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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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

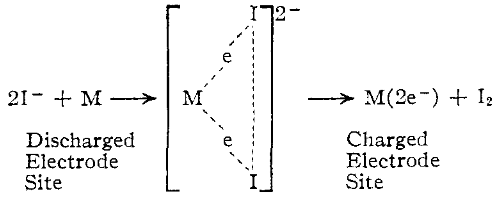
$$I_2 + 2e^- \xrightarrow{k'_{red}} 2I^- \qquad (4)$$

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

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

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_l 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



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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.