species may play an important role elsewhere in the reaction.

The stoichiometry of reaction 1 as a function of time was followed by GLC analysis[20] and measurement of consumed oxygen gas. A striking characteristic of the reaction was that the molar ratio of the epoxide formed vs. the molecular oxygen consumed was close to unity throughout the reaction. In the present epoxidation, oxygen is consequently required in twice the ideal stoichiometry. We therefore looked for products other than **2** in the reaction of **1** and found several oxidative degradation products, among them 3-methyl-2-butenal and 2-hydroxypropanal. Control experiments showed that these degradation products derived from neither the epoxide **2**, the allyl alcohol **19** corresponding to **8**, **11**, and **16**, nor hydroperoxide **20**. These facts suggested that one atom of the oxygen molecule is used for the epoxidation and the other atom is consumed in oxidative degradation of the substrate. These phenomena also appear to be characteristic of the silver-catalyzed epoxidation of ethylene.[6]

Although further systematic studies are necessary to clarify the mechanism of the reaction, the reaction described here may be a new type of epoxidation by molecular oxygen and is the first example of nonenzymatic iron-catalyzed regiospecific oxygenation of complicated olefins by molecular oxygen.

Registry No. 1, 105-87-3; **2**, 23519-09-7; **4**, 141-12-8; **5**, 63707-79-9; **6**, 115-95-7; **7**, 41610-76-8; **8**, 83221-21-0; **9**, 29171-21-9; **10**, 77743-54-5; **11**, 83221-22-1; **12**, 150-84-5; **13**, 1787-98-0; **14**, 19162-00-6; **15**, 83221-23-2; **16**, 83221-24-3; **17**, 1191-16-8; **18**, 83221-25-4; **20**, 33766-44-8; **22**, 33766-45-9; $\mathrm{[Fe_3O(piv)_6(MeOH)_3]Cl}$, 55216-31-4; $\mathrm{[Fe_3O(OAc)_6(H_2O)_3](OAc)}$, 60797-92-4; $\mathrm{[Fe_3O(OAc)_6Py_3]Cl}$, 69554-73-0; $\mathrm{FeCl_3}$, 7705-08-0.

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(20) GLC analysis was carried out by using a 20% XE-60 column (2 m) at 160 °C.

Relationship between the Freundlich Adsorption Constants K and $1/N$ for Hydrophobic Adsorption

Ikuo Abe,* Katsumi Hayashi, and Tsuneaki Hirashima

Osaka Municipal Technical Research Institute
Morinomiya, Joto-ku, Osaka 536, Japan

Mutsuo Kitagawa

Society for Activated Carbon Research
Morinomiya, Joto-ku, Osaka 536, Japan

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A good linear relationship has been obtained between the logarithm of K and $1/N$ of the Freundlich adsorption constants for hydrophobic adsorption. The linear equation is applicable to many adsorbent–adsorbate systems.

We now consider the adsorption of hydrocarbons onto a hydrophobic adsorbent such as activated carbon. For such adsorption the Polanyi adsorption potential theory may be applied as follows.[1-4]

The adsorption of solute takes place by the precipitation of the solute on the surface with potential estimated as

$$\epsilon_{s1} = RT \ln (C_s/C) \tag{1}$$

where C_s and C are the saturated and the equilibrium concentrations. We assume that the relation between the adsorption potential (ϵ_{s1}) and the volume of solute adsorbed (W) is given by the expression

$$W = W_0 \exp[-m(\epsilon_{s1}/V_s)] \tag{2}$$

where W_0 is the limiting volume of adsorption space, V_s is the molar volume of solute, and m is a parameter of the distribution function. This equation is another form of the Freundlich equation of the adsorption isotherm since it can easily be brought to the form

$$W = W_0 \exp\left(-\frac{mRT}{V_s} \ln C_s/C\right) = W_0(C/C_s)^{mRT/V_s} = KC^{1/N} \tag{3}$$

where

$$K = W_0(1/C_s)^{mRT/V_s} \tag{4}$$

and

$$1/N = mRT/V_s \tag{5}$$

By taking logarithms, eq 4 can be written in the form

$$\log K = \log W_0 - (mRT/V_s) \log C_s \tag{6}$$

It is well-known that the logarithm of the solubility of hydrocarbon in water is a linear function of the hydrocarbon molar volume:[5]

$$\log C_s = aV_s + b \tag{7}$$

where a and b are constants. By combining eq 5–7, we obtain

$$1/N = -(1/b) \log K + (1/b)(\log W_0 - amRT) \tag{8}$$

This equation indicates that a linear relationship is set up between the logarithm of K and $1/N$ of the Freundlich adsorption constants. The equation has been applied to actual adsorption data in order to examine the validity of eq 8. We have measured the adsorption isotherms of 139 organic compounds (including alcohols, ethers, ketones, aldehydes, amines, esters, fatty acids, amino acids, aromatics, saccharides, glycols, and surfactants, etc.) from aqueous solution onto an activated carbon (Pittsburgh Activated Carbon Co., grade CAL) at 25 °C.[3,6-13] The isotherms have been approximated by the Freundlich equation with the following units:

$$\log X = \log K + (1/N) \log C \tag{9}$$

where X is the amount of solute adsorbed (mg/g of adsorbent) and C is the equilibrium concentration of solute (mg/L). When the K value is expressed in weight unit instead of volume unit, eq 8 is changed to the following equation:

$$1/N = -(1/b) \log K + (1/b)(\log W_0 + \log \rho + 3 - amRT) \tag{10}$$

where $X = 1000\rho W$, ρ is the density of adsorbate (g/mL), and W_0 and W are expressed in mL/g of adsorbent. The slope of the line expressed by eq 10 is independent of the nature of adsorbent and adsorbate. Assuming that the density of each adsorbate is nearly equal, the intercept of the line depends on the nature of adsorbent and is independent of adsorbate. Figure 1 shows a plot log K vs. $1/N$ for the 139 compounds. The line is from linear least-squares analysis of the 136 data points excluding three points

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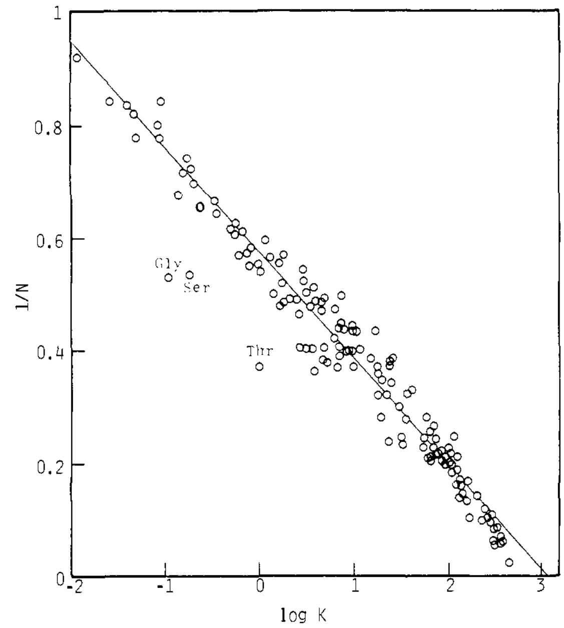

Figure 1. Plot of log K vs. $1/N$ for the adsorption of 139 organic compounds from aqueous solution onto CAL activated carbon at 25 °C.

for glycine, L-serine, and L-threonine. The equation of the line is

$$1/N = (-0.186 \pm 0.008) \log K + (0.572 \pm 0.011) \quad (11)$$

$$r = 0.973 \qquad s = 0.0477$$

In this equation, the errors are in the 95% confidence intervals, r is the correlation coefficient, and s is the standard deviation. Figure 1 indicates that eq 10 is also valid for compounds other than hydrocarbons. This result can be explained by considering that the adsorption of solute takes place by precipitation of the hydrocarbon portion of the solute.

Next we have checked the propriety of the numerical values in eq 11. McAuliffe[5] measured the solubilities in water at room temperature of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons. The solubility data for 60 hydrocarbons excluding methane, ethane, and ethene have been given to a NEC PC-8001 computer to determine the constants a and b in eq 7. The data could be expressed by the following equation:

$$\log C_s = (-0.0300 \pm 0.0049)V_s + (5.43 \pm 0.60) \quad (12)$$

$$r = 0.847 \qquad s = 0.450$$

where C_s is the solubility expressed in mg/1000 g of water and V_s is the molar volume expressed in mL/mol. Since the solubility of hydrocarbon is usually low, the solubility in mg/1000 g of water is nearly equal to the solubility in mg/1000 mL of solution. The coefficient of log K in eq 10 was calculated from eq 12 ($-1/b = -1/5.43 = -0.184$). This excellent agreement with the experimental value (−0.186) indicates that the assumption that the hydrophobic adsorption takes place by precipitation of the hydrocarbon portion of the solute is valid. The value of m in eq 2 was calculated from the adsorption data of anisole ($m = 0.0488$).[14] The value of W_0 was determined as the micropore volume of the adsorbent ($W_0 = 0.317$ mL/g).[14] The ρ value was calculated as the average of the densities of the 60 hydrocarbons ($\rho = 0.717$ g/mL). The value of second term of eq 10 calculated from these values (W_0, ρ, m, $a = -0.0300$, $b = 5.43$, $R = 1.99$, and $T = 298$) was 0.594 and was in agreement with the experimental value (0.572).

It can be seen from Figure 1 that the plots of glycine, serine, etc., deviate downward from the line because of the very small contribution of hydrophobic hydration to the adsorption.

These results indicate that the hydrophobic adsorption isotherm can be expressed by the following equation with only one parameter:

$$\log X = \log K + (0.572 - 0.186 \log K) \log C \quad (13)$$

These relationships were applicable to many other adsorbent–adsorbate systems. Equation 10 is an important equation characterizing hydrophobic adsorption isotherm and becomes a very powerful tool in the investigation of hydrophobic adsorption.

Registry No. C, 7440-44-0.

Supplementary Material Available: Adsorption data of 139 organic compounds on CAL activated carbon (3 pages). Ordering information is given on any current masthead page.

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Bis[(trimethylsilyl)methylidene]tetrakis(trimethylphosphine)dibromodimolybdenum (M≡M)

K. J. Ahmed, M. H. Chisholm,* I. P. Rothwell, and
J. C. Huffman

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

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We have proposed[1] that reactivity patterns presently well documented in mononuclear transition-metal chemistry will also be found for dinuclear compounds containing M–M multiple bonds. We wish here, in further support of this hypothesis, to report a phosphine-promoted α-hydrogen elimination reaction in the formation of a dinuclear bis-carbene compound. Interesting analogies with Schrock's[2] findings for related mononuclear early transition-metal chemistry are apparent.

Addition of PMe_3 (≥4 equiv) to a hexane or toluene solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$[3] causes an immediate reaction, even at −78 °C, and the solution turns from orange-red to dark green. When the reaction was carried out in a sealed NMR tube in benzene-d_6, Me_4Si (2 equiv) was detected by ^1H NMR spectroscopy. Analysis of the volatiles in this reaction by GC–MS revealed only benzene-d_6, PMe_3, and Me_4Si. Significantly, the latter was not enriched in Me_4Si-d_1, suggesting that the hydrogen atom required to form Me_4Si was originating from a Me_3SiCH_2 ligand. The ^{31}P NMR spectrum obtained on the NMR tube reaction described above showed the formation of a major product, ca. 85% based on ^{31}P signal intensities, having an AA′BB′ spectrum and two minor products showing ^{31}P singlets. (One of the minor products has been shown to be $Mo_2Br_4(PMe_3)_4$ (M–M quadruple bond).) On a preparative scale, crystallization of the crude reaction product from hexane gave the (trimethylsilyl)methylidene complex, I, as amber crystals in 60% yield based on eq 1.[4]

$$\underset{\mathbf{1}}{Mo_2Br_2(CH_2SiMe_3)_4} + 4PMe_3 \rightarrow \underset{\mathrm{I}}{Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4} + 2Me_4Si \quad (1)$$

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[4] All operations were carried out by using dried and deoxygenated atmospheres and solvents. $Mo_2Br_2(CH_2SiMe_3)_4$ (0.94 g, 1.34 mmol) was dissolved in toluene (40 mL). With the use of a calibrated vacuum manifold, PMe_3 (5.36 mmol) was condensed onto this solution frozen at −178 °C. The mixture was allowed to warm to room temperature slowly, and the resultant green solution was stirred for 1.5 h. The solvent was stripped and the residue extracted with hexane (100 mL). A small quantity of insoluble material was removed by filtration, the filtrate was reduced in volume to ca. 20 mL, and the solution was cooled to ca. −15 °C. The green-yellow microcrystalline precipitate so formed was collected and recrystallized from hexane slowly (cooling from 50 to 18 °C), yielding amber crystals, $Mo_2Br_2(CHSiMe_3)_2(PMe_3)_4$.

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