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# An Infrared Spectroscopic Study of the Photolytic Decomposition of Methyl Azidoformate[1]

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**Abstract:** Methyl azidoformate has been photolyzed in rare-gas matrices near 4°K and in the solid state at 77°K. Methoxy isocyanate, formaldehyde, and isocyanic acid are proposed as possible photolysis products which are consistent with the infrared spectra. Mechanisms based on band-intensity changes upon prolonged photolysis are also proposed.

Several investigations of the photolysis of the alkyl azidoformates[3-8] have led to a much better understanding of the mechanisms involved. It has become clear that singlet nitrene plays an important role in the photolytic decomposition of the alkyl azidoformates. It has also been discovered recently that these so-called "rigid" azides undergo rearrangement in hydroxylic solvents[9] as well as hydrocarbon solvents.[10]

In an effort to better understand the intermediates involved in the photolysis of the alkyl azidoformates, methyl azidoformate and methyl azidoformate-$d_3$ were photolyzed in rare-gas matrices near 4°K. The decompositions were studied by means of infrared spectroscopy. The methyl species was chosen for study because of its simpler spectrum.

## Experimental Section

Methyl azidoformate-$d_3$ was obtained by introducing 0.056 mol of methanol-$d_3$ into a solution of 30 g of phosgene in 50 ml of anhydrous ether at 0°, refluxing the mixture, then distilling the solvent and excess phosgene over a 12-in. helix-packed column. The pot residue was dissolved in ether and stirred with an aqueous solution of a small excess of sodium azide at 0° for 20 hr. Distillation of the ether and microdistillation of the residue at 40° (55 mm) gave 1.8 g (42% yield) of pure methyl azidoformate-$d_3$. We are greatly indebted to Dr. S. M. A. Hai for carrying out this preparation.

The methyl azidoformate was kept below 0° and protected from light until needed. All manipulations of the methyl azidoformate were carried out in high vacuum. One sample remained in the high-vacuum system at room temperature and unprotected from light for 6 months; no decomposition could be detected spectroscopically.

The methyl azidoformate was mixed with neon and argon at concentrations of 0.25–0.1 mol % azidoformate. The gases were allowed to mix for at least 24 hr before deposition.

Isocyanic acid was prepared according to the method employed by Herzberg and Reid.[11] Formaldehyde vapor was produced by heating paraformaldehyde (polyoxymethylene) until the required pressure of the vapor was obtained.

The cryostat employed was an Andonian Modular Design[12] with rotatable tail section designed to fit into the optical system of the Beckman IR-9 spectrophotometer. Temperature control was accomplished using the Teflon-plug technique[13] in conjunction with a 20-ohm resistance heater located immediately above the deposition-window frame. The temperature was measured with a Cryo resistor[14] mounted on the deposition-window frame. The temperature of the sample when in the infrared beam was estimated to be 6°K.

The photolysis was carried out through a fused-quartz window with a General Electric H4AB low-pressure mercury lamp from which the Pyrex envelope had been removed. The beam was focused with a spherical mirror so that the focal point was just behind the deposition window, thereby allowing the entire sample area to be exposed to the radiation.

All spectra were obtained with a Beckman IR-9 spectrophotometer. Under the experimental conditions, the probable error in the wave number is estimated to be ±1 cm$^{-1}$ throughout the spectral range (400–4000 cm$^{-1}$).

## Results

Comparison of the gas-phase and matrix-isolation infrared spectra of methyl azidoformate shows that the same number of bands with the same relative intensities are present in both the gas-phase and matrix-isolation spectra. The spectra of methyl azidoformate and its photolysis products are the same in both neon and argon matrices, except for small solvent shifts. For this reason, only the vibrational wave numbers of the neon-isolated samples are reported. The wave numbers of all new bands appearing in the neon matrix are listed

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(2) (a) Texas Tech University; (b) New Mexico State University.

(3) W. Lwowski and T. Mattingly, Jr., *Tetrahedron Lett.*, 277 (1962).

(4) R. S. Berry, D. Cornell, and W. Lwowski, *J. Amer. Chem. Soc.*, **85**, 1199 (1963).

(5) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *ibid.*, **85**, 1200 (1963).

(6) W. Lwowski, T. W. Mattingly, Jr., and T. J. Maricich, *Tetrahedron Lett.*, 1591 (1964); J. Hancock, *ibid.*, 1585 (1964).

(7) W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

(8) D. W. Cornell, R. S. Berry, and W. Lwowski, *ibid.*, **87**, 3626 (1965).

(9) W. Lwowski, R. DeMauriac, T. W. Mattingly, Jr., and E. Scheiffele, *Tetrahedron Lett.*, 3285 (1964).

(10) R. Puttner, W. Kaiser, and K. Hafner, *ibid.*, 4315 (1968).

(11) G. Herzberg and C. Reid, *Discuss. Faraday Soc.*, **9**, 92 (1950).

(12) Andonian Associates, Waltham, Mass.

(13) R. Savoie and A. Anderson, *J. Chem. Phys.*, **44**, 548 (1966).

(14) Cryo Cal, Inc., Riviera Beach, Fla.

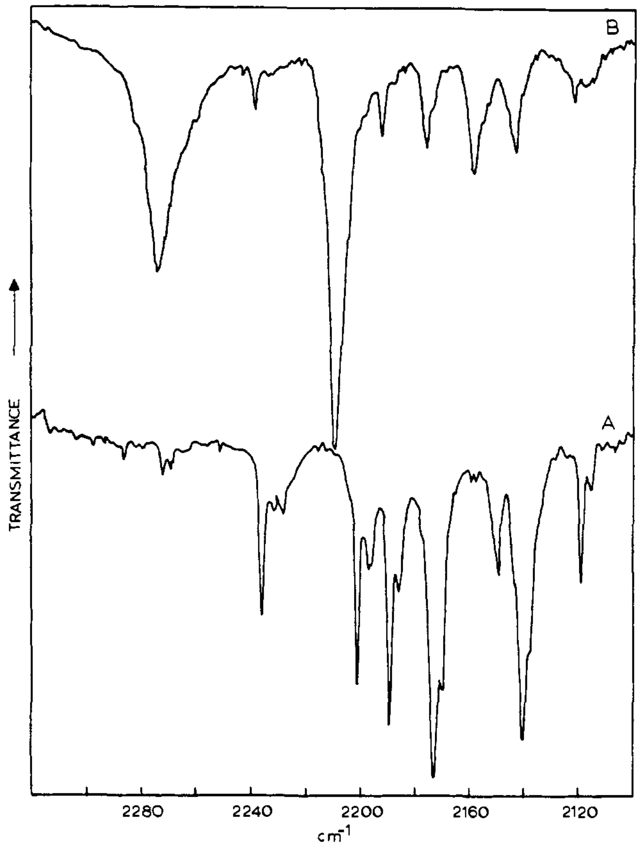

Figure 1. Infrared spectra of $N_3COOCH_3$ in neon (A) before and (B) after photolysis at 6°K.

in Table I along with relative intensities as observed after 1 hr of photolysis. Typical spectra are shown in Figure 1. It was observed that upon prolonged photolysis (up to 7 hr) some bands increased in intensity while others decreased. This effect was more pronounced in the spectra of the deuterated samples. However, it is believed that the ease with which this effect is observed is more a function of the amount of sample deposited than a characteristic of the deuterium content of the sample. The effect was difficult to observe in some of the extremely weak bands (90–100% transmittance), especially in the spectra of photolyzed $N_3COOCH_3$. For this reason not all bands are listed as increasing or decreasing upon photolysis.

**Table I.** New Bands Observed after Photolysis of $N_3COOCH_3$ and $N_3COOCD_3$ in a Neon Matrix

| $N_3COOCH_3$, cm$^{-1}$ | $N_3COOCD_3$, cm$^{-1}$ |
|---|---|
| 3318$^a$ m | 2495$^a$ w |
| 3293$^a$ vw | 2474$^a$ vvw |
| 2273$^a$ s | 2251 vvw |
| 2209$^b$ vs | 2231$^a$ m |
| 2158$^b$ m | 2199$^b$ vs |
| 2143$^{a,c}$ w | 2196$^b$ sh |
| 2115 vw | 2142$^a$ vvw |
| 1735$^a$ w | 2109$^b$ w |
| 1597 vvw | 2093$^a$ vw |
| 1560 vvw | 2181$^b$ vw |
| 1504 vw | 2072$^b$ vvw |
| 1481 vw | 1688$^a$ vw |
| 1462 vvw | 1560$^a$ vvw |
| 1240 vvw | 1125$^b$ w |
| 1052$^b$ m | 1016$^b$ vw |
| 1030 vvw | 995$^a$ vvw |
| 829$^b$ w | 974$^b$ w |
| 662$^b$ vw | 792$^b$ w |
| 518 vvw | 544$^a$ vvw |
|  | 536$^a$ vvw |
|  | 517$^b$ vvw |

[a] Increases in intensity upon prolonged photolysis. [b] Decreases in intensity upon prolonged photolysis. [c] Overlapped by strong 2142-cm$^{-1}$ $N_3COOCH_3$ band.

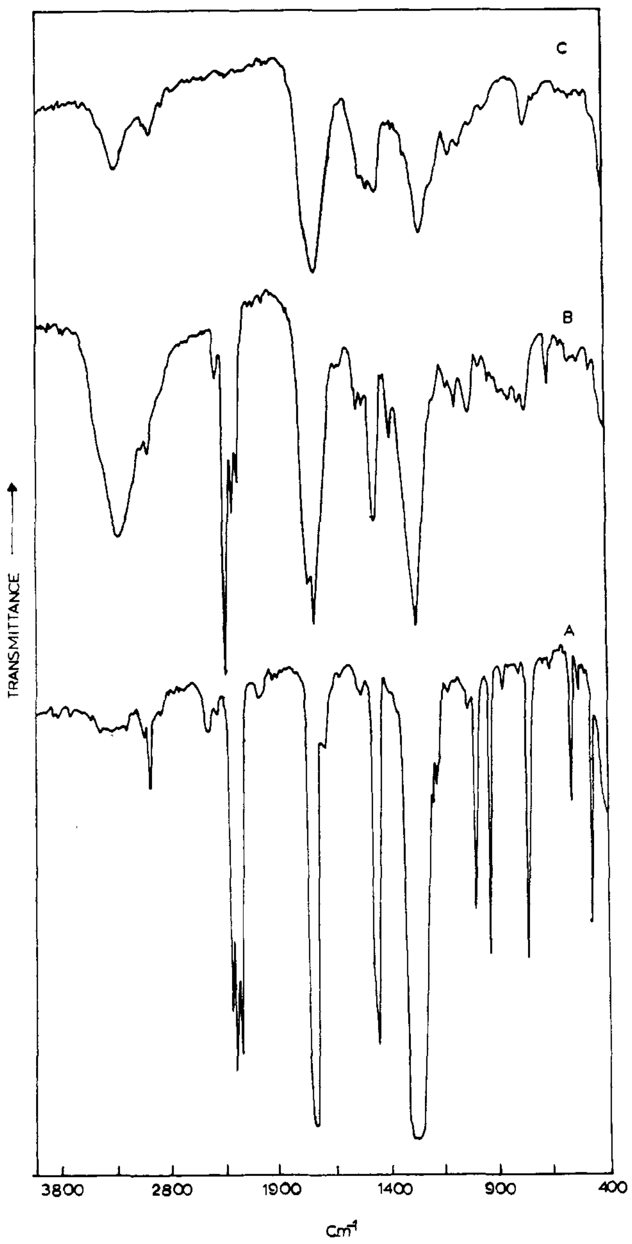

Figure 2. Infrared spectra of solid $N_3COOCH_3$ (A) before and (B) after photolysis at 77°K and after photolysis at 300°K (C).

The spectra of solid methyl azidoformate at 77°K and of its photolysis products at 77 and 300°K are shown in Figure 2. The spectrum of the photolysis products was obtained after photolyzing for 20 hr. Volatile products obtained from the cryostat upon warm-up were trapped with liquid nitrogen. The infrared spectra of these volatile products showed them to be $H_2O$, $CO_2$, and $N_3COOCH_3$.

## Discussion

**Identification of Photolysis Products.** There are apparently two reactions occurring during the photolysis. The initial reaction leads to a product which itself slowly undergoes photolysis to a final product. An exhaustive search of the literature revealed no reported possible products with absorption in the region of 2210 $cm^{-1}$. The possible products are limited because of the nature of the matrix-isolation experiment. At the concentrations employed in our experiments, it is assumed that the methyl azidoformate molecules are trapped as isolated monomers in the matrix. The fact that spectra obtained before and after photolysis are the same for the 0.25 and 0.10 mol % samples lends support to this assumption. Certainly clusters of two or more molecules do exist in the matrix, but their concentrations are not sufficient to be detected in the spectra. Furthermore, the molecules are trapped in their matrix "cages" so that diffusion through the matrix is limited mainly to atoms. Annealing of the argon matrix at ~40°K did not change the spectra.

Not being able to directly identify the initial reaction species, we concentrated on the identification of the final species. The rather broad band at 3318 $cm^{-1}$, shifting to 2495 $cm^{-1}$ upon deuteration, is characteristic of hydrogen-bonded N–H or O–H groups. The strong band at 2273 $cm^{-1}$, shifting to 2231 $cm^{-1}$ upon deuteration, is characteristic of $-C{\equiv}N$ or $-N{=}C{=}O$ groups. Finally, the band at 1735 $cm^{-1}$, shifting to 1688 $cm^{-1}$ upon deuteration, is characteristic of a carbonyl group. It was decided that the final species must be a formaldehyde–isocyanic acid molecule pair. In order to check this hypothesis, the infrared spectra of isocyanic acid and formaldehyde were obtained in a neon matrix at a concentration of 1 mol %. Then the two gas-phase samples were allowed to mix, and a spectrum of the $CH_2O$–HNCO mixture in a neon matrix was recorded. *Two new bands were observed in the spectrum of the $CH_2O$–HNCO mixture at 1733 and 3320 $cm^{-1}$.* These must be associated with $CH_2O$–HNCO molecule pairs. The isocyanate asymmetric stretching vibration in isocyanic acid occurs at 2268 $cm^{-1}$ in a neon matrix. The same vibration in DNCO occurs at about 2240 $cm^{-1}$ in a nitrogen matrix.[15] In a neon matrix the isocyanate symmetric stretch, $\nu_3$, and in-plane-bend, $\nu_5$, at 1320 and 600 $cm^{-1}$, respectively, are extremely weak and would not be observed in the photolysis experiment. The N–H bend, $\nu_4$, and isocyanate out-of-plane bend, $\nu_6$, at 777 and 577 $cm^{-1}$, respectively, in a neon matrix are stronger than $\nu_3$ and $\nu_5$, but it is questionable whether or not they would be observed in the photolysis-product spectrum. Certainly $\nu_4$ will be shifted upon hydrogen bonding. A weak broad band at 828 $cm^{-1}$ in the spectrum of matrix-isolated HNCO may be the N–H bend of the HNCO dimer. We hesitate to assign the 829-$cm^{-1}$ band (792 $cm^{-1}$ in the deuterated species) to this vibration because of its behavior upon prolonged photolysis.

The extremely weak bands at 544 and 536 $cm^{-1}$ in the spectrum of the deuterated photolysis product may be $\nu_6$, although there are no analogous bands observed in the spectrum of the protonated species. This is not surprising, however, when the intensity of these bands is considered.

Formaldehyde is a weaker infrared absorber than is isocyanic acid, and hence its bands are not expected to be as pronounced in the spectrum as the strongest bands of isocyanic acid. In a neon matrix, the most prominent bands in the formaldehyde spectrum are at 1745 (s), 2842 (m), 2778 (m), 1500 (m), and 1166 (w) $cm^{-1}$. There is no trace of the formaldehyde C–H stretching bands in the spectrum of the photolysis product. It is not unreasonable to assume that these bands lose intensity upon interaction with the isocyanic acid.

We believe that the evidence strongly supports the assignment of the "a" bands in Table I to a formaldehyde–isocyanic acid molecule pair.

The "b"-band spectrum in Table I is characterized by a very strong band at 2209 $cm^{-1}$, shifting to 2199 $cm^{-1}$ upon deuteration. This band is too high in frequency to be an azide vibration, and occurs at the low-frequency end of the isocyanate stretching region. As pointed out above, it has been postulated that methyl azidoformate rearranges to the isocyanate.[10] We therefore assign the b bands of Table I to the methoxy isocyanate monomer. Using the frequencies of methyl nitrite,[16] methyl isocyanate,[17] and methyl azidoformate as a guide, the assignments of Table II have been made.

**Table II.** Vibrational Assignments of Methoxy Isocyanate

| Normal mode | $CH_3ONCO$, $cm^{-1}$ | $CD_3ONCO$, $cm^{-1}$ |
|---|---|---|
| NCO stretch | 2209 | 2199 |
| $CH_3$ deformation | 1481 | 1125 |
| C–O stretch | 1052 | 974 |
| N–O stretch | 829 | 792 |
| NCO bend | 518 | 517 |

It is clear from the behavior of the frequencies of methoxy isocyanate upon deuteration that there is considerable coupling of the C–O and N–O stretches with the hydrogen motions. A similar coupling might occur in methyl nitrite, but, unfortunately, the frequencies of $CD_3ONO$ are not known.

The assignment of the –NCO bending motion to 518 $cm^{-1}$ may seem a little out of line, since this motion occurs at 577 $cm^{-1}$ in HNCO and at 596 $cm^{-1}$ in methyl isocyanate.[17] However, this assignment is reasonable in view of the low frequency of the –NCO stretching vibration.

Many of the extremely weak bands have not been assigned. These may arise from the formaldehyde–isocyanic acid molecule pair or from the methoxy isocyanate, or perhaps from some other decomposition which occurs to a slight extent. However, the main features of the infrared spectra have been accounted for.

**Mechanism.** In their study of the Curtius rearrangement of pivaloyl azide, Lwowski and coworkers[18] showed that the nitrene is not the precursor of the isocyanate. They also reached the conclusion that the rearrangement can proceed by two possible mechanisms. In one mechanism the rearrangment occurs simultaneously with loss of nitrogen in the same electronically excited state which gives rise to the singlet nitrene. The

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(15) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **40**, 2457 (1964).

(16) P. Klaboe, D. Jones, and E. R. Lippincott, *Spectrochim. Acta, Part A*, **23**, 2957 (1967).

(17) R. P. Hirschmann, R. N. Kniseley, and V. A. Fassel, *ibid.*, **21**, 2125 (1965).

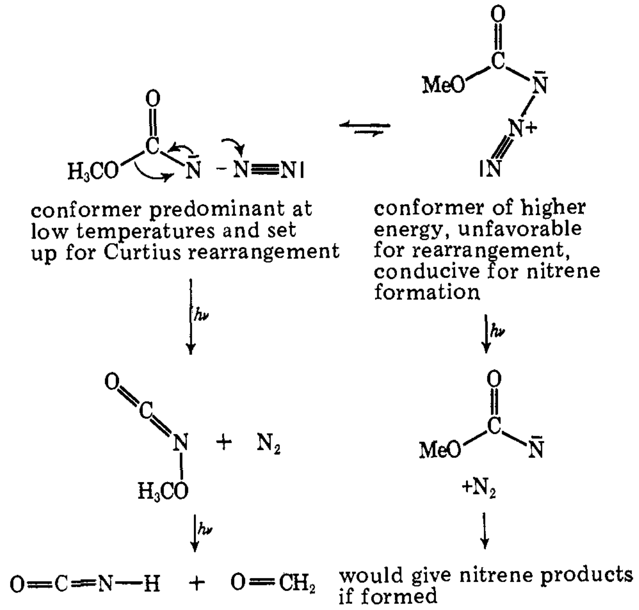
(18) S. Linke, G. T. Tisue, and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6308 (1967).

decomposition would probably be conformationally dependent in this case.

A second mechanism involves a competition between dissociation of the excited azide to give nitrene and its internal conversion to a vibrationally excited molecule. The rearrangement then proceeds *via* the vibrationally activated azide.

It is of interest to apply these mechanisms to the photolysis of methyl azidoformate. Because there is no evidence of the nitrene in the spectrum and because the spectrum did not change while warming the sample to the temperature at which argon leaves the window (55–60°K), it may be concluded that little or no nitrene is produced under the conditions of this study. Therefore, if the decomposition is conformationally dependent, reaction Scheme I is a possibility.

**Scheme I**



It was observed that the room-temperature gas-phase vibrational spectrum of methyl azidoformate is essentially identical with the 4°K matrix spectrum, even after annealing of the matrix. This observation argues for only one conformer, and thus the second mechanism discussed by ref 18 becomes an attractive possibility for the methyl azidoformate decomposition. The azide, being unable to decompose *via* the nitrene because of the cage effect in the matrix, is converted to a vibrationally excited state from which it simultaneously loses nitrogen and rearranges to form methoxy isocyanate. The methoxy isocyanate then slowly decomposes under photolysis to form formaldehyde and isocyanic acid.

However, it must be pointed out that no change would be expected in the infrared spectrum of methyl azidoformate in going from gas-phase to matrix near the limits of very high or very low conformational barriers. Also, overlap of bands and vibrational resonances could obscure conformational-dependent effects. Both mechanisms, therefore, must be considered as possibilities.

**Solid Methyl Azidoformate.** Evidence for rearrangement is present in the spectra of the photolysis products of solid methyl azidoformate. The new strong bands observed at 2258 and 2197 cm$^{-1}$ in Figure 2B and at 2216 and 2189 cm$^{-1}$ in the spectrum of photolyzed $N_3COOCD_3$ suggest that the same mechanism is operative in the solid as in the matrix. At wave numbers less than 2000 cm$^{-1}$ in the spectra of the photolysis products, there are deviations from the matrix-isolation spectra. In particular, the spectra of the photolysis products of $N_3COOCH_3$ (Figure 2B) and $N_3COOCD_3$ are characterized by strong bands at 1784 and 1782 cm$^{-1}$, respectively. These bands may arise from dimethyl azodiformate, which exhibits two strong bands in $CCl_4$ at 1785 and 1237 cm$^{-1}$; probably the 1237-cm$^{-1}$ band is obscured by the very strong 1252-cm$^{-1}$ band of methyl azidoformate. Diethyl azodiformate has been shown to be a product of photolysis in the gas and liquid phases of ethyl azidoformate.[6]

Upon warming the solid, the most striking changes in Figure 2B are the decrease in the relative intensity of the N–H stretching band and the disappearance of the bands in the 2100–2300-cm$^{-1}$ region. The room-temperature product is probably a polyurethane.

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