

Table 3.

$\eta$  denotes overvoltage in millivolts.  
C. D. » current density (amp/sq.cm.)

	% D.	C.D.	$\eta$
Copper in 1 N hydrochloric acid	0	10 <sup>-3</sup>	525
	75		546
	99.5		587
Nickel in 1 N hydrochloric acid	0	»	178
	30		186
	50		209
	75		235
	99.5		260
Lead in 1 N hydrochloric acid	0	»	1 044
	50		1 088
	80		1 127
	99.5		1 175
Iron in N potassium hydroxide	0	»	170
	50		188
	80		232
	98		269
Mercury in 0.2 N sulphuric acid	0	10 <sup>-4</sup>	828
	50		831
	80		894
	99.5		903

observations showed satisfactory agreement with the results reported in <sup>1</sup>. Some mean values are given in Table 2.

Experiments with aluminium in 4.5 N hydrochloric acid at 25° C gave the surprising result that the reaction rate was much higher with DCl (99 % D) than with HCl. Some mean values are given in Table 2. Similar results were obtained with 2 N hydrochloric acid.

Further a number of observations were made on the dissolving velocity of aluminium in 2 N potassium hydroxide. Some mean values are given in Table 2.

3. *Iron.* Experiments with commercial mild steel and high purity iron in 2 N hydrochloric acid also showed a marked reducing effect of the deuterium content on the dissolving rate.

*Measurements of overvoltage.* In the present work are included measurements on mercury, copper, nickel, lead and iron at 25° C.

Some mean values from the overvoltage-C. D. curves are tabulated in Table 3.

1. Johnston, H. L., and Davies, C. D. *J. Am. Chem. Soc.* **64** (1942) 2613.

Received November 8, 1951.

### Molecular Configuration of 1,2-Dichloro-4,5-Dibromocyclohexane ( $\epsilon\epsilon-\kappa\kappa \rightleftharpoons \kappa\kappa-\epsilon\epsilon$ ) in the Vapour State

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Some months ago the 1,2-dichloro-4,5-dibromocyclohexane corresponding to the 1,2,4,5-tetrachlorocyclohexane of m.p. 176° C and the tetrabromocyclohexane of m.p. 187° C was prepared in our laboratory<sup>1</sup>. We wanted to decide which of the two possible configurations is the energetically preferred one, that in which the chlorine atoms occupy  $\kappa$  positions and the bromine atoms  $\epsilon$  positions or the reversed configuration (Fig. 1).

The substance (m.p. 171°) turned out to crystallize isomorphous with the two substances mentioned above, the only element of symmetry required by the space group being a two-fold axis of symmetry. An X-Ray investigation, the result of which is now being published in this journal<sup>2</sup>, showed the chlorine atoms to be in  $\epsilon$  positions and the bromine atoms in  $\kappa$  positions (Fig. 1 a).

Although this result seemed entirely acceptable from a theoretical point of view, the objection could be raised that the

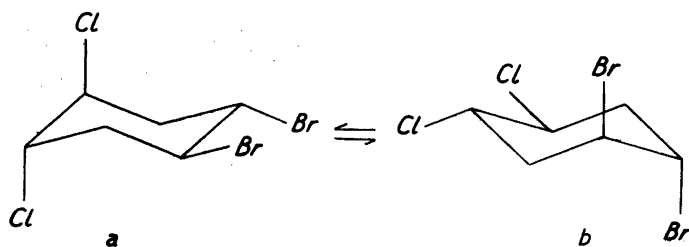


Fig. 1.

configuration b (Fig. 1) might be present to a considerable extent in the vapour. We have therefore investigated the substance in the gaseous state using the electron diffraction technique based upon the rotating sector.

The experimentally obtained distance distribution curve ( $\frac{\sigma(r)}{r}$  curve) is reproduced in Fig. 2, and below this curve line diagrams giving the internuclear distances (and their relative weights) for three

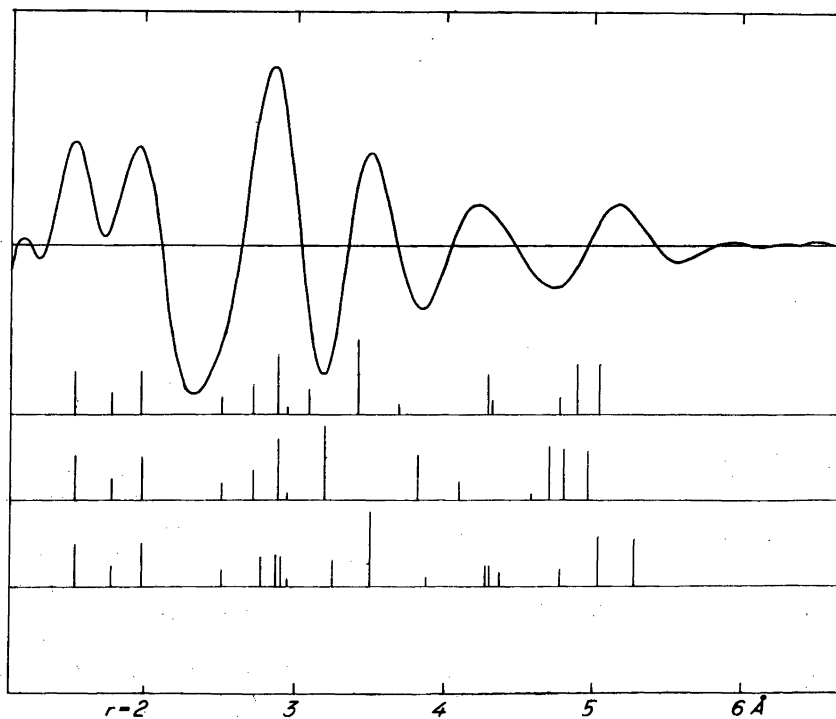


Fig. 2.

possible models: a) a model having the chlorine atoms in  $\epsilon$  position, the bromine atoms in  $\kappa$  positions (Fig. 1 a), and with all valency angles strictly tetrahedral, b) a corresponding idealized model of the second possible configuration (the chlorine atoms in  $\kappa$  positions, the bromine atoms in  $\epsilon$  positions, Fig. 1 b), c) a *distorted* model having the chlorine atoms in  $\epsilon$  position and the bromine atoms in  $\kappa$  position. It is easily recognized that the second line diagram cannot account for the maxima of the experimental curve and that the first is in fair agreement with the experimental result. It seems obvious, however, that some minor distortions of the valency angles will be necessary to bring the line diagram in full agreement with the experimental curve. First of all the C-Cl bond will have to be bent away from the chief axis of the carbon ring. We found that an angle of  $8^\circ$  between this bond and the directions of the chief axis leads to the best agreement with experiment. It is interesting to note that a distortion of the same kind and very nearly the same magnitude was observed in the corresponding tetrachloro-compound both in the crystal and in the vapour<sup>3</sup>. It is no doubt due to repulsive forces acting between the chlorine atoms and the nearest ( $\epsilon$  bonded) hydrogen atoms. In addition to this deviation from strictly tetrahedral valency angle a smaller distortion ( $3^\circ$ ) of the C-C-Br angle bringing the neighbouring bromine atoms a little further apart than in the idealized structure was introduced.

1. Hassel, O., and Lunde, K. To be published shortly.
2. Hassel, O., and Wang Lund, E. *Acta Chem. Scand.* In publication.
3. Hassel, O., and Wang Lund, E. *Acta Cryst.* 2 (1949) 309.

Received November 17, 1951.

## Hydrogen Peroxide Decomposition Catalyzed by Ferric Salt in Solutions acidified with Perchloric Acid

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In a previous work<sup>1</sup> the author has shown that the course of hydrogen peroxide decomposition catalyzed by ferric salt in solutions containing nitric acid deviates from the unimolecular scheme. Bray and Peterson<sup>2</sup> states in a paper published recently that this deviation should be ascribed to the presence of nitrate ions, as they have been able to reproduce the deviation in experiments made in solutions acidified with nitric acid, but not in solutions acidified with perchloric acid.

Abel<sup>3</sup> is likewise of the opinion that the deviation must be due to the influence of nitrate ions, although this author has not any experimental results on which to base this contention.

As the said deviation forms the actual experimental basis on which the author of the present work has established the mechanism proposed for the hydrogen peroxide decomposition catalyzed by ferric salt<sup>1,4,5</sup> the author considers it necessary once more to revert to this subject quite briefly by presenting the results of a single experiment with two repetitions. The experiment was made with hydrogen peroxide, ferric salt and acid in the same concentrations as those used for the purpose of the experiments of table 1 of the paper quoted above<sup>1</sup>, but this time the ferric nitrate and the nitric acid were replaced with ferric perchlorate and perchloric acid. The ferric perchlorate used was prepared by Robertson\* during his

\* C. A. Robertson, who has published several works dealing with this problem, *e. g.* *J. Am. Chem. Soc.* 45 (1923) 2493.