

NOTES.

Application of Constant Sulphite Solution to the Study of the Reaction between Sulphurous Acid and Iodic Acid. By ANDREW HENDERSON and WALTER P. McCULLOCH.

THE reaction between sulphurous acid and iodic acid has frequently been studied since it was first investigated by Landolt (*Ber.*, 1886, **19**, 1317; 1887, **20**, 745), and it was hoped that the use of a constant sulphite solution (this vol., p. 506) might eliminate some of the difficulties in the work.

Each of the three variables, (i) weight of total mixture, (ii) weight of iodic acid, and (iii) weight of sulphur dioxide, was in turn altered, the other two being kept constant, and the present communication records results obtained in experiments of type (i).

A constant weight of constant sulphite solution in a vessel thinly coated with paraffin is rapidly poured into a solution of a constant weight of Kahlbaum's iodic acid, J , and of sulphuric acid, A , in a volume of water which may be varied, and the time required for reaction, t , is noted. The sulphuric acid is calculated to suffice to liberate all the available sulphurous acid (taken as the anhydride), S , from the sulphite, very dilute starch emulsion is used as indicator, and the temperature is recorded on a standard thermometer. The total weight of the mixture of the two solutions, K (in kg.), is used as the variable.

As recommended by Landolt, wide beakers (Jena) are used for the mixtures, but the upper part of the inside walls is coated with a thin layer of paraffin so that pouring or stirring does not affect the mixture. Two observers note the time for reaction, taking their zero severally from the beginning and from the completion of the pouring. (These reaction times are denoted in the tables by "M." and "H." respectively.)

Even for experiments of considerable duration, the values of t were satisfactorily concordant.

Mathematical Expression of the Data.—Consideration of the data of many series of experiments showed that, for consecutive equal increments of K , the difference between the corresponding values of t/K^2 formed an arithmetical progression. Hence $d^2(t/K^2)/dK^2 = a$

i.e.,

$$t/K^2 = aK^2 + bK + c$$

or, with different constants,

$$t = AK^2(K^2 + BK + C).$$

Three observations, then, determine the curve, and the following examples, in each case selected from 18 time readings all of which fitted the curve accurately, demonstrate the accuracy of the above expression. Time is recorded in seconds and the observed values are means.

Series I.

Temp., 18.35°.

$S = 0.12$ g. } for each mixture.
 $J = 0.208$ g. }
 $t = K^2(103.06 + 232K - 36K^2).$

Series II.

Temp., 16.5°.

$S = 0.1150$ g. } for each mixture.
 $J = 0.175$ g. }
 $t = K^2(114 + 335.1K - 58K^2).$

K.	t , calc.	t , obs.		K.	t , calc.	t , obs.	
		M.	H.			M.	H.
1.25	526.265	526.85	526.33	1.25	691.016	693.53	694.10
1.00	299.060	299.00	298.30	1.00	391.100	391.28	390.48
0.75	144.456	144.58	143.43	0.75	187.144	187.25	186.03

It was of interest to find that Landolt's data (Part II; Series I and II) for sulphurous acid itself conform to expressions of this type, *viz.*,

$$\text{Series I: } t = K^2(35 + 139K - 30K^2)$$

$$\text{Series II: } t = K^2(23.24 + 71.4K - 13K^2)$$

Dilutions greater than those given have been tested with satisfactory results, but doubts as to the maintenance of concentrations and of temperature and particularly as to the increasing faintness of the iodine indication do not warrant their reproduction; throughout the above range the end-point is quite sharp.

Should the formula apply at all dilutions, the time should attain a maximum value and finally become zero, and in this connexion it is of interest that Patterson and Forsyth's data (J., 1912, 101, 40) show that replacement of water by increasing amounts of acetone causes the time to increase to a maximum and then decrease rapidly. A further examination of this effect might be illuminating.

The authors desire to record their very great thanks to Emeritus Professor G. G. Henderson, F.R.S., for his keen interest and advice.—THE UNIVERSITY, GLASGOW. [Received, November 18th, 1938.]

The Chemistry of Natural Rubber. By J. W. HAEFELE and E. M. MCCOLM.

ROBERTS (J., 1938, 215, 219) dissolved air-dried films from fresh latex in acetone-carbon tetrachloride and coagulated the solution by the addition of further acetone: the supernatant liquid contained an ingredient which was soluble in ligroin, contained sulphur, might be elastic, and was termed by Roberts, "caoutchol."

Roberts stated that removal of this "caoutchol" ingredient caused marked changes in the properties of the remaining rubber "characterised by its lack of tensile strength and the remarkably low viscosity of its solutions." This rubber was dried in air for 24 hours, dissolved in benzene, centrifuged, and emulsified with water, and the benzene removed by steam distillation. The rubber remaining was tacky and feebly elastic after drying in a vacuum, and was termed "caoutchene."

Roberts developed the theory that the elasticity of crude rubber is due to the presence of "caoutchol," and that without "caoutchol," rubber has very poor elasticity and low viscosity in solution.

Insufficient attention has been paid to the rôle of oxygen in the purifications described. Roberts states: "The process has been carefully examined, particularly with respect to the possibility of oxidative or other changes in the constituents. No evidence of such changes has been obtained." Yet the coagulated rubber, after removal of the "caoutchol," but prior to steam distillation, was milled in air, and dried in air for 24 hours, during which time considerable oxidation could have occurred.

The following analysis of "caoutchene" is given: C, 87.0; H, 11.8; N, 0.5; S, 0.1; O (by diff.), 0.6%. The oxygen content is stated to be equivalent to the nitrogen content, since the two occur in the same ratio as in most proteins, and therefore the oxygen found by difference is assumed to be protein oxygen, and not combined with the hydrocarbon. This assumption is not necessarily justified, in view of the error inherent in estimating oxygen by difference from combustion-analysis results of carbon, hydrogen, and sulphur, which is large relative to the low value of the nitrogen found. It must therefore be concluded that the analysis given does not constitute a proof that oxygen has not been taken up by the hydrocarbon in the "caoutchene" fraction during its preparation.

We prepared rubber free from the "caoutchol" fraction and found it to be elastic and non-tacky if sufficient precautions were taken to conduct the purifications in oxygen-free nitrogen. Fresh latex, an hour old, was coagulated by running it into 95% ethyl alcohol, to avoid any possible bacterial changes which may have occurred in Roberts's procedure of relatively slow air drying. The coagulum was pressed, and vacuum-dried to a moisture content of 0.15%. The dry rubber was dissolved four times in dry carbon tetrachloride-acetone under oxygen-free nitrogen and precipitated four times by the addition of further dry acetone, approximately Roberts's proportions of solvents being used. This solution and precipitation procedure for the removal of "caoutchol," Roberts carried out only once. The final precipitate of rubber was freed from solvent in a vacuum, milled thin, and dried in a vacuum over sulphuric acid, the air in the desiccator having been replaced by nitrogen before evacuation. The dry

piece of rubber so obtained was not tacky and was quite elastic as determined in the hand. It began to show tackiness after 24 hours' exposure to air.

This experiment with dry rubber and solvents fulfils Roberts's specification, given in a private communication, that the removal of "caoutchol" from rubber is complete only in the absence of moisture. The removal of "caoutchol" from rubber does not lead to tackiness and loss of elasticity. These properties appear when "caoutchol-free" rubber suffers oxidation, but do not appear if oxygen is excluded from the rubber, during or after its preparation.—UNITED STATES RUBBER PLANTATIONS, BOENOET, KISARAN, SUMATRA, EAST COAST. [Received, June 3rd, 1938.]

The Dipole Moment and Configuration of Arsenobenzene. By R. J. W. LE FÈVRE and C. A. PARKER.

No evidence appears to exist concerning the configuration of molecules containing arsenic atoms at the same time both doubly and singly linked to other atoms. Because of the obvious connexion with the azobenzenes (see this vol., pp. 531, 535) we have determined the dipole moment of arsenobenzene in benzene solution, in which, however, it was not very soluble. The results are tabulated below under the customary headings; it is evident from the relative magnitudes of the total molecular polarisations (P_1) and the molecular refractions for the three solutions that the solute has a vanishingly small moment.

Arsenobenzene in Benzene at 25°.

$w_1 \times 10^6$.	ϵ_{1200}^{25} .	d_4^{25} .	ρ_{12} .	P_1 .	η_D^{25} .	r_{12} .	$[R_L]_D$.
0	2.2725	0.87380	0.34085	—	1.49724	0.33502	—
886.6	2.2727	0.87405	0.34079	83.0	1.49728	0.33495	80.9
1404.1	2.2732	0.87439	0.34075	82.0	1.49746	0.33492	79.9
2041.9	2.2730	0.87440	0.34071	82.6	1.49742	0.33489	82.5

Arsenobenzene therefore has a symmetrical molecule, which by analogy with the stable form of azobenzene, is the *trans*-form. It may, however, be much more nearly rectilinear than is *trans*-azobenzene, owing to the larger volume and consequent easier deformability of the arsenic than of the nitrogen atoms.

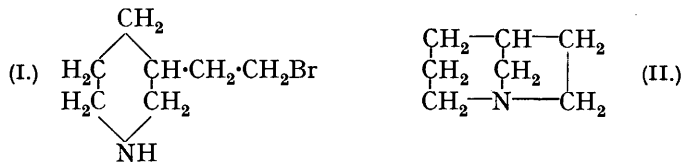
Preparation.—This was accomplished by reduction of phenylarsonic acid ("Organic Syntheses," Vol. XV, p. 59) with hypophosphorous acid at 60° as described by Palmer and Scott (*J. Amer. Chem. Soc.*, 1928, 50, 536) except in the following respects: (1) coal-gas was used as an inert atmosphere instead of carbon dioxide; (2) for the purification, the dried crude reduction product from 10 g. of phenylarsonic acid was dissolved in chloroform (100 c.c.) under coal-gas and dried with sodium sulphate. Rapid filtration and evaporation on the steam-bath with continued exclusion of air until crystallisation began gave, after cooling, filtration, and washing with alcohol, 0.5—1.0 g. of nearly colourless needles; m. p.'s, in different preparations, 201—203°, 205—206°, 209°, and 211—212°. The literature shows some variation in the m. p., the highest, however, being 212° (Palmer and Scott, *loc. cit.*) (cf. Michaelis and Schäfer, *Ber.*, 1913, 46, 1742).

The benzene solutions used in the above measurements quickly became cloudy (? oxidation) even when kept in the dark. The solution of $w_1 = 0.002042$ was exposed to direct sunlight in a white glass flask for 1 hour, after which its dielectric constant was 2.2735, but as the solution was then no longer clear, the slight increase could not be taken as evidence of any geometrical change (cf. this vol., p. 531).—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON. [Received, January, 25th, 1939.]

1-Azabicyclo[1 : 2 : 3]octane. By V. PRELOG, (MISS) S. HEIMBACH, and E. CERKOVNIKOV.

1-Azabicyclo[1 : 2 : 2]heptane is easily obtainable by intramolecular ammonium salt formation from α -dibromo- γ -aminomethylpentane (Prelog, Cerkovnikov, and Ustricev, *Annalen*, 1938, 353, 37). As the dicyclic amine must have a pyrrolidine derivative as an intermediate, which is then bridged in the 1 : 3-position of the pyrrolidine ring, there was no reason to suppose that piperidine could not be bridged in the 1 : 3-position. Our attempts to realise such a case have been successful. 3- β -Hydroxyethylpiperidine, synthesised by the procedure of Merchant and Marvel (*J. Amer. Chem. Soc.*, 1928, 50, 1197) from ethyl nicotinate, furnished with concentrated hydrobromic acid the hydrobromide of the corresponding bromo-derivative (I). By dropping the solution of 3- β -bromoethylpiperidine hydrobromide into a dilute solution of sodium

hydroxide a tertiary base was obtained which is certainly the expected 1-azabicyclo[1 : 2 : 3]octane (II). It is a water-soluble, steam-volatile substance. The determination of the molecular weight of the hydrochloride in alcoholic solution by the Barger-Rast method (*Ber.*, 1921, 54, 1979) proved its simple molecular weight. A molecular-weight determination of quinuclidine hydrochloride carried out under the same conditions showed that the low molecular weight is not due to dissociation of the hydrochloride. The new base has been characterised by the well-crystallised *platinichloride* and *picrate*.



Attempts to prepare 1-azabicyclo[1 : 3 : 3]nonane, as the further representative of 1 : 3-bridged piperidine derivatives, are being carried out.

3-β-Bromoethylpiperidine Hydrobromide.—3-β-Hydroxyethylpiperidine (0.35 g.) was heated for 4 hours in a sealed tube with concentrated hydrobromic acid (15 c.c., 69%). The excess of the acid was removed by distillation under reduced pressure, and the solid crystalline residue twice recrystallised from acetone-ether; m. p. 116—116.5° (Found: N, 5.2. Calc. for C₇H₁₅NBr₂: N, 5.1%). The recrystallisation was accompanied by great loss of material.

1-Azabicyclo[1 : 2 : 3]octane.—The crude 3-β-bromoethylpiperidine hydrobromide obtained from 0.35 g. of 3-β-hydroxyethylpiperidine was dissolved in water (25 c.c.) and dropped into N/10-sodium hydroxide (100 c.c.) at 50° during 1½ hours. After cooling, benzenesulphonyl chloride (8 g.) and 15% sodium hydroxide solution (10 c.c.) were added (Prelog, Cerkovnikov, and Ustricev, *loc. cit.*) and stirring was continued for 2½ hours. The volatile tertiary base isolated by steam-distillation needed 0.73 c.c. of N-hydrochloric acid (methyl-red) for neutralisation. Yield, 27% of the theoretical.

The *hydrochloride* separated from acetone-ether in white crystals, which sublimed above 300° without melting (Found: N, 9.7. C₇H₁₃N.HCl requires N, 9.5%). A solution of 5.4 mg. of the substance in 205.1 mg. of alcohol was between 0.151 and 0.209 N (Found: *M*, 126—174). 5.2 Mg. of quinuclidine hydrochloride in 197.4 mg. of alcohol behaved similarly.

The *platinichloride* was readily soluble in water and less soluble in alcohol. Recrystallisation from water yielded orange crystals, m. p. 215—215.5° (Found: Pt, 30.8. C₁₄H₂₆N₂.H₂PtCl₆ requires Pt, 30.9%).

The *picrate* crystallised from methyl alcohol in yellow needles, m. p. 294—295° (Found: C, 46.1; H, 4.75; N, 16.55. C₇H₁₃N.C₆H₃O₇N₃ requires C, 45.9; H, 4.7; N, 16.5%).—THE UNIVERSITY, ZAGREB, YUGOSLAVIA. [Received, January 3rd, 1939.]