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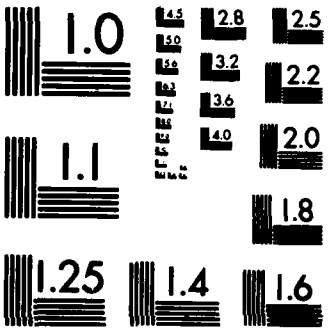

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

During this final contract period, we have completed several projects in the thermochemistry and chemistry of carbene anion radicals, expanded our survey of the gas-phase chemistry of various anionic transition metal complexes, and continued to carry out modifications of our flowing afterglow apparatus which will benefit studies for years to come.

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CHEMISTRY OF ENERGETIC FRAGMENTS: HYPOVALENT RADICALS

Final Technical Report
for the Period 7/1/83 to 2/29/84

Richard N. McDonald

June 25, 1984

U.S. Army Research Office

Contract DAAG29-80-K-0099

Kansas State University
Manhattan, Kansas 66506

Final Report on Contract DAAG29-80-K-0099

for the Period July 1, 1983 to February 29, 1984

A. Papers sponsored by ARO published during this period.

(1) R. N. McDonald and A. K. Chowdhury, "Nucleophilic Reactions of F_3C^- at sp^2 and sp^3 Carbon in the Gas Phase. Characterization of Carbonyl Addition Adducts," J. Am. Chem. Soc., 1983, 105, 7267.

(2) R. N. McDonald, P. L. Schell, and W. D. McGhee, "Oxidative-Addition Processes in the Reactions of $(OC)_4Fe^{\cdot-}$ with XCY_3 Molecules," Organometallics, 1984, 3, 182.

(3) R. N. McDonald, A. K. Chowdhury, and P. L. Schell, "The Series of Tricarbonyliron Hydride Anions $(OC)_3FeH_n^-$ (n = 1-3)," Organometallics, 1984, 3, 644.

B. Papers sponsored by ARO submitted during this period.

(1) R. N. McDonald, A. K. Chowdhury, and W. D. McGhee, "Gas Phase Generation of 1,1,1,3,3,3-Hexafluoroisopropylidene Anion Radical - Proton Affinity and ΔH_f° of $(CF_3)_2C^{\cdot-}$ and $(CF_3)_2CH^-$," J. Am. Chem. Soc., 1984, 106, in press.

(2) R. N. McDonald, A. K. Chowdhury, and P. L. Schell, "Generation and Reactions of $(OC)_3Fe^{\cdot-}$ In a Flowing Afterglow Apparatus," J. Am. Chem. Soc., submitted.

(3) R. N. McDonald and A. K. Chowdhury, "Diversity of Products from Reactions of $(OC)_3Fe^{\cdot-}$ with Some Organic Carbonyl Containing Molecules." Organometallics, submitted.

During this period, three important developments occurred:

(a) The simple method of introducing solid or high-boiling liquids into the flowing afterglow (FA) apparatus by placing the compound in a small beaker and inserting this beaker (attached to a glass rod on a vacuum seal) into the flow tube (see previous report) has been improved. Now the reservoir of

the compound is external to the flow tube for purposes of cooling or heating, and the vapors are swept into the flow tube using a controlled He or Ar flow. This method may allow further modification to enable kinetic measurements with such neutral compounds.

~~(b) We completed studies~~ on the thermochemical properties of $(CF_3)_2C^{\cdot}$ ~~(submitted paper 1),~~ and ~~began~~ studies on its chemistry as well as that of the carbanion $(CF_3)_2CH^-$. We also started investigations of the thermochemistry and chemistry of a new carbene anion radical $CF_3CH^{\cdot}$. These results when com~~pleted under~~ our present NSF grant will be published under joint ARO/NSF sponsorship.

(c) During this period, we continued to survey the capabilities of the FA method in various reaction types using anionic transition metal complexes. I believe this will become a most active area of gas-phase study in the near future. One important accomplishment is our development of a method in the FA to effect reductive-(double-decarbonylation) of transition metal carbonyl complexes, e.g. $Fe(CO)_5$ + "hot" $e^- \rightarrow (OC)_3Fe^{\cdot-}$ + 2CO. Such coordinatively unsaturated species should have a rich chemistry which we hope to define in the future.

The Scientific personnel supported by this project during this period:

Dr. A. K. Chowdhury
P. L. Schell - predoctoral student
M. T. Jones - predoctoral student
W.-Y. Gung - preM.S. student
W. D. McGhee- undergraduate
Dr. R. N. McDonald - PI

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