

Fading of Organic Artists' Colorants by Atmospheric Nitric Acid: Reaction Products and Mechanisms

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■ The reaction products formed upon exposure of selected artists' colorants to gas-phase nitric acid have been identified using chemical ionization mass spectrometry. The two organic colorants that were most nitric acid-fugitive were triphenylmethane derivatives: the chloride cationic dye basic fuchsin yielded the corresponding nitrate salt, and the carbinol pararosaniline yielded the corresponding organic nitrate ester. Both also yielded small amounts of benzophenones. Other colorants studied yielded only small amounts of oxidation (but not nitration) products, i.e., phenols and/or ring-opening products: benzoic acid and hydroxyquinacridone from acridones, isatin and isatoic anhydride from indigo, trihydroxyanthraquinone from alizarin, and phthalic acid from Alizarin Crimson. The corresponding reaction mechanisms are outlined. The results are discussed in terms of possible damage to colorants in museum collections resulting from exposure to atmospheric nitric acid.

Introduction

Studies carried out in this laboratory have shown that several categories of organic artists' colorants fade substantially when exposed, in the dark, to purified air containing 0.3–0.4 ppm of ozone over a period of 3 months (1–3). Such ozone concentrations can occur during urban photochemical smog episodes, and the total ozone dose (product of ozone concentration and exposure duration) delivered to the colorants during these experiments would accumulate over a period of less than 10 years within many museum environments.

Subsequent studies of the chemical reactions taking place between ozone and the ozone-fugitive colorants indicated that loss of chromophore, i.e., colorant fading, resulted from a number of oxidation pathways which involved carbon-carbon bond scission in organic colorants containing aromatic (4, 5) and unsaturated aliphatic functional groups (6, 7). These findings prompted concern regarding possible damage to paintings and other art objects due to exposure to ambient levels of ozone and led to surveys of indoor levels of air pollutants, including ozone, in museum air (8–10). These findings also led to investigations of possible mitigation measures (11) including the use of sorbents to minimize concentrations of ozone and other pollutants in museum display cases (12, 13).

While ozone is ubiquitous in urban air, other pollutants also are present that may have adverse effects on museum collections and other cultural property. Air pollutants that are formed, along with ozone, in the complex set of reactions involving emitted hydrocarbons and oxides of nitrogen include nitrogen dioxide, nitric acid, peroxyacetyl nitrate (PAN), and carbonyls such as formaldehyde. While ambient levels of these pollutants in urban smog are often (but not always) lower than those of ozone, a realistic

Table I. List of Colorants Studied

| colorant | MW | colorant index name and/or no. | supplier (purity) |
|--|-----|--------------------------------|-------------------|
| alizarin (1,2-dihydroxy-anthraquinone) | 240 | 58000 | Aldrich (97%) |
| Alizarin Crimson | | Pigment Red 83 | Winsor and Newton |
| pararosanine base | 305 | 42500 | Aldrich (95%) |
| basic fuchsin | 338 | 42510, Basic Violet 14 | Aldrich |
| acridone | 195 | | Aldrich (99%) |
| Quinacridone Red | 312 | 46500, Pigment Violet 19 | Binney and Smith |
| indigo | 262 | 73000, Natural Blue 1 | Aldrich |
| Thioindigo Violet (Paliogen Red Violet) ^a | | 73312, Pigment Red 88 | BASF |
| curcumin | 368 | Natural Yellow 3 | Aldrich (95%) |

^a Contains tetrachlorothioindigo; see Figure 1.

assessment of the possible effects of photochemical smog on art objects should include NO₂, nitric acid, PAN, and formaldehyde, all of which are known to induce oxidation and/or corrosion processes. Accordingly, we have investigated the effect of exposure to nitrogen dioxide (14), formaldehyde (15), and PAN (16) on a number of colorants. In this article, we describe the methods and findings of a study in which organic colorants have been exposed to low concentrations of nitric acid, with emphasis on the characterization of reaction products and reaction mechanisms.

Colorants Selection

Nine organic colorants have been selected for study. They are listed in Table I along with some relevant properties. The colorant structures are shown in Figures 1–6. These colorants have been selected to parallel previous work with ozone (1–7) and with nitrogen dioxide (14) so that comparisons can be drawn between the action of different pollutants toward the same colorants. Alizarin (a dihydroxy-substituted anthraquinone) and Alizarin Crimson (a calcium-aluminum lake obtained by precipitating alizarin as an aluminum complex according to the tentative structure given in Figure 1) are a yellow dye and a red pigment, respectively, and are representative of a number of alizarin derivatives employed in the formulation of artists' colorants. Many of these pigments, including Alizarin Crimson, are ozone-fugitive (1–4). Basic fuchsin (Basic Violet 14) is a typical member of an important group of colorants, the triphenylmethane cationic dyes (e.g., Malachite Green, Crystal Violet, Fuchsin, Rosaniline), which are derived from triphenylmethanes and from the corresponding triphenylcarbinols (5). Basic fuchsin is ozone-fugitive; the carbinol pararosaniline base, which is not ozone-fugitive (5), was included in this study for comparison. Quinacridone Red, which is not ozone-fugitive

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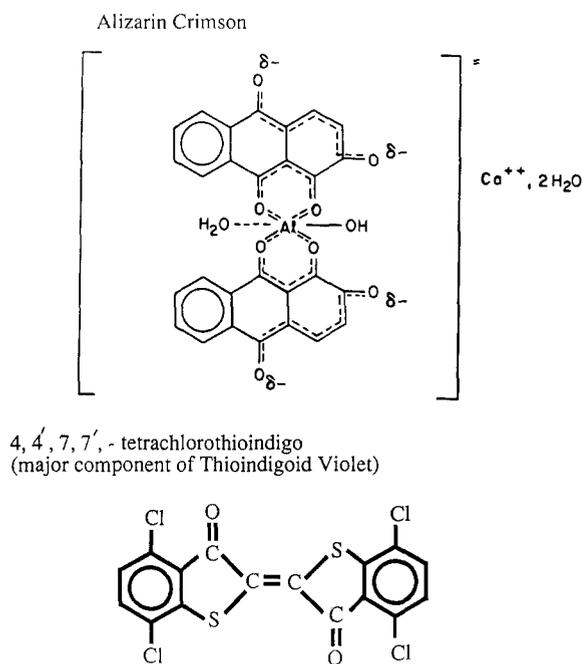


Figure 1. Structures of Alizarin Crimson and tetrachloroindigo.

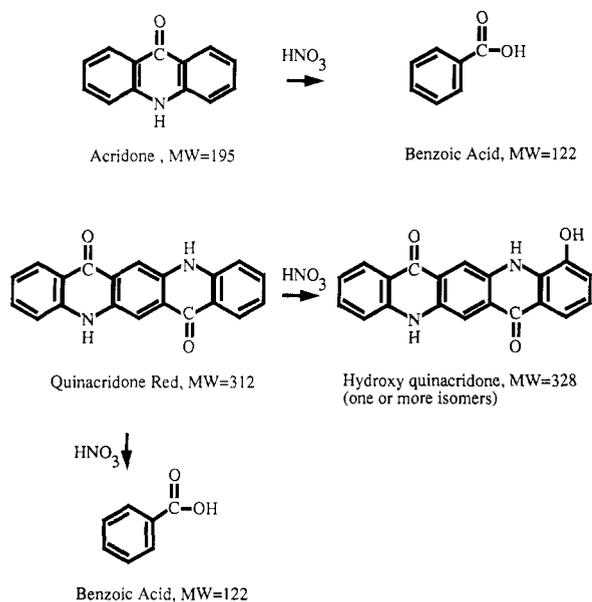


Figure 2. Reaction products of acridone and quinacridone.

(2), was included as a representative of the acridone family of colorants; its simpler structural homologue acridone was included as an aid to interpretation of the results. Indigo is a natural colorant which has been employed since antiquity, along with other indigo derivatives such as dibromoindigo, the Royal Purple dye traded by the Phoenicians in the first millennium B.C. (17). Indigo fades substantially when exposed to ozone (1-3) as a result of ozone attack on the unsaturated carbon-carbon bond (7). Another indigo derivative, Thioindigoid Violet (tetrachloroindigo), which is also ozone-fugitive (7), was included for comparison. Finally, we included the traditional natural colorant curcumin, which is the most ozone-fugitive of the colorants we have tested to date (1-3, 6, 18).

Experimental Methods

Compounds Studied. All colorants studied were obtained from commercial sources (see Table I) and were used without further purification. Verification of the organic colorants' structures was obtained by chemical ion-

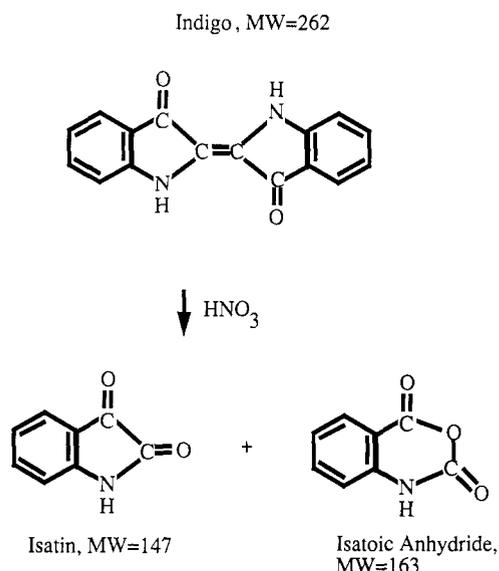


Figure 3. Reaction products of indigo.

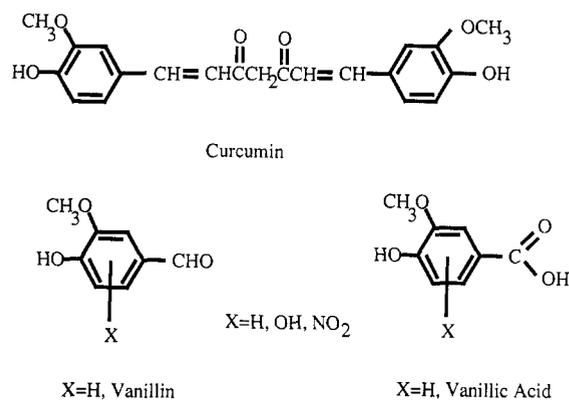


Figure 4. Structures of possible oxidation products not found upon exposure of curcumin to gas-phase nitric acid.

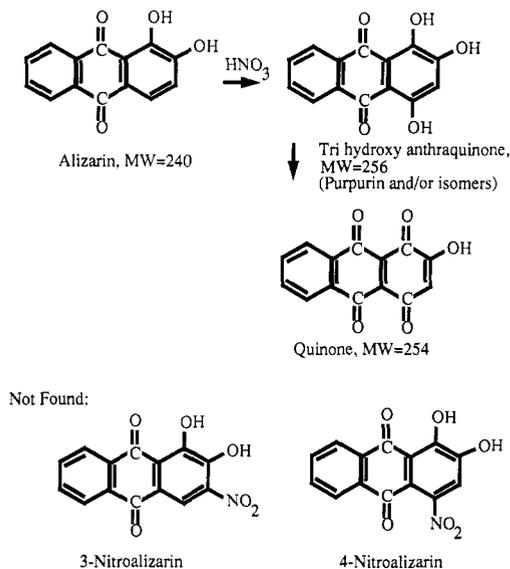


Figure 5. Reaction products of alizarin.

ization mass spectrometry; see Mass Spectrometry Analysis section below. The chemical ionization mass spectra of curcumin, alizarin, pararosaniline base, basic fuchsin, and indigo have been recorded in previous work (4-7) and were recorded again on a different instrument to verify colorant stability and purity. Good agreement was obtained with earlier data. Analysis of Alizarin Crimson by X-ray

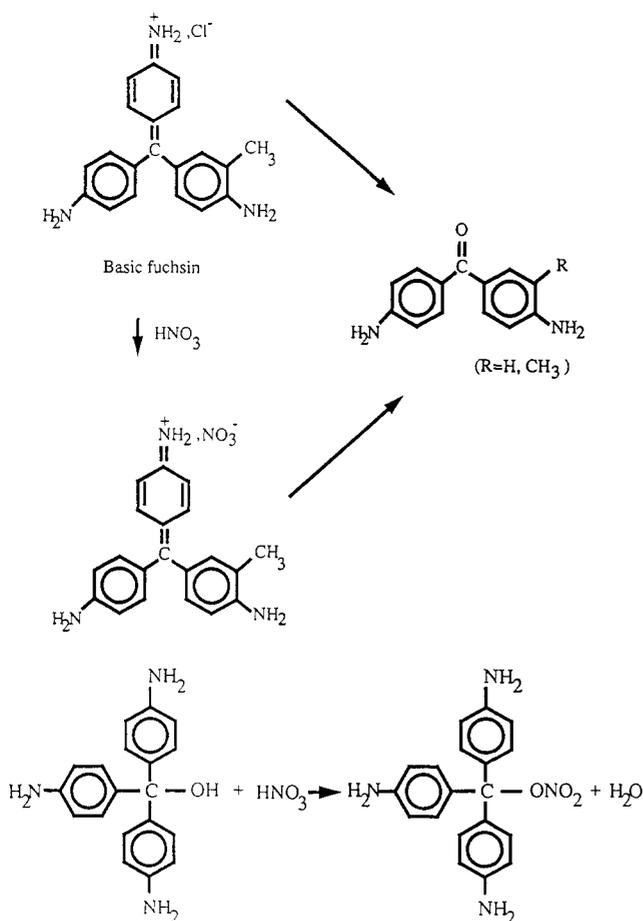


Figure 6. Reaction products of triphenylmethane colorants.

Table II. Chemical Ionization (Methane) Mass Spectra of Acridone and Quinacridone Red

| acridone, MW = 195 ^a | | | Quinacridone Red, MW = 312 ^a | | |
|---------------------------------|-----------|---------------------|---|-----------|----------------|
| <i>m/e</i> | rel abund | peak assignmnt | <i>m/e</i> | rel abund | peak assignmnt |
| 236 | 5 | M + 41 ^b | 341 | 45 | M + 29 |
| 224 | 18 | M + 29 ^c | 314 | 22 | <i>d</i> |
| 197 | 15 | <i>d</i> | 313 | 100 | MH |
| 196 | 100 | MH | 312 | 60 | M |
| 195 | 20 | M | 297 | 60 | MH-16 (MH-O) |
| 180 | 3 | MH - 16 (MH-O) | 283 | 40 | MH - 30 |
| 167 | 5 | MH - 29 (MH-HCO) | 209 | 25 | |
| | | | 196 | 50 | <i>f</i> |

^aSource temperature 140 °C, probe temperature 40 °C. ^bM + C₃H₅ adduct. ^cM + C₂H₅ adduct. ^d¹³C isotope peak. ^eSource temperature 320 °C, probe temperature 40 °C. ^fMay include MH of acridone as impurity.

fluorescence confirmed that aluminum and calcium were the major inorganic components (4) in agreement with the lake structure shown in Figure 1. Thioindigoid Violet was shown to contain tetrachlorothioindigo as expected and also contained other alkyl-substituted and chlorinated thioindigos (7). The presence of chloride in basic fuchsin was verified by liquid chromatography with ultraviolet detection (19). Chemical ionization mass spectra of acridone and Quinacridone Red, which we had not recorded in previous work and have not been published before, are summarized in Table II and are consistent with the structures shown in Figure 2.

Nitric Acid Exposure Protocols. Three types of exposures were carried out, using "high", "intermediate", and "low" levels of nitric acid, respectively (Table III). The

Table III. Summary of Nitric Acid Exposure Protocols

| compound | high concn | intermediate | low |
|---------------------|---|------------------------------------|-------------------------------|
| | exposure fumes of conc HNO ₃ | concn exposure, 800 ppb for 7 days | concn exposure ^{a,b} |
| alizarin | + | + | + |
| Alizarin Crimson | + | + | + |
| curcumin | +, c | + | + |
| acridone | | | + |
| Quinacridone Red | | | + |
| indigo | +, c | | + |
| Thioindigoid Violet | | | + |
| pararosaniline | | + | + |
| basic fuchsin | +, c | + | + |
| anthraquinone | + | | + |

^aAll colorants exposed on Teflon filters except curcumin and anthraquinone, which were exposed on watercolor paper. ^bA 12-week exposure to 12 ppb nitric acid followed by a second 12-week exposure to a higher concentration of nitric acid (40 ppb). ^cOn watercolor paper, color changes measured, exposed samples not analyzed by mass spectrometry for reaction products.

first exposure experiment was conducted simply to determine qualitatively whether or not any reactions or color changes would occur upon exposure even to high levels of nitric acid vapor. Some 30 colorants were exposed for 4–24 h by opening a bottle of concentrated nitric acid and letting the fumes flow over a glass beaker containing the colorant samples (Whitmore and Cass, unpublished results, California Institute of Technology, 1985). While this experiment was intended principally to assist the design of the lower level exposure studies described below, samples of HNO₃-exposed alizarin, Alizarin Crimson, and their simpler structural homologue, anthraquinone, were reserved for subsequent chemical analysis.

Having noted rapid fading and many color changes during the high-level HNO₃ exposure experiments, a controlled experiment of several months' duration was conducted at low nitric acid concentrations. Some 79 colorants (natural, synthetic, organic, and inorganic) including artists' pigments deposited on watercolor paper, Japanese colorants and dyes on silk, and several inks on paper were placed in sample holders facing the open interior of an exposure chamber similar to the one employed earlier in our colorant-ozone exposure studies (1–3, 18). The full set of 79 samples on paper and silk was intended for optical measurements of color changes induced by HNO₃ exposure, and these results are reported elsewhere (20). These optical samples on paper were accompanied by Teflon-deposited samples of all of the colorants listed in Table I (except curcumin) that were intended for subsequent chemical analysis. The samples prepared for chemical analysis consisted of 1.8–9.8 mg of colorant deposited uniformly on 47 mm diameter, 0.5 μm pore size Teflon filters placed such that the colored surface of the filter faced the open interior of the exposure chamber. Teflon was selected as the colorant support to minimize substrate-induced color changes and substrate-induced chemical reactions between the colorants and nitric acid (4, 6). Two consecutive exposures, each of 12 weeks' duration, were carried out. The protocol for these experiments is described in detail elsewhere (20) and is only briefly summarized here. The colorant samples were placed in a Teflon-lined glass and metal cabinet and were exposed, in the dark, and at a temperature of 22 °C and a relative humidity of 50%, to purified air containing ppb levels of nitric acid obtained from the diluted output of a permeation tube. The inlet airflow rate to the continu-

ously stirred exposure chamber was 1.5 L/min. In the first exposure, the chamber inlet nitric acid concentration was 113 ppb and the concentration within the chamber was 12 ppb. In the second exposure, the inlet nitric acid concentration was raised to 323 ppb and the concentration within the chamber was 40 ppb, in order to accelerate changes in those samples that reacted slowly during the first exposure experiment. The large difference between inlet concentrations and concentrations within the stirred chamber reflects substantial retention of nitric acid within the chamber, i.e., on the colorant samples and possibly on the Teflon-coated mounting frames and on the chamber walls. The amount of nitric acid to which the colorants were exposed was estimated by measuring the nitric acid flux to nylon filters that were placed beside the colorant samples within the chamber. Nylon filters collect nitric acid with $\geq 99\%$ efficiency (21). Analysis of the nylon filters' nitrate content by ion chromatography indicated that the nitric acid flux to the nylon filters was $0.03\text{--}0.07 \mu\text{g m}^{-2} \text{s}^{-1}$ in the first 12-week exposure and $0.15 \mu\text{g m}^{-2} \text{s}^{-1}$ in the second 12-week exposure.

Supplementary exposure experiments were carried out at "intermediate" levels of nitric acid, with purified air containing 800 ppb nitric acid flowing for 7 days at a flow rate of 1.0 L/min through 3.9–7.3 mg of colorant deposited on a Teflon filter housed in a 47 mm diameter filter holder. Alizarin, Alizarin Crimson, curcumin, basic fuchsin, and pararosaniline were studied further in this manner.

Mass Spectrometry Analysis. After exposure to nitric acid, the colorant samples were analyzed by chemical ionization (CI) mass spectrometry. All analyses were carried out directly by scraping small amounts (typically less than 0.1 mg) of the unexposed and exposed samples off the Teflon filters and using the instrument's solid insertion probe; i.e., no solvent extraction was involved.

Samples from the high nitric acid concentration exposure were analyzed using a Kratos Scientific Instruments Model MS-25 instrument. The source temperature was 140–320 °C (200 °C for most colorants), the solid insertion probe temperature was 40–340 °C (120–140 °C for most colorants), the electron beam energy was 100 eV, the acceleration potential was 2 kV, the reagent gas (methane) pressure was 0.1 Torr, and the reagent gas flow rate was 30 mL/min.

Samples from the intermediate and low nitric acid exposures were analyzed using a VG Analytical Model ZAB-SE instrument. High-purity methane (99.5%) was used as the reagent gas at a pressure of about 0.1 Torr inside the reaction chamber of the ion source. The electron beam energy was 100 eV and the ion source temperature was 120–250 °C, depending upon the melting point of the compound. The probe temperature was gradually increased until the protonated molecular ion (MH^+) was visible on the instrument data system monitor. The spectrum was recorded when the intensity of the MH^+ peak reached steady state.

Reaction products that could go undetected in our conditions include (a) volatile products that were no longer present on the Teflon filter at the completion of the nitric acid exposure experiment, (b) products formed in low yields of $\leq 1\%$, since the mass spectrometer's data acquisition systems did not record mass fragments whose abundances were less than 1% of that of the base peak, and (c) products of very low vapor pressure, of which no detectable amount could be introduced into the reaction chamber of the instrument's ion source even at high probe temperature. With these analytical limitations in mind, product identification was deemed probable when the

Table IV. Color Changes for Colorants Exposed to Nitric Acid on Teflon Filters and on Other Substrates

| colorant | qualitative color change, Teflon filters | | final color change, ΔE units ^a | |
|-------------------|--|-------------------------|---|------------------------------|
| | unexposed | after exposure | first 12 weeks ^b | next 12 weeks ^{c,d} |
| alizarin | orange | darker orange | 7.8 | 4.4 |
| Alizarin | purple | no change | 1.4 | 2.8 |
| Crimson | | | 2.2 ^e | 5.2 ^e |
| pararos-aniline | violet | dark green | 27.8 | 3.1 |
| basic fuchsin | violet | dark green | 22.2 | 28.4 (ns) |
| | fluorescent green | fluorescent dark yellow | 3.8 | 7.3 |
| Quinacridone Red | pink | no change | 0.4 | 0.1 |
| acridone | pale yellow | no change | 0.3 | 1.0 (ns) |
| indigo | dark blue | no change | 0.2 | 0.8 |
| | | | 0.2 | 0.9 |
| | | | 0.2–1.0 ^f | 0.3–1.0 ^f |
| Thioindigo Violet | purple | no change | 0.2 | 0.3 |
| curcumin | orange | orange, slightly faded | 6.5 | 4.3 |
| | | | | 6.0 (ns) |

^a On watercolor paper unless otherwise indicated. ^b Nitric acid concentration 12 ppb. ^c Nitric acid concentration 40 ppb. ^d ΔE listed in this column are for additional color change after the second of two consecutive exposures unless otherwise indicated by the footnote (ns), new sample. ^e On Whatman 41 cellulose filter. ^f On silk, Japanese colorant Ai, four shades tested on silk without mordant.

sample mass spectrum could be matched to that of an authentic sample recorded under the same conditions, and possible when no authentic sample was available for comparison and the structure of the product was derived solely from interpretation of its CI mass fragmentation pattern.

Results and Discussion

Color Change. Listed in Table IV are color changes following exposure of the colorants studied to nitric acid on watercolor paper, on cellulose paper, and on silk. These color changes, expressed in ΔE units, were obtained from detailed optical measurements made by reflectance spectroscopy (20). Measured ΔE values of 0.5 or less indicate no perceptible color change, and measured ΔE values of 1.0 or less indicate that a good color match still exists between exposed and unexposed samples. Exposure to low levels of nitric acid for 12 or 24 weeks led to essentially no color change (ΔE of 1 or less) for acridone, Quinacridone Red, indigo, and Thioindigoid Violet, to some color change for Alizarin Crimson ($\Delta E = 1.4\text{--}5.2$), and to substantial color changes for curcumin and alizarin ($\Delta E = 4.3\text{--}7.8$) and for the two triphenylmethane derivatives, basic fuchsin ($\Delta E = 3.8\text{--}7.3$) and pararosaniline. The most nitric acid-fugitive colorant tested, pararosaniline, yielded final ΔE values of 22–28; the corresponding color change was from deep purple to dark green.

At the much higher levels of nitric acid used in the "high-concentration" screening test, most colorants tested exhibited substantial color changes: $\Delta E = 70$ for Alizarin Crimson (color change from red purple to yellow); $\Delta E = 23$ for basic fuchsin (green to yellow); $\Delta E = 11$ for alizarin; $\Delta E = 13\text{--}43$ for curcumin (yellow to completely faded); $\Delta E = 33\text{--}35$ for indigo (blue to completely faded). Acridone, Quinacridone Red, Thioindigoid Violet, and pararosaniline were not included in the high nitric acid concentration screening tests.

Acridones. The reaction of aromatic compounds with nitric acid leads to nitro aromatic products (22, 23) as well

as to oxidation products such as phenols which may result from oxygen transfer between the nitronium ion (NO_2^+) and the aromatic ring (24). Benzoic acid is also frequently observed as an oxidation product of polycyclic aromatic compounds (25, 26).

Chemical ionization mass spectra (Table II) and 380–700-nm reflectance spectra of samples of acridone and Quinacridone Red exposed to nitric acid were essentially identical to those of the unexposed samples. The exposed samples both contained a small amount of benzoic acid ($\text{MW} = 122$, $\text{MH}^+ = 123$) which therefore may be indicative of some oxidation by nitric acid. The exposed Quinacridone Red sample also contained a small peak, $m/e = 329$ ($\text{MW} = 328$), consistent with the presence of a phenol oxidation product, i.e., hydroxyquinacridone (one or more isomers); see Figure 2. There was no $m/e = 358$ peak which would have indicated the presence of an aromatic ring nitration product of $\text{MW} = 357$. The oxidation product yields are estimated to be less than 3% from the relative abundance of mass fragments in the samples' mass spectra. Thus, Quinacridone Red is not fugitive when exposed to low concentrations of nitric acid vapor in air. Quinacridone Red and several artists' pigments that include Quinacridone Red as the red colorant (e.g., Winsor and Newton's Permanent Rose, Permanent Magenta, Rose Doré) are also resistant to fading by ozone (2).

Indigos. Even though the exposure of indigo to low levels of nitric acid resulted in only a very small color change ($\Delta E < 1$), the mass spectrum of the exposed sample indicated the presence of two reaction products, isatin and isatoic anhydride (Figure 3). The CI spectrum, while containing abundant mass fragments corresponding to a large amount of unreacted indigo (5), also included the fragment ions $m/e = 148$ (MH^+ of isatin, $\text{MW} = 147$), 120 ($\text{MH}^+ - \text{CO}$, isatin), 119 ($\text{MH}^+ - \text{HCO}$, isatin), 164 (MH^+ of isatoic anhydride, $\text{MW} = 163$), and 146 ($\text{MH}^+ - \text{H}_2\text{O}$, base peak of isatoic anhydride). These fragments and their relative abundances matched well those of authentic samples of the two compounds, the CI mass spectra of which have been recorded and discussed in earlier work (5). Using the relative abundance of the fragment ions as a guide, we estimate that the spectrum of the exposed indigo sample is consistent with a product ratio (isatin/isatoic anhydride) of about 3–4, and that the yield of the oxidation products is 5% or less. Indigos also undergo oxidation to form isatin and other products upon reaction with gas-phase ozone (7) and with ozone in water (27) and upon exposure to light (28, 29). Peaks corresponding to aromatic ring oxidation products (phenols) or to nitration products (nitro compounds) were not present in the spectrum of the exposed indigo sample. Further oxidation of isatin and/or isatoic anhydride to form anthranilic acid ($\text{MW} = 137$, $\text{MH}^+ = 138$) was not observed. Further oxidation of isatin to anthranilate has been observed upon reaction of indigo with hypohalites in the liquid phase (30) but not upon exposure of isatin and isatoic anhydride to low levels of ozone in air (7).

The CI mass spectra of exposed and unexposed samples of Thioindigoid Violet were identical; both were complex and probably reflected significant thermal decomposition. The corresponding 380–700-nm reflectance spectra were also identical. There was no evidence for chemical reaction between nitric acid and Thioindigoid Violet under the conditions of our experiment. In particular, there was no evidence for the formation of dichloroisatin and dichloroisatoic anhydride, the structural homologues of the products found in low yields in the nitric acid-exposed indigo sample. We have observed before (7) that thio-

indigos are less reactive than indigos toward ozone. This reactivity trend is similar to the one observed here with nitric acid, i.e., only slow reaction for indigo and no reaction for Thioindigoid Violet.

Curcumin. The CI spectra of exposed and unexposed samples of curcumin were essentially identical, even though the corresponding 380–700-nm reflectance spectra showed measurable differences: the reflectance of the exposed sample increased by 10% in the 400–430-nm region, with the wavelength of maximum reflectance shifting from 420 to 400 nm. A similar fading of curcumin has been observed upon exposure to other air pollutants (1–3, 14) and even to purified air (15). The presence of likely oxidation products, i.e., vanillin and vanillic acid (Figure 4), could not be unambiguously confirmed from examination of the exposed sample's CI spectrum, even though this spectrum contained small mass fragments, not present in the spectrum of unexposed curcumin, at $m/e = 169$ (MH^+ and base peak of vanillic acid) and 152 (MH^+ and base peak of vanillin). However, the relative intensity of these fragments was only 2% and 5%, respectively. Vanillin and vanillic acid form readily upon exposure of curcumin to ozone (6). Vanillin also forms in high yields in the oxidation of lignin, which contains derivatives of a structural homologue of curcumin, coniferyl alcohol (31). No other reaction products could be detected. In particular, the exposed sample's spectrum did not include the following peaks that would have indicated aromatic ring oxidation (phenol) or nitration (nitro aromatic): hydroxycurcumin ($\text{MW} = 384$), nitrocurcumin ($\text{MW} = 413$), hydroxyvanillin ($\text{MW} = 169$), nitrovanillin ($\text{MW} = 198$), whose mass spectrum has been recorded (32), hydroxyvanillic acid ($\text{MW} = 185$), or nitrovanillic acid ($\text{MW} = 214$).

Alizarins. Two products were observed in low yields ($\leq 5\%$) upon exposure of alizarin to both high and low concentrations of nitric acid (Figure 5). The first product, trihydroxyanthraquinone, $\text{MW} = 256$, was confirmed by comparison with the CI mass spectrum of an authentic sample of one of the possible isomers, purpurin (1,2,4-trihydroxyanthraquinone). The second product, $\text{MW} = 254$, is most likely the corresponding quinone shown in Figure 5. The oxidation of alizarin by nitric acid to form purpurin has been documented in the liquid phase (33). The corresponding quinone observed as a product is likely to result from further oxidation of purpurin (4). Ring-opening products including phthalic acid were not observed. Products resulting from nitration rather than from oxidation, for example, nitroalizarin isomers which are produced by nitration of alizarin in the liquid phase (34, 35), were not observed either.

The 380–700-nm reflectance spectrum of exposed Alizarin Crimson was similar to that of the unexposed colorant, the only difference being a slight increase in reflectance near 510 nm. The CI spectrum of the exposed sample contained fragments at $m/e = 150$, 149, 105, and 104 in the relative abundance ratio 8:100:5:20 and therefore indicated the presence of small amounts of phthalic acid or phthalic anhydride, which have identical CI spectra (4).

That phthalic acid is indeed a reaction product was confirmed by analysis of a sample of Alizarin Crimson from the high nitric acid concentration screening test. The CI spectrum of this sample indicated the presence of phthalic acid as the major product, along with trace amounts of benzoic acid and of anthraquinone, which was present as an impurity (anthraquinone, when tested independently and exposed to concentrated nitric acid vapor for 23 h, did not react with nitric acid). Phthalic acid is a frequently observed oxidation product of polycyclic aromatic hydro-

Table V. Comparison of Color Change Resulting from Exposure, for 3 Months, of Organic Colorants on Watercolor Paper to Ozone, Nitrogen Dioxide, Nitric Acid, and Purified Air

| colorant and chemical functionality | color change, ΔE units | | | |
|-------------------------------------|--------------------------------|--------------------------------|--|--------------------------------|
| | ozone, 310–400 ppb (1–7) | NO ₂ , 500 ppb (14) | HNO ₃ , 12 ppb ^a | purified air (15) ^b |
| natural | | | | |
| indigo | 14.2 | 2.8 | 0.2 | |
| curcumin | 41.8 | 14.5 | 6.5 | 2.7 ± 0.3 |
| alizarins | | | | |
| alizarin | | | 7.8 | |
| Alizarin Crimson | 11.3 | 2.9 | 1.4 | 1.6 ± 0.3 |
| acridones | | | | |
| acridone | | | 0.3 | |
| Quinacridone Red | no fading | | 0.4 | 1.3 ± 0.3 |
| triphenylmethanes | | | | |
| basic fuchsin | substantial fading | | 3.8 | 1.9 ± 0.6 |
| pararosaniline base | no fading | | 22.2, 27.8 | 1.8 ± 1.0 |
| others | | | | |
| Thioindigo Violet | modest fading | 0.7 | 0.2 | 1.5 ± 0.3 |
| AATCC ribbon ^c | | 26.3 | 5.2 | 1.8 ± 0.2 |
| watercolor paper | 1.15 | 0.7 | 0.8 | <0.5 |

^aThis study. ^bMean ± one standard deviation for triplicate samples. ^cDisperse Blue 3 (an amino-substituted anthraquinone) on cellulose acetate, used by the American Association of Textile Chemists and Colorists as a standard for fugitiveness to oxides of nitrogen.

Table VI. Indoor Levels of Ozone, Nitrogen Dioxide, and Nitric Acid at Southern California Museums

| location | ozone, ppb 1-h max ^a | nitrogen dioxide, ppb | | nitric acid, ppb | | |
|---|------------------------------------|---|--|-----------------------------------|---------------------------------|----------------------------------|
| | | range of 6-h samples ^b | max ^b | range of 6-h samples ^b | av of 24-h samples ^c | highest 24-h sample ^c |
| | | El Pueblo de Los Angeles State Historical Park, Los Angeles | | 33–56 | 123 ^e | 0.3–7.6 |
| Olivas Adobe Historical Park, Ventura | | | | 0.8–5.7 | | |
| Los Angeles County Museum of Art, Los Angeles | 10 | 40–62 | 108 ^e | 0.8–10.4 | | |
| Henry E. Huntington Library and Art Gallery, San Marino (Scott Gallery) | 43, 65, <5 ^d | 1–27 | 27 | 1.0–3.6 | 0.08 | 0.22 |
| Natural History Museum, Los Angeles | | 0–35 | 35 | 0.4–3.7 | | |
| George C. Page Museum, Los Angeles | | 4–42 | 42 | 0.4–5.0 | | |
| University of California, Los Angeles (Research Library) | | 9–45 | 45 | 2.0–9.7 | | |
| Southwest Museum, Los Angeles | 90, 143 | 21–56 | 56 | 0.7–3.7 | 0.08 | 0.17 |
| The J. Paul Getty Museum, Malibu | 9, 22, 28 | | | | 0.04 | 0.10 |
| Gene Autry Western Heritage Museum, Los Angeles | 3.3–4.3 ^f | 9–22 | 30 ^g 7–24 ^{e,f} | | | |
| Junipero Serra Museum, San Diego | 34, 22 | | | | | |
| Pasadena Historical Society Museum, Pasadena | 98, 25, 19 | | | | | |
| Lang Gallery, Claremont | 17, 30 | | | | | |
| Villa Montezuma, San Diego | 14, 22 | | | | | |
| Montgomery Gallery, Claremont | 60, 67 | | | | | |
| Norton Simon Museum, Pasadena | | | | | <0.04 | <0.04 |

^aFrom ref 8, unless otherwise indicated; measured in July–August 1984. ^bFrom ref 9, unless otherwise indicated; measured in July–October 1988. ^cFrom ref 41; measured in July–August 1987; lower values, not listed, were also obtained at the same museums during the winter (November 1987–January 1988). ^dThe last (and lowest) value was obtained in 1988 after a chemical filtration system had been installed (Hisham and Grosjean, unpublished results, 1988). ^eInstantaneous maximum measured with continuous analyzer; see ref 9. ^fFrom ref 42. ^gFrom ref 10.

carbons and of a number of quinones (4, 25, 26). Phthalic acid is also a product of the ozone–Alizarin Crimson reaction when this colorant is exposed to (and rapidly faded by) ozone at levels relevant to urban air quality (4).

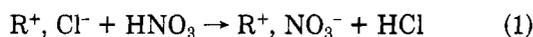
Oxidation to colorless phthalic acid is consistent with the optical observations (see above) made on the sample exposed to low levels of nitric acid. However, the sample of Alizarin Crimson that was exposed to concentrated nitric acid vapor changed from deep red to bright orange, so either there was a change in the alizarin lake structure or products that contain a chromophore were formed in addition to phthalic acid.

Triphenylmethanes. Upon exposure to nitric acid, the two triphenylmethane colorants tested exhibited substantial color changes. The chemical reactions responsible for these color changes were different, i.e., nitrate salt formation for basic fuchsin and organic nitrate (ester) formation for pararosaniline.

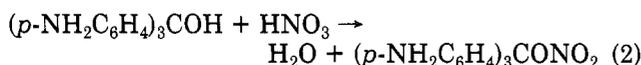
The mass spectrum of exposed basic fuchsin contained two new and small peaks (yield ≤2–3% each) corresponding to products of MW = 212 and 226, respectively. These products, identified in earlier work involving the exposure of triphenylmethane colorants to ozone (5), are the two substituted benzophenones whose structures are shown in Figure 6. Benzophenone products have been identified in the oxidation of triphenylmethane dyes by gas-phase ozone (5), by ozone in methanol (36), by hydrogen peroxide in the presence of light, both with dye powders and in solution (37), and by photooxidation of the dyes as powders, on cellulose, and in aqueous solutions (37–39).

Liquid chromatography analysis of the unexposed and exposed samples of basic fuchsin for their chloride and nitrate content (19) showed that the substantial color change observed corresponded mainly to the displacement of the colorant's chloride ion by nitric acid to yield the

corresponding nitrate; see Figure 6:



The CI mass spectrum of pararosaniline, MW = 305, contains peaks at $m/e = 306$ (MH^+) and 290 (base peak, possibly $MH^+ - NH_2$) along with smaller mass fragments. After exposure to nitric acid, these peaks have been replaced by an abundant fragment at $m/e = 351$, which corresponds to the pseudomolecular ion of a reaction product of MW = 350. This product is most likely the organic nitrate ester resulting from reaction of nitric acid with the colorant's carbinol group (40), as is shown in Figure 6:



We synthesized this nitrate ester in the liquid phase by reaction of 5 μ L of concentrated nitric acid with 20 μ g of pararosaniline in 12 μ L of carbon tetrachloride. The color change observed and the CI spectrum of the reaction product were identical to those resulting from exposure of pararosaniline to gaseous nitric acid.

As was the case for basic fuchsin, the two benzophenones shown in Figure 6 were identified as minor oxidation products of pararosaniline (yield 1–3%). They may form directly from pararosaniline, its nitrate ester reaction product, or both.

Implications for Museum Collections. Of the several chemical functionalities studied, i.e., natural organic colorants and synthetic organic colorants including acridones, alizarins, and triphenylmethanes, the two triphenylmethane colorants tested were found to be most susceptible to damage (color change) by nitric acid. Since fugitiveness is closely correlated with colorant chemical functionality, as we had observed earlier for ozone (4–7), triphenylmethane colorants besides those tested in this study may also be susceptible to damage when exposed to atmospheric nitric acid. These colorants include Malachite Green, Brilliant Green, Crystal Violet, Methyl Green, and pararosaniline chloride, among others.

Also of interest in the context of this study is a brief comparison of color changes resulting from exposure to nitric acid to those resulting from exposure to other pollutants such as ozone and nitrogen dioxide, which are often present in museum air (8–10). Compared in Table V are color changes resulting from exposure, for about 3 months, to ozone, nitrogen dioxide, nitric acid, and purified air. Typical levels of ozone, nitrogen dioxide, and nitric acid measured inside southern California museums are compiled in Table VI (8–10, 41, 42). Comparison of the color changes vs pollutant concentrations given in Table V and of the pollutant concentrations in museums given in Table VI indicates that, for most colorants, ozone is the pollutant of greatest concern with respect to damage to colorant-containing objects in museum collections. However, nitric acid may be of greater concern than ozone for at least one category of artists' colorants, the triphenylmethanes. For these, the chemical oxidation processes and the resulting color change observed in our experiments could take place within about 7 years within an unprotected museum such as the Sepulveda House at El Pueblo de Los Angeles State Park [mean annual HNO_3 concentration 0.42 ppb indoors (41)] as a result of exposure to ambient (indoor) levels of nitric acid.

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NMR Spectroscopic Investigation of Hydrogen Bonding in Atrazine

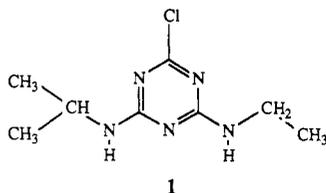
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■ The solution properties of atrazine are investigated using NMR spectroscopy. In aprotic solvents, atrazine exists as a mixture of four conformational isomers related by rotation of the alkylamino side chains. The partial double-bond character responsible for this restricted rotation implies that there is a separation of charge within the atrazine molecule. As a result of this separation of charge, atrazine is able to both donate and accept hydrogen bonds. One consequence of this cooperative H-bonding is that atrazine dimerizes in aprotic solvents. In CCl_4 solvent, the dimerization constant is 49 M^{-1} .

Introduction

Atrazine (1), a herbicide frequently used by corn and sorghum growers has been detected in many surface streams through the Midwest (1). Recent surveys have also detected low levels of atrazine in some Wisconsin groundwaters (2). In spite of the widespread use of atrazine and its persistence in the environment, very little is known about the chemistry of the interactions between atrazine and the soil or between atrazine and any agents that may carry it through the soil.



An illustration of this situation is provided by recent experience in the Lower Wisconsin River (LWR) and Central Sands (CS) agricultural regions in Wisconsin. In both these regions corn is grown under similar irrigation practices and atrazine application rates, yet atrazine is detected in LWR groundwater at levels far above those observed in the CS groundwater. This despite the fact that both these areas have predominantly sandy soils that are similar in organic matter content, mineralogy, surface area, and pH—factors known to affect atrazine adsorption.

We are investigating the chemistry of atrazine interactions through the use of nuclear magnetic resonance (NMR), a spectroscopic technique that provides details about interactions at the molecular level. These molecular interactions control the solvation of atrazine, its adsorption onto soil surfaces, and its degradation into nonphytotoxic hydroxyatrazine. These same interactions govern the important adsorption parameters K_d and K_{oc} , as well as the octanol/water partitioning coefficient, K_{ow} . Understanding

the chemistry behind these phenomena will increase the ability to predict and control the environmental impacts of atrazine use. In this paper we present and discuss the NMR spectra of atrazine in five aprotic solvents and show that these spectra provide important clues about the solution behavior of atrazine.

Two brief NMR investigations of atrazine have been published. The proton NMR spectrum of atrazine in chloroform (CDCl_3) and trifluoroacetic acid (TFA) solvents has been reported (3). Atrazine in TFA was found to have its NH proton signal shifted downfield and split into two signals when compared to the spectrum of atrazine in CDCl_3 . This was interpreted as showing that atrazine is protonated by the strong acid TFA, and it was suggested that protonation takes place on the triazine ring nitrogens.

Subsequently, the ^{13}C NMR spectrum of atrazine was reported in these same solvents (4). It was found that TFA rapidly converted atrazine into hydroxyatrazine, instead of the protonated atrazine reported earlier. The hydroxyatrazine was then protonated by TFA. From the published results it is not possible to determine whether the proton NMR spectrum of atrazine in TFA shows a protonated form of atrazine, an atrazine spectrum shifted due to a solvent effect, or the spectrum of hydroxyatrazine.

Recently, high-resolution ^1H and ^{13}C NMR spectral data for atrazine in dimethyl sulfoxide (DMSO) solvent were published (5). On the basis of the NMR data and accompanying variable temperature experiments, it was proposed that atrazine exists as a mixture of four conformational isomers, related by restricted rotation of the side-chain alkylamino groups.

We present the results of high-resolution ^1H NMR experiments on atrazine in aprotic solvents of different polarity. The results confirm that atrazine exists as a mixture of four conformational isomers, related by restricted rotation about the alkylamino side chains. The NMR data imply that there is significant development of charge polarity in the atrazine molecule. Dilution experiments show that atrazine dimerizes in these inert solvents, and the formation constant is calculated for CCl_4 solvent.

Materials and Methods

Chemicals. Technical grade atrazine (98% pure) was supplied by the Ciba-Geigy Corp. and was recrystallized twice from hexane. NMR solvents were obtained from the Aldrich Chemical Co. and stored over 4-Å molecular sieves.

NMR. High-resolution proton spectra were obtained on a 400-MHz Bruker spectrometer at the National Magnetic Resonance Facility in Madison, WI. Spectra were acquired by applying a 5.6- μs (90°) pulse over a