Gas Phase Recoil Phosphorus Reactions. III. Systematic Study of Hydrogen-Abstraction Reactions[1]

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Abstract. The relative efficiencies of H abstraction by recoil ^{32}P atoms from eight hydrogen-containing molecules (AH_x) have been measured. A plot of the H-abstraction efficiency vs. AH_x bond dissociation energy yielded a good correlation curve identifying bond strength as a major controlling parameter for such reactions. Moreover, when the heats of reaction for $^{32}PH_3$ formation with assumed one-, two-, or three-step abstraction mechanisms were compared with the experimental results, the conclusion was reached that the abstraction of three H atoms from SiH_4 occurs simultaneously, and that the H abstraction from hydrocarbons requires energetic ^{32}P atoms and is likely to involve a stepwise mechanism.

Abstraction together with insertion, substitution, and addition are the four fundamental reaction modes for free atoms.[2-10] For "univalent" atoms[11] abstraction is always the most predominant process.[2-5] However, for "multivalent" atoms, abstraction appears to be at most of minor importance.[6-10]

The abstraction of hydrogen by various free atoms has been studied in detail by a number of investigators.[2-10] It is actually the only possible mode for reactions of thermal hydrogen atoms with saturated hydrocarbons.[2,3] In the case of energetic hydrogen atoms, although other reaction modes such as direct substitution become feasible, H abstraction remains one of the most predominant.[4] For "divalent" and "tetravalent" atoms such as O, S, C, and Si,[6-10] even if H abstraction is proposed as one of the initial steps in the reaction mechanism, the yields of the expected stable hydrides are normally very small. The only "trivalent" atom whose chemical interactions have been extensively studied is nitrogen.[8,12] In active nitrogen systems the major reaction product of N atoms with hydrocarbons is always HCN, while the H-abstraction product, NH_3, is formed only in minor amounts.[8] In recoil ^{13}N systems containing either methane or ethylene $HC^{13}N$ was also found to be the predominant product while the formation of $^{13}NH_3$ was not reported.[12]

In the present work we wish to report a detailed study of H-abstraction reactions by another "trivalent" atom, phosphorus. The nuclear recoil technique has been the only successful method thus far for producing phosphorus atoms in the form of ^{32}P and studying their chemical interactions. For recoil ^{32}P atoms, abstraction is the only well-established reaction channel[1,13,14] and has been shown to be definitely the most predominant pathway for certain molecules such as PH_3 where absolute yields of $^{32}PH_3$ as high as 78% are observed.[14] In the present work we have measured the relative efficiencies of H abstraction by phosphorus atoms from various molecules and have revealed bond strength as the fundamental controlling factor for such abstraction reactions. This is the first systematic study of abstraction reactions by "multivalent" atoms.

Experimental Section

Sample Preparation. The general procedure used in this study was the same as that used in other typical nuclear recoil experiments.[15] Phosphorus trifluoride along with the desired hydrogen-containing compounds (AH_x) were sealed in Pyrex 1720 bulbs using standard high-vacuum techniques. A typical set of samples consisted of two pure PF_3 samples and eight samples of varying PF_3-AH_x composition in bulbs of similar sizes.

Extreme care was required when preparing the pure PF_3 samples because traces of a compound with easily abstractable hydrogens gave significant quantities of $^{32}PH_3$. These interfering hydrogen-containing compounds probably came from one or more of the following sources: (1) the wall of the sample bulb, (2) the vacuum line, or (3) impurities in PF_3 itself. In order to remove H-containing contaminants such as water vapor from the wall, the sample bulbs were all well-flamed in vacuo before introducing any components into the bulbs. Similarly, the vacuum line was conditioned by flaming the appropriate storage bulb and occasionally the entire line in vacuo to remove any hydrogen-containing compounds which may have been absorbed on the glass surfaces. In order to remove possible H-containing impurities from PF_3, a bulb-to-bulb distillation was performed and only the middle fraction of the PF_3 was used. In addition, pure phosphorus trifluoride samples were commonly sealed before any hydrogen-containing compound was introduced into the line again in an effort to keep contaminants in the pure samples to a minimum.

Irradiation. Phosphorus-32 from the $^{31}P(n,\gamma)\ ^{32}P$ nuclear transformation[13] was formed using thermal neutrons from the Texas A&M University Nuclear Science Center Reactor. A rotisserie which rotated at 2.5 rpm and held ten samples was used for the irradiations. Reactor irradiations typically lasted for 20 min while exposing the outside of the rotisserie to a neutron flux of approximately 5×10^{11} n/(cm^2 sec).

Sample Analysis. After irradiation the samples were transferred to an injection loop using liquid nitrogen to trap the sample. Such a procedure was sufficient for our purposes since the products of interest, $^{32}PF_3$ and $^{32}PH_3$, were condensable at 77°K. A 0.25 in. × 12 ft aluminum column of Porapak Q, 50-80 mesh, was employed for the analyses. $^{32}PH_3$ and $^{32}PF_3$ had retention times of 11 and 36 min respectively when the column was operated at 25° with a helium flow rate of 33 ml/min. Mass peaks were measured using thermal conductivity response while an internal gas proportional counter of 85 ml active volume was used for radioactivity detection. No $^{32}PHF_2$ or $^{32}PH_2F$ was observed during the analyses, but the presence of these molecules may have gone undetected since no carrier was used for these compounds. Furthermore, in a backflush experiment of the radiogas chromatographic system no indication of volatile products other than $^{32}PF_3$ or $^{32}PH_3$ was obtained.

Since certain ^{32}P-containing products in minute quantities may be removed by materials present in the radio-gas chromatographic system, the corresponding unlabeled compounds were always added in sufficient amounts as carriers to preserve the labeled products. For example, although the PF_3 in each sample served as a carrier for $^{32}PF_3$, a small quantity of PH_3 had to be added to the sample before the analysis was performed in order to ensure the preservation of all the $^{32}PH_3$ activity.

Occasionally it was found that a nonradioactive sample of PH_3 carried out radioactivity after passing through the radio-gas chromatographic system. The activity was found to be due to tritium exchange with PH_3 producing PH_2T. This problem arose because the same experimental setup was used to analyze not only ^{32}P products but also other labeled compounds including tritiated ones. The interfering activity was removed by alternately injecting quantities of NH_3 and PH_3. Samples were only analyzed when no further tritium activity was carried out by PH_3.

No noticeable quenching of the internal counter was observed by compounds used in connection with this research nor was any increase in the specific activities observed when the surface area was grossly enhanced by the addition of glass fragments to the reaction bulbs.

Chemicals. Phosphorus trifluoride (>97%) was obtained from PCR, Inc. and purified by bulb-to-bulb distillation. Phosphine (99.5%), silane (99.9%), methane (>99.0%), ethane (>99.0%), neopentane (>99.0%), hydrogen (>99.9%), ethylene (>99.5%), and acetylene (>99.6%) were all obtained from Matheson and used without further purification except for degassing.

Results

Normalized Specific Activities of $^{32}PF_3$ and $^{32}PH_3$ as a Function of Composition. The AH_x molecules studied in connection with this work were saturated and unsaturated species such as H_2, PH_3, SiH_4, CH_4, C_2H_6, C_2H_4, C_2H_2, and neo-C_5H_{12}. Samples were prepared so that roughly equal intervals were covered in the 0.1–0.8 AH_x mole fraction range. After irradiating and analyzing the samples as described earlier, the activity of ^{32}P-containing product peak areas of the ^{32}P precursors as taken from the disk integrator was calculated. After correcting for radioactive decay of ^{32}P species, the specific activity of $^{32}PF_3$ or $^{32}PH_3$ was calculated in the following manner.

$$\text{specific activity } ^{32}PF_3(^{32}PH_3) = \frac{\text{corrected } ^{32}PF_3(^{32}PH_3) \text{ activity}}{\text{mass peak area of } ^{32}P \text{ precursor}} \qquad (1)$$

As a cross check for reactant quantity, both the pressure and volume of the reacting system were accurately measured. The pressure-volume measurements were used to calculate specific activity only when the mass peak areas were unavailable. The calculated specific activities were then normalized by comparing their values with that of the pure PF_3 standard.

$$\text{normalized specific activity (NSA)} = \frac{\text{specific activity}}{\text{specific activity of standard}} \times 100 \qquad (2)$$

In Figure 1 normalized $^{32}PF_3$ specific activities, NSA($^{32}PF_3$) values,[16] have been plotted as a function of sample composition for all of the molecules studied here. It can be seen from the graph that with the exception of PH_3 and SiH_4 systems, straight lines could be drawn through the experimental points correlating log NSA($^{32}PF_3$) and AH_x mole fraction. Qualitatively, the trend of the data indicates that the addition of these AH_x molecules continuously decreases the NSA($^{32}PF_3$) values in all the systems. The relative efficiencies for the depression of NSA($^{32}PF_3$) values as observed in Figure 1 was: $H_2 < CH_4 < C_2H_6 < C_2H_4 < C_2H_2 \approx$ neo-$C_5H_{12} < SiH_4 \approx PH_3$.

The NSA($^{32}PH_3$) values are presented in Figures 2 and 3 as a function of AH_x mole fraction. The three saturated hydrocarbons were plotted separately to clarify the positions of the actual points in order to avoid the possible confusion arising from overlapping H_2 data points. A general feature of the points in each line is that the NSA($^{32}PH_3$) values increase with increasing AH_x mole fraction. The intermolecular comparison shows that the obtained NSA($^{32}PH_3$) values differ by as much as three orders of magnitude with the following order of decreasing reactivity: $PH_3 \approx SiH_4 \gg C_2H_6 >$ neo-$C_5H_{12} \approx H_2 > CH_4 > C_2H_4 > C_2H_2$. There was actually no $^{32}PH_3$ observed in the acetylene system.

A comparison of NSA($^{32}PF_3$) and NSA($^{32}PH_3$) values in Figures 1–3 reveals a reciprocal relationship between these two quantities. The only minor exception among saturated molecules is that ethane and neopentane are the only pair that do not strictly follow this reciprocal order. For the unsaturated molecules, C_2H_4 and C_2H_2, although the NSA($^{32}PF_3$) values are in the same range as those of their saturated counterparts, the NSA($^{32}PH_3$) values are nevertheless virtually zero.

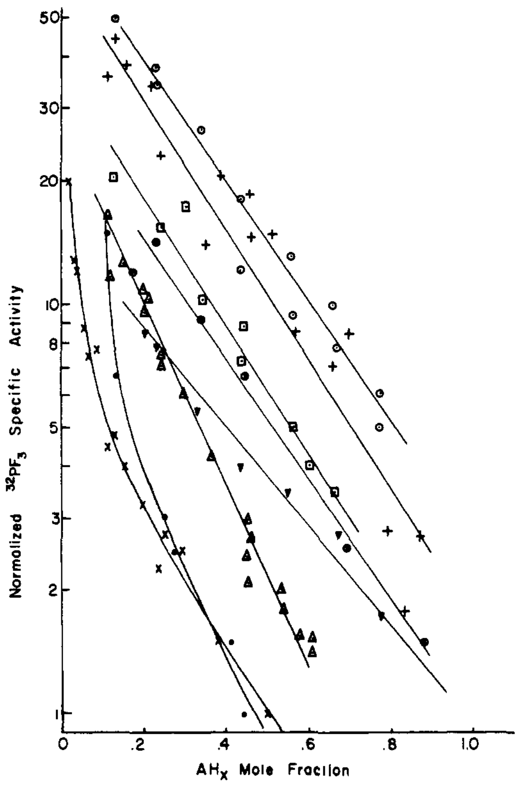

Figure 1. Normalized $^{32}PF_3$ specific activity vs. AH_x mole fraction: H_2 (⊙); CH_4 (+); C_2H_6 (◻); C_2H_4 (⊕); C_2H_2 (▼); neo-C_5H_{12} (▲); SiH_4 (●); PH_3 (x).

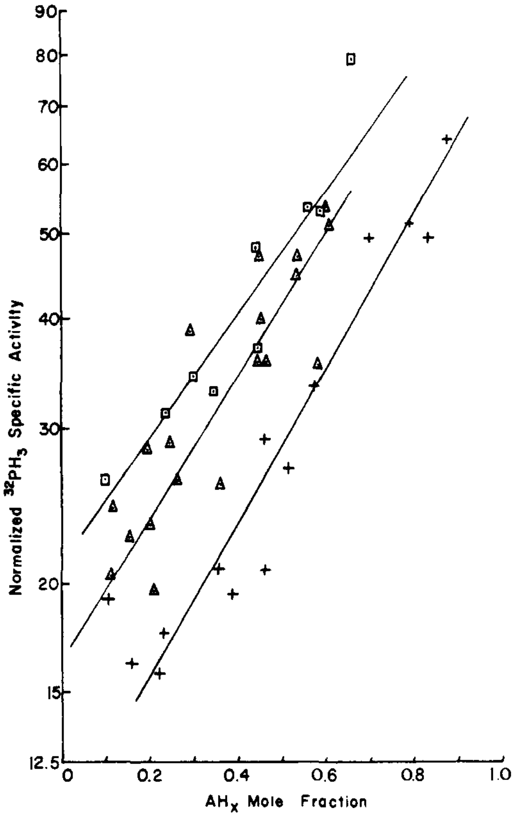

Figure 2. Normalized $^{32}PH_3$ specific activity vs. AH_x mole fraction for saturated hydrocarbons: C_2H_6 (◻); neo-C_5H_{12} (▲); CH_4 (+).

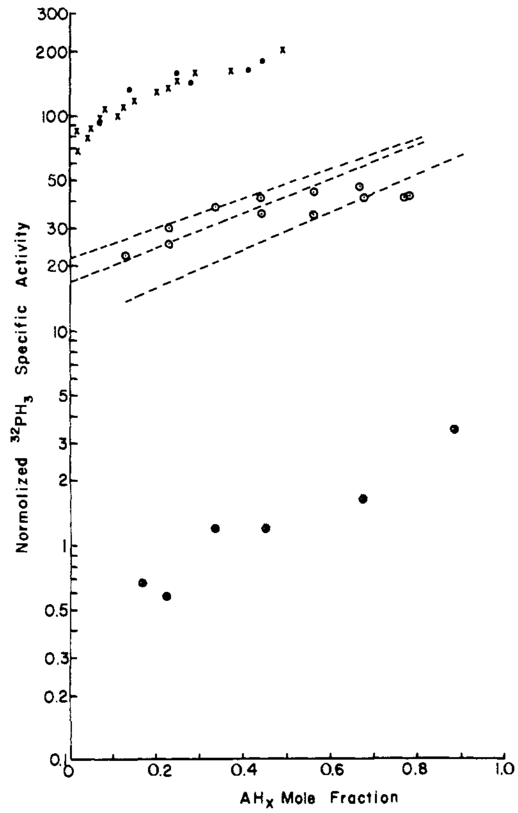

Figure 3. Normalized $^{32}PH_3$ specific activity vs. AH_x mole fraction: PH_3 (x); SiH_4 (●); H_2 (○); C_2H_4 (⊕); (- - -) lines drawn in Figure 2.

Specific Activity Ratio per Molecule. In order to have a more meaningful comparison of the relative reactivities, an additional quantity was calculated which involved correcting the NSA($^{32}PH_3$) or NSA($^{32}PF_3$) values for the relative amounts of AH_x or PF_3 in the sample composition. The specific activity ratio per molecule (SARPM) is therefore an indication of the relative H vs. F abstraction efficiencies on a molecular basis.

$$\mathrm{SARPM} = \frac{\mathrm{NSA}(^{32}\mathrm{PH}_3)/F_{\mathrm{AH}_x}}{\mathrm{NSA}(^{32}\mathrm{PF}_3)/F_{\mathrm{PF}_3}} \qquad (3)$$

(F denotes mole fraction)

The SARPM values have been plotted as a function of sample composition in Figure 4. The extreme diversity of the abstraction efficiencies is apparent from the fact that the SARPM values cover more than three orders of magnitude. It appears that straight lines drawn through the points for each molecule fit the data well. The ordering of these lines is: $PH_3 \approx SiH_4 \gg$ neo-$C_5H_{12} > C_2H_6 > CH_4 \approx H_2 > C_2H_4$.

As can be seen in Figure 4, some of the SARPM lines slope up with increasing AH_x concentration (e.g., neopentane) while others are essentially horizontal (e.g., H_2). Although we cannot address ourselves to the full explanation of this phenomenon here, it is reasonable to speculate that one of the major reasons may be the presence of different moderating properties in samples of different composition. The energy spectrum of the reacting ^{32}P atoms may be drastically different in such unnormalized systems which in turn may affect the overall abstraction efficiencies.

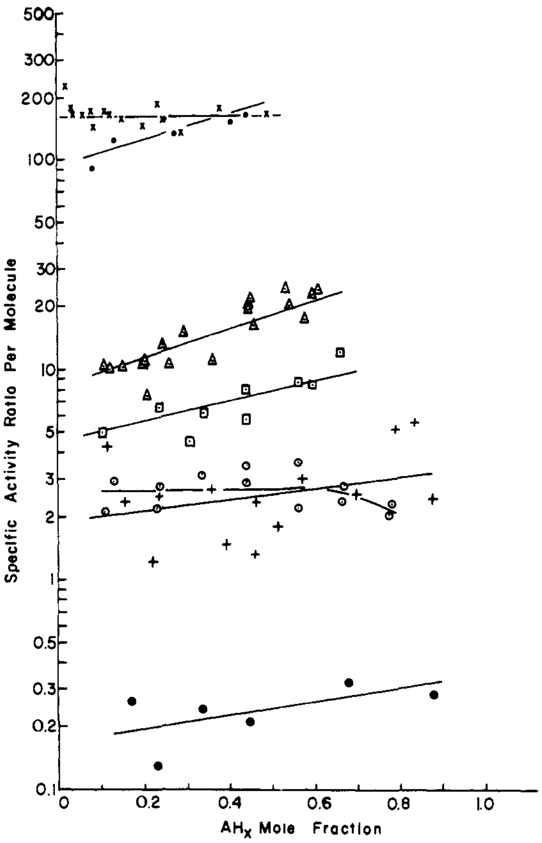

Figure 4. Specific activity ratio per molecule vs. AH_x mole fraction: PH_3 (x); SiH_4 (●); neo-C_5H_{12} (▲); C_2H_6 (▣); H_2 (⊙); CH_4 (+); C_2H_4 (⊕).

Discussion

Specific Activities and Specific Activity Ratios in Systems Containing 80% PF_3. Recoil ^{32}P atoms are formed with a maximum recoil energy of 800 eV,[14] but the energy spectrum of the *reacting* ^{32}P atoms in the chemical reaction range will be basically determined by the moderating property of the system. Therefore in the present case the comparison of the H-abstraction efficiencies for different molecules by ^{32}P is meaningless unless we are dealing with systems of similar moderating properties. Experimentally the best we could do was to choose a normalized system where the bulk of the sample was identical. In practice, systems containing 80 mol % PF_3 could be employed for this comparison. Systems with a PF_3 content higher than 80 mol % could not be used because such a system would give a low $^{32}PH_3$ yield and therefore a large statistical error.

In Table I the NSA($^{32}PF_3$), NSA($^{32}PH_3$), and SARPM values for systems containing 80% PF_3 are listed for the eight AH_x molecules studied. They were taken from the lines drawn in Figures 1–4. In the table the SARPM value of 2.1 for methane implies that the overall abstraction of three H atoms from methane molecules is 2.1 times more likely than the overall abstraction of three F atoms from PF_3 molecules.

Comparisons of H-abstraction efficiency may alternatively be expressed on a per bond rather than a per molecule basis. The specific activity ratio per bond (SARPB) is defined as

$$\mathrm{SARPB} = \mathrm{SARPM} \times \frac{\text{No. of P–F bonds in PF}_3}{\text{No. of A–H bonds in AH}_x} \qquad (4)$$

The eight SARPB values for systems containing 80% PF_3 are also listed in Table I.

Bond Strength Effect. From the values quoted in Table I it can be seen that with few exceptions both the SARPM and SARPB values vary inversely with the bond dissociation energy of the A–H bond. Such a relationship is alternatively demonstrated in Figure 5 where an exponential plot

Table I. Normalized Specific Activities and Specific Activity Ratios for the Abstraction Products in an 80% PF_3 System

Molecule (AH_x)	Normalized $^{32}PF_3$ specific activity at 80% PF_3	Normalized $^{32}PH_3$ specific activity at 80% PF_3	SARPM	SARPB	D(A–H)	Ref for D(A–H)
PH_3	3.2	125	162	162	83.9	17
					90.3	18
SiH_4	4.3	130	128	96	94.0	19
					95.3	18
C_2H_6	28	29	5.7	2.8	98.0	20
neo-C_5H_{12}	17.7	23.5	11.3	2.8	99.3	20
H_2	39	25	2.7	1.8	104.0	20
CH_4	31	15.8	2.1	1.5	104.0	20
C_2H_4	14.2	0.8	0.2	0.5	108.0	21
C_2H_2	8.7	~0	~0	~0	115	22

of SARPM or SARPB vs. bond dissociation energy is shown. The most significant feature of the plotting shows that as the D(A–H) values increase by a mere 20 kcal/mol, the specific activity ratios vary by more than three orders of magnitude. In this figure the values for acetylene have not been shown because of the zero yield for $^{32}PH_3$. All the other data points correlate reasonably well with the straight lines drawn through them. However, it must be cautioned that a strict exponential relationship is neither necessarily followed nor easily explained. Nevertheless, the results here unmistakably identify bond strength as a major factor controlling the H-abstraction efficiency by recoil ^{32}P atoms.

Inverse correlation between the yields of the H-abstraction product and the A–H bond dissociation energy similar to that observed here has long been convincingly established in a series of recoil tritium studies by Rowland and coworkers,[23-25] and successfully explained by their proposed energy cut-off model.[23] An extension of the energy cut-off model to the present ^{32}P-abstraction reactions implies that molecules with weaker A–H bonds permit abstraction of H atoms by ^{32}P at lower energies and as a result gives rise to higher $^{32}PH_3$ yields. A weaker A–H bond may also increase the probability of reaction per collision in the energy range available for abstraction.

Although bond strength has been established here as a major controlling factor for the H-abstraction reactions by ^{32}P atoms, other parameters such as the possible participation of d orbitals in the PH_3 and SiH_4 systems and the possible removal of abstraction intermediates such as ^{32}PH and $^{32}PH_2$ in the C_2H_4 and C_2H_2 systems may tend to modify the specific activity ratios.

Heats of Reaction for the Three-Step H-Abstraction Process. The interpretation of the bond strength effect by the energy cut-off model basically reflects the overwhelming role played by the activation energy of the H-abstraction reactions. Although a smaller bond dissociation energy normally gives rise to an abstraction reaction of lower activation energy, these two quantities are not always parallel. In fact a term which is also fundamental in determining the H-abstraction efficiency is the heat of reaction which represents the absolute lower limit of activation energy. In the absence of any direct knowledge about the activation energy of a reaction, its heat of reaction value may give certain penetrating insights of a process which would otherwise be unattainable.

A stepwise mechanism is generally assumed for the abstraction reactions by a "multivalent" atom. For the formation of $^{32}PH_3$ through the H abstraction from AH_x, a three-step mechanism dictates the following.

$$^{32}P + AH_x \rightarrow {}^{32}PH + AH_{x-1} \quad (5)$$

$$^{32}PH + AH_x \rightarrow {}^{32}PH_2 + AH_{x-1} \quad (6)$$

$$^{32}PH_2 + AH_x \rightarrow {}^{32}PH_3 + AH_{x-1} \quad (7)$$

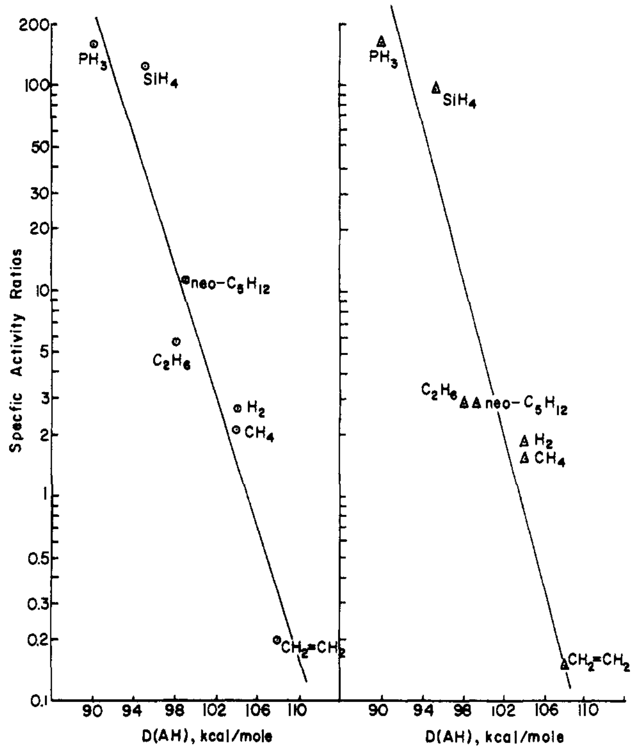

Figure 5. Specific activity ratios vs. D(A–H); specific activity ratio per molecule (⊙); specific activity ratio per bond (▲).

The heat of reaction for the formation of $^{32}PH_3$ from each one of the eight AH_x molecules via a three-step H-abstraction mechanism has been evaluated. These values are listed in Table II following the same decreasing order of the specific activity ratios as shown in Table I. It is apparent that there is a rough inverse relationship between these two quantities. A major conclusion which can be drawn from these positive heat of reaction values is that the formation of $^{32}PH_3$ via a three-step mechanism is a highly endothermic process for all the molecules studied except PH_3 and requires energies in the order of 60 kcal/mol or more. Under the heading "three-step mechanism" in Table II, the three values included in parentheses behind each heat of reaction value represent the heats of reaction for the three individual steps, eq 5–7, respectively. In each case the second abstraction is always the most endothermic among the three.

One- and Two-Step Mechanisms for the Formation of $^{32}PH_3$. Although there is no concrete experimental evidence for its occurrence, the possibility of simultaneous abstraction of two or more atoms by a multivalent species such as O, N, and P has long been proposed. Oxygen atom reactions with both methane and ethylene have been viewed as proceeding through the simultaneous abstraction of two

Table II. Heats of Reaction for Various H Abstractions[a]

Molecule (AH_x)	Heats of reaction One-step mechanism	Two-step mechanism	Three-step mechanism	Ref for ΔH_f°
PH_3	0	−8.6 (−8.6, 0)	8.5 (−8.6, 17.1, 0)	26–28
SiH_4	−8.0	43.1 (27.0, 16.1)	56.8 (7.5, 33.2, 16.1)	29–32
C_2H_6			63.4 (9.7, 35.4, 18.3)	26, 33
neo-C_5H_{12}			61.6 (9.1, 34.8, 17.7)	26, 34
H_2		−22.2 (−46.7, 24.5)	82.0 (15.9, 41.6, 24.5)	26
CH_4	85.6	92.1 (67.8, 24.3)	81.4 (15.7, 41.4, 24.3)	26, 33, 36
C_2H_4			93.4 (19.7, 45.4, 28.3)	26, 33
C_2H_2			99.1 (21.6, 47.3, 30.2)	26, 36

[a] All ΔH values are expressed in kcal/mol and expressed for species in their gaseous state.

hydrogen atoms.[37,38] It has also been suggested that in active nitrogen systems, NH_3 was formed in mono-, di-, or trimethyl substituted silane systems by a simultaneous abstraction process.[39] For recoil ^{32}P reactions with methane, Halmann and Kugel have mentioned the possibility that the $^{32}PH_3$ formation may proceed through a one-step mechanism.[40] Although this suggestion was disputed and termed "unlikely" by Stewart and Hower based on the observation that the $^{32}PH_3$ yields are highly susceptible to scavenging,[14] the disputing argument nevertheless ignores the fact that a one-step abstraction mechanism involving ^{32}P atoms which possess odd electrons should also be suppressed by suitable scavengers. As a result it is unwise to prejudge the occurrence of simultaneous abstraction by ^{32}P atoms from these published reports.

It is conceivable that a detailed examination of the energies of the simultaneous abstraction process may reveal certain valuable insights. The simultaneous abstraction of three hydrogen atoms by ^{32}P constitutes a one-step mechanism.

$$^{32}P + AH_x \rightarrow {}^{32}PH_3 + AH_{x-3} \tag{8}$$

A two-step mechanism may proceed in two alternative ways, with either an initial abstraction of two hydrogens followed by the abstraction of a third one or vice versa. The heats of reaction for both the one- and two-step mechanisms were calculated for some of the molecules studied and are also included in Table II. Both alternatives of the two-step mechanism should have the same overall heat of reaction, while the numbers in parentheses behind this overall heat of reaction value in Table II refer to the reactions where two hydrogen atoms are abstracted in the initial step.

By comparing the data in Table I with the heat of reaction values in Table II, the following conclusions concerning H abstraction by energetic ^{32}P atoms can be reached. (1) For the abstraction of H from SiH_4 by ^{32}P to give $^{32}PH_3$, the heat of reaction for a one-step mechanism is exothermic while those of the multiple step mechanisms are both highly endothermic. Since the extremely high $^{32}PH_3$ yields call for a low energy or even thermal process, it is in obvious contradiction with the stepwise processes. As a result the abstraction from SiH_4 most likely proceeds through a one-step mechanism. (2) For the abstraction of H from PH_3, the heats of reaction for all three possible mechanisms have low values, suggesting a low-energy process which accords well with the observed high $^{32}PH_3$ yield. However, it is impossible to single out the predominant mechanism of the three. While the three-step mechanism may have the highest overall activation energy, it should nevertheless have the most favorable steric factor. (3) For the saturated hydrocarbons which are typified by the CH_4 molecule, the heats of reaction for all three possible mechanisms have high values which is in accord with the relatively low $^{32}PH_3$ yield observed. For these molecules the H-abstraction process by ^{32}P must involve "hot" phosphorus atoms. Mechanistically a three-step process is likely to predominate because of the expected favorable steric factor. (4) In the H_2 system, a two-step mechanism is expected to be highly favored over a three-step one judging from the heat of reaction values. Such a two-step mechanism may in fact be an insertion of ^{32}P into the H-H bond of hydrogen giving $^{32}PH_2$, followed by the abstraction of a final H atom. If the H abstraction by ^{32}P in the H_2 system did actually involve a two-step exothermic mechanism, $^{32}PH_3$ yields would be expected to be high and similar to those found in the PH_3 system. On the other hand if the abstraction from H_2 proceeds through the three-step endothermic mechanism, $^{32}PH_3$ yields would be expected to be low and similar to those found in the CH_4 case. As Table I shows, the actual yield of $^{32}PH_3$ in this system is substantially less than that observed in PH_3 but is similar to that in CH_4. This comparison points to the conclusion that for some unknown reasons the H abstraction from H_2 by ^{32}P probably proceeds through a three-step mechanism. It is worthwhile to note that Kistiakowsky and Volpi[41] have observed no detectable reaction between active N and H_2 although the insertion process giving NH_2 is highly exothermic. (5) Stereochemical considerations rule out a one-step mechanism process for C_2H_4 by ^{32}P atoms and for similar reasons a three-step H-abstraction process for C_2H_2 must be proposed. The extremely low $^{32}PH_3$ yields observed from these two molecules accord well with the extremely high endothermicity for the three-step processes. Such an abstraction must require highly energetic ^{32}P atoms.

Abstraction Reactions by Other Atoms. As previously mentioned, "univalent" atoms abstract very readily while "multivalent" species only undergo abstraction reactions to a small extent. The reluctance of divalent species such as O and S to undergo abstraction may be due to the intense competition from insertion reactions where the insertion products are always stable species.

The H-abstraction process by active N from the eight AH_x molecules studied here is summarized below. There is no NH_3 observed from the H_2,[41] PH_3,[42] and SiH_4[39] systems. In the case of the hydrocarbons the yields vary from 10 to 50% that of HCN.[43-46] A detailed comparison of the H abstractions from hydrocarbons by active N and recoil ^{32}P atoms is not warranted here because the moderation properties of the nitrogen systems are not normalized and the HCN yields from different systems are not identical. However, a common ground here is that H abstraction from hydrocarbons by neither of these two atoms is a very efficient process.

The most interesting comparison between active N and recoil ^{32}P atoms is the contrast between their H abstraction from PH_3 and SiH_4. The heats of reaction for the stepwise H abstraction from PH_3 by N have values of −6.2, −11.6, and −23.4 kcal/mol for the three steps, respectively. The corresponding values for the SiH_4 system are 9.9, 4.5, and −7.3 kcal/mol. The heats of reaction for a one-step H-abstraction mechanism from PH_3 and SiH_4 by active N are both highly exothermic with values of −49.7 and −57.7 kcal/mol, respectively. The fact that no NH_3 was observed in either one of these two systems points to the conclusion that: (1) N atoms cannot abstract from PH_3 or SiH_4 with a one-step mechanism; and (2) the NH species formed in the initial abstraction of a three step mechanism undergoes reactions other than abstraction in the active N systems where free radical concentration is extremely high.[8,42]

The conclusion that ^{32}P can undergo a one-step simultaneous abstraction of three H atoms from SiH_4 while nitrogen atoms cannot is most significant. The presence of d orbitals on both the reacting atom and interacting molecule is probably the necessary condition for the formation of a long-lived complex where the transfer of two or more atoms may occur before the complex disintegrates.

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