NOTES

The Crystal Structure of Calcium Cyanamide

By M. A. Bredig*

When the reactivity of calcium carbide as a function of its crystal structure was studied by means of X-ray diffraction methods,[1] calcium cyanamide, product of its reaction with nitrogen, also was included. Very considerable discrepancies were observed between the positions of the X-ray lines obtained and those reported in a previous attempt to determine the structure by U. Dehlinger.[2] Recently, calcium cyanamide was listed among the first thousand substances of which X-ray data were assembled for use with the Hanawalt X-ray method of chemical analysis.[3] An examination of the figures given for calcium cyanamide indicated that the preparation used must have contained very little calcium cyanamide and that merely the X-ray interferences of calcium carbonate, of calcium hydroxide, and of graphite, major impurities and decomposition products of calcium cyanamide, were recorded. A reëxamination of the X-ray data of this industrially important compound appeared desirable.

A Debye–Scherrer–Hull powder diagram of a commercial grade, finely pulverized calcium cyanamide, containing approximately 70% calcium cyanamide, was obtained with copper K_α radiation in an X-ray camera of 57.5 mm. diameter. The sample was contained in a thin-walled Lindemann glass tube, and was not rotated during the exposure. The X-ray interferences of calcium hydroxide, principal impurity of this sample, were very easily distinguished from the dotted lines of calcium cyanamide, due to the much coarser grains of the latter. They were used as reference lines with which the data, for calcium hydroxide, of Hanawalt, Rinn and Frevel, and those of Landolt-Börnstein, Supplement Vol. IIb, were in perfect agreement, as the table shows. The interplanar distances of calcium cyanamide, as measured and as calculated with new rhombohedral lattice constants, $\alpha = 39°55'$ and $a_{rh} = 5.40$ Å., corresponding to a hexagonal lattice with the constants $c =$

(1) H. H. Franck, M. A. Bredig, G. Hoffmann and Kin-Hsing Kou, Z. anorg. allgem. Chem., 232, 61, 75 (1937).

(2) U. Dehlinger, Z. Krist., 65, 286 (1927).

(3) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, Ind. Eng. Chem., Anal. Ed., 30, 479 (1938).

TABLE I

X-RAY POWDER DIAGRAM OF CALCIUM CYANAMIDE

Indices	$d_{exp.}$	$d_{calcd.}$	Intensities exp.	Intensities calcd.
111	4.92	4.95	m	140
C	3.39	3.38	v.w.	..
110	2.93	(2.93)	v.s.	370
$Ca(OH)_2$	2.63	2.63	s	..
211	2.422	(2.422)	m	80
221	2.170	2.180	m	110
$Ca(OH)_2$	1.928	1.93	s	..
$\bar{1}10$	1.853	1.840	m	82
$Ca(OH)_2$	1.786	1.79	m	..
322	1.753	1.760	w	62
102	1.723	1.725	w	35
$Ca(OH)_2$	1.685	1.690	w	..
333	1.637	1.650	v.w.	8
332	1.593	1.606	w	14
$\bar{1}11$		1.590		3
200	1.556	1.568	w-m	46
$Ca(OH)_2$	1.478	1.485	m	
220		1.470		17
$Ca(OH)_2$	1.442	1.450	w	..
$\bar{2}01$	1.447	1.455	v.w.	5

v.s. = very strong, s = strong, m = medium, w = weak, v.w. = very weak.

14.85 and $a = 3.67$ Å., are in very satisfactory agreement. The specific gravity becomes 2.29.

The rhombohedral lattice constants $\alpha = 43°50'$ and $a_{rh} = 5.11$ Å., and the hexagonal lattice constants $c = 14.1$ and $a = 3.91$, as given by Dehlinger, do not agree with his own experimental data, nor are they even compatible with each other. Dehlinger pointed to the agreement between the rhombohedral angle, calculated by him for the larger unit cell, containing four molecules of calcium cyanamide, with a figure (74°), determined on single crystals under the microscope by C. H. Warren.[4] However, two different angles were erroneously compared by Dehlinger, namely, the angle between the rhombohedral axes of the larger cell, calculated by him as 73°, and the cleavage angle of 74°, measured by Warren. Actually, 68°, as measured by Warren for the angle of the rhombohedral axes of the cleavage rhombohedron would have been the figure with which to compare Dehlinger's figure 73°, with no agreement to be observed. With Warren's figure 68°, however, the angle 68°15', as calculated from the data of the present investigation, agrees very well, and the

(4) C. H. Warren, Am. J. Science, [5] 2, 120 (1921).

same is true for the cleavage angle of 74°15′ (this paper) and 74° (Warren).

The structure of calcium cyanamide is entirely analogous to that of sodium azide, NaN_3, determined by S. B. Hendricks and L. Pauling[5] and confirmed recently by M. Bassière.[6] The cations occupy the positions 000, the carbon atoms the positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the nitrogen atoms the positions $\pm$ (uuu). The parameter u was assumed by Dehlinger as 0.37. With this figure, the distance C–N was calculated by Dehlinger as 1.59 Å., while actually the calculation from his own data, 14.1·(0.50 − 0.37), should have yielded 1.84 Å., an impossibly large value, compared with 1.17 Å. for the distance N–N, in sodium azide. A comparison of the intensities, as observed in the present investigation, with those calculated by using ionic scattering factors, as compiled by James and Brindley,[7] yields the parameter u = 0.422 ± 0.005. The distance C–N becomes 1.16 ± 0.08 Å., and the distance Ca–N 2.49 ± 0.04 Å., which compares with 2.48 Å. for Na–N in sodium azide.

No attempt was made to refine the discussion of the X-ray intensities as much as to find the possible asymmetry in the position of the two nitrogen atoms, and to thereby determine whether the cyanamide anion has the carbodiimide structure —N=C=N— or the true cyanamide form =N—C≡N. The agreement between the values of the distances in the azide anion, in sodium azide, as obtained by M. Bassière[6] through a discussion of the X-ray intensities, 1.10 and 1.26 Å., and those previously determined for the azide radical in cyanogen azide $(CN)N_3$ by E. Knaggs,[8] 1.11 and 1.26 Å., and in methyl azide by Brockway and Pauling,[9] has not been supported by the former with sufficiently convincing proof. The asymmetry in the N_3^- ion is, in fact, highly improbable.[10] It also seems quite doubtful whether the accuracy of the method employed was sufficient to determine, from the agreement of the X-ray intensities, as observed and as calculated, the

(5) S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925).

(6) M. Bassière, Compt. rend., **208**, 659 (1939).

(7) "Internat. Tabl. Determ. Cryst. Struct.," **II**, 571 (1935).

(8) E. Knaggs, Proc. Roy. Soc. (London), **A150**, 576 (1935).

(9) Brockway and Pauling, Proc. Nat. Acad. Sci. (Wash.), **19**, 860 (1933).

(10) The author is indebted to Professor K. Fajans, University of Michigan, for the private communication that the polarization theory of chemical binding leads to a symmetrical structure for ions such as N_3^- and CN_2^{2-}, while asymmetry is expected in the group N_3 when connected by bonds of small polarity with other atoms or radicals, as in HN_3, $(CN)N_3$, or CH_3N_3.

asymmetry in the distances C–O (1.13 Å.) and C–N (1.21 Å.),[11] in sodium isocyanate, NaNCO, another compound, isomorphous with calcium cyanamide.

The thanks of the author are due to Professor L. Thomassen for the permission to use the X-ray equipment of the Department of Chemical and Metallurgical Engineering of the University of Michigan.

(11) M. Bassière, Compt. rend., **206**, 1309 (1938).

Photoactivation of Adsorption of Hydrogen on Thorium Oxide[1]

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It is known[3] that activated adsorption of hydrogen requires an energy of activation. The hydrogen so adsorbed is supposed to be dissociated into atoms, this dissociation occurring on the surface of the catalyst during the adsorption. Confirmation of this assumption has been sought in the following experiments.

The temperature at which activated adsorption is observable is often several hundred degrees higher than the temperature of van der Waals adsorption, notably on oxide surfaces. We have sought to employ light instead of heat as the activating agent. In earlier work it has been found[4] that adsorption of certain solutes in solution could be photoactivated. Also, at 230°, the reaction between nitrous oxide and hydrogen in presence of boron nitride phosphors indicated a slight rise in reaction rate when irradiated with ultraviolet light. Other reactions on several catalysts and at different temperatures gave negative results.

We have studied the photo-activation of hydrogen adsorption on various catalysts with positive results which we shall illustrate with thorium oxide, prepared by calcination of the nitrate. The oxide so obtained was heated and evacuated in a quartz vessel at 700° for several hours. Electro-