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HOT ATOM REACTIONS INVOLVING MULTIVALENT AND UNIVALENT SPECIES

MASTER

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Progress Report

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Texas A&M Research Foundation

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II. A list of publications supported by the AEC-ERDA-DOE Contract No. DE-AS05-76ER03898:

(1) Recoil Tritium Reactions with Trimethylfluorosilane. A Study on Parameters Affecting Hot Atom Substitution Reactions, J. Phys. Chem., 75, 301-307 (1971), S.H. Daniel and Y.-N. Tang

(2) Secondary Unimolecular Reactions Subsequent to Substitution Reactions by High-Energy Chlorine-38 and Chlorine-39 Atoms, J. Phys. Chem., 75, 440-442 (1971), Y.-N. Tang, W.S. Smith, J.L. Williams, K. Lowery, and F.S. Rowland.

(3) Recoil Tritium Reactions with Hexamethyldisilane in the Gas Phase, J. Phys. Chem., 76, 1249-1254 (1972), S.H. Daniel, G.P. Gennaro, K.M. Ranck, and Y.-N. Tang.

(4) Direct Evidence for the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene, J. Am. Chem. Soc., 94, 4355-4357 (1972), Y.-N. Tang, G.P. Gennaro, and Y.Y. Su.

(5) Unimolecular Processes Subsequent to Recoil Tritium Reactions with Spiropentane, J. Phys. Chem., 76, 2187-2195 (1972), Y.Y. Su and Y.-N. Tang.

(6) Reactions of Recoil Chlorine Atoms with cis- and trans- Olefins, J. Phys. Chem., 76, 2711-2715 (1972), W.S. Smith, S.H. Daniel, and Y.-N. Tang.

(7) Gas Phase Recoil Phosphorus Reactions I-Complete and Partial Retention of Bonds in PF_5, J. Inorg. Nucl. Chem., 35, 3087-3094 (1973), G.P. Gennaro and Y.-N. Tang.

(8) Addition of Singlet and Triplet Silylene to Buta-1,3-diene, J.C.S. Chem. Comm., 637-638 (1973), G.P. Gennaro, Y.Y. Su, O.F. Zeck, S.H. Daniel and Y.-N. Tang.

(9) Gas Phase Recoil Phosphorus Reactions II- A Detailed Study of Pressure and Scavenger Effects, J. Inorg. Nucl. Chem., 36, 259-262 (1974), G.P. Gennaro and Y.-N. Tang.

(10) Relative Efficiencies of Hydrogen Abstraction by Recoil Phosphorus Atoms, J.C.S. Chem. Comm., 52-53 (1974), O.F. Zeck, G.P. Gennaro and Y.-N. Tang.

(11) The Ground Electronic State of Silylene, J. Amer. Chem. Soc., 96, 5967-5973 (1974), O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.-N. Tang.

(12) Consecutive Unimolecular Decomposition Following Recoil Tritium Activation of 1,1-Difluoroethane, J. Phys. Chem., 78, 2186-2189 (1974), W.S. Smith and Y.-N. Tang.

(13) Interaction of Triplet Silicon Difluoride with Paramagnetic Molecules, J.C.S. Chem. Comm., 156-157 (1975), O.F. Zeck, Y.Y. Su and Y.-N. Tang.

(14) Gas Phase Recoil Phosphorus Reactions III-Systematic Study of Hydrogen-Abstraction Reactions, J. Amer. Chem. Soc., 97, 4498-4503 (1975), O.F. Zeck, G.P. Gennaro and Y.-N. Tang.

(15) Effect of Additives on the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene, J. Amer. Chem. Soc., 98, 3474-3477 (1976), O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.-N. Tang

(16) Relative Reactivities of Conjugated Dienes towards Silicon Difluoride, J.C.S. Chem. Comm., 6-7 (1977), R.A. Ferrieri, E.E. Siefert, M.J. Griffin, O.F. Zeck and Y.-N. Tang.

(17) Use of Radio-Gas Chromatography in the Study of Plant Metabolism, Anal. Biochem., 87, 466-476 (1978), D.A. Baltuskonis, Y.-N. Tang and R.J. Newton.

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(19) Reactions of Energetic Tritium Atoms with Organic Compounds, a chapter in "Isotopes in Organic Chemistry," Volume 4 (E. Buncel and C.C. Lee, Eds.), Elsevier Scientific Publishing Company, 85-177 (1978), Y.-N. Tang.

(20) Gas Phase Recoil Phosphorus Reactions IV-Effect of Moderators on Abstraction Reactions, J. Inorg. Nucl. Chem., 41, 785-789 (1979), O.F. Zeck, R.A. Ferrieri, C.A. Copp, G.P. Gennaro and Y.-N. Tang.

(21) Reactions of Silicon Atoms and Silylenes, a chapter in "Reaction Intermediates," Volume 2, (R.A. Abramovitch, ed.), Plenum Publishing Company Limited, (total 107 pages), to be published in 1979, Y.-N. Tang.

(22) Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions, J. Amer. Chem. Soc., in press, E.E. Siefert, K.-L. Loh, R.A. Ferrieri, and Y.-N. Tang.

(23) Unusual Compounds Synthesized via Nuclear Recoil Methods, to be published as a chapter in "Nuclear Applications in Biological, Environmental, and Pure Chemistry," (K.A. Krohn and J.W. Root, eds.), to be published in 1980, Y.-N. Tang.

Accumulated support level for this project from 1968-1980 is $256,267.00.

III. Progress Report for the Year, 1979-1980

A. Abstract

The major progress during this period was in the study of recoil ^{31}Si and recoil ^{11}C reactions and in the initiation of the studies on the interaction of molecular tritium on solid surfaces. For the recoil ^{31}Si systems, heterogeneous hydrogenation experiments have been designed to positively confirm that a major unknown product, derived from the interaction of ^{31}Si atoms with 1,3-butadiene, is 1-silacyclopenta-2,4-diene. This compound has been shown to be very sensitive to γ-ray irradiation and to be thermally unstable at a temperature higher than 100°C. Another recoil ^{31}Si experiment was designed to review the mechanism of the ^{31}Si abstraction reactions. From the fact that high yields of [^{31}Si]-1-fluorosilacyclopent-3-ene was obtained as a product from a mixture of PH_3 and PF_3 together with 1,3-butadiene, the stepwise abstraction mechanism is definitely much more predominant than the possible simultaneous abstraction. Other recoil ^{31}Si works involved a detailed systematic composition study of $^{31}SiF_2$ reactions with 1,3-butadiene, some neon moderator studies, and the continuation of the studies on the reactions of $^{31}SiF_2$ and $^{31}SiH_2$ with conjugated hexadienes.

By using 2-$^{14}\underline{C}$-propanone and 1,3-$^{14}\underline{C}$-propanone, the mechanism of solvent-free oxidative cleavage of propanone by $KMnO_4$ has been elucidated. Information thus derived was used to degradate the ^{11}C-labelled propadiene derived from the reactions of recoil ^{11}C atoms with ethylene. Results indicate that 73% of the ^{11}C-labelled propadiene was center-labelled. This value was observed to change with additives: (i) to 100% with 40% oxygen; (ii) to 83%

with 92% xenon; and (iii) to 6% with 94% neon. Such results indicate that while singlet carbon atoms are selective in undergoing double bond interactions, triplet carbon atoms are the sole reactants in the C-H insertion process. It also suggests that a direct double bond insertion process is operative at high energy. Besides this, recoil ^{11}C atom reactions with butadiene have been extended to moderator studies.

Various mechanistic studies on the heterogeneous interactions of molecular T_2 on solid surfaces such as Pd supported on active carbon have been initiated. This includes the studies of the temperature programmed desorption of tritium on catalysts, the "spilled-over" phenomenon for supported catalysts, the hydrogenation of $CH_2=CHF$ and $CH_2=CF_2$ with H_2/T_2 mixture over Pd/C together with the temperature effect on such interactions. The mechanism of the heterogeneous hydrogenolysis of fluorocarbons by molecular H_2 has also been elucidated.

Other progress includes the completion of two review articles, one on the reactions of silicon atoms and silylenes, and the other on the unusual compounds synthesized via nuclear recoil methods. Recoil tritium reactions with benzene and with toluene have also been performed. A paper concerning the effect of moderators on ^{32}P abstraction reactions has recently been published.

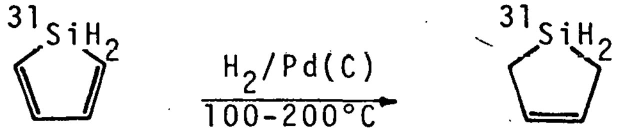
B. Significant Results

During the past year (1979-1980), the major progress was in the continuation of recoil silicon-31 and recoil carbon-11 studies, and in the initiation of the studies on the interaction of molecular tritium on solid surfaces. The details are summarized below.

(1) Reactions of Recoil Silicon-31 Atoms

Silicon-31 atoms were formed *via* the nuclear transmutation, $^{31}P(n,p)^{31}Si$, initiated by fast neutrons either from a nuclear reactor or from a cyclotron source with a 16-MeV deuteron beam impinging on a beryllium target. The major accomplishment during this period is as follows.

(a) Formation of [^{31}Si]-1-Silacyclopenta-2,4-diene through Recoil ^{31}Si Atom Reactions with 1,3-Butadiene. The synthesis of silacyclopentadienes has been a long-term challenge to chemists during the past two decades. During the reactions of recoil ^{31}Si atoms with 1,3-butadiene, a major unknown product was observed which was tentatively identified by Gaspar and co-workers as 1-silacyclopenta-2,4-diene. This supposition was confirmed by us through catalytic hydrogenation processes. The unknown compound was first individually trapped and then was injected together with H_2 through a catalyst tube containing Pd supported on active carbon. The fact that silacyclopenta-3-ene was observed repeatedly as a hydrogenation product provides the strongest chemical evidence that the trapped compound is indeed 1-silacyclopenta-2,4-diene.



(1)

Subsequent studies have shown that this unusual compound is very sensitive to γ-ray irradiation, and it is also thermally unstable at a temperature higher than 100°C.

A paper entitled "Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions" has been accepted by J. Am. Chem. Soc. for publication. A preprint (DOE/ER/03898-41) of this paper is included with this report.

(b) Mechanism of ^{31}Si Abstraction Reactions. It has been established that when PH_3 was used as the ^{31}Si precursor, the H-abstraction will give rise to $^{31}SiH_2$ which subsequently adds to 1,3-butadiene to give silacyclopentadiene. Correspondingly, when PF_3 is used as the ^{31}Si precursor, the F-abstraction will give rise to $^{31}SiF_2$ which subsequently reacts to give 1,1-difluorosilacyclopent-3-ene as the final product. However, it is not sure whether the abstraction proceeds in a stepwise manner or whether the abstraction of two entities is simultaneous. Information on the abstraction mechanism has been obtained by generating ^{31}Si atoms in the presence of PH_3 and PF_3. If simultaneous abstraction is the only operating mechanism, $^{31}SiH_2$ and $^{31}SiF_2$ will be the only silylenes formed and accordingly, we should only obtain silacyclopent-3-ene and 1,1-difluorosilacyclopent-3-ene. On the other hand, if stepwise abstraction mechanism prevails, in addition to the above mentioned intermediates and products, ^{31}SiHF should also be formed as an abstraction product which in turn will give rise to 1-fluorosilacyclopent-3-ene. The reactions involved are shown below.

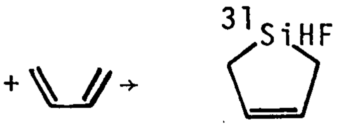
$$^{31}Si + PH_3 \rightarrow {}^{31}SiH + PH_2 \qquad (2)$$

$$^{31}SiH + PF_3 \rightarrow {}^{31}SiHF + PF_2 \qquad (3)$$

$$^{31}Si + PF_3 \rightarrow {}^{31}SiF + PF_2 \qquad (4)$$

$$^{31}SiF + PH_3 \rightarrow {}^{31}SiHF + PH_2 \qquad (5)$$

^{31}SiHF +



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The recoil ^{31}Si experiments with PH_3-PF_3 mixtures have been carried out and a new product appeared at the tail-end of 1,1-difluorosilacyclopent-3-ene during radio-gas chromatography analysis. Since there is some overlapping between the two peaks, graphic separation of their yields has been performed. As seen in figure 1, the yield of this new product thus obtained changes with the mole fraction of PH_3 from zero through a maximum and then back towards zero. Correspondingly, the yield of silacyclopent-3-ene decreases while that of 1,1-difluorosilacyclopent-3-ene increases with the mole fraction of PH_3 in the mixture. The characteristic of the yield variation of this new product is exactly what we would have expected for 1-fluorosilacyclopent-3-ene through a stepwise abstraction mechanism. On the quantitative side, if we employ a situation where the efficiency of H-abstraction is identical with the efficiency of F-abstraction, the expected yields of the silacyclopent-3-enes would be as shown in the table on the following page for the two possible mechanisms. As indicated in the table, the yield of 1-fluorosilacyclopent-3-ene would be <u>twice</u> as high as each of the other two silacyclopent-3-enes under such equal reactivity conditions. In figure 1, for samples with a PH_3 mole fraction of about 0.7 where the efficiencies of the H- and F-abstractions are about identical, the yield of the tentatively identified 1-fluorosilacyclopent-3-ene is actually about twice as high as that of the other two silacyclopent-3-enes.

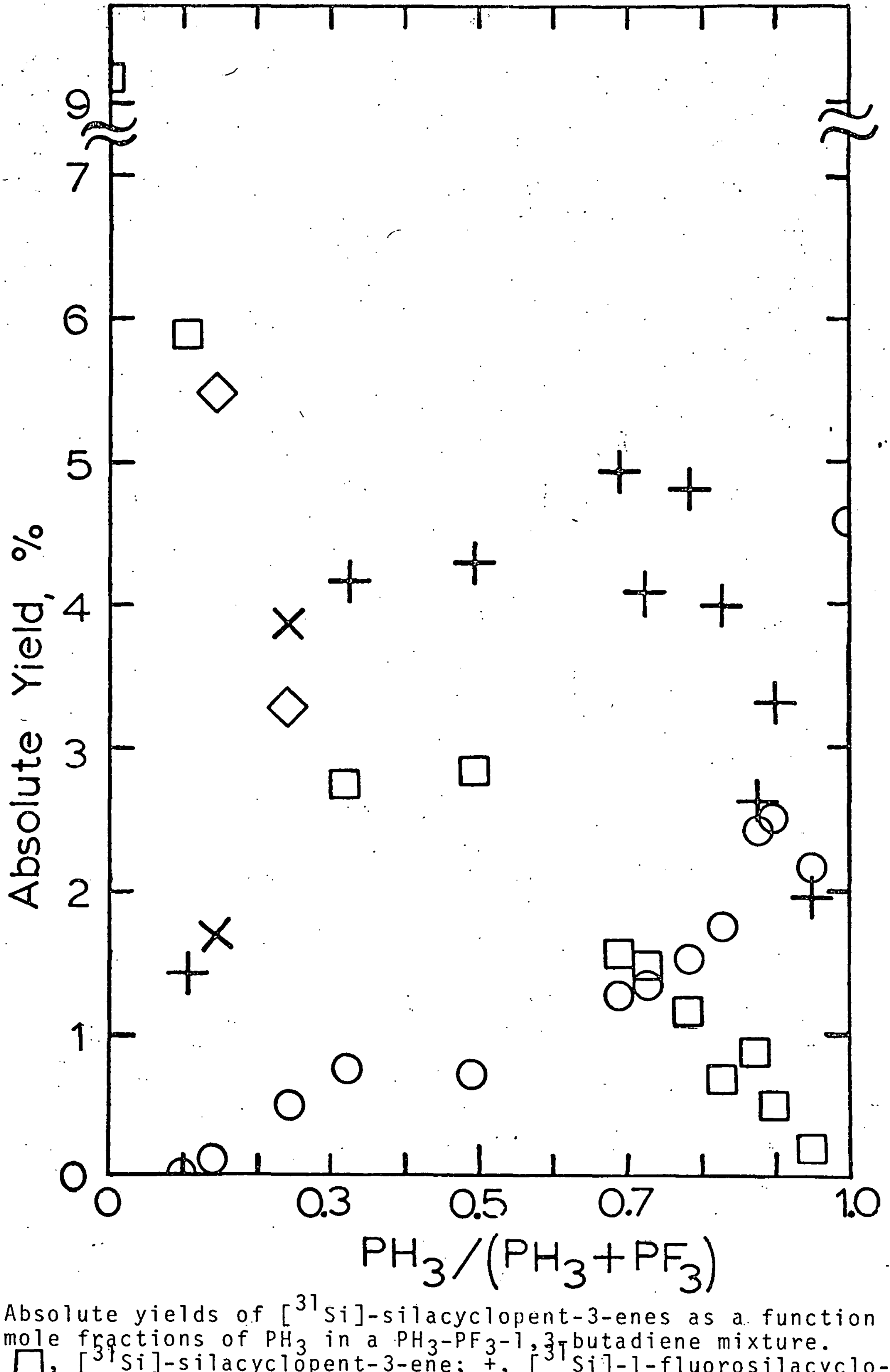
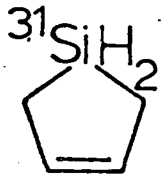
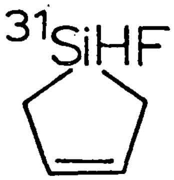
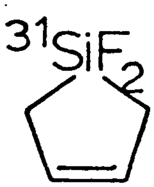


Figure 1. Absolute yields of [^{31}Si]-silacyclopent-3-enes as a function of mole fractions of PH$_3$ in a PH$_3$-PF$_3$-1,3-butadiene mixture. □, [^{31}Si]-silacyclopent-3-ene; +, [^{31}Si]-1-fluorosilacyclopent-3-ene; ○, [^{31}Si]-1,1-difluorosilacyclopent-3-ene.

Mechanism	Expected Yields		
			
Stepwise	(1.0)	2.0	1.0
Simultaneous	(1.0)	0.0	1.0

This indicates that the stepwise mechanism is definitely the predominant, if not the only, one operating for the ^{31}Si abstraction reactions.

This work will be continued and completed during the next period of time.

(c) <u>A Detailed Systematic Composition Study of $^{31}SiF_2$ Reactions with 1,3-Butadiene</u>. It has been previously demonstrated that $^{31}SiF_2$ added to 1,3-butadiene gives ^{31}Si-labelled difluorosilacyclopent-3-enes. Very recently, we have performed a detailed systematic composition study of this reaction system. The results are shown in figure 2. For the PF_3-1,3-butadiene system with no other additives, it is seen that difluorosilacyclopent-3-ene is formed with the addition of as little as 0.01% butadiene. Its yield increases exponentially with further butadiene addition until a maximum of 30% absolute yield is obtained at about 0.5% butadiene. However, the yield declines

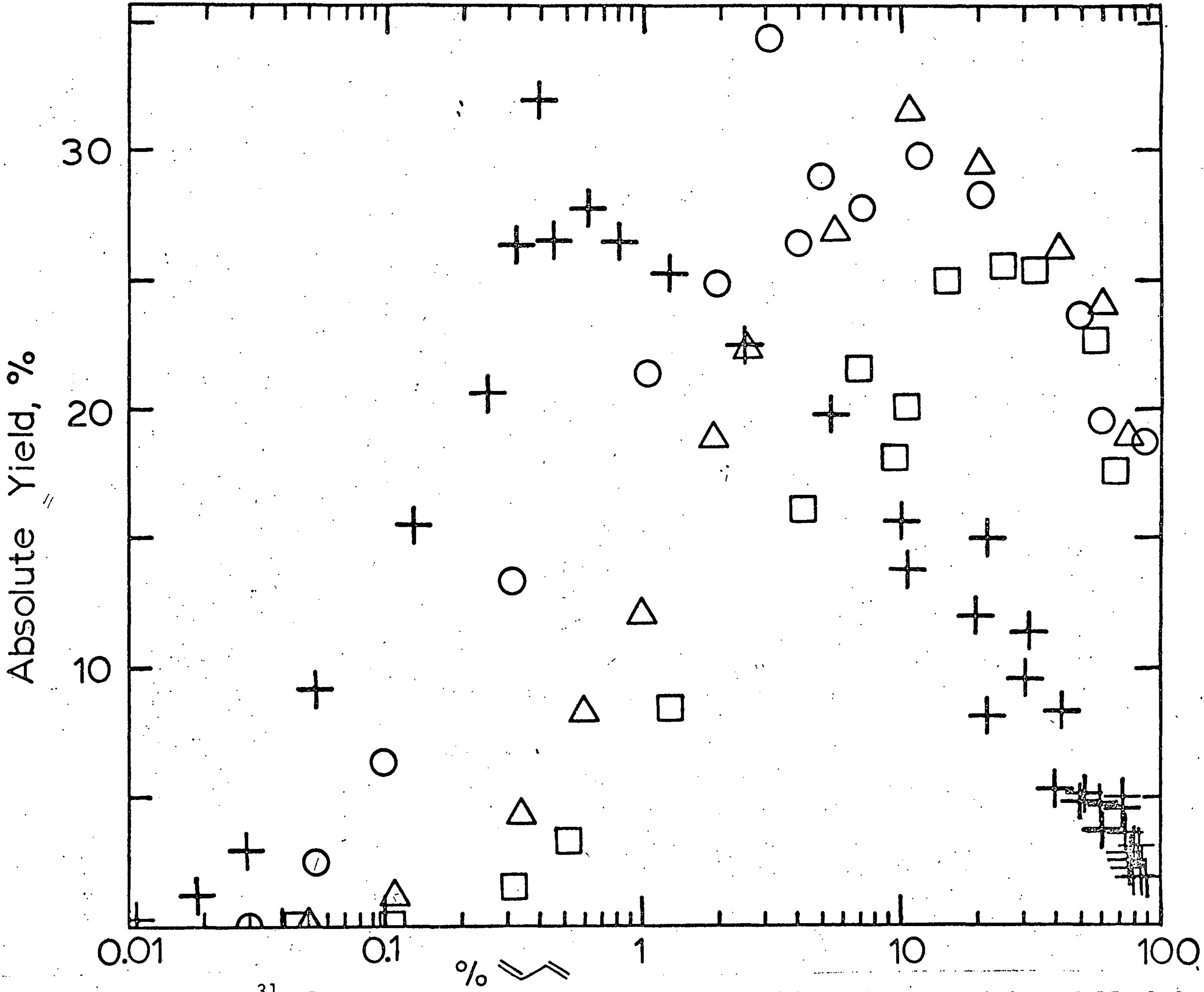
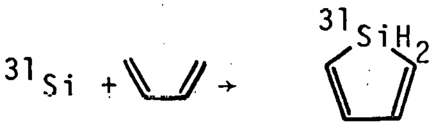


Figure 2. Dependence of [^{31}Si]-1,1-difluorosilacyclopent-3-ene yield on the composition of PF$_3$-1,3-butadiene samples. +, no additives; ○, with 1% NO; △, with 5% NO; □, with 20% NO.

again exponentially thereafter. At 90% butadiene the absolute yield of [^{31}Si]-difluorosilacyclopent-3-ene only amounts to 2%. Similar trends are observed when 1%, 5%, or 20% nitric oxide is added, but the position of the maximum yield is shifted to higher butadiene concentrations. Such results could provide a lot of insight into the chemical properties of ground state singlet $^{31}SiF_2$ and the complex formed by triplet $^{31}SiF_2$ with NO. It could also give the relative reactivities of triplet $^{31}SiF_2$ towards butadiene and NO.

This work will be continued and completed during the next period of time.

(d) Neon Moderator Studies on the Reactions of ^{31}Si Atoms with 1,3-Butadiene. Very recently we have initiated moderator studies on the reactions of ^{31}Si atoms and $^{31}SiX_2$ silylenes with 1,3-butadiene. Neon is the only inert gas which has been employed thus far. For the PH_3 -butadiene systems, the results are shown in figure 3. It is seen that the yields of [^{31}Si]-silacyclopentadiene, formed *via* reaction (7), increase with moderation while that of [^{31}Si]-silacyclopent-3-ene, formed *via* reaction (8), stayed essentially constant. In figure 4, the results from the corresponding Ne-moderator study on the PF_3-butadiene system are shown. Similarly, the [^{31}Si]-silacyclo-



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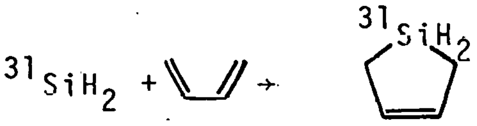

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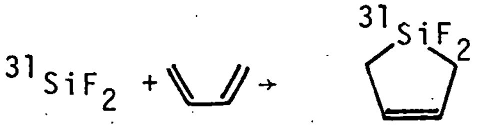

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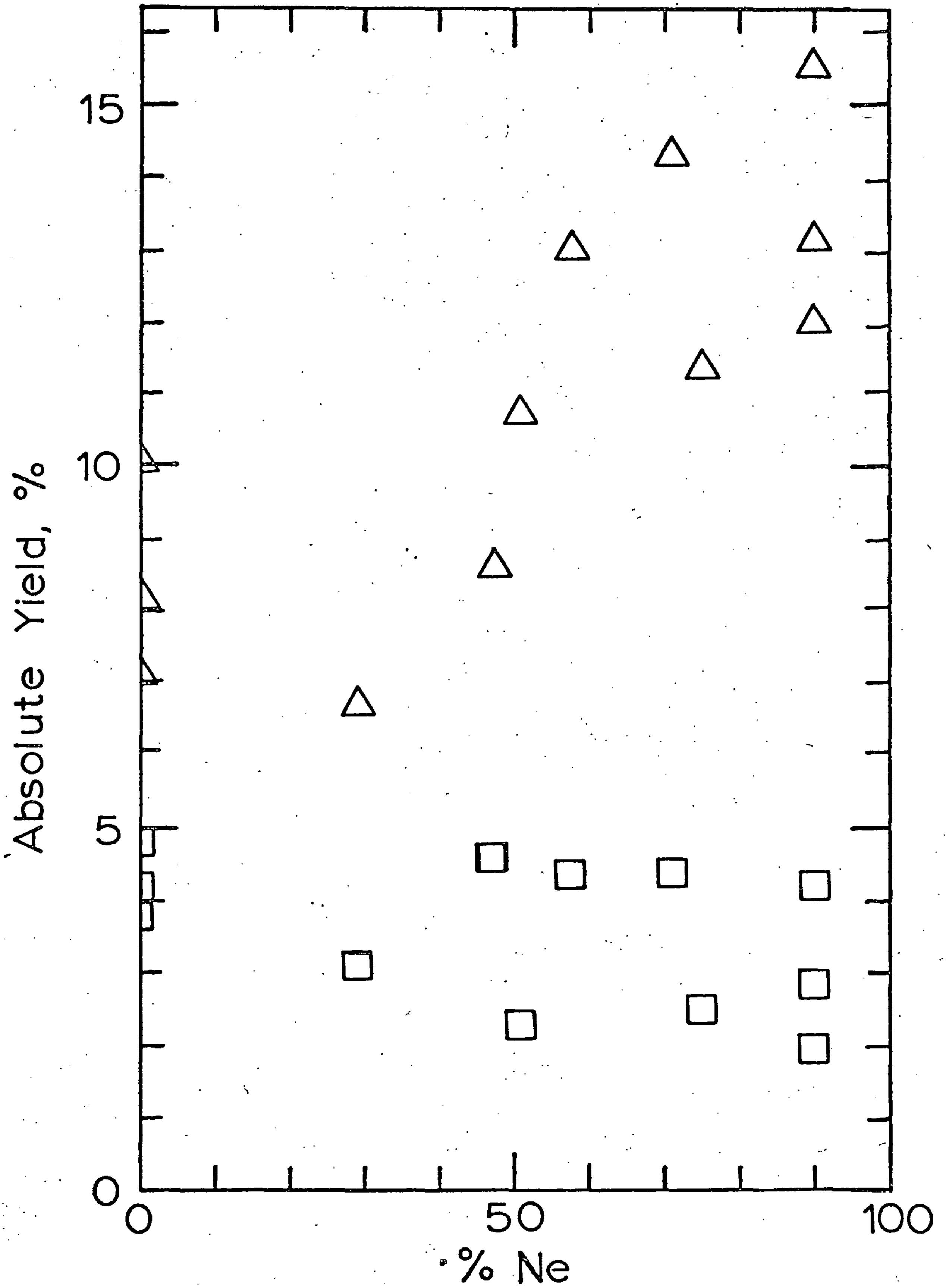


Figure 3. Effect of neon as a moderator on the reactions of recoil ^{31}Si atoms in a PH_3-1,3-butadiene system. △, [^{31}Si]-1-silacyclopenta-2,4-diene; □, [^{31}Si]-silacyclopent-3-ene.

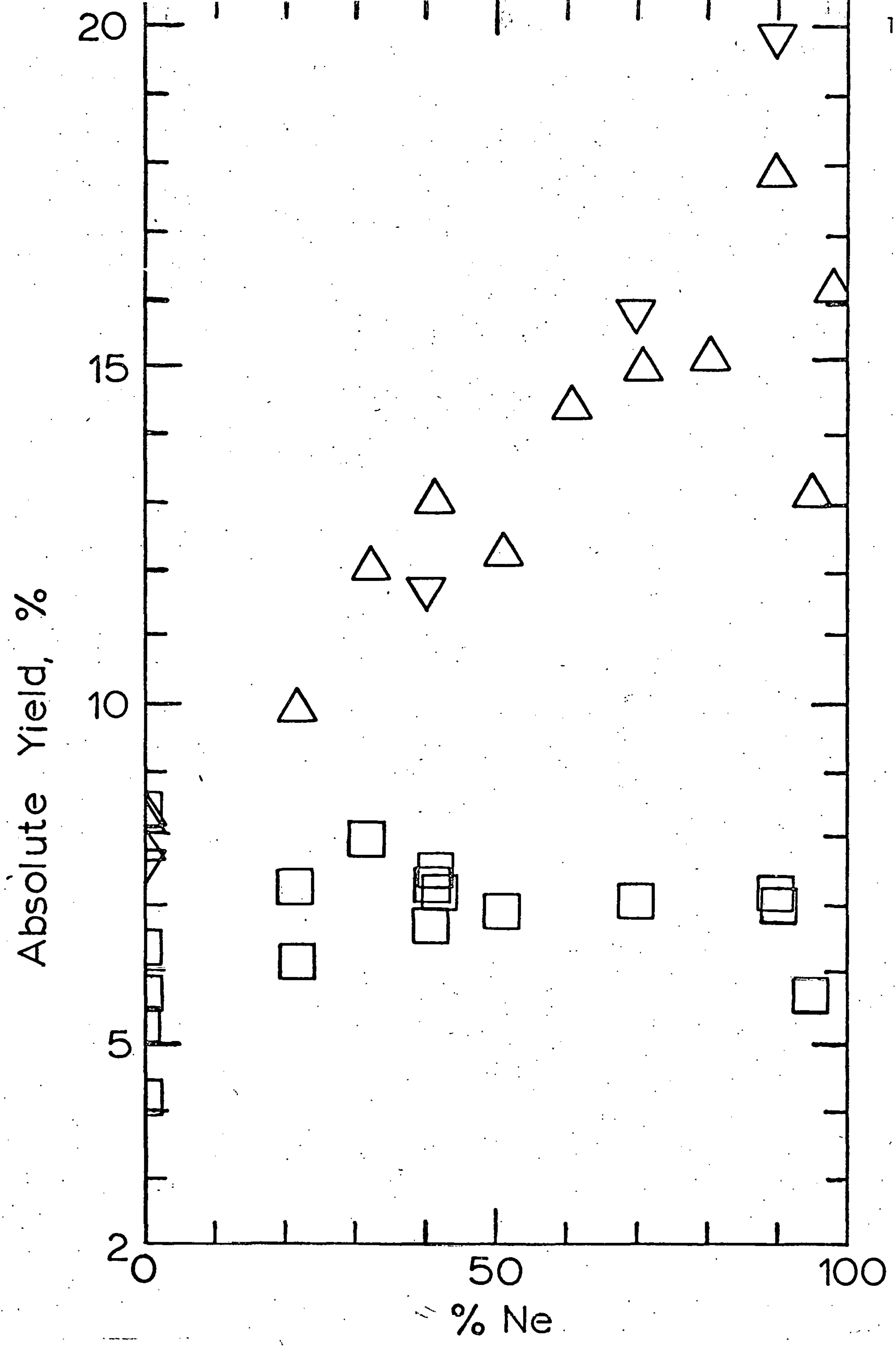


Figure 4. Effect of Neon as a moderator on the reactions of recoil ^{31}Si atoms in a PF_3-1,3-butadiene system. △, [31Si]-1-silacyclopenta-2,4-diene; □, [31Si]-1,1-difluorosilacyclopent-3-ene.

pentadiene yield increases while the [^{31}Si]-1,1-difluorosilacyclopent-3-ene yield, derived from reaction (9), stayed nearly constant. These preliminary results imply that it is the translationally thermalized ^{31}Si atoms which are more likely to add to butadiene for the occurrence of reaction (7). Further detailed studies with other moderators are definitely required.

(e) Reactions of $^{31}SiF_2$ and $^{31}SiH_2$ with Conjugated Hexadienes. During the previous research period, reactions of $^{31}SiF_2$ and $^{31}SiH_2$ with conjugated hexadienes such as trans-2-trans-4-hexadiene, its cis-trans-isomer, and its cis-cis-isomer have been studied. The most surprising observation is that for $^{31}SiF_2$ reactions with the three hexadienes, only one stereoisomer of the two expected [^{31}Si]-2,5-dimethylsilacyclopent-3-enes is observed as product, and the same one has been formed from either one of the three reactant molecules. In the case of $^{31}SiH_2$ reactions with the three hexadienes, although both cis- and trans- stereoisomers of the product molecule are observed, they are formed in the ratio of approximately four to one. All of these experiments were performed with a single gas chromatographic column for product analysis. During this period of time, we have repeated some of the experiments by employing various types of columns for product separation. The results uphold the earlier quantitative data.

(f) A Review Article on the Reactions of Si Atoms and Silylenes. During the previous period of time, a preliminary copy of a review article entitled "Reactions of Silicon Atoms and Silylenes," was written. During this period of time, this article has been finalized with extensive amending, modifying, and up-dating. The final version of this article amounts to 107 pages. It is currently in the process of publication as a chapter in "Reaction Intermediates," volume 2. A preprint of this revised version (DOE/ER/03898-42) is included with this report.

(2) Reactions of Recoil Carbon-11 Atoms

(a) Mechanism of Solvent-Free Oxidative Cleavage of Propanone by $KMnO_4$. In order to degradate the [^{11}C]-propadiene formed from recoil ^{11}C atom reactions with ethylene, a method was developed where propadiene was hydrolyzed to propanone and subsequently degraded through oxidative cleavage by $KMnO_4$. This method of degradation was novel in that it employed a solvent-free system where propanone was oxidized over solid $KMnO_4$ at elevated temperatures. A complete reaction flowscheme had been established from the results of the solvent-free heterogeneous oxidations of 2-$^{14}\underline{C}$-propanone and 1,3-$^{14}\underline{C}$-propanone by $KMnO_4$. Under most of the oxidative conditions for the 2-$^{14}\underline{C}$-propanone system, $^{14}CO_2$ was observed as the major product with an average yield of 92% total product activity. In the case of 1,3-$^{14}\underline{C}$-propanone, the product trends are shown in figure 5. As seen in the figure, when the oxidative conditions were mild, formaldehyde and acetic acid were the major ^{14}C-labelled products. Intermediate oxidative conditions predominately gave rise to ^{14}C-labelled formic acid. On the other hand, when the oxidative conditions were harsh, carbon dioxide became a major ^{14}C-labelled product. Such results are consistent with the following oxidative degradation mechanism of propanone by $KMnO_4$.

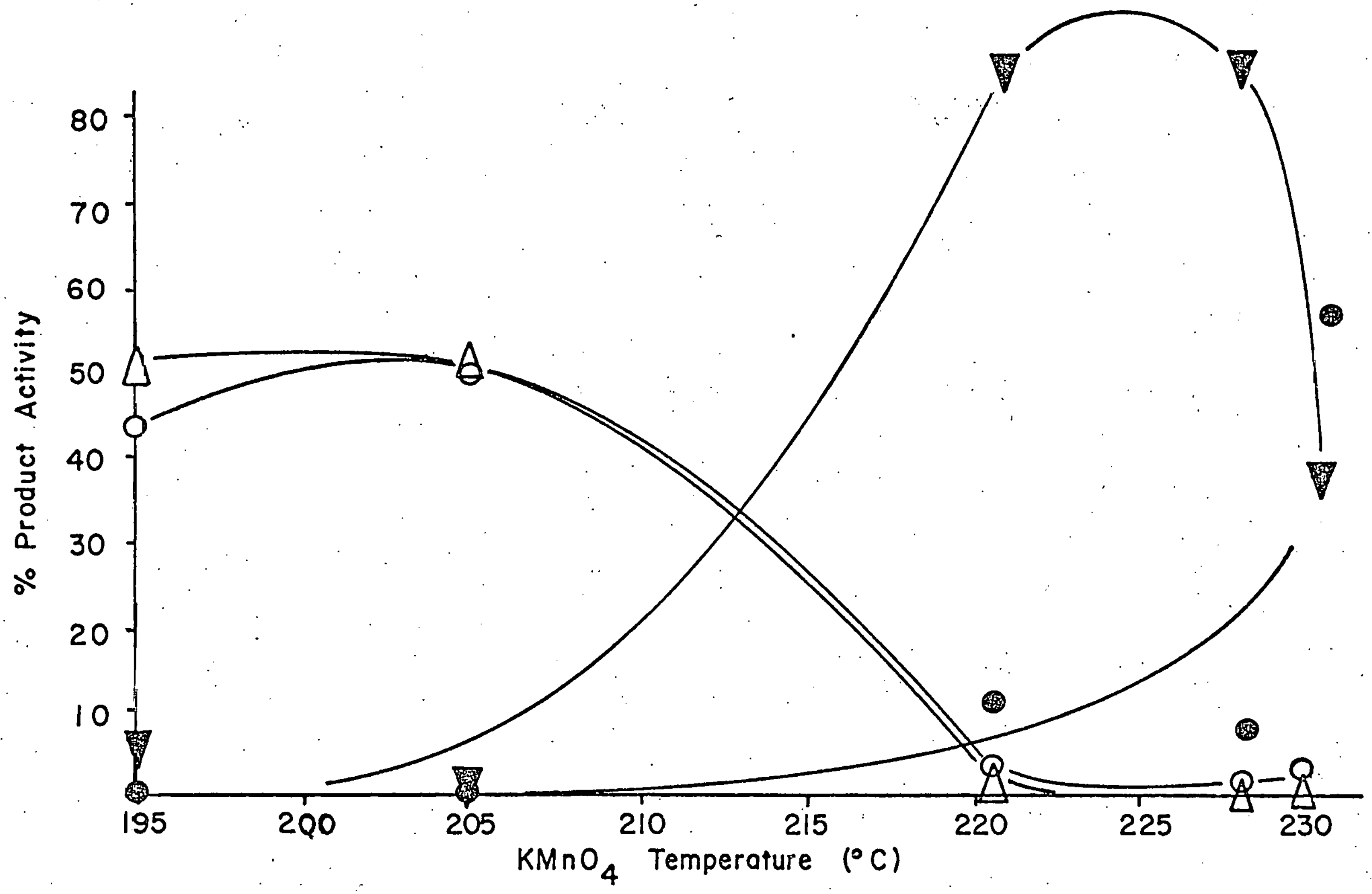
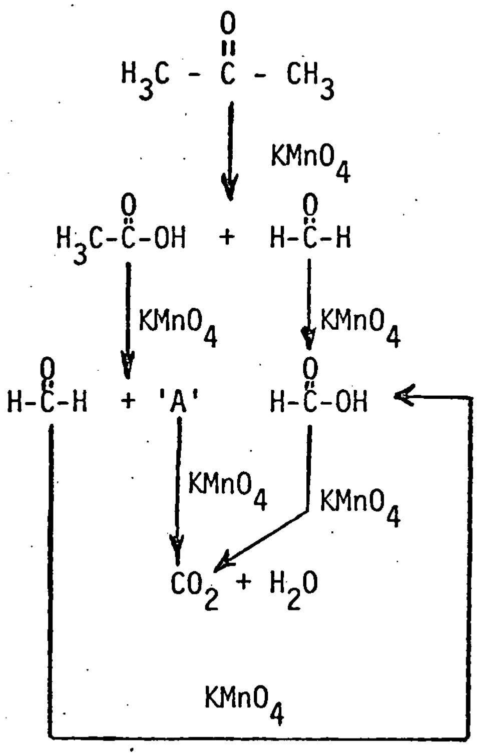


Figure 5. Plot of product yield distributions as a function of $KMnO_4$ temperature (●, CO_2; ○, HCHO; ▼, HCO_2H; Δ, CH_3O_2H).



(10)

(b) The Effects of Energetics and Electronic States on the Reactions of Recoil Carbon-11 Atoms with Ethylene. Since May, 1978, we have collaborated the study on recoil ^{11}C reactions with Dr. A.P. Wolf of Brookhaven National Laboratory by sending Mr. Richard A. Ferrieri, a graduate student, to work there. The nuclear transformation $^{12}C(p,pn)^{11}C$ was employed for the formation of recoil ^{11}C atoms.

The interaction of ^{11}C atoms with the double bond in ethylene gives rise to center-labelled propadiene while the insertion of ^{11}C atoms into a C-H bond gives rise to end ^{11}C-labelled propadiene. By using mild oxidation conditions in the $KMnO_4$ degradation technique described in the previous section, it was possible to oxidize the central carbon of [^{14}C]-propanone derived from the ethylene system mainly to CO_2 and the end carbons to HCHO and HCO_2H. Results indicated that 73% center ^{11}C-labelled propadiene was observed for ethylene samples of 160-1600 torr. This value was observed to change with additives: (i) to 100% with 40%

oxygen; (ii) to 83% with 92% xenon; and (iii) to 6% with 94% neon. The detailed results are shown in figure 6. The oxygen scavenging effects of C(^{3}P) suggest that singlet carbon atoms undergo exclusive double bond interactions. The neon moderator results indicate that this interaction is a higher energy process than C-H insertion. This suggests that a direct double bond insertion process is operative at high energy. In addition, these results indicate that while singlet carbon atoms are selective in undergoing double bond interactions, triplet carbon atoms are the sole reactants in the C-H insertion process.

Part of these results have been written as a communication to be submitted to J. Am. Chem. Soc. in the near future. A preprint (DOE/ER/03898-45) is included with this report.

(c) Recoil ^{11}C Atom Reactions with Butadiene. This topic was initially studied by employing the nuclear transformation $^{12}C(n,2n)^{11}C$, where the fast neutron is produced with a deuteron beam from the Texas A&M University cyclotron via the $^{9}Be(d,n)^{10}B$ transmutation. Mr. Ferrieri has also extended this study at Brookhaven National Laboratory.

For the reactions of recoil ^{11}C atoms with pure 1,3-butadiene, eight major ^{11}C-labelled products were identified with the following measured total gas yields: carbon monoxide (0.92); acetylene (25.5); propadiene (1.2); methyl acetylene (1,3); 1,2,4-pentatriene (6.2); vinyl cyclopropane (1.6); cyclopentadiene (1.8); and 1,2,3-pentatriene (5.2).

Product yields were monitored as a function of the pressure of butadiene and the concentration of oxygen, neon and xenon additives. Four initial reaction channels are available to the

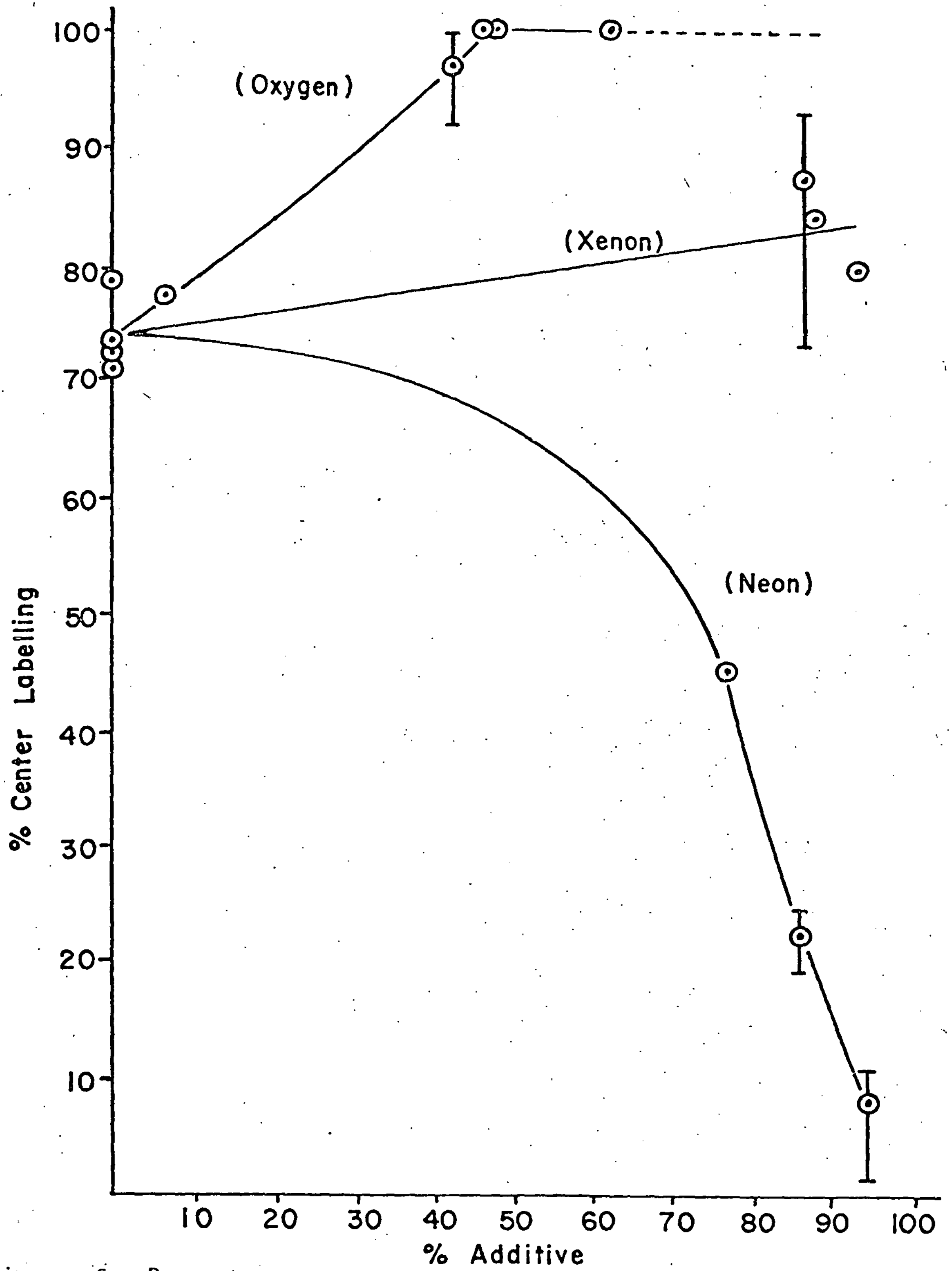


Figure 6. Percent center labelling as a function of additive concentration.

carbon atoms: (i) double bond insertion; (ii) terminal and middle C-H insertion; (iii) π-addition; and (iv) H-abstraction. The primary C_5 intermediates formed from carbon atoms undergoing one of these first three reaction modes may decompose, isomerize, be stabilized, or react further bimolecularly with a second butadiene molecule. Since butadiene has conjugated carbon π-bonds, isomerization of the C_5 intermediate may involve intramolecular reactions with these π-bonds.

Products formed via the higher energy insertion processes (acetylene and 1,2,4-pentatriene)accounted for 74% of the observed product yield which decreased with neon moderation to 37%. Products formed via the lower energy π-addition process (cyclopentadiene and 1,2,3-pentatriene) accounted for 16% of the observed product yield which increased to 51% with neon moderation. Propadiene and methyl acetylene are likely to be formed from methyne reactions, while vinyl cyclopropane was definitely derived from methylene. Results also indicated that vinyl cyclopropane was derived by both higher energy singlet and triplet methylene while lower energy triplet methylene gave rise to cyclopentene instead.

(d) A Ph.D. Dissertation by R. A. Ferrieri. Richard A. Ferrieri completed his Ph.D. degree requirements at the end of August, 1979. The title of his dissertation is "The Effects of Energetics and Electronic Spin States on the Reactions of Carbon Atoms in Non-Thermal Systems," which amounts to 330 pages.

(3) Interactions of Molecular Tritium on Solid Surfaces

During this period, we have initiated various mechanistic studies on the heterogeneous interactions of molecular T_2 on solid surfaces such as Pd supported on active carbon. This work is also partially supported by a small internal grant provided by the Texas A&M Center for Energy and Mineral Resources. The major progress is summarized below.

(a) Temperature Programmed Desorption of Tritium on Catalysts. We have employed the method of temperature programmed desorption of tritium on catalysts such as Pd on active carbon. The results indicate that there are three types of adsorbed tritium. Two of them, being released from the catalyst at temperatures below 300°K, are likely to be adsorbed as T_2 molecules on the surface, bounded by van der Waals forces. The third kind which requires a temperature of about 500°K for desorption, is likely due to adsorbed T atoms on Pd, bounded by chemical bonds. These results agree with those obtained by Cvetanovic and co-workers which they labelled as α-, β-, and γ-hydrogen adsorbed on catalytic surfaces.

(b) "Spilled-Over" Phenonmenon for Supported Catalysts. It is a recently known fact that supported catalysts sometimes give different results from the unsupported catalysts in that certain reactants could be adsorbed on the support and "spill-over" to the active catalyst during a reaction. We have investigated such a phenonmenon by comparing the results from an unsupported paladium black reactor and a reactor with Pd supported on active carbon. Both of them were first saturated with a H_2/T_2 mixture with a known specific activity. Afterwards aliquots of C_2H_6 were injected into each reactor with He as a carrier. In the case of unsupported paladium black, no tritium-labelled C_2H_6 was obtained. However, in the presence of active carbon as a support, tritium-labelled C_2H_6 was continuously observed even after ten aliquots of C_2H_6 were injected. The specific activity of tritium-labelled C_2H_6 decreases from about the same level as the original H_2/T_2 value to about 25% of that value after ten exchanges. In a second set of experiments, aliquots of C_2H_5F were injected through the active carbon supported Pd reactor which was pre-saturated with H_2/T_2. It was observed that the specific activity of tritium-labelled C_2H_5F, the T-for-H exchange product, decreases with the number of torr-ml of C_2H_5F injected. But, suprisingly, the specific activity of tritium-labelled C_2H_6, the T-for-F exchange product, increases with the amount of C_2H_5F eluted through the reactor.

(c) Heterogeneous Hydrogenation and Hydrogenolysis of Fluorocarbons by Molecular H_2. As a background experiment for the interaction of molecular T_2 on solid surfaces, the hydrogenation and hydrogenolysis of several fluorocarbons were studied in a flow catalytic system with H_2 as the carrier gas and Pd on active carbon as the catalyst. Hydrogenation was observed to take place instantaneously. Hydrogenolysis of the C-F bonds took place readily in molecules such as CHF=CHF which contain a maximum of one F atom attached to each carbon, but was essentially absent in molecules such as $CH_2=CF_2$ which contain two or more F atoms attached to the same carbon.

A preprint of this work (DOE/ER/03898-44) is included with this report, which is ready to be submitted to J. Phys. Chem. for publication.

(d) A Detailed Study on the Hydrogenation of CH_2=CHF with H_2/T_2 Mixture over Pd/C. A series of about 30 experiments have been performed on the hydrogenation of CH_2=CHF with H_2/T_2 mixture over Pd/C at 423°K. Helium was used as carrier gas for the flow reactor. In these experiments, the amount of CH_2=CHF used was held constant at about 100 torr-ml, while the amount of H_2/T_2 added varied from 10-1800 torr-ml. The following are the major observations. (a) The mass peak of the hydrogenation product, C_2H_5F, increases sharply while that of the parent compound, CH_2=CHF, decreases sharply when 10-200 torr-ml of H_2/T_2 is used. Beyond this range, essentially all of the CH_2=CHF molecules converted to C_2H_5F. The mass peak of C_2H_6 is always very small. (b) The observed tritium radioactivity in both C_2H_5F and C_2H_6 increases to a maximum at about 300 torr-ml of H_2/T_2, and decreases with further addition of H_2/T_2. The yield of tritium-labelled C_2H_6 remains essentially constant when the amount of H_2/T_2 increases from 500-1800 torr-ml. Quantitatively, the yield of tritium-labelled C_2H_5F is about 50 times higher than that of C_2H_6. (c) The specific activity of C_2H_5F is slightly higher than the original specific activity of H_2/T_2, while that of C_2H_6 is about four times higher. The specific activity of the unreacted CH_2=CHF is also as high as four times that of the original H_2/T_2 specific activity. (d) The specific activity ratio of C_2H_6/C_2H_5F fluctuates in the range of 2-3.

Similar studies have also been performed for $CH_2=CF_2$. Further experiments are required for the elucidation of the reaction mechanism for such heterogeneous systems.

(e) Temperature Effect on the Hydrogenation of Fluorocarbons. Some preliminary studies of the temperature effect on the hydrogenation of CH_2=CHF over Pd/C have been performed with H_2 as the carrier gas for the flow reactor. It was observed that as temperature increases from 348°K to 530°K, the yield of C_2H_5F decreases while that of C_2H_6 increases sharply. Beyond 530°K, (up to 770°K), C_2H_6 is essentially the only product observed.

Studies of the temperature effect on the hydrogenation of fluorocarbons such as CH_2=CHF, C_2H_5F, CH_2=CF_2, and CH_3CHF_2 with H_2/T_2 mixtures over Pd black have also been initiated. Helium was used as the carrier gas for the flow reactor. Preliminary results indicate that as temperature increases, from 350° to 770°K, the mass peak and the observed tritium radioactivity generally increases. As for the specific activities of products, the value for the direct hydrogenation product stays approximately constant, while that of the defluorination products decreases with increasing temperature. The latter observation is probably due to that as temperature rises, the product molecules will be desorbed from the catalytic surface at a faster rate, and as a result, less T-for-H exchange will take place in these product molecules.

(4) Other Progress

(a) A paper entitled "Gas Phase Recoil Phosphorus Reactions-IV: Effect of Moderators on the Abstraction Reactions" has been published by *J. Inorg. Nucl. Chem*. A reprint (DOE/ER/03898-40) is included with this report.

(b) An invited presentation entitled "Unusual Compounds Synthesized *via* Nuclear Recoil Methods" was given at the 178th National ACS Meeting in Washington, D.C, as part of the symposium on "Recent Developments in Biological and Chemical Research with Short-Lived Radioisotopes." The contents of this presentation will be published as a chapter in a book with K.A. Krohn and J.W. Root as editors. A preprint (DOE/ER/03898-43) of this paper is included with this report. It contains certain previously unpublished results such as the formation of ^{11}C-labelled 1,2,3-pentatriene from the reactions of recoil ^{11}C atoms with 1,3-butadiene.

(c) As the initiation of aromatic hydrocarbon studies, the reaction of recoil tritium atoms with benzene and with toluene has been performed. The results are generally in agreement with the published work in the literature.

(d) An effluent combustion type of radio-gas chromatographic set-up has been constructed for the study of high boiling ^{14}C-labelled compounds. It is being modified to analyze high boiling tritium-labelled compounds which are expected to be derived from the reactions of recoil tritium atoms with aromatic hydrocarbons.

(e) The use of ^{14}C-labelled compounds to study the carbohydrate transport and metabolism in seedlings is continued.

(f) Two electrical engineering graduate students are modifying the currently used radio-gas chromatographic set-up. The new design will involve integrated circuits and it will be coupled with a microcomputer unit for data processing.

C. List of Reprints Included with this Report

DOE/ER/03898-40	"Gas Phase Recoil Phosphorus Reactions-IV: Effect of Moderators on the Abstraction Reactions," O.F. Zeck, R.A. Ferrieri, C.A. Copp, G.P. Gennaro, and Y.-N. Tang, J. Inorg. Nucl. Chem., 41, 785-789 (1979).

D. List of Preprints Included with this Report

DOE/ER/03898-41	"Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions," E.E. Siefert, K.-L. Loh, R.A. Ferrieri, and Y.-N. Tang, J. Am. Chem. Soc., in press.	Removed
DOE/ER/03898-42	"Reactions of Silicon Atoms and Silylenes," a chapter in "Reaction Intermediates," Volume 2, (R.A. Abramovitch, ed.), Plenum Publishing Company Limited, (total 107 pages), to be published in 1979, Y.-N. Tang.	Removed
DOE/ER/03898-43	"Unusual Compounds Synthesized via Nuclear Recoil Methods," to be published as a chapter in "Nuclear Applications in Biological, Environmental, and Pure Chemistry," (K.A. Krohn and J.W. Root, eds.), to be published in 1980, Y.-N. Tang.	Removed
DOE/ER/03898-44	"Heterogeneous Hydrogenation and Hydrogenolysis of Fluorocarbons," Y.-N. Tang, E.-C. Wu, and S.D. Witt, J. Phys. Chem., submitting for publication, 1979.	Removed
DOE/ER/03898-45	"Double-Bond Insertion by Energetic Carbon Atoms," R.A. Ferrieri, Y.-N. Tang, and A.P. Wolf, to be submitted to J. Am. Chem. Soc. for publication.	Removed

E. List of Presentations During this Period

(1) "Reactions of Recoil Silicon-31 Atoms with 1,3-Butadiene," E.E. Siefert, R.A. Ferrieri, and Y.-N. Tang, presented at the 177th National ACS Meeting in Honolulu, Hawaii, April, 1979.

(2) "Composition Effect on the Reactions of Monomeric Silicon Difluoride with 1,3-Butadiene," E.E. Siefert, R.A. Ferrieri, K.-L. Loh, and Y.-N. Tang, presented at the 10th International Hot Atom Chemistry Symposium, Loughborough, England, Sept. 1979.

(3) "Unusual Compounds Synthesized *via* Nuclear Recoil Methods," Y.-N. Tang, presented at the 178th National ACS Meeting in Washington, D.C., Sept. 1979.

(4) "Effect of Energy and Electronic States on Recoil ^{11}C Reactions with Ethylene," R.A. Ferrieri, Y.-N. Tang, and A.P. Wolf, presented at the 178th National ACS Meeting in Washington, D.C., Sept. 1979.