Four runs were made and the data are summarized as expt 16–19 in Table I.

^{13}C Nmr.[3] The ^{13}C spectra were obtained under steady-state (cw) conditions using a Varian XL-100-15 instrument equipped with a V-3512 proton decoupler and a C-1024 time-averaging device. The camphene samples were examined as 10% (w/v) solutions in benzene-d_6. With normal samples, operating conditions were adjusted so that the signals for each carbon bearing hydrogen exhibited the same integrated intensity; these conditions were then employed for each enriched sample. The signals for the four carbons absorbing at highest field were recorded using a 250-Hz sweep width and 500–800 scans to obtain relatively high signal to noise ratio. These signals are (in parts per million downfield from TMS): 24.2 (C-5), 26.0 (*endo*-Me), 29.2 (C-6), 29.7 (*exo*-Me). Off-resonance decoupling was employed to establish these assignments and it may be noted that these differ from those reported previously.[13] Careful integration of the four signals allows one to follow the increase in ^{13}C at the methyl carbons quantitatively since the two methylene signals (C-5, C-6) provide a measure of the natural-abundance ^{13}C as an internal standard. In addition, proton spectra of the olefinic region of the enriched samples were carefully integrated (HA-100). Because of the large ^{13}C–H coupling constants, the ^{13}C satellites are readily observed and their intensities relative to those of the main absorption bands (^{12}C–H) were determined to obtain values for the ^{13}C content at C-8. Integrated intensities were determined, in triplicate, for each sample and the results averaged; these data are listed in Table I.

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(13) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

Spectroscopic and Photochemical Study of Diaminomaleonitrile and Diaminofumaronitrile[1]

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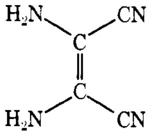
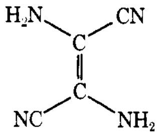
Abstract: Based on a wavelength study of the excitation of pure diaminofumaronitrile (DAF) in a polar solvent, we conclude that either (1) DAF cannot form 4-amino-5-cyanoimidazole (ACI) but can be converted to diaminomaleonitrile (DAM) which can or (2) there is a wavelength dependence for the formation of ACI from DAF. The highly dominant result of irradiation of DAF at wavelengths well within the absorption onset is trans (DAF) → cis isomerization to produce DAM. Irradiation of initially pure DAM in a polar solvent at wavelengths within (but relatively near) the absorption onset results in photoisomerization to DAF and production of the imidazole, ACI. The photochemical formation of ACI has an overall activation energy which is larger than that necessary for isomerization. There is evidence for the existence of an intermediate(s) between DAM (also potentially DAF) and ACI. Excitation of DAM or DAF in a rigid matrix at −196° produces a species which has been assigned as aminocyanocarbene, in addition to photoisomerization (but no ACI).

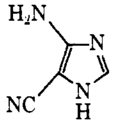
Diaminomaleonitrile (DAM) (I) and diaminofumaronitrile (DAF) (II) are respectively substituted cis and trans derivatives of ethylene. These can undergo photochemical interconversion.[2] Also, photochemical conversion of DAM to 4-amino-5-cyanoimidazole (ACI) (III) is believed to be an important step toward the chemical evolution of purines.[3–6]



I



II



III

A mechanistic proposal of the photochemical conversion of DAM (I) to ACI (III) has been given.[3–7] The trans isomer, DAF (II), was given as one of the intermediates in the transformation of DAM (I) to ACI (III).[3] Lamps with principal emissions at 253 and 350 nm have been successfully used to convert DAM to ACI (in the latter case, wavelengths other than 350 nm must be effective since DAM has no absorption at 350 nm). Yamada, *et al.*,[2] reported that irradiation with wavelengths longer than 320 nm enhanced the photochemical conversion of DAF back to DAM.[1] This was noted to be in contrast to the results of Ferris and Orgel[4] who indicated ACI was formed. Nonetheless, the former authors[2] maintained the opinion[3,4] that the photochemical rearrangement of DAM to ACI proceeds *via* DAF.

As a part of our continuing interest in photoisomerization and photochemistry, we have investigated DAM and DAF. In particular, we have studied the interconversion of DAM and DAF and the conversion of DAM and DAF to ACI as a function of temperature and exciting wavelengths.

Experimental Section

DAM was synthesized and purified by multiple crystallization.[7] DAF was prepared using the procedure described by Yamada, *et al.*[2]

All samples used for photochemistry and spectroscopy were care-

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(1) Supported by the National Aeronautics and Space Administration, Grant No. NGR 44-205-091.

(2) Y. Yamada, N. Nagashima, Y. Iwashita, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, 4529 (1968).

(3) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, **30**, 223 (1967).

(4) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, **88**, 1074 (1966).

(5) J. P. Ferris, J. E. Kuder, and A. W. Catalano, *Science*, **166**, 765 (1969).

(6) J. P. Ferris and J. E. Kuder, *J. Amer. Chem. Soc.*, **92**, 2527 (1970).

(7) J. P. Ferris and R. A. Sanchez, *Org. Syn.*, **48**, 60 (1968).

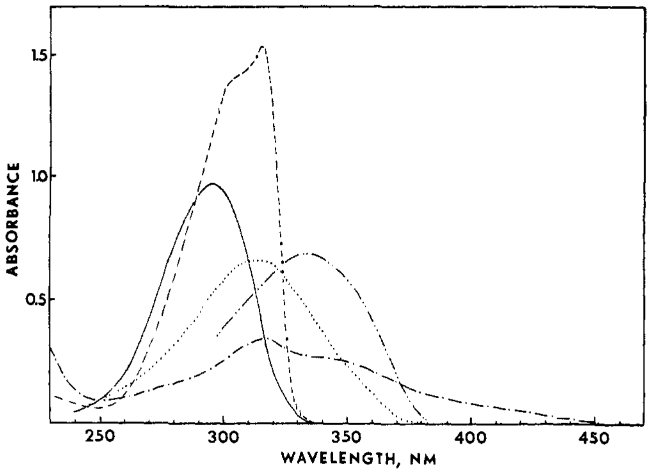

Figure 1. Diaminomaleonitrile (DAM) in EPA, at room temperature (———), at −196° (-------); diaminofumaronitrile (DAF) in EPA, at room temperature (......), at −196° (-·-··-), after irradiation with source I at −196° for 25 min (-·-·-·-·-).

fully degassed using four freeze–pump–thaw cycles (vacuum 10^{-5} Torr). For irradiation, the following sources were used.

Source I: 1-kW Hg–Xe high-pressure arc, 5-cm water and Corning glass filter CS 7-54 (bandpass maximum at ~320 with ~2% transmission at 240 and 410 nm, respectively, manufacturer's data).

Source II: 100-W Hg high-pressure arc, 5-cm water and a filter as indicated in the text.

254-nm Hg line +358-nm excitation: Hg resonance lamp and 150-W Xe high-pressure lamp, 5-cm water filter and Corning CS 7-60 filter. Isolation of 254 nm as above. The bandpass using the Xe lamp and filter is broad and has a maximum at 358 nm with 79% transmission and cutoffs at 300 and 395 nm (~1.5% transmission at 310 and 395 nm).

254-nm Hg line excitation: Hg resonance lamp using microwave excitation and filter of 10 cm of Cl_2 and 1 cm of Br_2 gases. The bandpass maximum is at 240 nm with 47% transmission at 254 nm and cutoff at 290 nm (~1% transmission).

366-nm Hg line excitation: 100-W Hg high-pressure lamp and filter consisting of 5-cm water, Balzer 365-nm interference, and Corning CS 0-52 filters. The bandpass maximum is at 366 nm with 12% transmission and cutoffs are at 365 and 383 nm (<0.5% transmission).

366- + 334-nm Hg lines excitation: 100-W Hg high-pressure lamp and filter consisting of 5-cm water, 341-nm Balzer interference, and Corning CS 4-69 filters. The bandpass maximum is at 346 nm with 10% transmission. Approximately three times as much 366-nm light is passed than 334-nm light and cutoffs are at 325 and 385 nm (<0.5% transmission).

254- and 366-nm Hg lines excitation: Hg resonance lamp and 100-W Hg high-pressure lamp using filters as noted above.

It is particularly important to note that extensive effort was made in the last four cases above to isolate narrow excitation bands *and* to eliminate shorter wavelength lines. Particularly in the case of irradiation of DAF, any leakage of 313-nm light irradiates DAM. We found that only combinations of filters would truly eliminate any unwanted light as 313 nm.

A Cary Model 15 spectrophotometer was used for all absorption spectra. Quartz cells of 2-mm pathlength were used together with a quartz dewar equipped with flat optical windows. All quartz in the optical path was Suprasil-II. For studies at −196° liquid nitrogen was the coolant. At temperatures intermediate between −196° and 22°, vapor from boiling liquid nitrogen was the coolant. A Wheelco Model 402 capacitrol was used for temperature control.

DAM to ACI conversion is known to proceed not only in water, but in a variety of organic solvents[5] including alcohol and ether. In our experiments, EPA (5:5:2 by volume ether–isopentane–alcohol) was used unless otherwise noted. The photolysis pattern in 2-methyltetrahydrofuran (2-MeTHF) appeared to be the same as that in EPA including that in a rigid matrix.

Results

Diaminomaleonitrile (DAM). Considering that DAM is a substituted ethylene, the maximum of the first absorption band is at an unusually long wavelength. Consequently, we did a spectroscopic study to assess whether DAM showed any indication of forming self-intermolecular charge transfer complexes. There was no indication of such a complex in water in the concentration range of 2×10^{-6} to 2×10^{-3} *M*. Because of the similar absorption in EPA, we assume no charge transfer complexes existed in this solvent. The first absorption band has been assigned as arising from an intramolecular charge transfer transition. This is in agreement with another similar suggestion.[6]

A comparison was also made between DAM and tetracyanoethylene to assess whether other types of intermolecular charge transfer complexes could form with DAM. While tetracyanoethylene gave an intensely colored charge transfer complex with hexamethylbenzene (in 2-MeTHF, benzene, and acetonitrile), DAM did not display a similar behavior. Thus, we are confident that DAM existed in the monomolecular state in all experiments at the concentrations used (10^{-3}–10^{-4} *M*). Based on the results with DAM, we have assumed DAF also exists in the monomolecular state.

When a sample of DAM in EPA solution was irradiated by light from 240 to 410 nm (source I, see Experimental Section) at room temperature (~22°), practically complete conversion to ACI occurred. This was followed in absorption by the disappearance of the 296-nm band of DAM and the development of ACI absorption with a maximum at 245–250 nm. In rigid glass at −196° the picture was quite different. On cooling to −196°, the room-temperature absorption band maximum of DAM at 295 nm shifted to longer wavelengths (maximum 315 nm) and showed some structuring (Figure 1). Therefore, it is possible that the band is actually composed of two bands with charge transfer character. Upon ultraviolet irradiation from 240 to 410 nm (source I) in EPA glass at −196°, the original DAM absorption rapidly decreased in intensity, but no ACI absorption developed. However, a broad absorption from 370 to 460 nm, giving a yellow color to the sample, developed as a band shoulder on the long-wavelength edge of photochemically produced DAF (Figure 1). On warming to room temperature, the yellow color disappeared around −160° and part of the intensity of the DAM absorption was restored (~30%). Also, absorption of DAF was increased as can be seen especially clearly on the long-wavelength side of the DAM band after recooling to −196°. The absorption maximum of DAF at room temperature is 314 nm and at −196° is 333 nm (Figure 1).

Absorption in the ~380–460 nm region (Figure 1) appears to originate from aminocyanocarbene. We prepared what has been assigned as aminocyanocarbene by photolysis of the lithium salt of 1-cyanoformamide *p*-toluenesulfonylhydrazone at −196° in a 2-MeTHF matrix.[8,9] A yellow color developed with absorption in the 350–460-nm region with a maximum at ~393 nm. Upon warming, the yellow color disappeared at the same temperature as did the yellow intermediate from the photolysis of DAM. The aminocyanocarbene from photolysis of salts of 1-cyanoformamide *p*-toluene-

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(8) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Amer. Chem. Soc.*, **89**, 5673 (1967).

(9) We wish to thank C. N. Matthews for supplying the hydrazone salt.

sulfonylhydrazone is said to dimerize and DAM is isolated.[8] From all the evidence, it appears that in a rigid glass DAM is in part photochemically split into two molecules of aminocyanocarbene. When the rigidity of the glass is removed, these recombine to give both DAM and DAF.

Three samples of DAM in EPA were irradiated with source I at three different temperatures for 40 min. Cis → trans isomerization was only slightly influenced by the changes of temperature, but varying amounts of ACI were formed. The relative amounts of ACI formed at −150, −50, and 22° were in the ratio 1:2.3:3.6. The latter data indicate a thermal barrier in at least one of the steps of the sequence leading to ACI.

Room-temperature photochemistry of DAM was carried out with different wavelengths. Irradiation of DAM with source I (wavelengths between ~240 and 410 nm) in EPA solution at room temperature resulted in conversion to ACI. Practically 100% conversion occurred in a 10^{-3} *M* solution within 40 min. During the irradiation, the DAF absorption could be seen as a long-wavelength shoulder on the DAM band. Finally both DAM and DAF were consumed, and ACI was formed.

DAM and EPA was irradiated at room temperature with source II and a Corning filter CS 7-60 (maximum at 358 nm with 79% transmission and ~1.25% transmission at 310 and 395 nm) for 1 hr. The DAM band was slowly reduced in intensity, absorption due to DAF clearly developed, but no definite indication of ACI could be observed (some slight increase in absorption in the region of the minimum near 250 nm did occur). Comparable results were obtained with a 150-W Xe source utilizing the same filter. In the latter case, an absorption maximum from ACI was clearly discernible after 3 hr and increased absorption was present in the 250-nm region after 2 hr.

When DAM was irradiated at room temperature with the source II and Corning filter CS 0-53 (Pyrex, ~1% transmittance at 275 nm), conversion proceeded to both DAF and ACI. The ACI band at ~250 nm was clearly present after 30 min of irradiation. The DAM band was reduced in intensity by ~25% and simultaneously, DAF absorption developed. With continued irradiation, the ACI absorption continued to grow while both the DAM and DAF bands were reduced in intensity. After 2 hr of irradiation, essentially no DAM or DAF was present, and the only absorption above 235 nm was that of ACI.

It is important that we point out an observation pertinent to the last experiment above. During the first 30 min of irradiation the absorption of DAM appeared to decrease without a sufficient concomitant increase in both the DAF and ACI absorption (DAM, ϵ ~12,000; DAF,[3] ~8000; ACI,[10] ~11,000 for the first absorption bands). This result indicated the presence of an intermediate with only weak absorption in the region above 280 nm.[11]

In order to obtain further verification of the foregoing observation, DAM was irradiated at room temperature with light near its onset of absorption (150-W Xe lamp, 358-nm maximum, 1.5% transmission at 310 nm; see Experimental Section) alone and simultaneously with 254 nm (2 hr). The absorption of ACI using 254 nm and simultaneously light near the onset of absorption increased approximately twice as fast compared to using light near the onset of absorption alone. Irradiation of DAM with 254-nm light alone for 2 hr and longer apparently did not produce imidazole but did produce DAF. In fact after 1 hr, the magnitude of the absorbance in the region of ACI (~250 nm) decreased because the absorption of the DAF produced is less than DAM in this region. After 3.5 hr, some slight increase in absorption occurs in the 225–245-nm region which results from some unidentified product.

Diaminofumaronitrile (DAF). DAF was irradiated in an EPA rigid glass at −196° with source II plus Corning filter CS 4-69 as a short-wavelength cutoff filter (for wavelengths below 310 nm, ~0.5% transmission at 313 nm). This light is absorbed principally by DAF but somewhat by DAM which has an onset near 335 nm (for DAM and DAF absorption see Figure 1). Trans → cis interconversion occurred as well as the formation of a yellow color. The absorption of the yellow intermediate was the same as the one observed during rigid matrix photolysis of DAM (*vide supra*) and therefore probably results from aminocyanocarbene. No ACI absorption was observed even after 3 hr of irradiation. Upon melting of the glass, the yellow color rapidly disappeared and the absorption of both DAM and DAF increased in intensity. Surprisingly enough after the melting, a weak band was observed in the region of ACI absorption.

Irradiation of DAF was done with the same source and filter as above in EPA at room temperature. In this case no yellow intermediate was observed, and the trans → cis conversion proceeded faster than in the rigid glass. Also, apparently little or no ACI was produced after 2 hr of irradiation at which time the DAF was largely converted to DAM.

Upon irradiation of DAF in EPA solution with the same source and filter as above at −150°, trans → cis isomerization took place. Furthermore, ACI was apparently not produced after 1 hr but was seen after 3 hr of irradiation.

Unfortunately in the foregoing experiments except for the 254-nm filter system, the filter systems permit light leakage of shorter wavelengths, particularly the Hg lines. Consequently, additional experiments were performed where rigorous isolation of an exciting Hg line or bandpass occurred (see Experimental Section for details).

When DAF alone was irradiated in EPA at room temperature with the carefully isolated 366-nm Hg line, only DAM appeared to be produced even after 4 hr of irradiation. There was an increase in the magnitude of the absorbance of the minimum (at ~250 nm), but it was the result of the increased absorption by DAM compared with DAF in this region and no absorption of ACI could be observed. An isosbestic point (broad)

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(10) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, **88**, 3829 (1966).

(11) In one experiment, we irradiated DAM at room temperature and performed a tlc separation of the products. In addition to DAM and DAF another product existed. The unidentified product showed an absorption beginning at ~290–300 nm with a shoulder at ~255 nm and another stronger band at ~225 nm. This latter band was also seen in other photolysis experiments; for example, see Figure 1. Unfortunately, there was insufficient material for identification and the potential significance of the product could only be seen in retrospect.

occurred in the region of ~308 nm, and the composition of the solution after 4 hr was ~62% DAM and ~38% DAF. Irradiation of DAF with 254-nm light alone for 1.25 hr caused very slight isomerization to DAM, but no ACI could be observed. Some of the DAF appeared to be photochemically converted to unidentified species with low (or no) absorption in the near-uv. Simultaneous irradiation with 254- and 366-nm Hg lines for 1.25 hr resulted only in the formation of DAM and an isosbestic point (sharp) at ~303 nm. The DAM was formed much faster than with 254-nm Hg line alone and only slightly faster than the rate with the 366-nm Hg line alone.

Irradiation of DAF alone in EPA at room temperature with (366 + 334)-nm Hg lines for 3 hr produced DAM and an isosbestic point (broad), but no absorption from ACI was observed. A new absorption arose as a band shoulder on the long-wavelength edge of the DAF absorption (maximum ~395 nm). We did not identify the nature of this new species.

Irradiation of DAF alone in EPA at room temperature with the 366-nm Balzer filter alone or simultaneously with 254-nm light clearly produced ACI in 2 hr. We have determined that the 366-nm filter alone passes ~2.5% of the 334-nm, ~1% of the 313-nm, and ~0.6% of the 303-nm Hg lines. Thus, the ACI arose from these latter wavelengths (recall when 366-nm light is carefully isolated, no ACI is formed; *vida supra*).

4-Amino-5-cyanoimidazole (ACI). ACI was prepared by irradiation of DAM in EPA at room temperature with a 100-W high-pressure Hg lamp (plus 5-cm water filter). The assignment of ACI as the product was based on the absorption spectrum assigned to ACI by others.[10] Following this, the ACI was irradiated with 254-nm light for 3 hr. The maximum change in absorbance was about 5% indicating that ACI was quite resistant to photochemical degradation (at least to 254-nm light). This experiment was done to obviate any possible misinterpretation of the foregoing DAM and DAF results because of potential photochemical decomposition of any ACI caused by the 254-nm exciting light employed.

Discussion

It is important to point out first that the data clearly indicate the wavelength of excitation has a marked influence on the photochemical results. We shall allude to this as the discussion proceeds. A salient feature is the fact that, based on the wavelength study (*vide supra*), *excitation of DAF alone at wavelengths well within the absorption onset* (*or at 254 nm*) *appears not to produce the imidazole ACI* (up to room temperature). This is also true if 254-nm light is coupled with the other light. In fact, the highly dominant result of exciting DAF alone is trans → cis isomerization to produce DAM. This conclusion is based on the results obtained (*vide supra*), where exciting Hg lines of 366, 254, 366 + 254 nm and (366 + 334 nm) were carefully isolated and other wavelengths (including Hg lines) were excluded. On the other hand, inclusion of light of other wavelengths, particularly 313 and 303 nm, which are within the absorption region of the first electronic transition, does definitely result in the production of ACI. These wavelengths are not only absorbed by DAF but also by DAM. The data show that irradiation of DAM with excitation that contains 313-nm light results in the formation of ACI, but apparently neither DAF nor DAM is converted to ACI with 334-nm light. It is also true that in the case or irradiation of DAM, the addition of 254-nm light (to say 313-nm light) increases the rate at which ACI is formed, although 254-nm light alone apparently gives no ACI.

It is clear that excitation well within the onset of absorption of DAF rapidly produces DAM which essentially does not absorb the exciting light, and, furthermore, no ACI is produced. Even coupling such exciting light with 254-nm excitation (or 254 nm alone) does not result in ACI. Based on all the information, we are forced to two possible conclusions: (1) DAF cannot form ACI but can be converted to DAM which can form ACI; (2) there is wavelength dependence for the formation of ACI from DAF (potentially true also for DAM). Unfortunately a broadly varying exciting wavelength dependent study for the conversion of DAF alone to ACI cannot be carried out since DAM is immediately formed and excitation of both would occur at shorter wavelengths (<325 nm). On the other hand, relatively long wavelength excitation for DAM, as 310–325 nm, also results in production of DAF and such excitation is relatively short-wavelength excitation for DAF.

The data indicate that DAF cannot be converted to ACI with exciting wavelengths as short as 334 nm (or 254 nm alone as is also true for DAM) which is well into the absorption region of the first transition. However, irradiation of DAM or DAF with 313-nm light (and perhaps up to 325 nm) can produce ACI. The real question is whether this latter result originates from DAM (itself or produced from DAF) or DAF (itself or produced from DAM). If the ACI originates from DAM, there would seem to be no real concern about a wavelength dependence since 310–325 nm is near the 0–0 band of the first transition (of DAM). However, if it is from DAF, then there is a wavelength dependence for production of ACI (*vide infra*). It is interesting based on our discussion above that *DAM and not DAF*[2,3] *may have to be the intermediate* (*the reactant*) *to produce ACI.* In any event, our data indicate that DAF as an intermediate or prime reactant must be excited at relatively short wavelengths (325 nm or less) to form ACI, if indeed it does at all.

The source of a wavelength dependence for the production of ACI could come from (1) a vibronic effect[12] where excitation of a particular quantum level of a given fundamental vibration is required or excitation of a particular fundamental vibration is required or (2) there are two intermixed electronic transitions and excitation of the higher energy one is required.

The one fact that is clear is that cis (DAM) ⇄ trans (DAF) isomerization occurs at the onset of absorption of both DAM and DAF and no wavelength dependency need be invoked. The DAM (cis) ⇄ DAF (trans) photoisomerization occurs both in a rigid matrix and in fluid solutions (faster in the latter). In addition, there is only a very small activation energy in the excited state(s) for the cis ↔ trans isomerization. Thus, excitation of either would lead to a common species in which twisting by 90° has occurred around the double

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(12) R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969).

bond. Internal relaxation (conversion) would then lead to either the cis or trans form. The results regarding the activation energy requirements for photo cis → trans isomerization parallel other similar processes studied by us.[13–15] The trans → cis processes generally have a higher barrier than the cis → trans isomerization processes. However, in the case of both DAM and DAF, the first absorption band has appreciable charge transfer character. Consequently, the nature of the excited states and shape of the potential energy curves may be different from the usual considerations where they are π,π^* (or n,π^*).

The results of the irradiation of DAM with relatively long-wavelength light alone, 254-nm light alone, and these in combination point to the existence of at least one intermediate between DAM and ACI, not including the possibility of DAF. It should be kept in mind that we cannot be assured that it is not the DAF produced that is reacting (resulting from the shorter wavelengths of light used to irradiate DAM being beyond the onset of ACI formation). Based on the data, the production of the ACI is consistent with a minimum requirement of two photons as

$$\text{DAM (DAF)} \xrightarrow{h\nu_1} \text{intermediate} \xrightarrow{h\nu_2} \text{ACI} \qquad (1)$$

It has been stated[2,3] that DAF is a necessary intermediate in the DAM → ACI process. If indeed this were to be true, then the photochemical formation of ACI from DAM would appear to require at least three photons as

$$\text{DAM} \xrightarrow{h\nu_3} \text{DAF} \xrightarrow{h\nu_1} \text{intermediate} \xrightarrow{h\nu_2} \text{ACI} \qquad (2)$$

assuming DAF goes through an intermediate comparable to that from DAM, if DAF does react.

The imidazole, ACI, essentially is not formed in a rigid matrix but is in fluid solution. Based on the temperature data for the formation of ACI with initial irradiation of DAM, an activation energy exists for the process. It is not possible to determine if the activation energy requirement(s) originate(s) in a photo or thermal step(s) or both.

Recall that for both DAM and DAF, irradiation in a rigid matrix apparently produces aminocyanocarbene. Also, in the case of DAF, melting of the rigid matrix in the dark resulted in the formation of some ACI. This warns us of a potential complication to the previous mechanism(s) postulated[6] for formation of ACI from either DAM or DAF. Although the aminocyanocarbene cannot be observed in fluid solution, it could nonetheless exist as a transient. Based on the foregoing results with DAF, the carbene could participate in the formation of an intermediate (reactions 1 and 2) or react with an intermediate or something else to produce ACI. Others have postulated that an azetine is an intermediate in the formation of ACI.[6] However, we feel we do not have sufficient data to warrant identification of our suspected intermediate. We are performing further experimental and theoretical investigation regarding the formation of aminocyanocarbene and the relation of this to the bond energy of DAM and DAF in both the ground and excited states.

Summary

It is not possible to develop an unequivocal interpretation of the mechanism for photochemical formation of ACI from DAM and DAF. This situation results from the facts that (1) these geometric isomers are photochemically interconverted with high quantum yield, (2) the absorption spectra of DAM and DAF overlap quite significantly, and (3) DAF does not form ACI at wavelengths not simultaneously absorbed by DAM. We have been forced to conclude that either (1) DAF does not produce ACI but DAM does or (2) that for DAF, there is a wavelength dependence for the formation of ACI (onsetting at 325 nm or less). Because of this latter possibility and the rapid formation and coexistence of DAM and DAF (with consequent absorption overlap), we cannot determine if a wavelength dependence exists for the formation of ACI from DAM. Irradiation with 254-nm light alone, which is absorbed by both DAM and DAF and appears not to result in the formation of ACI, does cause isomerization and produces other unidentified photochemical products (from both pure DAM and DAF).

The photochemical production of ACI is consistent with the requirement that a minimum of two one-photon steps occur. No ACI appears to be produced in a rigid matrix at low temperature even when irradiation includes wavelengths as short as 240 nm; however, aminocyanocarbene appears to be generated. Upon melting of the rigid matrix in the dark, the aminocyanocarbene dimerizes to produce both DAM and DAF, and can apparently react to produce some ACI (at least in the one case of irradiation of what originally was DAF).

Cis ⇄ trans photoisomerization occurs with a high quantum yield and has only a very small activation energy. The photochemical formation of ACI has an overall activation energy which is greater than that necessary for isomerization.

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(13) R. S. Becker, K. Inuzuka, and J. King, *ibid.*, **52**, 5164 (1970).

(14) R. S. Becker, K. Inuzuka, J. King, and D. Balke, *J. Amer. Chem. Soc.*, **93**, 43 (1971).

(15) K. Inuzuka and R. S. Becker, *Bull. Chem. Soc. Jap.*, **44**, 3323 (1971).