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Hot Atom Reactions Involving Multivalent and Univalent Species

Progress Report

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I. Research Personnel

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Post-doctoral Fellows:

Dr. O. F. Zeck (February, 1976)
Dr. E. E. Siefert (April, 1976 - January, 1977)

Graduate Student:

Mr. R. A. Ferrieri
(Mr. Ferrieri is majorly supported by a teaching assistantship from Texas A&M University, but working exclusively researchwise on the project of this contract).

Undergraduate Scholars:

Michael J. Griffin
John F. Copp
Pamela W. Liu

II. A list of publications supported by the U. S. Atomic Energy Commission Contract No. AT-(40-1)-3898:

(1) Recoil Tritium Reactions with Trimethylfluorosilane. A Study on Parameters Affecting Hot Atom Substitution Reactions, J. Phys. Chem., 75, 301 (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 (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 (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 (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 (1972), Y. Y. Su and Y.-N. Tang.

(6) Reactions of Recoil Chlorine Atoms with cis - and trans-Olefins, J. Phys. Chem., 76, 2711 (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 (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., 1973, 637. 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 (1974). G. P. Gennaro and Y.-N. Tang.

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

(11) The Ground Electronic State of Silylene, J. Amer. Chem. Soc., 96, 5967 (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 (1974). W. S. Smith and Y.-N. Tang.

(13) Interaction of Triplet Silicon Defluoride with Paramagnetic Molecules, J. C. S. Chem. Comm., 156 (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 (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 (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., 000 (1976). (in press) R. A. Ferrieri, E. E. Siefert, M. J. Griffin, O. F. Zeck and Y.-N. Tang.

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

Accumulated support level for this project from 1970-1977 is $152,267. The principal investigator is also in a process of preparing the following three review articles as chapters in books where ERDA support will be acknowledged:

(1) "Reactions of Energetic Tritium Atoms with Organic Compounds," a chapter in "Isotopes in Organic Chemistry," Volume 4, Elsevier Scientific Publishing Company, to be published in 1977.

(2) "Reactions of Silicon Atoms and Silylenes," a chapter in "Reaction Intermediates," Volume 1, Plenum Publishing Company Limited, to be published in 1977.

(3) "Reactions of Fluorine-Containing Carbenes and Silylenes," a chapter in "Structure and Reactivities of Fluorine-Containing Compounds," ACS publication, to be published in 1977.

III. Progress Report for the Year 1976-1977

A. Abstract

Work has been performed during this period in the study of three kinds of multivalent hot atoms formed by the nuclear recoil method: silicon-31, phosphorus-32 and carbon-11.

For the recoil ^{31}Si reactions, we have completed the study on the relative reactivities of conjugated dienes towards monomeric $^{31}SiF_2$. The relative reactivities of 1,3-butadiene, trans-pentadiene, cis-pentadiene and 2-methyl-1,3-butadiene towards $^{31}SiF_2$ have been measured as: 1.0:0.89:0.91:1.06 for singlet $^{31}SiF_2$; and as 1.0:0.80:0.52:0.89 for the triplet. The large steric effect detected here between cis- and trans-pentadienes for their reactivities towards triplet $^{31}SiF_2$- donor indicates that a direct 1,4-addition process is possible for such $^{31}SiF_2$ donating complexes. In the process of this study, we have also successfully synthesized 2-methyl-1,1-diflorosilacyclopent-3-ene and its 3-methyl isomer by the co-pyrolysis technique. We have also initiated experiments to evaluate the relative addition efficiencies of $^{31}SiH_2$ towards various conjugated dienes; and to study to H- and F-abstraction mechanism by ^{31}Si atoms.

For recoil ^{32}P reactions, some progress has been made towards evaluating the mechanism of abstraction reactions by recoil ^{32}P atoms in PF_3-PCl_3 system, and the moderator effect for recoil ^{32}P reactions with PF_3-CH_4 mixtures. The possible formation of ^{32}PH, and the formation of ^{32}P atoms via the $^{32}S(n,p)^{32}P$ process have also been explored.

For recoil ^{11}C reactions, major progress has been obtained in the moderator studies of its reactions with 1,3-butadiene. With the successive addition of Ne as a moderator, the yield of acetylene-^{11}C decreased, the yield of cyclopentene-^{11}C increased while those of both 1,2,4-pentatriene-^{11}C and cyclopentadiene-^{11}C went through a minimum. Some progress for the identification of the last unknown ^{11}C-labeled product from this system has also been made.

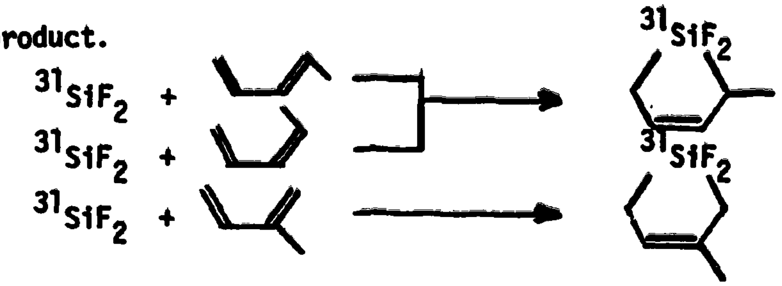
B. Significant Results

The total progress during the period of the past year (1976-1977) is not as productive as the previous year (1975-1976) majorly because of the turnover of the personnel in the research project. Dr. Otto F. Zeck, who has been working diligently on the project for the past three years, left for a good position at Texas Technical University in February, 1976. His substitute, Dr. E. Edwin Siefert, did not arrive until April. Since Dr. Siefert is a gas kineticist with no prior knowledge in handling radioactive material it takes an additional period of time for him to be oriented towards hot atom chemistry and radioactivity. Nevertheless some major progress has been made during this year period on the study of three multivalent hot atoms formed by the nuclear recoil technique: silicon-31, phosphorus-32 and carbon-11. The details of the progress are described below:

(1) Reactions of Recoil Silicon-31 Atoms

Recoil ^{31}Si 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) We have completed the study on the relative reactivities of conjugated dienes towards silicon difluoride. Monomeric $^{31}SiF_2$ was formed in the recoil ^{31}Si systems through the abstraction of F atoms from PF_3. Its reactions with <u>trans</u>- and <u>cis</u>-penta-1,3-diene will both give 2-methyl-1,1-difluorosilacyclopent-3-ene-^{31}<u>Si</u> (2MDFSCP*) as a product, while the reactions of $^{31}SiF_2$ with 2-methylbuta-1,3-diene will give the 3-methyl isomer (3MDFSCP*) of the above product.



(1)

(2)

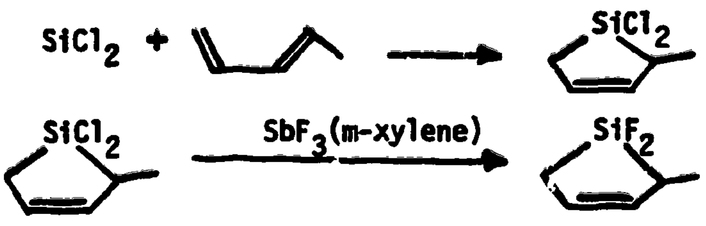
Three types of experiments have been performed. First, butadiene standards and pentadiene samples, with or without the addition of nitric oxide were irradiated simultaneously in separate ampoules using a rotisserie system to normalize the neutron flux. The samples without NO indicate that an equivalent amount of <u>singlet</u> $^{31}SiF_2$ was captured by butadiene and each of the pentadienes, while the NO-addition samples yielded the same conclusion for triplet $^{31}SiF_2$. Moreover, since a four-fold increase in the product yields is always observed with the addition of NO, it was confirmed that for $^{31}SiF_2$ produced by the present nuclear recoil method, the singlet to triplet ratio is about 1:3, irregardless of the type of diene present in the system. Such agreement further strengthens and broadens the previous deduction that singlet $^{31}SiF_2$ reacted with dienes to give the DFSCP*'s directly, but triplet $^{31}SiF_2$ only gave these products in the presence of paramagnetic molecules such as NO.

In the second type of experiments, varying amounts of NO or O_2 were added to both the <u>trans</u>- and <u>cis</u>-penta-1,3-diene samples. In the nitric oxide case, a sharp rise in the 2MDFSCP* specific yield was observed in the range of 0.01 to 0.1% NO concentration, and is followed by a constant plateau which is about 4 times higher than the yield from samples without NO. In the oxygen case, a sharp rise in the 2MDFSCP* specific yield was observed in the low O_2 concentration range which is followed by an eventual decline to the level of non-additive samples. This phenomenon is again consistent with the supposition that triplet $^{31}SiF_2$ reacts with paramagnetic molecules to give $^{31}SiF_2$ donating complexes, while in the oxygen systems, the $^{31}SiF_2$-O_2 complex is further removed by a higher concentration of oxygen.

In the third type of experiments, approximately equal amounts of buta-1,3-diene and one of the pentadienes were mixed so the competition for the available $^{31}SiF_2$ in the system could be observed. From the results measured in both the presence and absence of NO, it is deduced that the reactivities of buta-1,3-diene, trans-penta-1,3-diene, cis-penta-1,3 diene and 2-methylbuta-1,3-diene towards singlet $^{31}SiF_2$ are: 1.0:0.89:0.91:1.06; and towards triplet $^{31}SiF_2$ are: 1.0:0.80:0.52:0.89. From these results, the most surprising feature is that for the addition of $^{31}SiF_2$ donor derived from triplet $^{31}SiF_2$, trans-pentadiene is about 50% more reactive than its cis-counterpart. This observation implies the operation of an 1,4-addition process of the $^{31}SiF_2$-donor to the conjugated double bonds. If such an 1,4-addition process requires the two double bonds to be oriented on the same side of the molecule, it is obvious that the methyl group in the cis-compound will introduce some hindrance to the approach of the reactants, while in the trans-compound such additional hindrance is absent.

(b) We have successfully synthesized 2-methyl-1,1-difluorosilacyclopent-3-ene (2MDFSCP) and its 3-methyl isomer (3MDFSCP) by the co-pyrolysis technique. A flow system has been assembled for the co-pyrolysis experiment. Mixtures of Si_2Cl_6 vapor and vapor of one of the pentadienes were passed through a reaction tube operated at 500°C. The collected dichloro-derivatives were then fluorinated with SbF_3 to yield 2MDFSCP or 3MDFSCP. The reactions involved are illustrated below with trans-pentadiene.

$$Si_2Cl_6 \xrightarrow{\Delta} SiCl_2 + SiCl_4 \qquad (3)$$



(4)

(5)

The IR spectra of the synthesized compounds have very similar features as that of 1,1-difluoro-silacyclopent-3-ene. The preparation of the authentic samples of these compounds is essential for the product identification in the recoil ^{31}Si experiments as described in part (a) of this section.

(c) We have initiated experiments to evaluate the relative addition efficiencies of $^{31}SiH_2$ towards various conjugated dienes. Some preliminary results have already been obtained for the reactions of $^{31}SiH_2$ with trans- or cis-pentadiene in the absence of nitric oxide. These results indicate that an equivalent amount of $^{31}SiH_2$ was captured by 1,3-butadiene and each of these two pentadienes. However, this topic is still a long way from completion.

(d) Some prerequisite work, for the study of H- and F-abstraction mechanism by ^{31}Si atoms have been performed. Since the key to such a mechanistic study is the synthesis of 1-fluorosilacyclopent-3-ene (FSCP) as a carrier, (see the accompanying renewal proposal for detail), large amounts of silacyclopent-3-ene, the starting material for the synthesis of FSCP, has been synthesized and accumulated. A flow system to carry out the FSCP synthesis is presently in a designing stage, where construction of the reaction apparatus will be initiated shortly.

(2) Reactions of Recoil Phosphorus-32 Atoms

Recoil ^{32}P atoms were formed via the nuclear transformation, $^{31}P(n,\gamma)^{32}P$, initiated by thermal reactions from a nuclear reactor. The major achievement of this period is as following:

(a) Some progress has been made to evaluate the mechanism of abstraction reactions by recoil ^{32}P atoms. In the PF_3-PCl_3 system, it is further confirmed that a definite but small yield of $^{32}PF_2Cl$ is observed in the presence of a PF_2Cl carrier. In the PF_3-PH_3 system, neither $^{32}PH_2F$ or $^{32}PHF_2$ was detected. However, this was done in the absence of PH_2F and PHF_2 as carriers. The search of a possible gas chromatographic column for the separation of PH_2D and PHD_2 is also in progress.

(b) The moderator study for recoil ^{32}P reactions with PF_3-CH_4 mixtures has been initiated. Preliminary results indicate that the H-abstraction from CH_4 to give $^{32}PH_3$ decreases sharply with the addition of He, while the F-abstraction from PF_3 to give $^{32}PF_3$ is essentially unaffected.

(c) One preliminary experiment has been performed to explore the possibility of detecting ^{32}PH reactions. Recoil ^{32}P reactions with PH_3-C_2H_4 mixture was carried out in the presence of synthesized phosphiran, PH-CH_2-CH_2, as a carrier. However, no radioactivity accompanied the phoshiran mass peak.

(d) As an alternate source of ^{32}P atoms, the successful formation of ^{32}P-labeled products via the $^{32}S(n,p)\ ^{32}P$ process with high energy neutrons has been firmly established by following the half-life of the radioactive entity being formed.

(3) Reactions of Recoil Carbon-11 Atoms with 1,3-Butadiene

The study of recoil ^{11}C atom reactions is undertaken as a shortrange topic and not as a long range project. The interest is restricted to its reactions with 1,3-butadiene which was aroused by our interesting results obtained in the analogous studies of recoil ^{31}Si atoms with 1,3-butadiene.

Previously, recoil ^{11}C atom reactions with 1,3-butadiene have been carried out by employing the nuclear transformation, $^{12}C(n,2n)\ ^{11}C$, for the formation of the hot atom. Carbon-11 labeled acetylene, allene, 1,2,4-pentatriene, cyclopentadiene, and vinylcyclopropane have been identified as reaction products, and their variations with pressure and with scavenger concentration have been extensively studied. The majority of the observations thus far are generally consistent with the known reaction modes of recoil ^{11}C atoms. The major achievement of this period is as following:

(a) Some moderator studies have been performed for the reactions of recoil ^{11}C atoms with 1,3-butadiene. With the successive addition of Ne as a moderator, the yield of acetylene-$^{11}\underline{C}$ decreased while the yields of both 1,2,4-pentatriene-$^{11}\underline{C}$ and cyclopentadiene-$^{11}\underline{C}$ went through a shallow minimum. However, the most interesting feature is the appearance of cyclopentene-$^{11}\underline{C}$ as a product whose yield increases with moderation. This compound presumably is derived from triplet $^{11}CH_2$ reactions. Studies along this line would be helpful in providing information about the energetics and the electronic states of the reacting entities in the recoil ^{11}C systems.

(b) Serious attempts have been made to identify an unknown product in the recoil ^{11}C reaction with 1,3-butadiene system. This unknown compound was first trapped with liquid nitrogen during a radio-gas chromatographic analysis. It was then passed through a Pd/Charcoal catalyst together with H_2 at various temperatures. N-Pentane, 1-pentene, *trans*- and *cis*-2-pentenes, *trans*- and *cis*-pentidienes were observed as hydrogenation products. From these results, it may be deduced that the likely candidates for this unknown compound are: $CH_2{=}CH{-}C{\equiv}C{-}CH_3$, $CH{\equiv}C{-}CH{=}CH{-}CH_3$ and $CH_2{=}C{=}C{=}CH{-}CH_3$. The first candidate was eliminated by calibration with authentic samples. In order to distinguish between the last two, this unknown compound was passed through a $AgNO_3$ column which is known to completely remove molecules with terminal triple bonds such as 1-butyne. The observation is that there is no decrease in the yield of this compound. However, follow-up experiments demonstrate that conjugated compounds such as $CH{\equiv}C{-}CH{=}CH_2$ are also unaffected by $AgNO_3$ column. As a result, it is still inconclusive at the present stage as to the actual identity of this unknown compound.

C. List of Presentations (1976-1977)

(1) "Reactions of Monomeric Silicon Difluoride with Conjugated Dienes," Y.-N. Tang, O. F. Zeck, R. A. Ferrieri and M. N. Griffin. Presented at the Eighth International Symposium on Fluorine Chemistry, Kyoto, Japan, August, 1976.

(2) "Reactions of Monomeric Silicon Difluoride with Conjugated Dienes," R. A. Ferrieri, E. E. Siefert, M. N. Griffin, O. F. Zeck and Y.-N. Tang. Presented at the 172nd ACS National Meeting, San Francisco, California, August, 1976.

(3) "The Effect of Pressure and Moderator on the Reaction of Carbon-11 Atoms with 1,3-Butadiene," D. A. Baltuskonis, R. A. Ferrieri, O. F. Zeck and Y.-N. Tang. Presented at the 32nd Southwest Regional ACS Meeting, Fort Worth, Texas, December, 1976.

D. List of Preprints Included with this Report

Removed

ORO-3898-28 "Relative Reactivities of Conjugated Dienes towards Silicon Difluoride." R. A. Ferrieri, E. E. Siefert, M. J. Griffin, O. F. Zeck and Y.-N. Tang, J. C. S. Chem. Comm., in press.

E. List of Reprints Included with this Report

Removed

ORO-3898-25 "Effect of Additives on the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene." O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y.-N. Tang, J. Amer. Chem. Soc., 98, 3474 (1976).