These findings are strongly indicative of a common "active center" in thrombin, chymotrypsin and trypsin, and phosphoglucomutase, enzymes of varying specificity from serum, pancreas, and muscle, respectively. Further sequence analysis of phosphopeptides obtained by acid and enzymatic hydrolysis are in progress and will be reported in a later publication.

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RECEIVED JANUARY 17, 1958

RATE AND MECHANISM OF THE ELECTROOXIDATION OF IODIDE[1]

Sir:

We wish to report the first known instance of an electrode reaction involving an electron transfer process which has substantiated second order kinetics. In a range of potentials between +0.6 and +1.1 v. (*versus* the normal hydrogen electrode), the anodic current component of the polarographic wave of iodide in 0.1 M perchloric acid at a conical platinum microelectrode corresponded to the reaction

$$2I^- \xrightarrow{k''_{ox}} I_2 + 2e^- \qquad (1)$$

and was found to obey the rate law

$$i_a = -10^{-6} FAk''_{ox}(a^0_{I^-})^2 \qquad (2)$$

where i_a (expressed in amperes) denotes the anodic component of the current, F is the faraday (expressed in coulombs), A is the effective area (in sq. cm.) of the indicator electrode, k''_{ox} denotes a rate constant (expressed in cm.^{4}/mole sec.) referred to unit electrode area, and $a^0_{I^-}$ denotes the molal activity of iodide at the electrode surface. In accordance with concepts of the absolute rate theory,[2] it was postulated that the second order rate constant in Eq. 2 was correlated with the relevant electrode potential E

$$k''_{ox} = (k''_{ox})^0 \exp\left[(1-\alpha)(E - E^0)\frac{2F}{RT}\right] \qquad (3)$$

where $(k''_{ox})^0$ defines a "specific rate constant" which is operative at the standard potential E^0 of the iodine–iodide couple and $(1 - \alpha)$ is the transfer coefficient. It was assumed that the converse process

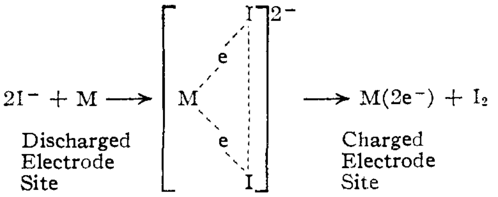
$$I_2 + 2e^- \xrightarrow{k'_{red}} 2I^- \qquad (4)$$

which yielded the cathodic component i_c on the current-voltage wave, was governed by first order electrode kinetics.[2] Using Eq. 2 and 3 as specific premises, the wave equation (5) was derived for anodic current–voltage curves of iodide

$$-i/(i - i_1)^2 = [(FAm^2_{Red}/f^2_{Red}k''_{ox}) + (k'_{red}f_{Ox}FAm^2_{Red}/k''_{ox}f^2_{Red}m_{Ox})]^{-1} \qquad (5)$$

Eq. 5 is based on principles[3] generally applicable to steady state situations in which both mass transfer (by diffusion and forced convection) and electron transfer are current-controlling factors. The symbol m in Eq. 5 denotes "mass transfer coefficients" which depend on the prevailing conditions of diffusion and flow, f represents activity coefficients, i_1 is the anodic limiting current, and i (the net current) = $i_a + i_c$; the subscripts Ox and Red refer to iodine and iodide, respectively.

Under judiciously controlled experimental conditions, Eqs. 2, 3 and 5 have been verified for ten current–voltage curves of iodide obtained in flowing solutions, covering a range of flow velocities between 100 and 700 cm./sec. The values of the relevant specific rate constants were determined as $(k''_{ox})^0$ = 0.03 cm.^{4}/mole sec. and $k'_{red})^0$ = 60 cm./sec. The corresponding rate laws are accounted for by the reaction mechanism



Acknowledgment.—This investigation was supported in part by Research Grants H-2342 and H-2342(C) from the National Heart Institute, National Institutes of Health, Public Health Service.

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RECEIVED JANUARY 20, 1958

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[1] From a thesis by R. A. Javick.

[2] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, pp. 575–580.

A NOVEL REARRANGEMENT OF TWO γ-BENZOYLOXYCYCLOALKANONES

Sir:

Treatment of 4-benzoyloxycyclohexanone,[1] m.p. 63–64.5°, $\lambda_{max}^{CCl_4}$ 5.80 μ, with 1.1 molar equivalents of potassium *t*-butoxide in *t*-butyl alcohol gave, in 53% yield, an *acidic isomer*, I, m.p. 67–68°, $\lambda_{max}^{CCl_4}$ 3.0–3.5, 5.84, 5.97 μ, λ_{max}^{EtOH} 244 mμ (ϵ 16,700) (*Anal.* Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.46; equiv. wt., 218. Found: C, 71.68; H, 6.55; neutralization equiv., 219), which gave a 2,4-dinitrophenylhydrazone of the corresponding methyl ester, m.p. 161–162° and 172–173°, $\lambda_{max}^{CHCl_3}$ 5.78, 6.20, 6.29 μ, $\lambda_{max}^{CHCl_3}$ 384 mμ (ϵ 29,400) (*Anal.* Calcd. for $C_{20}H_{20}N_4O_6$: C, 58.25; H, 4.89; N, 13.58. Found: C, 58.43; H, 5.09; N, 13.74). I is assigned a 2-benzoylcyclopropanepropionic acid structure on the basis of this evidence and these considerations: (i) it failed to add bromine and to reduce aqueous potassium permanganate, indicating the absence of ethylenic unsaturation; (ii) its infrared band at 5.97 μ bespoke the presence of a benzoylcyclopropyl system (*cf.* benzoylcyclopropane,[2] $\lambda_{max}^{CCl_4}$ 5.96 μ, with acetophenone, $\lambda_{max}^{CCl_4}$ 5.91 μ); although the position of this band could also be

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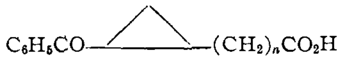
[1] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

[2] Sample kindly supplied by Dr. W. J. Close, Abbott Laboratories.

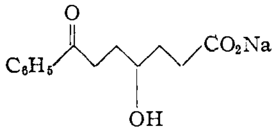
consistent with a $C_6H_5COC{=}C$ system, the strong C=C stretching band characteristic of this system was absent; (iii) its ultraviolet spectrum was consistent with the presence of either a simple benzoyl group or a benzoylcyclopropyl system, but not of a $C_6H_5COC{=}C$ system [*cf.*[3] acetophenone, $\lambda_{\max}^{EtOH}$ 242 mμ (ϵ 12,300), benzoylcyclopropane, $\lambda_{\max}^{EtOH}$ 244 mμ (ϵ 14,100), and crotonophenone, $\lambda_{\max}^{EtOH}$ 256 mμ (ϵ 17,400)]; further, the ultraviolet maximum of its 2,4-dinitrophenylhydrazone lay at a wave length slightly higher than that usual for alkyl phenyl ketone 2,4-dinitrophenylhydrazones (379 ± 1 mμ in $CHCl_3$)[4]; (iv) its n.m.r. spectrum, with peaks at 821, 944, 960, 1161, 1197 and 1225 cycles,[5,6] was consistent with the structure I (*cf.* the n.m.r. spectrum of benzoylcyclopropane, peaks at 947, 964, 1160, and 1222 cycles); (v) treatment with zinc chloride, acetic anhydride and acetic acid followed by alkaline hydrolysis gave a salt, formulated as II, which was oxidized with chromium trioxide and pyridine to 4,7-dioxo-7-phenylheptanoic acid (III) identified by comparison with an authentic sample.[7]

The reaction is considered to proceed *via* the intermediates IV and V. Sodium borohydride reduction of III gave 4,7-dihydroxy-7-phenylheptanoic acid γ-lactone, $n^{20}D$ 1.5390, $\lambda_{\max}^{liq.}$ 2.86, 5.64 μ (*Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.08; H, 7.16) which was oxidized with chromium trioxide and sulfuric acid in acetic acid to V, m.p. 75–76°, $\lambda_{\max}^{KBr}$ 5.59, 5.92 μ (*Anal.* Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.46. Found: C, 71.71; H, 6.49); acidification of II also gave V. Treatment of V with potassium *t*-butoxide under the conditions used for the original isomerization gave I in 64% yield.

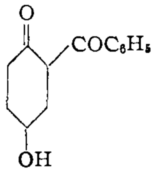
Similar treatment of 4-benzoyloxycycloheptanone, $n^{20}D$ 1.5363, $\lambda_{\max}^{CCl_4}$ 5.80, 5.84 (shoulder) μ (*Anal.* Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.12; H, 7.06), with potassium *t*-butoxide gave in 58% yield an *acidic isomer*,



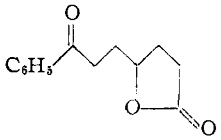
I, *n* = 2
VI, *n* = 3



II



IV



V

as a liquid, molecularly distilled at 65–75° (bath temperature; 10^{-3} mm.), $n^{20}D$ 1.5416, $\lambda_{\max}^{CCl_4}$ 3.0–3.5, 5.84, 5.96 μ, $\lambda_{\max}^{EtOH}$ 244 mμ (ϵ 14,700), n.m.r. peaks at 813, 944, 964, 1164, 1198 and 1225 cycles[5,6] (*Anal.* Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.43; H, 7.10), which gave a semicarbazone, m.p. 133.5–135° (*Anal.* Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.51; H, 6.72; N, 14.53) and a 2,4-dinitrophenylhydrazone of the corresponding ethyl ester, m.p. 127.5–128.5°, $\lambda_{\max}^{CHCl_3}$ 5.78, 6.18, 6.26 μ, $\lambda_{\max}^{EtOH}$ 377 mμ (ϵ 24,400). (*Anal.* Calcd. for $C_{22}H_{24}N_4O_6$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.79; H, 5.58; N, 12.91). This product is formulated as VI on the basis of the close similarity of its properties to those of I.

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[3] R. P. Mariella and R. B. Raube, THIS JOURNAL, **74**, 521 (1952).

[4] F. Ramirez and A. F. Kirby, *ibid.*, **75**, 6026 (1953).

[5] On the Bothner-By scale, in which the aromatic and methyl proton resonance peaks of toluene are assigned values of 1000 and 1197 cycles, respectively.

[6] We thank Mr. Edwin A. Chandross for these measurements.

[7] E. A. Kehrer, *Ber.*, **34**, 1263 (1901).

BOOK REVIEWS

Bacterial Fermentations. CIBA Lectures in Microbial Chemistry. 1956. By H. A. BARKER, Professor of Microbial Biochemistry, University of California, Berkeley, California. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1957. vii + 95 pp. 13 × 19 cm. Price, $3.00.

This is the first book in the series: CIBA Lectures in Microbial Biochemistry. These lectures were established in 1955 at the Institute of Microbiology, Rutgers, The State University of New Jersey, through the support of the CIBA Pharmaceutical Products, Inc., Summit, N. J. The lectures are delivered in the spring of each year at the Institute.

This little volume of ninety pages, plus index, is packed with a gratifying amount of factual material. The topics covered in this volume are: Biological Formation of Methane (Chap. 1), The Chemistry of Butyric Acid-Butanol Fermentations (Chap. 2), and Fermentations of Nitrogenous Compounds (Chap. 3).

In the first chapter the taxonomy of the methane-producing bacteria is discussed together with a very useful account of the author's methods for isolating and culturing these organisms. Progress on this phase of the problem has been slow the author states since the isolation of pure cultures, "has been difficult and in many instances impossible to achieve." In the other two chapters the reader is referred to standard texts and the literature for information on classification and details of culture methods.

Primarily the emphasis is on the chemical pathways by which the various substrates are or appear to be broken down