g/cm³; four (calc. 4.03) mols. in the unit cell. The only systematic absences occur in the $h0l$ reflexions for h odd and in the $0k0$ reflexions for k odd, and the space group is therefore $P2_1/a$.

KD, violet form. Plates {100}, elongated along the c axis. Monoclinic, with $a = 15.12$ Å, b = 13.70 Å, c = 9.15 Å, and $\beta = 115°$. Density 1.84 g/cm³; four (calc. 4.00) mols. in the unit cell. Systematic absences and space group as for the red form, $P2_1/$a.

RbD. The crystals have the same shape as those of the red form of KD. They are monoclinic, with $a = 15.97$ Å, $b = 13.22$ Å, $c = 11.02$ Å, and $\beta = 130°$. Density 1.96 g/cm³; four (calc. 4.03) mols. in the unit cell. The space group is $P2_1/$a. The $00l$ reflexions are very weak for odd values of l.

CsD. Monoclinic plates {001}, with $a = 13.90$ Å, $b = 10.64$ Å, $c = 11.54$ Å and $\beta = 92°$. Density 2.25 g/cm³; four (calc. 4.05) mols. in the unit cell. The hkl reflexions are absent for $h + k$ odd, and the $h0l$ reflexions for l odd. Possible space groups are $C2/c$ and Cc, the latter being the most likely one, as the molecule probably is asymmetrical.

Discussion of results. It will be seen that the red and violet forms of KD have the same space groups and fairly similar unit cell dimensions. The development of crystal faces is, however, quite different in the two cases, as {001} is predominant in the red form and {100} in the violet form. This may possibly be connected with the difference in reactivity of the two forms towards nitric acid. Red KD is isomorphous with RbD. An attempt was made to solve the structure of the latter by Patterson and Fourier projections along the b axis. The vector map indicated x = 0.10 and $z = 0.24$ as possible co-ordinates for the Rb atom, but we did not succeed in interpreting the corresponding Fourier map.

Grison [4] has determined the structure of. three polymorphic forms of N-picryl-p-iodoaniline, a compound which differs from HD in having no nitro groups in one of the benzene rings. Grison finds that the angle C-N-C at the amino-nitrogen is 138° and that the two benzene rings are rotated relative to one another through 65°. It appears likely that the corresponding angles in the dipicrylamine molecule are of the same order of magnitude, as it can be shown by means of a model that the introduction of nitro groups also in the other benzene ring may be compensated by suitable rotation of the ortho nitro groups.

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Polymorphism and Thermal Instability of 1ᴋ, 2ᴋ, 4ᴋ, 5ᴋ-Tetrabromocyclohexane

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Recently 1ᴋ, 2ᴋ, 4ᴋ, 5ᴋ-tetrachlorocyclohexane (m.p. 226° C) and 1ᴋ, 2ᴋ-dichloro-4ᴋ,5ᴋ-dibromocyclohexane (m.p. 240° C) have been prepared [1]. It was shown that both substances are dimorphous, corresponding modifications being isomorphous. The transition temperatures are 60−65° C and 90−95° C respectively. The tetrachloro-compound is stable above the melting point, but the dichloro-dibromo-compound, when heated above the melting point is transformed — at least to a large extent — into the stereoisomer of m.p. 171°

which has been shown to be the 1ε, 2э-dichloro-4ϰ, 5ϰ-dibromo-compound. The melting point of the "four kappa" dichloro-dibromo-compound found on rapid heating is 240° C, but heating slowly considerably lower values may be obtained.

The crystals of the "four kappa" tetrabromo-compound described by Haak and Wibaut [2] are isomorphous with the high temperature (β) forms of the corresponding tetrachloro- and dichloro-dibromo-compounds. It would therefore seem possible that this substance is also dimorphous, the crystals obtained by Haak thus being the high temperature (β) modification. The fact that Haak and Wibaut reports a melting ·point of 218° C, a figure lower than those found for the two isomorphous crystals containing chlorine, indicates a thermo-instability similar or even more pronounced than that of the dichloro-dibromo-compound.

Professor Wibaut kindly placed some crystals of the tetrabromo-compound at our disposal. The melting point of these crystals turned out to depend markedly on the rate of heating. On rapid heating (using a heating table) a melting point of 255° C was observed, however. If the melt is allowed to solidify and heated again the melting point is 180° C. This finding would seem to indicate that a nearly hundred per cent transformation into the ε,ε,ϰ,ϰ-isomer (m.p. 187° C) has taken place. Actually on addition of a nearly equal amount of the 187° isomer the m.p. is *not* lowered, but raised to 183° C.

In order to obtain the low temperature (α) modification of the "four kappa" tetrabromocompound, crystals of the β modification were dissolved in ethyl acetate Some drops of this solution were isolated, seeded with a very small crystal of the α modification of the "four kappa" dichloro-dibromo-compound and the solvent evaporated at room temperature. One of the crystals thus obtained was used as seeding crystal for the main part of the solution. The crystals obtained at room temperature turned out to be isomorphous with the α modifications of the tetrachloro- and dichloro-dibromo-cyclohexanes (comp. Table 1). The crystals heated above 125° C undergo a transition into the β modification. It is difficult, however, to determine the transition point with accuracy (compare what has been said about the other α—β transitions [1].

When solutions of halogens are added to the 1,4-diene the yield of the higher melting ("four kappa") compound seems to be very poor in the case of bromine, but very high in the case of chlorine. Starting with the 1,2-dichlorocyclohexene (4) the yield of the corresponding dichloro-dibromocyclohexane seems to be intermediate between those found in the two other cases. It appears rather surprising that the "four kappa" compounds containing bromine are so easily transformed into the ε, ε, ϰ, ϰ-compounds as one would expect the energy of the *free* molecule to be smaller for the "four kappa" compounds. The mechanism of transformation would indeed

Table 1. Crystallographic data, melting points and approximate transition points of 1ϰ, 2ϰ, 4ϰ, 5ϰ-tetra-halogeno-cyclohexanes.

	a	b	c	β	M.p.	Transition point
α $C_6H_8Cl_4$	6.13	6.74	10.72	98°	226° C	60— 65° C
α $C_6H_8Cl_2Br_2$	6.29	6.93	10.81	98°	> 240° C	90— 95° C
α $C_6H_8Br_4$	6.40	7.03	10.80	98°	> 255° C	120—125° C
β $C_6H_8Cl_4$	6.40	11.41	6.20	110°	226° C	60— 65° C
β $C_6H_8Cl_2Br_2$	6.79	11.75	6.20	110°	> 240° C	90— 95° C
β $C_6H_8Br_4$	7.23	12.32	6.32	110.5°	> 255° C	120—125° C

be worth while studying. In the case of the dichloro-dibromocompound, however, we have observed the evolution of hydrogen bromide both when melting the solid substance and when heating the substance in carbon tetrachloride solution to 200° C.

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Oxidation of Thiol Groups by Catalase

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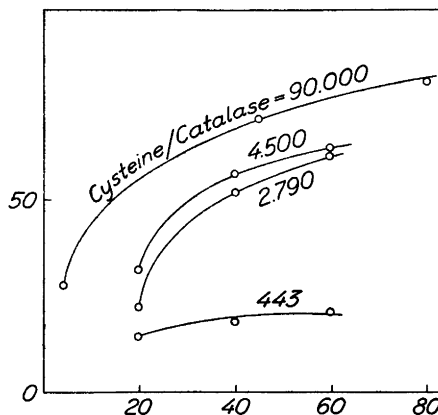

Fig. 1. *Guinea-pig liver catalase. 20° C. Phosphate buffer M/100. Ordonates: percent decrease of the rate constant for the hydrogen peroxide decomposition as determined according to Bonnichsen, Chance and Theorell [6]. Abscissae: time in minutes of the incubation of the catalase solution with cysteine.*

It is known that cytochrome-oxidase preparations in the presence of cytochrome-c and oxygen oxidize cysteine (Keilin [1]). We have found that the same reaction is effected by blood and liver catalase: oxygen is required, but neither cytochrome-c nor hydrogen peroxide.

The disappearance of the thiol groups was followed by titration of the thiol groups with the amperometric method of Kolthoff and Stricks [2] using a rotated platinum electrode, and the end product was identified by titrating the disulfide groups according to the same authors, after reduction with Na amalgam.

The rate of the catalytic action of catalase on cysteine oxidation is comparable to that of the system oxidase plus cytochrome-c: we obtained on a 10^{-3} M cysteine solution at pH 7 the same effect with 4.7×10^{-9} moles of catalase per ml as with a cytochrome-oxidase preparation whose Q_{O_2} was 212 per mg dry weight per hour (using 0.02 M succinate as substrate)

with the addition of 1.25×10^{-8} moles of cytochrome-c per ml.

The catalytic effect of catalase on the oxidation of cysteine (and similarly on the oxidation of reduced glutathione and thioglycolic acid) is much higher than the hemin catalysis shown by Krebs [3]. No
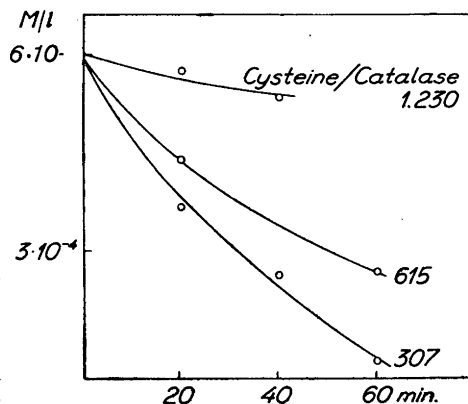

Fig. 2. *Horse blood catalase. 20° C. Phosphate buffer M/100. Ordonates: cysteine concentration per liter: Abscissae: time in minutes.*

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