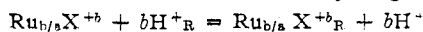ruthenium solution, all divided by the gram atoms of ruthenium per liter in the eluted solution.

The charge per species is found from the concentration dependence of the exchange of ruthenium with a known ion—in our case hydrogen ion

$$Ru_{b/a}X^{+b} + bH^+_R = Ru_{b/a}X^{+b}_R + bH^-$$

$$Q = \frac{[RU_{b/a}X^{+b}]_R [H^+]^b}{[Ru_{b/a}X^{+b}][H^+]^b_R}$$

where X denotes anions in the ruthenium species, R designates the resin phase and concentrations are indicated by brackets. The ratio of ruthenium concentrations is proportional to the ratio of hydrogen ion concentrations to the $-b$ power. From two equilibrations at different hydrogen ion concentrations b may be calculated. Conditions were chosen such that the great majority of the resin was in the hydrogen ion form and most of the ruthenium was present in the resin phase. There is an unpredictable change in activity coefficients in the aqueous phase but the method is believed to be sufficiently accurate in most cases because b must be an integer as well as a multiple of a.

It can be shown that any changes in hydrolysis on exchange do not affect the results.

This method has been used to establish the formulas of the species Ru^{+3} and $RuCl^{+2}$.

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SEMI-QUANTITATIVE GAS CHROMATOGRAPHY

Sir:

We have found relationship (1) reasonably accurate in relating the fraction by weight of a component in a mixture to the corresponding area in a liquid–vapor chromatogram obtained using helium as the carrier gas and a tungsten wire thermal conductivity gage as detector

$$\left(\frac{m_i}{W}\right) = \frac{A_i \sqrt{M_i}}{\sum_i A_i \sqrt{M_i}} \tag{1}$$

where (m_i/W) is the fraction by weight of the ith component, A_i the planimeter-determined area under the peak on the chromatogram corresponding to the ith component and M_i the molecular weight of the ith component.

Clearly the equation may be applied only to mixtures which are completely resolved and such that all components appear in the chromatogram.

Component	Known mole %	wt. %	Found area %	Calcd. wt. %
Ethanol	43.4	45.4	47.3	44.6
Water	46.6	19.1	31.1	18.3
1,8-Cineole	10.0	35.5	21.5	37.1

The equation has been applied with comparable results to chromatograms of several mixtures: α and β-pinene plus ethanol; α and β-pinene plus benzene; methyl ethyl ketone, n-propyl alcohol and p-xylene.

Although the expression was arrived at empirically, the appearance of the square root function is not unreasonable on the basis of kinetic theory.

Further, it is apparent that the expression may be utilized to determine the molecular weight of a component from the chromatogram of a mixture of known weight composition of the material of unknown molecular weight with a known substance. Although the square root function through its leverage places a premium on accurate determination of the areas on the chromatogram, we have had some success in this utilization of the relationship.

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TETRAACETYL DIBORATE AND SO-CALLED "BORON ACETATE"

Sir:

There has been considerable confusion in the literature over the constitution of the product obtained by the reaction between orthoboric acid and acetic anhydride. Two types of compounds have been reported at various times. One, said to melt around 121°, has been called boron triacetate, $(CH_3CO_2)_3B$,[1,2,3] and the other, m.p. 150–152°, pyroboron acetate, $(CH_3CO_2)_2BOB(O_2\text{-}CCH_3)$.[4,5,6] Both have been supported by analytical data but, in several cases, the authors used identical procedures only to obtain different products.

We have repeated some of the previous preparations, our results agreeing with those of Gerrard and Wheelans[6]; no evidence was obtained for boron triacetate, although the methods described for its preparation[1,2] were carefully followed. The analytical data for $(CH_3CO_2)_2BOB(O_2CCH_3)_2$ were improved and extended and the name tetraacetyl diborate is proposed.

The reaction between orthoboric acid and acetic anhydride was found to occur according to the equation

$$2H_3BO_3 + 5(CH_3CO_2)_2O \longrightarrow$$
$$(CH_3CO_2)_2BOB(O_2CCH_3)_2 + 6CH_3CO_2H$$
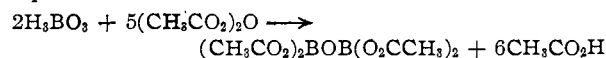
Orthoboric acid (0.534 mole) and acetic anhydride (1.96 mole) were heated together at 50–100° with vigorous stirring in a nitrogen atmosphere until all the solid had dissolved. On cooling, the product crystallized as colorless needles. One sample was purified by recrystallization from a benzene–chloroform mixture, another by precipitation from solution in dry acetic acid by the addition of ether. Both melted at 147–148°.

All filtrations were carried out using a pressure of dry nitrogen and the products were dried in vacuum at room temperature before being transferred to a dry box for subsequent handling.

The acetate content was determined by titration with standard base, the end-point (around pH 6.7)

(1) A. Pictet and A. Geleznoff, Ber., 36, 2219 (1903).
(2) H. Cook, L. Ilett, B. Saunders and G. Stacey, J. Chem. Soc., 3125 (1950).
(3) T. Ahmad and M. Khundkar, Chem. and Ind., 248 (1954).
(4) O. Dimroth, Ann., 446, 97 (1925).
(5) H. Meerwein and H. Maier-Hüser, J. prakt. Chem., 134, 51 (1932).
(6) W. Gerrard and M. Wheelans, Chem. and Ind., 758 (1954).

being detected with a Beckmann pH meter. Boron was estimated, using the same solution, by further titration with base in the presence of excess mannitol to the phenolphthalein end-point. Analysis with the Karl Fischer reagent under anhydrous conditions caused the reaction

$$(CH_3CO_2)_2BOB(O_2CCH_3)_2 + 2MeOH \longrightarrow$$
$$H_2O + 2(CH_3CO_2)_2BOMe$$
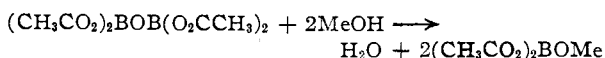
to be driven to the right, the reagent quantitatively removing the water.[7] The "hydroxyl equivalent" was calculated as mg. water/g. of sample. This reaction afforded unequivocal proof of the nature of the product, because boron triacetate could not react at all with the Karl Fischer reagent. The molecular weight measurement was carried out ebullioscopically in dry chloroform, the concentrations of the solutions being given in g. of sample per 1000 g. of solvent in parentheses after each value.

EXPERIMENTAL VALUES

Sample crystallized from	M.p., °C.	% CH₃CO₂	% B	Hydroxyl equiv. mg. H₂O/g.	CH₃CO₂/B ratio
Chloroform–benzene	147–148	85.0	7.86	67.2	1.98
		85.6	7.96	67.9	1.97
Acetic acid–ether	147–148	85.6	7.67	...	1.99

Molecular weight of sample crystallized from chloroform-benzene: 345 (1.30), 302 (3.30), 312 (5.51), 302 (9.40)

CALCULATED VALUES

Compound	Mol. Wt.	% CH₃CO₂	% B	Hydroxyl equiv. mg. H₂O	CH₃CO₂/B ratio
(CH₃CO₂)₂BOB-(O₂CCH₃)₂	273.6	86.3	7.90	65.9	2
(CH₃CO₂)₂BOH	145.9	81.0	7.42	123.4	2
(CH₃CO₂)₃B	187.9	94.2	5.76	0	3

These data clearly establish the product of the reaction to be $(CH_3CO_2)_2BOB(O_2CCH_3)_2$, tetraacetyl diborate.

X-Ray powder diffraction patterns were taken with copper K_α radiation (nickel filter).

X-RAY POWDER DIFFRACTION DATA FOR TETRAACETYL DIBORATE

d	I	d	I	d	I
7.37	M	3.59	W	2.39	W
6.28	MS	3.46	VW	2.28	VW
5.55	MS	3.32	VW	2.19	VW
4.72	VW	3.11	VW	2.12	VW
4.41	W	2.94	VW	1.94	VW
4.11	W	2.74	VW	1.83	W
3.78	VS	2.51	M		

A sample of the tetraacetyl diborate was heated in acetic anhydride in an attempt to cause further acetylation, the product being precipitated by the addition of ether, m.p. 120–140°. Analysis showed that slight decomposition with decrease in acetate content occurred under these conditions, analogously to Dimroth's observation[4] that tetraacetyl diborate lost acetic anhydride on heating. How-

(7) H. C. Mattraw, C. E. Erickson and A. W. Laubengayer, THIS JOURNAL, 78, 4901 (1956).

ever, an X-ray powder photograph was identical with the one we obtained for tetraacetyl diborate.

A further experiment in which we followed as closely as possible the method of Cook, *et al.*,[2] yielded a crystalline product, m.p. 149–150° (Cook gave m.p. 120°). This checks very well with the melting point of tetraacetyl diborate.

From the above evidence, we reach a conclusion similar to that of Gerrard and Wheelans.[6] Although it may be possible to prepare boron triacetate, our experience confirms the existence of only tetraacetyl diborate.

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REACTIONS OF GASEOUS IONS. III.
FORMATION OF PROTONATED METHANE

Sir:

Recent publications[1,2,3,4] have reported the formation of CH_5^+ (or CD_5^+) in a bimolecular reaction between CH_4^+ (or CD_4^+) ions and CH_4 (or CD_4) molecules taking place in the ionization chamber of a mass spectrometer. However, the formation of protonated methane by reactions involving methane ions and molecules other than methane has not been reported.

We have observed the formation of CD_4H^+ in mixtures of CD_4 with other hydrogen-containing substances. The formation of CD_4H^+ is first-order in CD_4^+ and first-order in the hydrogen-containing substance and appearance potential measurements of CD_4H^+ more closely correspond to the ionization potential of CD_4 than to any other possible ionic species in the system. We thus write for the formation of CD_4H^+

$$CD_4^+ + XH \longrightarrow CD_4H^+ + X \qquad (1)$$

We have calculated rate constants relative to the rate constant taking $XH = CH_4$ for several such reactions by the relationship

$$\frac{k_{XH}}{k_{CH_4}} = \frac{[CH_4]}{[XH]} \frac{\left(\frac{I_{CD_4H^+}}{I_{CD_4^+} + I_{CD_4H^+}}\right)_{XH}}{\left(\frac{I_{CD_4H^+}}{I_{CD_4^+} + I_{CD_4H^+}}\right)_{CH_4}} \qquad (2)$$

where the I's are the observed ion-currents and $[CH_4]$ and $[XH]$ are the ionization chamber gas concentrations. We assumed that the ratio of ionization chamber concentrations was equal to the ratio of gas reservoir partial pressures, an assumption well within experimental error. The values obtained (averages of replicate measurements) are shown in Table I.

Within experimental error the appearance potential of CD_4H^+ coincides with the ionization potential of CD_4. If we assume that (1) cannot be endothermic (any exponential term involving significant activation energy would so decrease the

(1) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, 86, 909 (1952).

(2) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, 23, 1353 (1955).

(3) F. H. Field, J. L. Franklin and F. W. Lampe, THIS JOURNAL, 78, 5697 (1956).

(4) G. G. Meisels, W. H. Hamill, and R. R. Williams, Jr., *J. Chem. Phys.*, 25, 790 (1956).