Final Report
John F. Hershberger
North Dakota State University
DE-FG02-96ER14645

Abstract

We report study of the chemical kinetics and/or photochemistry of several chemical reactions of potential interest in understanding the gas phase combustion chemistry of nitrogen-containing molecules. Studies completed during the final grant period include determination of quantum yields of the photolysis of HCNO, fulminic acid, a kinetics and product channel study of the reaction of CN radicals with methyl bromide, and study of the products of the reaction of hydroxymethyl radical with nitric oxide.

1) HCNO Photochemistry

The fulminic acid (HCNO) molecule is a higher energy isomer of HNCO, isocyanic acid. HCNO was shown in our laboratory to be a major product channel of the HCCO + NO reaction. Since HCCO had been previously known to be a product of the O + C_2H_2 reaction, HCNO is a possible product in acetylene combustion.

In our laboratory, we used laser photolysis combined with high-resolution infrared laser absorption spectroscopy to probe the kinetics of several radical-molecule reactions involving HCNO, including OH+HCNO, CN+HCNO, O+HCNO, and NCO+HCNO. During these studies, the radical of interest (OH, CN, etc.) was produced by a UV photon from a pulsed Nd:YAG or excimer laser, typically at 248 or 266 nm. Product molecules were then detected and quantified by IR spectroscopy. It was noted over the course of these experiments that several product molecules were produced even in the absence of the radical precursor, indicating that the HCNO molecule was absorbing UV light and undergoing photodissociation. This is not surprising, as there is a substantial literature on HNCO photodissociation. Nevertheless, it represented background signals in the reaction kinetic studies.

More recently, we chose to study the photodissociation of HCNO explicitly, with the goal of determining photolysis quantum yields. This turned out to be a surprisingly complex system, with six possible photodissociation and/or isomerization pathways:

HCNO + hv	→ O + HCN	(1a)
	→ H + NCO	(1b)
	→ OH + CN	(1c)
	→CO + NH	(1d)

→ HNCO (1e)
→ CH + NO (1f)

All six channels are energetically accessible at the 193-nm excimer laser wavelength. At 248 nm, only the first five channels (1a)-(1e) are accessible. Because many of the products are reactive radicals, such as CN, O, etc., that are known from our previous studies to react with HCNO, there is substantial secondary chemistry involved in these experiments. Our approach to simplifying the secondary chemistry was to include an excess of an additional reagent, such as NO or O_2, that would redirect the secondary chemistry. For example, HCN from channel (1a) is fairly easily detectable, but HCN could also arise from the NCO+HCNO reaction if NCO is produced in (1b). We suppressed the NCO+HCNO reaction, however, by including excess NO, resulting in the NCO radicals reacting with NO, without producing HCN. Other secondary reactions could produce HCN, but the use of labeled reagents such as ^{15}NO resulted in the production of $HC^{15}N$ from secondary chemistry, but $HC^{14}N$ from channel (1a). Similar procedures were used to quantify the quantum yields of all of the above photolysis channels. Our results are summarized as follows:

Table 1: Quantum Yields of HCNO Photolysis Products at 248 and 193nm

Product Channel	ϕ(248 nm)	ϕ(193nm)
O + HCN	0.39 ± 0.07	0.38 ± 0.04
H + (NCO)	0.21 ± 0.04	0.07 ± 0.02
CN + OH	0.16 ± 0.04	0.24 ± 0.03
NH + CO	0.19 ± 0.03	<0.22 ± 0.04
HNCO	0.05 ± 0.02	0.02 ± 0.01
CH + NO	0.00	0.21 ± 0.06
Total	1.00 ± 0.15	0.92 - 1.11

The NH+CO product channel at 193 nm was the least well determined, with only an upper limit reported. This was due to secondary chemistry that could not be completely suppressed.

Overall, our results show a total photolysis quantum yield within experimental uncertainties of unity. At least four photolysis channels are active at both wavelengths, as well as a very small quantum yield for isomerization to HNCO. The major difference between the two photolysis wavelengths studies is that the H+NCO channel is significant at 248 nm, but very minor at 193 nm. Also, at the higher photon energy, the sixth channel, CH+NO, becomes active as well.

2) CN + CH_3Br Reaction

The reaction kinetics of the CN radical is of interest due to the role this species plays in combustion and possibly atmospheric chemistry. There is a substantial literature of CN kinetic studies involving reactions with O_2, NO, NO_2, hydrocarbons, etc. Prior to our study, no experimental study of the CN+CH_3Br reaction had been reported. Our interest in this reaction was partly motivated by a recent ab initio study, that predicted that Br atom abstraction (possibly forming BrCN) may compete with hydrogen atom abstraction (which would form HCN), unlike the CN+CH_3Cl reaction, for which hydrogen abstraction is likely the dominant channel. Because we can readily detect and quantify HCN production in a transient kinetics experiment, this reaction was a good candidate for study by our techniques.

First, we measured total rate constants over the temperature range 298-523 K. The data could be fit by an Arrhenius expression:

$k(T) = (2.20\pm0.6)\times10^{-12} \exp(453\pm98/T)$ cm^3 $molecule^{-1}$ s^{-1}

This corresponds to a small but definitely negative activation energy of -3.76±0.8 kJ/mol. This is in contrast to typical hydrogen abstraction reactions, which generally show a significant positive activation energy.

We then measured the product yield of HCN in this reaction, using the CN+C_2H_6 reaction (which proceeds by H abstraction, forming HCN) as a calibration. We found that the HCN yield in the CN+CH_3Br reaction is only 12±2% of that in the CN+C_2H_6 reaction. This confirms the ab initio prediction that other channels (probably Br abstraction to form BrCN) compete with hydrogen abstraction. We attempted to detect BrCN products, but were unsuccessful because the infrared spectral features of BrCN are extremely weak. We were able to estimate an upper limit of ~1% for HBr production. Therefore, although not detected, we propose that BrCN + CH_3 is likely the major product channel of this reaction.

2) CH_2OH + NO Reaction

The spectroscopy and kinetics of CH_2OH, the hydroxymethyl radical, are of interest. This species may be formed by the reaction of a halogen atom such as Cl with methanol. We also recently showed in our laboratory that the CN radical behaves similarly, i.e. CN + CH_3OH results in abstraction of a methyl hydrogen to produce CH_2OH (hydroxymethyl), and not CH_3O (methoxy). We have therefore used the CN+CH3OH reaction as a source of CH_2OH, in order to study the CH_2OH + NO reaction. As is typical in the

radical chemistry of nitrogen-containing small molecules, many product channels are possible:

CH_2OH+ NO	→ $CH_2(NO)OH$	(2a)
	→ HNO + CH_2O	(2b)
	→ HCNO + H_2O	(2c)
	→ HNCO + H_2O	(2d)
	→ HCO + NH_2O	(2e)
	→ NCO + H_2 + OH	(2f)
	→ HCN + 2 OH	(2g)

There was only one previous literature report of the kinetics of this reaction, which quoted a bimolecular rate constant of 2.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 T and 1 atm pressure, along with the suggestion that adduct formation ($CH_2(NO)OH$ or similar) likely dominated the reaction, but there was very little evidence for this assertion. In our laboratory, we cannot measure the total rate constant (we unfortunately don't have infrared lasers at the correct wavelength to detect CH_2OH), but we can probe and quantify many of the possible reaction products. We were able to detect small yields of HNO, which we believe to originate primarily from secondary chemistry. No HCNO, CO, or HCN is detectable (CO would be expected from the NCO+NO reaction from (6f), or the HCO+NO reaction from (6e), if either of these channels were significant). Most surprisingly, we found a substantial transient signal for isocyanic acid, HNCO. These results are rather unexpected, as the most obvious route to bimolecular products would be a single hydrogen migration to form HCNO + H_2O. Ab initio calculations performed by ourselves as well as previous workers have shown, however, that this hydrogen migration involves a high potential energy barrier. We have calculated pathways to other products, and found a fairly complex multi-step but energetically plausible route to HNCO products, channel (2d). Calibration of the experimental transient signal shows that this pathway in relatively minor, with a yield of only ~10% of the overall reaction. The major pathway is probably adduct formation and collisional stabilization, channel (2a). Nevertheless, this was a surprising result, as this pathway had not been previously reported or even proposed.

Publications acknowledging DOE support (2014-present)

1. “Quantification of the 248 nm Photolysis Products of HCNO (Fulminic Acid)”, W. Feng and J.F. Hershberger, J. Phys. Chem. A 118, 829 (2014).

2. “Reaction Kinetics of the CN radical with primary alcohols”, E. Janssen and J.F. Hershberger, Chem. Phys. Lett. 625, 26 (2015).

3. “Reaction Kinetics of the CN radical with methyl bromide”, M. Hodny and J.F. Hershberger, Chem. Phys. Lett. 645, 88 (2016).

4. “Product Channels in the 193-nm photodissociation of HCNO (fulminic acid)”, W. Feng and J.F. Hershberger, Chem. Phys. 472, 18 (2016).

5. “Product Channels in the Reaction of the Hydroxymethyl Radical with Nitric Oxide”, W. Feng, E. Janssen, and J.F. Hershberger, J. Phys. Chem. A, 120, 1145 (2016).