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INVESTIGATION OF THE DISSOCIATION
CHEMISTRY OF -NF_2 COMPOUNDS

Quarterly Summary Report for
February through April 1963

TM-1423

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SUMMARY

During this report period dissociation experiments have been carried out by both thermal and photolytic means. As yet no meaningful thermal-dissociation data have been obtained with the adiabatic-compression apparatus; however, the apparatus appears to be operating properly. Preliminary flash photolysis experiments on NF_3 sensitized by NO indicated no dissociation by light of wave length greater than 2200 Å. Some N_2F_4 experiments are reported which indicate a flash-induced formation of NF_2 which reaches a maximum about 200 μsec after the photolysis flash. It seems likely that this effect is due to flash heating of the sample. A study of the NF_2 spectra in the region of 2600 Å has revealed a previously unreported band structure superimposed on a continuous background. The flash-photolysis cell has been modified to include a concentric flash source around a high-purity quartz cell which permits photolysis with radiation down to 1700 Å or sensitization of the photodissociation by oxygen.

INTRODUCTION

The high-energy propellant possibilities associated with the NF_2 group have led to the development of an extensive new field of chemistry. The synthetic possibilities of now-available reagents such as N_2F_4 , NF_3 , HNF_2 , N_2F_2 , etc. are suggested by the host of new compounds already prepared. It appears, however, that these and similar compounds could be more effectively exploited, both as high-energy oxidizers and as synthesis reagents, if more were known about their dissociation chemistry. It is known, for example, that N_2F_4 is in equilibrium with NF_2 radicals, and appreciable concentrations of NF_2 can be formed with only moderate heating. Mechanisms have been proposed for the subsequent participation of the NF_2 radical in reactions; however, the rate of dissociation of N_2F_4 is not known at various temperatures, nor is the rate of dissociation of the NF_2 radical known. One can conceive of situations where the desired chemistry is frustrated because thermal-dissociation reactions take place more rapidly than displacement or addition reactions, and vice versa. Because of the potential importance of this class of compounds, it seems important to conduct research designed to give fundamental knowledge of the dissociation chemistry of the $-\text{NF}_2$ compounds.

FLASH PHOTOLYSIS

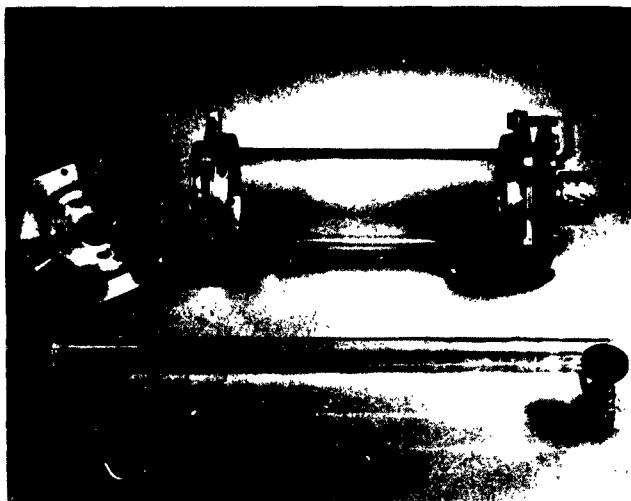
The flash-photolysis and kinetic-spectroscopy studies of the dissociation chemistry of -NF_2 compounds are continuing.

With the apparatus described in previous quarterly reports (1, 2), mixtures of NF_3 and NO were flashed and the spectrum searched from 7000 to 2200 Å. No absorption features were observed other than the (0, 0) band of the NO gamma system at 2270 Å and absorptions in the source flash itself. Rather than pursue the NF_3 dissociation further at this time, it was decided to modify the flash apparatus and study the photolysis of N_2F_4 . Further investigations on NF_3 will be made later.

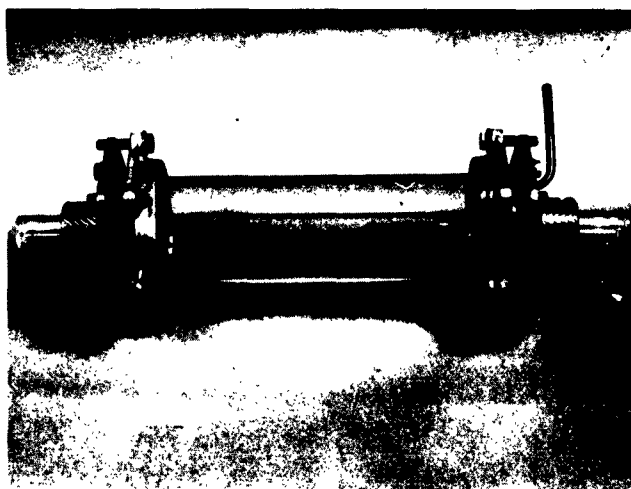
In the device previously described (1, 2), the lower limit to the wavelengths available for photolysis lies near 2000 Å. Thus cut-off is due to both absorption by air and by the quartz used in constructing cells and flash tubes. So that more of the ultraviolet can be used for photolysis, a concentric flash-tube-sample-cell configuration was devised using extremely pure quartz for the sample cell. The sample cell lies along the axis of a large-diameter section of Double Tough Pyrex pipe. Electrodes in the end plates then make the space between the two concentric cylinders effectively into four flash tubes. Figure 1 displays the construction of the device. The electronics of the system are the same as before, and no change has been made in the source flash. It has been found that air at low pressure is satisfactory as a gas for the flash tubes. Figure 2 shows the system in operation. In the current experiments the sample cell is constructed from General Electric high-purity quartz, which has a 10% transmittance at 1700 Å. A cell made from Suprasil (Englehard Industries) is being constructed. Suprasil has a 50% transmittance at 1700 Å.

The new apparatus makes possible the use of oxygen as a sensitizer where one is needed and permits the study of some compounds directly without a sensitizer.

With the new apparatus, studies were started on the photolysis of N_2F_4 . The motivation for shifting to N_2F_4 stems from the fact that it is always in equilibrium with NF_2 radicals, which give rise to an absorption near 2600 Å (3). Thus by studying the effect of photolysis on the absorption in this region, an insight into the photolytic behavior of N_2F_4 may be obtained. In addition, because of the presence of NF_2 as such, the chances of observing NF produced



DISASSEMBLED



ASSEMBLED

FIGURE 1. CONCENTRIC FLASH TUBE AND REACTION TUBE



FIGURE 2. KINETIC-SPECTROSCOPY APPARATUS IN OPERATION

by photolysis of NF_2 are greater than observing it in the photolysis of NF_3 . It should also be pointed out that an examination of the 2600 Å absorption with the plane-grating spectrograph (dispersion 10 Å/mm) is of intrinsic interest since previous studies were made with spectrophotometers of low dispersion (3).

The spectral features in the 2600 Å region were studied at pressures near 100 torr and a variety of delay times. In each exposure the delay was monitored as previously described (2). Both the nature of the absorption features observed and the variation of the absorption with the delay time between the photolysis and source flashes were examined.

The 2600 Å absorption may be described as either:

- (a) three (perhaps more) intense features superimposed on a continuous background, or
- (b) three or more bands with unresolved or predissociated rotational structure; the shading seems to be to the red.

Estimated wavelengths of some maxima are 2574, 2597, 2608 (?), and 2646 Å (?). These numbers are merely estimates. The bands must be better developed before meaningful measurements are made. There is also the "apparent" continuous background which obscures the issue. NO is an impurity in the N_2F_4 and clearly appears at 2270 Å. It is not easy to remove. The possibility of impurity contributions to the features near 2600 Å must still be resolved. In any case there seems no doubt that in general the absorption in this region is due to NF_2 . If the two strongest features (2574 and 2597 Å) are construed as part of a progression, then an upper-state vibrational frequency of about 350 cm^{-1} would be indicated. This would probably be the ν_2 bending frequency. Walch's correlation diagram for AB_2 molecules (4) would predict a progression in the bending mode in the lowest NF_2 electronic transition. Such considerations are, of course, highly tentative at this stage of the investigation. Both a continuum and predissociated rotational structure would indicate photochemical activity for this region of the spectrum.

Figure 3 is a reproduction of a spectrographic plate showing the variation of absorption in the 2600 Å region as a function of delay time between the photolysis and source flashes and thus gives the variation of NF_2 concentration with time. It will be seen that there is no immediate increase in NF_2 concentration but rather a gradual increase, which reaches a maximum near 200 μsec and then starts falling off. The pressure in the sample cell was 105 torr.

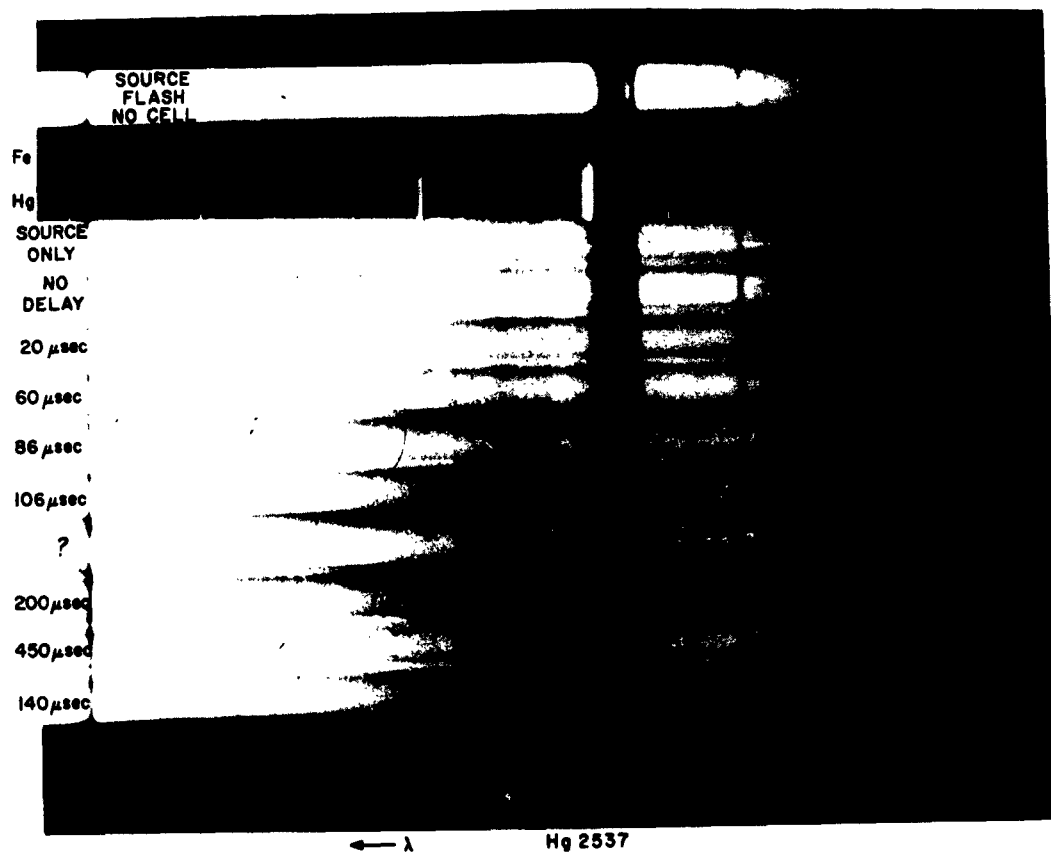


FIGURE 3. FLASH PHOTOLYSIS OF N_2F_4
 SPECTRA VERSUS TIME IN THE 2600 Å REGION

It seems likely that at this pressure the main effect of the photolysis flash with respect to NF_2 is flash heating. The delay in the production of NF_2 is then indicative of the relaxation time for a process in which some species absorbs the flash radiation and degrades it as heat. At present it is not clear if the absorbing species is N_2F_4 at short wavelengths, NF_2 , or the NO impurity.

Work is to continue on N_2F_4 as follows:

1. By varying temperature and pressure, an attempt will be made to obtain better developed structure in the 2600 Å absorption region for spectral measurements.
2. By variations of pressure and temperature as well as the use of inert gas diluents, the mechanism of the flash photolytic formation of NF_2 will be investigated.
3. Under conditions which seem optimum in the light of what is learned about NF_2 , a search will be made for the NF radical spectrum.

Following these studies, attention will be turned to other -NF containing molecules.

THERMAL-DISSOCIATION EXPERIMENTS

The rationale of the thermal-dissociation experiments and a description of the adiabatic-compression apparatus to be used in carrying them out have been described in a previous report (1). At the time of the last report (2) the apparatus was operable; however, photographic registry of the oscilloscope output of the mass spectrometer had not been optimized. Good high-contrast pictures of successive oscilloscope traces are now being routinely obtained with Kodak SO-234 film and a P-16 phosphor on the cathode ray tube driven at 14.1 kv.

A complication appeared at this point which made a further modification of the apparatus necessary. In attempting to carry out experiments on the apparatus, it was observed that the high-pressure nitrogen used to drive the piston in the compressor was leaking past the two O-ring seals on the piston to the extent that the spectra of interest could not be observed, and the pressure in the reaction cylinder was raised to an intolerable level. This problem was solved by adding a third O-ring to the sealing system and machining a pumpable annulus into the space between the two rear O-rings. By this means any nitrogen that leaked by the first seal was pumped away before it could find its way into the

reaction chamber. The effect of the added drag of a third O-ring on the compression speed has not yet been determined, but it is thought to be slight.

A further refinement to the apparatus has been the addition of a 34-liter ballast volume to the ion-source region of the mass spectrometer. The purpose of this volume is to increase the capacity of the spectrometer so that the surge of gas into the spectrometer when the compressor is fired does not cause such a large pressure rise that the spectra become unreadable due to pressure broadening of the mass peaks. The problem of pressure build-up in the ion source has been further aided by taking two side walls off the Bendix ion source of the spectrometer so that molecules streaming into this small volume, where they are ionized by the electron beam, are confined as little as possible. The idea is for molecules streaming out of the reaction cell to pass through the electron beam and then out of the ion source as rapidly as possible, so that there is a minimum possibility of reactions taking place in the ion source and complicating the mass spectra. The mass spectrometer with the adiabatic compressor installed and the auxiliary equipment are shown in Figure 4.

A series of preliminary experiments have been carried out using NF_3 in concentrations up to 7% and compressed to give temperatures of from 350-600°K. These temperatures are of course too low to cause dissociation of NF_3 , but were useful for establishing the proper experimental conditions and procedures for future experiments. It was found that a mixture of 5% NF_3 in helium containing 1% argon gave good mass spectra as shown in Figure 5.

In future experiments we will attempt the dissociation of NF_3 at higher temperatures (the maximum temperature achievable in the compressor will be about 1500°K), and attempts will be made to cause further dissociation of NF_2 produced either from NF_3 or N_2F_4 . It is hoped that this temperature will be adequate to permit the study of the thermal NF_2 dissociation. In the very near future it will be necessary to measure experimentally the temperature actually achieved in the apparatus. This can be done by measuring the concentrations of species formed in reactions that are known to reach equilibrium rapidly at the temperatures of interest and by making kinetic runs on well-studied reactions.

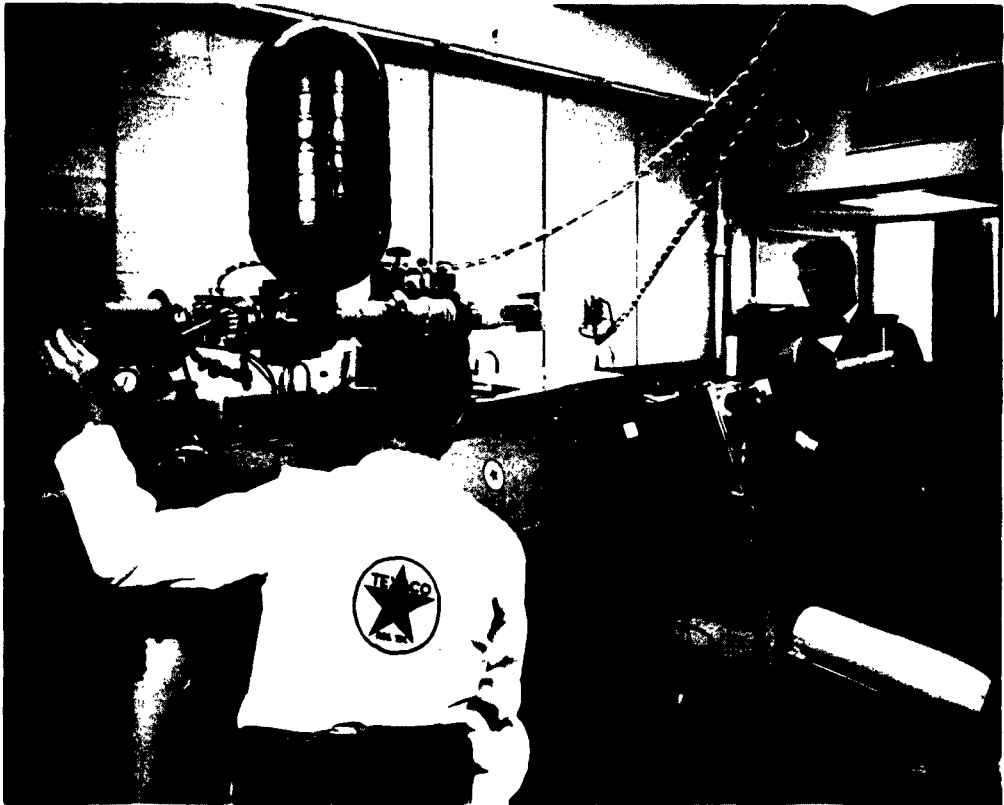


FIGURE 4. ADIABATIC-COMPRESSION APPARATUS

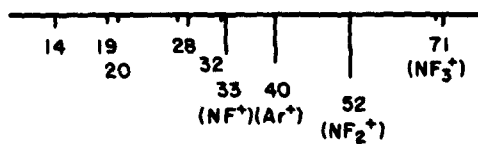
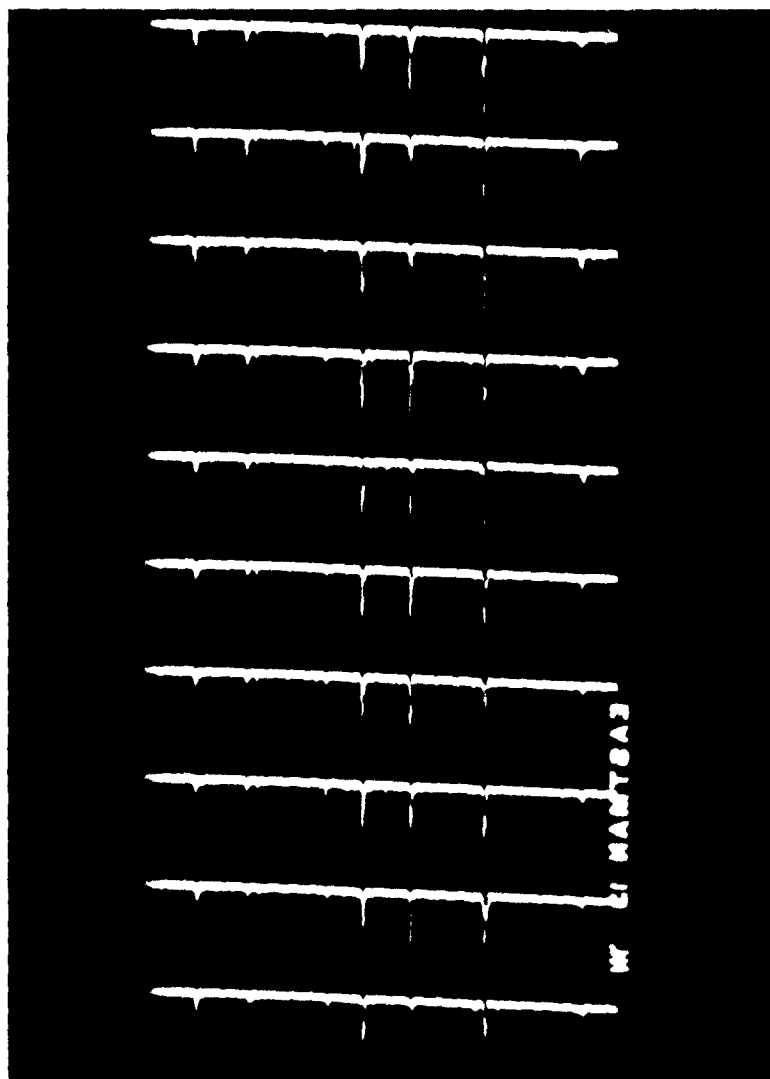


FIGURE 5. SEQUENTIAL MASS SPECTRA OF NF₃

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