melting at 164–167°. It is believed that these preparations were less pure. The resolidified phase exhibited the X-ray powder diffraction diagram recorded by Werner[5] for α-D-galactopyranose. It is probable that an equilibrium between the two anomers was established in the melt. In this equilibrium melt the α-D-pyranose anomer was capable of crystallizing, and as it crystallized the equilibrium in the molten part generated more of it, so that the whole melt solidified as α-D-galactopyranose, which then melted at the higher temperature of 164–167°, slightly below that of the pure α-D-form, 168–170°.

Equal parts of α-D-galactopyranose, m.p. 168–170°, and α-L-galactopyranose, m.p. 168–170°, were crystallized by dissolving in water, concentrating to a sirup and dissolving the sirup in methanol. The resultant optically inactive, crystalline phase melted at 145–148°. Previously reported values are: 163°,[7] 140–142°,[8] 143–144°.[9] The X-ray powder diffraction diagram of this preparation was identical with that of α-D-galactopyranose. This racemic phase is therefore a mechanical mixture of the α-D and α-L anomers.

(7) E. O. von Lippmann, *Ber.*, **55**, 3038 (1922).

(8) E. Fischer and J. Hertz, *ibid.*, **25**, 1247 (1892).

(9) C. Neuberg and J. Wohlgemuth, *Z. physiol. Chem.* **36**, 219 (1902).

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COMMUNICATIONS TO THE EDITOR

DISCONTINUITIES IN THE ADSORPTION ISOTHERM OF *n*-HEPTANE ON MOLYBDENUM DISULFIDE

Sir:

In the course of a recent investigation at Walker Laboratory of Rensselaer Polytechnic Institute, certain interesting experimental results were found regarding the appearance of discontinuities in the adsorption isotherm of *n*-heptane on molybdenum disulfide. These results, heretofore referred to in a discussion of observed transitions by Young, Beebe and Bienes,[1] were not included in the original publication on water and benzene adsorption on molybdenum disulfide.[2]

Reproducible discontinuities in the adsorption isotherm of *n*-heptane on molybdenum disulfide at 26.0° were observed at a relative pressure near 0.01 when five to ten minutes was allowed for equilibrium between doses. However, when more time was allowed after the initial and succeeding doses, the discontinuity disappeared, and a smooth isotherm, concave to the pressure axis, resulted. If the sample was reactivated and the shorter time between admission of doses resumed, the discontinuity again appeared. This was observed when the sample was previously degassed at room temperature as well as when "activated" at 200°. At higher pressures (above p/p_0 = 0.05) the time after each dose could be shortened considerably without effect.

The low pressure portion of an *n*-heptane adsorption isotherm showing the discontinuity as well as the low pressure portion of a smooth isotherm, in which several hours elapsed between the initial and second dose, is shown in Fig. 1. The adsorbent is "activated adsorbent 1" of molybdenum disulfide, as previously described.[2] The desorption isotherms showed the same appearance of discontinuities, except that several small steps were observed in the same pressure range. Numerous experiments with benzene and water adsorption on the same surface showed no vertical rises in the adsorption or desorption curves, but in experiments with toluene adsorbate a vertical rise at p/p_0 = 0.003 was obtained when allowing five to ten minutes between doses. The apparatus used was similar to that described by Harkins and Jura.[3]

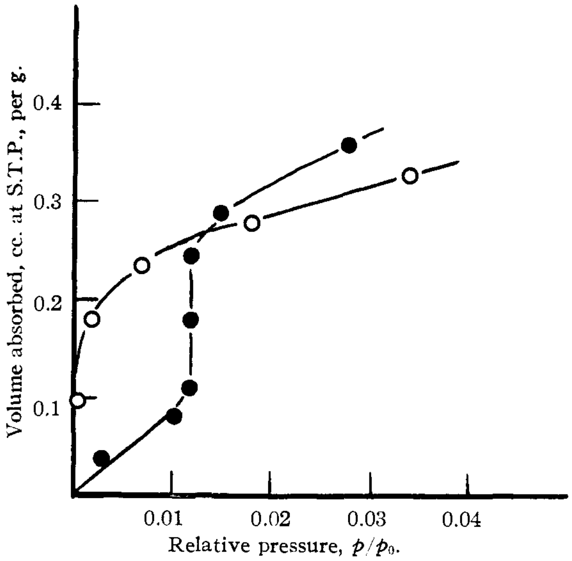

Fig. 1.—The absorption of *n*-heptane on molybdenum disulfide activated adsorbent 1: ●, five to ten minutes between doses; ○, up to eight hours between doses.

Although the appearance of a discontinuity in an isotherm may be a non-equilibrium condition which disappears in sufficient time, this does not eliminate the reality of the observation. As physical adsorption is a rapid process, an adsorbate which

(1) D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

(2) E. V. Ballou and S. Ross, *J. Phys. Chem.*, **57**, 653 (1953).

(3) W. D. Harkins and G. Jura, This Journal, **66**, 1356 (1944).

comes to equilibrium slowly occupies some surface positions which are either relatively inaccessible or are associated with an appreciable activation energy.

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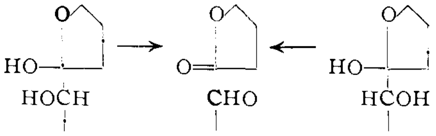
HARVARD UNIVERSITY E. VERNON BALLOU

RECEIVED JANUARY 11, 1954

ON THE NATURE OF THE GERMINE–ISOGERMINE–PSEUDOGERMINE ISOMERIZATIONS

Sir:

Shortly before discontinuance of research on the ester alkaloids of germine at the Squibb Institute, one of us (J.F.) found that germine acetonide hydrochloride (I) consumes one mole of potassium periodate and affords a crystalline oxidation product which reduces Tollens reagent, m.p. 274–276° dec., $[\alpha]^{23}\mathrm{D}$ $+2°$ (c 1.54, alc.). Calcd. for $C_{30}H_{45}O_8N$: C, 65.79; H, 8.28. Found: C, 65.85; H, 8.37. Further characterization of the substance at Harvard showed it to be an aldehydo-γ-lactone (II).



I II III

Thus infrared absorption bands at 3.65 and 5.79 μ are attributable to an aldehyde group, and a band at 5.62 μ is indicative of the γ-lactone function. Furthermore, the substance forms an oxime, m.p. 278–279° dec., $[\alpha]^{23}\mathrm{D}$ $+4°$ (c 1.47, alc.). Calcd. for $C_{30}H_{46}O_8N_2$: C, 64.03; H, 8.24; N, 4.98. Found: C, 63.93; H, 8.09; N, 5.12.

The close analogy of the germine–isogermine–pseudogermine isomerizations to the veracevine–cevagenine–cevine isomerizations suggests similar structures in the two series,[1] and indeed Barton and Brooks[2] have obtained an aldehydo-γ-lactone analogous to ours by periodic acid oxidation of anhydrocevine.

We have now oxidized pseudogermine acetonide hydrochloride (III) with potassium periodate and isolated an aldehydo-γ-lactone identical with that derived from germine (mixed m.p. and infrared spectral comparisons of aldehyde and oxime). Pseudogermine was prepared by isomerization of germine and of isogermine with sodium ethoxide in ethanol. The acetonide hydrochloride, m.p. 283–284° dec., was prepared by the standard procedure.[3] Calcd. for $C_{30}H_{47}O_8N \cdot HCl \cdot H_2O$: C, 59.63; H, 8.34. Found: C, 59.86; H, 8.44. The acetonide free base showed m.p. 238–239° dec., $[\alpha]^{23}\mathrm{D}$ $+27°$ (c 1.51, alc.). Calcd. for $C_{30}H_{47}O_8N$: C, 65.53; H, 8.62. Found: C, 65.46; H, 8.65.

The fact that the same aldehydo-γ-lactone is formed from both germine and pseudogermine indicates that these alkaloids contain the same α-ketol-5-membered hemiketal system and differ only in the orientation of the hydroxyl group of the α-ketol system as in I and III. These experimental results (coupled with the results of bismuth oxide oxidation in the cevine series[1c]) thus establish a deduction made by Dr. R. B. Woodward in September, 1953.

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RECEIVED FEBRUARY 4, 1954

(1) (a) S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **75**, 3248 (1953); (b) S. M. Kupchan, D. Lavie, C. V. Deliwala and B. Y. A. Andoh, *ibid.*, **75**, 5519 (1953); (c) S. M. Kupchan and D. Lavie, *ibid.*, **76**, 314 (1954).

(2) D. H. R. Barton and C. J. W. Brooks, *Chemistry and Industry*, **51**, 1366 (1953). We are indebted to Dr. Barton for communicating these results to us prior to publication.

(3) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **148**, 57 (1943).

THE SIGN OF OXIDATION–REDUCTION POTENTIALS

Sir:

The choice of sign for oxidation–reduction couples is indeed arbitrary, but it is not generally recognized where the arbitrary choice is made. If (1) the measured voltage of a cell is taken as positive and (2) the equation for the spontaneous cell reaction is written with the products on the right; then there is no choice of signs for the "half reaction." For example, consider the spontaneous reaction

$$Zn + 2H^+ = Zn^{++} + H_2 \qquad E° = +0.76 \qquad (A)$$

one must then write

$$H_2 = 2H^+ + 2e^- \qquad E° = 0.0 \qquad (B)$$

and

$$Zn = Zn^{++} + 2e^- \qquad E° = +0.76 \qquad (C_1)$$

This is necessary since the hydrogen and zinc couples must add up to give the equation and the potential for the completed reaction A. We then must also write

$$Zn^{++} + 2e^- = Zn \qquad E° = -0.76 \qquad (C_2)$$

because the laws of thermodynamics require that the sign of the free energy of a reaction be reversed if the equation is reversed. The sign conversion of C_1 and C_2 is, however, the same.

There is general agreement throughout the world, with regard to the arbitrary choices (1) and (2). G. N. Lewis in his selection of thermodynamic conventions was therefore compelled to choose the signs of his "standard electrode potentials" or "half reactions" consistent with C_1 and C_2. Unfortunately the older European conventions were

$$Zn = Zn^{++} + 2e^- \qquad E° = -0.76$$
$$Zn^{++} + 2e^- = Zn \qquad E° = +0.76$$

The resulting confusion has been most distressing. It was hoped that the Commissions of the Congress of Pure and Applied Chemistry meeting in Stockholm (1953) had resolved the difficulty but such does not seem to be the case. Thus, J. O'M. B.[1] has criticized my use of the Lewis conventions. To quote, "The author can be parochial in important matters. The sign convention for electrode potentials is presented dogmatically without mention that the one used is not that of the majority and that an International Commission has recently recommended its withdrawal."

The facts are that the Commission voted to accept the arbitrary choices (1) and (2) and the

(1) J. O'M. B., *Trans. Faraday Soc.*, **49**, 1503 (1953).