X-Ray Photoelectron Spectroscopic Evidence for Novel Surface Nitrogen Species in Irradiated $NaNO_3$

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Summary Irradiation of $NaNO_3$ *in situ* at low temperatures produces NO_2^-, N^{3-}, two other thermally unstable intermediates, tentatively assigned as NO^- and N^-, and gaseous N_2, O_2, and NO

Despite the many published studies[1] on the radiolysis of the alkali metal nitrates, when the final products have been found to be NO_2^- and O_2(g), the detailed decomposition mechanism for any one salt is still not clearly understood,[2] partly owing to the problems[3] inherent in the bulk chemical analyses of irradiated solids A promising new approach has been to apply certain important advantages of *X*-ray photoelectron spectroscopy (*X*-p e s) to the study of radiation damage at the surfaces of ionic solids [4,5] Prompted by some recently published *X*-p e s work[6] on electron-irradiated $LiNO_3$, I now report preliminary results on the low-temperature photo-induced decomposition of $NaNO_3$, where evidence for an initial mechanism substantially different from that currently accepted for the bulk decomposition has emerged, involving some novel surface nitrogen-containing species

Sodium nitrate samples (AnalaR grade) were examined as thin films, deposited from ethanol solution on to gold plates, in a Kratos ES200B photoelectron spectrometer Unmonochromatised Al-K_α radiation was used, both to induce the radiation damage and to excite the photoelectron spectra Sample temperatures were controlled with a liquid nitrogen feed coupled with resistive heating, and the gaseous composition of the sample chamber was monitored with a Vacuum Generators' Q8 quadrupole mass spectrometer Samples were annealed at 433 K for at least 16 h at a base pressure of 5×10^{-9} Torr prior to the experiments $Na^{15}NO_3$ (enriched to 99 1 atom % in ^{15}N) was also examined.

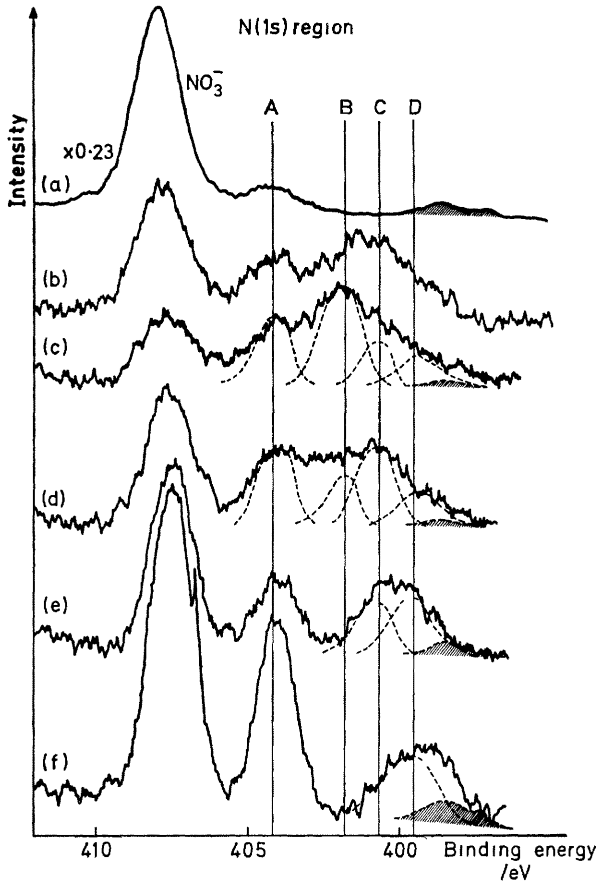

FIGURE N(1s) region of the X-p e s spectrum of a sample of $NaNO_3$ (a) 263 K, after 25 min irradiation [Al-$K\alpha$, 1487 eV], (b) after cooling to 123 K and then irradiating for a further 153 min (c) further 215 min irradiation at 123 K, (d) immediately after warming to 273 K, (e) immediately after warming to 329 K, (f) after heating at 433 K for 30 min The hatched areas correspond to $\alpha_{3,4}$ satellites

In contrast with irradiations at room temperature[6] or 203 K[7], where the N(1s) region of the photoelectron spectrum shows the growth of only one new peak at 3·7 eV higher kinetic energy with radiation dose (assigned[8] to NO_2^-), irradiation at 123 K produces a much more complex N(1s) photoelectron spectrum (see Figure) The most plausible curve-fitting indicates that no fewer than *four* reduction products are present on the sodium nitrate surface, the strong positive correlation invariably observed between N(1s) binding energy and (formal) oxidation number[8] for many compounds of nitrogen leads to the assignment of species A and D to NO_2^- (nitrite) and N^{3-} (nitride) respectively Using this simple method of interpolation it is difficult to avoid the conclusion that B corresponds to NO^- and C to N^- Support for the assignment of these unusual and highly reactive species comes from the warming-up experiments [scans (d)→(f)], and from mass spectrometric evidence for the evolution of O_2 (*m/e* 16, 32) $*N_2$ (*m/e* = 15, 30), and *NO (*m/e* 31) during irradiation of $Na^{15}NO_3$ The loss of surface nitrogen during irradiation is evident from the reduction in total integrated intensities in scans (a)→(c) The possibility of differential surface charging during the X-p e s measurements leading to peaks B and C is discounted because of the stability of these peaks at low temperature in the absence of radiation

It is conceivable that peaks B or C might correspond to adsorbed molecular products such as NH_3 (by reaction of N^{3-} with traces of H_2O), in fact NH_3(g) was detected by mass spectroscopy However, recooling an irradiated sample containing a high concentration of surface nitride [*e g* as in the scan (f)] did not produce any new N(1s) feature On balance, the most likely assignment for species B and C remains NO^- and N^- respectively, and these intermediates could only be observed after prolonged annealing at 433 K prior to irradiation, it appears that adsorbed H_2O acts as an efficient scavenger for these species The N(1s) chemical shift of *ca* 1 eV observed between NO^- and N^- is much smaller than the shift of *ca* 6 eV, previously measured between $N^{\delta-}$(ads) and $NO^{\delta-}$(ads) from studies[9] of the interaction of nitric oxide with aluminium surfaces The electronic structures of these two substrates are vastly different however, and polarisation and relaxation effects must be taken into account

It seems clear that apart from the primary radiolysis step (1), previously observed in the NO_3^- system, further decomposition occurs in the initial stages at the surface of $NaNO_3$, probably due to collisional abstraction by oxygen atoms, *e g* steps (1)—(9) Steps (6), (7), and (9) appear to form the

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O \qquad (1)$$

$$O + NO_2^- \rightarrow NO^- + O_2\uparrow \qquad (2)$$

$$O + NO^- \rightarrow N^- + O_2\uparrow \qquad (3)$$

$$2e + N^- \rightarrow N^{3-} \qquad (4)$$

$$N^- + N^- \rightarrow N_2\uparrow + 2e \qquad (5)$$

$$NO^- \rightarrow N + O^- \qquad (6)$$

$$N + N \rightarrow N_2 \qquad (7)$$

$$O^- + O \rightarrow O_2^- \qquad (8)$$

$$NO^- \rightarrow NO\uparrow + e \qquad (9)$$

most feasible route to the production of molecular nitrogen, and nitric oxide, though (3) and (5) cannot be ruled out entirely at this stage

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