NOTES.

Potassium Hexathionate. By James Riddick Partington and Albert Fred Tipler.

The preparation of potassium hexathionate as described by Weitz and Achterberg (*Ber.*, 1928, **61**, 5399) has been repeated. Analysis of a specimen, very well washed and dried for several days in a vacuum desiccator, gave K, 21·5, 21·8; S, 50·3, 50·6 (Calc.: K, 21·3; S, 52·5%). The sulphur was determined by oxidation with bromine water and precipitation as barium sulphate. The percentage of potassium was found as described by Weitz and Achterberg, by igniting the dry substance and weighing the residue as potassium sulphate, the assumption being made that neither potassium chloride nor other such impurity was present.

Further analyses were carried out by the following method, which, with careful adjustment of details and of apparatus, gave easily reproducible results. (i) 10 C.c. of a solution of potassium chlorate (approx. 0·6*N*), 30 c.c. of water, and 45 c.c. of concentrated hydrochloric acid were boiled for 1 hour, the evolved gases were absorbed in a solution of potassium iodide (3·5 g. in 35 c.c. of water), and the liberated iodine was titrated with 0·098*N*-thiosulphate: the normality of the potassium chlorate solution was found to be 0·64. (ii) This procedure was repeated with the addition of 20 c.c. of a solution of the substance (0·2406 g. of a less highly purified specimen in 100 c.c.), but only 10 c.c. of water being used. The volumes of 0·098*N*-thiosulphate used were 65 c.c. in (i) and 34·5 c.c. in (ii) (mean values).

As the percentage of sulphur in this specimen was 47·2, the ratio of the number of oxygen atoms added to the number of sulphur atoms in the molecule of the oxidised substance is 2·121, which agrees sufficiently well with the ratio 2·167 for hexathionic acid (the ratios for two other possible polythionic acids are heptathionic acid, 2·286; pentathionic acid, 2·000).

Potassium hexathionate was obtained only when the potassium thiosulphate used had been prepared by Foerster and Mommsen's method (*Ber.*, 1924, **57**, 258), represented by the equation $2KSH + 4KHSO_3 = 3K_2S_2O_3 + 3H_2O$. The thiosulphate was obtained as the hydrate $K_2S_2O_3,1\frac{2}{3}H_2O$ (Found: $K_2S_2O_3$, 86·2. Calc.: $K_2S_2O_3$, 86·4%). Several commercial specimens of thiosulphate yielded hardly any hexathionate. A thin film of sulphur produced on the walls of the preparation flask appeared to be prejudicial to the formation of hexathionate. These experiments seem to confirm in their main details the observations of Weitz and Achterberg.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [*Received, April 29th*, 1929.]

The Photobromination of Coumarin. By DAVID MATTHEW WILLIAMS.

BERTHOUD and NICOLET (*J. Chim. Phys.*, 1928, **25**, 40) have shown that the photobromination of α-phenylcinnamonitrile in carbon tetrachloride leads to an equilibrium. α-Phenylcinnamonitrile resembles coumarin, in that both will not react with bromine in the dark in a non-hydroxylic solvent (J., 1928, 343). It has now been found that the photobromination of coumarin leads to an equilibrium. In the case of the nitrile it is possible to reach the equilibrium from both ends, since the dibromide is stable for that purpose, but the dibromide of coumarin is too unstable to allow velocity measurements of its decomposition.

The reaction was studied in light from a mercury-vapour quartz lamp and the reacting solutions were placed in tubes of quartz glass on a rotating table at an average distance of 18 inches from the lamp.

When the concentrations of the coumarin and bromine were $1/60M$, carbon tetrachloride being used as solvent, equilibrium was reached in 25 minutes and 85·6% of the bromine had reacted. With chloroform as solvent, equilibrium was reached in 45 minutes and 65·8% of the bromine had reacted. With the nitrile under identical conditions, equilibrium was reached in about 60 minutes in carbon tetrachloride at 40·2% addition and in about 150 minutes in chloroform at 35·4% addition.

In the thermal reaction (*loc. cit.*) the velocity of bromination was invariably greater in chloroform. It seems that the reverse is true for the photobromination.—THE EDWARD DAVIES CHEMICAL LABORATORIES, ABERYSTWYTH. [*Received, May 9th*, 1929.]

A Micro-method for determining Semicarbazones and its Application to the Analysis of Ketones. By RALPH PERCIVAL HOBSON.

HYDROLYSIS with hydrochloric acid decomposes semicarbazide into ammonia and hydrazine. Rimini (*Atti R. Accad. Lincei*, 1903, **12**, II, 376) determined semicarbazones by oxidising the hydrazine with an alkaline solution of mercuric chloride and measuring the nitrogen evolved. Maselli (*Gazzetta*, 1905, **35**, i, 267) analysed the pure base and its salts by estimation of the ammonia formed.

Maselli's method was adapted to a micro-scale for semicarbazones, with the modification that the mercuric chloride was added to the acid so as to oxidise the hydrazine as it was formed during the hydrolysis. The essential reactions are :

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + H_2O = NH_3 + CO_2 + NH_2{\cdot}NH_2.$$
$$NH_2{\cdot}NH_2 + 2HgCl_2 = N_2 + 2Hg + 4HCl.$$

A solution containing 15% hydrochloric acid and 5% mercuric chloride was used and hydrolysis was carried out by boiling under reflux for several hours in a hard-glass test-tube. The ammonia was then determined by Pregl's modified micro-Kjeldahl method (" Quantitative Organic Microanalysis," 1924, p. 99. Transl. by Fyleman); the solution used for making the mixture alkaline was prepared by diluting a 40% solution of sodium hydroxide with an equal volume of a saturated solution of sodium thiosulphate (which is necessary for the decomposition of the mercury ammonium complex).

Experiments were carried out with semicarbazide hydrochloride and the semicarbazones of acetone and *d*-camphor. The results (Table I) show that the reaction is complete in 6 hours for semicarbazide, one of the three nitrogen atoms appearing as ammonia.

TABLE I.

The ammonification of semicarbazide and semicarbazones by hydrolysis with a solution of hydrochloric acid containing mercuric chloride (*a* = ammonia nitrogen expressed as percentage of total nitrogen).

Substance.	Mg.	Hydrolysis (hrs.).	*a*.	Substance.	Mg.	Hydrolysis (hrs.).	*a*.
Semicarbazide	9·8	1½	28·3	Acetonesemi-	191·4	7	33·2
hydrochloride	9·4	4	32·8	carbazone	182·2	,,	33·15
	22·3	,,	32·7	*d*-Camphor-	21·0	,,	32·1
	9·4	6	33·2	semicarbazone	24·2	,,	32·6
	22·1	,,	32·7	Semicarbazide	19·3*	8	34·1
	20·5	8	33·5	hydrochloride	14·8†	,,	36·7
Acetonesemi-	64·4	7	33·4	Acetonesemi-	180·5‡	7	34·1
carbazone	30·4	,,	33·3	carbazone			

* 0·1 G. of sucrose added. † 0·1 G. of sucrose added and mercuric chloride omitted. ‡ Mercuric chloride omitted.

The semicarbazones after 7 to 8 hours' hydrolysis react in the same way, yielding one-third of their total nitrogen as ammonia. It is important when dealing with semicarbazones to destroy the hydrazine, as the ketone released or organic impurities, if present, may cause a partial reduction to ammonia; this has been shown to occur when the mercuric chloride is omitted in the hydrolysis of semicarbazones and of a mixture of semicarbazide and sucrose.

This method affords a means for the micro-determination of ketones, provided they can be converted quantitatively into their semicarbazones when present only in small amounts, and has been applied in this way for the analysis of pyrethrum (Tattersfield, Hobson, and Gimingham, *J. Agric. Sci.*, 1929, **19**, 266). It is not necessary to obtain the semicarbazones pure, but the excess of semicarbazide (and, if present, any impurities yielding ammonia on acid hydrolysis) must be removed. The separation of the semicarbazone from the remaining semicarbazide may be carried out (*a*) by precipitation of the semicarbazone with water, (*b*) by evaporating the mixture to dryness and removing the semicarbazide by washing with water, (*c*) by evaporating the mixture to dryness and extracting the residue with ether, the ethereal solution being shaken with water to remove the semicarbazide.—ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN. [*Received, May 8th*, 1929.]