where triphenylmethylperoxy radical decomposes. Triphenylacetic acid was found most suitable because its critical temperature is above the temperatures used in this study.

The solid state appears to be a promising medium for obtaining thermochemical and kinetic data for stable radicals and oxygen. Preliminary results have been obtained for other radicals, e.g., 9-phenylfluorenyl.

(13) University of Georgia Alumni Foundation Fellow, 1965–1966.

Caroline L. Ayers,[13] Edward G. Janzen, F. J. Johnston
Department of Chemistry, The University of Georgia
Athens, Georgia 30601
Received March 18, 1966

Substitution Reaction of 3-Ev Tritium Atoms with Methane[1]

Sir:

We have produced 3-ev tritium atoms by the photolysis of TBr with 1849-A radiation and have observed both the abstraction and substitution reactions 1 and 2

$$T^* + CH_4 \longrightarrow HT + CH_3 \qquad (1)$$
$$T^* + CH_4 \longrightarrow CH_3T + H \qquad (2)$$
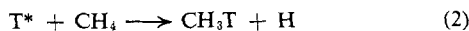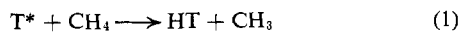
with methane. Previous experimenters have demonstrated that deuterium atoms from the photolysis of DI with 2537-A radiation, and from the photolysis of DBr with 1849-A radiation, undergo hot reactions with methane,[2,3] but the experimental systems did not permit the separation of the contributions of the reactions corresponding to (1) and (2), or even to demonstrate the qualitative presence of both reactions.[4] Tritium atoms formed with much higher energy by nuclear-recoil processes react by both reactions 1 and 2 in the yield ratio of approximately 0.8–1.0 for halogen or oxygen-scavenged methane.[5–7] Our experiments indicate that the yield ratio of reactions 1 and 2 is approximately 3.5–4.0 for 3-ev atoms in methane and depends to some extent on the ratio of scavenger molecule to methane.

The abstraction and substitution reactions cannot be separated in these photolytic systems if the photolytic source also serves as the scavenger molecule in this system; the CH_3 radical from (1) abstracts T from TBr and forms CH_3T, while the H from (2) forms HT by abstraction. Such combination photolytic source and scavenger experiments have been used in successful measurements of the total hot reaction in methane for D

(1) This research has been supported by AFOSR Grant No. 62–15 at the University of Kansas, and by AEC Contract No. 34, Agreement No. 126, at the University of California, Irvine.
(2) R. J. Carter, W. H. Hamill, and R. R. Williams, Jr., *J. Am. Chem. Soc.*, 77, 6457 (1955).
(3) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, 40, 3007 (1964).
(4) The yield of the substitution reaction has been shown to be quite small for 0.9–1.8-ev T atoms from the 2537-A photolysis of TI in the presence of I_2: M. C. Sauer, Jr., Ph.D. Thesis, University of Wisconsin, 1958.
(5) M. F. A. El-Sayed and R. Wolfgang, *J. Am. Chem. Soc.*, 79, 3286 (1957); M. Henchman, D. Urch, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, p 83.
(6) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, 79, 3284 (1957).
(7) J. W. Root, Ph.D. Thesis, University of Kansas, 1964; J. W. Root and F. S. Rowland, unpublished results.

Table I. Distribution of Tritium Radioactivity after 1849-A Photolysis of TBr in Methane

Sample no.	— Pressure of reactants,[a] mm —			Measured product ratios after photolysis, HT/CH_3T
	CH_4	Br_2	O_2	
31	220	86	...	3.37[b]
32	430	10	...	4.19[b]
65	350	32	...	3.57[c]
64	350	33	...	3.58[c]
63	350	32	...	3.57[d]
59	320	<3	30	3.75[e]
60	310	30	...	3.64[e]

[a] TBr present in carrier-free quantities; $\sim 10^{-3}$ mm. [b] 1-min irradiation with lamp current at 39 ma. [c] 1-min irradiation with lamp current at 49 ma. [d] Fused quartz lamp was used instead of Suprasil quartz lamp; irradiation at 50 ma for 1 min. [e] 2-min irradiation with fused quartz lamp at 50 ma.

atoms[2,3] and in hexane for T atoms.[8] We have carried out our experiments using carrier-free TBr and utilizing Br_2 as the scavenger molecule, thereby avoiding the formation of a radioactive molecule in the second reaction following (1) and (2).

Appropriate mixtures of TBr, CH_4, and Br_2 were introduced into Suprasil quartz photolysis cells, and irradiation was carried out in a nitrogen atmosphere with a low-pressure Hg lamp, also of Suprasil quartz. While the main output of the lamp is in the ultraviolet region at 1849 and 2537 A, the absorption of TBr at 2537 A is sufficiently small relative to that at 1849 A[9,10] that the irradiations were carried out without using any filters. The tritiated products were analyzed by radio gas chromatography. Similar experiments have also been carried out with C_2H_6. Typical results are shown in Table I.

Carrier-free TBr was prepared by passing an electric discharge between two gold electrodes in a vessel containing a mixture of T_2 and Br_2, and then by pumping off the unreacted T_2 at $-196°$. Mixtures of TBr, Br_2, and methane showed negligible radioactivity as molecular hydrogen or hydrocarbons, whether analyzed immediately, or after storage for 24–48 hr. Mixtures prepared as usual, but substituting Vycor glass for the Suprasil quartz in the reaction vessel, showed no radioactivity in either HT or CH_3T, confirming that the hot T atoms are formed almost entirely through photolysis with 1849-A radiation. The actual TBr pressure is estimated to be 10^{-3} mm.

Since the abstraction reaction of H atoms with methane is well established, the qualitative question of importance is whether or not the observed yield of CH_3T was formed by the substitution reaction 2. The most likely other source of CH_3T would be from the reaction with TBr of CH_3 radicals formed by some other process in the system.[11] An estimate of this contribution can

(8) D. Perner and R. H. Schuler, *J. Phys. Chem.*, 70, 317 (1966). These authors have demonstrated the equivalence in yield of HT and $C_6H_{13}T$ in the photolysis of TI in hexane.
(9) C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc.* (London), A152, 221 (1935).
(10) J. Romand, *Ann. Phys.* (Paris), 4, 527 (1948).
(11) There is no positive evidence for CH_3 radicals in our system. However, the absorption cross section for methane for 1849-A radiation is extremely small at low pressures but has been reported as nonnegligible at pressures approaching 1 atm; see A. B. F. Duncan and J. P. Howe, *J. Chem. Phys.*, 2, 851 (1934), and S. W. Leifson, *Astrophys. J.*, 63, 73 (1926).

be obtained from the amount of CH_3Br formed in the vessel during photolysis, combined with the known value of 0.1 for the rate constant ratio for methyl radical reaction with HBr and Br_2.[12] In photolyses lasting 1 min, about 20% of the TBr was decomposed, and the final ratio of CH_3Br to Br_2 was between 1 and 5×10^{-3}. The conversion of TBr to CH_3T by methyl radicals would be less by at least a factor of 10, and would therefore represent not more than $1-5 \times 10^{-4}$ of the total TBr present and could not account for the $>10^{-2}$ actually converted to CH_3T.[13]

The relative yields of HT and CH_3T indicate that the abstraction reaction proceeds with a higher relative yield than the substitution reaction, when suitably averaged over the energy range from 3 ev down to thermal energies. This is not surprising, since the activation energy for the abstraction reaction is certainly lower than that of the substitution reaction. Since the total yields of hot reaction measured by Martin and Willard[3] are only 17% for 3-ev D atoms reacting with CH_4, as compared to the yields of approximately 50% for the sum of the abstraction and substitution products from recoil tritium reactions,[5-7] it is clear that a substantial fraction of the reactions of both substitution and abstraction occurs at energies above 3 ev. Crude estimates from the 3.5–4.0 ratio below 3 ev and 0.8 ratio for the entire range suggest that approximately 90% of the substitution reactions and 40% of the abstraction reactions occur at energies above 3 ev.[14] The estimates for ethane are similar.

(12) G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

(13) The measured CH_3Br yield probably arises chiefly or entirely from photolytic reactions of molecular bromine, and hence leads to a great overestimate of the extent of methyl radical reaction in the system; see T. A. Gover and J. E. Willard, *J. Am. Chem. Soc.*, **82**, 3816 (1960), for the reactions of I_2^* in similar systems.

(14) This estimate is based on the fragile assumption that the 17% hot yield with CH_4 below 3 ev will be the same for energetic D and T atoms. This assumption is almost certainly not quantitatively accurate but may not be too much in error. Measurement of the total hot yield in our system has not yet been performed, largely because of the uncertainties introduced through the use and handling of carrier-free TBr.

C. C. Chou, F. S. Rowland

Department of Chemistry, University of California
Irvine, California

The Preparation of Triphosphine.
An Intermediate in the Pyrolysis of Diphosphine

Sir:

It has been suggested[1] that hydrides of phosphorus containing three or more phosphorus atoms may exist. Presently, however, phosphine (PH_3) and diphosphine (P_2H_4) are the only stable hydrides well known.[1-3] In this communication we report the preparation and initial characterization of a phosphorus hydride containing three atoms of phosphorus.

Evidence for triphosphine was first uncovered during a mass spectrometric examination of the pyrolysis of diphosphine.[4] Briefly these experiments consisted of

(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p 217.

(2) E. C. Evers and E. H. Street, Jr., *J. Am. Chem. Soc.*, **78**, 5726 (1956).

(3) The Raman spectrum of pyrolyzed diphosphine suggests the presence of higher hydrides of phosphorus; however, none were isolated and characterized: M. Baudler and L. Schmidt, *Naturwissenschaften*, **46**, 577 (1959).

pumping diphosphine through an electrically heated tubular flow reactor and examining the efflux of the reactor mass spectrometrically.[5] At pressures of *ca.* 0.1 torr and speeds of *ca.* 0.02 l./sec, the efflux of the reactor consisted of P_2H_4, P_2H_2, and PH_3 as shown by appearance potential measurements and by the change in the relative ionic abundances with reactor temperature.[4] At pressures of *ca.* 0.5 torr and speeds of *ca.* 10^{-4} l./sec, ions containing three phosphorus atoms and up to five hydrogen atoms were just detectable.[6] Further characterization with this apparatus was prevented by the inability to produce more than trace quantities of this substance.

However, it was felt that a triphospine might be stable enough to be prepared in macroquantities. Consequently a hot–cold reactor was constructed.[7] The inner tube was maintained at a temperature of 65–70° while the outside tube was immersed in a cold bath at $-63°$, a temperature at which diphosphine has a vapor pressure of 2 mm². In a typical preparation diphosphine, which was prepared in a mercury-free system by the hydrolysis of calcium phosphide[2] and which was purified by trap-to-trap distillation, was held in the annular space between the two tubes (*i.e.*, pyrolyzed) for 1 hr under the above conditions. Roughly half the diphosphine decomposed into phosphine and a white solid (at $-63°$). Phosphine and diphosphine were distilled away; the hot bath was removed and the white solid sublimed out at $-23°$. On warming, this product decomposed before or during melting into a yellow solid while giving off phosphine in the process.[8] Fortunately the white solid had sufficient vapor pressure and stability at $-23°$ for the mass spectrum to be obtained.[9] A partial mass spectrum at 70 ev of the vapor over the purified product at $-23°$ is given in Table I.[10]

The neutral progenitor of the $P_3H_x^+$ ions contains three phosphorus atoms as no ions with leak-dependent intensities were observed above mass 98.[11] Also samples known to contain P_2H_4 were examined and the ratio of the intensities of $P_3H_x^+$ and $P_2H_x^+$ varied accordingly. Further, the $P_3H_x^+$ ions are assigned to the P_3H_5 molecule for the following reasons. First the ion of highest mass corresponds to $P_3H_5^+$, and as PH_3, P_2H_4, P_2H_2, and P_2H_3 produce parent ions of substantial intensity[4,12] one might expect the same behavior for a triphosphine. Second, the appearance potential of

(4) T. P. Fehlner, *J. Am. Chem. Soc.*, **88**, 1819 (1966).

(5) The technique used incorporated a collision-free sampling system capable of strong discrimination against products of decomposition in the source and other background effects; see, for example, S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **21**, 1374 (1953).

(6) Approximately 0.1% of the $P_2H_4^+$ intensity.

(7) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Am. Chem. Soc.*, **80**, 4149 (1958).

(8) Shown mass spectrometrically.

(9) A Bendix Model 12-107 time-of-flight mass spectrometer with conventional sampling was used to obtain the following data. Because of the characteristics of this compound the advantage of rapid acquisition of data outweighed the advantages of collision-free sampling.

(10) Ion masses were obtained by counting background peaks from a known ion peak. The ion intensities contained in Table I were dependent on the leak setting and were a linear function of the pressure. With the exception of small amounts of P_4^+ and P_3^+, no ions whose intensity was dependent on the leak setting were observed at masses greater than m/e 66 when pure P_2H_4 is introduced into the spectrometer. Consequently, the ions contained in Table I are not due to pyrolysis of diphosphine in the source.

(11) See also ref 10.

(12) The mass spectrum of diphosphine is given in Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964).