

A Neutron Diffraction Study of Polycrystalline

 HCrO_2 and DCrO_2 *

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On the basis of powder neutron diffraction data the O-O bond in DCrO_2 is shown to be asymmetric. Results for the O-H-O bond in HCrO_2 are less certain, but tend to support a symmetric hydrogen bond.

A neutron diffraction study of polycrystalline HCrO_2 and DCrO_2 has been carried out in an attempt to resolve the question of the symmetries of the O-H-O and O-D-O bonds in these substances. The O...O distance is sufficiently short (2.5Å) to make a symmetric bond seem credible.

Douglass¹⁾ in an X-ray study found HCrO_2 to be trigonal, Laue symmetry $\bar{3}m$, with $a = 4.787\text{\AA}$, $\alpha = 36.3^\circ$, one molecule per unit cell. The simplicity of the structure encouraged us to carry out a neutron diffraction study, even though single crystals were not available. The simplicity of the structure and its interesting structural and magnetic properties have also prompted other studies, including one by nuclear magnetic resonance techniques²⁾ and another by infrared techniques.³⁾ On the assumption of a center of symmetry the space group of HCrO_2 must be $R\bar{3}m$, and Douglass found reasonable agreement with observation upon putting Cr in 0, 0, 0; 2O in $\pm(x, x, x)$ ($x = 0.405$). The hydrogen atoms can either be at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ or statistically distributed with an average of one-half hydrogen in each of the positions $\pm(x, x, x)$. The structure itself consists of sheets of Cr atoms between two sheets of O atoms. The O atoms are close packed and each Cr atom is surrounded by a distorted octahedron of O atoms. The O-Cr-O layers are stacked normal to the [111] axis with a three layer repeat.

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The separate layers are joined together by hydrogen bonds.

Owing to the overlap of the powder data, all peaks could not be resolved completely. On the partially resolved peaks, however, estimates of the individual intensities could be made. Such observations are correlated, and since the data were refined by least squares, these correlations were included in the form of a non-diagonal weight matrix. All computations were carried out on an IBM 704. The program employed enabled us to refine the scale factor, the oxygen x parameter, the half-hydrogen x parameter, the scattering factors, and two temperature factors for each atom, one parallel to [111] ($B_{\parallel}$) and one perpendicular to [111] ($B_{\perp}$), as demanded by symmetry.

For DCrO_2 several cycles of least-squares were carried out with variations of the scale factor and the deuterium and oxygen positional parameters. This refinement converged to $x_o = 0.4082 \pm 0.0011$; $x_D = 0.4834 \pm 0.0025$. Use of these parameters, $B_{\parallel} = B_{\perp} = 0$, and neutron scattering factors of 0.35, 0.58, and 0.65 for Cr, O, and D led to a generalized agreement factor of 0.079 for this set of intensities. The generalized agreement factor is defined as

$$R = \left[\frac{\sum_i \sum_j (I_o - I_c)_i w_{ij} (I_o - I_c)_j}{\sum_i \sum_j I_{oi} w_{ij} I_{oj}} \right]^{\frac{1}{2}}$$

No significant improvement in the agreement was obtained when temperature factors for D were varied; the resultant temperature factors were not significantly different from zero.

These parameters lead to $0 \cdots 0 = 2.48 \pm 0.03 \text{ \AA}$, $\text{O}-\text{D} = 1.02 \pm 0.04 \text{ \AA}$. On the basis of appropriate variance ratio tests, it may be concluded that there is less than 0.5% probability that the observed data could have been produced by a structure with $x_D = 0.5$. We conclude, with high probability, that the hydrogen bond in DCrO_2 is not symmetric.

The data for HCrO_2 were similarly refined. Owing to the singular nature of the normal equations' matrix when $x = \frac{1}{2}$, refinements were carried out with x_H held constant. Some results, with $B_{\parallel} = B_{\perp} = 0$, are

x_H	x_O	R
0.47	0.4068 ± 0.0009	0.157
0.48	0.4062 ± 0.0009	0.116
0.49	0.4053 ± 0.0009	0.120
0.50	0.4050 ± 0.0009	0.126

Hence the agreement is rather insensitive to the hydrogen parameter in the range of interest.

Attempts to refine the hydrogen temperature factors shed further light on the hydrogen bond. In contrast to the DCrO_2 case, there is significant improvement upon the introduction of temperature factors for hydrogen. The results are more sensible for the cases with an x_H parameter near 0.5, and the amplitude of thermal motion is then found to be greater perpendicular to the bond, in accordance with the predictions of the nuclear magnetic resonance study²¹. In fact, a fit almost as good as the best is obtained when the nuclear magnetic resonance condition on the thermal parameters is quanti-

tatively applied ($B_{\perp} - B_{\parallel} = 4.7 \text{ \AA}^2$). In this case we obtain ($x_H = 0.50$); $x_O = 0.4045 \pm 0.0006$; $B_{\parallel} = -0.6 \pm 1.1$; $B_{\perp} = 4.1 \pm 1.1$; $R = 0.098^{(1)}$. This much greater apparent motion perpendicular to the bond lends support to the hypothesis that the hydrogen atom is indeed centered. The fact that the $\text{O} \cdots \text{O}$ distance, calculated for an x_O parameter of 0.4045, is longer ($2.55 \pm 0.02 \text{ \AA}$) than that found for DCrO_2 is surprising in view of the expansion of the lattice constants upon substitution of D for H ($c(\text{HCrO}_2) = 13.36 \text{ \AA}$; $c(\text{DCrO}_2) = 13.50 \text{ \AA}$).

Thus the hydrogen atom in HCrO_2 is probably centered, rather than being statistically distributed on either side of a potential hump. It must be emphasized however, that this result is not nearly so unambiguous as the statement that the deuterium is definitely not centered. It is encouraging that these results are in complete agreement with the infrared study³; the infrared data are most readily interpreted in terms of a symmetric hydrogen bond and an asymmetric deuterium bond.

References

1. R. M. Douglass: *Acta Cryst.* **10** (1957) 423.
2. J. A. Ibers, C. H. Holm, and C. R. Adams: *Phys. Rev.* **121** (1961) 1620.
3. R. G. Snyder and J. A. Ibers: *J. Chem. Phys.* **36** (1962), in press.
4. Since this work was submitted for publication, further refinements of the data have been carried out with the condition that the Cr-O distance be constant in both compounds. The results, to be reported later, lead to distances of approximately 2.51 and 2.57 $\text{\AA}$ for O-H-O and O-D-O, respectively.

DISCUSSION

S.W. PETERSON: I would like to mention that this is quite similar to the work that we did on KH_2AsO_4 and KD_2AsO_4 system, where the $\text{O}-\text{D} \cdots \text{O}$ bond was significantly longer and in any case we could very clearly see two positions, whereas in $\text{O}-\text{H} \cdots \text{O}$ bond which was shorter, as far as we could tell, the bond was symmetric.