INTRODUCTION

The goal of this research is the understanding of elementary chemical and physical processes important in the combustion of fossil fuels. Interest centers on reactions involving short-lived chemical intermediates and their properties. High-resolution, high-sensitivity, laser absorption methods are augmented by high temperature flow-tube reaction kinetics studies with mass-spectrometric sampling. These experiments provide information on the energy levels, structures and reactivity of molecular free radical species and, in turn, provide new tools for the study of energy flow and chemical bond cleavage in the radicals in chemical systems. The experimental work is supported by theoretical and computational work using time-dependent quantum wavepacket calculations that provide insights into energy flow between the vibrational modes of the molecule. The work of group members Fockenberg and Muckerman described in separate abstracts of this volume.

HIGHLIGHTS OF RECENT PROGRESS

(i) Infrared Spectroscopy of C2H5

Much progress has been made in the analysis of the infrared spectrum of C2H5 near 500 cm⁻¹. Hundreds of new vibration-rotation-torsion transitions have been assigned. A new absorption cell based on the Herriott configuration developed for the near-ν2 spectrometers was completed and new spectra recorded, following predictions from the ongoing analysis. Ethyl is the simplest alkyl radical that exhibits the torsional and low-frequency vibrational motions expected to dominate the internal dynamics of all heavier members of this radical class. We had previously recorded part of this spectrum of ethyl and reported a preliminary analysis some time ago. The new data permit good estimates of the torsional barrier in the zero-point level and its change on excitation of the CH2 rocking (umbrella) vibration. Extensive aihito calculations performed in collaboration with Prof. Philip Johnson (SUNY, Stony Brook) guided the spectral analysis and provided physical insight into the coupling between the various motions. Analysis of the spectrum leads to estimates of the torsional barrier of 16.6 cm⁻¹ in the zero-point level, decreasing to 10.3 cm⁻¹ on excitation of the CH2-rocking fundamental. The electronic structure calculations provided estimates of the change in the vibrational frequencies as a function of torsional angle as well as the electronic contribution to the barrier. Together, these were used to provide purely theoretical estimates of the torsional barriers, which are 17.6 cm⁻¹ and 10.9 cm⁻¹ respectively, in excellent agreement with the observations. With the spectroscopy in hand, preliminary measurements of the kinetics of ethyl radical reactions with HBr and O2 were made in collaboration with Craig Taatjes and Eileen Clifford (Sandia, Livermore) using the BNL spectrometer. We plan further measurements at elevated temperatures in the future. Related diode laser measurements, described in more detail below, have been used to calibrate quantum yields for photochemical processes used to generate C2H5 for radical-radical kinetics studies.
(ii) Near Infrared Spectroscopy of Carbenes

Last year, we reported new measurements of the near infrared spectrum of CH2, methylene, by transient frequency-modulated absorption spectroscopy. We have extended the work to the study of HCBr and its deuterated isotopomer, a species that provides an interesting contrast to CH2 because the lowest singlet and triplet states, while separated by energies similar to those in CH2, are reversed in their ordering. In HCBr the singlet is lower by approximately 2000 cm⁻¹. A precise determination of this quantity is one of the goals of this work. Like CH2, HCBr has a singlet band system which extends from the near infrared through the visible and is dominated by a progression in the bending vibrational mode because of the large change in equilibrium bond angle between the two states. Unlike methylene, the rotational structure in the spectrum is free from large perturbations and thus rotational assignment is comparatively straightforward. Vibrionic assignments have been the subject of uncertainty in the past due to an inability to follow the band system down to the origin region where Franck-Condon factors are smaller and spectroscopic sources have been less powerful.

With the advent of tunable near-IR diode laser-based spectrometers, this has changed and we find the origin of the band system is at 11973 cm⁻¹ and 11966 cm⁻¹ for HCBr and DCBr respectively.

(iii) Dynamical Studies of Photoinitiated Reactions

The barrierless unimolecular decomposition of ketene to singlet CH2 and CO has long served as a prototype for ground-state bond-fission reactions. We have observed surprising new experimental results derived from FM Doppler spectroscopy applied to this system in a slit jet expansion. Removal of the effects of the parent energy distribution provides greatly enhanced resolution in the measured Doppler lineshapes. Measurements of CH2 product lineshapes provide clean information on the internal energy distribution of the undetected CO partner fragment. These correlated product distributions can be compared to correlated state measurements from the Wodtke laboratory, and extensive related work from the Moore laboratory. Energy-dependent deviations from statistical or partially adiabatic behavior become more clear in such correlated state distributions, and provide new challenges to and tests of approximate statistical theories widely used to interpolate, extrapolate and even predict rates of relevance to combustion models.

We have used transient FM Doppler spectroscopy in a study of ICN photodissociation at several wavelengths throughout the unresolved UV absorption band. This extensively studied, but still 'incompletely understood, direct dissociation proceeds on several interacting potential energy surfaces. It offers an excellent opportunity for experimental and theoretical investigations of mixed adiabatic and diabatic dynamics, and coherent effects in polyatomic dissociation. Direct comparisons are being made between the semiclassical bipolar moment framework for Doppler profile analysis of polarized photofragments, and a new, explicitly coherent formalism due to Zare and co-workers. Preliminary theoretical work has uncovered an unexpected generality of the older, semiclassical formalism, which apparently makes it able to identify and quantify coherent effects. Our extensive high-resolution measurements of ICN photodissociation by FM Doppler methods will provide a rigorous test of the theoretical comparisons.

(iv) Diode Laser Probes of Combustion Kinetics

Characterization of radical-radical kinetics of combustion-related species using time-of-flight mass
transfer. This model is currently being investigated by taking into account the coupling of the molecular modes with those of a model zeolite framework (15).

CONCLUSIONS

The large changes observed in the $^{13}$C NMR isotropic chemical shifts for CH$_3$CN in H-MFI with temperature are the result of dynamical processes associated with the excitation of low-frequency, vibrational modes. We find no evidence for changes in the chemical structure of CH$_3$CN resulting from either partial or complete proton transfer.

ACKNOWLEDGEMENTS

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15. M. Allavena, private communication.

HYDROCHLOROFUOROCARBON REACTIVITY AND STRUCTURAL CHARACTERIZATION OF ZINC EXCHANGED NAX

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ABSTRACT

Solid-state MAS NMR and synchrotron X-ray powder diffraction have been used to study the reactivity of fluorocarbons and to study the cation positions of Zn$^{2+}$-exchanged NAX. The structure of dehydrated ZnX was refined in the space group P4$_3$3m and zinc cations were located in the SII position in the supercages. Tetrahedral extra-framework aluminum was found (by $^{27}$Al MAS NMR and diffraction) in the center of the sodalite cage. The HFCF-124a (CF$_2$HCF$_2$Cl) over ZnX were studied with NMR and by temperature programmed desorption/mass spectrometry (TPD/MS). The unsaturated products of dehydrofluorination and dehydrochlorination reactions (CF$_2$CFCl and CF$_2$CF$_2$) were the TPD experiments, while saturated products such as HFC-125 (CF$_3$CF$_2$H) were products as observed by $^{19}$F NMR.

INTRODUCTION

Basic zeolites have been proposed as materials for separating different mixtures of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) produced in the environmentally-friendly replacements to the CFCs. However, HCFCs are also decomposed in basic zeolites. For example, the conversion of CHCIF$_2$ (HCFC-22) to CHF$_2$CFCl (HFC-124a) at ambient temperatures, over the molecular sieve 5A, was reported a number of years prior. The HFCs will also undergo dehydrofluorination reactions at higher temperatures. We are studying the adsorption and reactivity of HFCF-124a (CF$_2$HCF$_2$Cl) on cation exchanged zeolites, with solid state NMR, powder diffraction and mass spectrometry, to understand the HFC reactions. We have chosen to study HFCF-124a since this molecule in principle, undergoes dehydrofluorination reactions via a carbenium mechanism. In dehydrochlorinations, the carbonium ion is formed, leading to the production of chlorine. The latter can then react with other molecules in the zeolite framework, leading to the formation of other products. The mechanisms of dehydrofluorination and dehydrochlorination reactions are not well understood, and further investigation is needed to understand the reactivity of these compounds.
as the electrostatic field of the cation in the zeolite increases. Thus, in theory, the preference for dehydrofluorination versus dehydrochlorination may be related to the relative importance of the interactions with the basic oxygen atoms versus with the cations.

EXPERIMENTAL

Zeolite ZnX was prepared by ion-exchanging zeolite NaX (Aldrich Chemicals) with 0.1 M Zn(NO$_3$)$_2$ at a temperature of 60 °C over a period of 48 hours. Dehydration of the exchanged sample was carried out by ramping the temperature under vacuum to 450 °C over 12 hours then holding at 450 °C for an additional 24 hours. HCFC-124a (Dupont) loading levels were established by monitoring the drop in pressure, on exposure of the dehydrated sample to an HCFC atmosphere, with a calibrated vacuum line and an absolute-pressure gauge. ICP elemental analysis, (Galbraith) of the exchanged Zn-X sample gave a composition (weight %) of Na 1.13, Zn 11.76, Si 14.36, and Al 11.56, giving a composition for the unit cell of Na$_{16.17}$Zn$_{11.76}$Si$_{14.36}$Al$_{11.56}$O$_{144}$.

Variable-temperature $^{27}$Al and $^{19}$F MAS NMR experiments were performed with a double resonance Chemagnetics probe, on a CMX-360 spectrometer. Chemical shifts for $^{35}$Na, $^{27}$Al and $^{19}$F are quoted relative to aq. sodium chloride, aq. aluminum sulfate and CCl$_3$F, respectively, as external standards.

X-ray synchrotron powder diffraction data were collected at the beamline X7B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), with a FUJI imaging plate (25 x 400 mm, spatial resolution 100 x 100 μm) mounted perpendicular to the incoming beam. Reactions were performed with a RXM-100 Multifunctional Catalyst Testing and Characterization Machine equipped with a MKS 100C Precision Quadrupole Mass Analyzer.

RESULTS

The room temperature structure of dehydrated ZnX has been refined in the cubic space group Fd3m and agreement factors of $R_w = 2.22\%$ and $\chi^2 = 5.34$ were obtained. A total of 41.4 zinc and 8.6 sodium cations per unit cell were found (Table 1). Sodium cations were only located in the SiI position in the supercage and $^{35}$Na NMR demonstrated the lack of any Si sodium cations. The number of zinc cations is slightly higher than expected from the chemical analysis (37), while the number of sodium cations is lower. This is, most likely, due to the correlation between the occupancies of the Zn and Na SiI positions, due to the overlap of the electron density, and is reflected in the larger e.s.d.s for these sites. It is, therefore, difficult to refine the occupancies of these two sites independently. Zinc cations were located on a split, lower symmetry (32e), Si position, consistent with the previous report for ZnY. Attempts to model the electron density with a true SiI position (16c), resulted in a very low occupancy for this site, and considerable residual electron density on the split position. A difference Fourier map revealed residual electron density at the center of the sodalite cage. This was attributed to extra-framework AlO$_4$ species, which have been previously reported in Zeolite A and in dealuminated X. A resonance at 92 ppm is observed in the $^{27}$Al MAS NMR of dehydrated ZnX, consistent with this species.

Table 1. Occupancies, per unit cell, for the refined cation positions and extra-framework AlO$_4$ ion. Standard deviations for the occupancies are given in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>SI (32e)</td>
<td>5.7(2)</td>
</tr>
<tr>
<td>Zn</td>
<td>Si' (32e)</td>
<td>16.8(3)</td>
</tr>
<tr>
<td>Zn</td>
<td>SiII (32e)</td>
<td>12.7(4)</td>
</tr>
<tr>
<td>Zn</td>
<td>SiIII (32e)</td>
<td>6.2(6)</td>
</tr>
<tr>
<td>Na</td>
<td>SiI (32e)</td>
<td>8.6(16)</td>
</tr>
<tr>
<td>Al</td>
<td>(8a)</td>
<td>1.62(2)</td>
</tr>
<tr>
<td>O</td>
<td>(32e)</td>
<td>5.41(35)</td>
</tr>
</tbody>
</table>

Reactions of HCFC-124a (CF$_3$CFHCl) adsorbed on ZnX were studied with $^{35}$F and $^{27}$Al variable temperature MAS NMR. Reactivity of the HCFC-124a was observed with $^{35}$F MAS NMR after heating the sample for only 3 minutes at 150 °C. Two additional resonances were detected at -141 and -89 ppm which were assigned to HFC-125 (CF$_3$CFH), HFC-123 (CF$_3$CHCl) and HFC-116 (CF$_3$CF$_2$). A much broader, less intense resonance at ca. -126 ppm is observed. The linewidth, and the sidebands observed for this resonance, indicate that it does not come from a gaseous species, and it is assigned to either a longer chain saturated fluoro- or chlorofluorocarbon, or a silicon fluoride species. When the sample is ramped to 225 °C (for 20 mins), this resonance disappears and small broad peak at -168 ppm with associated spinning sidebands is observed. Simultaneously, a noticeable change in the $^{27}$Al NMR spectrum is observed: the resonance from the extra-framework AlO$_4$ species at 92 ppm disappears, and a
broad peak from an octahedral aluminum species at ~0.8 ppm begins to appear. After 45 minutes at this temperature, the intensity of this resonance has increased, presumably as the framework aluminum atoms are attacked and more Al-F species are produced.

Products from TPD studies of samples of excess HFC-124a-loaded ZnX were studied with mass spectroscopy. As the temperature was ramped above 50 °C, the dehydrochlorination and dehydrofluorination products (HFC-1114 (CF2CF2) and HCFC-1113 (CF2CFCI), respectively) were observed in approximately equal amounts as the most abundant products. HCFC-124a was not observed and thus must completely react before desorption. Some HCl was observed, but no HF was seen, the latter presumably attacking the zeolite framework, at the temperatures required for desorption. Only very small concentrations of saturated products were detected.

DISCUSSION

Rietveld refinement of bare partially zinc-exchanged NaX has shown that there are both zinc and sodium cations in the supercages available for gas binding after the sample has been dehydrated. The zinc position lies only 0.53 Å above the plane formed by the 3 O2 atoms in the supercage, so will be less exposed to gas sorbates than the sodium cations which lie 1.1 Å above the O2 plane. Clearly, further ion-exchange is required to remove these sodium cations. The products in an open reaction system (TPD/MS) differed considerably from those detected in the closed reaction vessel (NMR). No unsaturated products were observed with NMR, the major product being HFC-125. Both dehydrofluorination and dehydrochlorination reactions are clearly occurring, as the products from these reactions were observed by MS. The saturated products are proposed to result from the addition of HF or HCl to the unsaturated products. Thus, HFC-125 is formed from the addition of HF to CF2CF2, the product of the dehydrochlorination reaction, the driving force presumably being the formation of the thermodynamically-stable CF3 group. However, fluorine and chlorine substitution reactions cannot be ruled out. Coking is also observed in the sealed systems, which may account for the loss of some of the products of the dehydrohalogenation reactions. Although HCFC-124a dehydrohalogenation reactions were observed at 150 °C, attack of the extra-framework AlO4 species by HF did not occur until higher temperatures. Rapid attack of the framework and further dealumination was observed at 225 °C.

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