The surface chemistry of double based (nitrocellulose-nitroglycerin) propellants as revealed by e.s.c.a.

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Introduction

Many of the important properties of double based propellants formulated from nitrocelluloses and nitroglycerin depend to a greater or lesser extent on the surface chemistry in the outermost few tens of angstroms[1]. Since it is the surface of a material which communicates with the outside world the question of initial burn rate and of environmental stability for example both represent questions of some technical, scientific and commercial importance[1]. Despite this importance of surface properties the fact remains that little is known of the surface chemistry of double based propellants and this contrasts with extensive studies of bulk properties[2].

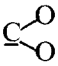
In a recent series of papers[3] we have shown how e.s.c.a. provides a powerful tool for investigating the complex nature of the surface chemistry of the nitration and denitration of nitrocelluloses and in this paper we address the problem of the surface chemistry of a series of double based propellants. Such studies are an important prerequisite to the understanding of weathering phenomena in such materials which forms part of our current research programme in this area.

Experimental

The double based propellants examined in this work were supplied by the Ministry of Defence, Waltham Abbey, in various wt/% ratios of NG/NC.* Approximately 1% by weight of diethyldiphenyl urea stabilizer was incorporated in all samples. The propellants in sheet form (~ 3 mm in thickness) were cut to probe tip size (18 x 8 mm), and mounted on a special cooling probe, the temperature of which can be accurately controlled by pumping liquid nitrogen to the probe tip. Samples considered in this work were pre-cooled to ~ −110°C in a dry nitrogen atmosphere by the use of a glove bag attached directly to the insertion lock of the spectrometer. This procedure precludes the deposition of water vapour onto the propellant surface. The samples were then pumped down in the insertion lock ($\approx 10^{-3}$ torr) before introduction to the sample chamber ($\approx 5 \times 10^{-8}$ torr). It was found that the pressure of the chamber was maintained during this procedure and there was no evidence for loss of NG from the surface under normal operating conditions (viz. the spectra were independent of time on the typical time scale of the measurements). However it should be noted that it is possible to instigate a steady loss of NG to the chamber by increasing the temperature of the probe tip (cf. Results section). The spectra were run on an AEI E.S. 200A/B electron spectrometer using a $MgK\alpha_{1,2}$ X-ray source operated in the fixed retardation ratio mode. Under the conditions of these experiments the $Au_{4f_{7/2}}$ level used for energy calibration had a fwhm of 1.15 eV.

Spectra were analysed using a DuPont 310 curve resolver.

Results and discussion

Detailed e.s.c.a. investigations have previously been presented for both simple model systems and for nitrated and denitrated cellulosic materials[3,4]. To put the discussion which follows in perspective it is important to briefly consider the main points arising from these investigations. The cotton linters which have been employed in these studies have been subjected to standard dewaxing, depectinization and Kiering processes[5]. The C_{1s} core level spectra for samples of this material show two main components in the C_{1s} spectrum at 288.0 eV and 286.5 ev in the intensity ratio of 1:5 corresponding to , and $\underline{C}$–O structural features for each *βD* glucopyranose residue. An additional component at 285 eV is also evident and the intensity varies depending on the source of the linters. That this component is not associated with hydrocarbon contamination arising during the e.s.c.a. experiment is readily demonstrated both by the variability in intensity of the 285 eV component with the source of linters and the absence of any time dependence of the C_{1s} spectra. Indeed detailed studies have been made of the core level spectra for nitrocelluloses as a function of X-ray irradiation time to demonstrate that on the time scale involved no degradation occurs. With a fibrous sample it is not routinely possible to perform angular dependent measurements at a fixed photo-emission energy to investigate the nature of the 285 eV component. With a dual X-ray source however it is possible to show that this extraneous component present in all celluloses (both nitrated and un-nitrated) is in the form of a patched overlayer. Thus whereas with a photon energy of 1253.7 eV ($MgK\alpha_{1,2}$) the 285 eV component is readily detected; with $TiK\alpha_{1,2}$ (hν 4510 eV) this component contributes so little to the overall line shape that it is not detected. The difference in mean free paths for photo-emission from the C_{1s} levels (~15Å for $MgK\alpha_{1,2}$ and ~90Å for $TiK\alpha_{1,2}$) therefore reveals the surface nature of the impurity and indeed microanalysis provides confirmatory evidence. The analysis of the core levels to obtain stoichiometries is straightforward once account has been taken of this extraneous component which remains even after the extensive pre-treatment which the fibres receive.

In the particular case of the double based propellants the surface chemistry could conceivably involve not only

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* The propellants were fabricated as rolled sheets and were prepared using 12.2% N nitrocellulose obtained from the nitration of wood cellulose

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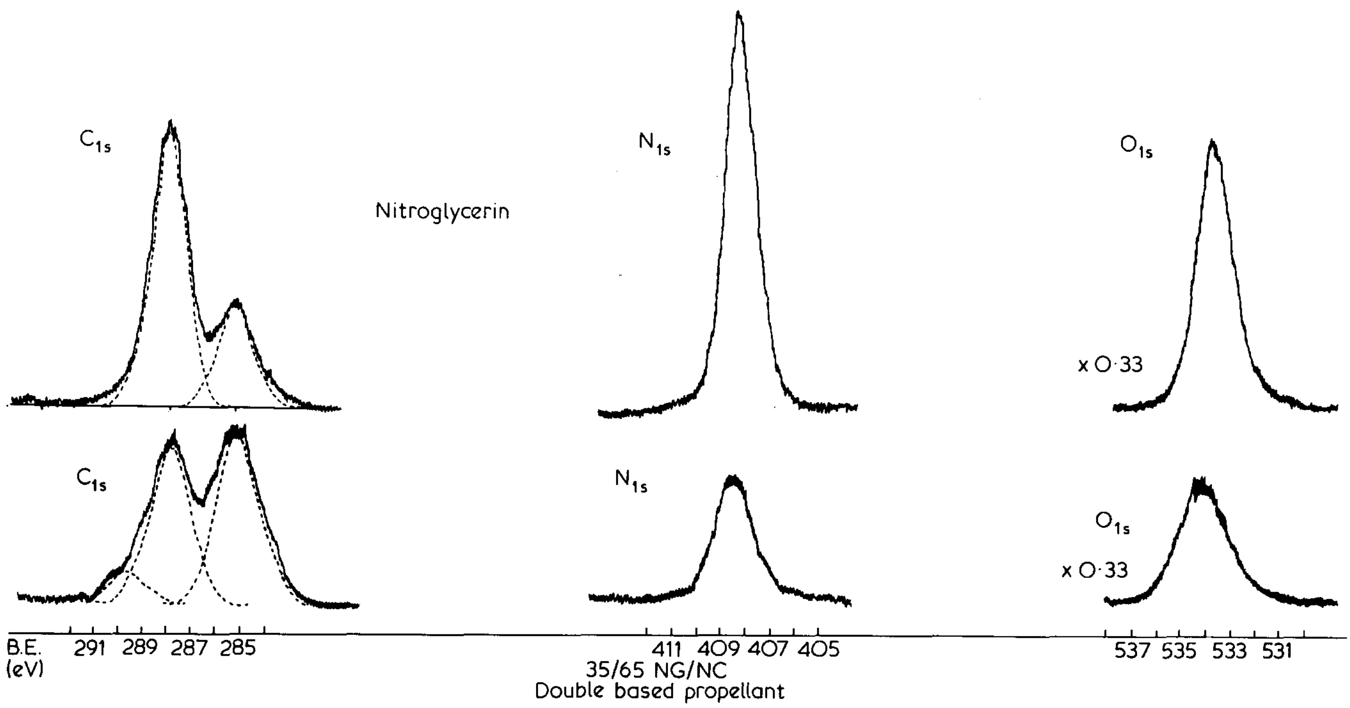

Figure 1 Core level spectra of Nitroglycerin (NG) and 35/65 NG/NC double based propellant. The NG spectra were obtained by the overlayer technique described in the text, the low binding energy component arises from the NC substrate and from DEDPU

the nitrocellulose (NC) and nitroglycerin (NG) components but also the stabilizing component diethyldiphenyl urea which although only present at low levels could conceivably segregate at the surface. The surface composition is therefore defined in terms of two parameters representing the relative proportions of the three components. The C_{1s}/O_{1s} and C_{1s}/N_{1s} intensity ratios provide the two measurable parameters which allow the surface composition to be determined.

Before considering the data for the double based propellants it is of interest to note the e.s.c.a. spectrum of NG itself since this has not previously been reported. The sensitivity to detonation of NG implies that especial caution is necessary in measuring the core level spectra. To this end a cooled sample (cf. Section 2) of the 60/40 NG/NC material was slowly allowed to warm whilst the sample was maintained in high vacuum ($\sim 5 \times 10^{-8}$) in the spectrometer chamber. By monitoring the pressure in the chamber it was found possible to determine when appreciable amounts of NG started to desorb from the surface. By re-cooling the samples to $-110°C$ at this stage it has proven possible to obtain the C_{1s}, O_{1s} and N_{1s} levels of an NG overlayer on NC and the spectra are shown in *Figure 1*. For comparison purposes we also include core level spectra for the 35/65 formulation and distinctive differences in intensity ratio and in the binding energies of the components of the C_{1s} levels are readily apparent.

The surface compositions of the four double based propellant systems studied in this work are shown in *Table 1* where comparison is drawn with the bulk compositions. It is clear from this that there is a close correspondence between the surface and bulk chemistries and this is best illustrated by means of the comparison drawn in *Figure 2*. Several distinctive features are of note. Firstly the correspondence between surface and bulk composition is closest for the two samples which are close to 50 mol% in the two major components. For the samples with a low bulk composition in NG there is a tendency for the surface to be somewhat lower in this component than for the bulk.

Table 1 Surface compositions of double based propellant systems

Wt./% NG/NC Ratio		Mol %		
		NG	NC	DEDPU
35/65	Calculated	38	62	
	e.s.c.a.	31±1	68±1	1.0±0.2
40/60	Calculated	45	55	
	e.s.c.a.	49±1	49±1	2.0±0.2
50/50	Calculated	54	46	
	e.s.c.a.	53±1	46±1	1.0±0.2
60/40	Calculated	63	37	
	e.s.c.a.	82^{+0}_{-1}	5^{+0}_{-2}	13.0±1

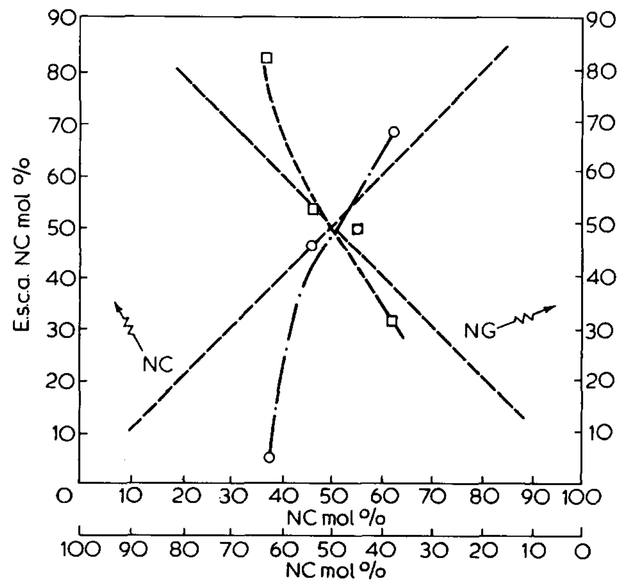

Figure 2 Graph of Bulk mol % of NC/NG in double based propellants *versus* mol % NC/NG determined by e.s.c.a. (The broken curves link the NC(○) and NG(□) data points whilst the dotted lines represent the correlations expected if surface and bulk compositions were identical)

By contrast for the sample with a larger composition in NG there is a tendency for the surface to become comparatively enriched in this component and this is accompanied by significant surface segregation of the stabilizer. This surface segregation may be directly confirmed by analyzing the low binding energy region of the N_{1s} levels. The main component of the N_{1s} spectrum originating from the nitrate ester groups centred at $\sim$408.3 eV unfortunately provides obscuring $K\alpha_{3,4}$ satellites in the region $\sim$400 eV appropriate to urea type nitrogen. In the case of the samples for which the DEDPU is computed to be at the 1–2% level the satellite intensity from the main component does not allow a statistically significant subtraction to be made and it is clear that the level of DEDPU in such materials is extremely low. In the 60/40 NG/NC material however the intensity of the peak at low binding energy is substantially larger than would be expected for a $K\alpha_{3,4}$ satellite and subtraction of the expected intensity, (14% of the main nitrate ester peak)[6] provides a value of 10 mol % of DEDPU in the surface regions in close agreement with the analysis based on the integrated intensities as set out above.

The e.s.c.a. data clearly adds a new dimension to current knowledge of the surface chemistry of double based propellants and the information will undoubtedly be of considerable importance in understanding many of the properties which depend on surface composition.

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A double helical model for some alkali metal ion-poly(ethylene oxide) complexes

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Introduction

The crystalline complexes of poly(ethylene oxide) (PEO) with potassium, sodium and lithium ions so far reported all have stoichiometries of 1 mol of cation to four mols of ethylene oxide (EO) unit. They are the open chain analogues of the 'crown-ether' complexes and such complexes are characterized by interactions between the cation and lone pairs of electrons from adjacent oxygen atoms brought about by a *gauche* rotation of the intervening C–C bond. Although single strand helical arrangements have been proposed[1,2], recent investigations[3,4] of the morphology and conductivity of some sodium ion and lithium ion complexes have led us to conclude that the physical properties are best described by a double strand helical arrangement of the PEO chains. In this communication we present some crystallographic data on KSCN and NaSCN complexes to support this proposal.

Experimental

X-ray fibre photographs of oriented fibres drawn from concentrated methanolic solutions were taken on a Pye-Unicam oscillation camera with the fibre stationary and using CuKα radiation[5]. Exposure times of 24 h were used but only relatively few low angle reflections were observed. Using a trial and error procedure to index the reflections the real space cell dimensions were determined to be:

For KSCN-PEO $a=11.37$ Å $b=8.18$ Å $c=8.10$ Å

$\alpha=80.3°$ $\beta=65.7°$ $\gamma=88.6°$

cell volume $=676$ Å^3

For NaSCN-PEO $a=10.25$ Å $b=8.43$ Å $c=7.23$ Å

$\alpha=91.2°$ $\beta=61.2°$ $\gamma=103.7°$

cell volume $=529$ Å.

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