

Progress in Permanence: Improved Dyes for “Gas Fading”

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Approaches to Improved “Gas Fading” Products

This paper discusses some approaches to understanding the chemical mechanisms of gas fading, and how we have been able to use these to intervene in the principal degradation pathways to improve longevity of printed images.

We have used ozone as the reactive chemical oxidant and present some justifications for this. We discuss the methodology for the mechanistic investigation and some of the issues we have found, followed by some example kinetics and mechanisms.

We then relate the kinetic and mechanistic conclusions to performance of dyes on real ink jet media (porous type). Finally we present data from some example dyes resulting from our investigations

Introduction

Previously we have discussed the importance of airborne pollutants in the degradation of images on porous ink jet media (1). In many systems and situations, degradation by pollutants is the primary mechanism for image loss and is much more rapid than degradation due to light.

A number of authors have looked at ozone and other pollutants as a root cause of air or gas fade, and in general have concluded that ozone appears to be significantly more destructive than other common pollutants in the systems studied so far. Ozone is a significantly stronger oxidizer than *e.g.* NO or NO_x, and is well known to react very readily with conjugated molecules as present in many chromophoric systems of dyes and pigments.

We have therefore looked principally at the kinetics and mechanisms of the reaction of a variety of chromophores with ozone both on ink jet media surfaces and in solution. An understanding of these basic processes is obviously key in designing more resistant systems.

Solution Studies

Studying the reaction of dyes with ozone in solution is relatively well known and a number of studies have been reported in the literature with the objective of understanding the decolouration of wastewaters (2). This method has the advantage of been established with many of the issues

known. In addition analysis of the kinetics and products is much simpler as a much wider range of analytical techniques is available in solution. A major assumption is that the same chemistry will be observed in the solid state (on ink jet media) and we deal with some aspects of this later and comment on the similarities and differences.

To this end we have built a small-scale lab ozonolysis rig outlined in Fig 1. Ozone is generated by electric discharge and is continuously sparged through a frit into dye solution of a known concentration. This arrangement leads to a steady ozone concentration, which is related to the partial pressure of ozone in the sparging air, and the delivery can be controlled by both the flow rate and the electric discharge equipment. Samples can be taken at regular intervals and the concentrations of ozone, dye, and products established by conventional methodology including uv vis and HPLC, MS and nmr etc. The chemistry of ozone in water is well established and it is relatively stable at low concentrations over reasonable time periods, but is catalytically degraded by hydroxide ions into hydroxyl radicals.

Whilst the reaction of ozone with organic molecules can be quite fast it is relatively selective and will react with some molecules faster than others and attack at specific points. Hydroxyl radicals however are much more reactive and are amongst the strongest oxidizing species known and non selective. Most ink jet media are pH7 or below and we have therefore chosen to buffer our solutions at pH7 with an unreactive buffer in order to minimize the production of hydroxyl radicals – this is common practice.

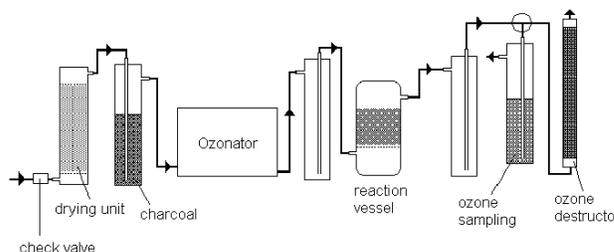
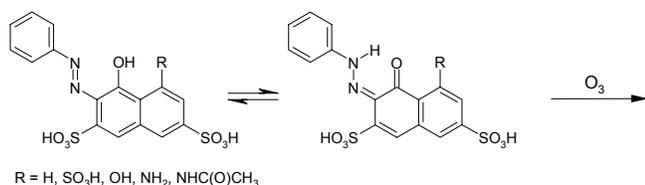


Figure 1. Ozonolysis Apparatus

Kinetic and Mechanistic Examples

Scheme 1 below incorporates a common ink jet chromophore. Examination of their solution properties to establish the tautomeric forms and aggregation state were first done. Analysis of its overall reactions with ozone by uv-visible spectroscopy shows eventual loss of the chromophore accompanied by a long wavelength tale relative to the main absorption (Fig 2). Rates can be calculated these spectra and fit reasonably well with the expected pseudo first order kinetics. HPLC analysis however demonstrate that the initial products from the react of ozone with these molecules is still strongly absorbing and therefore in order to calculate accurate pseudo first order rate constants and full second order rate constants some form of separation or deconvolution of the spectra need to be done.



Scheme 1

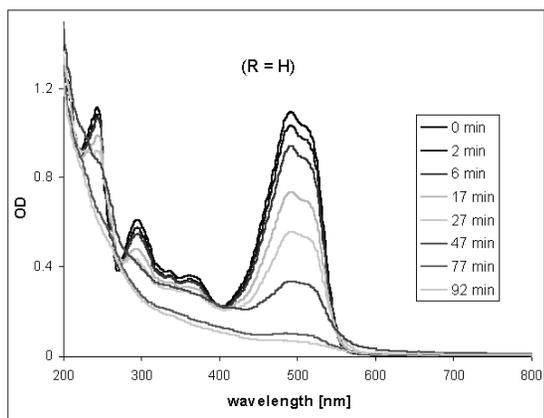


Figure 2

The products of the initial part of the reaction (first 10-15%) were separated by preparative HPLC combined with a DAD and subject to MS and nmr. The reactions were repeated at various concentrations of ozone and the peak areas were then used to calculate accurate and reproducible second order rate constants as in Table 1.

The concentration profile of the products can be plotted to follow the progress of all the components in the reaction as in Fig 3. Surprisingly for these molecules, ring hydroxylation para to the aza nitrogen is a dominant pathway for the initial reaction, which is subsequently followed by chromophore degradation.

Similar studies of have been done on a number of chromophores including phthalocyanines, metallised dyes, azo chromophores and azo chromophores substituted by numerous functional groups to examine substituent effects.

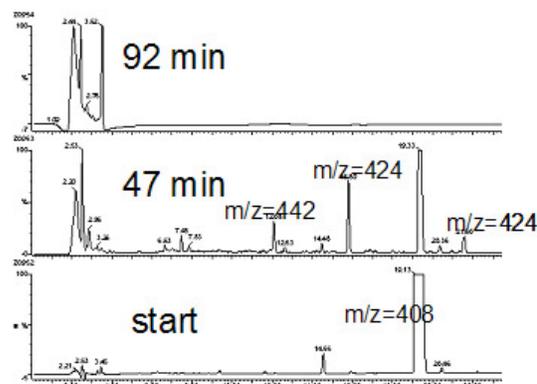


Table 1

R	$k_{\text{exptl, UV}}$ [10^{-4} s^{-1}]	$k_{\text{exptl, HPLC}}$	O 3	k_{UV} [M^{-1}]	k_{HPLC} C
H	12	20	4	27	46
SO ₃	11	16	3	31	43
NH ₂	11	16	2	44	73
OH	8	13	1	46	75
NHC	6	11	2	24	41

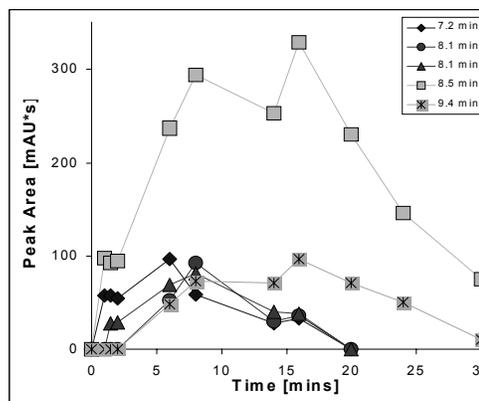


Figure 3

Correlation to Solid State Reactions

In order to make full use of this understanding we have attempted to relate the solution chemistry to that which happens in forced air flow and ozone chamber experiments on the same dyes when printed onto ink jet media.

Qualitatively the same changes in the uv spectra are seen when the reflection spectra are measured see Fig 4, the same overall rates are seen, and the same products are observed by analytical HPLC/uv-vis and MS when extracted. (The products are much simpler to identify once their retention times, uv-vis and MS spectral properties have been established from the solution experiments.)

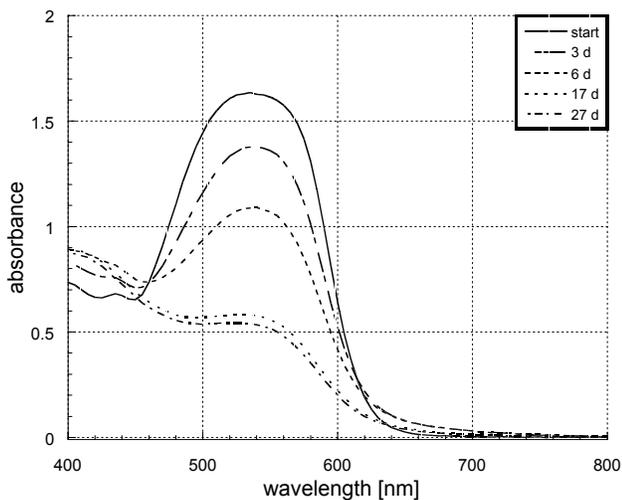


Figure 4

Improved Dyes

Using the above generated knowledge we have been able to synthesise dyes with improved ozone resistance. Some examples show 10-100 time better ozone fastness with the other properties being similar.

References

1. P Wight NIP 17 (2000) and NIP 18 (2001)
2. See e.g. VS Salvin J. Am. Dye Rep., 1969, 1, 245-251; RE Miller, J. Org. Chem., 1961, 26, 2327-2330; M Matsui, Dyes & Pigments, 1988, 9, 109-117

Biography

Paul Wight received his B.Sc from Durham University, UK in 1986, and a Ph.D. in organic chemistry from Nottingham University (UK) in 1990. He started work for the then ICI, on novel chromophores and disperse dyes. After 5 years he joined the ink jet research group, and has worked on a wide range of projects as the company reincarnated itself as Zeneca and now Avecia. He currently leads a team titled "Fundamental Understanding" using a combination of physical chemistry techniques, analysis and synthesis, with the objective of discovering useful new science underlying ink jet chemistry and processes.