Photoinduced Decomposition of Sodium Perchlorate and Sodium Chlorate when studied by *X*-Ray Photoelectron Spectroscopy

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The kinetics of the photoinduced decomposition of solid Na[ClO_4] and Na[ClO_3] have been derived from *X*-ray photoelectron spectroscopic data. Sodium perchlorate is shown to undergo reduction to the chloride *via* sodium chlorate in a consecutive first-order process, and evidence for a defect surface NaCl phase is presented.

THE application of *X*-ray photoelectron (*X*-p.e.) spectroscopy to the study of photoinduced effects on solid surfaces promises to be a fruitful area of research. Most work on radiation damage has been concerned with the interactions of high-energy photons, charged particles (*ca.* 1 MeV),† and neutrons with matter, leading to the production of gross defects in lattices.[1] The relatively low energy of the exciting radiation commonly employed in *X*-p.e. spectroscopy (*ca.* 1.5 keV) leads to more subtle interactions at the solid surface, which are readily amenable to investigation by the *X*-p.e. technique. Due to the chemical shift in core-electron levels,[2] both products and intermediates of a photoinduced reaction can, in principle, be quantitatively determined, and the surface sensitivity [3] of the method ensures that the outermost 50—100 Å of the solid are examined. Some further advantages of this technique include the small amount of sample required (*ca.* 1 mg), the maintenance of controlled conditions during the *X*-p.e. experiment (*ca.* 10^{-8} Torr vacuum), and the ease of accumulation of kinetic data without the necessity of perturbing the sample.

A few reports on photoinduced effects during *X*-p.e. investigations have appeared,[4-7] concerned with metal compounds where reduction to a lower valency state invariably occurred. Only one other kinetic analysis of *X*-ray-induced decomposition during an *X*-p.e. study has been reported,[8] which involved the conversion of some platinum(IV) complexes to Pt^{II} in a first-order process where the precise natures of the reduction products were not ascertained.

We have selected the Na[ClO_4] system for study because the photoinduced product (Cl^-) and an intermediate ([ClO_3]$^-$) are readily identified by the chemical shift of the Cl(2*p*) electron level.[9] Furthermore, detailed structural information from *X*-ray diffraction data is available for all the three compounds.[10-12] We have also applied a variety of data-processing techniques [13-15] in order to ensure maximum consistency in the kinetic analysis. The valence-band regions of the *X*-p.e. spectra of the perchlorate and chlorate of lithium have previously been reported [16-18] in molecular-orbital (m.o.) studies of a series of oxo-anions. In only one [18] of these papers is the occurrence of photodecomposition in the perchlorate system mentioned, as this leads to significant changes in the valence-band p.e. spectrum; complementary measurements in the Cl(2*p*) region were not reported.

EXPERIMENTAL

Materials and Instrumental.—Anhydrous sodium perchlorate and sodium chlorate (analytical grade) were finely ground in an agate pestel and mortar, lightly brushed on to double-sided sticky tape, and mounted on a copper sample block. The compounds were investigated in an A.E.I. ES200B p.e. spectrometer with a base pressure of 1.8×10^{-8} Torr using Al-K_α radiation (1 487 eV) at constant *X*-ray power (255 W). The Cl(2*p*) and O(1*s*) p.e. peaks were monitored as a function of time of exposure to the *X*-ray beam. Independent checks showed that no significant changes occurred in the p.e. spectrum with the *X*-ray beam switched off, or with only the *X*-ray gun filament on (no high voltage applied). A MAT AMP 3 quadrupole mass analyser, connected directly to the source chamber, was used to monitor the residual atmosphere and the pressure was measured with a cold-cathode Penning gauge situated *ca.* 10 cm from the sample. Variable-temperature studies in the range 120—300 K were undertaken using a liquid-nitrogen feed-through. Chemical shifts were measured with respect to both the C(1*s*) and Na(2*s*) levels, with good agreement. As the origin and chemical nature of the carbon signal present in all the samples could not be precisely ascertained, the relative binding energies of the chlorine-containing species were calculated with respect to the Na(2*s*) level. It was found that a mixture of Na[ClO_4],

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 Torr = (101 325/760) Pa; 1 cal = 4.184 J.

[1] D. S. Billington and J. H. Crawford, ' Radiation Damage in Solids,' Princeton University Press, Princeton, New Jersey, U.S.A., 1961.

[2] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsaliensis*, 1967, **20**, ser. 4.

[3] I. Lindau and W. E. Spicer, *J. Electron Spectroscopy*, 1974, **3**, 409.

[4] D. A. Wiegand and J. Sharma, *Bull. Amer. Phys. Soc.*, 1974, **19**, 283.

[5] D. C. Frost, A. Ishanti, and C. A. McDowell, *Mol. Phys.*, 1972, **24**, 861.

[6] D. C. Frost, C. A. McDowell, and I. S. Woolsey, *Mol. Phys.*, 1974, **27**, 1473.

[7] P. Burroughs, A. Hamnett, and A. F. Orchard, *J.C.S. Dalton*, 1974, 565.

[8] P. Burroughs, A. Hamnett, J. F. McGilp, and A. F. Orchard, *J.C.S. Faraday II*, 1975, 177.

[9] A. Fahlman, R. Carlsson, and K. Siegbahn, *Arkiv. Kemi*, 1966, **25** (28), 301.

[10] NaCl, W. L. Bragg, *Proc. Roy. Soc.*, 1913, **A89**, 248.

[11] $NaClO_3$, C. Aravindakshan, *Z. Krist.*, 1959, **111**, 241.

[12] $NaClO_4$, W. H. Zachariasen, *Z. Krist.*, 1930, **73**, 141.

[13] R. R. Ernst, *Adv. Magn. Resonance*, 1966, **2**, 1.

[14] J. J. Pireaux, *Appl. Spectroscopy*, 1976, **30**, 219.

[15] S. M. Roberts, D. H. Wilkinson, and L. R. Walker, *Analyt. Chem.*, 1970, **42**, 886.

[16] R. Prins and T. Novakov, *Chem. Phys. Letters*, 1971, **9**, 593.

[17] J. A. Conner, I. H. Hillier, V. R. Saunders, and M. Barber, *Mol. Phys.*, 1972, **23**, 81.

[18] R. Prins, *J. Chem. Phys.*, 1974, **61**, 2580.

Na[ClO$_3$], and NaCl gave a symmetrical Na(2*s*) line of full width at half-maximum (f.w.h.m.) *ca.* 2.5 eV and could be accurately described by a single Gaussian peak. The C(1*s*) level was of the same width and it was therefore assumed that the Na(2*s*) levels for all the three compounds are identical. A narrower f.w.h.m. of 1.9 eV was observed for both the Na(2*s*) and C(1*s*) levels in the irradiation experiments, and a consistent shift to higher kinetic energies of all the core levels was detected as the decomposition progressed.

Data Analysis.—As a preliminary study the characteristics of the Cl(2*p*) levels, arising from the three salts Na[ClO$_4$], Na[ClO$_3$], and NaCl, were investigated. Fourier-transform resolution enhancement was used to separate the $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ components by transforming the known Lorenzian *X*-ray width to a Gaussian of smaller f.w.h.m.[13]

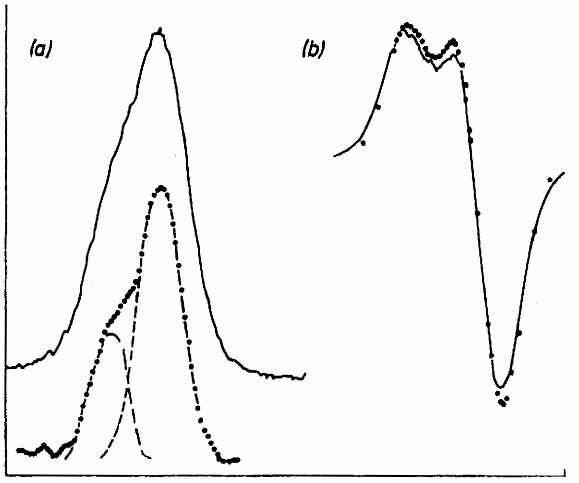

FIGURE 1 (*a*) Fourier-transform resolution enhancement of the Cl(2*p*) level in NaCl. (*b*) First derivative of experimental curve (*a*) (solid line), compared with the theoretical derivative of a Gaussian doublet

Relatively low signal-to-noise ratios prohibited complete separation in this case, however; as can be seen in Figure 1, the broad asymmetric singlet for NaCl is resolved into a shape much closer to the expected 1 : 2 doublet. Analyses of these spectra gave a $2p_{\frac{1}{2}}$–$2p_{\frac{3}{2}}$ separation of 1.60 ± 0.2 eV and a f.w.h.m. for each component of 1.90 ± 0.2 eV. This was confirmed by calculating the first-derivative spectrum, also shown in Figure 1, and comparing it with the theoretical curve.[14] All the three salts gave the same results, and good fits to the data were obtained by assuming that the pure spectra could be represented as two overlapping Gaussian peaks. The Cl(2*p*) levels from [ClO$_4$]$^-$ and [ClO$_3$]$^-$ are close in binding energy, resulting in considerable overlap (see Figure 2). Resolution enhancement, using the Fourier-transform method, indicated that the main components of each doublet are *ca.* 2 eV apart. Since all the positional and width parameters can be taken as fixed, it was only necessary to determine the relative heights of each component and to use these as quantitative measures for the kinetic analysis. As a check on this procedure a non-linear least-squares fit,[15] allowing all the parameters to vary, was carried out on an intermediate spectrum where an appreciable degree of reduction had occurred. The relative areas obtained by this method were in good agreement with the height measurement, but did not reproduce the expected 1 : 2 intensity ratios for the $2p_{\frac{1}{2}}, 2p_{\frac{3}{2}}$ spin-orbit doublet. This was thought to be due to the systematic reduction in the observed signal-to-noise ratio as the decomposition progressed. A correction was also made for the $\alpha_{3,4}$ satellites occurring in the Cl$^-$ region of the Cl(2*p*) spectrum by subtracting 8% of the observed Cl(2*p*) intensity arising from [ClO$_4$]$^-$. The O(1*s*) signal (see Figure 2) was found to be a broad singlet (f.w.h.m. 2.2 eV, kinetic energy 941.8 eV) with a smaller broader peak (f.w.h.m. *ca.* 3.5 eV, kinetic energy 939.0 eV) which, since it remained at constant absolute intensity throughout the irradiation period, was attributed to adsorbed molecular oxygen. The chemical shift of the main O(1*s*) peak between [ClO$_3$]$^-$ and [ClO$_4$]$^-$ was too small to be measured (<0.3 eV). Numerical integration, after correction for the tail of the smaller peak and inelastic scattering, was used to determine the peak areas for the kinetic analysis, where, in contrast to the Cl(2*p*) data, the measured areas referred to both [ClO$_4$]$^-$ and [ClO$_3$]$^-$.

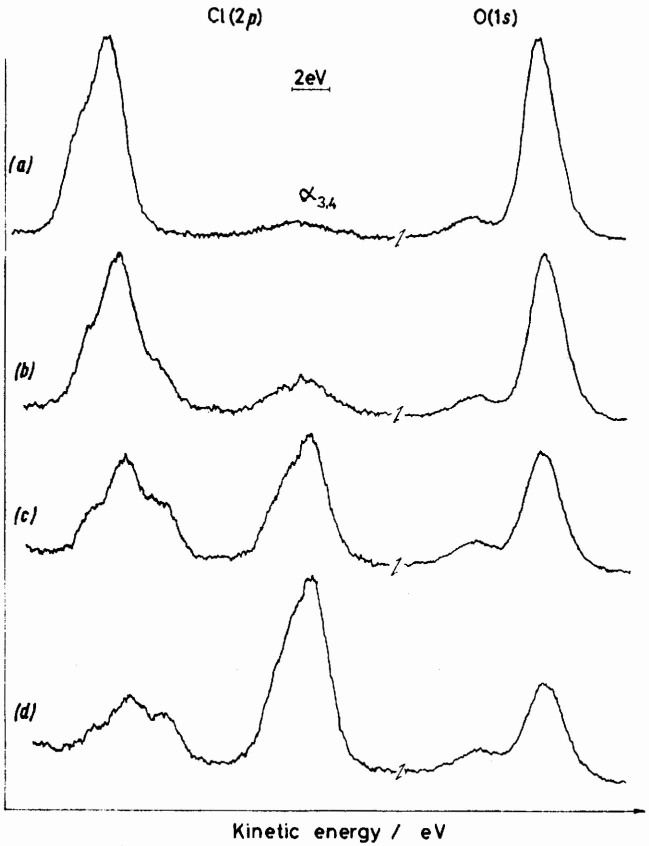

FIGURE 2 Photoelectron spectra in the Cl(2*p*) and O(1*s*) regions after exposure to 1 487-eV *X*-radiation at −20 °C for (*a*) 10, (*b*) 150, (*c*) 403, and (*d*) 705 min

RESULTS AND DISCUSSION

Typical p.e. spectra in the Cl(2*p*) and O(1*s*) regions, showing their dependence on the time of exposure to the *X*-ray beam, are shown in Figure 2. The assignment of the various chlorine-containing species was taken from the work of Fahlman *et al.*[9] and confirmed in a separate experiment on a mixture of Na[ClO$_4$], Na[ClO$_3$], and NaCl (Table 1 and Figure 3). Results were obtained for the photoinduced decomposition of *both* [ClO$_4$]$^-$ and [ClO$_3$]$^-$ species, as starting materials, in order to clarify the interpretation given later.

In Figure 4 an example is given of the first-order behaviour obtained for p.e. peak areas of Na[ClO$_4$] as a function of X-ray exposure time. Quantitatively similar results were obtained for Na[ClO$_3$], and in Table 2 the extracted kinetic data are summarised. All the results reported here were obtained at -20 °C; however, studies at significantly higher and lower temperatures gave only a random scatter with no evidence of any temperature dependence of the Arrhenius type. We may therefore conclude, at this stage, that both the starting material and the intermediate undergo, in isolation, first-order photoinduced decomposition with negligible activation energy (in contrast to studies on the thermal decomposition of Na[ClO$_4$] in fused Na[OH],[19] where activation energies of *ca.* 50 kcal mol^{-1} were obtained in a similar consecutive first-order process).

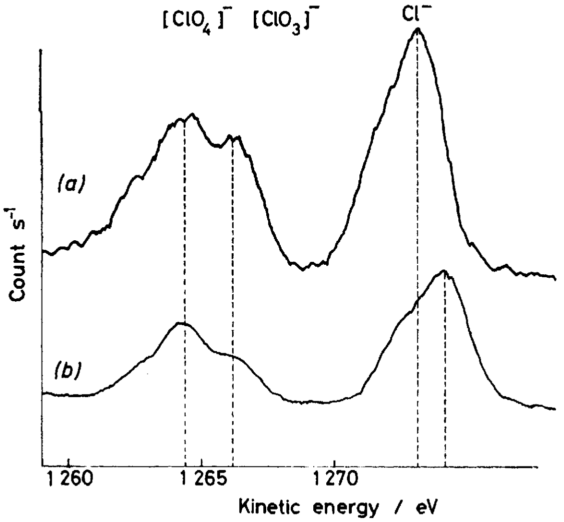

FIGURE 3 Chlorine($2p$) p.e. spectra for (*a*) a Na[ClO$_4$]–Na[ClO$_3$]–NaCl mixture, (*b*) Na[ClO$_4$] after 500-min irradiation

TABLE 1

Chlorine($2p$) binding energies and chemical shifts (in eV) with respect to the Na($2s$) level. Values are accurate, unless shown, to ± 0.1 eV. The chemical shifts for the irradiated samples were averaged over several irradiation times, while the typical relative binding energy is for an irradiation time of 500 min

	1 : 1 : 1 Mixture		Averaged results on irradiation of Na[ClO$_4$]		
Compound	E_b (relative)	Chemical shift	E_b (relative)	Chemical shift	Relative shift from ref. 9
Na[ClO$_4$]	144.4	0	144.6	0	0
Na[ClO$_3$]	142.2	2.2	142.8	2.0 ± 0.2	2.3
NaCl	135.8	8.6	134.8	10.0 ± 0.2	9.2

If we now suppose that the process $[ClO_4]^- \xrightarrow{k_1} [ClO_3]^- \xrightarrow{k_2} Cl^-$ is a consecutive first-order one, then an estimate of k_2 can be obtained from equation (1),[20] where $t_{max.}$ is the time at which the intermediate concentration

$$t_{max.} = \frac{1}{k_2 - k_1} \ln (k_2/k_1) \qquad (1)$$

is a maximum. From the experimental data for the Cl($2p$) levels and the value derived for k_1, k_2 was estimated to be 3.2×10^{-3} min^{-1}; as shown in Figure 5, this value provides an accurate description of the data for all the three species * up to $\sim 1.5t_{\frac{1}{2}}$.

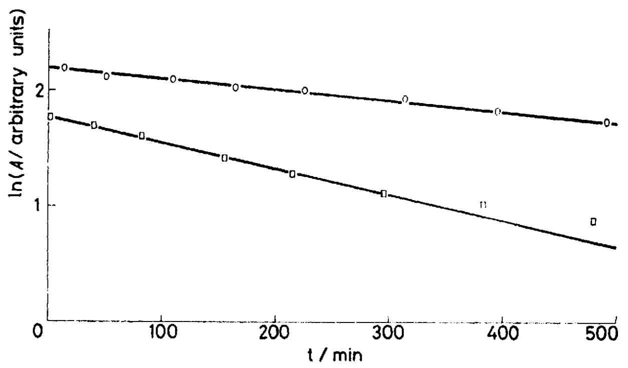

FIGURE 4 First-order plots obtained for the initial photo induced decomposition of Na[ClO$_4$], at -20 °C, from analysis of core-level peak areas: (○), O($1s$); (□), Cl($2p$). The deviations from linearity for Cl($2p$) observed at $t > 350$ min are real and were also observed in the Na[ClO$_3$] system

At longer X-ray exposures significant deviation from first-order behaviour was observed in the decompositions of both Na[ClO$_4$] and Na[ClO$_3$], invariably in the direction of decreasing rate constant. Inspection of Table 2 also shows that the rate constants for *total* oxygen decay are significantly smaller than those derived from the individual Cl($2p$) levels. This suggests that a substantial amount of molecular or atomic oxygen is trapped in the lattice during photodecomposition. As the reaction proceeds the evolution of oxygen gas is well established (see below), and we suspect that rupture of the crystallites leads to the exposure of small amounts of unchanged starting material, with an apparent reduction in its rate of removal, and some scatter in the data.

TABLE 2

Rate data for photoinduced decomposition of Na[ClO$_4$] and Na[ClO$_3$] at -20 °C obtained from linear regression analysis of the core-level peaks; $\sigma(k_1)$ is the standard deviation and the coefficient of determination was $>98\%$ in each case

	Cl($2p$)			O($1s$)		
System	10^3k_1/min^{-1}	$10^3\sigma(k_1)$	$t_{\frac{1}{2}}$/min	10^4k_1/min^{-1}	$10^4\sigma(k_1)$	$t_{\frac{1}{2}}$/min
Na[ClO$_4$]	2.06	0.12	336	8.70	0.40	800
Na[ClO$_3$]	2.07	0.064	334	11.7	1.5	593

The O($1s$) chemical shifts are too small to differentiate the various oxygen species in this system; however,

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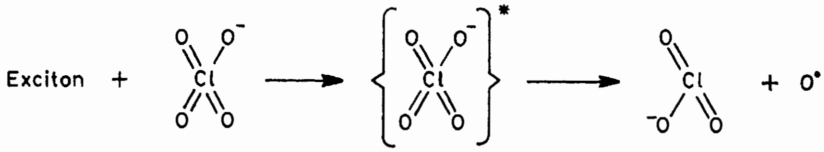
* The intensity of the Cl$^-$ ($2p$) level at completion is almost twice that of the [ClO$_4$]$^-$ level, and it was necessary to normalise the former to the latter value to allow for this.

[19] R. P. Seward and H. W. Otto, *J. Phys. Chem.*, 1961, **65**, 2078.

[20] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961.

magnetic-susceptibility measurements on irradiated solid nitrates [21,22] indicate that molecular oxygen forms in interstitial cavities, and similar evidence comes from monitoring the residual atmosphere of the sample chamber with the quadrupole mass analyser during the decompositions. With the mass analyser tuned to the O_2 peak (m/e 32), small bursts of oxygen gas were observed (after an initial induction period of $\approx 0.1t_{\frac{1}{2}}$), and these were further recorded as instantaneous pressure spikes on the Penning gauge, having an average magnitude of *ca.* 2×10^{-7} Torr s. We believe that these observations provide direct experimental evidence for the release of molecular oxygen from the surface crystallites. A search for other gaseous species such as Cl_2O, ClO_2, and Cl_2O_7 was unsuccessful within the detection limits of the instrument. This is in contrast to some earlier work [23] on the radiation-induced decomposition of a number of perchlorates, where the products were found to be $[ClO_3]^-$, ClO_2, $[ClO_2]^-$, $[ClO]^-$, Cl^-, O_2, and metallic oxide, identified by the u.v. absorption spectra of aqueous solutions of the irradiated salts. The use of solution methods to analyse irradiated solids has already been criticised,[24] however, because of the possibility of side reactions occurring in solution. Under the experimental conditions of this study, *viz.* a comparatively low radiation dose coupled with a specific surface decomposition, the stoicheiometry of the reaction can be represented by the process: $Na[ClO_4] \longrightarrow NaCl + 2O_2$.

The dissociation of the perchlorate anion is most probably due to the high flux of photoelectrons present during the experiment, produced by the ionisation of core levels by the *X*-rays. Since the maximum energies of the photoelectrons are only *ca.* 1.5 keV, the dissociation of an oxygen radical from the perchlorate ion cannot be achieved *via* inelastic collision; thus an electronic excitation, propagated by electron–hole pairs or *excitons*,[25] is envisaged; *e.g.* for the photoinduced dissociation of perchlorate we may write, following Burroughs *et al.*[8]:



The concentration of excitons within the solid will remain constant during the irradiation, and the observation of pseudo-first-order kinetics for the photoinduced decomposition is consistent with this mechanism. The oxygen atoms are small enough (*ca.* 12 Å^3 per atom) to diffuse rapidly through the lattice and combine to form clathrated molecular oxygen.

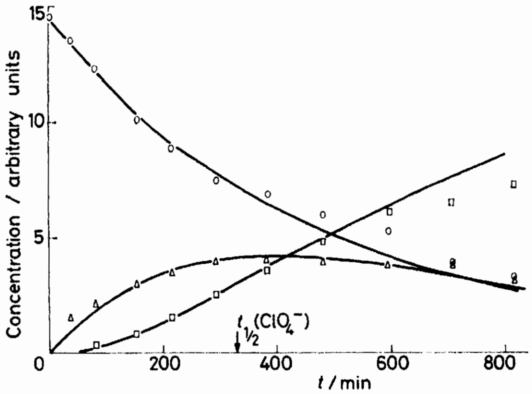


FIGURE 5 Comparison of data obtained for Cl(2*p*) levels in $Na[ClO_4]$ [(○), $[ClO_4]^-$; (△), $[ClO_3]^-$; and (□), Cl^-] with theoretical curves (——) based on a knowledge of k_1 and an estimate of k_2 assuming a first-order consecutive process to be involved (see text). The chloride intensities were normalised to that of $[ClO_4]^-$ at $t = 0$

There is a considerable amount of evidence, from the p.e. studies carried out here, to suggest that the NaCl produced has a grossly defective surface structure. Figure 3 and Table 1 show clearly that the Cl(2*p*) binding energy of the final product has decreased by *ca.* 1.3 ± 0.2 eV with respect to the Cl(2*p*) level in NaCl. The pale yellow colour of all the irradiated samples, which persists for many days after removal from the spectrometer, also suggests a severely defective structure for the surface NaCl; pure NaCl after irradiation develops a dark brown colour due to the production of *farben* centres,[26] with no change in the Cl(2*p*) level.[27] The Cl(2*p*) binding-energy difference between 'normal' and 'product' NaCl has been calculated with reference to the Na(2*s*) level (see Experimental section). We therefore believe that this difference is real, and is not due to an artifact such as sample charging. Distinct differences in the colour of these defect structures also support our interpretation.

The lower Cl(2*p*) binding energy of the defect NaCl produced by irradiation of $Na[ClO_4]$ suggests that a modified structure ensues, with effectively a higher concentration of negative charge at the anion sites. That such a modification should result is not surprising when the structures of the precursors and the final product are compared. The Cl–Cl distances in the unit cell of $Na[ClO_4]$ (two at 3.76 Å and two at 4.80 Å) and $Na[ClO_3]$ (four at 6.75 Å) are greater than in the sodium chloride lattice (four at 3.98 Å) so that the release of

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[21] J. Cunningham and H. G. Heal, *Trans. Faraday Soc.*, 1958, **54**, 1355.

[22] G. Hennig, R. Lees, and M. S. Matheson, *J. Chem. Phys.*, 1953, **21**, 664.

[23] L. A. Prince and E. R. Johnson, *J. Phys. Chem.*, 1965, **69**, 359 (and the following paper).

[24] H. G. Heal, *Canad. J. Chem.*, 1959, **47**, 979.

[25] A. S. Davydov, 'The Theory of Molecular Excitons,' McGraw-Hill, New York, 1962.

[26] R. Strumane, J. Nihoul, R. Gevers, and S. Amelinckx, 'The Interaction of Radiation with Solids,' North Holland, Amsterdam, 1964.

[27] R. G. Copperthwaite and J. Lloyd, unpublished work.

oxygen from these large anions leaves the resulting chloride lattice in a metastable configuration.

Further evidence for these conclusions resides in the p.e. intensity and kinetic data. Ng and Hercules[28] reported that the relative intensities for Cl(2*p*) levels in NaCl and Na[ClO$_4$] are approximately equal. In the present study we have found a ratio of 2 : 1 respectively, in contrast to those workers. Since they have shown that the p.e. intensity is proportional to the fractional escape solid angle, Ω, we can therefore conclude that the NaCl produced in this study has a larger Ω value, and hence a different structure, from that existing in the pure sample.

The value obtained for k_2 from the Na[ClO$_4$] data appears to be significantly larger than that obtained from the Na[ClO$_3$] measurement. This is again in tentative agreement with the arguments above, since [ClO$_3$]$^-$ produced by irradiation might be expected to have a structure more characteristic of Na[ClO$_4$] than Na[ClO$_3$]. There is therefore no requirement that k_2 observed in the consecutive process should be *identical* with k_1 for the pure intermediate; however, one would expect to observe order-of-magnitude agreement.

Conclusions.—We have shown that the soft *X*-ray-photoinduced decomposition of Na[ClO$_4$] proceeds, for exposure times of less than $1.5t_{\frac{1}{2}}$, *via* a simple consecutive first-order process involving Na[ClO$_3$] as an intermediate. The process is accompanied by evolution of clathrated *molecular* oxygen which suggests, together with analysis of the chemical shifts and relative intensities, that the final irradiation product, NaCl, has gross defects in structure in the surface regions.

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[28] K. T. Ng and D. M. Hercules, *J. Electron Spectroscopy*, 1975, **7**, 257.