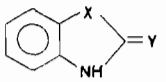
This study showed that K depends on the solvent, R and X. For the same solvent and R, K's increase in the order O < S < CH_2 < imidazolidines (NH, NMe and NEt).

On passing from thio- to seleno-ketonic compounds (Y = Se) the K's strongly increase, keeping the same dependence on the solvent and R. For the very high values of K, the simultaneous calculation of ϵ (molar extinction coefficient of the adduct) and K has presented some problems. In fact all the methods, based on a linear least square method, fail since they give not consistent values of K. *Viceversa,* good results have been obtained by employing the no-linear least square procedures of Gauss [3] and Conrow [4], working on several solutions within a large range of the saturation fraction [5].

This kind of investigation has been now extended to the following molecules



X = O, S, NH
Y = S, Se

in order to evidentiate the changes produced by the benzene ring on the donor properties of Y.

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Electronic, Steric and Lipophilicity Requirements in the Oxidation of Dialkylarylamines by Horseradish Peroxidase

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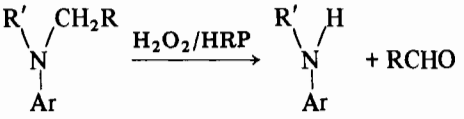
Horseradish peroxidase (HRP) catalyzes the oxidation of a wide variety of organic compounds by hydrogen peroxide. The mechanism has been established and described by the following scheme:

$$HRP + H_2O_2 \rightleftarrows HRP{-}H_2O_2 \rightarrow E_1$$

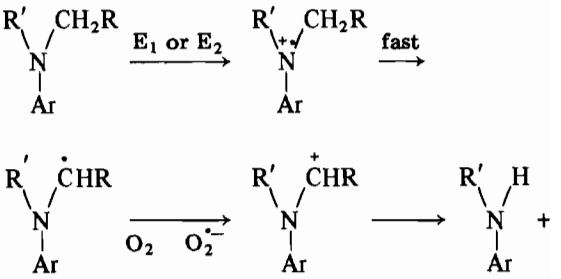
$$E_1 + AH_2 \rightleftarrows E_1{-}AH_2 \rightarrow E_2 + AH^{\bullet}$$

$$E_2 + AH_2 \rightleftarrows E_2{-}AH_2 \rightarrow HRP + AH^{\bullet}$$

where E_1 and E_2 are oxidized forms of the enzyme at respectively two and one level of oxidation. In previous work we have shown that HRP catalyzes the oxidation of aromatic tertiary amines with hydrogen peroxide yielding a secondary amine and an aldehyde according the reaction



In this reaction oxygen is consumed. From stoicheiometrical experiments the following mechanism has been proposed:



Since the hydrogen peroxide–peroxidase system is often regarded as a simple model for more complex biological oxidative systems, we have studied the structure requirements in the oxidation of some dialkylarylamines with this system.

A kinetic investigation was performed on a series of fifteen N,N-dimethyl (*1–8*) and diethylanilines (*9–15*). Within the experimental range of concentrations initial rates were linearly dependent on initial substrate concentrations. The apparent first order constants were calculated. Diethylanilines react on the average 2.6 times faster than dimethylderivatives. This parallelism reduces the possibility of dealing with random points distribution. In spite of this, statistical treatment of data by single or multiple regression does not show any linear expression of reactivity as a function of Hammett's σ, Hansch's π lipophilicity and MR steric parameters. Different rate determining steps may be supposed within the substrates series. However some empirical observations can be made. Reactivity is lowered by hydrophobic and electron withdrawing substituents and exalted by hydrophilic and electron donor substituents. Bulkiness of substrate has no peculiar importance. These results are in analogy with other data

(*1*)	X = 4-F	(*9*)	X = 4-F
(*2*)	3-Cl	(*10*)	3-Cl
(*3*)	4-Cl	(*11*)	4-Cl
(*4*)	3-Me	(*12*)	3-Me
(*5*)	4-$NHCOCH_3$	(*13*)	4-$NHCOCH_3$
(*6*)	4-*iso*C_3H_7	(*14*)	4-*iso*C_3H_7
(*7*)	4-CN	(*15*)	3-OCH_3
(*8*)	3-NO_2		

obtained for the oxidation of dialkylarylamines with rat liver microsomal P-450 dependent detoxifying system

Hydrophobic Host–Guest Interactions in Aqueous Media

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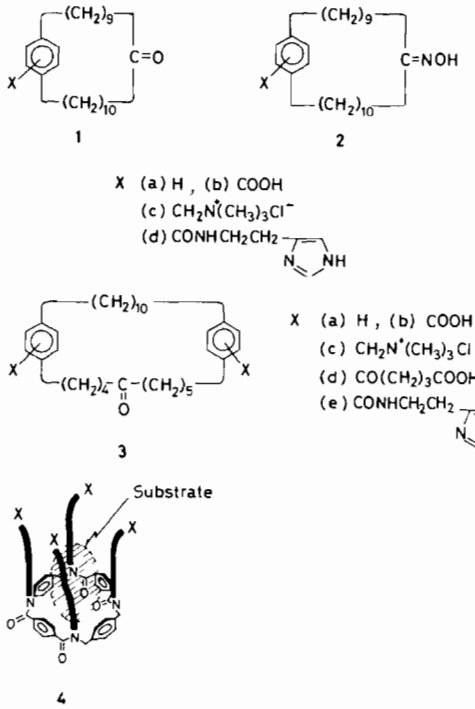
Three fundamental structures can be conceived for designing hydrophobic macrocycles as host molecules which interact with various hydrophobic guest molecules in aqueous media (a) macrocycles without capping at both top and bottom, (b) macrocycles with a flexible or fixed cap at one end, and (c) macrocycles with a fixed cap at one end and a flexible cap at the other The author and his coworkers have been mostly concerned with macrocyclic hosts of type (a) structural mode, and prepared various paracyclophanes illustrated by 1, 2, and 3 as typical examples [*20*] Paracyclophanes provide a hydrophobic binding site much more effective than cyclodextrins for hydrophobic substrates (binding constant $K_b = 10^3$–10^5), and exercise the following catalytic functions in the deacylation of hydrophobic carboxylic esters nucleophilic-electrostatic [1], nucleophilic-hydrophobic [2], and coordination-nucleophilic [3] A [*20*] paracyclophane having an ammonium group (1c) provides electrostatic-hydrophobic double-field and a hydrophobic ester undergoes effective aminolysis by glycine [4] A [*10 10*] paracyclophane bearing two imidazole groups (3e) shows complete turnover behavior in the hydrolysis of hydrophobic esters upon addition of copper(II) ion to the system, the catalysis proceeds through acylation and subsequent deacylation of the cyclophane [*10 10*] Paracyclophanes exercise two substrate-binding modes depending on the nature of substrates,



penetration and face-to-face [5] Azaparacyclophanes bearing multiple alkyl chains (octopus-cyclophanes) incorporate various substrates by the hydrophobic-electrostatic interaction of induced-fit type (4) [6]

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The Bis (salicylaldehyde) ethylenediiminecobalt (II) Catalysed Oxidation of Aromatic Amines with Oxygen

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The catalysis of complexed ions in the oxidation of aromatic amines with oxygen could mimic biological detoxification reactions