

## THE LIFETIMES OF NITRILES (CN) AND ACIDS (COOH) DURING ULTRAVIOLET PHOTOLYSIS AND THEIR SURVIVAL IN SPACE

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### ABSTRACT

Nitriles are one of the most common classes of molecules observed in the gas phase in space, with over a dozen having been positively identified in interstellar and circumstellar environments through the detection of their rotational transitions. Acids, in contrast, are much less common. In this paper we present laboratory data comparing the stability of two structurally related acid-nitrile pairs to ultraviolet (UV) photolytic destruction: acetic acid ( $\text{CH}_3\text{COOH}$ ) versus acetonitrile ( $\text{CH}_3\text{CN}$ ) and glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) versus aminoacetonitrile ( $\text{H}_2\text{NCH}_2\text{CN}$ ). We find that the nitriles are destroyed 10 and 5 times more slowly (respectively) by UV photolysis than are the corresponding acids. This suggests that whatever their relative formation rates, acids may be less abundant than nitriles in interstellar environments in part because they are more rapidly destroyed by photolysis. The results of this infrared (IR) spectral matrix isolation study indicate that during the lifetime of a typical interstellar cloud, even in its darkest regions, a population of acids in the gas phase will likely be diminished by at least half. Since aminoacetonitrile is a precursor to the amino acid glycine, and far more stable, presolar aminoacetonitrile may be a contributor to the deuterium-enriched glycine detected in meteorites. It would clearly be informative to search for aminoacetonitrile (the nitrile corresponding to glycine) in the regions where the amino acid glycine has been reported.

*Subject headings:* astrobiology — astrochemistry — ISM: molecules — molecular processes

### 1. INTRODUCTION

Nitriles (or cyanide compounds) are among the most commonly reported interstellar gas-phase organic molecules. Over a dozen different interstellar nitriles have been identified in dozens of sources through the detection of characteristic rotational transitions. For example, nitriles have been observed toward protostars (Kalenskii et al. 2000; Pankonin et al. 2001) and ultracompact H II regions (Akeson & Carlstrom 1996), and have been used as indicators of gas temperature (Schwartz & Mangum 1999). Nitriles are commonly identified, in part, because of the relatively strong dipole moment imparted to these molecules by their  $\text{C}\equiv\text{N}$  group, making these species amenable to detection through their rotational spectra. However, interstellar and circumstellar environments cannot be too inhospitable to these compounds, or they would not be detected so often.

Nitriles are of relevance to astrobiology because they are putative intermediates from which prebiologically important organic acids (such as amino acids) are proposed to form, whether by a Strecker synthesis or by Michael addition (see Ehrenfreund et al. 2001b). Nitriles are thought to be the parents of many of the acids extracted from primitive meteorites. It is interesting to note that while nitriles are common in space and organic acids are scarce, the opposite is true in primitive meteorites.

In this paper we present laboratory data comparing the photostability of acids and nitriles during exposure to ultraviolet (UV) photolysis. We examine two structurally related acid-nitrile pairs: acetic acid ( $\text{CH}_3\text{COOH}$ ) versus acetonitrile

( $\text{CH}_3\text{CN}$ ) and glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) versus aminoacetonitrile ( $\text{H}_2\text{NCH}_2\text{CN}$ ). We find that the acids are more rapidly destroyed by UV photolysis than are the corresponding nitriles, suggesting that whatever their relative formation rates, the acids may be less abundant in space because they are more rapidly destroyed by photolysis.

The photostabilities measured in these matrix isolation experiments suggest that a population of organic acids in the gas phase should be almost completely (97%) destroyed within 1000 yr on exposure to the UV field of the diffuse interstellar medium (ISM). Even in dense cloud regions with high  $A_V$ , where the only ambient UV is that formed inside the cloud from cosmic rays, more than half of these organic acids should be destroyed over the lifetime of a typical interstellar cloud. These results indicate that if glycine is observed in hot cores (Kuan et al. 2003), then the corresponding nitrile should be more abundant, if photodestruction (rather than formation) is the factor that determines the presence of these molecules.

### 2. EXPERIMENTAL METHODS

The samples discussed here were vapor deposited onto a 15 K infrared (IR) transparent CsI substrate in a vacuum chamber ( $P \sim 10^{-8}$  mbar) and UV photolyzed at 15 K. The equipment used for this work has been described in greater detail elsewhere (Allamandola, Sandford, & Valero 1988).<sup>4</sup>

The aminoacetonitrile was purchased as the free base (Sigma, 98%) and was vacuum transferred away from a nonvolatile yellow oil. The three liquids (aminoacetonitrile, acetonitrile [Aldrich, 99.5+%), and acetic acid [Sigma, glacial]), were all triply freeze-pump-thawed to remove dissolved gases prior to being mixed under vacuum in glass sample bulbs with either argon (Matheson, 99.999%) or  $\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  was purified with a Millipore Milli-Q water system to 18.2 M $\Omega$  and triply freeze-pump-thawed to remove dissolved

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gases prior to use.

For argon matrix experiments, the argon was premixed with the relevant nitrile or acid vapor in evacuated glass bulbs. Mixtures were made such that the argon was present in excess of the acid or nitrile by at least a factor of 300:1. If the organic molecules being studied are uniformly mixed with the argon, then at this concentration the majority of them should be separated from one another by argon atoms in the solid phase after deposition. This is intended to avoid intermolecular interactions between subject molecules. We recognize that acids can dimerize, but our kinetics for the acids show clean first-order behavior, so this is not a factor in the reaction. Similarly, mixed gas bulbs were made for the H<sub>2</sub>O experiments with H<sub>2</sub>O:acid or H<sub>2</sub>O:nitrile ratios of 100:1. We estimate that the contamination contributed from the sample preparation is less than 1 part in 10<sup>6</sup> relative to argon and less than 1 part in 10<sup>5</sup> relative to H<sub>2</sub>O. Trace CO<sub>2</sub> was often observed to be present in all of the samples, and comparisons of infrared spectra of matrix isolated aminoacetonitrile to theoretical calculations (Bernstein, Bauschlicher, & Sandford 2003) indicate that it contains a sulfate as a minor impurity, probably the same one used by Aldrich (the supplier) as an intermediate in synthesis of the aminonitrile. Given the overall low level of contaminants, they are not expected to have any appreciable effect on the results of our photolysis experiments.

The glycine (Sigma, 99%) is a solid at room temperature and therefore could not be premixed with argon or H<sub>2</sub>O in a gas bulb. Instead, it was vapor codeposited with argon or H<sub>2</sub>O, which entered the vacuum chamber through a separate inlet port. This method for vapor depositing solid amino acids is described in greater detail in Ehrenfreund et al. (2001a).

The rate of deposition for the argon mixtures was estimated from the growth rate of interference fringes in the baseline of the infrared spectra and from the integrated areas of relevant absorption features in the spectra. Both approaches indicated that the sample mixtures were deposited at a rate that produced ice samples a few  $\mu\text{m}$  thick after 10 minutes. For the H<sub>2</sub>O experiments, we estimate that the H<sub>2</sub>O ice mixtures were a few tenths of a  $\mu\text{m}$  thick after  $\sim 10$  minutes of deposit based on measured strengths of the H<sub>2</sub>O absorption features. This vapor deposition technique produces intimately mixed ices with the H<sub>2</sub>O in a high-density amorphous form that is only observed at low temperatures and pressures, and believed to be representative of H<sub>2</sub>O-rich ices in interstellar molecular clouds (Jenniskens et al. 1995). We maintained thin ( $<0.5 \mu\text{m}$ ) ice samples for the H<sub>2</sub>O matrix samples to ensure that the UV radiation penetrated the entire sample layer.

After deposition, all the samples were UV photolyzed with a microwave-excited hydrogen flow lamp that produces both Ly $\alpha$  and lower energy ( $\sim 160 \text{ nm}$ ) photons. Characteristics of the lamp are described in detail elsewhere (Warneck 1962). This hydrogen lamp produces  $\sim 2 \times 10^{15}$  photons  $\text{cm}^{-2} \text{ s}^{-1}$ . This flux is  $\sim 10^{12}$  times greater than the estimated UV flux induced by cosmic rays in the darkest regions of dense clouds (Prasad & Tarafdar 1983), and  $\sim 10^7$  times greater than the estimated flux of photons above 6 eV in the diffuse ISM (Mathis, Mezger, & Panagia 1983). Thus, 30 minutes of exposure to this lamp corresponds to  $\sim 500 \text{ yr}$  at the edge of a dense cloud, and  $\sim 1 \times 10^5 \text{ yr}$  within a dense molecular cloud of high  $A_v$ . Despite the high flux of the lamp, the time that elapses between photons arriving in the same molecular site in our samples is  $\sim 13$  orders of magnitude longer than typical molecular relaxation times, so multiphoton processes are not relevant. Each photolysis was preceded by a period in which

the lamp was powered up but no UV was shining on the sample, and each photolysis included a similar pause during the course of the experiment. In every case there was very little change in the areas of the peaks ( $<1\%$ ), demonstrating that changes in the peak area were caused by photolysis only, and contain no significant nonphotolytic component.

Both deposition of the samples and subsequent photodestruction of the nitriles and acids frozen in solid argon or H<sub>2</sub>O was monitored by measuring the 4000–500  $\text{cm}^{-1}$  (2.5–20  $\mu\text{m}$ ) infrared spectrum of the sample at regular time intervals using a Nicolet 740 spectrometer. Spectra were measured at a resolution of 1  $\text{cm}^{-1}$  (the width of an unresolved line). In argon matrix all peaks are visible and the photodestruction of the starting materials were monitored by following the decrease in the area of one or more of the absorption bands produced by original molecule, all of which give the same result. However, when the subject molecules were diluted in H<sub>2</sub>O many features, including the carbonyl stretching peak of the acids, are obscured by strong absorptions of H<sub>2</sub>O, so the reaction was followed by monitoring the disappearance of a CH deformation feature (see § 3).

The disappearance of our starting materials was assumed to be unimolecular, and therefore the loss of starting material with time was fitted to a first-order (simple exponential) decay, i.e.,

$$y = ae^{-kt} + b, \quad (1)$$

and in most cases this equation provided excellent fits to the data ( $R \sim 0.999$ ). However, this functional form was not adequate to fit the disappearance of acetonitrile in argon, which was better described by an equation that includes a term for shielding (see § 3 and Fig. 4) of the starting material by a product molecule, i.e.,

$$y = \frac{ae^{-kt}}{1 + b - bae^{kt}}. \quad (2)$$

### 3. RESULTS

#### 3.1. Photolysis of Acetic Acid

We used IR spectroscopy to monitor the UV photodestruction of two acids and two nitriles in the solid state at several temperatures. The procedure is exemplified by Figure 1, which shows the disappearance of the CO stretching vibration of the acid (COOH) group of acetic acid isolated in argon with increasing UV exposure. All the infrared absorption bands of acetic acid diminish in the same manner. We observed a simultaneous and concomitant formation of carbon dioxide (CO<sub>2</sub>), as shown in Figure 2. This is consistent with photodecarboxylation, i.e., a UV photon causes loss of the acid group to (ultimately) form CO<sub>2</sub>. The same correlation was observed in our previous study of the photodestruction of amino acids under astrophysical conditions (Ehrenfreund et al. 2001a), and in studies of the decomposition of acetic acid under terrestrial conditions (Ausloos & Steacie 1955).

A plot of the areas of the COOH and CO<sub>2</sub> infrared bands as a function of UV dose is shown in Figure 3. That these changes take a simple exponential form (eq. [1], § 2) is consistent with the photolysis of acetic acid in argon matrix being a unimolecular photodecomposition, i.e., individual acid molecules are breaking down as a result of photolysis without another acid molecule playing a role in the reaction. This is what is expected for molecules that are destroyed in single-photon events while

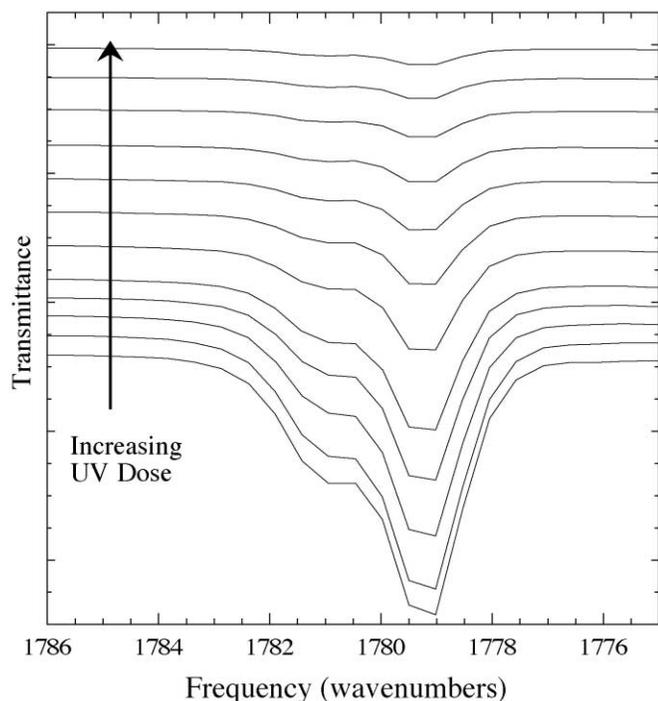


FIG. 1.—Plot of 1786–1775  $\text{cm}^{-1}$  (5.60–5.63  $\mu\text{m}$ ) IR spectra of an argon/ $\text{CH}_3\text{COOH} = 300$  ice on exposure to 0–90 minutes of UV photolysis at 15 K. The peaks corresponding to the acid (COOH) group diminish with increasing UV dose; this is depicted graphically in Fig. 3.

isolated in an argon matrix. In such a first-order decomposition, the half-life (the amount of time required for the acid peak area to diminish by half, or the  $\text{CO}_2$  peak area to double) should be constant over the course of the experiment. The half-lives for the diminishing  $\text{CH}_3\text{COOH}$  and the growing  $\text{CO}_2$  peaks de-

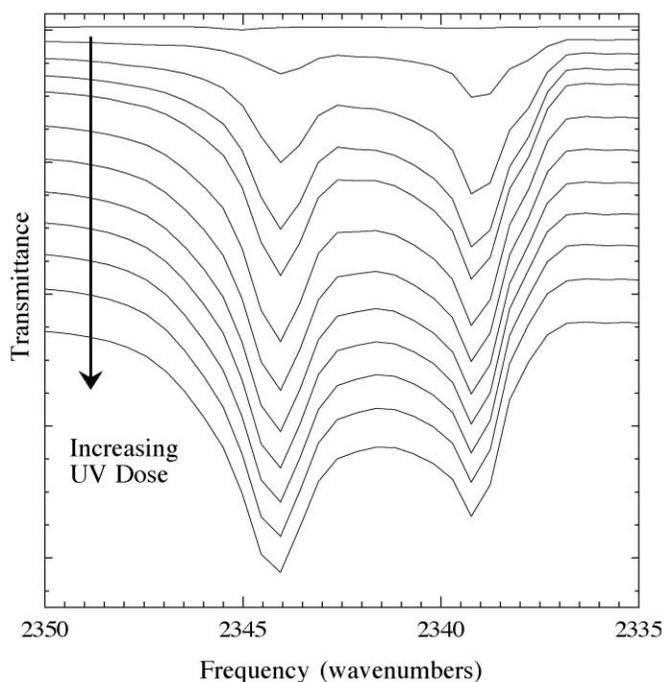


FIG. 2.—Plot of 2350–2335 (4.26–4.28  $\mu\text{m}$ ) IR spectra of an argon/ $\text{CH}_3\text{COOH} = 300$  ice on exposure to 0–90 minutes of UV photolysis at 15 K. The peaks corresponding to carbon dioxide increase with increasing UV dose; this is depicted graphically in Fig. 3.

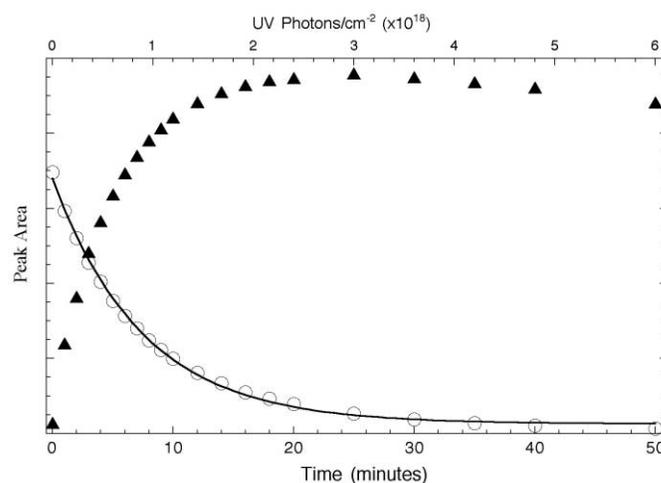


FIG. 3.—Diminishing area of the infrared features corresponding to the acid (COOH) functional group (*open circles*) with increasing UV exposure and concomitant increase in area of the  $\text{CO}_2$  peaks (*filled triangles*). An exponential fit to the diminishing acid peak area yields a half-life of  $\sim 5$  minutes for loss of acetic acid isolated in solid Ar.

rived from the fits in Figure 3 are 5.2 and 3.3 minutes, or  $\sim 3 \times 10^{17}$  UV photons  $\text{cm}^{-2}$ . These are similar enough, given experimental uncertainties, to be consistent with these processes being linked, i.e., a photodecarboxylation process mentioned above and previously reported for amino acids (Ehrenfreund et al. 2001a).

When the photolysis is repeated with acetic acid in  $\text{H}_2\text{O}$  rather than Ar, the acid features in the IR spectra are shifted by intermolecular interactions with  $\text{H}_2\text{O}$  from the positions seen in Figure 1, and are obscured by a strong, broad  $\text{H}_2\text{O}$  feature. As a result, the disappearance of the acid peak cannot be used to measure the progress of the reaction. Consequently, for experiments in which the acetic acid was UV photolyzed in a solid  $\text{H}_2\text{O}$  matrix, we ascertained the half-life for photodecomposition of the acid by measuring the disappearance of CH deformation feature at  $\sim 1295 \text{ cm}^{-1}$ . The half-life in solid  $\text{H}_2\text{O}$  was determined to be the same as the destruction of acetic acid in solid argon at the same temperature, within experimental uncertainties. In order to have an adequate signal-to-noise ratio (S/N) to follow the loss of acetic acid in  $\text{H}_2\text{O}$ , the concentration of acetic acid had to be higher than it was in argon (100:1 in  $\text{H}_2\text{O}$  vs. 300:1 in argon). To assess the affects of concentration, we also repeated the acetic acid photolysis in  $\text{H}_2\text{O}$  with the concentration of the acetic acid a factor of 10 higher (at  $\text{H}_2\text{O}/\text{CH}_3\text{COOH} = 10$ ), and the rate was within a factor of 3 of that at 100:1. If the reaction depended on two acid molecules interacting for the reaction to proceed, then one would have expected the rate to increase by a factor of 100. We attribute the more modest observed change to a bulk effect, such as a change in the pH of the ice. All the half-lives were derived from loss of starting material, which is considered more reliable than those from formation of a product such as  $\text{CO}_2$ , and all are summarized in Table 1.

### 3.2. Photolysis of Acetonitrile

In contrast to acetic acid, the infrared band areas of acetonitrile ( $\text{CH}_3\text{CN}$ ) diminish with time in a manner that deviates from that expected for a first-order process, as can be seen in Figure 4. The acetonitrile data is consistent with a simple exponential initially, but diverges from this first-order curve

TABLE 1

Compound and Matrix	Approximate Half-Life <sup>a</sup>			
	Minutes, Laboratory	Photons ( $10^{17} \text{ cm}^{-2}$ )	Years <sup>b</sup> $A_r = 0$	Years <sup>c</sup> $A_r \geq 5$
Acetic acid ( $\text{CH}_3\text{COOH}$ ) in argon .....	5	3	100	$1 \times 10^7$
Acetic acid in $\text{H}_2\text{O}$ ( $\sim 1:100$ ).....	3	1.8	60	$6 \times 10^6$
Acetonitrile ( $\text{CH}_3\text{CN}$ ) in argon .....	50 <sup>d</sup>	30	1000	$1 \times 10^8$
Acetonitrile in $\text{H}_2\text{O}$ ( $\sim 1:100$ ).....	60	36	1100	$1 \times 10^8$
Glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ) in argon.....	13	8	250	$3 \times 10^7$
Aminoacetonitrile ( $\text{H}_2\text{NCH}_2\text{CN}$ ) in argon .....	65	40	1300	$1 \times 10^8$

<sup>a</sup> The time it takes for the area of the peaks to diminish by half as determined from fitting the loss of starting material, not the formation of product such as  $\text{CO}_2$ . All of these values should be assumed to be accurate to  $\sim 30\%$ .

<sup>b</sup> In the diffuse ISM, assuming a flux of  $10^8 \text{ photons cm}^{-2} \text{ s}^{-1}$  (Mathis et al. 1983).

<sup>c</sup> Assuming a flux of  $10^3 \text{ cosmic-ray-induced photons cm}^{-2} \text{ s}^{-1}$  (Prasad & Tarafdar 1983).

<sup>d</sup> The fit to a pseudo-first-order decay is poor; see § 3.

(Fig. 4, *dashed line*), diminishing more slowly than one would expect for a standard first-order reaction after  $\sim 100$  minutes. We were able to greatly improve the fit to the acetonitrile decay by adding a second exponential term to the first-order curve that slows the loss of nitrile with increasing time (Fig. 4, *solid line*). This is intended to model the effects of a product molecule that slows the reaction rate by strongly absorbing UV and shielding the acetonitrile, and grows exponentially. This additional term was only needed in the case of acetonitrile in argon, the standard first-order simple exponential being adequate for all of the others, given our S/N. The difference between the two fits is fairly small, and the departure of the decay from the form of equation (1) was only apparent because of the good quality of our laboratory data and the fact that we followed the reaction to completion. Had we monitored the reaction for only one or two half-lives this difference might not have been evident. In any case, these features corresponding to the acetonitrile diminish much more ( $>10$  times) slowly upon photolysis than do the acetic acid under identical conditions. The UV dose required to decompose half of the acetonitrile isolated in solid argon is between 10 and 20 times greater

than was observed for acetic acid (Table 1 and Fig. 5). As was observed with acetic acid, the half-life for disappearance of the acetonitrile was, given the experimental uncertainty, the same in solid  $\text{H}_2\text{O}$  as in argon matrix at the same temperature.

### 3.3. Glycine versus Aminoacetonitrile

The photodestruction of the amino acid glycine and its corresponding nitrile, aminoacetonitrile, were observed to show the standard first-order exponential behavior with increasing UV dose described above for acetic acid. In addition, just as the photodestruction of acetic acid is faster than acetonitrile, glycine (the amino acid) is observed to break down more rapidly than aminoacetonitrile (the structurally corresponding amino nitrile). The half-life for photodestruction of the amino nitrile is approximately 5 times greater than that of the amino acid (Table 1), certainly significant given our experimental uncertainties. Thus, both nitriles are more stable against UV photodestruction than are their corresponding acids.

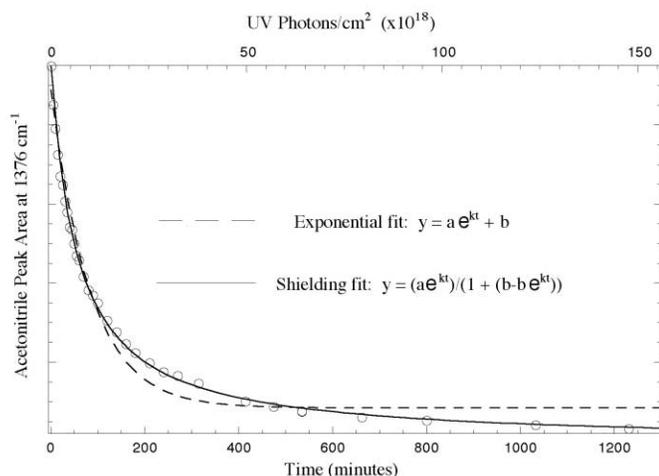


FIG. 4.—Demonstration of the failure of the standard exponential (*dashed line*) to fit the diminishing peak area of acetonitrile isolated in solid Ar with increasing UV exposure. The addition of a second exponential term to the denominator (*solid line*) improves the fit. That the deviation from first order occurs at later times ( $>100$  minutes) is consistent with shielding of the nitrile by a photoproduct.

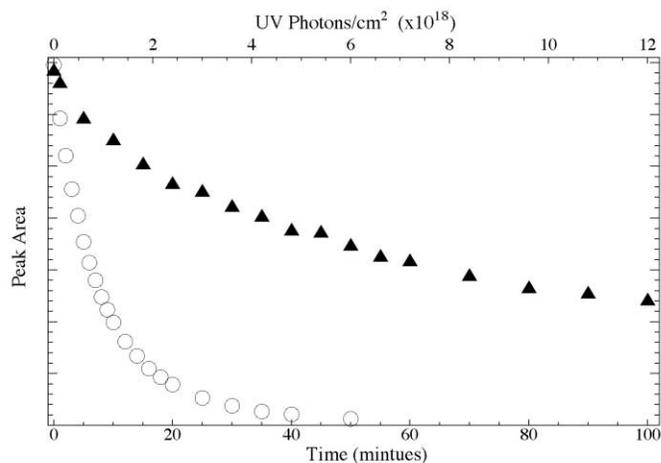


FIG. 5.—Comparison of the change in areas of IR peaks corresponding to acetic acid (*open circles*) and acetonitrile (*filled triangles*) on exposure to UV photolysis under identical experimental conditions and displayed on the same scale. Acetonitrile peak areas diminish at least 10 times more slowly during exposure to UV photons than do those of acetic acid, suggesting that nitriles may be more stable to UV photolysis in space than the corresponding organic acids.

#### 4. DISCUSSION AND IMPLICATIONS

These experiments demonstrate that organic nitriles survive longer than organic acids when exposed to UV photolysis at 15 K in the solid state. Furthermore, the rate of loss of acids and nitriles in solid Ar is within a factor of 2 of the rates in solid H<sub>2</sub>O. Loss of the acid functional group (COOH) was observed to correspond with the formation of CO<sub>2</sub>, consistent with a previous room-temperature gas-phase study of acetic acid (Ausloos & Steacie 1955). Presumably acids break down more readily than nitriles because this loss of CO<sub>2</sub> is energetically favorable, and this pathway is not accessible to nitriles. Since this difference is inherent to the structures of the compounds, and not an artifact of the matrix, the large differences in half-lives between acids and nitriles is probably relevant to the survival of these molecules in a number of astrophysical environments.

##### 4.1. Acids and Nitriles in the ISM

The half-lives reported in Table 1 can be used to estimate the relative proportion of acids and nitriles that will be destroyed in the ISM by UV photolysis, assuming that they are in the gas-phase or in ices that can be penetrated by UV photons. For example, we find that acetic acid has a half-life of  $2-3 \times 10^{17}$  photons cm<sup>-2</sup>, meaning that if suddenly exposed to UV radiation (e.g., following ice sublimation at the edge of a dense cloud) half of the acetic acid molecules originally introduced would be photolyzed (to CH<sub>4</sub> and CO<sub>2</sub>) in only 100 yr in the diffuse ISM. The corresponding nitrile, however, is more than 10 times more stable to photolysis, so their relative concentrations would change by roughly a factor of 2 every 100 to 200 yr. As a result, the relative proportions of acid and nitrile should change dramatically on exposure to UV radiation over extended periods, all else being equal. If these molecules were both formed or injected into the gas phase with similar efficiencies and UV radiation is present, then where acid is observed the corresponding nitrile should be more abundant. Given their relative proportions and the flux they have experienced, one should be able to back-calculate their relative formation rates (Balucani et al. 2000).

In dense molecular clouds, where the UV flux is greatly attenuated compared to the diffuse ISM, half-lives for even the acids approach or exceed typical cloud lifetimes. Since the relative proportions of acid and nitrile should vary in proportion to the UV flux, changes in acid-nitrile ratio with time should be less in dark clouds than in the diffuse ISM. For example, only half of the initial acid (and less than 10% of the nitrile) in the denser regions will be destroyed over the typical 10<sup>7</sup> yr lifetime of the cloud, assuming that the total flux of UV is that derived from cosmic rays (10<sup>3</sup> photons cm<sup>-2</sup> s<sup>-1</sup>; Prasad & Tarafdar 1983) and that all the material is in ices thin enough to be penetrated by UV photons. This means that if the acid and nitrile began with equal abundances, the ratio of nitrile to acid would change by only a factor of 2 over the lifetime of the cloud.

Obviously, the destructive fractionation process we describe here is only one component of a chemical network that also involves other creation and destruction processes (Rodgers & Charnley 2003). The relative importance of this photo-destruction is also likely to vary with environment, being different in the quiescent dense cloud medium, in hot cores, and in the vicinities of forming protostars. In environments where molecules were recently released into the gas phase we would

predict more acid relative to nitrile than in populations of molecules that had already been exposed to radiation.

##### 4.2. Acids and Nitriles in Solar System Ices

The general conclusion that nitriles are more stable to UV photolysis than acids should also apply to solar system environments where organic compounds are exposed to radiation on the surface of icy bodies. For example, the *Galileo* near-infrared mapping spectrometer (NIMS) spectra of Callisto and Ganymede display absorptions at 4.57 μm (McCord et al. 1997, 1998) that indicate the presence of nitrile (or isonitrile) chemical groups on the surface of these icy moons of Jupiter. Given the solar flux of UV and the rates we have measured in the laboratory, at the uppermost surface of Europa organic acids would be expected to survive days, and nitriles weeks. UV radiation therefore likely destroys such materials at the very surface at a rate faster than sputtering, impact gardening, or geologic processes could reveal or bury them. Thus, the observation of the 4.57 μm absorptions could be an indication that organic compounds have recently been introduced, either released onto the surface from below or the result of some kind of exogenous delivery. In any case, their concentrations in the very topmost layers of the surface are most likely defined by the equilibrium between their in situ creation and destruction.

Given that our previous study yielded similar destruction half-lives for molecules frozen in solid argon and nitrogen (Ehrenfreund et al. 2001a), the results presented here should also be relevant to the fate of organic molecules exposed to radiation in nitrogen-rich ices, such as are observed on Triton and Pluto.

##### 4.3. Astrobiological Implications

The paucity and instability of organic acids in space relative to nitriles is at odds with their prevalence in extracts of carbonaceous meteorites (Cronin & Chang 1993). Indeed, not only do meteorites contain a fair proportion of amino acids, but these amino acids (or their precursors) are thought to have an interstellar heritage because they contain substantial deuterium enrichments (Kerridge 1999).

However, nitriles can be easily converted to acids by heating in liquid H<sub>2</sub>O (hydrolysis). Liquid H<sub>2</sub>O is thought to have been at least briefly present in the asteroidal parent bodies of certain meteorites (Robert & Epstein 1982), and this hydrolysis is a step in various proposed parent body reactions that may lead to amino acids (Ehrenfreund et al 2001b). For example, the classic Strecker synthesis of the amino acid glycine is such a reaction, and this is perhaps the most popularly proposed pathway to meteoritic glycine. In this pathway to glycine aminoacetonitrile (one of the nitriles we have studied in this paper) forms first and then reacts with liquid H<sub>2</sub>O to form glycine. Rather than forming in the parent body by a Strecker-type reaction, perhaps some aminoacetonitrile was already present in space and was incorporated into the forming parent body. Thus, presolar nitriles may have been converted to acids by reacting with liquid H<sub>2</sub>O in asteroids or perhaps even comets. This is of relevance not only to amino acids, but also to other acids such as glyceric acid, found in meteorites.

Given the results presented in this paper, even if presolar amino acids do not survive the depredations of interstellar space perhaps the corresponding nitriles do persist to be

incorporated into a newly forming planetary system. Such interstellar nitriles could then be a significant source of amino acids in meteorites, with their deuterium enrichments being the result of the original interstellar heritage of the precursor nitriles.

Thus, the greater stability of nitriles, combined with their propensity to form acids on reaction with liquid H<sub>2</sub>O, make them logical precursors to amino acids in meteorites. While the hunt for the amino acid glycine has received considerable attention (Snyder 1997; Ceccarelli et al. 2000; Kuan et al. 2003), aminoacetonitrile has been neglected. We propose that it would be extremely useful to make a strong effort to search for this nitrile, both because it may be intrinsically more abundant and because it may be the precursor of the deuterium-enriched glycine in meteorites. In addition, the detection of related acids and nitriles in the same astrophysical environments should provide important insights into the processes by which these species are created and destroyed. It would be particularly interesting to search for aminoacetonitrile in those environments where the amino acid glycine has recently been reported.

## 5. CONCLUSIONS

The laboratory experiments presented here demonstrate that organic nitriles (cyanide compounds) survive 5 to 10 times

longer on exposure to UV photolysis than do the corresponding acids. This is true in both solid H<sub>2</sub>O and argon matrices. Acids are therefore expected to be much less stable than nitriles to UV in space environments and, all else being equal, nitriles should be much more abundant in space than their associated acids.

Interstellar nitriles could be a significant source of meteoritic amino acids, given their stability to UV and easy conversion into acids by reaction with liquid H<sub>2</sub>O.

It would therefore clearly be of interest to search for nitriles in dense clouds. It would be particularly interesting to search for both nitriles and their associated acids in the same locations, as their relative abundances would provide significant insights into the chemical process by which they are created and destroyed in space.

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