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

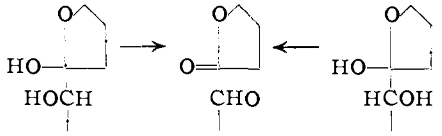
DIVISION OF APPLIED SCIENCE
HARVARD UNIVERSITY E. VERNON BALLOU

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., $[\alpha]^{23}\text{D}$ $+2°$ (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., $[\alpha]^{23}\text{D}$ $+4°$ (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., $[\alpha]^{23}\text{D}$ $+27°$ (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

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(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

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

sign conventions of C_1 and C_2. That is, they adopted the Lewis convention. They added, however, only C_2 could be called the *electrode potential*. I have no serious objection to this definition of electrode potential, although it is not really such, since the state of the electron is not defined. I would prefer to call C_1 the relative oxidation potential of Zn and C_2 the relative reduction potential of Zn^{++}. If anyone prefers to tabulate reduction potentials instead of oxidation potentials, he certainly has the right to do so, but it is ridiculous to claim that one is more fundamental than the other.

DEPARTMENT OF CHEMISTRY AND CHEMICAL
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RECEIVED JANUARY 30, 1954

A METHOD FOR THE STUDY OF CHLORINE ATOM REACTIONS. THE REACTION $Cl + CH_4 \rightarrow CH_3 + HCl$

Sir:

The reactions of chlorine with hydrogen and the hydrocarbons are chain reactions and as such their over-all rates are extraordinarily sensitive to the presence of traces of impurities, the condition of the reaction vessel and the intensity of the absorbed light in photochemical systems. Consequently, the many attempts which have been made to determine the rate constants of the elementary reactions of chlorine atoms, particularly those of type 1, have met with disproportionately little success.

$$Cl + RH = HCl + R \qquad (1)$$

However, the rate constant of the reaction 2 is known[1] to be given by $k_2 = 10^{13.9}$ exp. $(-5500 \pm 200/RT)$ moles^{-1} cc. sec.$^{-1}$. So that if the rate of

$$Cl + H_2 = HCl + H \qquad (2)$$

reaction 2 can be compared with that of reaction 1 in the same reaction system, k_1 may be found without having to make a direct estimate of chlorine atom concentrations: we have done this and determined k_1 for the reaction with methane in the following way.

Measured quantities of methane and hydrogen were sealed up in a 160 cc. Pyrex reaction vessel together with some 2.55×10^{-4} mole of chlorine, which is frozen out. The reaction is started by placing the vessel in a liquid or vapor bath which raises its temperature very rapidly. After a short interval to allow the vessel to attain the desired temperature, it is strongly illuminated. When a convenient period has elapsed the vessel is re-attached to a vacuum system and the residual hydrogen and methane separated from the products by low temperature distillations and adsorption in silica gel and measured.

The available evidence indicates that the hydrogen atoms and radicals formed will react with chlorine molecules for these reactions probably take place on every collision and hence the rate constants are approximately one hundred times those of any competing process, so that reactions 1 and 2 are the only ones by which methane and hydrogen are removed or formed. Then it can be readily shown[2] that if

$$-\,d[CH_4]/dt = k_1[CH_4]\,[Cl] \text{ and } -\,d[H_2]/dt = k_2[H_2][Cl]$$

then

$$k_1/k_2 = \log\{[CH_4]_1/[CH_4]_f\}/\log\{[H_2]_1/[H_2]_f\}$$

where the subscripts refer to the initial and final concentrations of the reactants. The reproducibility of k_1/k_2 for various ratios of methane to hydrogen is shown in the table. In Fig. 1 the logarithm of k_1/k_2 is plotted against $10^3/T$. The curvature of the points which is very small for a temperature range from 0° to 215° may be partially due to the effective temperature of the reaction being slightly below that of the bath at the higher temperatures. However, it seems that this can cause only a very small error in the slope of the line. It can be seen that the variation of k_1/k_2 with temperature is given by $k_1/k_2 = 10^{0.59}$ exp $(-1700/RT)$. Hence $k_1 = 10^{14.5}$ exp $(-3800/RT)$ mole^{-1} cc. sec.$^{-1}$.

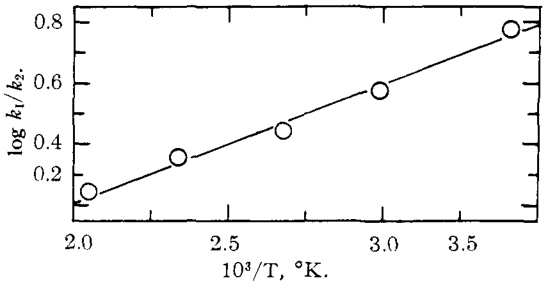

Fig. 1.

RUNS AT 100°

Initial concn., 10^{-7} mole cc.$^{-1}$ $[H_2]$	$[CH_4]$	Amount reacted, 10^{-7} mole cc.$^{-1}$ $\Delta[H_2]$	$\Delta[CH_4]$	k_1/k_2
28.34	27.96	2.22	6.96	2.76
35.98	44.81	2.75	8.98	2.81
58.15	52.19	4.72	7.54	3.01
66.57	33.80	5.27	6.46	2.57
76.77	33.27	5.24	7.72	2.88
81.34	51.16	4.09	8.62	2.79

Assuming that the standard entropy of the methyl radical is 45.5 e.u. and that the strength of the CH_3–H bond is 102.5 kcal./mole at 25°, we can make use of the approximate relation $k = \exp(\Delta S°/R)\exp(-\Delta H°/RT)$ which neglects the small variations of ΔS and ΔH with temperature. Then we find for the equilibrium constant of reaction 1

$$K_1 = 10 \exp(1000/RT)$$

Therefore the rate constant, k_{-1}, of the reverse reaction is $k_{-1} = 10^{13.6}$ exp $(-4800/RT)$ mole^{-1} cc. sec.$^{-1}$ which is equal to $10^{11.0}$ mole^{-1} cc. sec.$^{-1}$ at 150°. At this temperature Cvetanović and Steacie[3] find $k_{-1} = 10^{10.4}$ mole^{-1} cc. sec.$^{-1}$; although they report an activation energy of only 2.3 kcal./mole for reaction (−1). However, their activation energy is based on points at 25° and 150° only and it is known that the study of the reactions of methyl radicals derived from the photol-

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[1] P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953).

[2] W. M. Jones, *J. Chem. Phys.*, **19**, 78 (1951).

[3] R. J. Cvetanović and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158 (1953).