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Ozone Fading of Natural Organic Colorants: Mechanisms and Products of the Reaction of Ozone with Indigos

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■ Indigo, dibromoindigo, and colorants containing thioindigo and tetrachlorothioindigo were exposed in the dark to dry, purified air containing ozone (10 ppm) for 4 days, and the exposed samples were analyzed by mass spectrometry. Under the conditions employed, indigo and dibromoindigo were entirely consumed, and the major reaction products were isatin and isatoic anhydride from indigo and bromoisatin and bromoisatoic anhydride from dibromoindigo. Thioindigo and its chloro derivative also reacted with ozone, though at a slower rate; the corresponding substituted isatins and anhydrides were tentatively identified as reaction products. These results can be rationalized in terms of a mechanism involving electrophilic addition of ozone onto the unsaturated carbon-carbon bond. This mechanism adequately describes the observed loss of chromophore (fading) for all indigos studied and presumably applies to other indigo compounds as well. The reaction products of indigo, isatin and isatoic anhydride, were not ozone fugitive under our conditions.

Introduction

Studies carried out in this laboratory have shown that many artists' organic colorants fade substantially when exposed to ozone in the dark (1-3). These studies involved 12-week exposures to air containing 0.3-0.4 parts per million (ppm) of ozone at ambient temperature (21-25 °C) and humidity (RH = 46-50%). Examination of data for ambient levels of ozone in urban air, together with investigations of ozone levels inside museums (2, 4) and of the corresponding indoor-outdoor relationships (2, 5), indicate that the total ozone dose (concentration × duration of exposure) to which the colorants were subjected in those laboratory studies is equivalent to about 6 years inside a typical air-conditioned building in Los Angeles.

Organic compounds that were identified as ozone fugitive in our experiments included modern (synthetic) as well as natural colorants. Many alizarin lakes, including a synthetic indigo substitute, formulated from lamp black, copper phthalocyanine, and an alizarin lake, faded noticeably upon exposure to ozone (2). The products and mechanisms of the reaction of ozone with alizarin lakes and

related colorants have been investigated recently (6). Natural indigo was found to be even more ozone fugitive than its modern substitute (3). Although ancient works of art created with natural colorants such as indigo may have "survived" well before the recent introduction of ozone and other anthropogenic pollutants into urban air, the demonstrated ozone fading of these natural colorants has direct implications for current practices in the conservation of museum collections.

This paper describes the methods and results of a study focusing on the confirmation that ozone is indeed responsible for the fading observed in the above studies, on the identification of the products of the ozone-indigo reaction, and on the discussion of the corresponding reaction mechanisms that account for the loss of the chromophore, i.e., ozone fading. To test the general applicability of our findings, several indigo derivatives have been investigated as well. These include thioindigo, 6,6'-dibromoindigo, and several colorants containing chlorinated thioindigo. The chemical structures of these colorants are given in Figure 1. Thioindigo was included as a simple structural homologue of indigo. Dibromoindigo, the Royal Purple dye of fabrics widely traded by the Phoenicians in the first millennium B.C., has been used as a natural colorant since at least the 13th century B.C. (7, 8). The chlorinated thioindigos have found applications as artists' pigments and in the printing ink and paper industries (9). Also included in this study are the results of experiments involving the reaction of ozone with the major products of the ozone-indigo reaction.

Experimental Section

Colorants Studied. Indigo (*M*, 262, CAS Registry No. 482-89-3, CI no. 73000) was obtained from Aldrich Chemical Co., Milwaukee, WI, and was used without further purification following verification of its structure by mass spectrometry (see Mass Spectrometry Analysis). A second indigo sample was obtained from Fezandie and Sperrle (F&S). Dibromoindigo (*M*, 420, CI no. 75800) was obtained from Dr. F. D. Preusser of The Getty Conservation Institute, Marina del Rey, CA, and from the Forbes Collection (sample 7.01.8, Tyrian purple, murex) maintained at the Fogg Museum, Harvard University, Cambridge, MA. Thioindigo (*M*, 296), Vat Red 41, was obtained as a liquid emulsion and as a "press cake" from Hoechst. Thioindigoid Violet (Binney and Smith PR 88 MRS, CI no. 73312) and Thioindigo Red (BASF PR 88, CI no. 73312)

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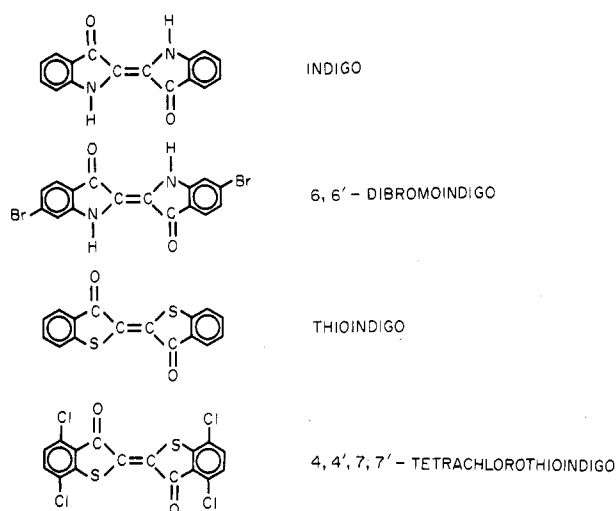


Figure 1. Structure of indigo and related compounds.

were shown by mass spectrometry to be mixtures containing tetrachlorothioindigo (as expected) along with alkyl-substituted and chlorinated thioindigo(s), e.g., tentatively dichlorothioindigo and dimethyldichlorothioindigo.

Ozone Exposure Protocol. Approximately 10 mg of each colorant was deposited on a 47 mm diameter, 0.5 μ m pore size, Teflon membrane filter (Ghia-Membrana Corp., Pleasanton, CA) of the type employed for the sampling of airborne pollutants by filtration. Teflon is a chemically resistant substrate, does not react with ozone under the conditions of our study, and has negligible absorption characteristics. Teflon filters were thus selected so as to minimize any spurious substrate-mediated (artifact) reactions between ozone and the colorants of interest. Filters with deposited colorants were mounted in an in-line, all-Teflon holder and exposed to purified air containing ~ 10 ppm of ozone as measured, following dynamic dilution, by ultraviolet photometry using a Dasibi Corp. (Glendale, CA) Model 1008-AH ozone analyzer. The matrix air was purified by passing through Purafil and activated carbon beds, which remove air contaminants including ozone, hydrocarbons, oxides of nitrogen and sulfur dioxide, followed by an in-line particle filter. Ozone was produced downstream of the beds with a Pen-ray ultraviolet lamp. Each colorant was exposed for 4 days (96 h) to air containing ~ 10 ppm ozone at a flow rate of 1 L/min. All exposures were carried out in the dark at room temperature ($T = 24^\circ\text{C}$) and low relative humidity ($\text{RH} \leq 5\%$). Control samples consisting of colorants deposited on Teflon filters but not exposed to ozone were included for each colorant studied.

Mass Spectrometry Analysis. Control and ozone-exposed samples were obtained simply by scraping the deposits off the Teflon filters. All samples were stored in the dark in glass vials with Teflon-lined caps prior to analysis.

Mass spectrometry analyses were carried out by direct insertion probe with electron impact (probe-EI) and chemical ionization (probe-CI), the latter using methane as reagent gas. Experimental conditions were as follows: (a) probe-EI, Kratos Scientific Instruments Model MS-25 hexapole, double-focusing magnetic sector mass spectrometer, electron energy 70 eV, probe temperature 250 $^\circ\text{C}$, source temperature 200 $^\circ\text{C}$, and acceleration potential 2 kV; (b) probe-CI, MS-25 mass spectrometer, reagent gas (methane) pressure ~ 0.1 Torr, reagent gas flow rate 30 mL min^{-1} , electron energy 100 eV, probe temperature 200–300 $^\circ\text{C}$, source temperature 320 $^\circ\text{C}$, and acceleration potential 2 kV.

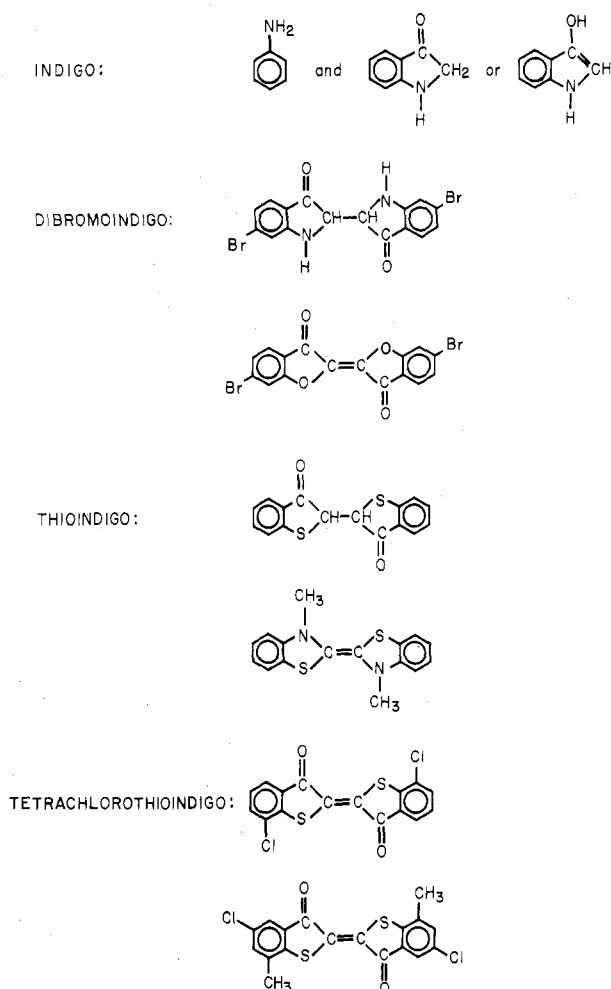


Figure 2. Probable impurities in samples of indigo and derivatives.

Results and Discussion

Mass Spectra of Reactants. The EI and CI spectra of indigo, dibromoindigo, thioindigo, and the thioindigoid samples (in fact containing chlorinated indigo compounds) were recorded, and their fragmentation patterns are discussed in detail elsewhere (10). Of the two indigo samples, the Aldrich sample contained no detectable impurity, while the F&S sample contained minor amounts of aniline and of a compound containing the indoxyl group (Figure 2). The higher purity Aldrich sample was thus selected for exposure to ozone. Structure confirmation was obtained by mass spectrometry for the two dibromoindigo and the two thioindigo samples, for which no literature data are available. All high-mass fragments in the spectrum of the dibromoindigo sample obtained from The Getty Conservation Institute could be accounted for on the basis of the structure given in Figure 1, with the exception of a triplet (isotopic distribution of ^{79}Br and ^{81}Br , two bromine atoms per molecule) at m/z 420, 422, and 424 atomic mass units (amu). This triplet was first attributed to the saturated homologue of 6,6'-dibromoindigo, as is shown in Figure 2, but may originate from an isobaric unsaturated compound, an example of which is also shown in Figure 2. The latter appears more likely since the m/z 420–422–424-amu triplet was absent from the spectrum after exposure to ozone, as would be expected for an unsaturated compound. The Forbes Collection dibromoindigo sample contained larger amounts of the same impurity. The thioindigo samples contained substantial amounts of an impurity at m/z $M_r + 2$, where M_r is the molecular weight of thioindigo. By analogy with dibromoindigo as discussed above, we suggest saturated and isobaric unsaturated compounds as possible

Table I. Chemical Ionization Mass Spectra of Indigo-Ozone Reaction Products

isatin, ^a <i>M</i> _r 147			isatoic anhydride, ^a <i>M</i> _r 163		
<i>m/z</i>	abundance, % of base peak	fragment structure	<i>m/z</i>	abundance, % of base peak	fragment structure
176	0.3	M + 29 ^b	178	1	M + 15 ^b
162	1.8	M + 15 ^b	165	3	^c
149	9.7	^c	164	34	MH
148	100 (BP)	MH	163	3	M
147	6.4	M	149	5	MH - NH
134	3.0	MH - N	148	18	M - NH, MH - O
133	1.0	MH - NH			
132	2.6	M - NH	147	10	^c
120	3.6	MH - CO	146	100 (BP)	MH - H ₂ O, M - OH
119	11.9	MH - HCO, M - CO	120	6	MH - CO ₂
92	2.6	MH - 2CO	119	15	M - CO ₂ , MH - CO ₂ H
91	1.2	MH - (HCO + CO), M - 2CO	104	2	C ₆ H ₄ CO
63	1.6	C ₆ H ₃ ^{+d}			

^a See structures in Figure 3. ^b Reagent gas adducts, these minor fragments have diagnostic value. ^c ¹³C isotope contribution to MH ion. This fragment has diagnostic value. ^d Characteristic of aromatic ring scission.

impurities (see Figure 2). Upon exposure to ozone, little, if any, of this impurity was consumed, thus suggesting that the impurity may be the saturated compound shown in Figure 2 (unsaturated compounds such as the benzothiazole shown in Figure 2 are expected to be ozone fugitive). Finally, the spectra of the two thioindigoid samples were complex and indicated (a) the presence of tetrachlorothioindigo, (b) the absence of thioindigo, (c) the presence of other chlorinated thioindigos (e.g., dichloro and dimethyldichloro, see Figure 2), (d) extensive thermal decomposition in the mass spectrometer source even at lower probe temperature, and (e) substantial amounts of unknown impurities. To our knowledge, 4,4',7,7'-tetrachloroindigo is not commercially available in pure form, and its synthesis was beyond the scope of this project.

Products Identification: Definitions and Limitations. Reaction products that could go undetected in our conditions include: compounds of molecular weight higher than 517, the upper limit of our spectrometer mass scan (e.g., polymeric reaction products), compounds of very low vapor pressure, no detectable amount of which could be introduced into the spectrometer source at the maximum probe temperature, volatile products that were no longer present on the Teflon filters at the completion of the 4-day ozone exposure experiment, and products formed in very low yields of $\leq 0.1\%$, since the mass spectrometer does not record mass fragments whose intensity is less than 0.1% of that of the most abundant ion (base peak).

Within these constraints, product identification was deemed *positive* when the sample mass spectrum was identical with that of an authentic sample recorded under the same conditions (e.g., isatin), *probable* when no authentic sample was available but mass spectral data were available for structural homologues, and *possible* when no authentic sample was available and the structure of the product was derived solely from interpretation of its CI and EI mass spectra.

Indigo. Comparison of the spectra of the control and ozone-exposed samples indicated that all of the indigo had been consumed at the end of the 4-day exposure. The CI spectrum of indigo (10) includes the high-mass fragments at *m/z* 291, 277 (indigo-reagent gas adducts), 264 (contribution of ¹³C to MH ion), 263 (MH ion, base peak), 262 (M), 247-249 (loss of N and NH), and 234-236 (loss of CO). All these fragments are absent in the spectrum of the ozone-exposed sample. The initial amount of indigo was ~ 10 mg; the amount of ozone flowing through the Teflon filter was ~ 108 mg, i.e., ~ 50 times more than needed to consume indigo in a bimolecular reaction. These results

are consistent with those obtained in our earlier study (3) with lower ozone levels (~ 0.4 vs 10 ppm), longer exposure times (12 weeks vs 4 days), a different substrate (watercolor paper vs Teflon membrane), and higher relative humidity (~ 50 vs $\leq 5\%$). These results are also consistent with those obtained in the liquid phase, where indigo has been shown to react readily with ozone in water (11); in fact, the reaction of indigo (as soluble sulfonate salts) with ozone in water serves as the basis for a spectrochemical method for the determination of ozone in aqueous environmental samples (11).

Major mass fragments in the CI spectrum of the ozone-exposed indigo sample included *m/z* 148 and 164, which correspond to compounds of molecular weight 147 and 163, respectively. Interpretation of the sample spectrum suggested isatin and isatoic anhydride as possible products (see structures in Figure 3). Authentic samples of isatin (Aldrich, *M*_r 147, purity = 98%) and of isatoic anhydride (Aldrich, *M*_r 163, purity = 96%) were obtained, and their spectra were recorded (Table I). These spectra gave an excellent match with that of the ozone-exposed sample, thus allowing positive identification of isatin and isatoic anhydride as the only detectable products of the indigo-ozone reaction under our conditions.

A tentative mechanism consistent with the experimental findings is given in Figure 3. This mechanism involves electrophilic addition of ozone onto the unsaturated carbon-carbon bond, which is far more reactive toward ozone than any other reaction center within the indigo molecule. The addition step is assumed to be identical to the well-documented addition of ozone onto the C=C bond of simple olefins (12). The initial addition step thus involves the formation of an ozone adduct (1,2,3-trioxolane), followed by scission of the carbon-carbon bond and rearrangement of the two resulting Criegee biradicals into isatin and isatoic anhydride, respectively.

The fate of the two products of the indigo-ozone reaction was investigated in experiments involving direct exposure of authentic samples of isatin and isatoic anhydride, respectively, to ozone under conditions identical with those employed for the indigo-ozone reaction. Mass spectra of samples before and after exposure to ozone were identical, i.e., isatin and isatoic anhydride were not ozone fugitive under our conditions.

Dibromoindigo. As for indigo, dibromoindigo was entirely consumed by ozone under the conditions of our study. The CI spectrum of dibromoindigo, discussed in detail elsewhere (10), contained major high-mass fragments at *m/z* 419, 421, 423 (MH ions, triplet due to ⁷⁹Br and ⁸¹Br,

Table II. Contribution of Bromoisatin and Bromoisatoic Anhydride to the CI Spectrum of the Ozone-Exposed Dibromoindigo Sample

<i>m/z</i>	bromoisatoic anhydride ^a		bromoisatin ^a		ozone-exposed dibromoindigo sample, % of base peak
	⁷⁹ Br (<i>M_r</i> 241)	⁸¹ Br (<i>M_r</i> 243)	⁷⁹ Br (<i>M_r</i> 225)	⁸¹ Br (<i>M_r</i> 227)	
245		MH (¹³ C)			1.5
244		MH			10.6
243	MH (¹³ C)	M			2.7
242	MH				12.8
241	M				1.0
230		MH - N			10.0
229		MH - NH		MH (¹³ C)	15.0
228	MH - N	M - NH, MH - O		MH ^b	84.6
227	MH - NH		MH (¹³ C)	M	22.4
226	M - NH, MH - O	MH - H ₂ O ^c	MH ^b		100 (BP)
225			M		8.8
224	MH - H ₂ O ^c				25.9
214				MH - N	10.1
213				MH - NH	10.0
212			MH - N	M - NH	46.5
211			MH - NH		11.0
210			M - NH		43.7

^a See structures in Figure 4. The relative abundance of ⁷⁹Br and ⁸¹Br is 50.54/49.46, i.e., ≈1:1. ^b MH is base peak in isatin; see Table I. ^c MH - H₂O is base peak in isatoic anhydride; see Table I.

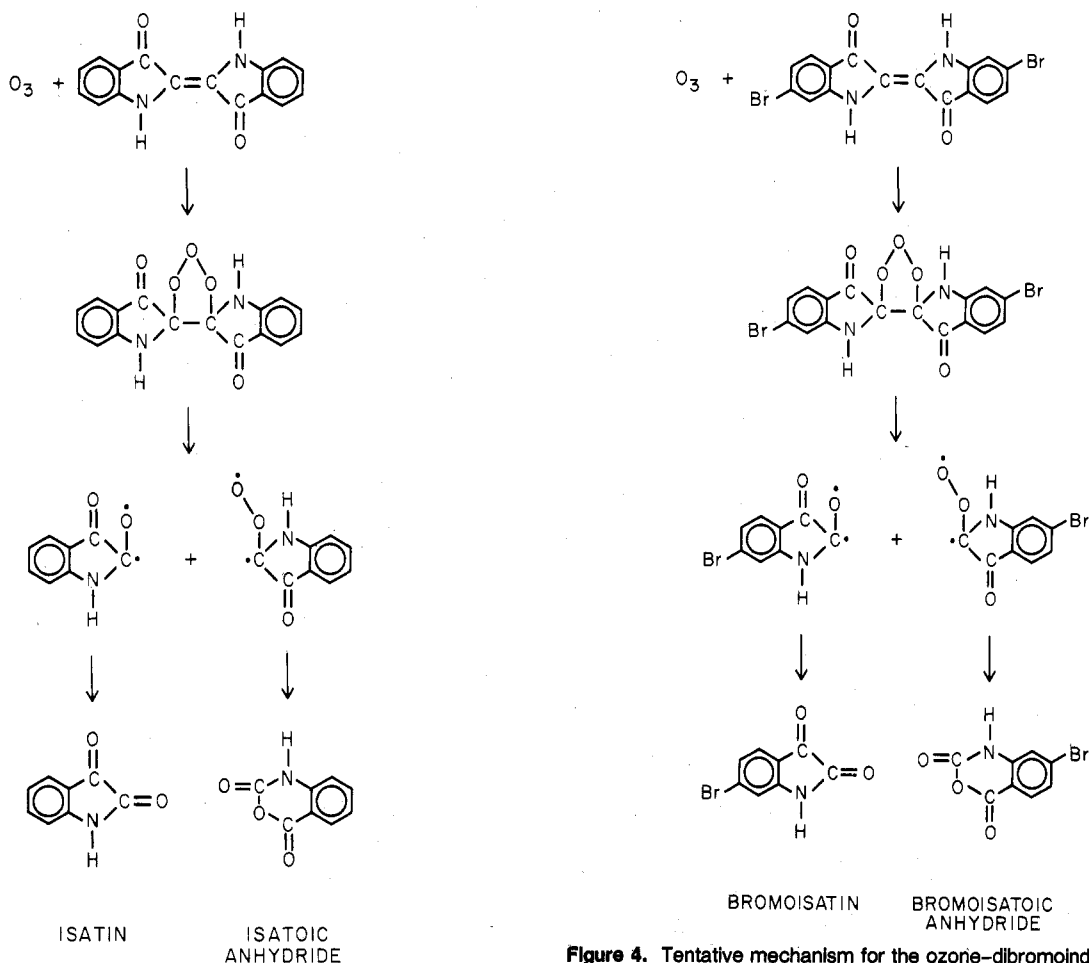


Figure 3. Mechanism of the ozone-indigo reaction.

two bromine atoms per molecule), 405 (loss of NH), 340 and 342 (loss of Br), 325–329 (loss of NH and Br), 261–264 (loss of two Br), and so on. All these fragments are absent from the spectrum of the ozone-exposed sample, whose prominent ion fragments include *m/z* 244 (11% of base peak), 242 (13%), 228 (84.6%), 226 (base peak, 100%), 224 (26%), and so on. Thus, the spectrum of the ozone-exposed sample can be accounted for (in terms of both fragment *m/z* values and their relative abundance in-

Figure 4. Tentative mechanism for the ozone-dibromoindigo reaction.

cluding ⁷⁹Br, ⁸¹Br, and ¹³C isotopes) by two reaction products, namely bromoisatin and bromoisatoic anhydride (Table II; see structures in Figure 4). While no authentic samples were available for comparison, the identification of these two products is deemed probable in view of the close similarity of the recorded spectra to those of the indigo-ozone system, for which positive identification could be made with authentic samples of isatin and isatoic anhydride.

A mechanism consistent with the experimental findings is given in Figure 4. As for indigo, this mechanism involves

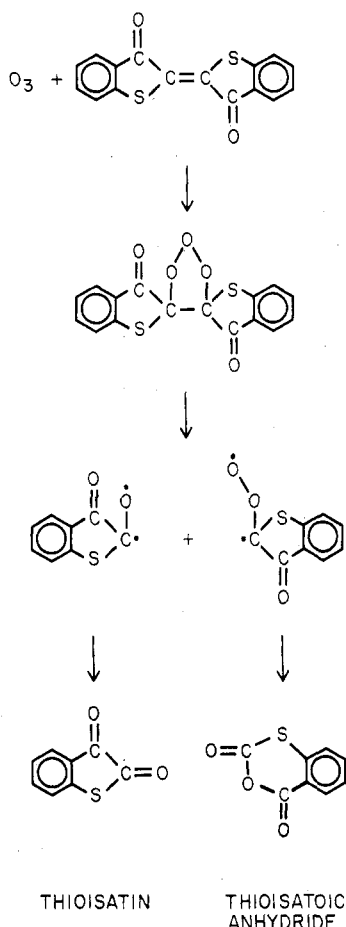


Figure 5. Tentative mechanism for the ozone-thioindigo reaction.

ozone addition onto the unsaturated carbon-carbon bond, followed by unimolecular decomposition of the trioxolane adduct to form two Criegee biradicals, whose rearrangement yields bromoisatin and bromoisatoic anhydride, respectively. It should be noted here that the mechanism of the dark reaction between ozone and dibromindigo is substantially different from that involving its photooxidation, i.e., exposure to sunlight in air: photooxidation involves loss of bromine atoms and the formation of indigo as a reaction product (7); the opposite is true of the ozone reaction, which involves the breaking of the indigo carbon skeleton and the retention of bromine atoms in the major products.

No attempts were made to isolate or synthesize bromoisatin and bromoisatoic anhydride in order to study their stability toward ozone. The dibromindigo sample, initially a deep violet, faded to a light gray after exposure to ozone. Whether the final color of the sample is attributable to bromoisatin, bromoisatoic anhydride, or to one or more of their ozone reactions products is not known at this time.

Thioindigo. The sample of thioindigo tested was significantly less reactive toward ozone than samples of indigo and dibromindigo. The exposed sample, while distinctly faded, still retained much of its original violet color. The mass spectrum of the exposed sample indicated a substantial amount of unreacted thioindigo. A comparison of the relative abundance of mass fragments of thioindigo and of those of the saturated impurity (which presumably did not react with ozone) indicates that only ~20-30% of the thioindigo had reacted with ozone after 4 days of exposure. In addition, thioisatin and thioisatoic anhydride, the expected reaction products (see Figure 5), were tentatively identified in the mass spectrum of the exposed

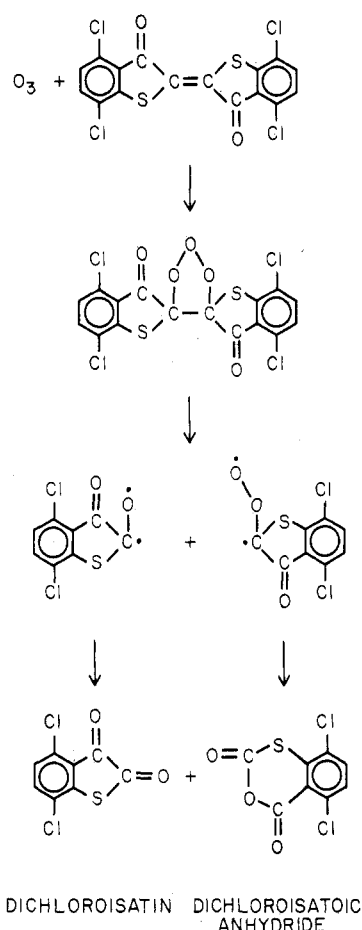


Figure 6. Tentative mechanism for the ozone-tetrachlorothioindigo reaction.

sample but accounted for only ~5-10% of the initial thioindigo. No other product could be detected, but some products may have escaped detection if their mass fragments coincided with those of unreacted thioindigo and/or sample impurities unreactive toward ozone.

Thus, it appears that thioindigo is less ozone fugitive than the nitrogen-containing indigos, but this conclusion should be verified by carrying out more detailed studies with colorant samples of higher purity.

Tetrachlorothioindigo. The behavior of the colorants containing tetrachlorothioindigo was similar to that discussed above for thioindigo, i.e., lower reactivity toward ozone than the nitrogen-containing homologues, spectra obscured by large amounts of unreacted materials and of impurities, with the added complexity of extensive thermal decomposition of the samples when subjected to mass spectrometry analysis. The expected reaction products (Figure 6), dichloroisatin and dichloroisatoic anhydride, were tentatively identified in low yields, along with chloroisatin (presumably from the dichlorothioindigo impurity) and methyl chloroisatin (presumably from the dimethyl-dichlorothioindigo impurity).

Relationship between Color and Ozone Reactivity for the Indigoid Colorants. The exact nature of the chromophore in colorants having the indigoid structure has been determined (13). The fundamental chromogen in such structures is the so-called "H-chromophore", the central arrangement of carbonyl-olefin-amine (or thioether) groups. This chromophore can be considered as a pair of extended donor (amine)-acceptor (carbonyl) chromogens linked by a common olefinic bond. It is the sharing of the central olefinic linkage that gives the molecule its low $\pi\pi^*$ excitation energy.

Since this chromophore is of a donor-acceptor type, the resulting color is very sensitive to the electron-donating/electron-accepting abilities of the component functional groups. Thus, the replacement of the amine by the thioether in going from indigo to thioindigo leads to an increase in the $\pi\pi^*$ excitation energy (and a shift in color from blue to red) because sulfur is a poorer electron donor than nitrogen. Other indigo derivatives, obtained by replacing the amine group with other heteroatoms, show similar shifts in color directly related to the electron-donating ability of these groups.

It has been found that the benzene rings attached on either side of this H-chromophore have only a secondary influence on the color of the molecule. Substituents on these rings, such as the halogen atoms in 6,6'-dibromoindigo and 4,4',7,7'-tetrachlorothioindigo, seem to have an effect on the color only insofar as they alter the electron-donating/electron-accepting ability of the groups of the central chromophore, either through mesomeric (through bond) or steric (through space) interactions. For example, the bromine atoms in 6,6'-dibromoindigo are para to the carbonyl groups in the central chromophore and thus reduce the electron-accepting ability of those carbonyls. The shift in $\pi\pi^*$ excitation to slightly higher energies accounts for the shift in color from the blue indigo to the violet dibromoindigo (Tyrian purple).

Since the apparent colors of indigo and its derivatives are such a sensitive measure of the electron-donating/electron-accepting ability of the groups adjacent to the central olefinic bond, it is not surprising that the reaction of these compounds with ozone, which proceeds by electrophilic addition onto the olefinic bond, should also show a wide range of apparent rates. It is well-known that, in both liquid-phase and vapor-phase ozonolyses (12), the rate of reaction of ozone with substituted olefins *increases* if the substituent is *electron donating* and *decreases* if the substituent is *electron withdrawing*. This trend seems to be in evidence in the ozone reaction of the indigoid colorants studied here. The observed products are consistent with an electrophilic addition of ozone to the olefinic bond, and the reaction rate seems to be greatest for those colorants having the greatest electron-donating capability adjacent to that double bond, i.e., indigo and dibromoindigo. In contrast, substitution of the amine by a sulfur atom decreases the electron-donating ability in thioindigo and tetrachlorothioindigo, and the corresponding ozone reaction rates are reduced. Just as the color of these compounds indicated this large change in electron-donating ability near the olefinic bond, the very slight shift in color upon halogenation (indigo to dibromoindigo, thioindigo to tetrachlorothioindigo) indicates a minor change in electron-donating capability in the chromophore, consequently, the ozone reactivities of the compound and of its halogenated analogues are very similar. These conclusions have diagnostic value for the selection of less ozone fugitive indigo colorants.

Comparison of Indigo Fading by Exposure to Ozone and by Exposure to Sunlight. In museum settings, indigo colorants may fade due to exposure to ozone and/or to sunlight. The poor lightfastness of indigos has long been documented in the textile industry (14, 15). When exposed to light (including sunlight) in air, i.e., photooxidation, indigo colorants undergo dehalogenation (loss of bromine and chlorine substituents) as well as oxidation (e.g., indigo \rightarrow isatin). Dehalogenation was not observed (and is not expected) in our experiments with ozone in the dark. Thus, the chemical characterization of the products in an art object containing faded indigo colorants may have

diagnostic value for the implementation of mitigation measures, i.e., removal of ozone or protection from light.

Conclusions

Several indigo colorants deposited on Teflon filters were exposed in the dark to purified air containing 10 ppm ozone. These exposures were carried out for 4 days at ambient temperature (24 °C) and low relative humidity (RH \leq 5%). Mass spectrometry analysis of the exposed samples indicated that indigo and dibromoindigo were entirely consumed, that the major reaction products of the ozone-indigo reaction were isatin and isatoic anhydride, and that the major products of the ozone-dibromoindigo reaction were bromoisatin and bromoisatoic anhydride. Under the same conditions, thioindigo and colorants containing tetrachloroindigo and/or other chlorinated indigos also reacted with ozone, though at a slower rate; the corresponding isatins and anhydrides were tentatively identified as reaction products.

The reaction products identified can be explained in terms of electrophilic addition of ozone onto the unsaturated carbon-carbon bond of the indigo molecule. This mechanism adequately accounts for the loss of chromophore for all indigos studied and for the lower reactivity of thioindigo and its derivatives as compared to that of indigo and its derivatives. The dose of ozone employed in our experiments, 10 ppm for 4 days, is equivalent to, for example, 0.04 ppm O₃ for 1000 days (2.74 years). Long-term average ozone concentrations of about 0.04 ppm are common in urban air, including indoor air such as in museums, in many urban areas of the world.

Acknowledgments

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Registry No. Indigo, 68651-46-7; dibromoindigo, 84-40-2; thioindigo, 522-75-8; tetrachlorothioindigo, 14295-43-3; ozone, 10028-15-6; isatin, 91-56-5; isatoic anhydride, 118-48-9.

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Sorption of Vapors of Some Organic Liquids on Soil Humic Acid and Its Relation to Partitioning of Organic Compounds in Soil Organic Matter

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■ Vapor sorption of water, ethanol, benzene, hexane, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and 1,2-dibromoethane on (Sanhedron) soil humic acid has been determined at room temperature. Isotherms for all organic liquids are highly linear over a wide range of relative pressure (P/P°), characteristic of the partitioning (dissolution) of the organic compounds in soil humic acid. Polar liquids exhibit markedly greater sorption capacities on soil humic acid than relatively nonpolar liquids, in keeping with the polar nature of the soil humic acid as a partition medium. The limiting sorption (partition) capacities of relatively nonpolar liquids are remarkably similar when expressed in terms of volumes per unit weight of soil humic acid. The soil humic acid is found to be about half as effective as soil organic matter in sorption of relatively nonpolar organic compounds. The nearly constant limiting sorption capacity for nonpolar organic liquids with soil humic acid on a volume-to-weight basis and its efficiency in sorption relative to soil organic matter provide a basis for predicting the approximate sorption (partition) coefficients of similar compounds in uptake by soil in aqueous systems.

Introduction

In a series of earlier studies (1-5), we considered the individual functions of soil organic matter and mineral matter in sorption of (nonionic) organic compounds by soil, as well as effect of humidity on soil uptake. In retrospect, the soil may be regarded as a dual sorbent for organic compounds, in which the mineral fraction functions as a conventional solid adsorbent and the organic matter as a partition medium. In water solutions and for water-saturated soils, adsorption of organic compounds by soil minerals is suppressed by water, and the soil uptake consists primarily of solute partitioning (dissolution) into the organic matter. By contrast, the markedly greater sorption by dry and subsaturated soils from the vapor phase (or from nonpolar organic solvents) is attributed to mineral adsorption, which predominates over the simultaneous uptake by partitioning into the organic matter.

While the predominance of solute partitioning into soil organic matter in wet soils is supported by observations such as the general dependence of soil uptake on organic matter content, isotherm linearity, small heat of sorption, and absence of solute competition, studies of sorption isotherms of organic compounds on mineral-free soil organic matter should constitute further tests of the sorption model. We have therefore investigated the vapor sorption of some organic liquids at room temperature on a purified (Sanhedron) soil humic acid whose elemental composition and other properties have been described previously (6,

7). To evaluate the sorption efficiency of soil humic acid relative to soil organic matter, the results have subsequently been compared with previously reported data on soil uptake from water solution, the data having been normalized for organic matter content of the individual soils. Since the proportions of humin, humic acid, fulvic acid, and other non-humic components vary to some extent between soils, this comparison gives an estimate of the efficiency of the surface-soil humic acid relative to soil organic matters in various soils used in previous studies. Through this comparison, one can determine the extent to which one can predict sorption (partition) coefficients of organic solutes between soil organic matter and water on the basis of results derived from soil humic acid.

Studies of vapor sorption have thus been carried out for a number of organic liquids (mostly priority pollutants) and water on a purified (Sanhedron) soil humic acid that was used in earlier work (6, 7). The high purity of the humic acid sample circumvents potential complications of the sorption data by concurrent adsorption onto mineral (ash) components of less pure humic materials. Finally, to facilitate a better understanding of the nature of sorption on humic acid, a comparative study was also carried out on the uptake of organic vapors by poly(styrene-co-divinylbenzene)(PSDVB), a synthetic organic polymer closely related to those whose solution properties have been well-characterized.

Experimental Section

The apparatus used for the determination of vapor sorption is shown in Figure 1, which is essentially the same as described elsewhere (8). The test liquid was purified by vacuum distillation before its vapor was introduced into the sorption chamber containing a Cahn electrical microbalance. The organic liquids for sorption experiments were reagent-grade chemicals from commercial sources (Aldrich and American Burdick and Jackson) with purities greater than 98+%. After vacuum distillation, the vapor pressures of the test liquids were monitored by the Baratron pressure gauge of the apparatus (with the sorption chamber isolated from the system). The distilled liquids showed vapor pressures in close agreement with the literature values at room temperatures, as shown in Table I.

The soil humic acid sample [or poly(styrene-co-divinylbenzene)] was suspended from the microbalance in a small glass container that was tared with a metal calibration weight. A heating tape was wrapped around the sample hang-down tube for controlling the sample outgassing temperature. The sample was baked at 100 °C for 10-12 h and cooled to room temperature for several hours under vacuum to remove moisture before initiation of