ing at 129° is anhydrous; $[\alpha]^{25}\mathrm{D}$ −128° (c 2.029 in 95% alcohol). In addition to the half menthyl ester, the half methyl ester, presumably formed by ester exchange from the methanolic potassium hydroxide solution, was isolated in 15% yield.

1-(−)**Menthyl 4-(+)menthyl 2-nitroterephthalate** was prepared by refluxing 3.49 g. of 1-(−)menthyl 2-nitroterephthalate with 5 cc. of pure thionyl chloride for one hour and removing the excess thionyl chloride at reduced pressure. To the residue was added 1.56 g. of (+)menthol[3] in 25 cc. of pyridine. After 24 hours the mixture was worked up in the usual way, and gave 4.09 g. of product that crystallized on standing. Recrystallization to constant melting point from 95% alcohol gave 2.76 g., m.p. 99.5–100.5°; $[\alpha]^{25}\mathrm{D}$ −59.7° (c 2.011 in benzene).

Anal. Calcd. for $C_{28}H_{41}O_6N$: C, 68.97; H, 8.48. Found: C, 69.08, 69.29; H, 8.53, 8.40.

(+)**Menthyl 2-nitroterephthalate** was prepared by the same procedure used to make the (−)menthyl ester. It melted at 86–88°; $[\alpha]^{25}\mathrm{D}$ +158° (c 2.031 in benzene). It was converted to the half ester, **1-(+)menthyl 2-nitroterephthalate**, m.p. 127.5–128.5°; $[\alpha]^{25}\mathrm{D}$ +127° (c 2.00 in 95% alcohol). The half ester was converted to 1-(+)**menthyl 4-(−)menthyl 2-nitroterephthalate**, m.p. 99.5–100.5°; $[\alpha]^{25}\mathrm{D}$ +59.1° (c 2.006 in benzene).

Anal. Calcd. for $C_{28}H_{41}O_6N$: C, 68.97; H, 8.48. Found: C, 69.03, 69.02; H, 8.48, 8.45.

A mixture of equal amounts of the two enantiomorphic esters melted at 80–87°.

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(3) J. Read and W. J. Grubb, *J. Soc. Chem. Ind.*, **51**, 329T (1932).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

Effect of Nearest Neighbor Substrate Interactions on the Rate of Enzyme and Catalytic Reactions

BY TERRELL L. HILL

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The object of this note is to illustrate with a simple example an approximate method of taking into account explicitly the effect of substrate interactions on the rate of surface-catalyzed reactions.

Let us consider nearest neighbor interactions on a surface with a large number B of equivalent adsorption sites. The problem of a linear enzyme, with B not necessarily large, has been discussed by Botts and Morales.[1] Consider the system (S is the substrate, S′ the product)

$$\mathrm{S}\begin{pmatrix}\text{solution, concentration } c;\\ \text{or gas, pressure } p\end{pmatrix} \underset{k_{-1}^{\circ}}{\overset{k_1^{\circ}}{\rightleftarrows}} \mathrm{S}\text{ (adsorbed)} \qquad (1a)$$

$$\mathrm{S}\text{ (adsorbed)} \xrightarrow{k_2^{\circ}} \mathrm{S}'\text{ (solution; or gas)} \qquad (1b)$$

The desorption of S′ is assumed fast enough that the number of S′ molecules on the surface is negligible.

In the absence of interactions we write the rates of the separate reactions as

$$v_1^{\circ} = k_1^{\circ}c(1-\theta) \qquad (2)$$

$$v_{-1}^{\circ} = k_{-1}^{\circ}\theta,\ v_2^{\circ} = k_2^{\circ}\theta$$

where $\theta = N/B$ and N is the number of adsorbed S molecules. Let the interaction free energy[2] between nearest neighbor S molecules be w_a, and between S and S′ nearest neighbors w_a'. At steady state, with N adsorbed S molecules, we assume that the probabilities of the various possible configurations of the adsorbed phase are given by a Boltzmann distribution (*i.e.*, the *adsorbed phase* is in *internal* equilibrium); the quasi-chemical approximation[3] is used to represent this equilibrium.

A consequence of the quasi-chemical approximation is the following: of the z sites nearest neighbor to a filled site, the probability that j will be filled is

$$P_j^{(f)} = \frac{z!}{j!(z-j)!}\,p^{z-j}(1-p)^j \qquad (3)$$

where

$$p = 2(1-\theta)/(\beta+1) \qquad (4)$$

$$\beta^2 = 1 - 4\theta(1-\theta)[1-\exp(-w_a/kT)]$$

Also, the probability that next to an empty site j will be filled is

$$P_j^{(e)} = \frac{z!}{j!(z-j)!}\,r^{z-j}(1-r)^j \qquad (5)$$

where

$$r = (\beta+1-2\theta)/(\beta+1) \qquad (6)$$

We assume that the rate constant for an S molecule being adsorbed onto an empty site with j nearest neighbor filled sites can be written as

$$k_1(j) = k_1^{\circ}\exp(-jw_b/kT) \qquad (7)$$

That is, the increase in the free energy of activation per nearest neighbor is w_b. Then the rate constant for an S molecule leaving a site with j nearest neighbor filled sites is

$$k_{-1}(j) = k_{-1}^{\circ}\exp[j(w_a-w_b)/kT] \qquad (8)$$

Similarly, the rate constant for an S′ molecule leaving a site with j nearest neighbor filled (with S) sites is written as

$$k_2(j) = k_2^{\circ}\exp[j(w_a'-w_b')/kT] \qquad (9)$$

The over-all rates in the presence of interactions are then

$$v_1 = c(1-\theta)\sum_{j=0}^{z} k_1(j)P_j^{(e)} \qquad (10)$$

$$v_{-1} = \theta\sum_{j=0}^{z} k_{-1}(j)P_j^{(f)} \qquad (11)$$

$$v_2 = \theta\sum_{j=0}^{z} k_2(j)P_j^{(f)} \qquad (12)$$

Equation (12) gives the desired rate of formation of product. Implicit in writing eq. (12) is the assumption that an S′ molecule, once formed, leaves the surface before the local nearest neighbor distribution determined by S–S interactions has time to readjust to S–S′ interactions. When simplified, eq. (12) leads to

$$v_2(\theta) = k_2^{\circ}\theta\left[\frac{2(1-\theta)}{\beta+1-2\theta}\right]^z\left(1 + \frac{2\theta\{\exp[(w_a'-w_b'-w_a)/kT]-1\}}{\beta+1}\right)^z \qquad (13)$$

The other rates become

$$v_1 = k_1^{\circ}c(1-\theta)f(\theta) \qquad (14)$$

$$v_{-1} = k_{-1}^{\circ}\theta\left[\frac{2(1-\theta)}{\beta+1-2\theta}\right]^z f(\theta) \qquad (15)$$

$$f(\theta) = \left\{1 + \frac{2\theta[\exp(-w_b/kT)-1]}{\beta+1}\right\}^z$$

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(1) D. J. Botts and M. F. Morales, to be published.

(2) E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).

(3) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, Chap. 10.

Although eq. (13) gives $v_2(\theta)$, to obtain $v_2(c)$ we need also $c(\theta)$. The steady state condition

$$v_1 = v_{-1} + v_2 \tag{16}$$

gives

$$c(\theta) = \frac{\theta}{1-\theta}\left[\frac{2(1-\theta)}{\beta+1-2\theta}\right]^z \left\{\frac{k_{-1}^\circ}{k_1^\circ} + \frac{k_2^\circ}{k_1^\circ}\left[\frac{\beta+1+2\theta\{\exp[(w_a' - w_b' - w_a)/kT] - 1\}}{\beta+1+2\theta\{\exp(-w_b/kT) - 1\}}\right]^z\right\} \tag{17}$$

When $k_2^\circ = 0$, eq. (17) reduces to the quasi-chemical equilibrium adsorption isotherm,[3] as expected. When $w_a' - w_b' - w_a = - w_b$, the $k_2^\circ = 0$ result is again obtained except k_{-1}° is replaced by $k_{-1}^\circ + k_2^\circ$.

One complication should be mentioned. Suppose w_a/kT and θ, at steady state, have values such that the adsorbed S molecules split into two surface phases[3] (determined by equal surface pressure and chemical potential in the two phases—since equilibrium within the adsorbed phase or phases has been assumed). Let θ_1 and θ_2 refer to the two different phases. Using eq. (13), (14) and (15), let us write the left-hand side of eq. (16) as $c\varphi_L(\theta)$ and the right-hand side as $\varphi_R(\theta)$. Then it is easy to show that in the region of phase splitting $c(\theta)$ is given by

$$c(\theta) = \frac{(\theta_2 - \theta)\varphi_R(\theta_1) + (\theta - \theta_1)\varphi_R(\theta_2)}{(\theta_2 - \theta)\varphi_L(\theta_1) + (\theta - \theta_1)\varphi_L(\theta_2)} \tag{18}$$

The present treatment applies to one, two or three dimensional lattices, the two dimensional case being the most important. The quasi-chemical method is exact in one dimension for B large, it may be recalled (Ising model).

This problem suggested itself in conversations with Drs. D. J. Botts and M. F. Morales concerning their work mentioned above.[1]

NAVAL MEDICAL RESEARCH INSTITUTE
BETHESDA, MARYLAND

Degradation of D-Glucose, D-Fructose and Invert Sugar in Carbonate-buffered Water Solutions

BY LAWRENCE J. HEIDT AND CATHERINE M. COLMAN[1]

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D-Glucose (dextrose), D-fructose (levulose) and the equimolar mixture of these sugars (invert sugar) have been found to be degraded completely into non-reducing substances under conditions commonly believed to result mainly in Lobry de Bruyn–van Ekenstein rearrangement into an equilibrium mixture of D-glucose, D-fructose and D-mannose[2] without the degradation of a large fraction of the sugars into non-reducing substances.[3] D-Fructose, for example, has been reported to establish in water at 100° and *p*H 7 to 12 an equilibrium value for the reducing power of the solution equal to about 93% of the initial value.[4]

The rate of degradation of the sugars to non-reducing substances in carbonate-buffered solutions at 100° is shown in Fig. 1. The reducing power decreases to about 10% of its initial value in 90 min. at *p*H 9.3 and in 16 min. at *p*H 10 in accord, for the most part, with the kinetics of a first order reaction with respect to the sugar and hydroxyl ion when the latter is estimated from the *p*H at 25° at constant total formal concentration of carbonate and bicarbonate. There is a slight induction period which is the longest in the case of D-glucose as is evident from Fig. 1. The small decrease in reducing power observed in earlier work[2a,4] at this temperature and over this range of *p*H may have been caused by a lowering of the *p*H by the acid produced in the reaction to the point where the rate of degradation became negligible before much of the sugar had been degraded.

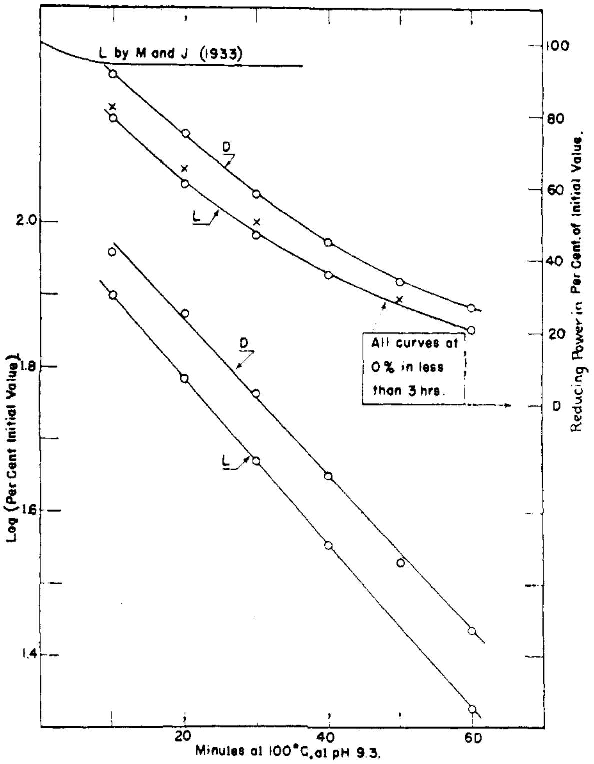

Fig. 1.—Rate of degradation at 100° of D-glucose (D), D-fructose (L) and invert sugar (X) to non-reducing material in water buffered with sodium carbonate and bicarbonate at 0.4 *M*. The solutions were initially 0.0042 *M* in hexose. The half-life of D-fructose at 100° is 6 min. at *p*H 10 and 28 min. at *p*H 9.3. Near the top of the figure is given the results reported by Mathews and Jackson[4] for D-fructose at 100° in water solution at *p*H 7 to 12.

The degradation of the sugars is accompanied by browning as is well known. The absorption spectra of the products have been found to exhibit a maximum which shifts from 2800 ± 25 Å. in the first stage of the reaction to 2650 ± 25 Å. as the reaction proceeds. This is shown in Fig. 2 which depicts the behavior of a solution of invert sugar 0.0042 *M* in hexose. Essentially the same results were obtained with D-glucose and D-fructose. The optical densities of the untreated solutions were negligible by comparison.

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[1] The authors are indebted to the Sugar Research Foundation, Inc., for a grant-in-aid in support of this work.

[2] (a) C. A. Lobry de Bruyn and W. Alberda van Ekenstein, *Rec. trav. chim.*, **14**, 203 (1895); (b) W. L. Evans, *Chem. Revs.*, **31**, 537 (1942).

[3] Some of the most convincing evidence supporting the rearrangement has been published by M. L. Wolfrom and W. L. Lewis, THIS JOURNAL, **50**, 837 (1928). Their results were obtained, however, under much milder conditions than we have employed.

[4] J. A. Mathews and R. F. Jackson, *Bur. Standards J. Research*, **11**, 619 (1933).