Acta Cryst. (1971). B27, 2700

The Study of Sodium Nitrate by Neutron Diffraction

By G. L. Paul
Physics Department, University of New South Wales, N.S.W. 2033, *Australia*

and A. W. Pryor
Australian Atomic Energy Commission, Lucas Heights, N.S.W. 2232, *Australia*

(*Received* 9 *November* 1970)

The sodium nitrate structure has been determined by neutron-diffraction methods between 20 and 290°C. Above the 275°C phase transition there is complete disorder between alternative orientations of the NO_3 group.

Introduction

Sodium nitrate crystallizes in the calcite structure, $R\bar{3}c$ (No. 167 in *International Tables for X-ray Crystallography*, 1965). In the triple hexagonal cell, which is used exclusively from this point, the Na atoms are in positions 6(*b*), the N atoms in positions 6(*a*) and the oxygen atoms in positions 18(*e*), with six formula units per cell. The structure consists of alternating layers of sodium ions and nitrate groups; alternate layers of nitrate ions differ in orientation by 60°. At a temperature near 275°C, there is a transition to a structure with a halved *c* axis and three formula units per cell (Inkinen, 1960). We believe this phase change to be a transformation to complete disorder between the two NO_3 orientations so that the structure becomes $R\bar{3}m$ (No. 166), with Na atoms in positions 3(*a*), N atoms in positions 3(*b*) and half-oxygen atoms in positions 18(*g*) with doubled *z* coordinates of layers.

The structure has been previously studied by X-ray diffraction most recently by Inkinen (1960) when all reflexions were measured at room temperature; and by Cherin, Hamilton & Post (1967) (referred to as CHP), who measured the oxygen-only, *l*-odd, reflexions at temperatures of 25, 100, 150 and 200°C.

Our aims in again studying the structure by neutron diffraction were:

(i) to explore the surprisingly rapid increase in the thermal vibration parameter of the O atoms reported by CHP at a temperature of 200°C;

(ii) to determine the structure above the phase transition;

(iii) to assess whether published X-ray data, in conjunction with neutron data, could provide information on the ionic state and bonding in the NO_3 group.

Experiment and analysis

An irregular specimen,† with faces of the class {104}, weighing 21 mg, was cleaved from a large crystal, mounted in a silica tube with a heater coil and thermocouple, and set up for measurement on the computer-controlled neutron diffractometer described by Pryor, Ellis & Dullow (1968). With a neutron wavelength of 1·07 Å most of the accessible reflexions were measured in at least two equivalent positions, at temperatures of 20, 100, 180, 230, 250, 268 and 290°C. Within our limits of accuracy the cell parameters of CHP were confirmed.

In the refinement there is one structural parameter, *x* (setting the N–O bond length) and eight thermal parameters. The Debye–Waller exponent *W* for the N and Na atoms is given by

$$-W=\beta_{11}(h_1^2+h_1h_2+h_2^2)+\beta_{33}h_3^2$$

and for the O atom at $(x,0,\frac{1}{4})$ by

$$-W=\beta_{11}h_1^2+\beta_{22}(h_2^2+h_1h_2)+\beta_{33}h_3^2+\beta_{13}(h_1h_3+2h_2h_3)\,.$$

Room temperature data, for which more equivalents

Table 1.

Temperature (°C)	Cell parameters (Å)		N–O bond length (Å)	Corrected N–O bond length (A)	Na		N	Vibration
	a	*c*			u_{11}	u_{33}	u_{11}	u_{33}
20	5·070	16·82	1·242 (1)	1·257 (1)	224 (3)	245 (3)	183 (2)	225 (2)
100	5·074	16·97	1·236 (1)	1·256 (1)	281 (4)	295 (5)	240 (3)	273 (3)
180	5·077	17·13	1·226 (1)	1·252 (1)	375 (6)	405 (9)	309 (3)	356 (4)
230	5·079	17·23	1·217 (2)	1·252 (2)	447 (9)	450 (15)	355 (5)	424 (6)
250	5·081	17·27	1·218 (2)	1·252 (2)	512 (11)	491 (20)	393 (4)	514 (9)
268	5·082	17·31	1·210 (4)	1·259 (4)	495 (12)	383 (22)	426 (6)	257 (8)
290	5·084	17·35	{ 1·188 (8)	1·238 (8)	668 (30)	769 (21)	524 (13)	740 (13)
			{ 1·198 (13)	1·301 (13)				

were taken than for higher temperatures, were analysed using the isotropic type 2 formulation for extinction due to Zachariasen (1967). This gave $r^* = 470 \pm 21$ Å as the mean radius of a perfect block. This value is unexpectedly small, so that the extinction corrections are likewise small. All other data sets were then analysed using this value of r^* to make extinction corrections.

The data above 250° were also analysed on the hypothesis that disorder in the orientation of the NO_3 group commences below the transition temperature. It was supposed that a fraction $1-\varepsilon$ of the O atoms were in the 'e' positions of the $R\bar{3}c$ structure and a fraction ε were in alternate positions $(\bar{x},0,\frac{1}{4})$, $(0,\bar{x},\frac{1}{4})$, $(x,x,\frac{1}{4})$, $(x,0,\frac{3}{4})$, $(0,x,\frac{3}{4})$, $(\bar{x},\bar{x},\frac{3}{4})$. When $\varepsilon = 0{\cdot}5$ this produces the $R\bar{3}m$ structure of the high temperature phase.

The curvilinear motion of the O atoms, as formulated by Pryor & Sanger (1970), was also incorporated in a series of refinements. This reduced the weighted R value by about 3% at room temperature and by about 10% at high temperatures. The thermal parameters and R values quoted in Table 1 below are for conventional refinements and only in the column, 'corrected bond lengths', are the results of the curvilinear refinements quoted.

Absorption corrections at all temperatures were based on $\mu = 0{\cdot}45 \pm 0{\cdot}03$ cm^{-1} obtained from cross section measurements on large crystals. This value corresponds to 28 barns per molecule which is surprisingly high. This could be partly explained by phonon processes. However, the total cross section measured on large crystals in probably not appropriate for the correction of Bragg intensities and the curiously low value of the extinction parameter may be due to this. Absorption probably increases with temperature particularly near the transition temperature, where critical scattering may occur. Weighting was determined from the variance of the intensity, being the sum of the variance due to counting statistics and a constant factor representing a level of confidence. The minimum observable intensity was determined from a plot of $\sigma(F)$ against F. 'Unobserved' reflexions were assigned an intensity and standard deviation equal to half of this intensity.

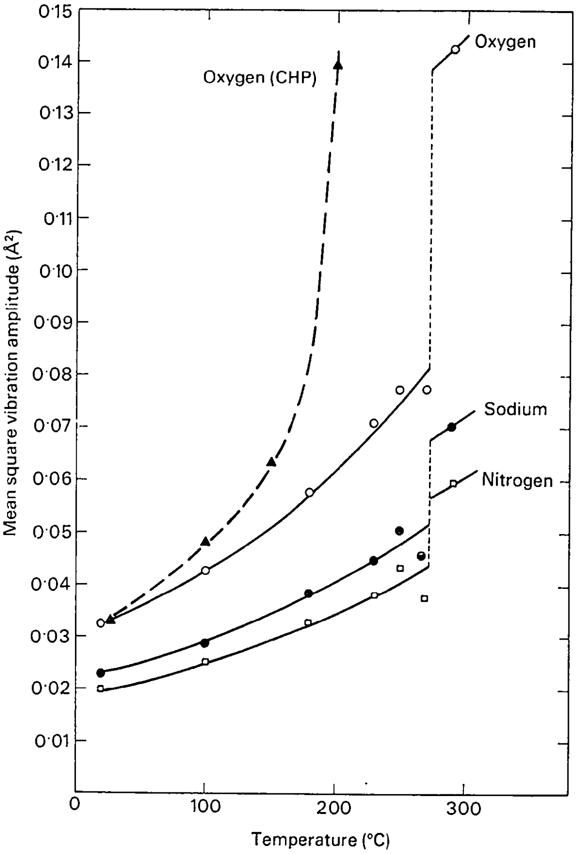

Fig. 1. Mean-square vibration amplitude for Na, N and O atoms.

Results and discussion

The results of the various refinements are given in Table 1. The vibration parameters are quoted in a Cartesian system with the 3-axis along the c axis of the crystal, and the 1-axis along the N–O bond. In this system, for Na and N, $u_{11} = \frac{3a^2}{8\pi^2}\beta_{11}$, $u_{33} = \frac{c^2}{2\pi^2}\beta_{33}$, and for O, $u_{11} = \frac{a^2}{2\pi^2}\left(\beta_{11} - \frac{\beta_{22}}{4}\right)$, $u_{22} = \frac{3}{8\pi^2}a^2\beta_{22}$, $u_{33} = \frac{c^2}{2\pi^2}\beta_{33}$, $u_{23} = \frac{\sqrt{3}ac}{4\pi^2}\beta_{13}$. These u's are real-space, mean-square vibration amplitudes in cm^2.

Refinements

Amplitudes

O				Occupancy.of alternate sites of oxygen	Number of reflexions	Weighted R value (%)
u_{11}	u_{22}	u_{33}	u_{23}			
184 (2)	378 (2)	416 (3)	−147 (2)	–	215	3·64
235 (2)	513 (2)	526 (4)	−199 (3)	–	248	4·29
314 (3)	723 (6)	696 (7)	−260 (4)	–	228	3·75
366 (4)	918 (9)	841 (11)	−331 (8)	–	154	4·64
407 (5)	1020(12)	892 (11)	−386 (8)	0·066 (4)	143	4·65
344 (12)	1240 (52)	737 (24)	−364 (25)	0·206 (12)	143	9·2
430 (25)	1197 (100)	1403 (106)	−222 (82)	'e', 0·50 fixed	76	2·7
657 (40)	2760 (170)	1343 (106)	−173 (80)	alternative 0·50 fixed		

---

† The crystals were obtained from Dr D. A. James, Department of Chemistry, University of Queensland.

In the refinements of the 250 and 268°C data, the occupancy of the alternate oxygen sites was a free parameter, and at 268°C it seems clear that there is partial occupancy of these sites. Above the 275°C transition, to refine the 290°C data we assumed equal occupancy of the '*e*' sites and the alternative sites and allocated the two sets of oxygen atoms separate positions and thermal parameters. The low *R* value, and the agreement between the two sets of oxygen position parameters, support this hypothesis of the structure.

The mean square vibration amplitude of Na, N and O atoms, calculated as $\frac{1}{3}(u_{11}+u_{22}+u_{33})$, is plotted against temperature in Fig. 1, together with the results of CHP. The spectacular increase in the O vibrations, reported by CHP, seems to be spurious. The 268° data gave anomalously low values for the vibration amplitudes and we suspect that this was caused by fairly intense diffuse scattering resulting in anomalous absorption.

If the NO_3 group is rigid, then u_{11} for N and O should be the same. Table 1 shows that this is indeed so, within the quoted error limits, up to 250°C. The rotational amplitude of the NO_3 group about the *c* axis (the 3-axis of our Cartesian system) is not unusually large (11·7° at 250°C).

The bond length from the conventional refinements decreases with temperature due to the well-known apparent shortening due to arc motion. Refinements incorporating a proper formulation of this effect gave a more-or-less constant value of the N–O distance at 1·256 (1) Å. The agreement with CHP on this point is excellent.

Analysis of X-ray data

Taking the thermal and positional parameters at room temperature from this experiment, and the X-ray data of Inkinen and CHP (put on a common scale by separate refinements), we prepared difference Fouriers.

The X-ray form factors of $Na^+N^{2+}O_3^-$ and of $Na^+N^{5+}O_3^{2-}$ were calculated after Clementi (1965). These difference Fouriers appeared, however, to show no systematic features which could be interpreted as clear information on the ionic state or bonding within the NO_3 group. We concluded that more accurate X-ray data would be needed to explore this question.

References

Cherin, P., Hamilton, W. C. & Post, B. (1967). *Acta Cryst.* **23**, 455.

Clementi, E. (1965). *IBM J. Res. Dev.* **9**, 2, plus Supplementary Tables of Atomic Functions.

Inkinen, O. (1960). *Ann. Acad. Sci. Fenn., Series A*, **55**, 1.

International Tables for X-ray Crystallography (1965). Vol. I. Birmingham: Kynoch Press.

Pryor, A. W., Ellis, P. J. & Dullow, R. J. (1968). *J. Appl. Cryst.* **1**, 272.

Pryor, A. W. & Sanger, P. L. (1970). *Acta Cryst.* A**26**, 543.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1972). B**28**, 2702

The Crystal Structure of *p*-Nitrophenyl Acetate

By R. Guttormson and B. E. Robertson

Division of Natural Sciences and Mathematics, University of Saskatchewan, Regina, Canada

(*Received* 2 *December* 1971 *and in revised form* 30 *March* 1972)

The crystal structure of *p*-nitrophenyl acetate, $C_8H_7NO_4$, is monoclinic, $P2_1/c$, $a=14{\cdot}115$ (10), $b=7{\cdot}437$ (9), $c=16{\cdot}158$ (10) Å, $\beta=90{\cdot}83$ (5)°, $Z=8$, $T=23$°C, $D_x=1{\cdot}42$ g.cm^{-3}, $D_m=1{\cdot}37$ g.cm^{-3}. The intensities of 2234 independent reflexions were measured with a four-circle diffractometer. The structure was solved using the symbolic addition method and refined by full-matrix least-squares analysis to a weighted least-squares residue of 0·048. In both of the two independent molecules, the plane of the acyl group is rotated approximately 65° from the plane of the phenyl ring and both molecules have the *trans* conformation. The C–NO_2 bond lengths are similar to those in related compounds with electron donating substituents.

Introduction

p-Nitrophenyl acetate has been used extensively in studies of alkaline hydrolysis and enzyme catalysed hydrolysis (see *e.g.* Boyer, Lardy & Myrback, 1960) because of the ease of estimation of nitrophenol by spectrophotometry and the relative simplicity of the molecule. Simple steric arguments suggest that either the acyl group must be rotated from the plane of the phenyl ring or the molecule must adopt the *cis* conformation rather than the more stable *trans* conformation. This study was undertaken to determine the conformation of the molecule and provide information on the bonding scheme in the acyl linkage.