being detected with a Beckmann *p*H 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.	% CH_3CO_2	% B	Hydroxyl equiv. mg. H_2O/g.	CH_3CO_2/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.	% CH_3CO_2	% B	Hydroxyl equiv. mg. H_2O	CH_3CO_2/B ratio
$(CH_3CO_2)_2BOB(O_2CCH_3)_2$	273.6	86.3	7.90	65.9	2
$(CH_3CO_2)_2BOH$	145.9	81.0	7.42	123.4	2
$(CH_3CO_2)_3B$	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. However, 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

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

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

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TABLE I

RELATIVE RATES OF FORMATION OF CD_4H^+

Reaction	k_{XH}/k_{CH_4}
$CD_4^+ + CH_4 \longrightarrow CD_4H^+ + CH_3$	1.00
$CD_4^+ + C_2H_6 \longrightarrow CD_4H^+ + C_2H_5$	0.11
$CD_4^+ + C_3H_8 \longrightarrow CD_4H^+ + C_3H_7$	$.05_6$
$CD_4^+ + \text{iso-}C_4H_{10} \longrightarrow CD_4H^+ + C_4H_9$	$.04_6$
$CD_4^+ + CH_3Cl \longrightarrow CD_4H^+ + CH_2Cl$	$.04_1$
$CD_4^+ + NH_3 \longrightarrow CD_4H^+ + NH_2$	$.08_8$
$CD_4^+ + H_2S \longrightarrow CD_4H^+ + HS$	.17
$CD_4^+ + HCl \longrightarrow CD_4H^+ + Cl$	.56

probability of a reactive collision that we could not observe the reaction), then the energetics of the reactions that do take place (Table I) lead us to the conclusion that the heat of formation of CD_4H^+ is $\Delta H_f \leq 234$ kcal/mole. On the other hand, we have not been able to find any evidence of CD_4H^+ formation in CD_4–H_2O and CD_4–H_2 mixtures. If these reactions are not observable for energetic reasons, one calculates the heat of formation of CD_4H^+ to be $\Delta H_f \geq 218$ and $\Delta H_f \geq 233$ kcal./mole, respectively. Thus, the implied value for the heat of formation of CD_4H^+ is 233–234 kcal./mole, and if this is correct, then the proton affinity of methane is 113 kcal/mole.

Although we have made no rate measurements, we have observed in the systems studied reactions (3), (4) and (5), which we believe have not been reported as yet

$$H_2S^+ + H_2S \longrightarrow H_3S^+ + HS \qquad (3)$$

$$H_2S^+ + CD_4 \longrightarrow H_2DS^+ + CD_3 \qquad (4)$$

$$HCl^+ + CD_4 \longrightarrow HDCl^+ + CD_3 \qquad (5)$$

Relative rate measurements have indicated that (5) has about the same rate as the reaction between CD_4^+ and HCl shown in Table I.

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THE REACTION OF TRIARYL PHOSPHITES WITH SULFONYL CHLORIDES

Sir:

Gilbert and McGough[1] reported that trialkyl phosphites react with sulfonyl chlorides to yield a mixture of the trialkyl phosphate, O,O-dialkyl-S-substituted thiophosphate and an alkyl chloride

$$3(RO)_3P + R'SO_2Cl \longrightarrow 2(RO)_3PO + (RO)_2P(O)SR' + RCl$$

This reaction has been confirmed recently by Hoffmann and his co-workers.[2] It is most likely that the reaction proceeds in three consecutive stages—the first two involving oxygen transfer

$$(RO)_3P + R'SO_2Cl \longrightarrow (RO)_3PO + R'SOCl \qquad (1)$$

$$(RO)_3P + R'SOCl \longrightarrow (RO)_3PO + R'SCl \qquad (2)$$

$$(RO)_3P + R'SCl \longrightarrow (RO)_2P(O)SR' + RCl \qquad (3)$$

Reaction 3 which is analogous to the Michaelis–Arbuzov reaction can occur only if one of the R groups is labile; in the case of trialkyl phosphites, this has been amply demonstrated by Gilbert and McGough[1] and by Morrison.[3]

With triaryl phosphites, however, O,O,S-trisubstituted thiophosphates are not formed under the same mild conditions. Thus, refluxing a mixture of triphenyl phosphite and benzenesulfonyl chloride (mole ratio 3:1) in dry benzene under a nitrogen atmosphere, then fractionating *in vacuo* gave triphenyl phosphate, diphenyl disulfide, chlorobenzene and possibly diphenyl phosphorochloridite (not definitely identified). The results support the stoichiometric equation

$$6(PhO)_3P + 2PhSO_2Cl \longrightarrow 5(PhO)_3PO + (PhS)_2 + PhCl + (PhO)_2PCl$$

The phosphate and disulfide were obtained almost quantitatively.

Diphenyl sulfide and O,O-diphenyl-S-phenyl thiophosphate were not found, thus indicating that triphenyl phosphite does not react with diphenyl disulfide. This inference was confirmed by demonstrating that triphenyl phosphite and diphenyl disulfide are recovered quantitatively after refluxing a mixture of them in benzene. With triethyl phosphite under the same conditions, however, diphenyl disulfide reacts quantitatively in refluxing benzene solution

$$(PhS)_2 + (EtO)_3P \longrightarrow (EtO)_2P(O)SPh + PhSEt$$

This reaction had been observed previously with dialkyl disulfides by Jensen and his co-workers[4] and it now appears to be generally applicable to trialkyl phosphites and diaryl disulfides.

Our conclusion is that the first two stages (reactions 1 and 2) occur with both triaryl and trialkyl phosphites but the third stage (reaction 3), in contrast to phosphites bearing at least one alkyl group, does not take place with triaryl phosphites. This is demonstrated readily by carrying out a reaction of triphenyl phosphite with benzenesulfenyl chloride when diphenyl disulfide but not O,O,S-triphenyl phosphate is formed

$$(PhO)_3P + 2PhSCl \longrightarrow Ph{-}S{-}S{-}Ph + (PhO)_3PCl_2$$

Unstable quasi-phosphonium intermediates seem likely at each stage of the reaction; however, the nature of these phosphonium complexes, the manner in which oxygen transfer occurs, and the interpretation of disulfide formation requires critical examination to clarify the course of this reaction. Disulfone or disulfoxide intermediates are unlikely—both are expected to react giving other products. However, the mechanistic and experimental details of this novel and convenient reduction of sulfonyl chlorides to disulfides by triaryl phosphites will be presented in a forthcoming publication.

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