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Light-induced transformations of aza-aromatic pollutants adsorbed on models of atmospheric particulate matter: Acridine and 9(10-H) acridone

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Abstract

The effect of the characteristics of the surface on the phototransformation of acridine, one of the most abundant azapolycyclic compounds encountered in urban atmospheres, and of one of its principal photoproducts, acridone, was studied when adsorbed onto models of the atmospheric particulate matter. For this purpose, relative photodegradation rates were determined from absorption or emission intensities as a function of irradiation times, and some products were isolated and characterized. The relative photodegradation rates of adsorbed acridine show the tendency $(\text{NH}_4)_2\text{SO}_4 > \text{MgO} > \text{Al}_2\text{O}_3 > \text{SiO}_2$. In general, the rates decrease as the fraction of protonated acridine species on the surface increases in MgO, Al_2O_3 , and SiO_2 , except for $(\text{NH}_4)_2\text{SO}_4$ where a fast surface reaction occurs. Oxygen reduces the photodestruction rates by as much as 40 to 60% when compared to an inert atmosphere, implying the participation of an acridine triplet state in the transformation processes on all surfaces except on $(\text{NH}_4)_2\text{SO}_4$. Acridone, a major product, undergoes a photoinduced tautomerization to 9-hydroxy acridine. The formation of a dihydrodiol, another photoproduct of acridine, is suggested by comparison to reported spectral properties of these compounds. This is formed through a singlet oxygen reaction. Photoproducts showing the absence of the narrow absorption band of 250 nm, characteristic of the $\pi \rightarrow \pi^*$ transition in tricyclic aromatics, were detected in small yields but not identified. These results suggest possible photochemical transformation pathways that could lead to the ultimate fate of these pollutants in the environment.

Keywords

Acridine; acridone; phototransformations; models of atmospheric particulate matter

1. Introduction

It has been proposed that polycyclic aromatic compounds (PACs) adsorbed on the atmospheric particulate matter can undergo chemical transformations leading to the formation of products more polar than the parent PAC (Daisey, 1980). Therefore, the harmful properties of the atmospheric particulate matter can depend on the probability of thermal and photochemical reactions that transform the parent compounds. Such transformation of PACs may occur via photodegradation on atmospheric particles (Arey et al., 1987; Kamens et al., 1988).

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More than 100 PAHs have been identified in urban air, and their photochemistry has been well studied using models of atmospheric particulate matter (Seinfeld and Pandis, 1998). Although, 47 azapolyaromatic compounds (aza-PACs) have been identified on atmospheric particulate matter, no information on their phototransformation on models of atmospheric particulate matter is available (Chen and Preston, 1998). Therefore, in this work we are concerned with phototransformations of azaarenes on the particulate matter. For the following reasons acridine (1) (Figure 1) was selected as a representative azaaromatic in order to study its phototransformations and interactions on different models of atmospheric particulate matter. First, it is one of the most abundant aza-PACs that have been detected (Carlsson and Ostman, 1997; Yamauchi and Handa, 1987). For example, in urban atmospheric particulate matter analyzed in Tokyo and air polluted by coal tar pitch, it was the aza-PAC present at the highest concentration (Yamauchi and Handa, 1987). Of 22 aza-PACs detected in a solvent refined coal heavy distillate, acridine was the third most abundant (Carlsson and Ostman, 1997). Furthermore, studies of the toxicity of acridine and its photoproducts on the marine diatom *Phaeodactylum tricornutum* revealed that after irradiation with a 350 nm lamp, the toxicity of acridine in the solution increased (Wiegman, 2002). Therefore, acridine photoproducts may be more harmful than the parent compound. Because acridine absorbs in the UV-A region of the solar spectrum it can undergo photodestruction on the atmospheric particulate matter in the troposphere. Additionally it is a convenient representative of aza aromatics because its symmetrical structure can reduce the number of photoproducts and simplify their characterization.

The ground and excited state of acridine species adsorbed on models of atmospheric matter (SiO_2 , $(\text{NH}_4)_2\text{SO}_4$, Al_2O_3 and MgO) and their decay pathways were determined in a previous study (Negrón-Encarnación et al., 2005). On silica, the ground state species present were hydrogen-bonded (AN ... HO), neutral (AN), and protonated (ANH^+), while on alumina hydrogen-bonded and neutral species were identified. The emission intensities of protonated acridine on silica and alumina were higher than expected. This was interpreted as resulting from photoprotolytic reactions on these surfaces. For acridine adsorbed on ammonium sulfate, protonated acridine was the only adsorbed species identified. Since the fluorescence intensity and lifetime of acridine on ammonium sulfate was smaller than for acridine in acidic water, at a similar ground state absorbance, quenching of the excited state or a rapid photochemical reaction with the surface was proposed. On magnesium oxide, neutral and hydrogen-bonded acridine species were characterized. That study (Negrón-Encarnación et al., 2005) demonstrated that acridine-adsorbed species and their decay pathways depended on the acidic properties of the models of atmospheric particulate matter.

Herein, the photodegradation rates and phototransformation pathways of acridine on the different solids surfaces are compared and interpreted. Because acridone (2) was identified as one of the main products of the photolysis of acridine, its light-induced degradation and transformation was studied on the inorganic solids used previously. Acridone may be present in the semipolar or polar fractions of atmospheric particulates. However, no information on the presence of acridone on these substrates is available because the analysis of the semipolar and polar fraction of particulates have been inhibited by the complexity of these substrates. Because acridone absorbs in the UV-A and visible regions of the solar spectrum, it may undergo photoinduced transformations. Thus, it is important to determine the principal products of the photolysis of acridone to shed light on the final fate of acridine in the atmosphere.

2. Experimental Section

2.1 Reagents and Sample Preparation

Acridine (99.2% of purity by HPLC), chromatographic grade 60 Å silica, and magnesium oxide were obtained from Aldrich, alumina from Sigma Chemical, ammonium sulfate from Alfa

AESAR, and the solvents (optima grade) from Fisher. The water content (Galbraith Laboratories) and BET surface area (Quantachrome Instruments) analysis were done for all solids examined. The results of these tests were: ammonium sulfate (0.10% water, $2.196 \times 10^{-2} \text{ m}^2/\text{g}$); alumina (8.59% water, $1.960 \times 10^2 \text{ m}^2/\text{g}$); silica (9.53% water, $4.100 \times 10^2 \text{ m}^2/\text{g}$); magnesium oxide (9.67% water, $1.016 \times 10^2 \text{ m}^2/\text{g}$). The adsorbed samples were prepared by adding a measured amount of a solution with a known concentration of acridine in hexane to a weighed amount of the adsorbent to obtain the desirable loading concentration. After the complete adsorption of the acridines the solvent was removed by rotoevaporation. The reproducibility of sample preparation and of the loading procedure was established from initial fluorescence or diffuse reflectance intensities. The surface loadings used were lower than a monolayer as determined from Langmuir adsorption isotherms. (Negrón-Encarnación et al., 2005). Methylene blue adsorbed onto alumina at a surface loading of $1 \times 10^{-6} \text{ mol/g}$ was used as a singlet oxygen sensitizer. Singlet oxygen sensitization studies were done by irradiating a mixture 1.0 g of acridine on alumina with 2.0 g of methylene blue on alumina under an O_2 atmosphere. Acridone samples were prepared by equilibrating an acridone in acetonitrile solution ($1 \times 10^{-4} \text{ M}$) with the corresponding solid.

2.2 Diffuse reflectance and emission spectroscopy

Fluorescence spectra were recorded with a SLM AMINCO spectrofluorometer model MCN320 upgraded with photon-counting electronics of ISS using a 4 nm wide excitation and emission slits. Diffuse reflectance spectra were obtained using a Varian Cary 1E double beam spectrophotometer with an integrating sphere.

2.3 Photolysis studies

The samples were irradiated with an Oriel 300 W or 1000 W Xe(Hg) lamp. A water filter was used to eliminate IR radiation, and a broad band Corning 7–51 filter was used to irradiate the samples of acridine and acridone. The lamp irradiance reaching the sample was $1.1 \times 10^{-2} \text{ W/cm}^2$ for the 300 W lamp and $3.0 \times 10^{-2} \text{ W/cm}^2$ for the 1000 W lamp. The photodegradation of acridine or acridone adsorbed on the solid surfaces was followed using diffuse reflectance techniques (for AN on MgO) or front face fluorescence (for AN on $(\text{NH}_4)_2\text{SO}_4$, SiO_2 and Al_2O_3) intensity measurements before and after the irradiation of the sample inside a 2 mm stationary quartz cell. For the HPLC analysis of the extracted samples, a pyrex rotatory cell was used to irradiate the samples. For the singlet oxygen sensitization studies a Corning 3–67 filter was used to irradiate the sample with methylene blue inside a rotatory cell and under an oxygen atmosphere.

2.4 Extraction procedure

The extraction efficiency of acridine and its products from the solid surface by methanol, ethanol, dichloromethane, acetonitrile, and ethylacetate was determined. The highest extraction efficiencies of acridine (90 to 100%) and acridone (95 to 100%) from the surfaces were obtained by using methanol (5–20 mL per extraction) as the solvent, with the assistance of ultrasound (5–10 min per extraction). The efficiencies were determined by measuring the emission and the absorption intensities before and after the extraction procedure. For $(\text{NH}_4)_2\text{SO}_4$ as the adsorbent a 1:1 mixture of methanol and acetonitrile was used to avoid dissolution of the salt. Four extractions were needed to obtain these high efficiencies. A 25 mm nylon syringe filter was used to filter the extracts. In the case of acridine samples adsorbed on MgO , centrifugation of the suspended solid was necessary prior to filtration, because the particles did not settle sufficiently rapid for the standard extraction procedure. The extracts were pre-concentrated with a rotoevaporator to produce a final volume at which the acridine concentration could be quantified by HPLC when following its photodestruction.

2.5 High performance liquid chromatography

Chromatographic analyses of non irradiated and irradiated acridine samples were done by injecting 75 μ L of the extracts into a Shimadzu HPLC/system equipped with two model LC10AD high-pressure pumps. The absorption spectra of the photoproducts and the quantification of the fractions were determined using a Shimadzu photodiode array detector (model SPD-M10A). The system was controlled with a Shimadzu SCL-10A system controller. A Prodigy C18 Phenomenex column (250 x 4.6 mm i.d.) was employed with a gradient composition of methanol and water and a total flow of 1 mL/min. The gradient was linearly varied, from 0 to 9 minutes with 60% to 80% methanol and from 9 to 18 minutes with 80% to 60% methanol. The chromatographic run was ended after 30 minutes. The chromatographic plots were recorded at 250 nm and the data analyzed from the chromatographic peak area. Because some thermal degradation of acridine on the solids surface occurred immediately after preparation of the sample, the chromatographic area of the peaks of an irradiated sample was compared to those of the unirradiated sample. If the chromatographic area of the peaks increased or appeared for samples irradiated with respect to those not irradiated, the peak was assigned to a photoproduct.

2.6 High performance liquid chromatography with mass spectrometry

To determine the mass of the major photoproducts, an HPLC coupled in parallel with a mass spectrometer (MS) detector was used, with an electrospray interface and Mass Lynx version 3.3 software. The chromatographic run was done using the same method employed for the analysis of the extracted samples as previously explained. The mass spectrometer was tuned using acetonitrile to verify its calibration and to optimize the position of the interphase. Standard solutions of acridine and acridone were used to optimize the electrospray interface voltage. These were introduced directly by means of a 250 μ L gas syringe mounted on a Kd Scientific Infusion Pump model 100. The flow speed was 0.1 mL/min. After tuning the instrument, the samples were injected using the HPLC autosampler.

3. Results and Discussion

3.1 Spectral changes during irradiation and phototransformation rates of acridine on different solids

Photolysis of acridine adsorbed on the surface of the inorganic solids used as models for atmospheric particulate matter resulted in the spectral changes presented in Figure 2. The absorbance at 250 nm decreased with increasing irradiation time on all surfaces indicating photodestruction. A simultaneous increase in the absorbance at the 260–320 nm wavelength region was observed in irradiations performed under N₂, air or O₂, suggesting the formation of adsorbed photoproducts. An increase above 380 nm was seen under those conditions in samples irradiated on silica, alumina, and magnesium oxide, and above 450 nm on ammonium sulfate. This increase in absorbance in the long wavelength region of the spectrum, common to photolysis on all solids, was later ascribed to the formation of acridone. During the irradiation the samples acquired a slightly darker yellow color.

Relative photodegradation rates of acridine were calculated using absorbance and fluorescence intensities measured at spectral regions and irradiation times where no interferences from absorbing or emitting photoproducts were evident. A simple first order photoprocess was assumed for complex photodegradation on the surfaces. Under a N₂ atmosphere, the rates of the photodegradation rates on (NH₄)₂SO₄, MgO, and Al₂O₃, relative to that on SiO₂ (the smallest observed) were 107, 25, and 18. The slower photodegradation rates observed on MgO, Al₂O₃, and SiO₂ surfaces in comparison to (NH₄)₂SO₄ could be explained in terms of the relative amounts of the different acridine species (neutral (AN), hydrogen bonded (AN ... HO) and protonated (ANH⁺)) adsorbed on each surface.

This dependence was also observed in the photodegradation rates of acridine in aqueous solution at different pHs (data not shown). At pH 2.5, protonated acridine photodegraded three times slower than neutral acridine at pH 8. In aqueous solution protonated acridine does not undergo an intersystem crossing process to the triplet state while neutral acridine does (Negrón-Encarnación et al., 2005). Therefore, the slower photodegradation rate of ANH^+ relative to AN can be related to the absence of a triplet photodegradation pathway.

The trend observed for the photodegradation rates on the substrates of $\text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{MgO}$ was attributed to the increasing proportion of the ANH^+ species on these surfaces. According to our diffuse reflectance, emission, and triplet-triplet (T-T) absorption data (Negrón-Encarnación et al., 2005), no ANH^+ was present on MgO. On alumina, although no ground state ANH^+ species were observed, excited proton addition reactions of AN were demonstrated by fluorescence studies. These reactions decreased the quantity of neutral AN available to transform to the triplet state, resulting in a lower photodegradation rate of neutral AN on alumina in comparison to MgO. The T-T absorption band of acridine on alumina appeared in the same wavelength region as that for the T-T absorption of neutral and hydrogen-bonded species. The absence of a T-T band from ANH^+ supported the hypothesis that intersystem crossing is not a major path for the deactivation of the protonated acridine singlet excited state (Negrón-Encarnación et al., 2005). On silica, ground-state neutral, hydrogen bonded, and protonated acridines were detected. Fluorescence measurements provided evidence for a photoprotolytic reaction, resulting in the transformation of AN into ANH^+ species. Triplet-triplet annihilation processes on this surface produced an intense delayed fluorescence signal obscuring the detection of triplet absorption signals. The delayed fluorescence signal suggested a high mobility of the protonated triplet species on silica, reducing the population of this state. No transient absorption signals from triplet or radical intermediates were observed for acridine absorbed on $(\text{NH}_4)_2\text{SO}_4$. Thus, the slower rates observed on SiO_2 , Al_2O_3 , and MgO surfaces can be explained in terms of the relative amounts of the ANH^+ species present. As its relative proportion increased, there is a decrease in the number of acridines reaching a reactive triplet state, and thus the photodegradation rate also decreased. The faster rates observed on $(\text{NH}_4)_2\text{SO}_4$ were explained in terms of an excited state reaction of acridine on this surface, supported by the steady state and lifetime fluorescence results (Negrón-Encarnación et al., 2005).

On all surfaces, the photodegradation under an N_2 atmosphere was faster than under O_2 , except for acridine on $(\text{NH}_4)_2\text{SO}_4$ where the rates were similar. The ratio of the rate constants calculated for samples irradiated under oxygen compared to a nitrogen atmosphere was 0.6 on MgO, 0.5 on SiO_2 and 0.4 on Al_2O_3 . This O_2 effect suggests the participation of the acridine triplet state in the photodegradation process. Indeed, in the presence of O_2 , the AN and AN ... HO triplets were quenched through efficient energy transfer from the acridine triplet to O_2 . This was demonstrated by the absence of T-T absorption bands from adsorbed acridine under those conditions (Negrón-Encarnación et al., 2005).

3.2 Product identification and quantification

To be able to detect acridine photoproducts, larger quantities of adsorbed samples (0.4 to 1g) were irradiated in a rotatory cell. On alumina, a 47% photodestruction was observed after 30 minutes of irradiation, and the chromatogram showed the formation of two major products with retention times of 9.0 and 10.7 minutes, respectively (Figure 3). Other peaks observed resulted from the thermal degradation of acridine on the surfaces. The absorption spectrum of the product with a retention time of 9.0 minutes presented a red shift relative to acridine (Figure 4a), therefore, it may have been responsible for the increase in absorbance at the 380–450 nm region observed during the irradiation. The mass spectrum (Figure 4b) presented a m/z of 196

(M+H) corresponding to acridine with one oxygen atom, which could have been due to the incorporation of a hydroxyl or a ketone functional group on to the acridine.

A common oxidation product of acridine is 9(10H)-acridone (ANO), (Wiegman et al., 2003). A standard of ANO was added to an extract of a photolyzed sample of acridine on alumina and the area corresponding to this product, which has a retention time of 9.0 min, increased in the chromatogram. Therefore, the photoproduct was characterized as ANO. The percent of formation of acridone was determined to be 0.4%, from less than 40% of photolyzed acridine. At higher photodegradation percentages, the rate of formation of ANO decreased and a photoproduct with a retention time of 10.7 min appeared (Figure 5). A similar behavior was observed on a silica surface. On MgO and $(\text{NH}_4)_2\text{SO}_4$, this secondary product was not observed. Because acridone absorbs in the wavelength region of 340–415 nm and the band pass filter transmits in this region (310–410 nm), it could absorb the incident radiation and undergoes photodestruction. Indeed, the photoproduct with retention time of 10.7 min arose from the photolysis of acridone, as discussed later.

Although additional photoproducts from irradiated acridine on alumina were not detected in the HPLC chromatogram, fluorescence measurements on the irradiated samples of acridine on alumina showed the formation of another photoproduct (Figure 6). The excitation spectra showed that this photoproduct absorbed in the 250–350 nm wavelength range. The emission of this fluorescent product was also observed on silica and magnesium oxide surfaces when excited at 290 nm. The maximum on the emission spectrum was at 366 nm, while excitation maxima were at 290, 328, and 344 nm on alumina, at 284, 330, and 344 nm on silica, and 289, 330 and 344 nm on magnesium oxide. The position of these wavelengths corresponded to those reported for 1,2-acridine dihydrodiol or 3,4-acridine dihydrodiol (McMurtrey and Knight, 1984; Sutherland et al., 1994), 290, 330, and 345 nm in a methanol water solution. The fact that the chromatographic peaks of these dihydrodiols were not observed in the extracts of photolyzed acridine on the solid surfaces was due to their low yields and instability on the surfaces.

The small quantities of photoproducts of acridine formed on alumina could be explained in terms of the formation of products with a blue shifted absorption band and small absorption coefficients. These result from photochemical reactions in which the acridine π conjugation in acridine is lost. The absence of the narrow absorption band at 250 nm for these products, characteristic of the $\pi \rightarrow \pi^*$ transition in tricyclic aromatic compounds, indicates the limited or absence of π conjugation. Products with similar absorption spectra to benzoic acid and benzaldehyde, which would indicate ring rupture of the parent acridine, were detected in the chromatographic analysis of the extracts of irradiated acridine on ammonium sulfate and silica.

After 9% photodegradation on MgO, the only acridine products detected were acridone and acridine dihydrodiol. Three major photoproducts were detected for the extracts of irradiated acridine on SiO_2 , where the largest fraction of protonated acridine was found in comparison to Al_2O_3 and MgO surfaces (Negrón-Encarnación et al., 2005). These included: acridone, a second resulting from the photodegradation of acridine (also observed on alumina), and a third with a shorter retention time (2.6 min) and an absorption spectrum with onset around 330 nm and maxima at 230 nm, demonstrating the loss of the π conjugation in acridine. The absorption spectrum of the third product was similar to that of benzoic acid, but was shifted towards the red. For irradiated acridine adsorbed on $(\text{NH}_4)_2\text{SO}_4$, three mayor products were detected, one of these being acridone. Only 5% of the acridine transformed to acridone after 65% photodestruction. On this surface, the photoproduct of ANO observed on the other solids was not detected. Therefore, its formation may not be favorable under acidic conditions. Two other products presented blue shifted absorption spectra relative to acridine due to significant loss of the π conjugation resulting from ring cleavage reactions.

Under the conditions used for the mass spectrometric analysis of the extracts these products were not detected, even in highly concentrated extracts. Therefore, mass balance on the amount of acridine destroyed and products formed could not be performed. The elusiveness of acridine photoproducts and their small yields have been reported. Phototoxicity studies of acridine to marine phytoplankton in aqueous solutions showed that although acridone was the main transformation product (Wiegman et al., 2003), only 10% of the acridine loss was transformed into it while other products were not identified.

3.3 Singlet oxygen reaction and mechanistic considerations

Singlet oxygen sensitization studies were performed to determine if any of the acridine photoproducts were produced by the reaction of acridine with $^1\text{O}_2$. The formation of $^1\text{O}_2$ by an energy transfer process from the acridine triplet has been reported in benzene (Wilkinson et al., 1993), although a self photosensitization reaction has not. Excitation of methylene blue, a singlet O_2 sensitizer, for five hours in presence of adsorbed acridine on alumina under an O_2 atmosphere resulted in a 2% photodegradation of acridine with the formation of three products that could be resolved from the chromatogram. Two of the products presented absorption spectra similar to that of acridine, while the third showed an absorption spectrum similar to an acridine dihydrodiol, 1,2-dihydroxy-1,2-dihydroacridine, or 3,4-dihydroxy-3,4-dihydroacridine. Acridone was not detected on the sensitization studies. The acridine dihydrodiol was also observed in the photolysis of acridine in hexane saturated with O_2 . To confirm the participation of a singlet oxygen reaction, the adsorbed samples containing methylene blue were irradiated in the presence of coadsorbed 2,5-dimethylfuran, an effective $^1\text{O}_2$ quencher. In this irradiation, no products were formed.

Acridone was the photoproduct observed on all the inorganic solids tested, and in water solutions saturated with O_2 or N_2 . In terms of these results, the following phototransformation route would be proposed for neutral acridine (Scheme 1).

It is hypothesized that once neutral acridine is excited to its singlet or triplet state it reacts with adsorbed water to produce 9-hydroxy-10-hydroacridine. A reaction in which water is dissociated and the hydroxyl undergoes nucleophilic addition to the 9th carbon and the proton forms a bond with the nitrogen is proposed.

For protonated acridine, the first excited singlet state would be the reactive state precursor to the formation of acridone. In this case, because in the first excited singlet state the acridine nitrogen acquires a higher electron density than in its ground state, the 9th carbon may have a lower electron density facilitating its oxidation. The 9-hydroxy-9,10-dihydroacridine would be formed through a nucleophilic addition of water at the 9th carbon followed by proton dissociation (Scheme 2).

The 9-hydroxy-9,10-dihydroacridine is thermally unstable because of the lower electron density at the 9th carbon atom due to the presence of the electron withdrawing hydroxyl group. In the presence of O₂, acting as an electron acceptor, the 9-hydroxy-9,10-dihydroacridine would be oxidized to acridone (Scheme 3).

An acridine dihydrodiol photoproduct was observed on alumina, silica, and magnesium oxide surfaces. Its absence on ammonium sulfate correlated well with the absence of formation of a triplet excited state acridine species (Negrón-Encarnación et al., 2005) on this surface that could sensitize singlet oxygen. A mechanism for the formation of the acridine dihydrodiol product is proposed to be initiated by the addition of singlet oxygen to the 1,2 or 3,4 C=C bond to produce a dioxetane; which may be reduced to the dihydrodiol (Scheme 4).

3.4 Phototransformation of acridone

Acridone was the photoproduct of acridine detected on all the inorganic solids examined, and it was observed that its formation rate decreased with increasing periods of irradiation. Additional photophysical and photochemical studies were done to determine its transformation on the surfaces, and to provide information on the ultimate fate of acridine on the models of the atmospheric particulate matter.

3.4.1 Adsorption and emission properties of adsorbed acridone—The UV-A band of the absorption spectrum of acridone on alumina, silica, and ammonium surfaces are shown in Figure 7. The maxima on this band for silica were at 384 and 399 nm, while for alumina at 387 and 402 nm, respectively. The position of these bands was similar to those observed for acridone in methanol (380 and 398 nm) and water (387 and 405 nm), while red shifted with respect to acridone in acetonitrile (373 and 391 nm). The similarity of the wavelength of maximum absorbance of acridone on alumina and silica, and in water and methanol was related to the formation of hydrogen bonds, and to the similar dielectric properties of these environments. On ammonium sulfate, maxima appeared at 396 and 418 nm, red shifted relative to those of acridone in water, suggesting a more effective electronic stabilization on ammonium sulfate. The ions on this surface can stabilize the charge separation in acridine induced by photon absorption more efficiently than in water or on neutral surfaces such as silica and alumina, where the excited molecule is stabilized by weaker dipole-dipole interactions. The emission spectra presented two well-defined maxima and two shoulders on the 410 to 450 nm region.

3.4.2 Spectral changes during irradiation—The photolysis of acridone on the solids surface was studied to determine its possible degradation on atmospheric particulate matter, and its dependence on the nature of the surface of the substrate onto which it is absorbed. The spectral changes observed during the irradiation of acridone on alumina are shown in Figure 8. The acridone UV-A band absorbance decreased demonstrating its photodestruction on the

surface. The emission intensity also decreased with increasing irradiation time. The absorbance above 450 nm increased showing the formation of adsorbed photoproducts. These presented a red-shifted absorption spectra with respect to acridone, implying that the transformation resulted in a more conjugated aromatic system or in the attachment of electron withdrawing groups to the aromatic rings. The absorbance in the 320 nm region also increased, but to a lower extent. Similar first order photodegradation rate constants of the order of 10^{-5} s^{-1} were calculated on the surfaces, suggesting that the surface pH and polarity did not have a significant effect on the photochemical behavior of acridone on the surface.

3.4.3 Photoproducts—The main photoproduct presented a retention time of 10.4 minutes in the chromatogram of the extracted samples of photolyzed acridone on alumina and silica. Its absorption spectrum was red-shifted relative to that of acridone. Therefore, it contributed significantly to the absorbance of the band in the 450 nm region of the diffuse reflectance spectra for photolyzed acridone on alumina and silica. Its retention time and absorption spectrum corresponded to that of a product observed on the chromatogram of photolyzed acridine on silica and alumina. The mass spectrum of this product showed a base peak of 195 m/z. This did not correspond to the M+H molecular cation because an even mass (194 g/mol) is not characteristic of molecules containing an odd number of nitrogens. Therefore, the base peak resulted from the ionization of the molecule and not from its protonation. Because the mass observed was equal to that of acridone, therefore, this product may have been an acridone isomer such as 9-hydroxyacridine. Chromatograms of extracts of irradiated samples of acridone on magnesium oxide and ammonium sulfate surfaces did not show the presence of the acridone photoproduct. Due to the pronounced light scattering properties of magnesium oxide powder, small photodestruction percentages were achieved (9%) that were not sufficient to detect the product. Its absence on ammonium sulfate was related to the stabilization of (π , π^*) states and destabilization of the (n , π^*) states in a highly polar environment. On this surface, a large red shift in the absorption and emission bands of acridine was observed relative to water; indicating stabilization of the (π , π^*) states. This could result in a higher energy difference between the $^1(\pi$, $\pi^*)$ and the $^3(n$, $\pi^*)$ states and therefore in a smaller population for the $^3(n$, $\pi^*)$ states. Because this state may be the precursor to acridone, its low yield on this surface could explain the absence of this product.

It is known that $^3(n$, $\pi^*)$ states of ketones are capable of abstracting a hydrogen atom from a suitable hydrogen donor to produce a ketyl radical (Turro, 1991). Acridone should not be an exception. Previous studies on the photolysis of acridone in benzene in the presence of phenol showed that acridone in its triplet excited state abstracts a hydrogen atom from the phenol to form a ketyl radical (Niizuma and Kawata, 1993). Also, the phototransformation of acridone can be compared to that of its isoelectronic analog, anthrone (Kanamaru and Nagakura, 1968; Redmond and Scaiano, 1989). Based on the phototransformation mechanism of anthrone and the evidence for the formation of the acridine ketyl radical in the presence of phenol, the following mechanism is postulated for the formation of 9-hydroxyacridine in the photolysis of acridone on the solids surfaces.

Where XOH could be a silanol or an aluminol group.

4. Conclusions

Because of the heterogeneity of atmospheric particulate matter, different acridine species (protonated, hydrogen bonded, and neutral) are expected to be present. The acridine photodegradation rates observed in this study on the different models of the atmospheric particulate matter depended on the nature of the surface which determined the proportion of the different species of acridine adsorbed on the surface in the ground and excited states. Therefore, the phototransformation rates of azaaromatics are expected to depend on the acidity and hydroxylic content of the surfaces. In general, in acidic particulate, the photodegradation of acridine decreases due to the formation of the less reactive protonated species on such surfaces. On $(\text{NH}_4)_2\text{SO}_4$ surfaces, higher rates observed are proposed to occur due to a reaction with the surface; thus with an increase in the concentration of this salt in the aerosol, higher acridine transformation rates could be expected. Triplet transformation routes are favored, and because oxygen quenches these states, a reduction in the photodegradation rates is expected. Singlet oxygen reactions contribute a lesser extent to the photodestruction of acridine, only leading to the formation of an acridine dihydrodiol.

Acridone, the major photoproduct formed on all surfaces could serve as a tracer of acridine oxidation on atmospheric particulate matter. Its formation can be considered as a potential environment hazard, because photoexcited acridine is known to induce DNA damage (Hirakawa et al., 2003). Photoinduced tautomerism of acridone on the surfaces resulted in the formation of 9-hydroxyacridine, its principal product. This reaction could be favored in the presence of hydrogen donors on these surfaces.

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Figure 1.
Schematic representation of acridine (1), 9(10-H)-acridone (2) and 9-hydroxyacridine (3).

Figure 2.

Diffuse reflectance spectra of acridine on silica, alumina, magnesium oxide, and ammonium sulfate at different irradiation times using a stationary cell and a 300 W lamp.

Figure 3.

Chromatogram of extracted samples of 6x10⁻⁷ mol/g acridine on alumina unirradiated (—) and irradiated (—) for 30 min (47% of destroyed acridine). Mass of acridine injected in to the unirradiated sample: 0.60 µg.

Figure 4.

Absorption (a) and mass spectra (b) of acridone produced on a sample of acridine on alumina photolyzed by 130 min (59% of photodestruction). Irradiation with the 300 W lamp.

Figure 5. Photodegradation of 6×10^{-7} mol/g acridine (■) on alumina and formation of its photoproducts, acridone (●) and tr=10.9 min (▲), at several irradiation times. Irradiation with a 300 W lamp.

Figure 6. Excitation spectrum (—) em 365 nm, and emission spectrum (---) ex 290 nm, of the acridine dihydrodiol on alumina

Figure 7. Diffuse reflectance spectra of acridone on silica gel (—), alumina (— —) and ammonium sulfate (—..—).

Figure 8. Diffuse reflectance spectra of 3×10^{-7} mol/g acridone on alumina at different irradiation times.