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I. RESEARCH TOPICS

A. The Reaction of Chlorodifluoromethyl Radicals with Molecular Oxygen

Our investigation of the reaction of CF_2Cl with O_2 stems from questions about the atmospheric chemistry of CHF_2Cl , CFCl_3 and CF_2Cl_2 , man made species which are unavoidably released into the atmosphere from their various technological applications. The reaction of CHF_2Cl with OH is a major tropospheric sink for this species,

while CF_2Cl_2 and CFCl_3 , which appear to be inert in the troposphere, are transported into the stratosphere where they can be photolyzed by solar radiation.^{1,2} The dominant primary photochemical process in the approximately 180 to 200 nm wavelength region where stratospheric photolysis occurs is the release of one Cl atom.³

The CF_2Cl radicals produced in the atmosphere by (1) and (2) are expected to react with molecular oxygen, but the reaction is only incompletely understood, and warrants further study.⁴

Our first efforts on this reaction were to investigate the suitability of 1,3-dichlorotetrafluoroacetone (DTA) as a source of CF_2Cl radicals, and to carry out a study of the products of 313 nm photooxidation of DTA.⁵ We have shown that DTA is a clean source of CF_2Cl radicals at 313 nm.

Information on the mechanism of reaction (3) was obtained, including evidence that CF_2ClO radicals can oxidize CO.

A reprint of a paper describing this work is included in the Appendix.

Over the past few months we have been using flash spectroscopy to continue our investigation of the DTA-O₂ photolysis system. Our observations are summarized below.

Mixtures of DTA and Ar photolyzed through Suprasil gave absorption spectra showing the 250 nm band system of CF₂. The $\nu_2' = 2$, $\leftarrow \nu_2'' = 0$ through $\nu_2' = 11$, $\leftarrow \nu_2'' = 0$ bands were observed. The band intensities increased with increasing time from 5 μs through 55 μs , and thereafter slowly decreased by second order kinetics. No CF₂ was present at $t = 0$, and no evidence for transitions originating from $\nu_2'' = 1$ was obtained. Furthermore, no CF₂ could be observed when the flashlamp was fitted with either Vycor or Pyrex tubular filters. These filters restrict DTA photolysis to the 300 nm band, or a portion of that band, respectively. Photolysis at total pressures of 50 torr and 200 torr, with $P_{\text{DTA}}/P_{\text{total}}$ ranging from 0.16 to 0.03 all gave similar results.

When O₂ was added to DTA-Ar mixtures, ClO bands due to a progression originating in $\nu'' = 0$ of the $\tilde{A}^2\pi \leftarrow \tilde{X}^2\pi$ system (265 nm to 292 nm) were obtained. These grew in intensity over a period of approximately 100 μs before slowly decaying over more than 10 ms. Fig. 1 shows the ClO vs. time profile. Weak CF₂ bands were present with the ClO bands, when photolyzing through suprasil and at low O₂ concentrations, but the CF₂ concentration was significantly lower than in experiments without oxygen. The CF₂ absorption band intensity decreased monotonically with increasing O₂ concentration. The use of a Vycor filter completely suppressed the CF₂ spectrum, but still showed a less intense ClO spectrum, while a Pyrex filter inhibited the spectra of both species.

With C₂H₆ added to the reaction mixture (2.5 torr DTA, 5 torr O₂, 15 torr C₂H₆ and Ar to a total pressure of 65 torr) no ClO could be observed, while the

Fig. 1

CF₂ spectrum appeared to be unaffected. A Vycor filter used in conjunction with the C₂H₆ experiments eliminated the CF₂ bands.

A kinetic and mechanistic analysis of these results is very nearly completed. The solid line in Fig. 1 is a numerical simulation using a mechanism consisting of known reactions of Cl, ClO and O₂, as well as reactions including and initiated by

which have previously been suggested in indirect studies.^{5,6}

B. Kinetics of Highly Vibrationally Excited Molecules

R. W. Carr spent the months of April through July in the laboratories of Professor J. Troe at Göttingen, West Germany, while on an academic quarter leave from the University of Minnesota. He became familiar with experiments using coherent antistokes Raman spectroscopy⁷ and laser flash photolysis - absorption spectroscopy⁸⁻¹¹, both of which are being used for direct detection of highly vibrationally excited (~100 kcal/mol) polyatomic molecules. Recent data obtained by the latter technique¹² show that collisional deactivation of toluene, ethylcycloheptatriene and isopropylcycloheptatriene occurs by removal of relatively small amounts of energy. For example, with n-pentane collision partner, the average amount of energy removed per collision, <ΔE>, is 2.2 kcal/mol, 2.2 kcal/mol, and 2.6 kcal/mol, respectively. This is not inconsistent with the correlation of <ΔE> with number of atoms in the excited molecule, which we recently published.¹³ Fig. 2 shows a replot of the correlation including the Göttingen data.

We have been attempting to develop another direct detection experiment for highly vibrationally excited polyatomics. The method requires that at least some of the vibrational energy content of a vibrationally excited molecule can be used to reduce the ionization energy. If the ionization energy were reduced to a value smaller than the ionization potentials of the other species present in

the reaction mixture, it would be possible to selectively photoionize the hot species by proper selection of photoionization wavelength. Observation of the resulting ion current would then provide the desired detection of excited species.

Thus far, progress has been slowed by difficulties with the flashlamp pumped dye laser that is being used as the photochemical excitation source to produce the hot species. These problems are largely solved at present. In the meantime, we used our double ion chamber to make some measurements of photoabsorption cross sections of some alkyl and aryl amines at 160 nm with a Xe resonance lamp. The cross sections showed pronounced maxima as sample pressure was increased from 0.1 torr to 1.0 torr. We are currently attempting to understand the origins of these unexpected maxima before submitting the results for publication.

C. Kinetics of $\text{CH}_2(^1\text{B}_1)$ Reactions.

This experiment uses the flashlamp pumped dye laser as a 400 nm excitation source (BBQ dye) to photolyze diazomethane.

The photon energy is sufficient to produce the second excited state of methylene, $\text{CH}_2(^1\text{B}_1)$, which is detected by its emission in the red.¹⁴ The previously mentioned difficulties with the laser have also slowed progress on this project. During the past few months improvements have been made in RFI shielding, and a new pre-amplifier has been added to amplify the photomultiplier output to the input level required by the boxcar integrator. Some measurements of laser power have been made with a disc calorimeter, and some measurements of the laser intensity-time profile have also been made.

Recently, we have tested the apparatus by measuring the phosphorescence decay of biacetyl excited at 450 nm. With very low intensity excitation ($E \ll 1$ mJ/pulse) biacetyl decay was exponential, and yielded triplet state life-

times in reasonable agreement with literature values. At higher laser intensities, around 25 mJ/pulse, the decay was non-exponential due to triplet-triplet annihilation. We intend to do a brief study of the triplet-triplet process over the next month or two, before moving along to the CH₂ experiments. The high intensity of our laser makes it well suited for such a study.

D. Flash Photolysis with Time Resolved Mass Spectrometry.

The ten year old home built quadrupole mass spectrometer was growing more difficult to operate and maintain. Thus, when the new Extranuclear quadrupole, which was budgeted in our last proposal, arrived at the beginning of the summer, we started fitting the apparatus to accept it. This necessitated fabrication of a metal vacuum housing, and a flange fitted with electrical feedthroughs. These have now been finished, and assembly is under way. Preliminary testing of the mass spectrometer and the redesigned apparatus will commence shortly.

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II. PUBLICATIONS

A. Published

Dynamic Sensitivity Analysis of Chemical Reaction Systems: A Variational Method. C. Seigneur, G. Stephanopoulos, and R. W. Carr, Jr., Chem. Eng. Sci., 37, 845 (1982).

The Photooxidation of 1,3-Dichlorotetrafluoroacetone: Mechanism of the Reaction of CF_2Cl with Oxygen. J. Y. Suong and R. W. Carr, Jr., J. Photochem. 19, 295 (1982).

B. Manuscripts in Preparation

Flash Spectroscopy Study of the Reaction of CF_2Cl Radicals with Molecular Oxygen. D. K. Peterson, R. W. Carr, Jr. and F. K. Smith.

Reduction and Analysis of a Photochemical Smog Mechanism by Dynamic Sensitivity Analysis. C. Seigneur and R. W. Carr, Jr.

III. PERSONNEL

A. Principal Investigator

R. W. Carr, Jr. devoted 25% of full time to research supported by this contract between 1 December, 1981 and 1 April, 1982. He gave 50% of full time from 1 April to 15 June and 100% of full time from 15 June to 15 July, 1982 while on single quarter leave at the University of Göttingen. From 15 September, 1982 to 1 April, 1982 he will spend 20% of full time on this DOE contract.

B. Visiting Scholars

Lu Shaoxing, professor of chemical engineering at the East China Petroleum Institute. Worked on measurements of photoabsorption cross sections and photoionization efficiencies of some amines until 1 May, when he left to spend a year in the Metallurgy Department, University of Utah.

Wu Fushiang joined the research group on 1 September, 1982. He is a mass spectroscopist from the Scientific Instrument Factory, Chinese Academy of Sciences, Beijing. He will spend two years here, working on flash photolysis with time resolved mass spectrometry. Wu's extensive experience with mass spectrometry will be most valuable to the project.

C. Postdoctoral Fellow

Joseph Sabol. Ph.D. from Oklahoma State University (1982). He has considerable experience with construction, maintenance and use of CW pulsed UV and visible laser systems. Sabol is investigating the kinetics of highly vibrationally excited molecules.

D. Graduate Students

Steven B. Moore. Design, construction and experiments in flash photolysis with time resolved mass spectrometry.

Don K. Peterson. Flash spectroscopy study of the reaction $\text{CF}_2\text{Cl} + \text{O}_2$.

Peter Gits. Design, construction and experiments in laser flash photolysis - time resolved luminescence.