16. *The Formula of Hypophosphoric Acid.*

By F. Bell and S. Sugden.

Considerable doubt exists as to the correct representation of hypophosphoric acid and its salts. Although many lines of investigation favour a formula $H_4P_2O_6$ (Parravano and Marini, *Atti R. Accad. Lincei*, **15**, ii, 203, 305; Cornec, *Bull. Soc. chim.*, 1909, **5**, 1121; van Name and Huff, *Amer. J. Sci.*, 1918, **45**, 103; Treadwell and Schwarzenbach, *Helv. Chim. Acta*, 1928, **11**, 405), yet Rosenheim and Pritze (*Ber.*, 1908, **41**, 2708) obtained molecular weights in solution for the esters which indicated the simpler formula R_2PO_3. These esters were prepared by the action of alkyl halides on silver hypophosphate and could not be distilled without decomposition. Later Miłobędzki and Walczyńska (*Rocz. Chem.*, 1928, **8**, 486) prepared the ethyl and menthyl esters by the reaction

$$(RO)_2P{\cdot}ONa + Cl{\cdot}PO(OR)_2 \longrightarrow (RO)_2P{\cdot}O{\cdot}PO(OR)_2 + NaCl$$

but could not distil the products. Recently Arbusov and Arbusov (*J. pr. Chem.*, 1931, **130**, 121) found that when bromine acted on sodium diethyl phosphite, $(EtO)_2P{\cdot}ONa$, in ligroin the chief product was ethyl hypophosphate, which was isolated after repeated fractional distillation at 2 mm. pressure. This ester had a density of 1·146, a molecular weight of 250—260 (calc. for $Et_4P_2O_6$, 274), and dissolved silver halides with evolution of heat. Arbusov and Arbusov conclude that the pure ester cannot be prepared by the action of alkyl halide on silver hypophosphate.

Since H_2PO_3 contains an odd number of electrons and $H_4P_2O_6$ does not, it follows that the hypophosphates, if they have the simpler structure, should be paramagnetic. We have therefore determined the susceptibility at 18—20° of some simple hypophosphates by the method described by one of us (J., 1932, 161). These substances (see table) are all diamagnetic and must therefore be derived from an acid of the formula $H_4P_2O_6$.

Salt.		Formula.	$\chi \times 10^6$.
Sodium hypophosphate		$Na_2H_2P_2O_6$	−0·38
,,	,,	$Na_2H_2P_2O_6,6H_2O$	−0·41
Silver	,,	$Ag_4P_2O_6$	−0·25
Guanidine	,,	$(CN_3H_5)_4H_4P_2O_6,2H_2O$	−0·41

Since it seemed possible that the liquids used by Rosenheim and Pritze might contain an ester of simpler formula, the preparation of the methyl and the ethyl ester as described by Sanger (*Annalen*, 1886, **232**, 9) was repeated. The products were all diamagnetic and did not give the reactions of true hypophosphates. The views of Arbusov and Arbusov are thus confirmed and the magnetism gives further evidence in favour of the formula $H_4P_2O_6$.

Experimental.

Sodium hypophosphate, $Na_2H_2P_2O_6,6H_2O$ (Found : H_2O, 34·4; P, 19·8. Calc. : H_2O, 34·4; P, 19·8%), was conveniently prepared by the method of Probst (*Z. anorg. Chem.*, 1929, **179**, 155).

Silver hypophosphate, $Ag_4P_2O_6$ (Found: Ag, 73·0. Calc.: Ag, 73·2%), was prepared (*a*) by the method of Philipp (*Ber.*, 1883, **16**, 749) and (*b*) by addition of a solution of the Na salt (40 g.) and $NaHCO_3$ (20 g.) to a solution of $AgNO_3$ (90 g.).

Guanidine hypophosphate, $(CN_3H_5)_4H_4P_2O_6,2H_2O$ (Found: P, 14·5. Calc.: P, 14·3%; cf. Müller, *Z. anorg. Chem.*, 1916, **96**, 29, and contrast Rosenheim and Pinsker, *Ber.*, 1910, **43**, 2003), was prepared by mixing hot solutions of the Na salt and guanidine carbonate. When a solution of guanidine carbonate was added to a solution of $Ag_4P_2O_6$ in NH_3 aq. there was formed a cryst. ppt., which after two crystns. from H_2O gave pure guanidine hypophosphate. This proves that the Ag salt does correspond in structure with hypophosphoric acid.

Interaction of $Ag_4P_2O_6$ *and* MeI.—(*a*) $Ag_4P_2O_6$ was covered with excess MeI and left for 4 days. The MeI was evaporated in vac., and the residue extracted with Et_2O. The Et_2O was evaporated in vac., and the resultant oil desiccated for several days. After being filtered from a small amount of AgI, it had *d* 1·307, immediately reduced $AgNO_3$ aq., and gave no ppt. on introduction into guanidine carbonate solution.

(*b*) $Ag_4P_2O_6$ was warmed for 4 hr. with a slight excess of MeI in Et_2O. The product when worked up in the above way gave an oil, *d* 1·303, with similar properties. There is therefore no indication of the formation of a methyl hypophosphate by this process.

Interaction of $Ag_4P_2O_6$ *and* EtI.—A brisk reaction took place when $Ag_4P_2O_6$ was slightly warmed with EtI, and after 2 hr. the product was worked up as before. The residual oil deposited AgI during several days. It then had *d* 1·173, reduced $AgNO_3$ aq., and gave no ppt. on introduction into guanidine carbonate solution.

$Ag_4P_2O_6$ was boiled with *p*-iodonitrobenzene or bromo-2 : 4-dinitrobenzene in Et_2O for 6 hr. No reaction occurred in either case. With bromo-2 : 4-dinitrobenzene in boiling xylene, darkening gradually occurred, but only bromo-2 : 4-dinitrobenzene was isolated on evapn. of the xylene.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11.
BIRKBECK COLLEGE, LONDON, E.C. 4.

[*Received, November 23rd*, 1932.]