

Aspects of the Surface and Bulk Nitration of Cellulose in Nitric Acid, Nitric Acid / Water, and Nitric Acid / Dichloromethane Mixes

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Synopsis

Electron spectroscopy for chemical analysis (ESCA) has been employed to follow the surface nitration of cellulose papers in nitric acid–water and nitric acid–dichloromethane mixes with the aim of: elucidating the identity of the nitrating species in these mixes and from comparison of surface and bulk degree of substitution (DOS) further understanding on the role that morphology plays in the nitration of cellulose in these mixes. In nitric acid, nitric acid–water and nitric acid–dichloromethane mixes, surface nitration was observed to be slow (cf. to that reported in mixed acids) and the concentration of nitronium ion was observed to be low (cf. to mixed acids). On the basis of these observations and from the results of kinetic experiments, reported herein, it is proposed that the nitronium ion, NO_2^+ , is the important nitrating species of cellulose in these nitric acid mixes. Nitration in all but the most concentrated nitric acid–dichloromethane mixes produced equal surface and bulk DOS; however, nitration in pure nitric acid produced different surface and bulk DOS. The latter result implies that the heterogeneous nature of the nitration reaction can influence the DOS achieved.

INTRODUCTION

Previous studies of cellulose nitration in nitric acid and nitric acid–water mixes have been limited to determining the extent and rate of nitration in the cellulose bulk and as a consequence of this the identity of the nitrating species and the mechanism controlling DOS in nitric acid mixes have remained the subject of considerable controversy: The nitronium ion is well established as the nitrating species in most organic nitrations; however, in cellulose nitration, molecular nitric acid is frequently cited as the nitrating species.^{1,2} The use of electron spectroscopy for chemical analysis (ESCA) to monitor the surface nitration of cellulose in technical mixed acids is well documented³: Many aspects of the nitration mechanism have been elucidated by ESCA that cannot be resolved from bulk studies.³

However, nitration in nitric acid (alone) or nitric acid–water mixes produces very brittle or shredded cellulose nitrates (depending on the water concentration of the mix) which are of little commercial importance: Further, materials of low DOS cannot be prepared in these mixes.⁴ With the addition of an “inert” miscible organic liquid to nitric acid the production of cellulose nitrates over the complete range of substitution, i.e., degree of substitution (DOS) = 0 → 3, without any appreciable destruction of the original cellulose fiber structure, is possible. The use of nitric acid–organic liquids to produce

very high DOS materials has been widely reported.^{2,5-9} Organic-nitric acid mixes are commonly employed to nitrate aromatic compounds and the mechanism of nitration in these mixes has been extensively studied.¹⁰ However, in cellulose chemistry the nitration mechanism has received scant attention.

In this paper ESCA has been employed to investigate the surface nitration of cellulose in different composition nitric acid-water and organic-nitric acid mixtures. The rates of nitration observed at the fiber surface in these mixes are compared to those previously reported for cellulose in mixed acids and important conclusions are drawn about the nature of the nitrating species and the mechanism of nitration. Further, the issue of "surface cracking" at the onset of nitration is addressed.¹¹

EXPERIMENTAL

One gram of Whatman cellulose papers was nitrated in 80 mL of nitrating mix at 24°C. The ratio of nitric acid:water or dichloromethane:nitric acid employed is described where relevant. Pretreatment of the cellulose is outlined elsewhere.³ Samples nitrated in nitric acid-water mixes were quenched immediately. Samples nitrated in dichloromethane/nitric acid mixes were either quenched immediately in 5 L of water or washed with dichloromethane in a Buchner funnel prior to quenching. The resulting surface and bulk DOS were found not to be affected by the chosen method of quenching.

Commercial fuming nitric acid was obtained from Aldrich Chemical Co. It was > 97% pure containing 2-3% N₂O₄. Pure anhydrous nitric acid was prepared by vacuum distillation from a KNO₃/H₂SO₄ mix and used immediately.¹² The dichloromethane (May and Baker Ltd.) was redistilled before use.

ESCA spectra were run on Kratos ES200 and ES300 electron spectrometers employing Mg_{Kα} and Ti_{Kα} X-rays. Peak fitting was achieved using the software on a Kratos DS300 data system. Raman spectra were run on a Varian Carey 82 Raman spectrometer using an Argon gas laser (514.5 nm, 200 mW).

Bulk % nitrogen was determined by either microkjeldhal analysis or employing a Carlo-Erba elemental analyzer (MoD 1106).

RESULTS AND DISCUSSION

Nitration with Pure Nitric Acid: The Nitrating Species

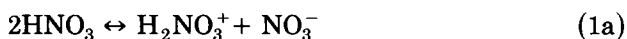
Nitration is a heterogeneous reaction and hence the order and rate of reaction cannot be deduced from bulk studies. However, as nitration is homogeneous over the top 50 Å, at the fiber surface the initial rate of nitration can be monitored: The data presented in Table I show the surface DOS calculated from the C_{1s} and N_{1s} core level spectra of the celluloses³ after a 1-s nitration in pure anhydrous nitric acid and in 90% nitric acid (10% water).

The results presented in Table I show that the addition of water to the anhydrous acid significantly reduces the extent of surface nitration achieved after 1 s immersion, while at longer nitration times (> 30 seconds) the two mixes produce cellulose nitrates of similar surface DOS (2.3 ± 0.1).

TABLE I
DOS Achieved after 1 s with Acid Mix Composition

% HNO ₃	DOS
100	1.7
90	0.2

The presence of the nitronium ion in anhydrous nitric acid is well established¹⁰; its formation is described by



It is assumed that the nitronium ion is responsible for the rapid nitration observed in pure nitric acid and reduction in the concentration of this ion is reflected by the dramatic change in DOS observed, after 1 s nitration, in the aqueous (90%) nitric acid. The anticatalytic effect, of added water, on the rate of reaction in anhydrous nitric acid has been reported in other organic nitrations; e.g., the addition of 5% water in the nitration of nitrobenzene reduces the rate by sixfold.¹⁰

Nitration in Fuming Nitric Acid: The Nitrating Species

The surface nitration of cellulose papers in fuming nitric acid–water mixes has been investigated as a function of immersion time; the surface DOS calculated from the Mg_{Kα} ESCA X-ray spectra are presented in Figure 1. From this figure it can be seen that the addition of water to fuming nitric acid dramatically reduces the DOS achieved in the top 50 Å after 1 s; e.g., nitration in the fiber surface with anhydrous nitric acid is almost complete after 1 s. However, in mixes diluted by > 10% the level of nitration in the cellulose surface achieved after 1 s is negligible.

Employing the greater sampling depth of Ti_{Kα} X-rays, it was found that nitration in all these mixes was vertically homogeneous to a depth of at least

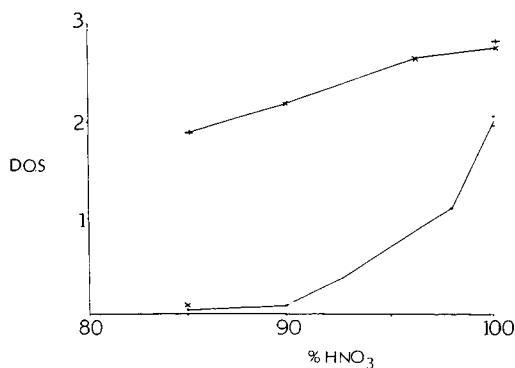


Fig. 1. Surface DOS with acid mix composition: (·) 1 s; (x) 30 s; (+) 30 min.

TABLE II
DOS Achieved with Nitration Time in Fuming Nitric Acid and Fuming
Nitric Acid-Potassium Nitrate Mixes

Immersion time (s)	DOS	
	HNO ₃	HNO ₃ /KNO ₃
1	1.86	0.77
5	2.26	1.62
30	2.40	2.20

100 Å after a 1-s immersion, establishing that it is the rate of nitration that is being monitored, by ESCA, and not the diffusion of the acid into the fiber surface.

The importance of the nitronium ion in the nitration of cellulose can be tested kinetically. From eq. (1) it can be seen that the addition of the nitrate ions to nitric acid will result in the suppression of nitronium ion formation. In Table II the levels of surface nitration achieved in fuming nitric acid and fuming nitric acid/potassium nitrate mixes, as monitored by ESCA, are compared after immersions of $t = 1, 5,$ and 30 s. The initial rate of nitration is of most interest; as the nitration reaction proceeds, water will be produced which will reduce the rate of nitration.

From Table II it is evident that the addition of potassium nitrate to nitric acid has reduced the level of surface nitration achieved at $t = 1$ and 5 s. The DOS in the top 100 Å was also monitored by Ti_{K α} X-rays and nitration was found to be vertically homogeneous at all immersion times; therefore, it can be concluded that the addition of nitrate ions had reduced the rate of nitration (and not the diffusion rate of the acid) in the surface region of the cellulose fiber.

The potential effect of the small N₂O₄ concentration in fuming nitric acid on the nitration reaction is thought to be negligible. This conclusion is based on several observations. First, the surface and bulk DOS achieved by nitration with fuming nitric acid is the same as that achieved with the pure acid. Second, the rate of nitration observed in the surface region with fuming nitric acid is comparable with that monitored in pure nitric acid. Finally, from the N_{1s} core level (Mg_{K α} X-rays) it is evident that only nitration has taken place in fuming nitric acid mixes,³ i.e., there is no significant nitrition or other side reaction.

The Nitrating Species in Aqueous Nitric Acid

In mixes of $> 5\%$ water content, nitration still takes place and moderately high DOS are still achieved in the surface, although physical techniques, spectroscopic and electrochemical, suggest that the ion is no longer present at such dilutions.¹⁰ However, it has been shown by kinetic studies that in aqueous nitric acid, containing as much as 60 mol % water, the nitronium ion is still an effective nitrating agent.¹⁰ It is possible that molecular nitric acid is responsible for nitration of cellulose in aqueous mixes; but it is thought more likely that the nitronium ion is still responsible for nitration. Miles¹ has pointed out that cellulose linters preferentially absorb nitric acid from nitric

acid-water mixes and therefore in the vicinity of the cellulose hydroxyls the true concentration of nitric acid may be very much higher than expected from the composition of the nitrating liquid. On the basis of the work presented above, it is not possible to establish the identity of the nitrating species in aqueous nitric acid. However, in all the other nitrating systems so far investigated, it has been shown that the nitronium ion is responsible for nitration.^{3,13,14}

A Study of Surface and Bulk DOS Achieved by Nitration in Nitric Acid Mixes

The final surface and bulk DOS of cellulose nitrates prepared from mixed acids have already been shown to differ.³ In nitric acid the highest bulk DOS generally reported is 2.8,² although a DOS of 3 has been reported by nitrating a 2.7 DOS cellulose nitrate in pure nitric acid.¹⁵ Gelatinization of the fiber may possibly prevent complete diffusion of the nitric acid throughout the fiber; however, from Table I it can be seen that at the fiber surface, where diffusion is not considered a problem, pure nitric acid will only nitrate cellulose to a DOS of approximately 2.4. The relationship between surface and bulk DOS and the effect (if any of gelatinization) on DOS have been further investigated.

Cellulose papers were nitrated at room temperature for 1 h in fuming nitric acid and a bulk DOS of 2.7 was measured. The nitrated product was extremely brittle and from visual examination it was evident that gelatinization of the fibers had taken place.

A cellulose nitrate (DOS = 2.7, prepared in a mixed acid) was further nitrated in fuming nitric acid; in Table III the surface and bulk DOS monitored are presented with nitration time. No gelatinization of the fibers was observed. From the data presented in Table III it is reasonable to assume that a DOS of 2.75 is the maximum bulk DOS obtainable in cellulose papers nitrated with fuming nitric acid. When a 2.83 bulk DOS material is immersed in fuming nitric acid it has been shown to denitrate to a DOS of 2.75.¹⁶ It therefore appears that a DOS of ~ 2.75 is the equilibrium DOS for cellulose papers nitrated with fuming nitric acid. If the nitronium ion is responsible for nitration from the data presently available, it must be concluded that molecular nitric acid is responsible for denitration. In mixed acids it has been shown that sulfuric acid can denitrate celluloses¹⁷; esterifications are usually reversible processes and it is not surprising that a strong acid can cause deesterification. In concentrated sulfuric acid cryoscopic and spectroscopic

TABLE III
DOS Achieved by Nitration in Fuming Nitric Acid

	Hours nitration		
	0	26	71
Surface DOS	2.4	^a	2.45
Bulk DOS	2.7	2.65	2.75

^a Not measured.

TABLE IV
Surface DOS with Nitration Time in a 1.5:1 ml Dichloromethane/Nitric Acid Mix

Time	Surface DOS
1 s	0.20
10 s	0.60
30 s	1.60
60 s	2.14
> 6000 s	2.35

evidence indicates that alcohol nitrate esters undergo complex ionization, yielding nitronium ion.¹⁸

The surface and bulk DOS achieved by nitration in fuming nitric acid are not the same. In the cellulose bulk the nitration–denitration equilibria are, for some reason, slightly more in favor of nitration (cf. the surface). The mechanism of denitration in nitric acid is unclear. However, from the above results it is certain that the heterogeneous nature of the nitration reaction influences the final DOS achieved in the cellulose fiber.

Nitration in Nitric Acid–Dichloromethane Mixes: The Nitrating Species

The results in Table IV refer to the surface nitration of cellulose papers in a 1.5:1 dichloromethane nitric acid mix: DOS were calculated from the $Mg_{K\alpha}$ X-ray spectra of the nitrated celluloses.

From this table it can be appreciated that surface nitration is comparatively slow; in an equivalent technical acid mix (where the dichloromethane component has been replaced by sulfuric acid) surface nitration is complete to a depth of 50 Å within the first second of immersion.³ Although the nitronium is prominent in the Raman spectra of technical mixed acids, in nitric acid:dichloromethane mixes the ion is not spectroscopically observable.¹⁹ However, kinetic studies have provided compelling evidence for the formation and effectiveness of this species in the nitration of aromatic compounds in organic–nitric acid mixes.¹⁰

The effect of added potassium nitrate on the rate of surface nitration in dichloromethane/fuming nitric acid mixes has been investigated. The surface DOS monitored after 1 s and 30 s nitration was found to be significantly reduced by the addition of 10% w/v of potassium nitrate to a 1:1 dichloromethane–fuming nitric acid mix. From this result it seems reasonable to assume that the nitronium ion is the important nitrating species of cellulose in dichloromethane/nitric acid mixes. The concentration of the nitronium ion in these mixes is low and this is reflected by slow rate of nitration monitored at the cellulose surface.

Surface and Bulk DOS with Nitric Acid / Dichloromethane Mix Composition

The factors controlling the DOS achieved in organic–nitric acid mixes are not particularly well understood; the mixes have been primarily used to prepare very high DOS cellulose nitrates and in comparison to their mixed

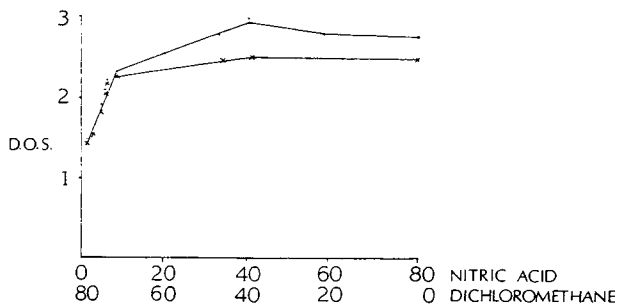


Fig. 2. Surface and bulk DOS with acid mix composition: (x) surface; (·) bulk.

acid counterparts little work has been reported on how the DOS is affected by mix composition.²

In Figure 2 the surface and bulk DOS achieved by nitrating 1 g cellulose papers in various nitric acid/dichloromethane mixes are reported. From the figure it can be seen that the surface and bulk DOS achieved in the cellulose fibers increase with increasing nitric acid concentration until the 40:40 mL situation is reached. Surface and bulk DOS do not appear comparable at high DOS; this may be the result of surface contamination which can seriously affect the DOS monitored by ESCA.¹⁴ However, two pieces of data argue against this interpretation:

- (i) As reported above, the surface and bulk DOS in cellulose nitrates prepared from fuming nitric acid are different; the surfaces of these cellulose nitrates were contaminant-free.
- (ii) In materials of lower DOS, surface and bulk are comparable and the level of hydrocarbon contamination in these materials was comparable to that observed for higher DOS materials.

The processes that have produced the curves in Figure 2 are clearly complex. Simple calculation reveals that there is a considerable excess of nitric acid to cellulose ($\times 3$) in all the mixes employed. The nitrating species is the nitronium ion and, in all but the highest concentration nitric acid mixes, it is thought that the predominant denitrating species is the hydrated nitric acid molecule,² water being produced by the nitration reaction. Since surface and bulk DOS are comparable (below a DOS of 2.2) it is clear that the "accessibility" of the crystalline and amorphous regions to these species must be equal. This is not necessarily always the case, as is evidenced by the difference in DOS observed in the mixes of high nitric acid content. A fuller explanation of this phenomenon will be presented in a future publication.²⁰

As the concentration of nitric acid increases, then the effect of hydrated nitric acid on the DOS is expected to diminish. For example, nitrating in a 40:40 mL mix and assuming complete reaction (i.e., a DOS of 3) the ratio of unreacted nitric acid to hydrated nitric acid in the used acid mix will be 160:1. In mixes of high nitric acid content it is possible that molecular nitric acid may act as a denitrating species (*vide infra* nitric acid).

In the 40:40 mL mix both surface and bulk DOS are at a maximum. Clearly the nitration reaction is at a maximum; i.e., nitration predominates over denitration.

Although a cellulose nitrate with a DOS of 3 cannot be prepared in fuming nitric acid, it can be seen, from Figure 2, that the addition of dichloromethane to fuming nitric acid facilitates near complete bulk nitration. It is perhaps possible to explain this observation in terms of the "polarity" of the nitrating mix and its ability to support charged species. The addition of dichloromethane to nitric acid will reduce the "polarity" of the nitrating mix and therefore its ability to stabilize charged species. If denitration proceeds via protonation of the nitrate ester and then ionization, to give the nitronium ion, then, as the "polarity" of the nitrating mix decreases, this mechanism will become less favorable. This argument is, to a certain extent, supported by data already presented, namely, that by physical measurements (spectroscopic and electrochemical) the presence of nitronium ion, or any charged species, cannot be detected in these mixes.^{10,19}

The Bulk Nitration of Cellulose Fibers

In mixed acids it is thought that the speed of bulk nitration observed is controlled by the diffusion rate of the nitrating mix through the cellulose polymer. This hypothesis is supported by comparing the rates at which the bulk nitration of cellulose takes place in a mixed acid and a dichloromethane/nitric acid mix respectively. From the data presented in Tables V and VI it is clear that complete bulk nitration in the mixed acid system requires a far greater immersion time than is required in the dichloromethane-nitric acid mix. Evidently, the speed of bulk nitration in the mixed acid is not equivalent to true rate of the nitration reaction as observed at the fiber surface by ESCA and from this it is concluded that bulk nitration is indeed diffusion-controlled.

TABLE V
Bulk DOS with Nitration Time: Mixed Acids^a

<i>T</i> (min)	DOS
2 min	0.54
11 min	1.10
21 min	1.50
41 min	1.90 ^b
120 min	2.70

^a75% H₂SO₄, 22.5% HNO₃, 2.5% H₂O, 24°C.

^bUnusually wide variation in DOS noted.

TABLE VI
Bulk DOS with Nitration Time: Dichloromethane/f. Nitric Acid^a

<i>T</i> (min)	DOS
10 min	2.53
35 min	2.66
60 min	2.74
180 min	2.73
2400 min	2.63

^a1.5:1 (mils) mix at +24°C.

However, from examination of the data in Tables IV and VI it can be seen that the rates of surface and bulk nitration, in the dichloromethane/nitric acid mix, are more comparable. Although bulk nitration is diffusion-controlled in this mix the faster rate of diffusion and the slower esterification reaction (as observed by ESCA) ensure that nitration is more even throughout the cellulose material at the shorter immersion times investigated. In mixed acids nitration occurs first at the fiber surface and then continues into the cellulose bulk. However, in dichloromethane/nitric acid mixes nitration must proceed almost simultaneously throughout the cellulose fiber. At low temperatures in mixed acids it has been reported that the cellulose fiber surface cracks at the onset of nitration.¹¹ This manifests as a drop in DOS, as monitored by ESCA, during nitration between $t = 20$ s and $t = 4$ min, depending on the nitrating temperature, and as extreme brittleness in materials removed from the nitrating mix. Cracking of the fiber surface with nitration has been confirmed by scanning electron microscopy (SEM).

Surface cracking has been attributed to stresses imposed in the fiber when nitration is limited to the very surface region of the fiber; the cellulose nitrate unit cell is considerably larger than that of cellulose and accommodation of these two unit cells in the cellulose polymer is thought to cause considerable stress and eventually cracking. At room temperature, in mixed acids, this cracking phenomenon is much more difficult to detect; it is neither as severe nor as persistent as it is at low temperature. This is to be expected since at low temperature mixed acids are very viscous and therefore penetration of the acid mix into the cellulose fiber is very slow; at room temperatures the mixes are no longer so viscous and penetration of the mixes into the cellulose bulk is appreciably faster. If this description of surface cracking is correct, it is to be expected only in mixes where nitration occurs from the surface inwards, e.g., mixed acids, nitronium ion salts.¹⁴ Surface cracking is not observed in the dichloromethane/nitric acid mixes. In nitric acid and nitric acid-water mixes the final products of nitration are so very highly degraded that it is not possible to detect cracking (if it is taking place) by SEM; however, the penetration of nitric acid and nitric acid-water mixes throughout the cellulose fiber has been observed to be complete in seconds (cf. mixed acids) and from ESCA no "dip" in surface DOS (with nitration time) was observed.

CONCLUSION

Summarizing, it appears that the nitronium ion is responsible for nitration in the mixes investigated and that the DOS established in a particular mix is equilibrium controlled. In aqueous mixes hydrated nitric acid is the predominant denitrating specie; in anhydrous nitric acid it is proposed that molecular nitric acid is responsible for denitration. In dichloromethane-nitric acid mixes, of low nitric acid concentration, the water produced by nitration limits the DOS. In mixes of high nitric acid concentration it is possible that molecular nitric acid is responsible for limiting the DOS achieved.

In anhydrous nitric acid and in dichloromethane-acid mixes, of high nitric concentration, cellulose nitrates of different surface and bulk DOS are produced, indicating the importance of the fiber structure on the nitration-denitration equilibria.

The rate of bulk nitration in dichloromethane–nitric acid mixes and in technical acid mixes has been examined. In the former mixes equilibrium surface DOS is shown to be established after approximately 1 min immersion. In the latter mixes surface DOS is known to be established in less than 1 s. Hence in the former mixes it is proposed that nitration proceeds fairly evenly throughout the entire cellulose material while in the latter systems nitration proceeds from the surface inwards. This conclusion is tied up with the cracking phenomenon observed in technical acid mixes.

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