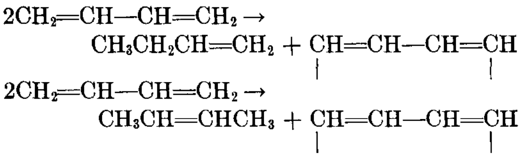
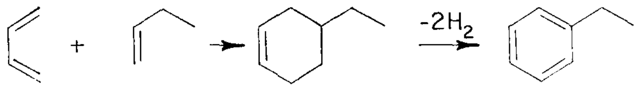


$$2CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_3CH_2CH{=}CH_2 + CH{=}CH{-}CH{=}CH$$

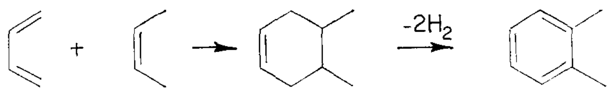
$$2CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_3CH{=}CHCH_3 + CH{=}CH{-}CH{=}CH$$

Much of the so formed olefinic material is desorbed and appears in the effluent gas stream but a considerable proportion remains on the catalyst surface where it is available for reaction with further diene molecules from the feed. (That these secondary reactions are in fact solid catalyzed is shown by the observation that when butene-1 or *cis*-butene-2 was included in the feed a decreased amount of liquid product was formed.) These reactions take the form of Diels-Alder type combinations and lead to the formation of adducts which are the precursors of the aromatic compounds found in the liquid products. For example:

(a) ethyl benzene:



(b) *o*-xylene:



The preponderance of these precursors in the liquid product from the reaction over the 5% cobalt oxide containing catalyst suggests that the cobalt is acting predominantly as a dehydrogenation center in this system. As is the case with the high temperature homogeneous reaction (*2*) it seems likely that the minor liquid products are formed by a series of isomerizations and decompositions involving the major products.

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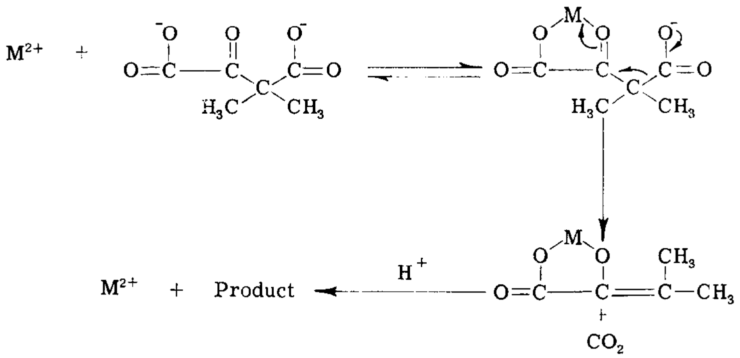
Enhancement of Metal-Ion Catalysis by Ligands: The Resonance Effect in Catalysis by Iron(II)

The ligands attached to a metal ion affect its ability to catalyze the decarboxylation of dimethyloxaloacetic acid (*1*). When it was observed that, like the enzyme protein in biological systems, 1,10-phenanthroline is a coordinating agent that enhances catalysis (*2*), we became interested in determining the physical basis of enhancement. Our method was to examine catalysts consisting of 1:1 complexes of metals and various sub-



stituted phenanthrolines to see whether the substituent caused a change in some physical property of the complex which could be simply correlated with a change in catalytic ability. These studies (*3*, *4*) were carried out on manganese(II) and zinc(II) ions. For substituents on the phenanthrolines that were distant from the point of attachment of the metal ion, the π electron system of the phenanthroline (and perhaps of the metal ion and substrate as well) seemed to be involved in the enhancement. In particular, it appeared that the phenanthroline substituent affected the catalysis rate by a resonance interaction with the π orbitals of the metal ion. The metal ions studied, zinc(II) and manganese(II), had symmetrically filled *d* shells. We have investigated catalysis by iron(II), which has more electrons in its π orbitals than in its σ orbitals, in the hope that a stronger metal–phenanthroline π interaction would occur so that the dependence on the resonance effect could be more firmly established.

The rise in CO_2 pressure in the reaction flask was used to measure the reaction progress as previously described. Good first-order kinetic plots were obtained, and the rate constants were corrected for autodecarboxylation and decarboxylation by other catalysts, so the reported constants represent catalysis by 1:1 metal–phenanthroline complexes (*3*). Particular care was taken to prevent oxidation of the iron(II) by oxygen. Although the iron was eventually converted to the catalytically inactive tris(phenanthroline)iron(II) complex, adequate time elapsed to determine the pseudo-first-order rate constants for the decarboxylation before this became significant. The results for 1:1 iron(II)-phenanthroline catalysts are listed in Table 1, along with the substituent constants σ para − σ meta, when available. These constants are generally considered to be the constants that most closely reflect that pure resonance effect of the substituents (*6*). Better correlation of rate constants with them was obtained than with any other measured properties of the catalyst. The other properties that have been examined include (*4*) other kinds of Hammett Substituent constants, pK_b values of the ligands, electron densities at various positions on the phenanthroline rings, and electronic transition energies. This result

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION OF DIMETHYLOXALOACETIC ACID BY IRON(II)–PHENANTHROLINE COMPLEXES[a]

Phenanthroline derivative	Corrected rate constant $\times 10^5$	*σ para − σ meta*[b]
Unsubstituted	20.5 ± 0.8	0.00
4,7-Dimethyl	24.5 ± 0.8	−0.10
3,5,6,8-Tetramethyl	27.0 ± 1.6	—
4,7-Diphenyl	28.6 ± 4.1	−0.07
5,6-Dimethyl	31.2 ± 0.5	—
4,7-Dichloro	35.0 ± 4.6	−0.15
4,7-Dibromo	37.9 ± 4.1	−0.16
3,4,7,8-Tetramethyl	40.4 ± 8.2	−0.17
5-Nitro	46.9 ± 5.2	—
4,7-Dihydroxy	50.6 ± 1.5	—
5,7-Dimethoxy	75.6 ± 4.3	−0.38

[a] Catalysts are 1:1 complexes at a concentration of 6.90×10^{-3} *M*. Other concentrations are the same as in Ref. (*3*).

[b] From Ref. (*5*).

corroborates more clearly than any previous one the conjecture that the π system of the phenanthroline and the resonance effect are responsible for enhancement of metal-ion catalysis.

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