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

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

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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[1] (a) E. E. Gilbert and C. J. McGough, U.S. Patent 2,690,450 (1954); (b) 2,690,451 (1954).

[2] F. W. Hoffmann, T. R. Moore and B. Kagan, THIS JOURNAL, **78**, 6413 (1956).

[3] D. C. Morrison, *ibid.*, **77**, 181 (1955).

[4] H. D. Jacobson, R. G. Harvey and E. V. Jensen, *ibid.*, **77**, 6064 (1955).