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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This is the final technical report for an Army Research Office Science and Technology Fellowship. The Fellow was Robert Ryther, a graduate student in the Department of Chemistry at Northwestern University. He worked under the direction of Professor Eric Weitz. His work involved the use of transient infrared diode laser spectroscopy to follow the reaction kinetics, photophysics and photochemistry of radicals and coordinatively unsaturated organometallic species.		

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Final Technical Report for DAAL03-86-G-0036

Introduction

Research Agreement No. DAAL03-86-G-0036 represented an award under the Army Research Office Science and Technology Fellowship Program. The overall objective of this award was the training of a graduate student in areas involving spectroscopic probes of the properties and reactions of transient, energetic, species. The graduate student designated under this program was Robert Ryther. He is currently a fourth year graduate student in the Ph.D. program in the Department of Chemistry at Northwestern University. He joined my research group in January of 1986 and his work has been associated with this project since its inception in April of 1986.

One of the important tools we use in our investigations of transient species is the technique of transient infrared spectroscopy. The probe source in most of our transient infrared spectroscopy experiments is a tunable infrared diode laser. As such Robert has been working with our diode laser based transient absorption apparatus and is now an expert in its operation. In the course of his work, to date, he has been involved with experiments on three systems: reactions of t-butyl radicals, reactions of vinyl radicals, and the reaction of coordinatively unsaturated organometallic species to produce polynuclear organometallic species. As part of his work he has learned a great deal of background information on the chemistry of these important transient species.

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Summary of Results

t-butyl radicals

The first set of experiments involves t-butyl radicals which are generated via ArF excimer laser photolysis of 4,4-dimethyl-1-pentene.¹ There is currently a controversy in the literature regarding the rate of reaction of t-butyl radicals with hydrogen halides and their deuterated counterparts^{1,2}. The primary goal in the literature studies was to determine the heat of formation of t-butyl radicals based on the measured rate constants and accepted rate constants for the reverse reactions. Unfortunately, the two groups that have measured these rate constants obtain values that differ by almost two orders of magnitude from each other. This clearly leaves the value for the heat of formation of t-butyl radicals in doubt. The value of the heat of formation of t-butyl radicals is important in a variety of hydrocarbon combustion schemes which are used to model various combustion processes. We entered this area in an effort to resolve the existing conflict and thus establish an accepted values for these rate constants.

We have now measured the rate of reaction of t-butyl radicals with HBr, DBr and HI³. Formation of the product of reaction, isobutane or d-isobutane, is followed via diode laser transient infrared spectroscopy.³ Our results agree well with those for HBr and DBr as measured by one of the two groups that have reported these values.¹ These measurements should now serve to end the controversy regarding the rates of reaction of t-butyl radical with hydrogen halides and to firmly establish a heat of formation for the radical.

Vinyl radicals

In the experiments in the second area involving vinyl radical reactions, we generate vinyl radicals via excimer laser photolysis of vinyl iodide⁴ and as with t-butyl radicals, we follow the reaction of vinyl radicals via diode laser probing of the product of the reaction.⁴ In virtually all

cases the reaction product is ethylene. To date, we have looked at reactions of vinyl radicals with HCl, DCl, O₂ and vinyl iodide⁴. Reactions involving O₂ were followed via competitive kinetics techniques. We have also measured the activation energy for the reaction of vinyl radicals with H(D)Cl. Robert Ryther will continue these studies and investigate the reaction of vinyl radicals with a number of other hydrogen containing species. Candidates for study are H₂, HBr, H₂O and a variety of alcohols.

Coordinatively Unsaturated Organometallics

In the third set of experiments involving the reactions of coordinatively unsaturated organometallic species we are generating these species via excimer laser photolysis of Fe(CO)₅. By varying photolysis wavelength we can vary the nature of the coordinatively unsaturated species that is produced. Using XeF photolysis we can produce almost exclusively Fe(CO)₃ while ArF photolysis produces almost exclusively Fe(CO)₂.⁵ We have observed the formation of a new polynuclear metal carbonyl via reaction of Fe(CO)₂ with Fe(CO)₃ and are in the process of characterizing its spectroscopy and the kinetics of formation.⁸ As expected, we observe the formation of Fe₂(CO)₈ on reaction of Fe(CO)₃ with Fe(CO)₃ and have studied the nature of the species produced and the kinetics of this reaction.⁶ We have found that the rate constants for reactions that form polynuclear iron compounds in this system are dominated by considerations of spin conservation in the reacting system. This has already been observed by us for the reactions of Fe(CO)_x (x=2-4) with CO. In this system, the reaction of Fe(CO)₄ with CO is slow since the ground state of Fe(CO)₄ is a triplet while the ground state of Fe(CO)₅ is a singlet. The other Fe(CO)_x species have triplet ground states so that their reactions with CO to eventually form Fe(CO)₄ are fast.⁵ From our studies of the formation of polynuclear species, we postulate that the two known forms of Fe₂(CO)₈, the bridged and unbridged forms, differ by one having a singlet ground state while the other has a triplet ground state.⁶

We have also been able to observe the formation of $\text{Fe}_2(\text{CO})_9$ both via reaction of $\text{Fe}(\text{CO})_4$ with $\text{Fe}(\text{CO})_5$ and via a new, heretofore unknown, pathway involving the direct addition of CO to $\text{Fe}_2(\text{CO})_8$.⁶ Rates of reactions for these systems also are compatible with spin control of reactions rates. The data we have obtained on the gas phase spectroscopy of $\text{Fe}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ represents the first gas phase IR data for these species.

We have also been able to use a diode laser to construct a spectrum of the CO stretching region of both species using a number of discrete points to construct the spectrum. To our knowledge this is the first time a diode laser has been used to construct a spectrum of a transient species over 10's of wavenumbers in the infrared. This capability will be very important to our future work involving transient high energy species.

These studies on the formation of polynuclear iron compounds are quite important as they represent initial steps in the formation of cluster compounds. This is the first time that such steps have been studied in real time and detailed microscopic kinetic data has been obtained.

In the course of our work on $\text{Fe}_2(\text{CO})_8$ we have also obtained additional information on the yield of $\text{Fe}(\text{CO})_4$ following excimer laser photolysis of $\text{Fe}(\text{CO})_5$.⁸ This information bears on the nature of the photodissociation process in $\text{Fe}(\text{CO})_5$.

Conclusions

This experimental program has provided Robert Ryther with a firm grounding in the study of energetic and highly reactive species via transient spectroscopy. As such, we feel the objective of the Fellowship Program has been well served. Robert Ryther is now well trained in the techniques of transient spectroscopy which are necessary to investigate highly reactive and energetic species.

It is anticipated that he will graduate from Northwestern with the Ph.D degree some time during the academic year 1989-1990. As discussed above, his remaining work will deal with reactions of vinyl radicals.

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8. R. Ryther and E. Weitz, to be published.

List of Publications

Manuscripts in Preparation

A Transient Infrared Spectroscopy Study of the Reactions of t-butyl Radicals with HBr, DBr and HI, P. Richards, R. Ryther, and E. Weitz.

A Transient Infrared Spectroscopy Study of the Formation of Polynuclear Iron Carbonyls, R. Ryther and E. Weitz.

Diode Laser Probes of Product Distributions in the Excimer Laser Photolysis of $\text{Fe}(\text{CO})_5$, R. Ryther and E. Weitz.

ARO will be provided with copies of these manuscripts when they become available.

Participating Personnel

R. Ryther — Army Research Office Science and Technology Fellow
Ph.D. expected; 6/90