over magnesium sulfate, and warmed to remove the solvent. The resulting residue was distilled under diminished pressure.

Picrates.—The picrates of the azomethines were prepared by adding a saturated solution of picric acid in either ethanol or benzene to a solution of about 0.2 g. of the base in the same solvent. The crude picrates were recrystallized from glacial acetic acid (except as noted in the table).

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Correlation of Cl³⁵ Nuclear Quadrupole Coupling Frequencies with Hammett's Sigma[1]

BY HARLAN C. MEAL

The nuclear quadrupole resonance frequency for Cl^{35} has been measured for some chlorobenzene derivatives with a frequency modulated super-regenerative spectrometer[2] (Table I). Signals

Fig. 1.

TABLE I

Cl³⁵ NUCLEAR QUADRUPOLE INTERACTION FREQUENCIES OBSERVED IN VARIOUS SUBSTITUTED CHLOROBENZENE COMPOUNDS

Substituent	196°K.	Cl³⁵ frequency at 77°K.	0°K. (extrapolated)	σ
o-NO₂	36.997 mc.[a]	37.260 mc.	37.47 mc.	+2.030
o-CF₃[b]	35.633			
o-Cl	35.496[a]	35.824	35.97	+1.260
	35.424[a]	35.755	35.92	
	35.278[a]	35.755	35.97	
	35.215[a]	35.580	35.75	
m-NO₂	35.225[a]	35.457	35.60	+0.710
m-COOH	35.053	35.227	35.26	+ .355
m-CF₃	34.632	35.073	35.23	+ .42[e]
m-Cl	34.732[a]	35.030	35.20	+ .373
	34.724[a]	35.030	35.20	
	34.523[a]	34.875	35.09	
	34.503[a]	34.809	34.96	
p-OH	34.672[a]	34.945[a]	35.19	− .317
	34.434[a]	34.700[a]	34.82	
m-N=C=O[b]	34.653			
p-OCH₃	34.433	34.753	34.94	− .268
o-N=C=O[b]	34.415			
None	34.026[a]	34.622[a]	34.90	0.00
p-Cl	34.562[a]	34.779[a]	34.88	+ .227
p-COOH	34.471	34.673	34.78	+ .728
p-COCH₃	34.327	34.618	34.73	+ .874
p-CHO	34.381	34.607	34.67	+1.126
	34.403	34.623	34.68	
p-CH₂Cl	34.303	34.567	34.69	+0.025
	32.840	33.754	34.24	
p-OC₂H₅	34.180	34.381	34.44	− .25
p-NH₂	33.974[a]	34.146[a]	34.20	− .660
p-CH=CHCOOH	34.227		34.40	+ .619
Benzyl chloride	32.417	33.630	34.14	

[a] Data from Dean and Pound (private communication). [b] Observations not yet complete, also, no σ-values available. [e] J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950).

too weak to be detected with frequency modulation and oscilloscope display were observed using magnetic field modulation, phase-sensitive detection and pen recording. Temperature dependences of the frequencies were determined (Fig. 1) and extrapolated to absolute zero. These, together with the data of Dean and Pound similarly extrapolated,
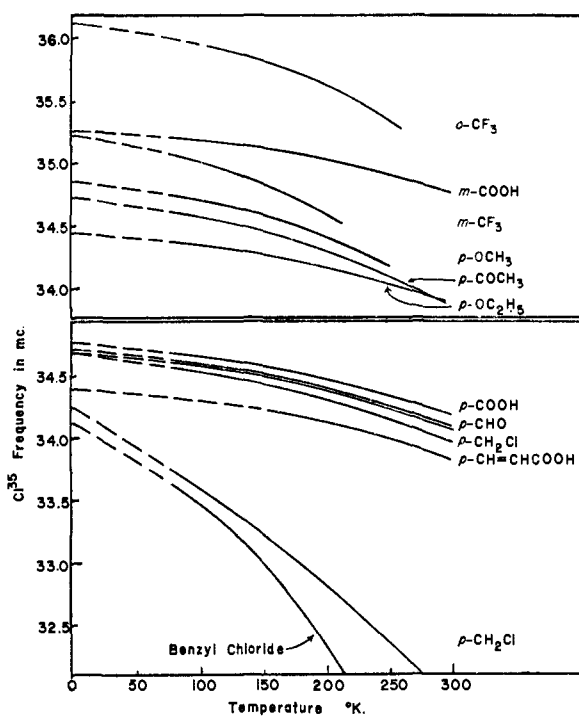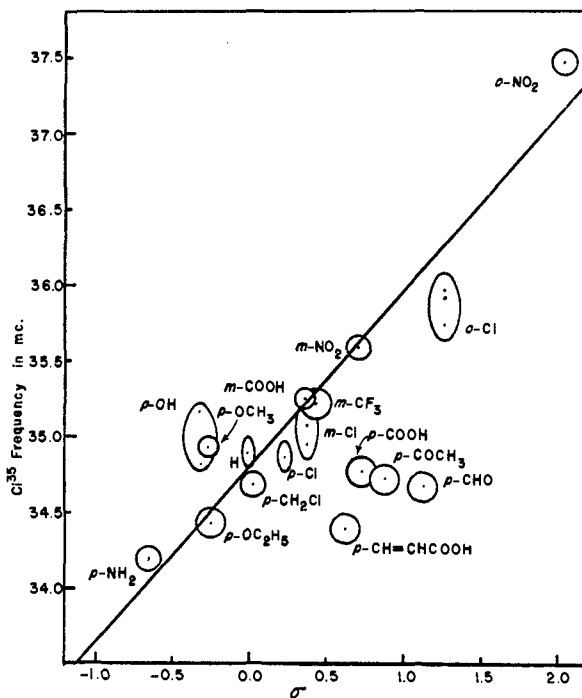
Fig. 2.

have been plotted against Hammett's substituent parameter sigma[3] (Fig. 2). Limits of error assigned are the mean deviations given by Hammett or arbitrarily taken to be 0.1 unit for sigma; for the frequencies the expected maximum error in the extrapolation is used. Where crystallographically non-equivalent chlorines give rise to multiple lines the frequencies of the several lines are plotted.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

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$_2$Cl 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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(4) J. F. J. Dippy and R. H. Lewis, J. Chem. Soc., 343 (1935); J. F. J. Dippy, F. R. Williams and R. H. Lewis, ibid., 1426 (1937).

(5) C. K. Ingold, et al., ibid., 575 (1949); 905, 918, 929 (1938); 1959 (1931).

(6) G. E. K. Branch and D. L. Yabroff, THIS JOURNAL, 56, 2568 (1934).

(7) R. W. Taft, Jr., ibid., 74, 2729, 3120 (1952).

(8) C. H. Townes and B. P. Dailey, J. Chem. Phys., 20, 35 (1952).

(9) H. C. Allen, THIS JOURNAL, 74, 6074 (1952).

(10) G. N. Burkhardt, C. Horrex and D. I. Jenkins, J. Chem. Soc., 1654 (1936); G. N. Burkhardt, W. G. K. Ford and E. Singleton, ibid., 17 (1936).

(11) E. Berliner and L. C. Monack, THIS JOURNAL, 74, 1574 (1952).

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Preparation of Radiohypophosphate Ion

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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 radioorthophosphate 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.

(1) G. H. Quinty, Doctoral Dissertation, University of Illinois, 1951.

(2) E. Leininger and T. Chulski, THIS JOURNAL, 71, 2385 (1949).

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