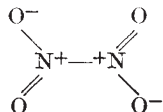


### Potential Barrier in Dinitrogen Tetroxide

THE communication<sup>1</sup> by C. K. and E. H. Ingold on the structure of  $N_2O_4$  reviews the chemical and physical evidence in favour of the various structures proposed for  $N_2O_4$ . The authors conclude that the structure is



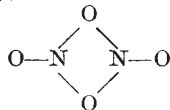
which is equivalent to the  $D_{2h}$  structure proposed by Sutherland<sup>2</sup> on the basis of the spectroscopic data. Using the fundamentals proposed by Sutherland and the following molecular dimensions, namely,  $\angle ONO = 120^\circ$ ,  $r_{NO} = 1.15 \text{ \AA}$ ,  $r_{NN} = 1.66 \text{ \AA}$ ,<sup>3</sup> the entropy at  $298^\circ \text{ K}$ . may be calculated by the usual methods of statistical thermodynamics<sup>4</sup>. In this way the entropy of translation for gaseous  $N_2O_4$  at  $298^\circ \text{ K}$ . is found to be  $39.44 \text{ cal./deg./mole}$ , and that due to vibration and rotation without taking torsion into account is  $30.00 \pm 0.3 \text{ cal./deg./mole}$ . (The error of  $\pm 0.3 \text{ E.U.}$  in the rotational entropy is estimated by assuming that the error in each molecular dimension is  $\pm 5$  per cent.) The entropy observed by Giauque and Kemp<sup>5</sup> was  $72.73 \text{ cal./deg./mole}$ . Thus the amount of entropy contributed by the degree of freedom associated with internal rotation is  $3.29 \pm 0.3 \text{ cal./deg./mole}$ . Assuming the potential energy is of the form  $V = B/2 (1 - \cos 2\phi)$  the torsional frequency and potential barrier  $B$  are related to the moment of

inertia about the torsional axis by  $\nu = \frac{1}{2\pi} \left[ \frac{8B}{I} \right]^{1/2}$

Then if the potential barrier is considered to be so high that the contribution to the entropy is simply due to a torsional oscillation, then the torsional frequency is  $108 \pm 20 \text{ cm.}^{-1}$ , with a corresponding barrier of  $8.5 \pm 2 \text{ cal./mole}$ .

On the other hand, if the barrier is not so high that a torsional oscillation may be used in the partition function, the tables of Pitzer and Gwinn<sup>6</sup> for a hindered rotator must be used. From these tables and the following values:  $I_m = I/4 = 27.5 \times 10^{-40}$  c.g.s. units,  $n = 2$ ,  $Q_f = 12.6$ , entropy of internal rotation =  $6.06 \text{ E.U.}$ , and  $S_f - S = 2.77 \pm 0.3$ , it is found that the barrier is  $9.2 \pm 2 \text{ cal./mole}$ . This corresponds to a frequency of  $112 \pm 20 \text{ cm.}^{-1}$ . The barrier is evidently so high,  $\sim 9 \pm 2 \text{ cal./mole}$ , that both calculations yield very nearly the same result.

The molecular model proposed by Longuet-Higgins<sup>7</sup>, namely,



with  $D_{2h}$  symmetry was introduced as an alternative to the ethylene-like structure of Sutherland to explain the spectrum and the abnormally long  $N-N$  distance<sup>8</sup> and low  $N-N$  force constant<sup>8</sup>. This model has no torsional mode, however, so that the calculated entropy and observed entropy differ by about  $3 \text{ E.U.}$ . This lack of agreement is strong evidence for excluding this model as a possible structure.

Since the repulsion of the oxygen atoms would stabilize the out-of-plane form ( $D_{2d}$ ), there must be a strong interaction ( $\geq 9 \pm 2 \text{ cal./mole}$ ) stabilizing the planar form. Resonance between the forms suggested by the Ingolds would be at a maximum when the structure is planar<sup>9</sup> and accounts for the stability of the planar form.

The heat capacity  $C_p^\circ$  at  $298^\circ \text{ K}$ . of  $N_2O_4$  is calculated to be  $17.11 \text{ cal./mole}$  for a barrier of  $9 \text{ cal./mole}$  and  $17.06 \text{ cal./mole}$  for a completely hindered rotator. The available experimental results on the heat capacity of  $N_2O_4$  are:  $11.4 \text{ cal./mole}$  at  $307^\circ \text{ K}$ .<sup>10</sup> and  $20 \text{ cal./mole}$  at  $300^\circ \text{ K}$ .<sup>11</sup>. An experimental re-determination of the specific heat seems to be indicated.

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<sup>2</sup> Sutherland, G. B. B. M., *Proc. Roy. Soc. A*, **141**, 342, 535 (1933).

<sup>3</sup> Maxwell, L. R., Mosley, V. M., and Denning, L. S., *J. Chem. Phys.*, **2**, 331 (1934).

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<sup>5</sup> Giauque, W. F., and Kemp, J. D., *J. Chem. Phys.*, **6**, 40 (1938).

<sup>6</sup> Pitzer, K. S., and Gwinn, W. D., *J. Chem. Phys.*, **10**, 428 (1942).

<sup>7</sup> Longuet-Higgins, H. C., *Nature*, **153**, 408 (1944).

<sup>8</sup> Duchesne, J., *C.R. Acad. Sci., Paris*, **204**, 1112 (1937).

<sup>9</sup> See, for example, Klotz, I. M., *J. Chem. Educ.*, **22**, 328 (1945).

<sup>10</sup> McCollum, E. D., *J. Amer. Chem. Soc.*, **49**, 28 (1927).

<sup>11</sup> Partington, J. R., and Shilling, W. G., "The Specific Heat of Gases", 188 (London: Ernest Benn, 1924).

### Synthesis of Thiazolid-2:5-Dione

RECENT interest in the synthesis of polypeptides has centred around the ability of oxazolid-2:5-dione and its 3- and 4-substituted derivatives to polymerize with loss of carbon dioxide or to condense with amino-acids or their esters. Cook and Levy<sup>1</sup> have now shown that the analogous 2-thiothiazolid-5-one and its 4-methyl derivative may also be used for the introduction of glycol or alanyl residues. Attempts by Cook, Heilbron and Hunter<sup>2</sup> to obtain the structural cross of the above heterocycles, that is, thiazolid-2:5-dione (III), were unsuccessful. These authors were interested in the latter compound and its derivatives, as they considered they would be of a stability intermediate between that of oxazolid-2:5-dione and 2-thiothiazolid-5-one and would consequently be more easily handled. The parent compound has now, unexpectedly, been obtained in good yield by the accompanying reaction scheme.

A variety of potassium alkylxanthates (alkoxy-dithioformates) were esterified to give ethyl alkoxydithioformates (I), which condensed smoothly with potassium aminoacetate to give N-thiocarbalkoxyglycines (II). Cyclization of (II) with acetic anhydride gave the expected 2-alkoxythiazol-5-one (IV), the

