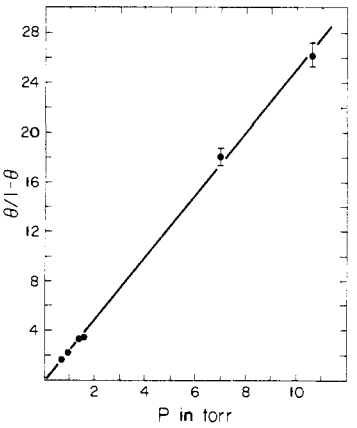

Figure 1. Isotherm of O_2 binding of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm) at 25.0°. Error limits set from accuracy of manometer. The least-squares fit to Langmuir isotherm equation $(\theta/(1-\theta) = (p_{1/2})^{-1}P_{O_2})$ is shown with a slope of 2.53 $Torr^{-1}$ measured over the range of θ = 65% to θ = 96%.

Table I. O_2 Binding by Representative Myoglobins and Myoglobin Models

Source[a]	$p_{1/2}^{20°}$, Torr	$\Delta H°$, kcal/mole	$\Delta S°$, eu[b]
This paper	0.31	−15.6	−38
Chang and Traylor model[d]	0.32	...	...
Human Mb, reconst.[e]	0.72	−13.4	−32[c]
Ox, Mb, adult[f]	0.55	−15	−37[c]
Tuna, Mb[g]	0.90	−13.2	−32[c]
Horse, Mb[h]	0.70	−13.7	−33[c]

[a] It should be noted that some variance exists in the literature concerning these constants due to both the experimental difficulties of the myoglobin systems, as well as to the possible inherent differences between myoglobins of different species. [b] Standard state of O_2 partial pressure = 1 atm. [c] Calculated from reported $p_{1/2}^{20°}$ and $\Delta H°$. [d] C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A.*, 72, 1166 (1975). [e] A. Rossi Fanelli and E. Antonini, *Arch. Biochem. Biophys.*, 77, 478 (1958). [f] A. Rossi Fanelli, E. Antonini, C. DeMarco, and S. Benerecetti, *Biochem. Hum. Genet., Ciba Found. Symp.*, 144 (1958), cited in E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands", American Elsevier, New York, N.Y., 1971, p 221. [g] A. Rossi Fanelli, E. Antonini, and R. Giuffre, *Nature (London)*, 186, 896 (1960). [h] E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands", American Elsevier, New York, N.Y., 1971, p 221.

tem argues that the apoprotein does not contribute significantly to the binding of oxygen,[14] and suggests that the primary role of the protein in myoglobin is to protect the heme from oxidation.

An independent analysis of these thermodynamic constants is possible. One can partition the entropy of an oxygen molecule into its translational, rotational, vibrational, and electronic (i.e., degeneracy) components.[15] Because the frequencies of the FeO_2 vibrations are not known, we cannot accurately calculate their contribution to the entropy of the complex; however, if we assume them to be of low frequency (400–100 cm^{-1}), then they would contribute an additional 3 to 11 eu. If one includes the loss of the fivefold electronic degeneracy of the Fe^{II} (S = 2) and treats the internal rotation of the bent Fe-O-O system as a free rotor (~7 eu), then

$$\Delta S°_{calcd} = -(S_{O_2}^{trans} + S_{O_2}^{rot} + S_{O_2}^{vib} + S_{O_2}^{elec} + S_{Fe}^{elec}) + S_{FeO_2}^{introt} = S_{FeO_2}^{vib}$$
$$= -(36 + 11 + 0 + 2 + 3) + 7 + (7 \pm 4)$$
$$= 38 \pm 4 \text{ eu (standard state of 1 atm)}$$

The agreement between the calculated and experimental values is consistent with the fit to the Langmuir isotherm, which requires independent binding sites, and with the absence of substantial systematic errors in the experimental determination. This demonstration that the "picket fence" porphyrin is a well-behaved system for solid-gas equilibrium studies sets the stage for further studies of parameters such as the nature and closeness of the axial base and the polarity of the oxygen binding site.

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(9) Barocell Model 523CH-12, from Datametrics, 340 Fordham Rd., Wilmington, Mass. 01887, whose ranges are 0–1, 0–10, 0–100, and 0–1000 Torr with a 3½ digit readout.
(10) Exposure of the sample to 300 Torr of O_2 for 15 hr resulted in better than 99% of stoichiometric binding of O_2.
(11) The half-life of approach to equilibrium was roughly an hour.
(12) Based on ln K_{eq} (°C): 5.34 ± 0.02 (50.0); 6.25 ± 0.05 (37.0); 7.56 ± 0.02 (25.0); 9.76 ± 0.13 (−0.1), with a standard state of 1 atm; error limits of these ln K_{eq} are the standard deviation of the least-squares fit to the Langmuir isotherm at each temperature. Error limits of ΔH and ΔS derived using the extremum method of Benson[13] yield maximum error limits of ±0.5 kcal/mol and ±1.6 eu, respectively. It should be noted that the statistical error limits given are derived from the least-squares fit and may not necessarily reflect the actual experimental error. The reproducibility of the equilibrium constants between separately synthesized samples is less than that of a single sample; K_{eq} varied less than 10% between samples, corresponding to a variation of less than 2% in ln K_{eq}.
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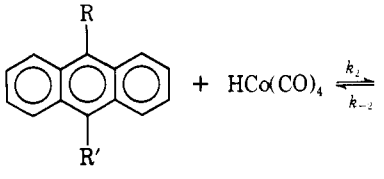
Mechanism of the Cobalt Carbonyl-Catalyzed Homogeneous Hydrogenation of Aromatic Hydrocarbons[1]

Sir:

A variety of polycyclic aromatic hydrocarbons (PAH) are homogeneously hydrogenated in a highly selective manner[2-4] in the presence of $Co_2(CO)_8$ and synthesis gas (CO + H_2) at elevated temperature and pressure ("oxo" conditions). The operation of this catalyst, being one of the few known homogeneous catalysts for aromatic hydrogenation, has special interest. By analogy with the generally accepted mechanism of hydroformylation of olefins with the same catalyst it has been assumed[5] that the key reaction is the

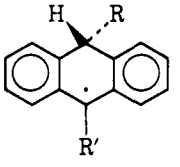
well-known,[6] concerted cis addition of H and $Co(CO)_n$ moieties (n = 3 or 4) of the active catalyst $HCo(CO)_n$ to an olefinic bond of PAH to form an alkylcobalt complex. We suggest instead that for aromatic hydrocarbons, at least, the mechanism of hydrogenation involves intermediate free-radicals rather than organocobalt complexes. Our proposed mechanistic sequence,[7] with an anthracene substrate (R,R′ = H or CH_3) as an illustrative example, is as follows:

$$Co_2(CO)_8 + H_2 \overset{K}{\rightleftharpoons} 2HCo(CO)_4 \quad (1)$$



$$+ HCo(CO)_4 \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}}$$

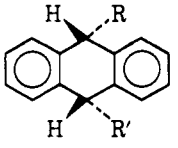
1



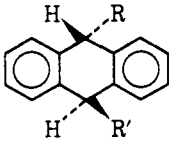
$$+ \cdot Co(CO)_4 \quad (2)$$

2

$$2 + HCo(CO)_4 \xrightarrow{\text{fast}}$$



and



$$+ \cdot Co(CO)_4 \quad (3)$$

3

$$2 \cdot Co(CO)_4 \xrightarrow{\text{fast}} Co_2(CO)_8 \quad (4)$$

This mechanism accounts for certain experimental results which appear anomalous when interpreted in terms of the conventional mechanism involving intermediate organocobalt complexes.

(i) Weil, Friedman, and Wender[8] have observed that deuteration of anthracene or pyrene with $DCo(CO)_4$ results in rapid isotopic exchange at the positions of addition only. Because of microscopic reversibility concerted cis addition and elimination of $DCo(CO)_4$ cannot lead to exchange since the nonequivalence of H and D is preserved by the cyclic structures. On the other hand, such isotopic exchange is a natural consequence of the reversibility of step 2 in our mechanism.

(ii) Hydroxymethylated compounds are not found among the products of catalytic hydrogenation of PAH,[2-4] although these are the usual products[2] derived from olefins under "oxo" conditions above 180°C. Absence of an alkylcobalt intermediate in our mechanism precludes the usual CO transfer reaction and formation of carbonylated products.

(iii) 2-Methylnaphthalene and acenaphthene are hydrogenated more readily than naphthalene,[4] and 9,10-dimethylanthracene more readily than anthracene.[5] Although concerted additions of metal hydrides to alkylated sp^2 centers are expected to be severely slowed by steric inhibition, the rate of step 2 should be less sensitive to steric influences, and might even be accelerated as a result of stabilization of the product radical by alkyl substituents.

(iv) Taylor and Orchin[5] observed nearly equal amounts of *cis*- and *trans*-dihydro products from the hydrogenation of 9,10-dimethylanthracene, although only *cis*-9,10-dihydro-9,10-dimethylanthracene was expected. The scheme[9] they used to rationalize this observation was rather elaborate and only applicable to alkyl substituents which possess α-hydrogens. On the other hand, our mechanism predicts this result because step 3 is expected to proceed by an approximately random approach of $HCo(CO)_4$ to an sp^2 center from either side of the nearly symmetrical molecular plane of **2**. Our mechanism predicts near equality of cis and trans isomers even for substituents not possessing α-hydrogens.

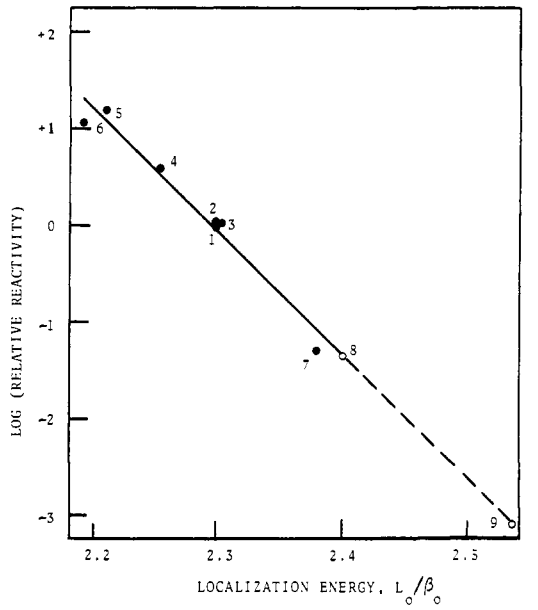


Figure 1. Correlation of relative hydrogenation reactivities at 200° with radical localization energies. The code is as follows: 1, naphthalene; 2, phenanthrene; 3, coronene; 4, chrysene; 5, fluoranthene; 6, pyrene; 7, triphenylene; 8, biphenyl; 9, benzene. (Reactivity of naphthalene ≡ 1). The points for benzene and biphenyl correspond to the relative rates predicted for these substrates by extrapolation of the line drawn through the other points.

(v) With this free-radical model we can also account both for the relative reactivities of various PAH and for the site preferences for hydrogen addition to each, as reported by Friedman et al.[4] It has been shown by Szwarc[10a-c] and by Coulson[10d] that there is a good correlation of the relative reactivity of a PAH toward hydrogen atom or free-radical addition with the localization energy for the formation of the resulting free-radical. Figure 1 shows such a plot of the log (relative reactivity), calculated[11] from the 200°C data[4] for unsubstituted PAH, vs. (HMO) radical localization energies.[13] The correlation is good and corresponds to an effective value of β[14] of -27.5 kcal. This large negative value (cf. $\cdot CH_3$, -11 kcal; $\cdot CF_3$, -20 kcal)[14] implies a transition state resembling the localized products.[15] In every case, the hydrogenation product(s) identified by Friedman et al.[4] are those expected[16] if the initial addition of a hydrogen atom at the most reactive position[13] of a PAH (step 2) is rapidly followed by additions at resulting odd-electron sites, the process continuing until the reactivity of the remaining substituted PAH is too low. This correlation predicts a reactivity for benzene which, although a thousandfold lower than that of naphthalene, should still be detectable.

One further distinctive prediction of our mechanism is that the rate of hydrogenation should be independent of CO pressure,[17] in contrast to the inverse CO pressure dependence observed for hydroformylation and predicted for the related hydrogenation proceeding through an intermediate organocobalt complex.

While we recognize that our proposed mechanism is unrelated to that of the η^3-$C_3H_5Co[P(OCH_3)_3]_3$-catalyzed

hydrogenation of benzene recently described by Muetterties and Hirsekorn[21] we do call attention to the similarity between our free-radical mechanism and that which has been advanced for the $HCo(CN)_5^{3-}$-catalyzed hydrogenation of conjugated olefins.[22] In this connection, we suggest that the hydrogenation of alkenes which typically accompanies hydroformylation, and which is especially pronounced for α,β-unsaturated compounds and at high temperatures, may also derive from this type of free-radical mechanism.[23]

We are continuing this investigation with a view to testing the above interpretations and predictions, and elucidating possible mechanisms of hydrogenation of coal-related substances.

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(11) Rate constants[12] were calculated from $k_i = -\ln f_i/tC$, where f_i = fraction of substrate i unconverted, t = time at temperature, C = concentration of active catalyst. Reactivities, $R_i = k_i/N_i$, where N_i is the number of equivalent positions of greatest reactivity.[13] The time, t, was assumed to be the same in each experiment (5 hr for the example described).
(12) The rate of hydrogenation has been shown to be first order in substrate concentration and proportional to the active catalyst concentration. H. M. Feder, R. D. Wolson, L. E. Ross, and J. Rathke, to be submitted for publication.
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(15) The position of the nonalternant hydrocarbon fluoranthene on this plot also implies that the transition state has little or no polarity because the localization energies of the corresponding fluoranthene anion and cation are widely different from that of the neutral radical.
(16) Both 9,10-dihydro- and 1,2,3,4-tetrahydrophenanthrene are products of phenanthrene hydrogenation in ~7:1 ratio.[2,5] Unfortunately, quantitative prediction of this ratio is hindered by the closeness of the localization energies corresponding to the alternative modes of attack, and the possibility of steric effects.[14]
(17) Under sufficiently high CO and H_2 pressures to maintain the catalyst predominantly in the $HCo(CO)_4$ form.[18,19]
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Bifunctional Catalysis of the Enolization of Acetone[1]

Sir:

We wish to report that the third-order term for acid-base catalysis of acetone enolization exhibits a Bronsted β_{AB} value of 0.15, a solvent isotope effect of $k_{H_2O}/k_{D_2O} = 2.0$, and a C-H isotope effect of $k_H/k_D = 5.8$. We conclude that this reaction represents true bifunctional catalysis with partial proton abstraction by acetate ion and a significant movement of the proton of acetic acid toward the carbonyl oxygen atom in the transition state.

The interpretation of the third-order term, $k_{AB}[HA][B]$, in the rate law for acetone enolization (eq 1)

$$k_{obsd} = k[H_2O] + k_{H^+}[H_3O^+] + k_{HO^-}[HO^-] + k_A[HA] + k_B[B] + k_{AB}[HA][B] \quad (1)$$

has been the subject of much controversy and has played an important role in the development of ideas on the mechanism of acid-base catalysis in solution and at the active sites of enzymes.[2] In particular, attempts have been made, and criticized, to interpret *all* of the rate terms as bifunctional, third-order acid-base catalysis in which water may cooperate in the rate-determining step as an acid-base species.[2,3] A reexamination of this problem appeared warranted because the mechanism for the k_A and k_B terms is now known. The k_A term has been shown to represent catalysis by the proton of the removal of a proton by acetate ion (k_2/K_{AcH^+}, Scheme I),[4,5] most directly by the demonstration that the rate of the reverse, ketonization reaction of RCH=CR′OH is entirely accounted for by the rate of protonation of the corresponding enol ether, RCH=CR′OCH_3, in which proton removal from $-OCH_3$ in the transition state is impossible.[5] Thus, the proton is fully transferred to the carbonyl oxygen atom in the transition state (i.e., $a = 1.0$). The k_B term (general base catalysis of C-H proton removal) can only involve stabilization of the transition state by hydrogen bonding of the carbonyl oxygen atom to water because there is no thermodynamic advantage to the transfer of a proton from water to the enolate ion ($pK \approx 11$); a for this reaction is, therefore, ca. 0-0.2.[6] One of us (W.P.J.) suggested that the third-order term represents simply a modification of the k_B term, in which acetic acid instead of water is hydrogen bonded to the transition state.[6] Since the value of a_A for hydrogen bonding is

Scheme I