Table I. Intepretation of Current–Voltage Waves

Current–voltage wave[a]	Applicable limiting current eq[b,c]	Corresponding electrode process
II$_2$	$-i_2 = $ (constant)$\cdot$ $D_{O_2^-}{}^{-2/3} C_{O_2^-}$	$O_2^- = O_2 + e$
II$_3$, cathodic portion	$i_{3,c} = $ (constant)$\cdot$ $D_{O_2^-}{}^{-2/3} C_{O_2^-}$	$O_2^- + e = O_2^{2-}$
II$_3$, anodic portion	$-i_{3,a} = $ (constant)$\cdot$ $D_{O_2^-}{}^{-2/3} C_{O_2^{2-}}$	$O_2^{2-} = O_2^- + e$

[a] Identified in Figure 1. [b] Based on eq IV; D and C denote diffusion coefficients and bulk concentrations, respectively. [c] Cathodic and anodic currents are assigned positive and negative values, respectively.

species (superoxide), both processes involving a one-electron transfer. This accounts for experimental result V. Our data also revealed the following correlation between the "nitrite wave" (II$_1$), on the one hand, and the superoxide and peroxide waves (II$_2$ and II$_3$), on the other hand.

$$|i_1|D_{NO_2^-}{}^{-2/3} = |i_{3,a}|D_{O_2^{2-}}{}^{-2/3} + 1.5|i_2|D_{O_2^-}{}^{-2/3} =$$
$$|i_{3,a}|D_{O_2^{2-}}{}^{-2/3} + 1.5|i_{3,c}|D_{O_2^-}{}^{-2/3} \quad (VI)$$

Equation VI is evidently consistent with the stoichiometry inherent in eq I$_1$ and I$_2$ (= generation of 1 mole of nitrite per mole of peroxide, and of 1.5 moles of nitrite per mole of superoxide).

Assuming the prevalence of Nernst-controlled electron-transfer equilibria, derivations based on well-known principles of polarographic theory yielded the "wave equations" VII and VIII, where $i(E)$ denotes the current at potential E and $E_{1/2}$ the half-wave potential. For II$_2$ at 265°

$$E = E_{1/2} + \frac{2.3RT}{F} \log \frac{i(E)}{i_2 - i(E)} \quad (VII)$$

For II$_3$ at 265°

$$E = E_{1/2}' + \frac{2.3RT}{F} \log \frac{i_{3,c} - i(E)}{i(E) - i_{3,a}} \quad (VIII)$$

The relevant Nernstian slopes determined from our experiments were 0.109 ± 0.002 v for II$_2$ and 0.106 ± 0.003 v for II$_3$, which is in good agreement with the theoretical assignment of $(2.3RT/F) = 0.107$ v in eq VII and VIII.

The "oxygen- and electron-transfer chemistry" postulated in equation sequence I–II was further confirmed by the following observations: (a) voltammograms similar to Figure 1 were obtained when sodium peroxide (in lieu of sodium oxide) was equilibrated with the alkali nitrate solvent melt, except that $|i_1|$ was relatively smaller (due to reaction I$_2$ occurring in the absence of reaction I$_1$); (b) direct equilibration of the solvent with pure potassium superoxide (in the absence of peroxide, oxide, and nitrite) yielded $i_{3,c} = -i_2$ (in accordance with eq V), but i_1 and $i_{3,a} = 0$.

The reproducibility of the results reported in this communication was critically contingent on the use of platinum-lined electrolysis cells (in order to obviate contact with silica) and on the presence of an inert and dry supernatant atmosphere. Otherwise, side reactions of the type $SiO_2 + O^{2-} = SiO_3^{2-}$ and $O^{2-} + H_2O = 2OH^-$ occurred, which may well account for discrepant reports in the literature. Furthermore, we found that bubbling of gaseous oxygen through the melts converted peroxide quantitatively to superoxide ($O_2^{2-} + O_2 \rightarrow 2O_2^-$) en-

gendering a decrease of $i_{3,a}$, accompanied by a concomitant enhancement of both $i_{3,c}$ and i_2; due to this effect, the superoxide generated *via* reaction II$_3$ did not contribute to i_2.

In the formulation of eq I and II, the customary "chemical shorthand" (as is practiced when writing H$^+$ in lieu of H$_3$O$^+$) was employed, ignoring solvation. However, solvation effects may be important in view of our (*a priori* unexpected) finding that nitrite could coexist with peroxide and superoxide. Further pertinent work is in progress.

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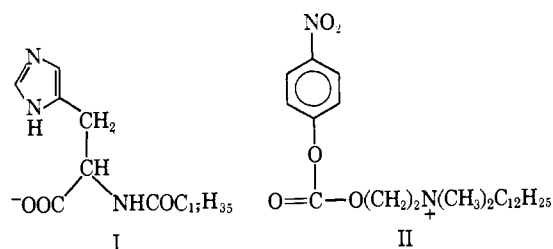*University Park, Pennsylvania 16802*
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Acceleration of *p*-Nitrophenyl Ester Cleavage Due to Apolar Bonding. A Model for Biologically Significant Apolar Interactions[1,2]

Sir:

There has been much speculation concerning the nature and significance of apolar bonding in biologically active molecules, specifically in the maintenance of structure and mode of action of enzymes.[3] The interdependence of all the weak forces involved in the maintenance of enzyme structure and function makes difficult the direct study of apolar bonding in such a complex system. An insight into the role played by apolar bonding in enzymatic catalysis may be gained without this difficulty by studying a model system. This model system should exhibit some of the important characteristics of enzyme-catalyzed reactions, characteristics dependent upon apolar interactions.

We wish to report such a model system exhibiting substantial catalytic effects which are the result of prior formation of a 1:1 catalyst–substrate complex held together by apolar bonding. Since the catalyst I con-

tains an anionic detergent portion and the substrate II a cationic detergent portion, interaction to form the catalyst–substrate complex appears to be similar to the strong binding observed between oppositely charged detergent molecules.[4] The demonstration of Michaelis–Menten (saturation) kinetics, product inhibition, large salt effects, and urea denaturation in this system serves to verify its enzyme-like nature.

(1) Part I in a series on selective catalysis.
(2) This research was supported by the Petroleum Research Fund, Grant 3190-B, and by a National Science Foundation Undergraduate Research Participation Grant to Wellesley College.
(3) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959); I. M. Klotz, *Science*, **128**, 815 (1958).
(4) R. L. Letsinger and T. E. Wagner, *J. Am. Chem. Soc.*, **88**, 2062 (1966).
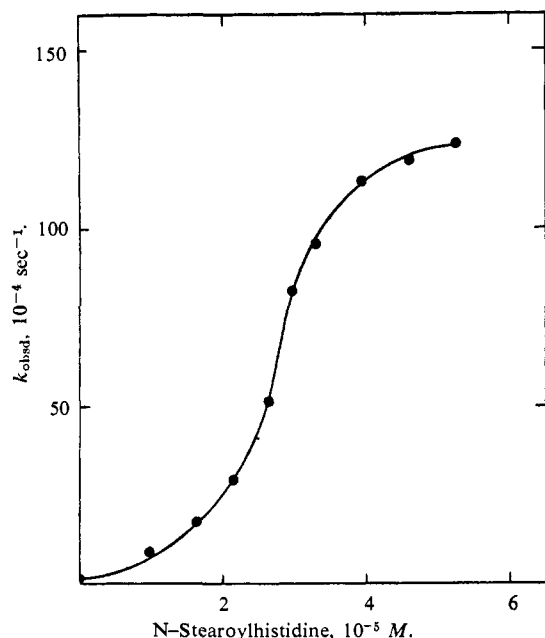
Figure 1. The effect of increasing catalyst concentration on the rate of reaction between I and II at 25°, pH 7.3; concentration of II (3.3 x 10^{-5} M) remains constant.

The substrate II was synthesized by refluxing 0.02 mole (1.78 g) of N,N-dimethylaminoethanol[5] and 0.02 mole (5.98 g) of 1-bromododecane in 25 ml of methanol for 24 hr, recovering the crystalline N-dodecyl-N,N-dimethylhydroxyethylammonium bromide following cooling, and treating 0.01 mole (3.384 g) of this compound with 0.01 mole (2.02 g) of p-nitrophenyl chloroformate[6] in 10 ml of dry pyridine. Evaporation of the pyridine yielded a residue which when taken up in 5 ml of dioxane afforded a white crystalline material (II), mp 168–169°. Prominent peaks in the infrared were observed at 2910, 1750, 1520, and 1480 cm^{-1}. A complementary catalyst molecule (I) was prepared by the addition of 0.02 mole (4.82 g) of histidine methyl ester dihydrochloride to a stirred 50-ml benzene solution, cooled to 5° and containing 0.05 mole (5.43 g) of ethyl chloroformate, 0.05 mole (14.20 g) of stearic acid, and 0.09 mole (9.09 g) of triethylamine. After 24 hr the insoluble methyl ester of N-stearoylhistidine was removed by filtration, dried, saponified with 0.5 N NaOH, and acidi-

(1)
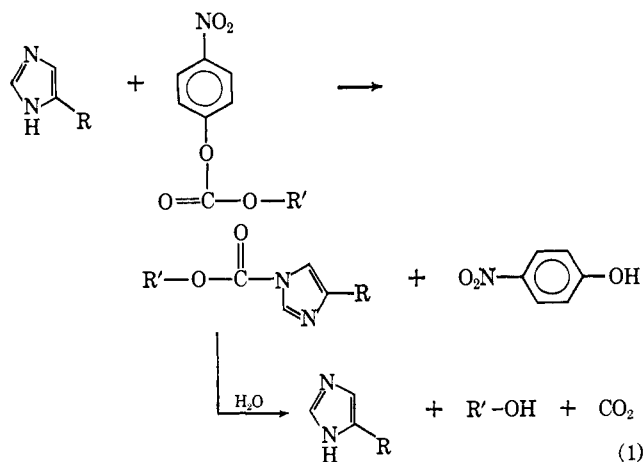
(5) Kindly provided by the Pennsalt Chemicals Corp., Philadelphia, Pa.

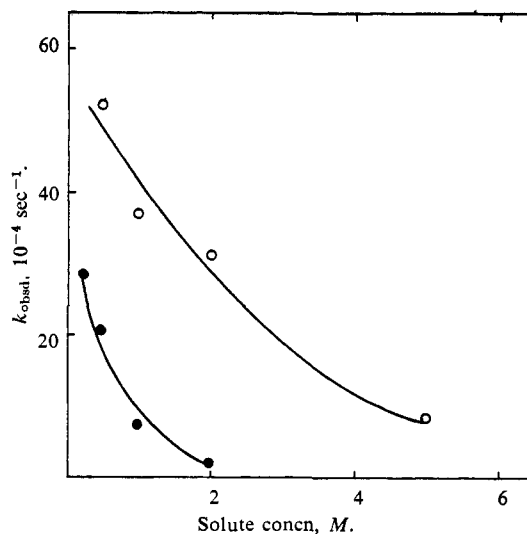(6) Prepared from phosgene and sodium p-nitrophenolate in dry benzene and purified by sublimation, mp 80–81°.

fied to yield N-stearoylhistidine hydrochloride, mp 250–252°. Prominent peaks in the infrared were observed at 2910, 1730, 1650, 1620, and 1550 cm^{-1}.

The net reaction between I and II in water may be represented by eq 1. Experiments were carried out in 3 ml of 0.01 M aqueous potassium phosphate solution, formation of nitrophenol being followed by the increase in absorbance at 400 mμ. Rate data are expressed in Table I as (pseudo) first-order rate constants, k_{obsd}.[7] A striking feature of this reaction is that N-stearoylhistidine at low concentration (3.3 $\times$ 10^{-5} M) is about 240 times as effective as an equivalent amount of N-acetylhistidine in releasing p-nitrophenol from II. This rate enhancement is apparently due solely to apolar interaction between the lyophobic groups in I and II, since N-acetylhistidine possesses each of the characteristics of I except for the long hydrocarbon group.

Table I. Reaction of Histidine Derivatives with II at 25.0°, pH 7.3[a]

Histidine derivative	Concn, $M \times 10^5$	$10^4 k_{obsd}$, sec^{-1}	$k_{obsd} - k_{solvent}$, M^{-1} sec^{-1}
None	0	1.0	
N-Acetylhistidine	3.3	1.4	0.12
N-Acetylhistidine	32	4.6	0.11
N-Stearoylhistidine	3.3	96	29

[a] The concentration of substrate II was 3.3 $\times$ 10^{-5} M in each experiment.

A plot of k_{obsd} vs. concentration of catalyst for the reaction between I and II (Figure 1) shows a sigmoidal shape due to product inhibition[8] at low (limiting) catalyst concentrations and catalyst saturation at high catalyst concentration (limiting substrate). In addition to these two characteristics of enzymatic catalysis, this reaction shows marked decreases in rate upon addition of NaCl or urea (Figure 2). Urea appears to destroy

(7) The rate constants were calculated from the slope of the line formed by the set of points time, log (absorbance − infinite absorbance) between 25 and 50% reaction, and division of the slope by − 0.4343.

(8) Competitive inhibition by N-dodecyl-N,N-dimethylhydroxyethylammonium bromide was demonstrated by addition of an excess of this reaction product to the reaction. In addition, a plot of initial k_{obsd} vs. concentration of catalyst showed usual Michaelis–Menten character.

much of the apolar bonding between I and II, perhaps by decreasing the structure of water,[9] thereby drastically reducing the rate of reaction between them. The effect of NaCl may be due to a similar decrease in water structure or to reduced electrostatic attraction between the reactants due to an increase in ionic strength.

Further studies utilizing this system to determine the thermodynamic characteristics of apolar bonding are in progress and will be discussed in a full paper.

(9) I. M. Klotz, "Horizons in Biochemistry," Academic Press Inc., New York, N. Y., 1962, pp 523–550.

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Eliminations of Neutral Metal Fluoride and Hydrogen Fluoride Fragments in the Mass Spectra of Transition-Metal Fluorocarbon Complexes

Sir:

A variety of fluorocarbon derivatives of transition metals have been prepared.[1] The mass spectra of a few such compounds have been investigated.[2-6] However, only in the mass spectra of the unusual cobalt complex[6] $[(CF_3)_2C_2S_2Co(CO)]_3$ and of the iron complex[7] $[(C_6F_5)_2PFe(CO)_3]_2$ has evidence been found by metastable ion analysis[8] for processes involving loss

gest that loss of neutral metal fluoride fragments is of widespread occurrence in the mass spectra of fluorocarbon transition metal derivatives. The compounds studied are of three different types: (a) fluoroorganosulfur derivatives[10] (*e.g.*, $C_2F_4S_2Fe_2(CO)_6$ (I) and $(CF_3)_2C_2S_2Fe_2(CO)_6$ (II)), (b) perfluoroaryl derivatives[11] (*e.g.*, $C_6F_5Fe(CO)_2C_5H_5$, p-$CF_3C_6F_4Fe(CO)_2C_5H_5$, and $3,4$-$H_2C_6F_3Fe(CO)_2C_5H_5$, all of type III (R_f = perfluoroaryl)), and (c) metal π complexes of the fluorinated bicyclo[2.2.2]octatriene ("barrelene") derivative[12] ($CF_3)_2(CH_3)_4C_8H_2$ (IV) (*e.g.*, $C_{14}H_{14}F_6Fe(CO)_3$ and C_5H_5-$CoC_{14}H_{14}F_6$). The limitation mainly to iron compounds is partially a consequence of the types of compounds available. The mass spectra of several fluorocarbon derivatives of molybdenum and tungsten have also been investigated, but the multiisotopic nature of these two metals has made observation of metastable ions involving metal-containing fragments in the mass spectra of their compounds much more difficult, since the intensity of any given ion is much less. The mass spectrum of the cobalt compound $C_5H_5CoC_{14}H_{14}F_6$ exhibits loss of C_5H_5CoF fragments rather than CoF_2 fragments (unlike $[(CF_3)_2C_2S_2Co(CO)]_3$).[6]

The data on the perfluoroaryl and $(CF_3)_2(CH_3)_4$-C_8H_2 derivatives in Table I indicate that elimination of metal fluoride fragments occurs only after the metal atom being eliminated has lost all of its carbonyl groups.[13] In both of the binuclear iron carbonyl derivatives of fluorinated organosulfur derivatives

Table I. Some Metal Fluoride Eliminations[a]

Compound	Process	Neutral fragment lost	Calcd	Found
$C_2F_4S_2Fe_2(CO)_6$[b]	$C_2F_4S_2Fe_2(CO)_3^+ \longrightarrow C_2F_2S_2Fe(CO)_3^+$	FeF_2	196.5	196.5
$C_4F_6S_2Fe_2(CO)_6$[b]	$C_4F_6S_2Fe_2(CO)_3 \longrightarrow C_4F_4S_2Fe(CO)_3^+$	FeF_2	254.7	255 (s)
$C_6F_5Fe(CO)_2C_5H_5$[c]	$C_6F_4FeC_5H_4^+ \longrightarrow C_{11}H_4F_2^+$	FeF_2	113.0	113.2 (vw)
$3,4$-$H_2C_6F_3Fe(CO)_2C_5H_5$[c]	$C_6F_3H_2FeC_5H_5^+ \longrightarrow C_{11}H_7F^+$	FeF_2	99.2	99.3 (cw)
$3,4$-$H_2C_6F_3Fe(CO)_2C_5H_5$[c]	$C_6F_2H_2FeC_5H_4^+ \longrightarrow C_{11}H_6^+$	FeF_2	82.1	82.3 (vw)
p-$CF_3C_6F_4Fe(CO)_2C_5H_5$[c]	$C_7F_7FeC_5H_5^+ \longrightarrow C_{12}H_5F_5^+$	FeF_2	176.1	176.3 (vw)
p-$CF_3C_6F_4Fe(CO)_2C_5H_5$[c]	$C_7F_6FeC_5H_4^+ \longrightarrow C_{12}H_4F_4^+$	FeF_2	157.9	158 (w)
$C_{14}H_{14}F_6Fe(CO)_3$[d]	$C_{14}H_{14}F_6Fe^+ \longrightarrow C_{14}H_{14}F_4^+$	FeF_2	189.0	189 (m)
$C_5H_5CoC_{14}H_{14}F_6$[d]	$C_5H_5CoC_{14}H_{14}F_6^+ \longrightarrow C_{14}H_{14}F_5^+$	C_5H_5CoF	182.8	183 (w)
$C_5H_5CoC_{14}H_{14}F_6$[d]	$C_5H_5CoC_{10}H_8F_6^+ \longrightarrow C_{10}H_8F_5^+$	C_5H_5CoF	135.8	136 (s)

[a] The mass spectra from which these data were obtained were all taken at 70-ev electron energies on the Mellon Institute MS-9 mass spectrometer (Associated Electrical Industries, Ltd.). Inlet temperatures were in the range 200–250° and source pressures in the range 5 × 10^{-7} to 5 × 10^{-6} mm. [b] Reference 10. [c] Reference 11. [d] Reference 12.

of neutral metal fluoride fragments. In the case of the cobalt complex, the reaction of this type involves fragmentation of the carbonyl-free trinuclear ion C_{12}-$F_{18}S_6Co_3^+$ to the binuclear ion $C_{12}F_{16}S_6Co_2^+$. In this process a neutral CoF_2 fragment is lost.

This paper presents the data[9] in Table I which sug-

studied in this work ($C_2F_4S_2Fe_2(CO)_6$ and $C_4F_6S_2Fe_2$-$(CO)_6$) loss of neutral FeF_2 fragments occurs from the tricarbonyl ions $(R_f)_2S_2Fe_2(CO)_3^+$. The apparent tendency for only carbonyl-free metals to be eliminated as their fluorides suggests that the first three carbonyl groups lost from the parent ions of $C_2F_4S_2Fe_2(CO)_6$ (I) and $C_4F_6S_2Fe_2(CO)_6$ (II) come off the same iron

(1) For a review of fluorocarbon derivatives of transition metals, see P. M. Treichel and F. G. A. Stone, *Advan. Organometal Chem.*, **1**, 143 (1964).

(2) H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

(3) R. B. King, M. I. Bruce, J. R. Phillips, and F. G. A. Stone, *Inorg. Chem.*, **5**, 684 (1966).

(4) M. I. Bruce, *J. Organometal. Chem.* (Amsterdam), **10**, 95 (1967).

(5) M. I. Bruce, *Inorg. Nucl. Chem. Letters*, **3**, 157 (1967).

(6) R. B. King and T. F. Korenowski, *Chem. Commun.*, 771 (1966).

(7) J. M. Miller, *J. Chem. Soc.*, *Sect. A*, 828 (1967).

(8) For a further discussion of metastable ions, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p xiii, and references cited therein.

(9) These mass spectra were run on the Mellon Institute MS-9 mass spectrometer (Associated Electrical Industries, Ltd.) under the direction of Mr. R. E. Rhodes. The standard conditions were 70-ev electron energies, 200–230° inlet temperature, resolution of 1000, 8-kv accelerating voltage, and sample introduction into the ion source with a metal probe.

(10) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963).

(11) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15 (1964).

(12) R. B. King, *J. Am. Chem. Soc.*, **84**, 4705 (1962).

(13) The stepwise loss of metal carbonyl groups is now a well-established feature of the mass spectra of metal carbonyl derivatives. For early observations of this phenomenon, see R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964); **4**, 157 (1965).