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GAS PHASE ION-MOLECULE CHEMISTRY OF CARBON NITROGEN AND
OXYGEN COMPOUNDS(U) COLORADO UNIV AT BOULDER DEPT OF
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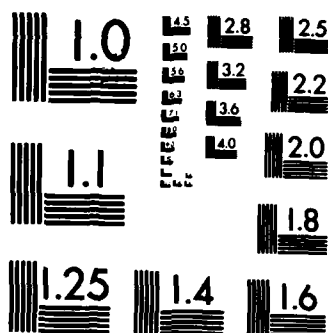
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The gas phase reactions of nitrogen, silicon, sulfur and phosphorus organic compounds with anions have been investigated using the flowing afterglow technique. Studies have been made which compare mechanisms by which first and second row elements react with anions. New methods for the generation of specific anions in the gas phase have been developed. A variety of new types of gas phase ions (PH_2^- , R_5Si^- , $\text{C}_3\text{H}_2\text{NO}_2^-$, etc.) have been prepared and their chemical reactions studied.
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GAS PHASE ION-MOLECULE CHEMISTRY OF CARBON,
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FINAL REPORT

CHARLES H. DePUY
VERONICA M. BIERBAUM

January 29, 1985

U. S. ARMY RESEARCH OFFICE

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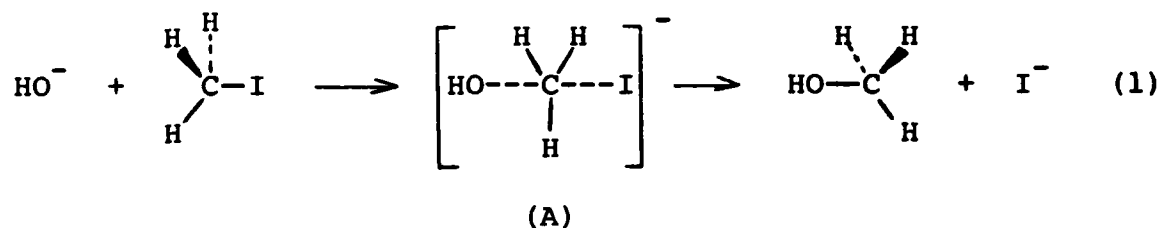
Summary of the Research Program

A. STATEMENT OF THE PROBLEM STUDIED

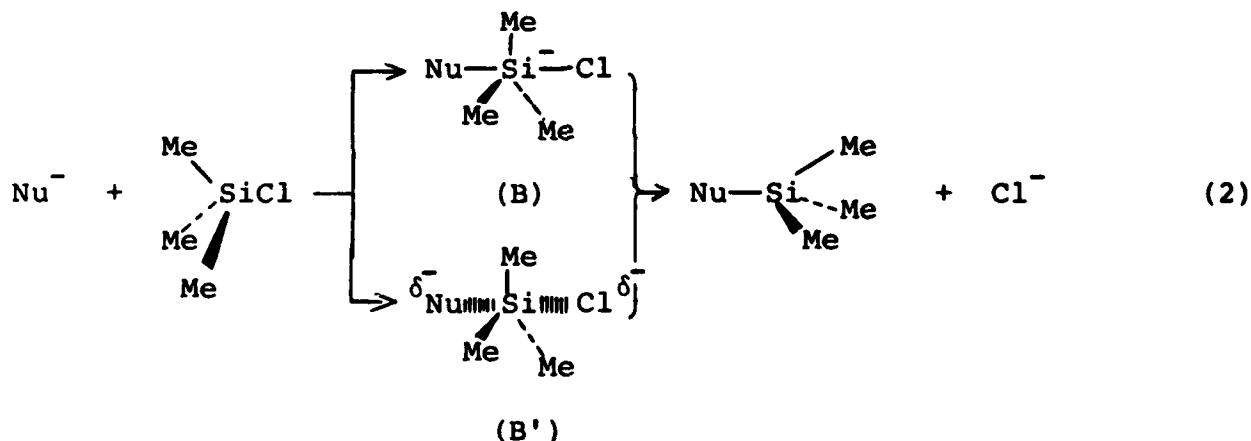
Our main interest in this work was to investigate the mechanisms by which first and second row elements, carbon, oxygen and nitrogen among the former, silicon, phosphorus and sulfur among the latter, react with nucleophiles. A related, secondary objective was to investigate the gas-phase ion chemistry of highly reactive compounds such as peroxides and nitro compounds. Our approach was to examine reaction rates and products for a number of neutral reagents reacting with anions at room temperature in the gas phase. The instruments used were a flowing afterglow (FA) and a selected ion flow tube (SIFT).

B. SUMMARY OF THE MOST IMPORTANT RESULTS

Details of the techniques used, and an overall view of our gas-phase ion chemistry work is contained in three review articles.^{4,11,18} We have made extensive studies of the reactions of silicon^{2,3,6,10,12,20} and phosphorus^{15,21} compounds with ions in the gas phase. One important, and basic, study was to compare and contrast the way an alkyl halide, CH_3I , and a silicon halide, $(\text{CH}_3)_3\text{SiCl}$, react with nucleophiles (H_2N^- , HO^- , H_2P^- , HS^- , etc).¹⁰ For CH_3I the process is the classical $\text{S}_\text{N}2$ displacement reaction proceeding through a single transition state with Walden inversion (eq. 1).



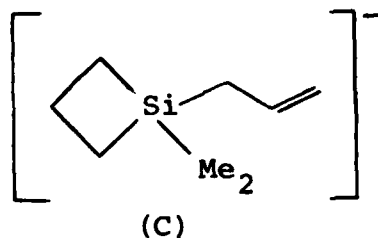
Because carbon can accommodate at most eight electrons in its bonding shell, (A) is a transition structure at the top of an energy hill. Second-row elements, for example Si, P and S, can in principle accommodate more than eight electrons and so the related structure could be either a transition structure (B') or a true intermediate (B). The difference is important because



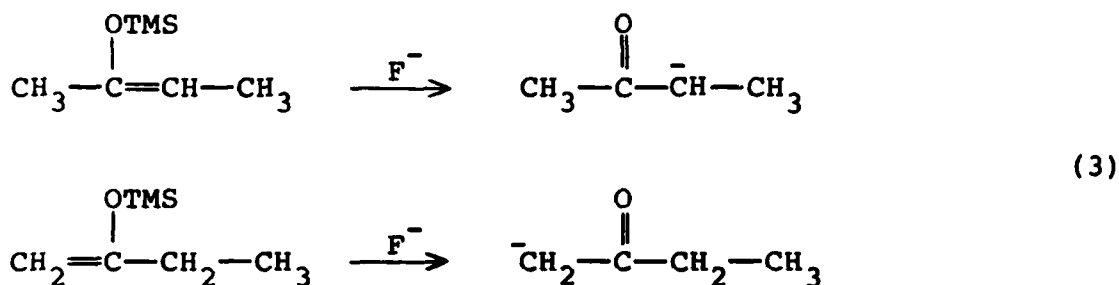
an intermediate can, in principle, be trapped or can undergo, for example, pseudorotation before being converted to product. We were able to show that the rates of reaction of the two halides differed profoundly in the way they responded to nucleophiles, and concluded that silanes did, indeed, react by way of a pentacoordinate intermediate.

In related work,⁶ we studied cyclic silanes and showed that silacyclobutanes formed particularly stable pentacoordinate

ions, including a unique pentaalkylsilyl anion (C). We also



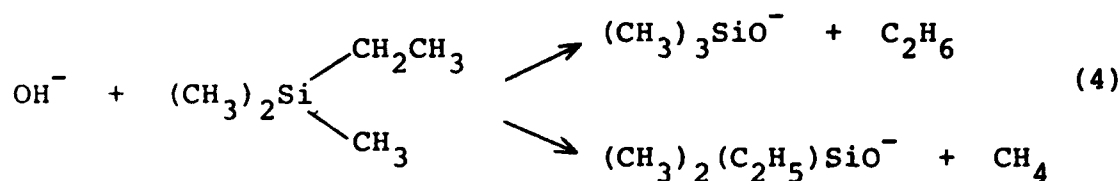
showed¹² how silyl derivatives of the isomeric enol forms of ketones can be used in the gas phase, as they are in solution, to generate regiospecific anions (eq. 3).



We made further use of silane chemistry to attack a problem of fundamental importance to all organic chemistry, the relative acidity of the alkanes.²⁰ While it is well known that a methyl group greatly stabilizes an adjacent carbocation (CH_3CH_2^+ is much more stable than CH_3^+), it is not known whether CH_3CH_2^- is much more stable than CH_3^- . Because of its stabilizing effect on a cation and based on its effect in solution, most organic chemists assume a methyl group will make an adjacent anion less stable. On the other hand, CH_3O^- is much less basic than HO^- , so in the alcohol series a methyl group appears to stabilize a negative charge. The problem is difficult to tackle experimentally because C_2H_5^- has never been prepared in the gas phase;

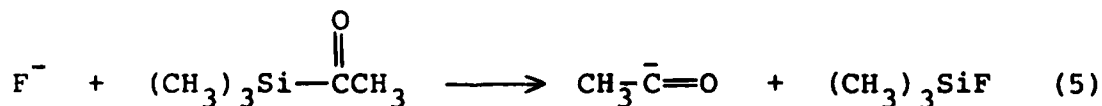
this anion is probably unstable with respect to electron detachment.

We discovered that alkyl silanes react with HO^- in the gas phase to form an alkane and a siloxide (eq. 4). In unsymmetri-



cally substituted silanes, we proposed that the relative amounts of alkane lost are a measure of the relative acidity of RH. For example, because ethane is lost less easily than methane, we believe that the ethyl anion (an intermediate) is more basic than the methyl anion and that, therefore, a methyl group makes an adjacent anion less stable. We are currently extending this study to other substituted silanes.

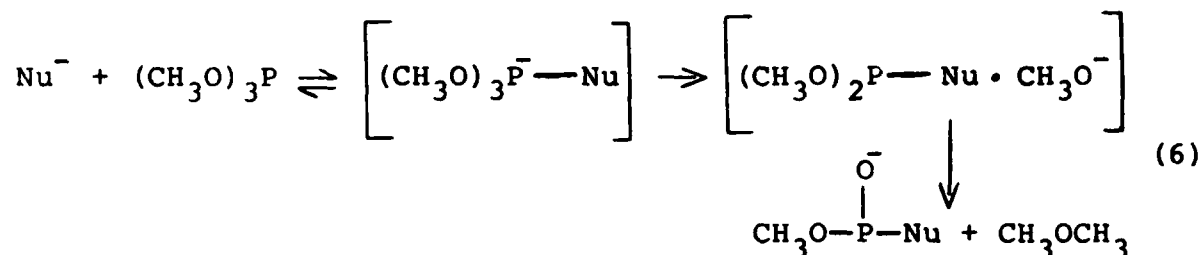
In recent, as yet uncompleted, work we have used silanes to generate the acyl anion (eq. 5). The gas phase chemistry of



this interesting and important anion can now be studied for the first time, and we also are determining (in collaboration with Prof. G. B. Ellison of this department) such crucial physical properties as its proton and electron affinities.

Phosphorus is next to silicon in the periodic table, and we have begun a study of the reactivity of phosphorus compounds. We recently published²¹ the first general study of the ion

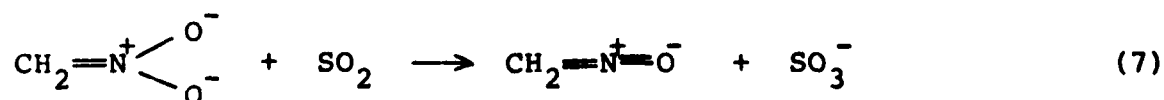
chemistry of trimethyl phosphite (eq. 6). Attack occurs



initially, and reversibly, on phosphorus, leading to displacement on one of the methyl groups.

In the study cited above, the phosphorus reagent served as the neutral electrophile. We also examined¹⁵ the nucleophilic chemistry of phosphorus in PH_2^- , and compared it to that of NH_2^- , which lies just above it in the first row of the periodic table. The phosphide anion is less basic and less nucleophilic than the amide ion.

Nitrites and nitro compounds are among the most reactive organic compounds. We have examined the gas-phase ion chemistry of both types of compounds. In published work^{3,7} we showed how nitrite esters undergo a variety of interesting and useful reactions with carbanions and other nucleophiles. In completed, but as yet unpublished work,²² we have studied nitroalkanes both as electrophiles in their reactions with anions of various types (NH_2^- , HO^-) and as nucleophiles as their anions, formed by proton abstraction. These anions react primarily in the aci-form by oxygen transfer (eq. 7).



In other studies we have determined the electron affinity of SO_2 ^{14,19} and of the important atmospheric radical $\text{HO}_2^\bullet$,⁵ developed a useful gas-phase ion synthesis of sulfides⁹ and studied the formation and reactions of a series of nitrogen and sulfur anions.¹⁷ We have also carried out collaborative studies of photodetachment with the Ellison group,¹⁶ of vibrational energy disposal in ion-molecule reactions with the Leone group,^{1,8} and of the mechanisms of reactions of some nucleophiles with phenyl acetate with the Nibbering and McIver groups.¹³

We have recently generated the novel methanimine anion ($\text{CH}_2=\text{N}^-$) and the 2-azallyl anion ($\text{CH}_2=\text{N}-\text{CH}_2^-$); the basicity, electron-binding energy and reactivity of these species have been studied.²³ We have also recently characterized the fragmentation processes for a variety of organic anions induced by exothermic addition reactions.²⁴

C. ARO SPONSORED PUBLICATIONS

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D. PARTICIPATING SCIENTIFIC PERSONNEL

Charles H. DePuy, Professor of Chemistry, Principal Investigator.

Veronica M. Bierbaum, Senior Research Associate, Co-Principal Investigator.

David Anderson, Post-doctoral research associate.

Stephen Barlow, Post-doctoral research associate.

Kathleen Carrigan, Graduate Student; M.A. awarded, Aug., 1984.

Jonathan Filley, Graduate Student.

Joseph Grabowski, Graduate Student; Ph.D. awarded, May, 1983.

Gary King, Graduate Student; Ph.D. awarded, July, 1980.

Matti Maricq, Post-doctoral research associate.

Robert Squires, Post-doctoral research associate.

Sally Sullivan, Post-doctoral research associate.

Jane Van Doren, Graduate Student.

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