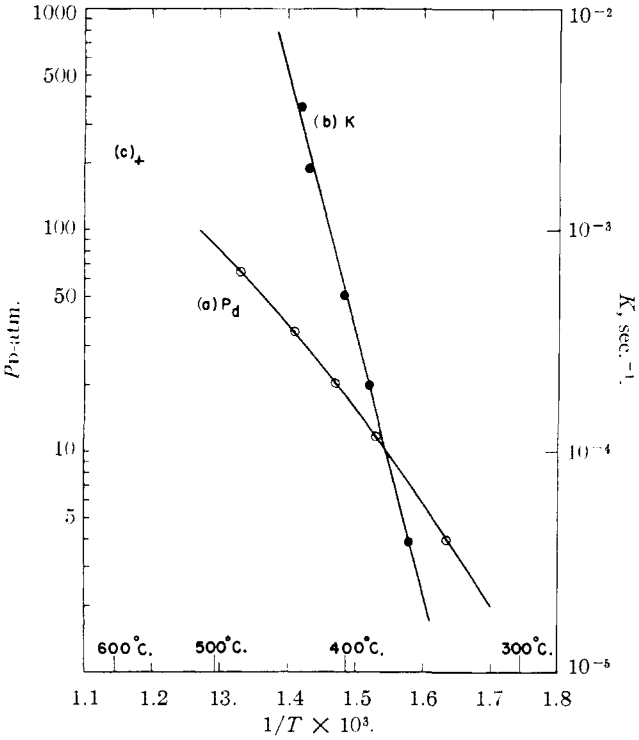

Fig. 1.—a, decomp. pressure of MgH_2; b, reaction rate constant for formation of MgH_2; c, Wiberg, Goeltzer and Bauer.[2]

The results here presented indicate that no catalyst is necessary.

Magnesium hydride prepared from fine turnings of high purity, doubly distilled magnesium by direct synthesis is a very light gray in color, is sensibly inert to laboratory air, and reacts slowly with water giving off bubbles of hydrogen. This behavior is in contrast to the high reactivity observed by Wiberg and Bauer for magnesium hydride prepared by the pyrolysis of diethylmagnesium.[3] The difference is probably due to the difference in particle size.

X-Ray examination of magnesium hydride shows that it crystallizes in the tetragonal system with a_0 = 4.516₈ Å. and c_0 = 3.020₅ Å. The measured density of 1.45 ± 0.03 g./cm.³ shows that there are two molecules in the unit cell. The calculated X-ray density is 1.419 g./cm.³.

The X-ray powder pattern shows that the two magnesium atoms in the unit cell are in a body-centered configuration, *i.e.*, 2Mg in (000) ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$). A consideration of all tetragonal space groups shows that there is one and only one possible choice of positions for the four hydrogen atoms leading to a plausible structure. This is

space group P4/mnm (D_{4h}^{14})
2Mg in (000) ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)
4H in $\pm (X,X,0)(X + \frac{1}{2}, \frac{1}{2} - X, \frac{1}{2})$
with $X = 0.306$

In this structure (rutile type) each magnesium is coördinated to six hydrogens at a distance of 1.95 Å., and each hydrogen is coördinated to three magnesiums. One H–H distance is 2.49 Å. and the others are 2.76 Å. The distance of 2.76 Å. compares favorably with the diameter of the H^- ion (2.72 Å.) as found in LiH. The one short H–H distance is characteristic of one anion–anion distance of the rutile type structure.

Magnesium hydride is optically uniaxial positive with refractive indices 1.95 for the ordinary ray and 1.96 for the extraordinary ray at the wave length 5893 Å.

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The Evaluation of Enzyme–Substrate Dissociation Constants[1]

BY RALPH LUTWACK AND CARL NIEMANN[2]

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For an enzyme-catalyzed reaction that can be described in terms of the steady-state process depicted in equation 1

$$E_f + S_f \underset{k_2}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_3} E_f + P_{1f} + P_{2f} \ldots \quad (1)$$

it is generally recognized that when $d[ES]/dt = 0$ and $[S_f] \doteq [S]$ the rate of disappearance of the specific substrate with respect to time is given by equation 2.

$$-d[S]/dt = k_3[E][S]/(k_2 + k_3)/k_1 + [S] \quad (2)$$

Briggs and Haldane[3] were the first to call attention to the fact that although the ratio $(k_2 + k_3)/k_1$ can be evaluated, and is numerically equal to the so-called Michaelis constant derived from the earlier equilibrium treatment of Michaelis and Menten,[4] knowledge of the value of this ratio for a particular system does not lead to an unambiguous estimate of the enzyme–substrate dissociation constant k_2/k_1 of that system. Because of many unsuccessful attempts to evaluate the ratio k_2/k_1, or the rate constants k_1 and k_2, from conventional kinetic data based upon the determination of the rate of disappearance of a specific substrate, or the rate of appearance of a reaction product, under the conditions specified above, we were surprised to find in a recent review[5] the statement that this goal had been achieved by Slater and Bonner[6] for the system succinic dehydrogenase–succinate. In view of the unquestioned acceptance of the treatment of Slater and Bonner[6] by Thorn,[7] by Dixon[8] and by Lindley[9] it appears worthwhile to call attention to the fact that the argument of Slater and Bonner[6] contains a tacit assumption which is not immediately apparent and which weakens, if it does not invalidate, their principal conclusion, *i.e.*, that k_1 and k_2 have

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(1) Supported in part by a grant from the National Institutes of Health, Public Health Service.

(2) To whom inquiries regarding this article should be sent.

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been evaluated for the system succinic dehydrogenase–succinate.

Slater and Bonner,[6] noting that fluoride and phosphate are competitive inhibitors of succinic dehydrogenase, determined the degree of inhibition obtaining under conditions in which the rate of the over-all reaction was varied by altering the concentration of the hydrogen acceptor, *i.e.*, methylene blue. In the course of their treatment, in which the symbols $e = [\mathrm{E}]$, $s = [\mathrm{S}]$, $v = -\mathrm{d}[\mathrm{S}]/\mathrm{d}t$ and $V = k_3'[\mathrm{E}]$ were employed, these authors arrived at the relation given in equation 3

$$V/v = 1 + (K_\mathrm{m}/s)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \quad (3)$$

where, in their symbolism, $K_\mathrm{m} = (k_2 + k_3')/k_1$, p and f the concentrations of phosphate and fluoride, and K_P, K_F and K_PF the respective enzyme–inhibitor dissociation constants. It was then argued that by expressing K_m in the form of its definition equation 3 may be transformed into equation 4

$$V/v = 1 + (k_2/k_1s)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) + (V/k_1se)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \quad (4)$$

and that in the case in which V/v and v are the only variables, the relation given by equation 5 results by setting $V/v = 1$.

$$-V = k_2e \quad (5)$$

The constant k_1 was then evaluated from the relation $K_\mathrm{m} = (k_2 + k_3')/k_1$. That this practice is dubious is evident from the following considerations.

(a) The necessary condition for the derivation of equation 5 is that V/v assume a value of unity.

(b) When this condition is applied to equation 3 it is seen that it is required that either $s \rightarrow \infty$ or $K_\mathrm{m} = 0$ since the quantity $(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \geq 1$.

(c) The condition is satisfactorily fulfilled when $s \rightarrow \infty$, this in fact being the definition of V, *i.e.*, $V = \lim\limits_{s \rightarrow \infty} v$.

(d) It is clear that the derivation of equation 5 by Slater and Bonner[6] is based upon setting $K_\mathrm{m} = 0$. In fact, the result itself is proof that this equality was assumed, since $V = k_3'e$ and hence $K_\mathrm{m} = (k_2 + k_3')/k_1 = 0$.

(e) The procedure used by Slater and Bonner[6] for the evaluation of k_1 is based upon the use of a value of k_2 obtained for the condition that $K_\mathrm{m} = 0$, *i.e.*, from equation 5, and the simultaneous use of values of K_m and k_3' for the system under conditions wherein $K_\mathrm{m} \neq 0$. It follows that the validity of a value of k_1 so obtained is entirely dependent upon a tacit assumed identity of the value of k_2 for the condition that $K_\mathrm{m} = 0$ with that for the condition that $K_\mathrm{m} \neq 0$. There is no reason to believe that such an extrapolation is necessarily valid.

Thus, even if it is granted that the system succinic dehydrogenase–succinate in the presence of fluoride and phosphate,[6] or of malonate,[7] can be described by equation 3 under the conditions employed by Slater and Bonner,[6] or by Thorn,[7] it is clear that this situation does not permit an unambiguous evaluation of k_1, k_2 or k_2/k_1 for the system succinic dehydrogenase–succinate.

The authors wish to express their indebtedness to Drs. R. Dilworth and R. J. Foster for their counsel.

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Observations on the Rare Earths. LXV. Naphthazarin Complexes of Certain Rare Earth Metal Ions

BY THERALD MOELLER AND MELVIN TECOTZKY

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A phase of rare earth metal chemistry which has received only limited attention is that of colored complexes formed with various organic reagents. In this connection, an early observation by Formánek[1] on the formation of red-violet to blue colors by reaction of the dye alkannet with thorium and rare earth metal ions is of interest. Major light absorptions in the wave length region 6120–6010 Å., with minor absorptions in the regions 5662–5559 Å. and 5262–5177 Å., were reported, with wave lengths decreasing in the series lanthanum to erbium. More recently, attention has been refocused upon this type of reaction by the development of a spectrophotometric beryllium determination using either alkannin or its unsubstituted parent, naphthazarin (5,8-dihydroxy-1,4-naphthoquinone),[2] and naphthazarin has been applied to the micro-determination of thorium.[3] Since in the determination of thorium interferences are caused by the rare earth metal ions, it has been of interest to study reactions of these species with naphthazarin. Spectrophotometric studies on such reactions and evaluations of the compositions of the colored complexes obtained are reported here.

Experimental

Materials.—Rare earth metal ions were used as 0.0021 *M* chloride stock solutions prepared from 98% to atomic weight purity oxides from the University of Illinois stocks. Naphthazarin was prepared and purified by the method of Toribara and Underwood.[4] It was used as 0.0021 *M* solution in absolute ethanol.

Absorption Spectra.—All absorption spectra were determined at *ca.* 25° with either a Beckman Model DU quartz spectrophotometer or a Cary Recording Spectrophotometer, using 1.00 cm. quartz cells with the former and 1.00 cm. demountable cells with quartz windows with the latter.

Color Reactions.—The colored complexes were obtained in solution merely by mixing the aqueous rare earth metal chloride solutions and the ethanolic naphthazarin solutions. Visible color changes resulted at concentrations as low as 0.31 mg. of rare earth metal ion per ml. In every instance, the red color of the naphthazarin was replaced by the reddish-blue of the complex. For absorption spectra measurements, solutions prepared from 5 ml. of the salt solution and 10 ml. of the naphthazarin solution and diluted to 100 ml. with absolute ethanol were found convenient.

Results and Discussion

Absorption Spectra.—Spectra obtained from solutions containing lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium and yttrium ions were all essentially similar except in

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[3] T. Moeller and M. Tecotzky, *ibid.*, **27**, in press (1955).

[4] T. Y. Toribara and A. L. Underwood, *ibid.*, **21**, 1352 (1949).