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Hot Atom Reactions Involving Multivalent and Univalent Species

Progress Report

Dr. Yi-Noo Tang
Texas A&M Research Foundation
College Station, Texas 77843

MASTER

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I. Research Personnel

Principal Investigator:
Dr. Yi-Noo Tang
Associate Professor
Department of Chemistry
Texas A&M University

Post-doctoral Fellows:
Dr. O. F. Zeck

Graduate Students:
Mr. D. A. Baltuskonis
Mr. R. A. Ferrieri
(These two graduate students are majorly supported by teaching assistantships from Texas A&M University, but working exclusively researchwise 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., 75, 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, 2186 (1974). W. S. Smith and Y.-N. Tang.

(13) Interaction of Triplet Silicon Difluoride 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, submitted to J. Amer. Chem. Soc., O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y.-N. Tang.

(16) Gas Phase Recoil Phosphorus Reactions IV-Effect of Moderators on Abstraction Reactions, submitting to J. Phys. 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 - 1976 is $122,267.)

III. Progress Report for the Year 1975-1976.

A. Abstract

Progress has been made 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 effect of additives on the reactions of monomeric $^{31}SiF_2$ with 1,3-butadiene and have concluded that recoil ^{31}Si reactions with PF_3 resulted in the formation of both singlet and triplet $^{31}SiF_2$ in the ratio of 1.0:3.3. We have also initiated the study on the addition reactions of $^{31}SiF_2$ to conjugated pentadienes such as trans-1,3-pentadiene, cis-1,3-pentadiene and 2-methyl-1,3-butadiene.

For recoil ^{32}P reactions, we have completed a moderator study on the effect of He, Ne and Ar on the ^{32}P abstraction reactions. It is concluded from these studies that the reaction probability curve for the H-abstraction from PH_3 to give $^{32}PH_3$ covers an extremely wide range but with a threshold somewhat above the thermal energy range, while the reaction probability curve for the F-abstraction from PF_3 to give $^{32}PF_3$ is narrow but with a threshold in or below the thermal energy range. We have also performed mechanistic studies for ^{32}P abstraction reactions with a PF_3/PCl_3 mixture and have concluded that both a single-step simultaneous abstraction and a stepwise abstraction mechansim must be present.

The effect of pressure and scavenger concentration on various products observed in the recoil ^{11}C reactions with 1,3-butadiene has been extensively studied. It is also observed that with the addition of a easily abstractable hydrogen source such as SiH_4 to the system, the acetylene-^{11}C yield decreases sharply while products corresponding to $^{11}CH_2$ reactions increases.

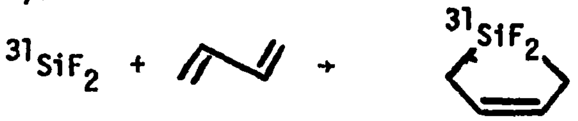
B. Significant Results

During the past year period, we have worked on the reaction of three kinds of multivalent hot atoms formed by the nuclear recoil technique: silicon-31, phosphorus-32 and carbon-11. The major progress obtained from these studies is 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 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 effect of additives on the reaction of monomeric silicon-31 difluoride to 1,3-butadiene to give difluorosilacyclopent-3-ene-^{31}Si (DFSCP*).

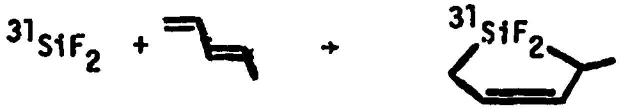


(1)

Additives present in this system exhibited 3 distinctive patterns. One such pattern is exhibited by N_2O, CO, propene and i-butene where the addition of as much as 20% of each of these molecules results in no apparent effect on the observed DFSCP* yields. The second types of additives includes NO and NO_2 which surprisingly increase the DFSCP* specific yield by a factor of 4.3. The third type of behavior is observed with the addition of O_2. In this case, the DFSCP* specific yield also increases sharply by a factor of 4 in the presence of 0.1% O_2, but further addition of O_2 gradually decreases the yield until at about 10% O_2, the DFSCP* specific yield returns to virtually the same as that of the pure sample. Further addition of O_2 beyond the 10% range causes no significant decrease in the observed specific yield. It was concluded from these results that recoil ^{31}Si atom reactions with PF_3

resulted in the formation of both singlet and triplet $^{31}SiF_2$ in the ratio of 1.0:3.3. Singlet $^{31}SiF_2$ reacted with 1,3-butadiene to give DFSCP* directly, but triplet $^{31}SiF_2$ only gave this product in the presence of paramagnetic molecules such as NO, NO_2 or O_2.

(b) Reactions of $^{31}SiF_2$ with conjugated dienes other than 1,3-butadienes have been initiated. Preliminary experiments with trans-1,3-pentadiene, cis-1,3-pentadiene and 2-methyl-1,3-butadiene have been preformed. The following addition reactions of $^{31}SiF_2$ are expected to take place: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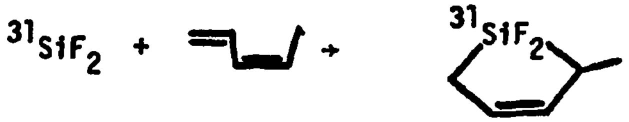
(3)


(4)

Although major radioactivity peaks do appear at retention times where such compounds might be expected, none of these methyl-substituted DFSCP compounds have yet been synthesized to establish the positive identification of these peaks. However, with the assumed tentative identification, these results do indicate that the conjugated pentadienes are more reactive than 1,3-butadiene.

(c) $^{31}SiF_2$ formed by the F-abstraction from PF_5 by recoil ^{31}Si atoms has been shown to have identical reactivity as those derived in the PF_3 systems.

(d) The F-abstraction from PF_3 has been confirmed to be about twice as efficient as the H-abstraction from PH_3 by recoil ^{31}Si atoms.

(e) The construction of a co-condensation system for the production of $(SiF_2)_2$, the dimer of SiF_2, for product identification purpose is in progress.

(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) The use of helium, neon and argon as moderators in recoil ^{32}P systems has shown that the F-abstraction from PF_3 to give $^{32}PF_3$ is totally unaffected by moderation while the H-abstraction from PH_3 to give $^{32}PH_3$ decreases to as low as 30% of the unmoderated value with the addition of 95% neon. The relative moderating efficiencies of these three inert gases in the PH_3 system is observed as: $He < Ar < Ne$. These results coupled with the extremely low yield of $^{32}PF_3$ in the PH_3-PF_3 mixtures prompted us to conclude that the reaction probability curve for the formation of $^{32}PH_3$ is high and covers an extremely wide energy range, but with a threshold somewhat above the thermal energy range. On the other hand, the reaction probability curve for the formation of $^{32}PF_3$ must be narrow, but with a threshold somewhat below the thermal energy range. The moderator studies in the mixture system have just been initiated to obtain information about the relative size and energy range of their reaction probability curves.

(b) Some valuable results have been obtained to answer the question whether ^{32}P atoms abstract univalent atoms one at a time or undergo simultaneous abstraction of a number of univalent atoms. We have formed recoil phosphorus atoms in PF_3/PCl_3 mixtures to examine the abstraction mechanism. If a simultaneous mechanism is valid, the only ^{32}P-labeled products expected from this system should be $^{32}PF_3$ and $^{32}PCl_3$. On the other hand if the reaction proceeded stepwise, the expected products would include $^{32}PF_2Cl$ and $^{32}PFCl_2$ in addition to the above pair. Based on a 1:1 mixture of PF_3 and

PCl_3, if the relative stepwise abstraction efficiencies for F and Cl atoms are identical, the expected ^{32}P product spectrum should be PF_3 (12.5%), PF_2Cl (37.5%), $PFCl_2$ (37.5%) and PCl_3 (12.5%). For a 4:1 F to Cl abstraction efficiency ratio, the expected quantitative product distribution should be: PF_3 (51%), PF_2CL (38%), $PFCl_2$ (10%), PCl_3 (1%). Note that for a stepwise abstraction there is no case where the PF_2Cl yield drops below <u>both</u> that of PF_3 and PCl_3. The actual experimental results are PF_3 (78%), PF_2Cl (6%) and PCl_3 (16%). The amount of PF_2Cl observed, being less than both PF_3 and PCl_3, points to the conclusion that in addition to the stepwise abstraction mechanism, simultaneous multiple abstraction must also be present.

(c) We have very recently initiated the work to study the isotope effect for the reaction of ^{32}P atoms with H_2 and D_2. Preliminary results have shown that their reactivities are essentially identical.

(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 <u>not</u> 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.

Preliminary studies of 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. In the scavenger study, 1,2,4-pentatriene-$^{11}\underline{C}$

and cyclopentadiene-$^{11}\underline{C}$ have exhibited similar oxygen dependence, indicating that they may have been derived from the same intermediate. In the pressure study, the 1,2,4-pentatriene-$^{11}\underline{C}$ yield is the only one to increase with increasing pressure. Besides these studies, some preliminary results have shown that in the presence of a easily abstractable hydrogen source such as SiH_4, the acetylene-$^{11}\underline{C}$ yield decreases sharply while products corresponding to $^{11}CH_2$ reactions increase.

C. List of Presentations (1975-1976)

Abstracts Removed

(1) "Reaction of Multivalent Hot Atoms", Y.-N. Tang, O. F. Zeck, D. A. Baltuskonis, G. P. Gennaro and Y. Y. Su. Presented at the Eighth International Hot Atom Chemistry Symposium, Spa, Belgium, May, 1975.

(2) "Mechanism of Abstraction by Recoil Phosphorus Atoms", O. F. Zeck, R. A. Ferrieri and Y.-N. Tang. Presented at the 170th ACS National Meeting, Chicago, Illinois, August, 1975.

D. List of Preprints Included with this Report

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, submitted to J. Amer. Chem. Soc. Removed

ORO-3898-26 "Gas Phase Recoil Phosphorus Reactions IV. Effect of Moderators on Abstraction Reactions". O. F. Zeck, R. A. Ferrieri, C. A. Copp, G. P. Gennaro and Y.-N. Tang, submitting to J. Phys. Chem. Removed

E. List of Reprints Included with this Report

ORO-3898-20	"Ground Electronic State of Silylene." O. F. Zeck, Y. Y. Su, G. P. Gennaro and Y.-N. Tang, J. Amer. Chem. Soc., <u>96</u>, 5967 (1974).
ORO-3898-21	"Consecutive Unimolecular Decomposition Following Recoil Tritium Activation of 1,1-Difluorethane." W. S. Smith and Y.-N. Tang, J. Phys. Chem., <u>78</u>, 2186 (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, J. Amer. Chem. Soc., <u>97</u>, 4498 (1975).
ORO-3898-24	"Interaction of Triplet Silicon Difluoride with Paramagnetic Molecules." O. F. Zeck, Y. Y. Su and Y.-N. Tang, J. C. S. Chem. Comm., 156 (1975).

Removed