E.s.c.a. studies of the nitration and denitration of cellulosic materials

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The relative rates of the nitration and denitration of cellulose and cellulose nitrate, respectively (in the form of linters paper), have been monitored in the outermost few tens of Angstroms of the fibres using e.s.c.a. (X-ray photoelectron spectroscopy). Important conclusions are drawn on the equilibrium conditions at the surface and it has been shown that in mixed acid nitrations sulphate esters, (often thought to be a cause of instability in cellulose nitrates), are confined to the outermost few tens of Angstroms of the material. Comparison of the degree of substitution at the surface and that determined for the bulk by Kjeldahl methods provides a new insight into this complex problem.

Keywords Electron spectroscopy for chemical application; nitration; denitration; cellulose; cellulose nitrates; equilibria

INTRODUCTION

The nitration of cellulose to produce the highly inflammable cellulose nitrates used in a range of applications including explosive formulations, surface coatings and photographic films is an extremely well documented reaction[1,2]. For example the expected degree of substitution of a given cellulose nitrate prepared in any composition of the most common nitrating media, (nitric acid/sulphuric acid/water), can be readily estimated from standard 3 component tables which have been in existence over 30 years[1].

The wide ranging nature of both the technological and academic investigations of the cellulose and nitrocellulose field over the past century, however, poses certain difficulties since relevant data is widely dispersed over a number of disciplines leaving many important questions unanswered.

The main point of interest in the technical nitration in mixed acid media, for example, is the question of the degree of substitution and how this relates to the acid mix composition. Thus, although the maximum theoretical degree of substitution is three, (corresponding to a nitrate group at each of the free hydroxyls throughout the cellulose chains), in practice this is never attained[1] and the maximum degree of substitution is ~2.8. A definitive answer as to why this should be so has not thus far been given since in a heterogeneous process the delineation between the possible explanations requires a technique which can clearly distinguish surface from bulk phenomena. The question of the limiting degree of substitution (usually extablished by a bulk nitrogen determination using a micro-Kjeldahl technique) in nitrocelluloses could *a priori* be rationalized in terms of two extreme models.

The first can be attributed to the micro and macroscopic structure of the cellulose. Thus, inhomogeneities in the bulk structure could give rise to accessible and inaccessible regions. Since nitration must depend on the diffusion of reagent throughout the bulk structure a further consideration is that there may well be a concentration profile throughout the structure. On this basis the less than maximum degree of substitution is attributable to an inhomogeneous bulk structure corresponding to regions of completely nitrated material and unreacted inaccessible regions[3].

A somewhat more plausible alternative is that since nitration is a reversible esterification process, then the ~2.8 degree of substitution typically observed represents the equilibrium situation[4]. Assuming an equilibrium reaction, however, another important question arises concerned with the relative rates of the forward (nitration) and backward (denitration) reactions. Many workers[5,6] monitoring bulk D.O.S. with time, (for materials prepared by nitration of cellulose and denitration of cellulose nitrate of high D.O.S.), have reported a slower backward reaction and have explained this in terms of a difference in the ease of diffusion of acids through the nitrated and denitrated materials.

These and many other important properties of nitrocellulose based formulations may be expected to depend on surface phenomena and it is surprising that so little attention has previously been directed at this aspect of the chemistry of nitrocelluloses. Since the initial reaction with any nitrating medium of cellulose fibrils is at the surface, and since it is the surface which interfaces with the surroundings, the question of the mechanism of synthesis, of initial burn rate, and of denitration, etc., are circumscribed by details of structure and bonding in not only the bulk but also in the outermost few tens of Angstroms of the surface. The advent of e.s.c.a., (X-ray photoelectron spectroscopy), in the last decade as a powerful tool for analysis of structure, bonding and reactivity of polymer surfaces[7,8] means that direct investigation of surface nitration and denitration of cellulosic material is now a realistic possibility. In this paper, therefore, we review detailed studies of the kinetics and mechanism of the surface nitration and denitration of celluloses using the wide range of information levels available from e.s.c.a. Comparison with bulk data provides considerable new insight into this important

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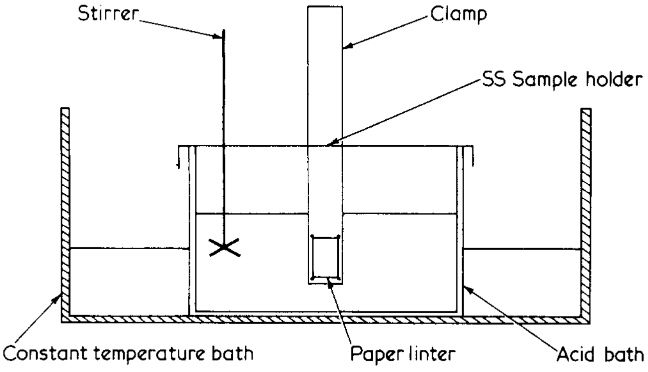


Figure 1 Nitrating apparatus used in e.s.c.a. studies

area which has been of interest to both science and technology for well over a century.

EXPERIMENTAL

The cellulose nitrates used in this work were prepared from commercially produced dewaxed, depectinized cotton linters of American origin, (Shirley fluidity 8.8 and approximate degree of polymerization 1100), which had been pressed into paper form for ease of analysis. The linters were pre-dried in a vacuum oven for 2 h at 50°C and stored for 24 h over P_2O_5 before nitration. This provides a starting cellulose containing $<2\%$ water. Nitrations were accomplished by immersion in the appropriate acid mix of sample strips, (4 x 4 cm), using an apparatus such as that depicted in *Figure 1*. The acid/cellulose weight ratio was never less than 100:1. Denitrated material was prepared by placing a high D.O.S. cellulose nitrate in acid mixes which would normally nitrate cellulose to a low level. For larger scale preparations the Mitchell[9] method was employed. After ~2 h of immersion in the required acid mix the nitrocellulose was removed, squeezed free of surplus acid and plunged into 2 l of rapidly stirred iced water. Several changes of water were used in the cold washing procedure before boiling the nitrocelluloses for periods of up to six hours in two changes of water. Drying was carried out in air initially followed by vacuum oven drying at low temperatures ~30°C for several hours followed by storage over P_2O_5 for several days before analysis. Bulk nitrogen determinations were carried out using a micro-Kjeldahl technique. Samples were cut to probe tip size (7 x 14 mm) and mounted using double sided scotch tape. They were analysed using a Kratos E.S. 300 electron spectrometer fitted with a dual $Mg/Ti_{K\alpha}$ anode and pumped with Alcatel air driven air bearing, hydrocarbon free, turbomolecular pumps. Spectra were deconvoluted using a DuPont 310 curve resolver and area ratios are determined by this means within $\pm 5\%$. The micro-analysis for nitrogen by means of micro-Kjeldahl provides an estimated uncertainty in D.O.S. of $\pm 4\%$.

RESULTS AND DISCUSSION

Preliminary analysis

Before considering the e.s.c.a. data on nitrocelluloses it is worthwhile briefly considering the core level binding energies for typical model systems. In an extensive series of studies on the influence of oxygen containing substituents on C_{1s} core binding energies we have recently shown that an additivity model may be used, the shift per single bond to oxygen being ~1.5 eV. The distinctive nature of nitrogen functionalities is evident from the data on simple nitrogen containing model systems shown in *Figure 2*. The N_{1s} binding energy for the nitrate ester is significantly higher than for either the nitroparaffin or nitrite ester and very much higher than for amide functionality as might be produced by photoreduction. The C_{1s} level for the carbon directly attached to oxygen in the nitrate ester is distinctively shifted to higher binding energy over and above that expected of a simple additivity model and it will become evident that the presence of nitrate ester groups provides a distinctive shift for the carbons involved.

The core level (C_{1s}, O_{1s}, N_{1s}) spectra for a typical nitrocellulose sample which has been commercially produced is shown in *Figure 3*. The C_{1s} spectrum shows 3 distinctive components (once a standard line shape analysis has been carried out). Thus the central component at ~287.4 eV arises predominantly from the carbons C2, C3 and C6 bearing the nitrate ester functionality with contributions from C4 and C5. C1 uniquely attached to 2 oxygens in the cyclic hemiacetal formulation of the *β-D*-glucopyranose ring is at highest binding energy. The component at 285 eV arises from extraneous hydrocarbon which we will show later is confined to the very surface of the sample. In cellulose samples irrespective of source or type (e.g. linters or staple fibres) the hydrocarbon signal observed is variable but inevitably present. The N_{1s} signal consists of an intense high binding energy component and comparison with

	Solid phase experimental e.v.			Theoretical e.v. (corrected)		
	C_{1s}	N_{1s}	O_{1s}	C_{1s}	N_{1s}	O_{1s}
CH_3NO_2	286·8	406·8	534·3	286·8	406·8	534·1
CH_3ONO				286·8	406·8	534·9 535·3
$CH_3CH_2CH_2CH_2ONO$	285·0 286·7	405·0	534·2 535·2			
CH_3ONO_2				287·4	407·7	536·2 534·5
$CH_3CH_2ONO_2$	285·0 287·0	408·1	535·0 534·1			
$CH_3CH_2CH_2ONO_2$	285·0 287·1	408·0	535·5 534·1			
$CH_3(CH_2)_3ONO_2$	285·0 287·0	408·1	535·3 534·1			
$CH_3\overset{O}{C}{-}NH_2$				284·8 288·8	399·9	533·1
$CH_3{-}O\underset{O}{C}{-}NH_2^{\cdot}$				286·8 290·2	400·3	534·4 532·6

Figure 2 Binding energy table of some simple nitrogen containing model systems

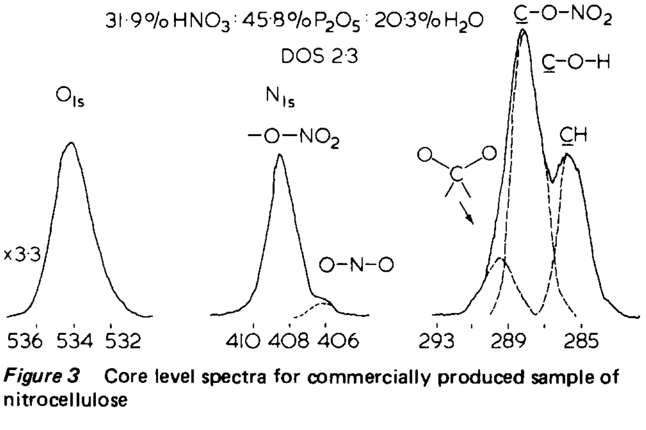


Figure 3 Core level spectra for commercially produced sample of nitrocellulose

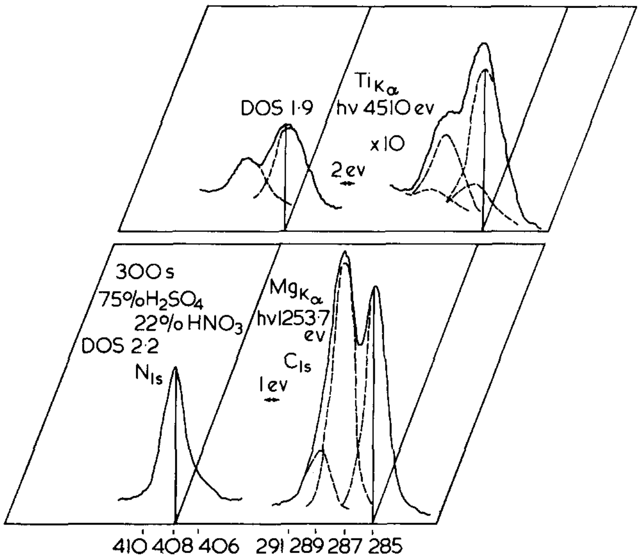


Figure 4 N_{1s} and C_{1s} spectra for nitrocellulose produced in mixed acid ($Mg_{K\alpha_{1,2}}$ and $Ti_{K\alpha_{1,2}}$ spectra)

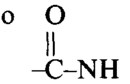
model systems unambiguously identifies this as originating from the nitrate ester groups $-O-NO_2$. In industrial scale nitrations a low binding energy component is often observed at ~406 eV and this is associated with nitrite ester groups. In the laboratory scale nitrations where conditions can perhaps be more precisely controlled such structural features are at a much lower level. Conventional nitrite traps (urea, ascorbic acid, etc.) dissolved in the nitrating mix to obviate the possibility of formation of nitrate esters does not seem to remove the very low levels of such structural features and it could be that they arise as a result of reactions occurring during stabilization and storage. The O_{1s} levels are an unresolved broad peak.

With a knowledge of sensitivity factors for the various core levels it is possible to work out the degree of substitution (D.O.S.) (average number of nitro-ester functionalities per glucose residue). Thus the integrated C_{1s}/N_{1s} area ratios (excluding the extraneous hydrocarbon component) yields a D.O.S. of 2.3 for the phosphoric/nitric nitrating mix identical with that determined from micro-Kjeldahl bulk analysis. The total C_{1s}/O_{1s} ratio indicates that there is little residual water in the nitrated sample.

With fibrillar samples such as linter papers any information on vertical inhomogeneities into the sample may only be inferred by looking at different levels corresponding to different escape depths. Clearly the good agreement between bulk and surface analyses suggests that the sample is uniformally nitrated and the extraneous hydrocarbon must therefore be localized at the surface perhaps in the form of a patched overlayer since in most cases there may well be significantly less than a monolayer present. One way of establishing the purely surface nature of this hydrocarbon (since the usual angular dependent studies are not feasible) is to compare D.O.S. averaged over different sampling depths. This can be achieved using the 'push button' dual anode facility of the E.S. 300 spectrometer which employs a standard $Mg_{K\alpha}$ X-ray source and a harder $Ti_{K\alpha}$ anode. Hence for $Mg_{K\alpha}$ the typical sampling depth will be say ~50 Å; for $Ti_{K\alpha}$ with photon energy 4510 eV a figure of ~150 Å would be more appropriate

Figure 4 shows N_{1s} and C_{1s} spectra for cellulose linters paper nitrated for 300 s in a low nitrating mix. Whereas the $Mg_{K\alpha}$ spectra for the C_{1s} levels show a significant contribution from the extraneous hydrocarbon the corresponding line shape analysis for the $Ti_{K\alpha}$ spectra is described with no contribution from hydrocarbon since even monolayer coverate (~5 Å) would contribute a negligible contribution to the C_{1s} levels for electrons having a mean free path at least an order of magnitude greater (~50 Å). This shows the great value of having a variable photon source routinely available.

The relative sensitivity of nitrocelluloses to photochemical decompositions is known and it is therefore necessary to investigate the sensitivity to interrogation by means of e.s.c.a. of nitrated and denitrated cellulose samples. It may readily be shown that on a typical time scale for the e.s.c.a. investigations photochemical degradation is negligible. At the typical dose rates involved (typical X-ray power ~150 watts) significant signs of decomposition require irradiation periods of > 2 h. The main reaction appears to be photoreduction. Thus the high binding energy component in the N_{1s} spectrum appropriate to $-O-NO_2$ structural features is accompanied in the case of material subjected to irradiation for extended periods by a small peak at low binding energy attributable to $\overset{\displaystyle O}{\overset{\|}{-C}}\text{-NH}$ functionality.



Even after 5 h irradiation however this component still only represents a small fraction of the total N_{1s} spectrum. We may conclude from this that X-ray degradation is negligible during the time scale of a typical e.s.c.a. investigation.

Detailed studies of nitration and denitration

For a nitrating mix of a given composition one of the most important features of interest is the question as to how rapidly an equilibrium D.O.S. is established in the surface regions accessible to e.s.c.a. As an example, *Figure 5* shows core level spectra for samples of the same batch of linters papers nitrated for differing periods in a nitrating mix consisting of 75% H_2SO_4: 22.2% HNO_3: 2.8% H_2O. The N_{1s} levels, which provide a ready means of following the nitration, remain constant in intensity from reaction times of 1 s to 1 h. This indicates that on the e.s.c.a. depth

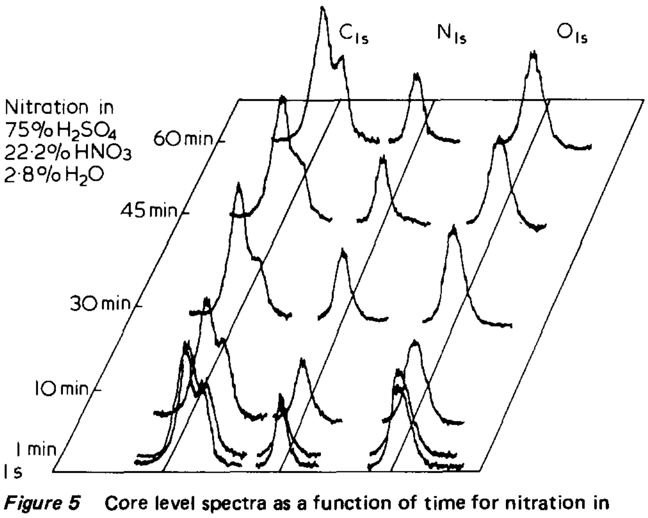


Figure 5 Core level spectra as a function of time for nitration in mixed acid

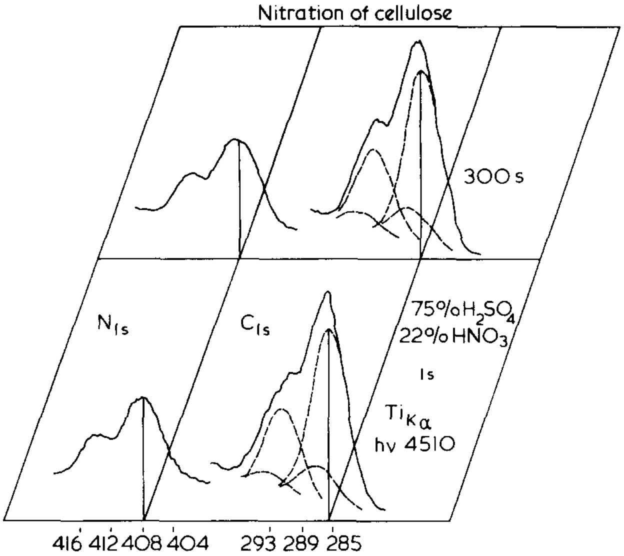


Figure 6 $Ti_{K\alpha}$ spectra for nitration of cellulose for 1 s and 300 s in mixed acid

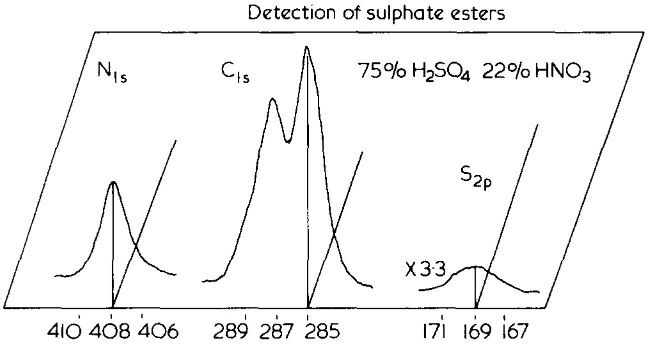


Figure 7 N_{1s}, C_{1s} and S_{2p} core level spectra for nitrated material

scale, equilibrium is very rapidly established. This is not entirely unexpected since the diffusion of nitrating mix into the outermost 50 Å or so of the cellulose fibrils is expected to occur rapidly. A similar comparison is shown in *Figure 6* for samples studied by means of the harder $Ti_{K\alpha}$ X-ray source. Here the sampling depth will be ~150 Å yet the spectra recorded after reaction times of 1 s and 300 s are closely similar. It is clear therefore that the equilibrium D.O.S. is rapidly established in the surface regions, during nitration in mixed acids. It is interesting to note that it has been proposed that the sulphuric acid component does not diffuse into the bulk[10,1] and this could obviously lead to differences in D.O.S. for the surface and bulk regions of samples since only in the surface regions is sulphonation competitive with nitration. An important question which e.s.c.a. is potentially capable of answering is whether sulphate esters may be detected in the surface regions of nitrated material.

$Mg_{K\alpha_{1,2}}$ spectra for the N_{1s}, S_{2p} and C_{1s} regions of cotton linters for nitrated material are shown in *Figure 7*. A low level S_{2p} signal is detected and the high binding energy of ~169 eV identifies this as arising from sulphate ester groups. It is clear therefore that sulphate esters are formed in the very surface regions. Comparable studies with the $Ti_{K\alpha}$ X-ray source with a larger sampling depth shows virtually no evidence for sulphate esters and e.s.c.a. therefore uniquely demonstrates the surface nature of such groups.

The final D.O.S. for a nitrocellulose, at least as far as the surface regions is concerned, depends on nitration, denitration, sulphonation equilibria. The fact that the D.O.S. is rapidly established suggests that denitration is competitive with nitration whilst the fact that even in high sulphuric mixes the D.O.S. is still appreciable illustrates that nitrate ester formation is more facile than sulphate ester formation. The rapidity with which denitration–nitration equilibria are established in the surface regions is nicely illustrated by the data displayed in *Figure 8*. Thus for starting material, D.O.S. 2.7 denitration of the outermost few tens of Angstroms is rapid and dependent on acid mix. In 79.1% HNO_3 denitration in 1 s is to D.O.S. 2.3 since this mix is close to the minimum necessary for nitration to be effected (77.8% HNO_3 corresponds to the mono-hydrate) whilst for 84.4% HNO_3 denitration is to a D.O.S. of 2.5 on a 1 s time scale. Corresponding spectra with a $Ti_{K\alpha}$ X-ray source indicates that the degree of denitration is slightly lower than for $Mg_{K\alpha}$ X-ray source.

The extreme sensitivity of e.s.c.a. in the detection of the initial stages of reactions is nicely displayed by the comparative data given in *Figure 9*. This shows the nitration and denitration of cellulosic samples. The

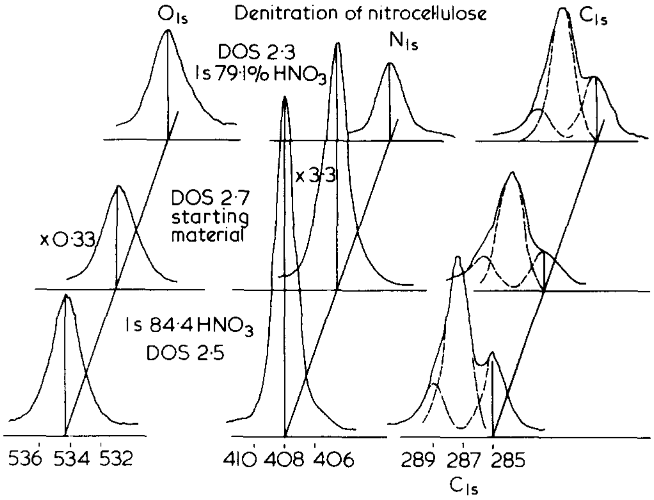


Figure 8 Denitration of nitrocellulose D.O.S. 2.7 as a function of denitrating mix ($Mg_{K\alpha_{1,2}}$)

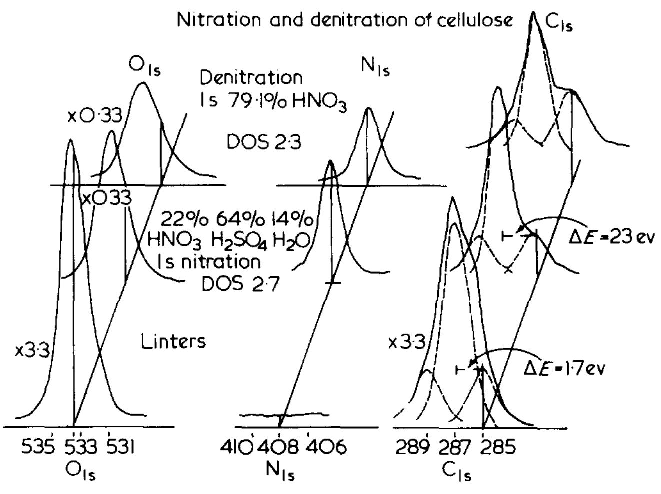


Figure 9 Comparison of surface nitration and denitration of cellulose

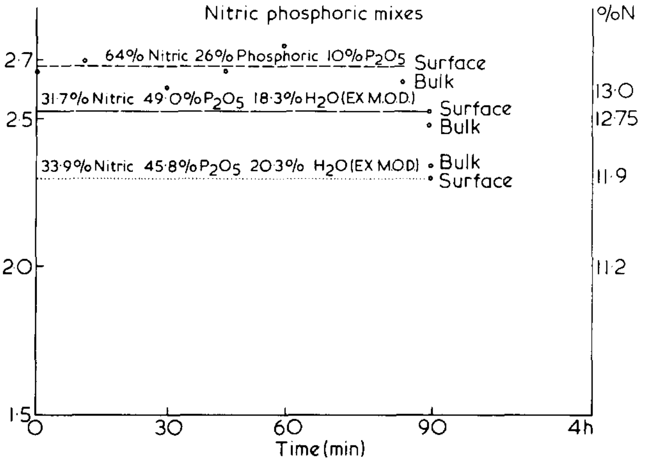


Figure 10 Comparison of surface and bulk D.O.S. as a function of time for the nitration of cellulose in nitric phosphoric acid mixes

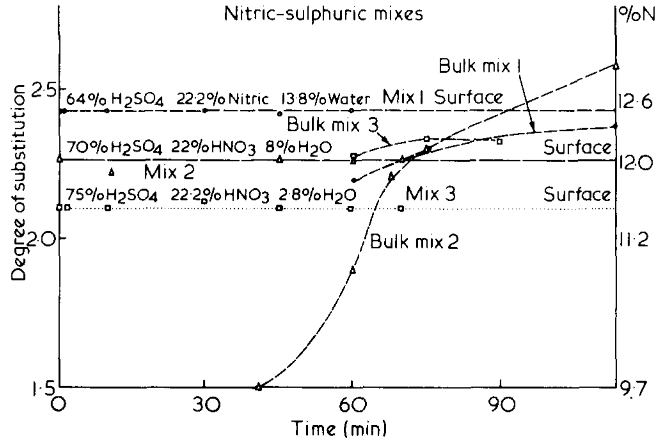


Figure 11 Comparison of surface and bulk D.O.S. as a function of time for the nitration of cellulose in nitric-sulphuric acid mixes

substantial secondary shift of the nitrate ester group is shown by the shift to high binding energy compared with the extraneous hydrocarbon peak (ΔE 2.3 eV for the $\underset{\sim}{C}$–O–NO_2 component compared with ΔE 1.7 eV for cellulose itself). The e.s.c.a. data presented, thus far therefore establishes that nitration–denitration–sulphonation equilibria are rapidly established in the surface regions.

Systematic studies have been made of nitrations in both nitric–phosphoric and nitric–sulphuric mixes, both from a surface and bulk point of view. For nitric phosphoric mixes the D.O.S. depends on the composition and there is little evidence for formation of phosphate esters. The D.O.S. in the surface region therefore represents the equilibrium between nitration and denitration. Since equilibration in the bulk requires diffusion of reagents then naturally establishment of this equilibrium occurs on a longer time scale than for the surface. The important feature however is that the D.O.S. obtained from bulk analyses is essentially the same as for the surface regions (*Figure 10*). The situation with regard to nitrations in mixed acid is considerably more complex and representative data for bulk and surface nitrations in mixed acid are given in *Figure 11*.

Considering firstly the data for the 64% sulphuric mix the surface D.O.S. as assessed by e.s.c.a. utilizing a $Mg_{K\alpha}$ source is essentially established after 1 s exposure and remains constant thereafter. The diffusion of nitrating mix into the bulk leads to a time dependent D.O.S. which tends to approach that of the surface. As the sulphuric content is increased and water content decreased the surface D.O.S. decreases. In terms of competitive equilibria we might anticipate that as the sulphuric content increases the formation of sulphate esters becomes relatively more favoured. The suggestion has been made that in mixed acid nitrations the sulphuric acid does not penetrate the bulk[5] and on this basis we might anticipate significant differences in surface and bulk chemistries irrespective of time scale. E.s.c.a. has demonstrated this in detail for the first time. Thus for both the 70% and the 75% sulphuric mixes the D.O.S. of the surface is actually lower than for the bulk and work recently completed has shown that with a $Ti_{K\alpha}$ X-ray source the D.O.S. is also close to that for the bulk.

CONCLUSION

E.s.c.a. provides a new dimension to this complex problem of the nitration–denitration of cellulose materials and the work described here provides a strong basis for the study of the even more complex systems represented by double and triple based propellant formulations.

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