ORO-3898-23

Hot Atom Reactions Involving Multivalent and Univalent Species

Progress Report

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Table of Contents

I. Research Personnel

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(These two graduate students are financially supported by Texas A&M University, but working partially on the project of this contract).

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 Spriopentane, 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, in press, scheduled for Nov., 1974. W. S. Smith and Y.-N. Tang.

(13) Gas Phase Recoil Phosphorus Reactions III. - Systematic Study of Hydrogen-Abstraction Reactions, submitted to J. Amer. Chem. Soc. O. F. Zeck, G. P. Gennaro and Y.-N. Tang.

III. Progress Report for the Year 1974-1975.

A. Abstract

Significant progress has been made during this period in the study of recoil silicon-*31* and phosphorus-*32* reactions. A study of recoil carbon-*11* reactions has also been initiated.

For the recoil ^{31}Si systems, we have completed the work designed to ascertain that the ground electronic state of silylene is a singlet. The effect of scavengers on the addition of silicon-*31* difluoride to 1,3-butadiene has also been studied. The observed results can be explained by the supposition that singlet $^{31}SiF_2$ always adds to 1,3-butadiene to give difluorosilacyclopent-3-ene-^{31}*Si*, while triplet $^{31}SiF_2$ forms complexes with scavenger molecules, possessing unpaired electrons. Such complexes then act as $^{31}SiF_2$ donors towards 1,3-butadiene to give the same final product.

For recoil ^{32}P systems, the relative efficiencies of H-abstraction from eight H-containing molecules have been measured and a major controlling parameter for such reactions was found to be bond strength. A significant deduction from these results is that the abstraction of three H atoms from SiH_4 by a ^{32}P atom occurs simultaneously in a single step.

The study of recoil ^{11}C atoms with 1,3-butadiene has been initiated. Carbon-11 labeled 1,2,4-pentatiene, 1-penten-4-yne and 1,3-cyclopentadiene were all observed as products.

B. Significant Results

During the past year period, major progress has been made in the study of two kinds of multivalent recoil atoms: silicon-31 and phosphorus-32. Some preliminary studies of recoil carbon-11 atoms have also been initiated. The significant results obtained from these studies are described in detail 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. During this period, we accomplished our objectives concerning this project by using scavenger and moderator studies to ascertain that the ground electronic state of silylene is a singlet. Evidence has also been presented to show that $^{31}Si^{+}$ ions are not responsible for the formation of silacyclopent-3-ene in the reaction of recoil ^{31}Si with 1,3-butadiene.

However, the major accomplishment in this period concerns the effect of scavengers on the addition of monomeric silicon-31 difluoride to 1,3-butadiene to give difluorosilacyclopent-3-ene-^{31}Si (DFSCP*). With the addition of as little as 0.25% NO, the DFSCP* yield rose sharply by a factor of 4.5 relative to that of pure samples and remained constant in the range of 0.25-20% NO. For the O_2-scavenged system, the DFSCP* yield also increased sharply to a factor of 4 in the presence of 0.04% O_2, but further addition of O_2 decreased the yield until at about 4% O_2, the DFSCP* yield was virtually the same as that of the pure samples. The addition of NO_2 gives results similar to that of NO. All three of these molecules possess unpaired electrons. On the other hand, additives such as N_2O, CO, $CH_3CH{=}CH_2$ and $(CH_3)_2C{=}CH_2$ which do not possess unpaired electrons exhibit no effect on the DFSCP* yield. These observations can be explained by the supposition that singlet $^{31}SiF_2$ always adds to 1,3-butadiene to give DFSCP*, while triplet $^{31}SiF_2$ forms complexes with scavenger molecules possessing unpaired electrons. Such complexes then act as $^{31}SiF_2$-donors towards 1,3-butadiene to give the same final product. In the presence of a high concentration of O_2, the complexes initially formed may undergo further reaction with O_2 to give products other than DFSCP*.

(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 neutrons from a nuclear reactor. The major achievement of this period is the completion of the systematic study of hydrogen-abstraction reactions by recoil ^{32}P. The relative efficiencies of H-abstraction from eight hydrogen-containing molecules (AH_x) have been measured. Their values compared on a per bond basis were: C_2H_2(~0), $C2H_4$(0.5), CH_4(1.5), H_2(1.8), neo-C_5H_{12}(2.8), C_2H_6(2.8), SiH_4(96) and PH_3(162). For these compounds, a plot of the H-abstraction efficiency per bond vs. AH_x bond dissociation energy yielded a good correlation curve identifying bond strength as a major controlling parameter for such reactions. Moreover, the heats of reaction for the $^{32}PH_3$ formation processes with assumed one-, two- or three-step abstraction mechanisms have been evaluated. A comparison with the experimental results indicate that the H-abstraction from SiH_4 is likely to be a one-step process and that although the H-abstraction from PH_3 could be a thermal process, the corresponding abstraction from the hydrocarbon molecules must require energetic ^{32}P atoms.

Other recoil ^{32}P research which has already been undertaken includes a study of the moderating effect on H- and F-abstraction reactions. Recoil

${}^{32}P$ reactions in PH_3-PF_3 and PF_3-PCl_3 mixtures have also been initiated in a search for mixed phosphines such as ${}^{32}PF_2H$, ${}^{32}PClF_2$ as possible products in an effort to determine the abstraction mechansim in these systems.

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

The study of recoil ${}^{11}C$ atom reactions is undertaken as a short-range 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.

The fast neutron irradiation of ${}^{12}C$ in 1,3-butadiene yields ${}^{11}C$ from the nuclear transformation ${}^{12}C(n^*,2n){}^{11}C$. For recoil ${}^{11}C$ reactions with butadiene in the pure form, acetylene was the major product comprising 51% of the total volatile activity. Other ${}^{11}C$-labeled products of significance in this system included: CO(5%), allene(4%), 1,3-cyclopentadiene(12%), 1,2,4-pentatriene(17%) and an additional product tentatively identified as 1-penten-4-yne(11%). With the addition of oxygen to the butadiene samples, ${}^{11}CO_2$(2%) was observed as well as an additional yield of ${}^{11}CO$(9% more). Similar to its formation in other hydrocarbon systems, acetylene-${}^{11}C$ is probably formed by the insertion of a ${}^{11}C$ atom in a C-H bond of butadiene followed by the breaking up of the energetic reaction complex. The formation of 1,2,4-pentatriene is likely to be due to the insertion of carbon atoms into the C=C bond of butadiene similar to the formation of allene-${}^{11}C$ from ethylene. 1-Penten-4-yne-${}^{11}C$ could conceivably result from secondary rearrangement of 1,2,4-pentatriene-${}^{11}C$. Formation of cyclopentadiene-${}^{11}C$ could proceed via one of three possible mechanisms: (1) 1,2-addition of ${}^{11}C$ to butadiene and rearrangement to cyclopentadiene-${}^{11}C$, (2) 1,4-addition of ${}^{11}C$ to butadiene, or (3) insertion of singlet ^{11}C into a C-H bond of butadiene followed by cyclization. In addition, the cyclopentadiene-$^{11}\underline{C}$ yields as a function of oxygen concentration have been studied to provide information as to the nature of the reacting ^{11}C. Tentative results indicate that at least 40% of it could be attributed to reactions involving triplet species.

C. List of Presentations (1974-1975)

(1) "Effect of Scavengers on the Addition of Silicon Difluoride to 1,3-Butadiene," O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y.-N. Tang. Presented at the 167th ACS National Meeting, Los Angeles, California, April, 1974.

(2) "Systematic Study of Hydrogen Abstraction Reactions by Recoil ^{32}P Atoms," O. F. Zeck, G. P. Gennaro and Y.-N. Tang. To be presented at the 30th Southwest Regional ACS Meeting, Houston, Texas, December, 1974.

(3) "Recoil Carbon Atom Reactions with 1,3-Butadiene," O. F. Zeck, D. A. Baltuskonis and Y.-N. Tang. To be presented at the 30th Southwest Regional ACS Meeting, Houston, Texas, December, 1974.

(4) "The Chemistry of Fluorine-Containing Divalent Species," Y.-N. Tang. Presented at the 2nd Winter Fluorine Conference, St. Petersburg, Florida, February, 1974.

D. List of Preprints Included with this Report

ORO-3898-20	"Ground Electronic State of Silylene." Revised version. O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y.-N. Tang. J. Amer. Chem. Soc., 96, 5967 (1974). (Reprints have not been received yet.)
ORO-3898-21	"Consecutive Unimolecular Decomposition Following Recoil Tritium Activation of 1,1-Difluoroethane." Revised version. W. S. Smith and Y.-N. Tang, J. Phys. Chem., 78, in press, scheduled for November, 1974.
ORO-3898-22	"Gas Phase Recoil Phosphorus Reactions III. Systematic Study of Hydrogen-Abstraction Reactions." O. F. Zeck, G. P. Gennaro and Y.-N. Tang, submitted to J. Amer. Chem. Soc.

E. List of Reprints Included with this Report

ORO-3898-14	"Addition of Singlet and Triplet Silylene to Buta-1,3-diene." G. P. Gennaro, Y. Y. Su, O. F. Zeck, S. H. Daniel and Y.-N. Tang, J. C. S., Chem. Comm., 1973, 637.
ORO-3898-15	"Gas Phase Recoil Phosphorus Reactions II. A Detailed Study of Pressure and Scavenger Effects." G. P. Gennaro and Y.-N. Tang, J. Inorg. Nucl. Chem., 36, 259 (1974).
ORO-3898-18	"Relative Efficiencies of Hydrogen Abstraction by Recoil Phosphorus Atoms." O. F. Zeck, G. P. Gennaro and Y.-N. Tang, J. C. S., Chem. Comm., 1974, 52.

Appendix

Abstracts of the four papers described in the "List of Presentations (1974-1975)"

Nuclear Chemistry and Technology

Effect of Scavengers on the Addition of Silicon Difluoride to 1,3-Butadiene

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EFFECT OF SCAVENGERS ON THE ADDITION OF SILICON DIFLUORIDE TO 1,3-BUTADIENE. O. F. Zeck, Jr., Y. Y. Su, G. P. Gennaro and Y.-N. Tang, Department of Chemistry, Texas A&M University, College Station, Texas 77843.

Highly energetic ^{31}Si atoms were produced by the fast neutron irradiation of ^{31}P involving the nuclear transformation $^{31}P(n,p)^{31}Si$. Monomeric silicon difluoride, $^{31}SiF_2$, formed as a result of fluorine abstractions from PF_3, adds to 1,3-butadiene to give difluorosilacyclopent-3-ene-^{31}Si(DFSCP*). In an effort to establish the electronic state of the reacting $^{31}SiF_2$, a scavenger such as nitric oxide or oxygen was added to the system. Experiments showed that with the addition of as little as 0.25% NO, the DFSCP* yield rose sharply by a factor of 4.5 relative to that of pure samples and remained constant in the range of 0.25-20% NO. For the O_2-scavenged system, the DFSCP* yield also increased sharply in the presence of 0.04% O_2, but further addition of O_2 decreased the yield until at ca. 4% O_2, the DFSCP* yield was virtually the same as that of the pure samples. A potential explanation for such behavior was thought to be due to a protective effect served by O_2 in that it removed radiation damaged species. However, experiments in which time was held constant and reactor power was varied from 20-200 KW failed to show that such an effect was operative. Other experimental results will be presented along with possible mechanisms to account for the observed behavior.

Physical Chemistry

Systematic Study of Hydrogen Abstraction Reactions by Recoil ^{32}P Atoms

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SYSTEMATIC STUDY OF HYDROGEN ABSTRACTION REACTIONS BY RECOIL ^{32}P ATOMS. O. F. Zeck, G. P. Gennaro and Y. N. Tang, Department of Chemistry, Texas A&M University, College Station, Texas 77843.

Phosphorus-32 produced from the nuclear transformation $^{31}P(n,\gamma)^{32}P$ has been shown to abstract either fluorine or hydrogen atoms in systems containing PF_3 and various hydrogen containing compounds (AH). Samples covering the entire PF_3/AH composition range were analyzed, but only systems containing 80 mole percent PF_3 were compared so that each system possessed similar moderation characteristics. The relative H- vs. F-abstraction efficiencies (as measured by the specific activity ratio for $^{32}PH_3$ vs. $^{32}PF_3$ on the per bond basis) for the molecules studied was: C_2H_2(0), C_2H_4(0.5), CH_4(1.5), H_2(1.[illegible]), neo-C_5H_{12} (2.0), C_6H_{12} (2.[illegible]), SiH_4(95) and PH_3(162). The abstraction of F atoms in pure PF_3 samples was used as a standard and has been arbitrarily assigned a value of 100. For these compounds, a plot of the H-abstraction efficiency per bond vs. AH bond dissociation energy yielded a good correlation curve identifying bond strength as a major controlling parameter for such reactions. Moreover, the heats of reaction for the ^{32}PH formation processes with assumed one-, two- or three-step abstraction mechanisms have been evaluated. A comparison with the experimental results indicate that the H-abstraction from SiH_4 is likely to be a one-step process and that although the H-abstraction from PH_3 could be a thermal process, the corresponding abstraction from the hydrocarbon molecules must require energetic ^{32}P atoms.

Physical Chemistry

Recoil Carbon Atom Reaction with 1,3-Butadiene

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X J. Phys. Chem.

RECOIL CARBON ATOM REACTIONS WITH 1,3-BUTADIENE. O. F. Zeck, D. A. Baltuskonis and Y.-N. Tang, Department of Chemistry, Texas A&M University, College Station, Texas 77843.

The fast neutron irradiation of ^{12}C in 1,3-butadiene yields ^{11}C from the nuclear transformation $^{12}C(n^*,2n)^{11}C$. For recoil ^{11}C reactions with butadiene in the pure form, acetylene was the major product comprising 51% of the total volatile activity. Other ^{11}C-labeled products of significance in this system included: CO(5%), allene(4%), 1,3-cyclopentadiene(12%), 1,2,4-pentatriene(17%) and an additional product tentatively identified as 1-penten-4-yne(11%). With the addition of oxygen to the butadiene samples, $^{11}CO_2$(2%) was observed as well as an additional yield of ^{11}CO(9% more). Similar to its formation in other hydrocarbon systems, acetylene-^{11}C is probably formed by the insertion of a ^{11}C atom in a C-H bond of butadiene followed by the breaking up of the energetic reaction complex. The formation of 1,2,4-pentatriene is likely to be due to the insertion of carbon atoms into the C=C bond of butadiene similar to the formation of allene-^{11}C from ethylene. 1-Penten-4-yne-^{11}C could conceivably result from secondary rearrangement of 1,2,4-pentatriene-^{11}C. Formation of cyclopentadiene-^{11}C could proceed via one of three possible mechanisms: (1) 1,2-addition of ^{11}C to butadiene and rearrangement to cyclopentadiene-^{11}C, (2) 1,4-addition of ^{11}C to butadiene, or (3) insertion of singlet ^{11}C into a C-H bond of butadiene followed by cyclization. In addition, the cyclopentadiene-^{11}C yields as a function of oxygen concentration have been studied, to provide information as to the nature of the reacting ^{11}C. Results indicate that about [illegible] of it could be attributed to reactions involving triplet species.

THE CHEMISTRY OF FLUORINE-CONTAINING DIVALENT SPECIES

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The best known fluorine-containing divalent species are carbenes such as CF_2, CHF, and CFX where X stands for halogen atoms other than F. The various methods of formation of these species in the gas phase as well as in solution will be summarized. The evaluation of the ground electronic states of these carbenes will be described in detail. The lack of ability to insert into C-H bonds and readiness to add to C=C double bonds will be discussed in the light of the stability of these carbenes. Over-all summaries of the relative efficiencies of their addition to various olefins will be tabulated and compared to those of similar species such as methylene and other halocarbenes.

Other possible fluorine-containing divalent species include SiF_2, SiHF, NF and PF. Their possible existence will be discussed. In particular, the dimerization and polymerization of SiF_2 will be summarized. The reaction of monomeric SiF_2 with 1, 3-butadiene will also be described in detail.