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The Crystallography of Solid Dinitrogen Trioxide at −115° C.

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The unit cell of N_2O_3 crystals at $-115°$ C. is tetragonal with $a = 16{\cdot}4$, $c = 8{\cdot}86$ Å, and contains 32 molecules of N_2O_3. Complete *hkl* data from single crystals indicate that the space group is D_4^{10}–$I4_12$. The presence of an abnormally high decline of intensities with increasing angle of scattering, and the presence of a marked transition at roughly $-125°$ C., suggest a disordered structure. Although the electron-density projection along c was refined to an agreement of $R = 0{\cdot}22$ (observed reflections only), an interpretation of this projection could not be made, and the structure remains unsolved.

Introduction

An investigation of the structure of N_2O_3 was undertaken because its enthalpy of dissociation (10·3 kcal./mole) is intermediate between that of N_2O_4 (14·6 kcal./mole) and that of N_2O_2 (4 kcal./mole). Since both N_2O_4 (Broadley & Robertson, 1949) and N_2O_2 (Dulmage, Meyers & Lipscomb, 1951) show anomalously long bonds, a similar anomaly was therefore expected for N_2O_3. However, as will be described, the presence of a probably disordered phase having a reasonably large, non-centrosymmetric unit cell has allowed us to determine only a partial structure of solid N_2O_3, and we have not obtained a chemically interesting interpretation of our results. However, it is to be expected that when calorimetric, magnetic susceptibility, spectroscopic, and other physical data are obtained for N_2O_3, interpretations of the diffraction data and electron-density map in terms of more complete crystal and molecular structures may become possible.

Experimental

The general experimental techniques have been described elsewhere (Reed & Lipscomb, 1953), so that only those additional details pertaining to N_2O_3 are described. Mixtures of NO and NO_2 were sealed in capillaries about 1 mm. in diameter attached to thick pyrex bulbs about 10 mm. in diameter. As is indicated by the phase diagram (see Wilson & Bremner, 1948, p. 14) the liquid phase above $-100°$ C. contains excess NO_2, and probably for that reason our preliminary attempts to freeze the liquid yielded N_2O_4 crystals. However, when the sample was maintained at a few degrees above the melting point of about $-100°$ C. for a few hours to allow solution of the equilibrium amount of NO, good large single crystals were obtained, unfortunately always along with small fragments of other crystals. We feel sure that the easily recognizable reflections due to the fragments caused neither ambiguities in indexing nor errors in the intensity estimates. The characteristically larger areas of the reflections from the single crystal and the high symmetry of the diffraction photographs were very helpful in avoiding these ambiguities and errors. It must be remarked that single crystals of N_2O_3 were many times more difficult to obtain than crystals of any substance so far studied in this laboratory. Unfortunately, the polarizing microscope was not useful for observation of the growth of crystals because of the opacity of the solid.

The crystals were maintained at $-115 \pm 5°$ C. during the photography. In the neighborhood of $-125°$ C. a major transition occurs. As the temperature is lowered the single-crystal reflections split up almost completely into a powder pattern.

The crystals, indicated by the diffraction patterns to be tetragonal, always grew with the c axis along the capillary. Consequently complete *hkl* data were obtained from precession photographs, all of which contained the $00l$ reflections. In addition Weissenberg photographs were taken of the $\{hk0\}$ zone. Mo $K\alpha$ radiation was used throughout. The integrated intensities of timed exposures on the precession photographs were measured by means of a Leeds and Northrup recording microdensitometer, and those on the Weissenberg photographs by means of visual estimates aided by the multiple-film technique and the usual type of standard scale made from timed exposures of a diffracted beam.

The complete three-dimensional Patterson function* was calculated on the X-ray Analogue Computer through the kind courtesy of Prof. R. Pepinsky. Computations of Patterson projections, Fourier projections and structure factors were made with the use of International Business Machines at the Computing Center of the University of Minnesota.

Results

The symmetry of the reciprocal lattice is D_{4h}. The unit cell dimensions

$$a = 16{\cdot}40 \pm 0{\cdot}10 \quad \text{and} \quad c = 8{\cdot}86 \pm 0{\cdot}04 \text{ Å}$$

lead to a volume of 2381 Å^3 and to a density of 1·70 g.cm.^{-3} if one assumes 32 N_2O_3 molecules in the unit cell. No value for the observed density is available, but the calculated densities of N_2O_2 (1·46 g.cm.^{-3}) and N_2O_4 (1·95 g.cm.^{-3}) lead to an average value of 1·70 g.cm.^{-3} as a 'predicted' density for N_2O_3. Observed reflections occurred only as follows: (1) hkl with $h+k+l = 2n$, (2) $00l$ only with $l = 4n$, and (3) $hk0$ only with $h = 2n$ and $k = 2n$. There is no space group which is in the Laue class D_{4h} and which shows only these extinctions and no others. However, we believe that the most probable space group is D_4^{10}–$I4_12$, which shows all extinctions except (3) when some atoms are in general positions. The additional extinction (3) is then to be attributed to two crystallographically non-equivalent peaks having x, y coordinates related by a translation of $\frac{1}{2}a$, but having different z coordinates. Since other possible explanations, such as reduction of the Laue symmetry to C_{4h}, are inconsistent with our experimental data, we have proceeded on the assumption that the space group is $I4_12$.

The analysis of the three-dimensional Patterson function was unsuccessful, and therefore the centrosymmetric projection along the c axis was considered. The extinction (3) further simplifies this projection to a pseudo-cell with $a' = \frac{1}{2}a = 8{\cdot}2$ Å, and all of the x and y coordinates in the following discussion refer to this pseudo-cell. The Patterson projection along the c axis showed prominent peaks at (0·50, 0·50) and (0·36, 0·12) plus those given by the symmetry operations. The (0·50, 0·50) peak, which is very nearly equivalent to the origin peak, requires the Fourier projection to have peaks at the origin and (0·50, 0·50); these peaks contribute in phase when $h+k = 4n$, and make only small contribution when $h+k = 4n+2$, so that nearly all of those reflections for which $h+k = 4n$ have positive signs. A Fourier synthesis with these reflections alone led to additional reasonably strong peaks at (0·36, 0·12) and equivalent positions. Although a refinement and molecular interpretation of this synthesis was attempted on the basis of four rotating NO molecules (radius of gyration = 0·55 Å) at positions I and II in Figs. 1 and 2 and one NO_2 molecule at III, the value of $R = \sum_{hk0} ||F_o| - |F_c|| \div \sum_{hk0} |F_o|$ could not be reduced below 0·47 so that this model, as well as a number of other stoichiometric models, were abandoned. An attempt was then made to adjust peak heights, areas and locations in order to give agreement between F_c and F_o and between $\varrho_c(x, y)$ and $\varrho_o(x, y)$. With the use of an average form factor for N and O it was found that if 6 atoms are placed at peak I (0, 0) with a temperature factor $B = 11{\cdot}5$, 6 atoms are placed at peak II (0·50, 0·50) with $B = 15{\cdot}3$, and three atoms are placed at peak III (0·35, 0·12) with $B = 15{\cdot}3$, a final agreement of $R = 0{\cdot}22$ is obtained from observed reflections only. A Fourier synthesis using $F_o - F_c$ as coefficients showed no peaks higher than 2 e.Å^{-2} at any point, while Fig. 1 shows peak heights of 22, 18 and 10 e.Å^{-2}. A com-

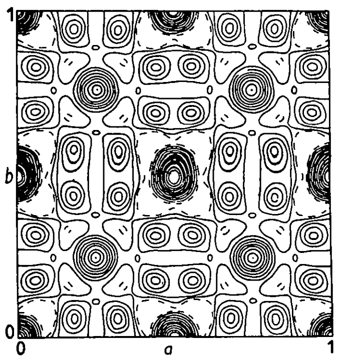

Fig. 1.

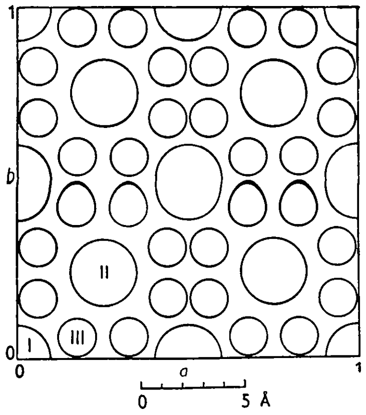

Fig. 2.

Fig. 1. Projection of the electron density along the c axis. Solid contours are at 2, 4, 6... e.Å^{-2}. The broken contour is at 1 e.Å^{-2}.
Fig. 2. Line diagram of Fig. 1, showing pseudo-cell and number of peaks.

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* This function is plotted in the Ph.D. Thesis of T. B. Reed, University of Minnesota, 1953, and can be obtained from University Microfilms, Ann Arbor, Michigan, U.S.A.

Table 1. *Comparison of observed and calculated hk*0 *structure factors*

*hk*0	F_o	F_c
000	—	137·0
200	<10	6·1
220	2·3	5·6
400	29·0	22·3
420	$<$ 1·0	−5·9
440	17·7	17·7
600	11·9	10·3
620	37·0	36·3
640	4·9	3·3
660	2·1	−0·5
800	3·2	3·9
820	$<$ 1·5	1·2
840	6·7	10·2
860	1·2	−1·0
880	10·0	8·5
10,0,0	2·3	−2·9
10,2,0	2·6	7·3
10,4,0	1·8	1·8
10,6,0	2·3	1·4
10,8,0	1·7	1·5
12,0,0	$<$ 1·7	−2·5
12,2,0	$<$ 1·7	2·0
12,4,0	2·4	1·3
12,6,0	1·4	−0·3
12,8,0	1·8	0·6

Table 2. *Observed general hkl structure factors*

hkl	F_o
004	3·4
008	4·5
112	4·1
202	2·8
211	3·6
213	3·8
215	3·4
222	26·5
303	6·8
321	3·6
323	4·3
332	12·8
402	19·0
404	9·9
406	4·6
411	4·9
413	8·1
444	6·6
503	7·0
512	5·3
521	10·5
532	5·3
541	5·4
552	5·9
554	4·1
611	15·1
613	5·2
631	8·8
633	4·3
662	9·1
664	4·3
732	3·2
734	4·4
743	4·7
752	4·5
772	9·0
774	4·9
802	19·3
806	5·0
811	4·9
813	5·6
831	4·9
842	5·1
844	4·9
851	5·9
884	4·8
905	4·7
952	4·8
10,0,4	4·4
10,2,2	3·8
10,2,4	5·5
10,3,3	3·7
10,4,2	2·8
10,4,4	3·7
10,6,2	4·6
10,7,3	5·5
10,10,2	5·0
12,0,4	4·1

parison of observed and calculated *hk*0 structure factors is shown in Table 1, and the remaining *hkl* experimental data are recorded in Table 2.

The model indicated by the Fourier projection in Fig. 1 can be varied only within relatively narrow limits. The most intense reflection is that for (620), for which the observed structure factor is 60% of its maximum possible value. Choice of the origin at one of the large peaks makes F_{620} positive. Now the contribution of peak III to F_{220} must be negative and large, since peaks I and II contribute positively. Peak III contributes negatively to F_{800} and positively to F_{880}, while the observed values are small and large respectively. Thus the contribution of peaks I and II to both F_{800} and F_{880} must be large and positive, a situation which demands concentration of the scattering matter of peaks I and II closer to the points (0, 0) and (0·50, 0·50) than the 0·55 Å radius of the rotating groups suggested by the molecular model which we later rejected.

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