

same is true for the cleavage angle of $74^{\circ}15'$ (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. Pauling⁵ 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 $\equiv (uuu)$. 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, $14.1 \cdot (0.50 - 0.37)$, 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 $u = 0.422 \pm 0.005$. 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 $-\text{N}=\text{C}=\text{N}-$ or the true cyanamide form $\equiv\text{N}-\text{C}\equiv\text{N}$. The agreement between the values of the distances in the azide anion, in sodium azide, as obtained by M. Bassière⁶ 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 $(\text{CN})\text{N}_3$ 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

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).

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Photoactivation of Adsorption of Hydrogen on Thorium Oxide¹

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It is known³ 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 found⁴ 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-

(1) The original version of this Note was received from the authors on August 13, 1941, and was accepted by the Editorial Board subject to some revisions which were embodied in a revised manuscript kindly prepared by Professor Hugh S. Taylor, which was sent to the authors on November 13, 1941, for their approval. Since it has proved impossible to get any word from occupied Belgium where the authors reside, it has seemed wisest, in order to avoid any further delay, to publish this present version now, in spite of the fact that the authors have had no opportunity to express their approval or disapproval of it.—THE EDITOR

(2) Associé du Fonds National Belge de la Recherche Scientifique.

(3) See "Catalysis," by G. M. Schwab, H. S. Taylor and R. Spence, D. Van Nostrand Co., New York, N. Y., 1937.

(4) See A. Hedvall, *Nature*, **143**, 330 (1939).

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

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

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

(8) E. Knaggs, *Proc. Roy. Soc. (London)*, **A160**, 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^- , 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 , $(\text{CN})\text{N}_3$, or CH_3N_3 .

lytic hydrogen was introduced to the cold adsorbent, to give a pressure of 2 mm. During the first seconds following the introduction of hydrogen a slight fall in pressure was observed owing to van der Waals adsorption.

Irradiation of the system, after the pressure becomes constant, with the light from a mercury lamp produces a regular and continuous decrease of pressure, which could be followed by means of a McLeod gage, during several hours. In favorable cases an irradiation of ten hours results in practically complete hydrogen adsorption. Further additions of hydrogen are adsorbed upon irradiation. Rates up to 1 cc. of hydrogen at 2.3 mm. pressure per minute, for 40 sq. cm. of irradiated surface and 18 g. of ThO_2 , have been observed. In one case, more than 8 cc. of hydrogen at N. T. P. was taken up by 100 g. of thoria. Thermally activated adsorption on our thoria sample was observable at 420° .

Adsorption is only observable with the irradiation from a cold mercury lamp, which indicates that resonance radiation is involved and that it is atomic hydrogen which is taken up by the adsorbent. The formation of atomic hydrogen may occur in the gas phase by the Frank-Cario mechanism with excited mercury atoms. We can also imagine molecules adsorbed on the surface by van der Waals forces being dissociated by transference of energy from mercury atoms. We cannot yet decide between these alternatives. Comparison with the rate of reduction of tungstic oxide in the Frank-Cario experiment suggests a diffusion of atomic hydrogen to the surface.

At 20–30 mm. pressure no photoactivation is measurable. After subsequent lowering of the pressure to 2 mm., photoactivation is again observable, but at one-half to one-third the normal rate. We interpret this as due to an adsorbed molecular layer of hydrogen protecting the adsorption centers. Lowering the pressure does not uncover all such centers. Complete evacuation is necessary. When this is done the normal rate of photoactivated adsorption at 2 mm. pressure is found.

After many days of alternate irradiation and evacuation at 700° the rate of adsorption slowly decreases and falls to one-tenth of its initial value. If after evacuation at 700° air is introduced at atmospheric pressure and room temperature and then evacuated at room temperature, introduction of hydrogen at 2 mm. pressure followed by

resonance irradiation restores the initial rate of hydrogen adsorption. The presence of oxygen on the surface of the catalyst is thus essential. This is confirmed by the observation that thoria samples heated in hydrogen to $700\text{--}800^\circ$ and then evacuated at this temperature do not show hydrogen adsorption on irradiation unless oxygen is again introduced. Analysis of the gas desorbed after either thermal or photoactivated adsorption shows the presence of oxygen only.

We have found an increase in the rate of thermally activated adsorption of hydrogen by chromium oxide and by reduced nickel when a certain amount of oxygen was introduced to the adsorbent.

Hedvall uses the term photoactivation of adsorption when the light is absorbed by the crystals and their activity is changed by the irradiation. We must consider, however, the cases in which adsorbent and gas are both excited by irradiation or the gas alone. In practice it will not be easy to decide between the several processes. We use the general term photo-activation of adsorption when we can measure an adsorption of gas by a surface owing to light irradiation.

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On the Structure of Fucosterol

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Fucosterol was first isolated from the alga, *Fucus vesiculosus*, by Heilbron, Phipers and Wright.¹ These workers showed that the sterol had the empirical formula $\text{C}_{29}\text{H}_{48}\text{O}$ and that it was a bond isomer of stigmasterol. They further stated that both double bonds were situated in the nucleus, since treatment with ozone failed to give ethylisopropylacetaldehyde. Additional evidence indicated the absence of a conjugated system, while the ease with which stigmastanol was formed on hydrogenation showed the lack of any "inert" double bonds. Later it was proved that one of the ethylenic linkages occupied the 5-6 position.² In view of Sobotka's³ suggestion that the second double bond might be located in the 11-12 position, which would render the sterol a suitable starting material for the synthesis of cortical

(1) I. M. Heilbron, R. F. Phipers and H. R. Wright, *Nature*, **133**, 419 (1934); *J. Chem. Soc.*, 1572 (1934).

(2) D. H. Coffey, I. M. Heilbron and F. S. Spring, *ibid.*, 738 (1936).

(3) H. Sobotka, "Chemistry of the Steroids," Williams and Wilkins Company, Baltimore, Md., 1938, p. 240.