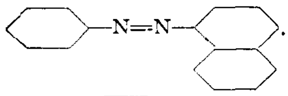
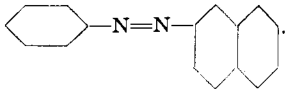
marked with an *x* in the tables and likewise the basic dyes which have the same structure as the acid dyes marked with an *x* were not available and therefore were not used in this study. Omitting the dyes marked with an *x* there are only thirty-one different formulas for dyes recorded which caused retardation of growth between a parallel pair of orthodome faces. Eighteen of these formulas represent nine pairs of dyes, one acid and one basic per pair which changed the crystal habit to type 1. Twenty-six of the forty-two dyes which changed the habit to type 1 possess nucleus A, . Sixteen possess nucleus B, . Five of the eight dyes which changed the habit in such a manner that stair-step-like planes were formed also possess nucleus A.

Acknowledgment.—The authors acknowledge their appreciation for suggestions offered by Dr. P. M. Harris, Department of Chemistry, Ohio State University.

Conclusions

The M and P dyes predominate in the formation of orthodome faces on cupric acetate while the A and O dyes predominate in the stair-step formation.

2. The majority of the dyes adsorbed possess nucleus A. This is in accordance with Rigterink and France's data[1] and a previous report by France and Wolfe.[1]

3. Nine pairs of dyes differing only in an —NH_2 group replacing an —OH group on the naphthalene ring have the same effect on the crystal habit of cupric acetate. This differs appreciably from the results obtained by Rigterink and France[1] in their studies of potassium sulfate.

4. Judging from the manner in which these dyes were adsorbed by crystals of known crystal lattice, one is led to conclude that the orthodome faces of cupric acetate are populated by alternate layers of positive and negative ions. It is also very probable that the carbon atoms of the acetate groups lie along the two-fold axis of symmetry. The lack of hardness and the boiling point of cupric acetate suggest the possibility of a layer lattice.

COLUMBUS, OHIO RECEIVED MARCH 3, 1941

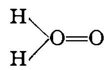
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 813]

The Crystal Structure of the Urea–Hydrogen Peroxide Addition Compound $CO(NH_2)_2 \cdot H_2O_2$

BY CHIA-SI LU, E. W. HUGHES AND PAUL A. GIGUÈRE

The molecular structure of hydrogen peroxide has been the subject of numerous investigations[1] during the last few years. No definite choice between the two proposed structures I and II[1,2] could be made from chemical evidence alone. Linton and Maass[3] favored structure II on the

I. HOOH

II 

$$\mathrm{\overset{H}{\underset{H}{>}}O{=}O}$$

basis of their determination of the dipole moments of hydrogen peroxide in solutions. Theilacker,[4] on the other hand, pointed out that the same dipole moment and parachor data could be equally well accounted for by structure I, if the OH groups were assumed to be free to rotate around the O–O bond. In 1934 Penney and Sutherland[5] made a quantum-mechanical calculation for this molecule by the method of electron pairs, and showed that the energy dependence on the azimuthal angle ϕ between the planes of the two OH groups is more dominantly governed by the interaction of the non-axis-symmetrical electronic distributions around the two oxygen atoms than by the interaction between the two hydrogen atoms. They found that structure III in which ϕ and θ ($= \angle$H–O–O) are both about 100° would be about 10,000 cal./mole more stable than either the *cis* or the *trans* configuration ($\phi = 0°$ or 180°). This structure gives a value of the dipole moment in good agreement with that determined

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[1] For a good summary, see W. Machu, "Das Wasserstoffperoxyd und die Perverbindungen," Verlag Julius Springer, Berlin, 1937.

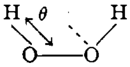
[2] See J. W. Mellor, "Treatise on Inorganic Chemistry," Longmans, London, 1922.

[3] E. P. Linton and O. Maass, *Can. J. Research*, **7**, 81 (1932).

[4] W. Theilacker, *Z. physik. Chem.*, **B20**, 142 (1933).

[5] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

III.



(*cf.* Fig. 5)

by Linton and Maass[3]; and also accounts for the Raman lines reported by Venkateswaran[6] and by Simon and Fehér,[7] which structure II fails to explain.

The O–O distance in hydrogen peroxide has been determined recently to be 1.48 Å.[8] by the electron diffraction method. The absorption spectrum in the photographic infrared has also been studied by Zumwalt and Giguère.[9] Their results confirm the above value for O–O distance; and also exclude definitely the possibility of either the *cis* or the *trans* configuration. Fehér and Klötzer,[10] in their preliminary investigation of the crystal structure of hydrogen peroxide, found that the crystals possess D_{4h} Laue symmetry, and that there are four molecules in a unit cell of the following dimensions: a_0 = 4.02 Å., c_0 = 8.02 Å. No detailed structure has yet been reported.

More complete information about the molecule of hydrogen peroxide is still very desirable. In view of experimental difficulties involved in X-ray diffraction work with hydrogen peroxide crystal itself, resulting from its instability and low melting point, we have chosen to investigate the crystal structure of the comparatively stable molecular compound which hydrogen peroxide forms with urea. This substance was first prepared by Tanatar,[11] and was found to be a stable addition compound with composition $CO(NH_2)_2 \cdot H_2O_2$. (The compound has found commercial use as a source of hydrogen peroxide and has been manufactured under the name of "hyperol" by a number of chemical manufacturers.) We expected that the molecules in this crystal would be held together only by hydrogen bonds, and that the molecular configuration of hydrogen peroxide would not be appreciably affected by the presence of urea. The well-established structure of the urea crystal[12] simplified the investigation to a considerable extent by providing information as to the dimensions of the urea molecule.

Method of Preparation.—The crystals used were prepared by the following procedures. A solution of urea in 30% hydrogen peroxide, in the molecular ratio 2:3, was heated in a Pyrex dish for a few minutes at a temperature of about 60°. When cool it was transferred to a crystallizing dish for slow evaporation and crystallization. Usually the crystals grew in the shape of needles, elongated in the *b* direction. If a small crystal of hyperol was added to the solution just before crystallization began and the solution was shaken gently for a few seconds, small plates would appear and would grow along the (010) basal plane. Crystals of this shape were useful for preparing X-ray photographs around the *a* and *c* directions.

These crystals, after removal from the solution, would retain their transparent faces and sharp edges for a few hours. Then the transparency would be gradually lost; and the crystals would be no longer suitable for goniometric work. In order to preserve good crystals before mounting on goniometer heads, we kept them in tightly stoppered vials and cooled them in solid carbon dioxide.

The hydrogen peroxide content of the hyperol crystals was determined to be 35.4% (calcd. 36.2%) by dissolving a small amount of the crystals in water and titrating with standard potassium permanganate in acid solution. Blank tests showed that the presence of urea does not interfere at all with this titration.

Physical Properties.—The density of the hyperol crystals was determined by the flotation method in a mixture of carbon tetrachloride and benzene to be 1.39 ± 0.01 g./cc.

The optical properties have been studied with the aid of Professor Ian Campbell and Mr. David Varnes of the Geology Department, to whom we are grateful for these measurements. The crystals are biaxial and show small positive birefringence. There are two rather good cleavages, one parallel to (100) and one nearly parallel to (110). There is probably a very poor cleavage parallel to (001). The indices of refraction have been determined by Professor Campbell by means of the immersion method in α-bromonaphthalene standards (which had been standardized interferometrically) to be α = 1.480 ± 0.003, β = 1.500 ± 0.002, γ = 1.550 ± 0.006, along the three crystallographic axes *a*, *b*, *c*, respectively.

X-Ray Examination.—A number of Laue photographs of the crystals, both needles and plates, were taken with "white" tungsten radiation ($\lambda_{\min}$ = 0.24 Å.). They showed D_{2h} symmetry, and established the identity in structure of the crystals with these two habits. Oscillation and rotation photographs around the three crystallographic axes were then taken with nickel-filtered CuKα radiation. The unit cell was found to have the following dimensions: a_0 = 6.86 ± 0.03 Å., b_0 = 4.83 ± 0.05 Å., c_0 = 12.92 ± 0.02 Å. Since the density is 1.39 g./cc., there are four molecules per unit cell, the calculated density being 1.45.

The presence of a few spurious spots on the oscillation photographs made the indexing somewhat uncertain. For further confirmation of the indexing, Weissenberg photographs were taken with unfiltered CuK radiation, two each for the three equators 0*kl*, *h*0*l*, *hk*0; one each

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(6) S. Venkateswaran, *Phil. Mag.*, vii, **15**, 263 (1933).

(7) A. Simon and F. Fehér, *Z. Elektrochem.*, **41**, 290 (1935).

(8) P. A. Giguère and V. Schomaker, unpublished preliminary results.

(9) L. R. Zumwalt and P. A. Giguère, results to be published shortly.

(10) F. Fehér and K. Klötzer, *Z. Elektrochem.*, **41**, 850 (1935); **43**, 822 (1937). See also G. Natta and R. Rigamonti, *Gazz. chim. ital.*, **66**, 762 (1936).

(11) S. Tanatar, *J. Russ. Phys.-chem. Soc.*, **40L**, 376 (1906); *Chem. Zentr.*, **79**, II, 583 (1908); *Chem. Abstr.*, **3**, 383 (1909).

(12) S. B. Hendricks, THIS JOURNAL, **50**, 2455 (1928); R. W. G. Wyckoff, *Z. Krist.*, **75**, 529 (1930); R. W. G. Wyckoff and R. B. Corey, *ibid.*, **89**, 462 (1934).

for the three first layer lines $1kl$, $h1l$, $hk1$, and the higher layer lines $h2l$, $h3l$. The presence of $(0kl)$ only with $k + l$ even, of $(h0l)$ only with l even, and of $(hk0)$ only with h even establishes the space-group as D_{2h}^{14}–$Pnca$.

As a powder pattern, probably arising from an accelerated decomposition of the crystals, heavily fogged the photographs when the exposure was extended to over twenty hours, each crystal specimen was used for one exposure only, and the length of exposure was reduced as much as possible. The Weissenberg photographs which were intended for intensity measurements were taken in sets of either three or five films, packed one behind another in the camera. The intensities of the CuKα reflections were then estimated by making use of an experimentally determined absorption factor of the films for CuKα radiation. (This is the technique of de Lange, Robertson and Woodward.[13]) As needle-shaped crystals could be readily grown and their dimensions could be easily chosen so that correction for absorption was negligible, the intensity data for the reflections $(h0l)$, $(h1l)$, $(h2l)$ are by far the most reliable (the exposure for the $(h3l)$ photograph was too short to be useful for intensity measurements). The dimensions of the plate-formed crystals were also so chosen that the correction for absorption was small and nearly the same for all reflections under examination. Thus, even for the $(0kl)$ and $(hk0)$ intensity data, the intensities as estimated from duplicate sets of photographs taken with different crystal specimens agreed fairly well. All intensities were corrected for Lorentz and polarization factors.

Determination of the Structure.—In the space-group D_{2h}^{14}–$Pnca$[14] there are three sets of four-fold special positions: (a), 000, $\frac{1}{2}00$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; (b), $00\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}0$; (c), $\frac{1}{4}0z$, $\frac{3}{4}0\bar{z}$, $\frac{1}{4},\frac{1}{2},\frac{1}{2} + z$, $\frac{3}{4},\frac{1}{2},\frac{1}{2} - z$; and one set of eight-fold general positions: (d), $\pm(xyz)$, $\pm(\bar{x},\frac{1}{2} + y,\frac{1}{2} - z)$, $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z)$, $\pm(\frac{1}{2} - x, \bar{y}, z)$. Since the urea molecules cannot have the molecular symmetry C_i, their carbon and oxygen atoms, four each in the unit cell, cannot occupy the special positions (a) or (b), which are centers of symmetry, and must be in two sets of special positions (c) with two parameters z_O and z_C. The eight nitrogen atoms must then take a set of general positions (d) with three parameters x_N, y_N, z_N. The eight oxygen atoms of the hydrogen peroxide molecules (designated later as OH to differentiate them from the oxygen atoms of the urea molecules) cannot be in the special positions (a) and (b), as is evident from bond length considerations. Nor can they be in the special positions (c), because of the following reasons. If these oxygen atoms should lie on the two-fold axes, F_{hk0} could not be numerically less than $4(f_O + f_C + 2f_{OH}) - 8f_N$ for even values of k, and all $(hk0)$ reflections with k even would be strong. Moreover, when k is odd, the value of $\frac{\sin 2\pi h x_N}{\sin 2\pi h' x_N}$ would be given by the ratio $\frac{F_{hk0}}{F_{h'k0}}\Big/\frac{f_{N(h'k0)}}{f_{N(hk0)}}$, regardless of the value of k. The facts that (260) was not observed experimentally; and that the ratios I_{210}/I_{410} were both greater than 1, while the ratio I_{250}/I_{450} was definitely less than 1, hence conclusively rule out this possibility. Therefore these oxygen atoms must occupy a set of general positions (d) with three parameters x_{OH}, y_{OH}, z_{OH}. With the hydrogen atoms ignored, there are eight parameters to be determined.

A preliminary structure model was constructed from the following considerations, based on the assumption that the molecules in the crystal are held together only by hydrogen bonds, and hence their molecular configurations would not be appreciably affected. For the urea molecules the following interatomic distances are given by Wyckoff and Corey's structure[12]: C–O = 1.25 Å., C–N = 1.37 Å., N⋯N = 2.32 Å. Hence we take $z_C - z_O \cong 0.097$, $z_N - z_C \cong 0.056$, and $r_N \cong$ 1.16 Å., where r denotes the distance from the respective two-fold axis. On the other hand, the O–O distance in the hydrogen peroxide molecules may be taken as 1.48 Å.,[8] so that $r_{OH} \cong$ 0.74 Å.

Along a two-fold axis each hydrogen peroxide molecule would be held to its neighboring urea molecule by hydrogen bonds N–H⋯O of about 3.0 Å. length; and because of the partial double-bond character of the C–N bonds in urea, the hydrogen bonds formed by the NH$_2$ groups would tend to be coplanar with the urea molecule. This leads to the condition $z_{OH} - z_N \cong 0.230$. We infer from the small birefringence of the hyperol crystal that the plane of the urea molecule is intermediate between the planes (100) and (010).

There are two other hydrogen atoms in the two NH$_2$ groups of urea and two more in the hydrogen peroxide molecule available for hydrogen-bond formation. From considerations of these hydrogen bonds we were led to a structure with the following preliminary parameters.

	O	C	N	OH
x	($\frac{1}{4}$)	($\frac{1}{4}$)	0.115	0.155
y	(0)	(0)	.175	.076
z	0.020	0.117	.173	.403

This suggested structure is confirmed by the

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(13) J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

(14) See "International Tables," Vol. I, Gebrüder Borntrӓger, 1935.

Patterson function[15] $P(\frac{1}{2},0,z)$, which shows maxima at the following values of z $(0 \leqq z \leqq \frac{1}{2})$: O–O: 0.000; O–C: 0.137; OH–OH: 0.194; N–N: 0.346; and N–OH: 0.424 (the two O–O peaks at $z = \pm 0.040$ combine into a peak at the origin; and the C–C peak at $z = 0.234$ is so small as to fall into the background).

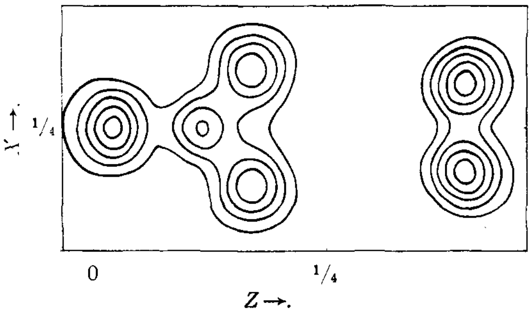

Fig. 1.—$\rho(x, z)$. Projection of electron density on (010).

These preliminary parameters were next tested by computing the $(h0l)$ and $(0kl)$ structure factors. In these computations the interpolated atomic scattering factors of James and Brindley[16] were used with a temperature factor $e^{-2.0(\sin \theta/\lambda)^2}$ (λ in Å.). The factors for the atoms N and OH were taken as $f_N + 2f_H$ and $f_O + f_H$. The agreement between the calculated and the observed structure factors was reasonably good, and it was possible to proceed to refine the parameters by Fourier synthesis.

The Fourier summations of $\rho(x, z) = \sum\sum_{hl} F_{h0l} \cos 2\pi(hx + lz)$ and $\rho(y, z) = \sum\sum_{kl} F_{0kl} \cos 2\pi (ky + lz)$ were carried out, first on Lipson–Beevers strips[17] at intervals of $\frac{1}{60}$; and next (using all available intensity data) on International Business Machine Corporation punched cards[18] at intervals of $^1/_{500}$. In the contour diagram $\rho(x, z)$ (Fig. 1) all atoms except the oxygen atoms of urea were satisfactorily resolved. From the contour diagram of $\rho(y, z)$ (Fig. 2), which gave almost identical values for the z-parameters, the parameters y_N and y_{OH} were obtained; the value of y_{OH} being poorly resolved on the diagram, was refined in the usual manner. The parameters so obtained are collected in Table I. We consider them to be reliable to ±0.002. A perspective drawing of this structure is shown in Fig. 3.

TABLE I

PARAMETER VALUES FOR HYPEROL

	O	C	N	OH
x	($\frac{1}{4}$)	($\frac{1}{4}$)	0.131	0.159
y	(0)	(0)	.169	.079
z	0.019	0.115	.168	.399

The agreement between the structure factors calculated on the basis of this set of parameters and the experimental values is in general satisfactory. Some of these structure factors are listed in Tables II–IV. In addition similar agreement was obtained for 193 forms $\{hll\}$ and $\{h2l\}$. Tables of observed and calculated structure factor values for these forms may be obtained from these laboratories.

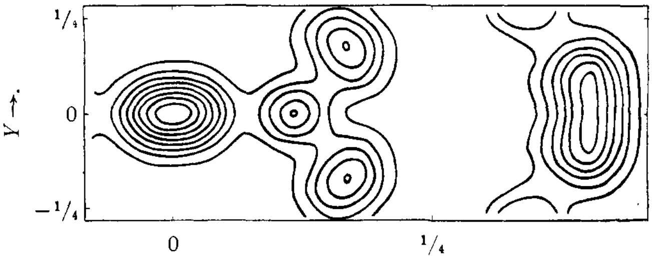

Fig. 2.—$\rho(y, z)$. Projection of electron density on (100).

Discussion.—Figure 4 shows a normal projection of a unit cell of the hyperol crystal onto the (001) plane. In these figures, underscored numbers give the heights, in Å., of the respective atoms

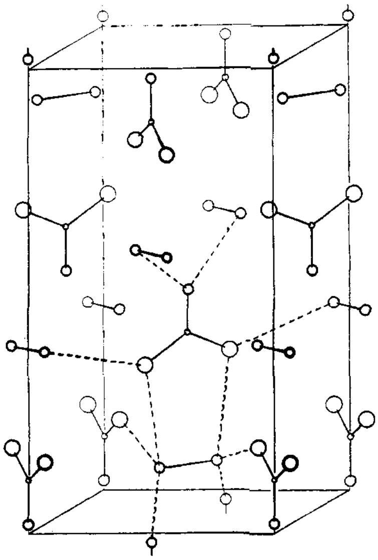

Fig. 3.—A perspective view of the unit cell of the urea-hydrogen peroxide crystal.

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(15) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935); D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

(16) R. W. James and G. W. Brindley, *Phil. Mag.*, **12**, 81 (1932); "International Tables," Vol. II.

(17) H. Lipson and C. A. Beevers, *Proc. Phys. Soc.* (London), **48**, 772 (1936).

(18) An account of this method will be published soon by P. A. Shaffer, Jr., and L. Pauling.

TABLE II

STRUCTURE FACTORS OF ($h0l$) REFLECTIONS

$h0l$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$	$h0l$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$
002	19	+17.2	604	7	−12.5
102	13	− 9.8	0.0.12	9	+11.9
200	64	−63.8	1.0.12	0	− 0.3
004	47	−56.8	508	12	+15.1
202	35	−28.1	4.0.10	0	+ 1.5
104	42	+38.1	2.0.12	0	+ 0.4
204	8	+ 7.8	606	4	− 8.7
006	12	+13.2	3.0.12	8	+ 8.5
302	5	+ 1.7	702	9	+15.3
106	22	−22.0	5.0.10	12	−13.4
304	28	+26.0	704	2	+ 2.5
206	< 1	+ 0.1	608	4	− 3.8
400	18	−21.0	0.0.14	14	−17.0
402	19	+19.5	1.0.14	3	− 3.0
008	15	+10.7	4.0.12	12	−11.2
108	41	−40.7	2.0.14	6	+ 6.2
306	< 1	+ 0.8	706	4	− 3.6
404	20	+26.0	3.0.14	0	− 1.4
208	16	−14.4	6.0.10	< 1	+ 3.3
502	17	−15.1	800	6	+12.1
406	< 1	− 1.0	5.0.12	7	−12.0
308	4	− 6.2	802	0	+ 0.1
0.0.10	17	+17.8	708	0	− 0.2
1.0.10	4	− 1.5	804	0	− 2.1
504	24	−27.2	0.0.16	5	− 6.9
2.0.10	11	−12.5	4.0.14	2	+ 4.9
408	14	+12.1	1.0.16	0	+ 0.2
506	8	+ 9.5	806	2	+ 7.6
600	3	+ 4.9	2.0.16	0	+ 1.6
3.0.10	14	+17.5	6.0.12	1	+ 4.2
602	3	− 4.6	7.0.10	< 1	+ 3.1

TABLE III

STRUCTURE FACTORS OF ($0kl$) REFLECTIONS

$0kl$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$	$0kl$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$
002	26	+17.2	044	6	+ 8.9
011	12	+10.5	0.0.12	11	+11.9
013	9	+ 6.5	039	18	+17.8
004	66	−56.8	046	3	+ 1.9
020	31	+33.2	0.2.12	6	− 5.9
015	54	+51.0	0.3.11	5	− 5.0
022	33	+32.7	0.1.13	0	+ 1.5
006	11	+13.2	048	6	+ 7.2
024	2	− 2.9	051	17	+16.7
017	23	+23.6	053	4	− 5.0
008	14	+10.7	0.0.14	15	−17.0
026	15	−16.0	055	4	− 3.9
031	9	+ 5.2	0.4.10	0	+ 1.7
033	26	+27.4	0.2.14	4	− 4.2
019	10	−13.1	057	3	+ 3.7
035	5	− 4.7	0.1.15	2	+ 1.8
028	17	+19.3	0.3.13	5	− 5.6
0.0.10	17	+17.8	0.0.16	4	− 6.9
037	5	+ 1.2	0.4.12	3	− 2.5
040	5	+ 1.4	060	3	+ 5.7
042	10	+ 9.4	059	4	+ 5.0
0.1.11	6	− 5.0	062	0	+ 1.2
0.2.10	18	+16.2	064	0	+ 0.9

TABLE IV

STRUCTURE FACTORS OF ($hk0$) REFLECTIONS

$hk0$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$	$hk0$	$\|F\|_{\text{obsd.}}$	$F_{\text{calcd.}}$
200	49	−63.8	610	7	+12.0
210	52	−56.5	620	7	− 5.2
020	54	+33.2	440	15	+16.3
220	31	−30.6	250	0	+ 2.0
400	17	−21.0	630	4	+ 2.2
410	16	+12.4	800	6	+12.1
230	17	−19.8	810	4	− 5.2
420	18	+17.7	450	2	+ 2.5
040	4	+ 1.4	640	5	−10.0
430	5	+11.6	820	1	+ 2.5
240	12	− 9.0	060	4	+ 5.7
600	5	+ 4.9	260	0	− 3.3

above the plane of projection or perspective; hydrogen bonds are represented by double lines. Interatomic distances are listed in Table V. The probable error of a bond length would be about ±0.03 Å. It is obvious that the urea molecules have the same configuration, to within experimental error, as in the urea crystal.[12]

TABLE V

INTERATOMIC DISTANCES IN HYPEROL

Chemical bonds Å.		Van der Waals distances Å.	
O–C	1.24	In same double layer	
C–N	1.34	N···N	3.68
N···N	2.31		3.98
HO–OH	1.46	O···OH	3.62
Hydrogen bonds Å.		C···OH	3.46
N–H···OH	3.04	N···OH	3.56
(along a two-fold axis)		Between adjacent double layers	
	2.94		
(between different two-fold axes)		C···O	3.46
		C···C	3.84
O–H···O	2.63	C···N	3.62
		C···OH	3.25
		C···OH	3.50
		N···OH	3.72
		HO···OH	3.48

Figure 5 shows a perspective view of the configuration of a hydrogen peroxide molecule. This configuration is essentially that proposed by Penney and Sutherland.[5] The two angles θ' (= the angle between an O–O bond and one of the adjoining hydrogen bonds) and ϕ' (= the azimuthal angle between the two hydrogen bonds from a hydrogen peroxide molecule) are 101.5° and 106°, respectively, each with a probable error of ±2°. These angles might differ considerably from the angles θ and ϕ, if we allow for the possibility of the hydrogen atoms not lying exactly along the hydrogen bonds. This skew configuration of hydrogen peroxide molecule admits of two possible stereochemical forms, and both

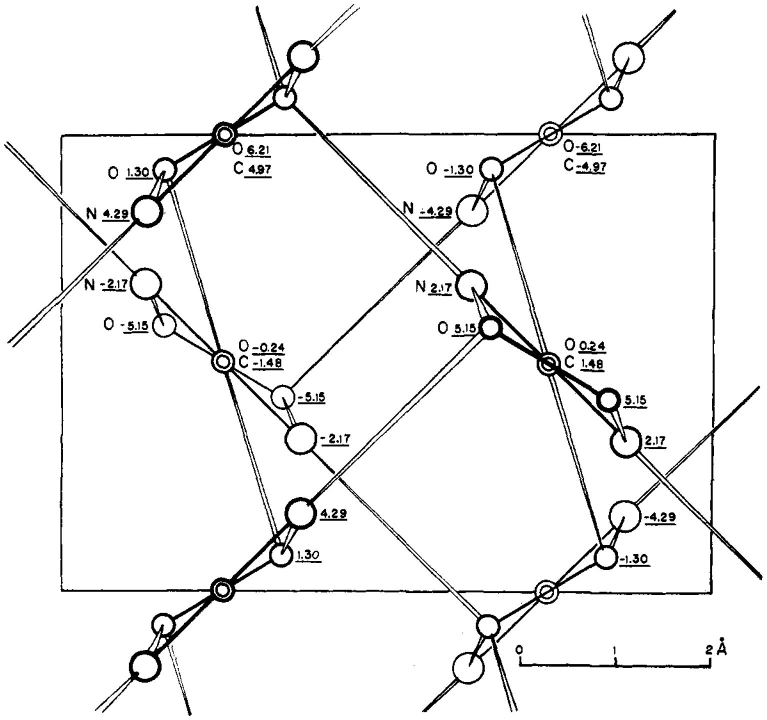
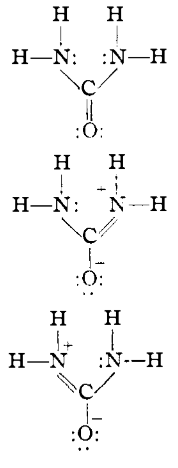


Fig. 4.—A normal projection of the unit cell onto (001). Underscored numbers are heights of atoms in Å. above plane of diagram. Tapered double lines represent hydrogen bonds.

forms are present in the hyperol crystal. By placing two hydrogen atoms on the two respective hydrogen bonds and taking the length of the O–H bond as 0.96 Å., we estimated the moments of inertia to be 33.2, 32.5 and 2.7 × 10^{-40} g. cm.^{2}, as compared with the following spectroscopic values of Zumwalt and Giguère[9] for hydrogen peroxide molecules in the vapor: 33.9$_5$ (harmonic average of two) and 2.79 × 10^{-40} g. cm.^{2}. We infer that our model is a possible configuration for the free hydrogen peroxide molecule. Dr. L. R. Zumwalt has pointed out to us that his analysis of the photographic infrared spectrum indicates the possible existence of two minima, separated by unequal potential barriers, one of which is quite low. It is interesting to note that our value of 1.46 ± 0.03 Å. for the O–O distance also confirms Giguère and Schomaker's value of 1.48 Å.,[8] which has been adopted recently by Schomaker and Stevenson[19] as a basis for revising the single covalent radius of oxygen.

Hydrogen bonds are mainly responsible for the packing of the molecules in the crystal. Each nitrogen atom of a urea molecule makes two hydrogen bonds, one of 3.04 Å. length to a peroxide oxygen atom lying near the same two-fold axis; and the other of 2.94 Å. length to another lying near a diagonally adjacent two-fold axis. Thus, half of the hydrogen bonds from urea molecules hold the hydrogen peroxide molecules in position to form "molecules" of hyperol, and the other half pack these "molecules" to form double layers. These double layers are held together by pairs of hydrogen bonds of 2.63 Å. length from hydrogen peroxide molecules to the carbonyl oxygen atoms lying on pairs of neighboring two-fold axes along the *b* direction. The double-layer feature is, however, not distinctly shown in the whole structure, on account of the very small separation of the double layers.

The partial double-bond character of the C–N bonds in a urea molecule, as discussed by Pauling,[20] results from the resonance of this molecule among the three following structures



On account of the formal charge on the carbonyl oxygen atom, the two hydrogen bonds O· · ·H–O to this atom tend to be stronger than in the ab-

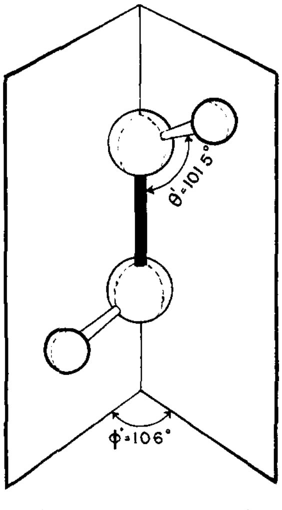


Fig. 5.—A perspective view of the hydrogen peroxide molecule. The hydrogen atoms (represented by smaller spheres) are assumed to lie along hydrogen bonds, and the length of the O–H bonds is taken as 0.96 Å.

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[19] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[20] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

sence of such resonance. This accounts for the fact that the value of 2.63 Å. for the length of these hydrogen bonds is much smaller than the corresponding value of 2.76 Å. in ice.[21] On the other hand, each oxygen atom of a hydrogen peroxide molecule serves as an acceptor of two hydrogen bonds O· · ·H–N of lengths 2.94 Å. and 3.04 Å. These are comparable in length to the hydrogen bonds N–H· · ·O of lengths 2.93 and 3.05 Å. connecting neighboring layers of glycine molecules in the crystal of glycine.[22] They are, however, distinctly longer than the hydrogen bonds N–H· · ·O of lengths 2.76 and 2.88 Å. in the same layer, since, in the case of glycine, resonance in the molecule leads to formal charges on both nitrogen and oxygen atoms, which then tend to make much stronger hydrogen bonds.

Our structure satisfactorily accounts for the cleavages. The crystal may be cleaved parallel to (100) or (110) by breaking only four hydrogen bonds of the type N–H· · ·O per unit cell. The strong hydrogen bonds O–H· · ·O and the close double-layer structure are mainly responsible to the poor cleavage parallel to (001). Cleavages along other planes would break more bonds.

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Summary

The crystal structure of the addition compound between urea and hydrogen peroxide, "hyperol," $CO(NH_2)_2 \cdot H_2O_2$, has been investigated. Its space group is D_{2h}^{14}—*Pnca;* and there are four molecules in a unit cell of the following dimensions: a_0 = 6.86 Å., b_0 = 4.83 Å., c_0 = 12.92 Å. The eight atomic parameters have been evaluated (Table I). The urea molecules have the same configuration, to within experimental error, as in the urea crystal. The configuration of the hydrogen peroxide molecules is that proposed by Penney and Sutherland, the two OH bonds lying in planes making a dihedral angle of about 106°. The O–O distance is 1.46 ± 0.03 Å. The packing of the molecules is essentially effected through hydrogen bonds.

PASADENA, CALIFORNIA RECEIVED FEBRUARY 18, 1941

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[21] W. H. Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).

[22] G. Albrecht and R. B. Corey, THIS JOURNAL, **61**, 1087 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA]

The Reaction between Hydrogen and Pyrex Glass

BY LATHROP E. ROBERTS AND CLARENCE BITTNER[1]

In a recent investigation of the thermal decomposition of dimethyl carbonate in this Laboratory,[2] hydrogen was identified as one of the principal products. Analysis showed, however, that a considerable portion of the hydrogen originally present remained unaccounted for. It seemed possible that this hydrogen had either diffused through the Pyrex glass wall of the reaction vessel, had been adsorbed by the glass, or had reacted with it. An extensive darkening of the glass indicated that reaction had occurred to some extent. Since hydrogen is frequently a product of thermal decompositions, and since a reaction of the hydrogen with the glass, or its adsorption, might affect the course of the decomposition, further investigation of the phenomenon was desirable.

Williams and Ferguson[3] found that, at 1 atmosphere and 640°, quartz glass was permeable to helium and hydrogen, the rate of diffusion for helium being 22 times that for hydrogen. They found that hydrogen did not diffuse through Pyrex under the same conditions. They attributed an observed darkening of the Pyrex to its reaction with hydrogen, and stated that this was not a surface reaction; but did not further investigate the phenomenon. Alyea,[4] working with bulbs packed with Pyrex powder, found that Pyrex adsorbed no hydrogen at 25°, but adsorbed it rapidly at 480°. He found the adsorption to be reversible, and recovered the greater part of the adsorbed gas, but did not attempt to measure accurately

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[1] Taken in part from a thesis submitted by Clarence Bittner to the Graduate College, University of Arizona, in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry, in May, 1939.

[2] D. Olson, "The Pyrolysis of Dimethyl Carbonate," Thesis, University of Arizona, 1938.

[3] Williams and Ferguson, THIS JOURNAL, **44**, 2160 (1922).

[4] Alyea, *ibid.*, **53**, 1324 (1931).