positive set. The center doublet must then be attributed to coincidence of the peaks owing to B-3 and B-5. It should be again noted that the assignment of the two doublets is not completely certain but is to be preferred on the basis of present knowledge.

The proton spectrum of $B_{10}H_{14}$ shown in Fig. 2b is not sufficiently well resolved to permit new interpretation. Note, however, that there is a slight suggestion of a shoulder at the low field side of the large quartet whose lowest member has been chosen as an arbitrary zero for decaborane derivatives. This suggestion is beautifully confirmed in the boron spin saturated spectrum shown in Fig. 2c. Furthermore, the high field peak in this spectrum arises from the collapse of the poorly split bridge protons and provides a standard of intensity since there are just four protons of this type. Two of the remaining ten protons fall into the space between the two peaks of Fig. 2c as shown in Fig. 2d taken with slightly different tuning of the boron saturating frequency. Furthermore, peak b of Fig. 2d has been shown by a study of halogen-substituted decaboranes to arise from the protons bonded to B-2 borons.[7] The remaining eight hydrogens in the molecule occur as sets of two, two and four and must together make up the partially resolved peak at the left of Fig. 2c. It is at once apparent that better resolution if it could be obtained would lead to peaks of relative intensity two and six. The set of four equivalent protons wholly bonded to the four B-1, B-4 boron atoms must then contribute to the high field component of the pair. No unambiguous way exists at present to decide which of the remaining two sets of two protons joins with the fourfold set to lead to the sixfold peak in Fig. 2c. However, it is more satisfying to assume that the protons attached to B-3 borons will more nearly resemble the fourfold set than will those attached to B-5 borons since the former are bonded to borons more similar in their bonding environment to B-1 and B-4 atoms than are the latter.

Figure 3 shows the B^{11} saturated proton spectrum of pentaborane-9. The possibility of "tuning" in the center peak by slight variation of the saturating field has been previously mentioned but not supported by spectra.[3b] The center peak by reason of its relative intensity must arise from the single proton attached to the apex boron atom of the B_5H_9 molecule.

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[Contribution from the Department of Chemistry of the University of Wisconsin]

Gas Phase Reactions Activated by Nuclear Processes

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It is known from previous work that I^{128} and Cl^{38} activated by radiative neutron capture are able to replace hydrogen in organic compounds by unique processes. The work of the present paper shows that: (1) Br^{80} can undergo similar reactions, following either radiative neutron capture or isomeric transition; (2) all three halogen species can replace hydrocarbon radicals as well as hydrogen atoms; (3) several modes of replacement are possible for reaction of a single type of halogen with a single type of target molecule—at least nine different organic iodides being formed by reaction of I^{128} with *n*-butane; (4) the nature of the compound in which the halogen is contained prior to neutron capture has little or no effect on the reactivity of the activated atom, but the nature of the parent compound seems to affect this reactivity when activation is by isomeric transition; (5) tritium produced by the $He^3(n,p)H^3$ process in gaseous hydrocarbons enters organic combination by a process which is apparently similar to the halogen reactions noted. It is suggested that these reactions are of the ion-molecule type. The demonstration that such reactions occur in the gas phase makes it probable that they contribute to organic yields in the more extensively studied condensed phases, where it is impossible to distinguish them experimentally from radical combination reactions. The application of gas phase chromatography to the analysis of mixtures of tracer amounts of radioactive materials is illustrated in this paper.

Introduction

^{128}I[1,2] and ^{38}Cl[3] freshly produced by the $I^{127}(n,\gamma)I^{128}$ and $Cl^{38}(n,\gamma)Cl^{38}$ processes are able to form organic halides by reacting with gaseous hydrocarbon molecules by displacement processes (*e.g.*, $I + CH_4 \rightarrow CH_3I + H$). This is of particular interest because photochemically or thermally produced halogen atoms which react with hydrocarbons do so by abstraction of hydrogen[4] to form the hydrogen halide and a free radical (*e.g.*, $Cl + CH_4 \rightarrow CH_3 + HCl$), with organic halide formation occurring by reaction of the radical with a halogen molecule ($CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$). The activation energy for hydrogen abstraction reactions by iodine atoms is so high that photoiodination of hydrocarbons cannot take place.

Speculation that this unique displacement type of reaction requires positive halogen ions rather than neutral atoms is strengthened by the observation[2] that a few mole per cent. of additives of ionization potential lower than that of I^+ greatly reduces the yield of the reaction of I^{128} with methane. No similar reactions, of which we are aware, have

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[1] J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

[2] G. Levey and J. E. Willard, *ibid.*, **25**, 904 (1956).

[3] (a) J. C. W. Chien and J. E. Willard, This Journal, **75**, 6160 (1953); (b) J. B. Evans, J. E. Quinlan and J. E. Willard, Paper 68 presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the September, 1956, Atlantic City Meeting.

[4] (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941; (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

been reported for halogens but there is growing evidence that ion-molecule reactions are important in systems involving hydrogen, hydrocarbons and the rare gases,[5] and it seems possible that they will prove to be the explanation of a number of puzzling problems of mechanism in the fields of chemical effects of nuclear transformations and of radiation chemistry.

It is the purpose of this paper to describe experiments designed to explore further such reactions of halogens activated by nuclear processes, with the aim of determining how the yield and product distribution varies with the identity of the halogen, the nature of the nuclear process, the nature of the parent compound, and the nature of the alkane reactant.

Experimental[6]

Reaction Mixtures.—All reaction mixtures for neutron irradiations were prepared by vacuum line techniques and sealed in quartz flasks, tubes, or thin-walled bublets.

The CH_4, C_2H_6, C_3H_8 and n-C_4H_{10} were Phillips Petroleum Co., Research Grade. CH_3Br, HBr and HCl were obtained in tanks from the Matheson Co. With the exception of CCl_4 (Merck Reagent Grade) and CCl_3Br (Michigan Chemical Corp.), all of the other alkyl halides were Eastman Kodak Co. white label. These were all further purified by H_2SO_4 treatment, photohalogenation followed by distillation, passage through silica gel, passage through alumina, or other appropriate means. Merck Reagent I_2 and Baker Purified Br_2 were used. HI was prepared from 55% aqueous solution by vaporizing through P_2O_5 after removing I_2 with red phosphorus. DI gas was prepared by dissolving HI gas in D_2O followed by distilling through P_2O_5.

The introduction of Br^{80m} into alkyl bromides (except CCl_3Br) was accomplished by exposing the alkyl bromide gas to solid $AlBr_3$ which had been prepared by treating Br-Br^{80m} (obtained from the Argonne National Laboratory) with heated aluminum metal. When samples of CH_3Br, CH_2Br_2, $CHBr_3$, C_2H_5Br, n-C_3H_7Br and i-C_3H_7Br were labeled with Br^{82} by this method, and then analyzed by gas chromatography, the Br^{82} activity was all found in the form of the original organic bromide, except for the propyl bromides where 30 to 40% isomerization occurred.

CCl_3Br^{80m} was prepared by the photochemical exchange of $BrBr^{80m}$ with CCl_3Br in the gas phase.[7] HBr^{80m} was formed by illuminating a mixture of radiobromine and hydrogen at 200°.

Determination of Organic Yields.—In all of the experiments of this paper (except those on the isomeric transition, where the Br^{80m} was in organic combination) the organic yields were determined by separating the organic species from the inorganic, counting each with a Geiger counter and computing the ratio of the organic to the total activity after appropriate corrections for counting efficiencies in different media, coincidence loss and decay. Many variations[6] in method of extraction were tested. For the experiments on activation by the (n,γ) process these include those described earlier[1,2] and others such as breaking irradiated bulbs (0.7 ml.) of the gases under the liquid layers in a separatory funnel containing chloroform and aqueous sulfite solution.

Reaction mixtures for study of activation by the Br^{80m} isomeric transition were contained in flasks attached to the vacuum line through a stopcock, or in all-glass flasks with a break-seal to allow attaching to the vacuum line for extraction, or in all-glass flasks with a "break-tip" which could be fractured under $CHCl_3$–aqueous sulfite extraction mixtures. Extraction with the aid of the vacuum line was accomplished by passing the gases through a copper train to remove free halogen, following which the organic fraction was counted as a gas in a Geiger tube jacket which was sealed off from the vacuum system.[7] In test experiments with CCl_3Br and CH_3Br labeled with Br^{82} a 4″ train of freshly reduced copper removed *ca.* 70 and 15% of the organic activity, respectively. Copper, which had not been freshly reduced, removed considerably less. When the Br^{80m} was in the organic fraction, the organic yield was deduced by the growth curve method[7] and hence quantitative recovery was not necessary, only a representative sample of the organic fraction being required. When extraction was done in the liquid phase, it was assumed that 50% of the Br^{80} formed from organically bound Br^{80m} during the 25 second extraction time was lost to the aqueous phase.

Gas Chromatographic Analysis.—Gas chromatographic analyses were made by methods similar to those described earlier.[8] A 12 ft. spiral column 4 mm. i.d. filled with 40–60 mesh Johns-Manville C-22 firebrick coated with 40% of its own weight of General Electric SF-96(40) silicone oil was used with nitrogen as the flow gas. Detection of the radioactive products was by means of a scintillation counter. The oil thermostat, containing the column, was heated at a constant rate of heat input during each separation run. Irradiated gas samples in fragile quartz bulblets were introduced to the gas stream by breaking the bulblets in the flowing gas.

Neutron Irradiations.—Neutron irradiations were made at the Argonne National Laboratory in the "isotope tube" and "rabbit tube" of the CP5 reactor. A typical irradiation involved exposure of a 0.7-ml. sample in the rabbit tube for 1 min. at a neutron flux of about 3×10^{12} neutrons $cm.^{-2}$ $sec.^{-1}$, and a background radiation dosage of about 4×10^4 r./min. (as determined by the change in absorbancy at 3500 Å. of silver activated phosphate glass[9]).

Results and Discussion

Organic Yields and Chromatograms for (n,γ) Activation.—Table I summarizes the organic yields obtained in this work for the (n,γ) activation of three different halogens in a variety of source compounds, in reactions with a variety of target molecules. Figures 1 and 2 show normalized gas chromatograms for the products in some of the systems. In transcribing the chromatograms from the recorder traces, the absolute peak heights have been adjusted to fit conveniently in the figures but the relative peak heights within each chromatogram have been preserved. The time scales have also been normalized to compensate for slight differences in heating rate or flow rate. No corrections have been made for decrease in relative peak height due to radioactive decay during the time of running the chromatogram. It should be noted that the organic yields for the different systems represented in the chromatograms vary widely (Table I).

A tentative identification of the compound represented by each peak has been made, both by a comparison of the peaks from different reactants, and by a consideration of the temperature of appearance of the peaks relative to their boiling points. Peak a of Fig. 1 can be assigned definitely because earlier work[1] on carrier fractionation gave CH_3I^{128} as the only organic product of the neutron irradiation of iodine in methane. Peak c must then be due to C_2H_5I because of its appearance when C_2H_5I is present in the CH_4 (7 and 8), and also in the I_2–C_2H_6 system (6). The other peak assignments are listed with the titles of the figures and are discussed in the sections below.

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(5) (a) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936); (b) V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 909 (1952) (*C. A.*, **47**, 2590 (1953)); (c) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); (d) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956); (e) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **25**, 790 (1956).

(6) Further details are given in the Ph.D. thesis of A. A. Gordus filed with the University of Wisconsin library in December, 1956, and available from University Microfilms, Ann Arbor, Michigan.

(7) R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **74**, 6213 (1952).

(8) J. B. Evans and J. E. Willard, *ibid.*, **78**, 2908 (1956).

(9) J. H. Schulman, C. C. Klick and H. Rabin, *Nucleonics*, **13**, 30 (1955).

TABLE I

ORGANIC YIELDS OF REACTIONS OF ALKANES WITH HALOGEN ATOMS ACTIVATED BY THE (n,γ) PROCESS

Source of halogen[a]	Alkane (p = 1 atm.)	Organic yield, %[b] Individual determinations	Av.
I_2	CH_4	42, 52, 39, 46, 52, 51	46
HI	CH_4	39, 36, 57	45
DI	CH_4	57, 43, 54, 57	53
CH_2I_2	CH_4	63, 54, 62	60
C_2H_5I	CH_4	73, 63, 69	68
$C_2H_5I(I_2)$	CH_4	53, 56, 53	54
I_2	C_2H_6	1.5, 3.0, 2.4	2
C_2H_5I	C_2H_6	26, 21, 25	24
$C_2H_5I(I_2)$	C_2H_6	2.7, 3.3, 3.3	3
I_2	C_3H_8	2.5, 2.7	3
$C_2H_5I(I_2)$	C_3H_8	4.6, 3.1, 4.1	4
I_2	n-C_4H_{10}	3.5, 5.6	4
$C_2H_5I(I_2)$	n-C_4H_{10}	4.3, 5.8, 4.5	5
Br_2	CH_4	16, 16, 17[c], 21	18
HBr	CH_4	42, 40, 41	41
C_2H_5Br	CH_4	58, 54	56
$C_2H_5Br(Br_2)$	CH_4	20, 19	20
Br_2	C_2H_6	9.6, 9.3, 9.6	9
HBr	C_2H_6	7.5, 8.5, 9.0	8
$C_2H_5(Br_2)$	C_2H_6	10, 10, 9	10
Br_2	C_3H_8	8.3, 9.7, 8.3	9
Br_2	n-C_4H_{10}	10, 11	11
n-C_3H_7Cl	CH_4	17, 17	17
CCl_4	CH_4	39, 17.23	27
HCl	CH_4	17, 16, 17	17
HCl	C_2H_6	10, 8, 12	10
10 mm. Br_2 and 1 atm. CH_3Br		3.9, 4.1	4

[a] (I_2) and (Br_2) indicate the presence of these elements as scavengers at pressures of 0.1 and 0.2 mm., respectively. When I_2 was used as the source of halogen, it was also at 0.1 mm. When Br_2 or alkyl halides were the source, their pressure was 1–4 mm., when HCl was the source the pressure was 14 mm. [b] Fraction of I^{128}, Br^{80} (18 min.) or Cl^{38} produced by the (n,γ) process which entered organic combination. [c] The yield of 17% was obtained for the Br^{80m} (4.5 hr.) isomer on the same sample which gave 16% for Br^{80} (18 min.).

Significance of the Generality of the Displacement Type Process and the Multiplicity of Products.—The data of Tables I and II and Figs. 1 and 2 indicate that I^{128}, Br^{80} and Cl^{38} activated by the (n,γ) process and Br^{80} activated by isomeric transition are all able to displace[10] H atoms or hydrocarbon radicals from gaseous organic molecules. With target molecules containing more than one carbon atom a variety of products may be formed from a single type of activation process.

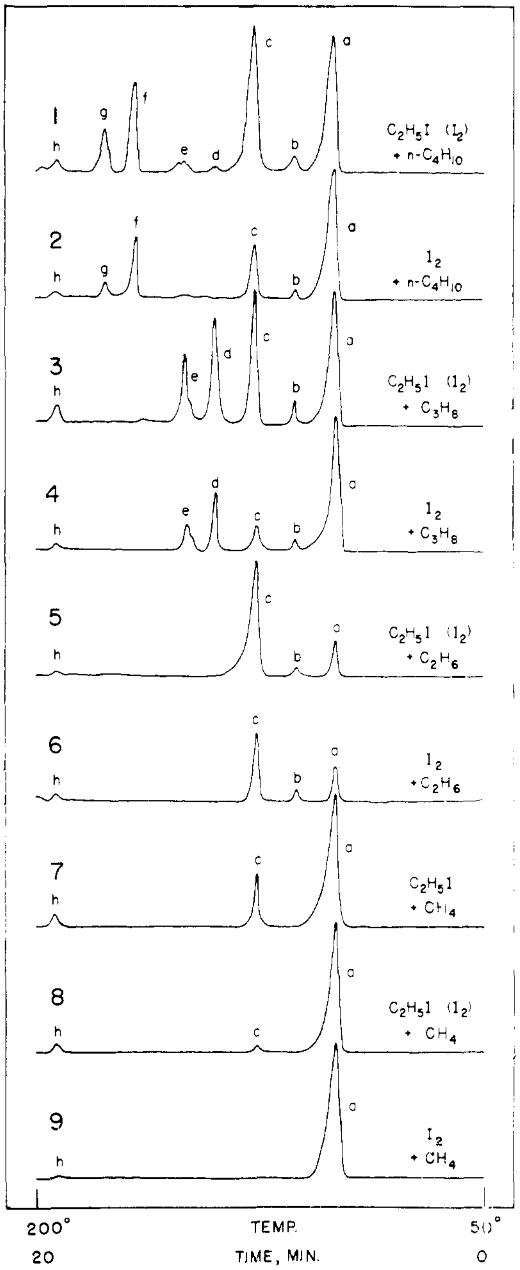

Fig. 1.—Gas chromatograms of organic products containing I^{123} as the result of neutron irradiation of iodine or iodine compounds in gaseous alkanes. Alkane pressure 350 mm.; C_2H_5I, 1 to 3 mm.; I_2, 0.1 mm. Peak assignments for Figs. 1 and 2 (letting X denote I or Br, and the numbers (1), (2) and (3) the decreasing order of certainty) (a) CH_3X (1); (b) C_2H_3X (2); (c) C_2H_5X (1); (d) *iso*-C_3H_7X (1); (e) n-C_3H_7X and t-C_4H_9X (2); (f) *sec*-C_4H_9X or *iso*-C_4H_9X (3); (g) n-C_4H_9X (3); (h) CH_2Br_2 (2), CH_2I_2 (3); (i) $CHBr_3$ (3); (j) dibromides other than CH_2Br_2.

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(10) In gas phase reactions activated by nuclear processes, the entry of the newly activated and tagged atom or ion into organic combination by combination with a free radical which it has formed, or which has been formed by background radiation is not possible if the system contains free halogen added to serve as scavenger. The scavenger reacts with all organic radicals to form stable organic halides. Those tagged atoms or ions which do not enter organic combination by a bimolecular non-radical step abstract hydrogen from a molecule of the medium or become stabilized in organic combination by reaction with a scavenger molecule. The probability of hydrogen atom abstraction by thermalized halogen atoms is related to the activation energies which are of the order of 1–4 kcal./mole for Cl,[11] 10 kcal./mole for Br and 50 kcal./mole for I. Only a few to a few hundred collisions at room temperature are necessary for reaction of Cl; 10^7 or so for reaction of Br; and 10^{35} for reaction of I.

Those tagged atoms which exchange with scavenger ($X^* + X_2 \rightarrow XX^* + X$) have negligible opportunity to enter organic combination because the fraction of the X_2 molecules which are used up by the $R + X_2 \rightarrow RX + X$ process is negligible unless the X_2 concentration is extremely low. This has been demonstrated[1] for the reaction of I^{128}, activated by the (n,γ) process in CH_4 by tagging the I_2 scavenger with I^{131}.

(11) H. O. Pritchard, J. B. Pyke and A. F. Trotman Dickenson, THIS JOURNAL, **77**, 285 (1955).

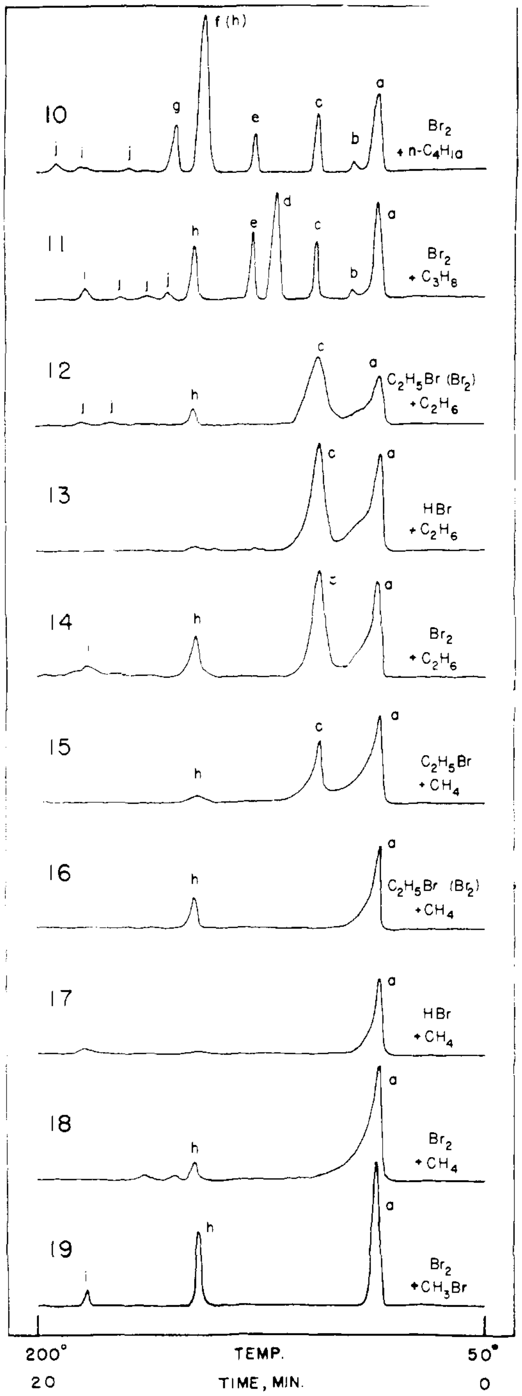

Fig. 2.—Gas chromatograms of organic products containing Br^{80} as result of neutron irradiation of bromine and bromine compounds in gaseous alkanes. Alkane pressures, 350 mm.; C_2H_5Br, Br_2 and HBr, 1 to 3 mm., except sample 19 in which 10 mm. of Br_2 and 760 mm. of CH_3Br were used; (Br_2) as scavenger, 0.2 mm. Peak assignments listed under Fig. 1 title.

In the liquid phase an atom activated by the (n,γ) process may, after becoming nearly thermalized, but before diffusing as a thermalized atom, be held in a solvent cage with a radical it has just formed, and consequently react with it to form a stable compound.[12,13] Such processes cannot occur in the gas phase because there is no caging effect. In solution they cannot be distinguished from "hot" displacement processes because neither is affected by low concentrations of scavenger. High enough concentrations of scavenger to interfere with one would interfere with the other. The present evidence that displacement processes are rather common in the gas phase and can give a multiplicity of products indicates that a part of the "hot" organic yield observed in liquid systems probably results from such processes. This conclusion has been rather clearly substantiated by John E. Quinlan in our laboratory who has found nearly identical organic yields and gas chromatograms of the Cl^{38} activity from $n\text{-}C_3H_7Cl$ when it was irradiated in the gas phase, with Cl_2 scavenger present, and when it was irradiated as the liquid. In each case at least 15 different peaks were observed. Radical reactions certainly account, however, for the easily scavengeable portion of the organic yield observed in liquid iodides,[14] bromides[13,15] and non-hydrogenous chlorides.[3a] They probably are also responsible for a considerable fraction of that portion of the organic yield which is relatively insensitive to scavengers in liquid systems; this "hot" yield is often much higher than the "hot" yield in the gas phase (*e.g.*, for C_2H_5I *ca.* 32% in the liquid and 2% in the gas).

Effect of Nature of Source Molecule and Target Molecule when Activation is by the (n,γ) Process.—In agreement with previous work[1,2] the organic yields of I^{128} from the $I^{127}(n,\gamma)I^{128}$ process have been found (Table I) to be in the range of 40–55% for I_2 in excess CH_4 and 60–70% for *unscavenged* alkyl iodides in CH_4. As a further test of the effect of the nature of the source molecule, we have determined the yields from the neutron irradiation of HI, DI and CH_2I_2 in CH_4. These species were chosen with the particular aim of determining whether the lower yields for I_2–CH_4 mixtures than for RI–CH_4 mixtures might be the result of the difference in the masses of the groups attached to the recoiling iodine atom (an iodine atom which recoils directly toward its parent partner loses all of its recoil energy if the partner is an I atom but only part if the partner is an alkyl radical). The data of Table I show that the yields using HI and DI are, within experimental error, the same as with I_2 while that from CH_2I_2 is the same as with the other organic iodides, indicating that the mass of the parent partner is not a controlling factor. DI as well as HI was tested because the fraction of the recoil energy which can go into internal energy in HI and thus be available for bond rupture $(1/(1 + 128))$ is so small that the *maximum* energy available for rupture is only 2.1 e.v. which is only slightly greater than the bond energy (1.6 e.v.), whereas this maximum energy for DI is 4.2 e.v.

The data of Table I and Fig. 1 indicate that the higher organic yields observed for unscavenged RI–

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[12] Investigations of reactions of this type are reviewed in: (a) J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); (b) J. E. Willard, *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

[13] S. Goldhaber and J. E. Willard, THIS JOURNAL, **74**, 318 (1952).

[14] G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

[15] J. F. Hornig and J. E. Willard, *ibid.*, **75**, 461 (1953).

CH_4 mixtures than for I_2–CH_4 mixtures result from a radiation induced reaction of the alkyl halide rather than from a difference in the average reactivity of I^{128} atoms born from alkyl iodides and from I_2. The pertinent evidence is as follows: (1) the average yield for the scavenged $C_2H_5I(I_2)$–CH_4 system is 54%, similar to that for I_2–CH_4, and in contrast to that for unscavenged C_2H_5I–CH_4 (68%) and other RI–CH_4 mixtures[2]; (2) a similar scavenger effect is observed for $C_2H_5I(I_2)$–C_2H_6 mixtures as compared to C_2H_5I–C_2H_6 and for $C_2H_5Br(Br_2)$–CH_4 as compared to C_2H_5Br–CH_4; (3) the reduction in yield caused by scavenger in the $C_2H_5I(I_2)$–CH_4 system is at the expense of the $C_2H_5I^{128}$ rather than the CH_3I^{128} product (Fig. 1, chromatograms 7 and 8). Since no $C_2H_5I^{128}$ is formed in I_2–CH_4 mixtures, and since the pressure of CH_4 for the experiment of chromatogram 7 was 400 times the pressure of C_2H_5I, it seems improbable that $C_2H_5I^{128}$ should be formed by a hot atom process, particularly since the organic yield from the neutron irradiation of pure C_2H_5I[1] is very low. The fact that the yield is reduced by I_2 confirms the fact that the $C_2H_5I^{128}$ is formed by a reaction of thermalized radicals or ions. It is probable that these are produced from the C_2H_5I[16] by the γ-radiation to which the system is exposed. Since, at the CH_4/C_2H_5I ratios used, most of the radiation energy is absorbed by the CH_4, charge transfer from CH_4^+ to yield $C_2H_5I^+$ may be a step contributing to the C_2H_5 yield. The radicals or ions are converted back to C_2H_5I by reacting with I_2. In the absence of added I_2 scavenger, the only I_2 in the system is the very small amount produced by radiation damage, so the specific activity of the I_2 with respect to I^{128} is enormously greater than in the presence of scavenger.

In the presence of scavenger the organic yields attributed to activation by the (n,γ) process in this type of study are not caused by the γ-radiation to which the sample is exposed during neutron irradiation. This has been established in the earlier work[1,2] by using I_2 tagged with I^{131} to distinguish reactions initiated by γ-radiation from those caused by activation by the $I^{127}(n,\gamma)I^{128}$ process. It has been confirmed for the bromine investigations in the present work, using Br_2 containing Br^{82} both in pile irradiations of bromine alkane mixtures, and also in irradiations of 1 atm. of C_3H_8 with 15 mm. of Br_2 with a Co^{60} γ-ray source. In the Co^{60} test, the dosage of 8×10^6 r. was some 40 times the maximum received by any of the samples of Table I and the fraction of the Br_2 which entered organic combination was less than 2%, if any.

From the data of Table I and Figs. 1 and 2 it may be concluded that, with possibly one exception, the organic yields and the pattern of products for each of the three halogens tested are independent of the type of molecule in which the halogen resides when it undergoes the (n,γ) process in a scavenged system. Thus the organic yields of I^{128} from I_2, HI, DI and scavenged C_2H_5I in CH_4 are all 50% within the limits of error; those for I^{128} from I_2 and C_2H_5I in C_2H_6, C_3H_6 and n-C_4H_{10} are 3%; those for Br^{80} from Br_2, HBr, and C_2H_5Br in C_2H_6 and from Br_2 in C_2H_8 and C_4H_{10} are 9%; and those for Cl^{38} from n-C_3H_7Cl and HCl and in CH_4 are 17%. The yields are, however, different for different halogens and different for different alkanes reacting with a single halogen. No satisfactory explanation is yet available for these variations and for contrasts such as the fact that the yields for I, Br and Cl reacting with CH_4 are in the approximate relation of 2.5, 1, 1, while for the reactions with C_2H_6 the relation is 0.3, 1, 1.

The one apparently definite exception to the observation that the yield is independent of the source compound for a single halogen is the yield from HBr in CH_4 which is 41% as compared to *ca.* 19% from Br_2 or C_2H_5Br. The result is particularly surprising in view of the fact that HI and DI in CH_4 and HBr in C_2H_6 give "normal" yields. The deviation cannot be attributed to the absence of added Br_2 as scavenger, since even trace amounts of Br_2 would by rapid exchange[17] maintain the same specific activity as the macro quantities of HBr and so reaction of Br_2 with radicals produced by radiation would not introduce significant quantities of Br^{80} into organic combination. If partial failure of the recoil to rupture the H–Br bond were important, or if a difference in the magnitude of the charge remaining on the Br^{80} following internal conversion and Auger electron emission played a role, these factors might be expected to affect the yield from C_2H_6 as well as that from CH_4.

In view of the variation in the individual determinations of the yields when CCl_4 is the source of chlorine for reaction with CH_4 (Table I), the fact that the average organic yield is higher than for n-C_3H_7Cl or HCl may not be significant. If it is significant, it may be because small amounts of Cl_2 formed by radiolysis of CCl_4 react with radicals to return Cl^{38} to organic combination, whereas in the experiments with HCl as the source of chlorine all of the inorganic Cl^{38} is present as HCl at low specific activity. In the C_3H_7Cl system, radiation decomposition would be expected to produce HCl exclusively rather than Cl_2. If radicals react at all with HCl it is probable that they do so solely by hydrogen abstraction.

$C_2H_5I^{128}$ Formed from the (n,γ) Process on C_2H_5I in Hydrocarbons Containing Scavenger.—Comparison of the chromatograms of Fig. 1 in which the I^{128} originated predominantly from neutron capture by the I atom in C_2H_5I with those where it originated from I_2 shows that the ratio of $C_2H_5I^{128}$ to CH_3I^{128} was always higher when C_2H_5I was the parent compound. As discussed above, part of the increase observed in the absence of scavenger was removed when 0.1 mm. of I_2 was present as scavenger. In no case, however, was all of the $C_2H_5I^{128}$ eliminated by the scavenger. The difference in the percentage of the total I^{128} present as $C_2H_5I^{128}$ in systems where scavenged C_2H_5I was the source as compared to those where I_2 was the source was in all cases about 1%. Thus in chromatogram 8 the CH_3I peak contains about 50% of the I^{128} and the C_2H_5I peak about 1% as contrasted to no C_2H_5I in 9. In 6 the total yield

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[16] R. J. Hanrahan and J. E. Willard, THIS JOURNAL, **79**, 2434 (1957).

[17] (a) L. C. Liberatore and E. O. Wiig, *J. Chem. Phys.*, **8**, 349 (1940); (b) W. F. Libby, *ibid.*, **8**, 348 (1940).

represented by the three peaks is 2 to 3% while in 5 it is 3 to 4% due to the higher yield of ethyl iodide. Similar relationships hold for the C_3H_8 and C_4H_{10} systems. This residual $C_2H_5I^{128}$ in the presence of scavenger may be an indication of failure of the C–I bond to rupture following about 1% of the (n,γ) events. If, however, a considerable fraction of the energy absorbed by the hydrocarbons was transferred to C_2H_5I to sensitize its decomposition to ethyl radicals which then reacted with the I_2 in the system, a residual $C_2H_5I^{128}$ activity of this magnitude might be observed. The two types of effect could be distinguished by use of a neutron source with a lower ratio of γ-radiation to neutrons, or by irradiation at a higher temperature which would permit use of a higher iodine scavenger pressure.

Absence of Isotope Effect.—Incidental to the other experiments reported here, a few comparisons were made of the organic yields of the three different bromine nuclei produced by the (n,γ) process. They indicate that there are no large differences in the yields. They were not exhaustive enough to eliminate the possibility of small differences. They include results on the (n,γ) activation of Br_2 in CH_4 (Table I, footnote c) and several observations in preliminary experiments in which the yields of the Br^{80m}, Br^{80} and Br^{82} species were identical within the experimental error.

Evidence that the Displacement Reaction may Produce Radicals.—Peak h of Fig. 2 is highest for Br_2 in CH_3Br and does not appear significantly for HBr in CH_4 or C_2H_6 but does appear for Br_2 in CH_4 and C_2H_6. The most probable assignment, therefore, seems to be CH_2Br_2 and this is consistent with the column temperature at which this peak appears. This compound cannot form in a one-step bimolecular process with CH_4 or C_2H_6. The recoil Br^{80} atoms which form it must first form an organic species which can subsequently react with Br_2 to give the final product. Further evidence on the reactions of molecule-ions with molecules should be helpful in elucidating these steps.

Reactions Activated by the Br^{80m} Isomeric Transition.—The isomeric transition of $Br^{80m} \rightarrow Br^{80}$ is known to produce the Br^{80} daughter atoms with a high positive charge[18] as a result of internal conversion and Auger electron emission. The energy of the electrons and γ-rays emitted is too low to give appreciable recoil energy. For these reasons it was of particular interest to determine whether the daughter atoms would react with hydrocarbons in inversion reactions similar to those of the halogens activated by the (n,γ) process. Table II shows the results of such experiments in CH_4, for the Br^{80m} in six different parent compounds.[19]

The data given are those obtained by the techniques which we consider to be the most reliable of several investigated.[6] Even so, the reproducibility is not good enough to allow all of the quantitative comparisons to be made which would be desirable. It is shown conclusively, however, that bromine activated by the isomeric transition in Br_2 and alkyl bromides can react with CH_4 to produce organically bound bromine. The extent of reaction is less than in the case of activation by the (n,γ) process and unlike the latter, is dependent on the parent compound of the bromine.

TABLE II

PARTIAL FAILURE OF BOND RUPTURE, AND REACTION WITH METHANE FOLLOWING ISOMERIC TRANSITION

Molecule containing Br^{80m} [b]	Total organic yield with CH_4, %	Failure of bond rupture, %[b]	Av. org. yield with CH_4 in excess of fail. of bond rupt., %
HBr	<0.1 <0.1	<5[a]	<0.1
	<0.1		
CH_3Br	7.1 4.5 7.9	0.7 0.6 0.7	
	4.6 3.0 6.2	0.7 0.9 0.3	4
	4.9 3.8	5.1 1.3	
C_2H_5Br	8.0 5.9 4.5	2.1 2.7 3.5	
		4.1	3
Br_2	6.1 10.3 7.4 8.4		
	5.8 9.0 11.0 5.5		
	8.8 7.7 10.6 5.4	...	8
	8.5 9.2 9.4 9.5		
	8.4 8.5		
CCl_3Br	10.1 9.3 10.0	1.5 2.7 1.7	
	10.5 9.2 11.2	1.1 2.9 2.2	8
	7.5 10.7	1.8 3.1 2.3	
		0.9	
$CHBr_3$	16.8 13.9 12.0	6.2 7.1 4.5	
	12.4 12.6	4.8 2.9 5.7	8
		6.6	

[a] Determined by R. Luebbe of our laboratory. [b] In the CH_4 experiments the ratio of CH_4 to Br_2 or organic bromide was always 100 to 1 or greater. Low concentrations of nonradioactive bromine were present in the organic bromide experiments as scavenger. In the bond rupture experiments, the ratio of Br_2 to organic bromide was always greater than 50 to 1.

In order to determine what fraction of the organically bound Br^{80} in the methane mixtures resulted from failure of the parent C–Br bond to rupture[7] rather than from reaction with CH_4, experiments were done in which the parent organic Br^{80m} compound was allowed to stand in excess gaseous Br_2 and then extracted. Under these conditions any Br^{80} which split out of its parent molecule would have no chance to re-enter organic combination. Definite failure of bond rupture was observed for $CHBr_3$, C_2H_5Br and CCl_3Br, while CH_3Br gave values of essentially zero which became positive only on applying a correction of 0.8% for reaction occurring in the liquid phase during the 25 sec. extraction time. The values for failure of bond rupture in CCl_3Br and CH_3Br are lower than those obtained for these compounds earlier[7] (*i.e.*, 7.1 and 5.6%). A rather exhaustive investigation of various separation techniques in the present work, and re-examination of techniques used in the previous work, has failed to demonstrate with certainty the cause of the discrepancy. If failure of the C–Br bond to rupture was accompanied by rupture of another bond and subsequent formation of a dibromide (*e.g.*, $CH_3Br^{80m} \rightarrow CH_2Br^{80} + H$; $CH_2Br^{80} + Br_2 \rightarrow CH_2Br^{80}Br$), and if the different bromides were partially fractionated in passing through the copper train (see Experimental section) the results might depend on the history of the copper train. Experiments in which

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[18] S. Wexler and T. H. Davies, *Phys. Rev.*, **88**, 1203 (1952).

[19] The first experiments which showed that Br^{80} activated by the isomeric transition process can enter organic combination by reaction with CH_4 were made by Leo Spinar in our laboratory in 1952.

the mixture of bromine with organic bromide undergoing isomeric transition was exposed to a greased stopcock tended to show higher values of failure of bond rupture than those done in sealed flasks, possibly because some of the organic material dissolved in the grease and thus allowed isomeric transition to occur in a condensed phase where organic yields are higher. In many of the determinations of Table II the reactants were contained in sealed flasks during the standing period and the extractants were admitted by breaking a side arm under the extracting solution; consequently possible errors from the use of a copper train or stopcock grease were precluded. Incidental to the gas phase determinations the failure of bond rupture of CCl_3Br and $CHBr_3$ in liquid bromine was determined, the values obtained being *ca.* 10 and 4%, respectively. Previous work[7] has given 13% for liquid CCl_3 Br.

Although the Br^{80} ions formed by the isomeric transition do not receive significant recoil energy from the γ-ray or electrons emitted, they may be ejected from the parent molecule with appreciable kinetic energy as a result of coulomb repulsion if charge distribution[20] over the molecule occurs before dissociation resulting from loss of binding electrons[21] takes place. If this occurs, conservation of momentum requirements will result in a different kinetic energy for the Br^{80} ion for each type of parent compound from which it is born. Thus the Br^{80} will carry away 0.013 (*i.e.*, $M_H/(M_H + M_{Br})$) of the energy when bound in HBr but may carry larger fractions for other compounds as follows: CH_3Br, 0.15; C_2H_5Br, 0.26; Br_2, 0.5; CCl_3Br, 0.60; and $CHBr_3$, 0.69. If account is taken of the fact that the maximum distance of charge separation varies with the respective molecules,[22] and if it is assumed that the charge distribution between the Br^{80} and its parent radical partner is the same, irrespective of the compound, then the relative kinetic energy of the Br^{80} from different compounds is: HBr, 1.0; CH_3Br, 9.6; C_2H_5Br, 10.4; CCl_3Br, 22.3; $CHBr_3$, 24.4; Br_2, 25.0. The energy of coulomb repulsion for a +9 Br^{80} ion leaving an H^+ ion is 1.1 e.v. while that for departure from a $CHBr_2^+$ ion is 27.4 e.v. It is tempting to ascribe the differences in the organic yields with methane (Table II) to these differences in energy since they parallel each other in relative magnitude and since there is no other obvious explanation of variation in yield with parent partner. Explanations based on differences in charge of the bromine escaping from different parent partners (and such differences are to be expected) are unsatisfactory if it is assumed that the ions must all be reduced to a +1, or possibly +2 charge by charge transfer collisions before entering combination.

Comparisons of reactions of bromine activated by isomeric transition and by the (n,γ) process in the liquid phase have shown similar distributions of products for the two even when the product spectrum is quite complex,[8] but in some cases the organic yields of the isomeric transition have been higher.[13,15] The gas phase reactions of Table II are the only reported case of which we know where the yields from isomeric transition is lower than that from the (n,γ) process.

Reactions of Tritium Activated by the $He^3(n,p)H^3$ Process.—A number of reasons make it of interest to compare the reactions of recoil tritium atoms from the $He^3(n,p)H^3$ process with those of the halogens discussed above. They include the following: (1) tritium atoms are lower in mass than the target alkane molecules and therefore most of their kinetic energy can be used as internal energy of the activated complex; (2) important work has been done on the labelling of complex compounds with tritium by the "heterogeneous recoil" process using the $Li^6(n,\alpha)H^3$ process,[23] but its mechanism is not yet well understood; (3) a comparison of the products from this type of activation with those obtained when tritium is allowed to interact with alkanes under the influence of its own decay and β-emission may throw light on the mechanism of this latter[24] important type of labelling process.

In collaboration with M. Sauer of our laboratory we have irradiated bulblets of methane, ethane and propane containing He^3 and small amounts of carrier hydrogen in the Argonne CP5 reactor and have analyzed them for tritiated organic products by gas chromatography with the aid of a flow-type proportional counter,[6] using silica gel as the column packing and methane as the carrier gas. The recoil tritium is found to produce tritiated methane even in a methane atmosphere scavenged with as much as 200 mm. of bromine, and to produce a variety of organic products when formed in an ethane or propane atmosphere scavenged with iodine or bromine. In the absence of scavenger, methane yields at least six higher tritiated hydrocarbons.[25,26]

Analogous Reactions.—Wolfgang, Eigner and Rowland[27] have reported the production of a mixture of tritiated alkanes and alkenes ranging from C_1 to higher than C_4 by the neutron irradiation of suspended lithium salts in liquid methane or ethane; Wolfgang, Pratt and Rowland[28] have found that organically bound tritium is formed when gaseous T_2 at low pressures is subjected to a potential of 500 volts between electrodes coated with various organic compounds; and Lemmon, Mazzetti, Reynolds and Calvin[29] have demonstrated that C^{14} ions formed in a mass spectrometer and allowed to impinge on benzene yield

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[20] (a) E. Cooper, *Phys. Rev.*, **61**, 1 (1942); (b) J. L. Magee and E. F. Gurnee, *J. Chem. Phys.*, **20**, 894 (1952); (c) R. L. Platzman, "Symposium on Radiobiology," John Wiley and Sons, Inc., New York, N. Y., 1952, Chap. 7.

[21] E. Segre and A. C. Helmholtz, *Rev. Mod. Phys.*, **21**, 271 (1949).

[22] F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).

[23] See for examples and references: R. Wolfgang, J. Eigner and F. S. Rowland, *J. Phys. Chem.*, **60**, 1137 (1956).

[24] K. E. Wilzbach, THIS JOURNAL, **79**, 1013 (1957).

[25] A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3284 (1957); R. W. Ahrens, M. C. Sauer, Jr., and J. E. Willard, *ibid.*, **79**, 3285 (1957).

[26] M. F. A. E. Sayed and R. Wolfgang, *ibid.*, **79**, 3286 (1957).

[27] R. Wolfgang, J. Eigner and F. S. Rowland, *J. Phys. Chem.*, **60**, 1137 (1956).

[28] R. Wolfgang, T. Pratt and F. S. Rowland, THIS JOURNAL, **78**, 5132 (1956).

[29] R. M. Lemmon, F. Mazzetti, D. L. Reynolds and M. Calvin, *ibid.*, **78**, 6414 (1956).

both benzene and toluene labeled with C^{14}. Earlier work has shown that C^{14} produced by the N^{14} $(n,p)C^{14}$ reaction is able to substitute for C and for N atoms in compounds such as acridene,[30] and pentane.[31] All of these reactions, like the halogen reactions described in the present paper, have been difficult to explain in terms of available theories of reactions activated by nuclear processes and it appears that a good working hypothesis is that they all involve steps of the ion-molecule type.

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[30] A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955).

[31] A. G. Schrodt and W. F. Libby, *ibid.*, **76**, 971 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN RESERVE UNIVERSITY]

Tetrakistriphenylsiloxytitanium and Some Related Compounds[1]

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Tetrakistriphenylsiloxytitanium was prepared in good yield by the reaction of triphenylsilanol with tetrabutoxytitanium and by the reaction of triphenylsilanol with titanium tetrachloride in the presence of ammonia. This compound shows an unusually high melting point, 501–505°, and possesses considerable inertness toward acids and bases. Some physical and chemical properties are discussed. Related compounds such as tetrakistriphenylsiloxysilane, tetrakistrimethylsiloxysilane are described and some properties of the compound triphenylbutoxysilane are given.

Prior to 1955 no silicon–oxygen–titanium molecular type compound had been reported in the literature. Titanated siloxanes[3] have been mentioned, but no information was given as to the compositions or the properties associated with the siloxy groups attached to titanium. In 1955 English and Sommer[4] described the preparation of $[(CH_3)_3SiO]_4Ti$ by the reaction of the appropriate silanol with titanium tetrachloride.

Calculations of bond strengths indicate that the Ti–O bond (~112 kcal./mole) should be approximately the same strength as the Si–O bond (~103 kcal./mole). In addition it has been shown that Si–C bonds are somewhat resistant to hydrolysis and that phenyl groups attached to silicon exhibit greater thermal stabilities than the alkyl silicon derivatives. As a consequence, the preparation of phenylsiloxy derivatives of titanium was undertaken with the hope of preparing substances of moderate to high thermal and chemical stability.

Experimental

Since the chlorides and esters of titanium and silicon hydrolyze readily, adequate precautions were taken to prevent exposure of these substances to water. Necessary operations were carried out in a dry atmosphere. All solvents were dried by means of an appropriate desiccant and distilled, or dried by azeotropic distillation. Tetra-*n*-butyl titanate from the Pigments Department, E. I. du Pont de Nemours Co., Inc., was purified by fractional distillation (b.p. 139–140° at 2 mm.). Tetraethoxysilane, Distillation Products Industries, was fractionally distilled (b.p. 165–167°). Titanium tetrachloride was of C.P. grade from Fisher Scientific Co. The triphenylsilanol was of purified (98%) grade.

Tetrakistriphenylsiloxytitanium

Preparation of $[(C_6H_5)_3SiO]_4Ti$. **Method 1.**—The reaction of triphenylsilanol with tetrabutoxytitanium was carried out, both in benzene and without solvents. The products were *n*-butyl alcohol and tetrakistriphenylsiloxytitanium, according to the equation

$$Ti(OC_4H_9)_4 + 4(C_6H_5)_3SiOH \longrightarrow 4C_4H_9OH + [(C_6H_5)_3SiO]_4Ti$$

When an excess of triphenylsilanol was used, triphenylbutoxysilane, a new compound, was also a product. Otherwise the reaction is essentially quantitative with respect to the formation of the above products. Variations in the mole ratios of reactants *did not* give partially substituted titanium esters.

In a typical preparation, equal molar quantities of tetrabutoxytitanium and triphenylsilanol were mixed. The reaction was slow, but quantitative amounts of *n*-butyl alcohol were recovered by distillation from the mixture. The *n*-butyl alcohol was identified by its refractive index.

The addition of tetrabutoxytitanium to a benzene solution of triphenylsilanol resulted in an instantaneous formation of a white precipitate as the desired product. In one reaction, 0.12 mole of tetrabutoxytitanium was treated with 0.60 mole of triphenylsilanol in one liter of benzene. The crude product (0.12 mole) was removed by filtration. Distillation of the filtrate to remove solvent also yielded 0.12 mole of triphenylbutoxysilane.

Method 2.—Tetrakistriphenylsiloxytitanium has also been prepared by the method of English and Sommer, according to the equation

$$TiCl_4 + 4(C_6H_5)_3SiOH + 4NH_3 \longrightarrow 4NH_4Cl + [(C_6H_5)_3SiO]_4Ti$$

$TiCl_4$ (0.1 mole), dissolved in 25 ml. of dry benzene, was added dropwise to 0.2 mole of triphenylsilanol dissolved in 1500 ml. of dry benzene. The apparatus consisted of a three-neck, three-liter flask equipped with a Trubore stirrer, reflux condenser and an ammonia delivery tube coaxial with the condenser. The flask was cooled in an ice-bath during the addition of the titanium tetrachloride. The ammonia was bubbled through the solution from the start of the $TiCl_4$ addition to the beginning of reflux. A strong yellow color developed. This color disappeared with the further addition of 0.22 mole of triphenylsilanol. The solution was refluxed for several hours to remove the ammonia and then filtered. The precipitate was washed with benzene, acetone and finally with water to remove the ammonium chloride. The white product was dried and purified by vacuum sublimation at 370°. Soxhlet extraction of impure tetrakistriphenylsiloxytitanium is an effective, but slow, method of purification.

Properties of $[(C_6H_5)_3SiO]_4Ti$.—Tetrakistriphenylsiloxytitanium is only slightly soluble in benzene, toluene, chloro-

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[3] H. C. Gulledge, U. S. Patent 2,512,058 (June 20, 1950).

[4] W. D. English and L. H. Sommer, THIS JOURNAL, **77**, 170 (1955).