

Carbon Black Catalyzed Olefin Isomerization

I. A Heterogeneous Site Model Based on Rate Dependence on Catalyst Concentration

J. A. MEIER* AND L. W. HILL

*Department of Chemistry, North Dakota State University,
Fargo, North Dakota 58102*

Received June 26, 1973

The carbon black catalyzed interconversion of 2-methyl-1-pentene and 2-methyl-2-pentene has been studied in slurry in the range 0 to 52.5°C. The reaction goes to equilibrium with first order reversible kinetics without formation of detectable amounts of other products. The reaction is competitively inhibited by trace amounts of residual water in the partially dried reactant. Poisoning results and deuterium uptake by reactant and product over deuterated catalysts indicate that a range of activity exists for acidic surface groups and that only a fraction of the Bronsted sites are catalytically active. Dependence of the apparent first order rate constant on catalyst concentration has been determined and analyzed rigorously in terms of a proposed mechanism and a heterogeneous site model. The mechanism involves direct protonation of adsorbed olefin and reversible adsorption of water on active sites. The heterogeneous site model consists of an exponential distribution of site activity and preferential adsorption of water on sites of higher activity.

INTRODUCTION

There has been considerable interest in the surface chemistry of carbon blacks as indicated by publication of six review articles in recent years (1-6). The chemical properties of blacks containing substantial amounts of bound oxygen are determined to a large extent by the functional groups on the surface of carbon particles. In comparison with other blacks, channel blacks are characterized by small particle size, high bound oxygen content, and a relatively high ratio of acidic surface groups.

Channel blacks have been shown to catalyze olefin isomerization and polymerization reactions. The reactions reported include the polymerization of 2-methylpropene at 120°C, the simultaneous isomerization and polymerization of 2-

methyl-1-butene at 120°C, the reversible interconversion of 2-methyl-1-pentene and 2-methyl-2-pentene at 60°C and at lower temperatures, the isomerization of 1-decene at 170°C (7), the isomerization of 3,3-dimethyl-1-butene to the methyl shift products 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, and the interconversion of three 3-methylpentene isomers (8). The interconversion of 2-methyl-1-pentene and 2-methyl-2-pentene has been studied in greatest detail. This reaction is first order reversible in olefin and proceeds to equilibrium with no other products present in detectable amounts (7).

The purpose of this paper is to develop a kinetic analysis for identifying the occurrence of competitive inhibition in a reversible system and to present a model which incorporates a distribution of site activity. The mechanism and site model are tested by determination of the rate dependence on the amount of carbon black

* Present address: Inmont Corporation, 6125 Industrial Parkway, Whitehouse, OH 43571.

in the olefin-black slurry. Evidence for a distribution of site activity is presented in terms of deuterium uptake by olefin over deuterated catalysts and poisoning of the catalysts by water. This study deals with the 2-methyl-1-pentene \rightleftharpoons 2-methyl-2-pentene interconversion; however, the mechanism and site model can be generalized by obvious extensions to explain all of the carbon black catalyzed reactions mentioned above. Furthermore, it is hoped that the kinetic analysis will be useful in understanding other liquid-solid systems.

METHODS

A vacuum system capable of maintaining pressures below 10^{-6} Torr was used to degass blacks for kinetic runs. Reactant was added to degassed black samples by vacuum distillation, and the slurry was stirred magnetically under an inert atmosphere. Samples were removed by syringe and analyzed by gas chromatography on a 9 ft 4% squalane column. Rate dependence on black was studied by adding a fixed amount of olefin from a single batch to varying amounts (80 to 900 mg) of degassed black. Temperatures were selected to avoid rapid reaction so that diffusion limitation of the rate did not occur; temperatures ranged from 0 to 52.5°C. The absence of diffusion limitation was established by determining the activation energies which ranged from 12.0 to 15.2 kcal/mole depending on the level of water contamination (9). These activation energies exceed those reported for activated diffusion in carbons by a factor of 2 to 3 (10).

Product and reactant from runs over deuterated catalysts were trapped separately from the gc eluate and analyzed for deuterium on two mass spectrometers, a Hitachi Perkin-Elmer RMU6-E and a Varian M-66. Deuterated catalysts were prepared by adsorbing D₂O on degassed carbon blacks. Mass changes that resulted from H-D exchange were followed by determining the extension of a thermostated helical quartz spring in a McBain balance system. The apparatus for H-D exchange studies has been described previously (11).

Standard drying procedures were used

for drying the olefin with Drierite, barium oxide, calcium hydride, and sodium. Partially activated, molecular sieves were used because highly activated sieves caused isomerization. The objective was to obtain a reduced and constant level of water contamination for a given drying agent. Extremely dry olefin gave very rapid and erratic rates. In most cases, the olefin was initially dried off the vacuum rack, and subsequently the drying procedure was repeated in the vacuum system.

Olefins were obtained from Phillips Petroleum Co., pure grade. The carbon black was obtained from Cabot Corp. and is identified as Black Pearls 2. The properties of this high oxygen channel black have been studied quite extensively. The black consists of spherical particles having a fairly uniform diameter of about 120 Å and a surface area of 744 m²/g (12). The acidic hydrogen content indicated by H-D exchange is 1.3 mE/g (11), and the weight percentage of bound oxygen is 9.5% (12).

RESULTS AND DISCUSSION

A typical first order reversible plot for the reaction 2-methyl-1-pentene \rightleftharpoons 2-methyl-2-pentene is shown in Fig. 1. The slope yields the sum of the forward and reverse rate constants, k_f and k_r . An independent determination of the equilibrium constant gives the ratio k_f/k_r ; thus, the

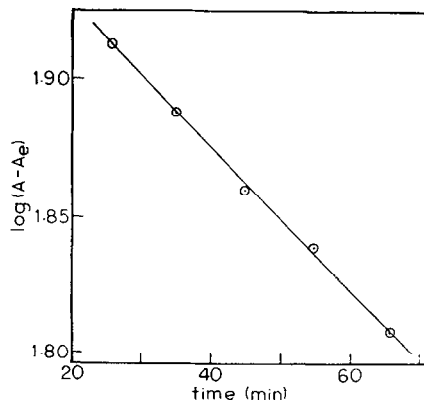
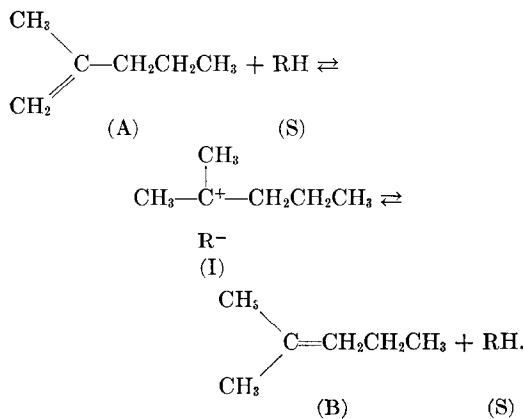


Fig. 1. Reversible first order plot for 2-methyl-1-pentene \rightleftharpoons 2-methyl-2-pentene at 19.1°C with 15.56 ml olefin and 562.8 mg black; $A_e = 9.7\%$ and $k_f = 0.326 \text{ hr}^{-1}$ using the method of least squares.

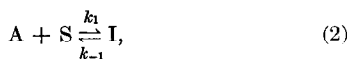
two rate constants can be evaluated. In all cases the first order reversible plots are linear, but the value of the empirical rate constant was found to vary with catalyst degassing conditions, trace levels of water in the olefin, and the amount of carbon black in the slurry.

Rate dependence on the degassing conditions was eliminated by heating the black at 105 to 110°C for 40 hr or at 160 to 165°C for 20 hr at a final pressure of less than 10^{-6} Torr. Longer degassing periods caused no additional increase in k_f . No catalytic activity was observed for blacks in equilibrium with atmospheric moisture.

Before the poisoning effect of water was fully appreciated, the mechanism proposed for the 2-methyl-1-pentene \rightleftharpoons 2-methyl-2-pentene equilibration was



The olefins are assumed to be physically adsorbed prior to protonation (7, 8). The symbol RH (subsequently indicated as S) represents a Bronsted acid site. If P represents water acting as a catalyst poison, the proposed elementary steps are



It is assumed that equilibrium is maintained in reaction 1 and that P and A (or B) compete for the same sites. According to this mechanism, the rate of disappearance of A is:

$$-\frac{dA}{dt} = k_1AS - k_{-1}I. \quad (4)$$

A steady state treatment applied to I yields

$$I = \frac{(k_1A + k_{-2}B)S}{k_{-1} + k_2}. \quad (5)$$

Replacing I in Eq. (4) and rearranging,

$$-\frac{dA}{dt} = \left[\frac{k_1k_2S}{k_{-1} + k_2} \right] A - \left[\frac{k_{-1}k_{-2}S}{k_{-1} + k_2} \right] B. \quad (6)$$

The empirical rate expression for the disappearance of A, as confirmed by plots such as Fig. 1, is

$$-\frac{dA}{dt} = k_fA - k_rB. \quad (7)$$

Comparison of Eqs. (6) and (7) relates the empirical rate constants to those for the proposed elementary steps:

$$k_f = \frac{k_1k_2S}{k_{-1} + k_2} \quad \text{and} \quad k_r = \frac{k_{-1}k_{-2}S}{k_{-1} + k_2}. \quad (8)$$

The linearity of the first order reversible plots indicates that S is constant within a given run. However, as a result of the poisoning indicated in reaction (1), the values of k_f vary with olefin drying procedures.

The effect of intentionally introducing water to a thoroughly dried catalyst sample is indicated in Table 1. The results are consistent with competitive inhibition by water in accordance with the proposed mechanism. After degassing as described above, water was reabsorbed and then partially removed by pumping for only 30 min. Independent absorption-desorption

TABLE 1
EFFECT OF WATER ON k_f AT 0°C WITH 0.568 g
BLACK AND 15.65 ml OF SODIUM
DRIED 2-METHYL-1-PENTENE

Water added (mmoles)	Addition procedure	k_f (hr ⁻¹)
None	—	0.56
0.035	Readsorption	0.078
0.035 + 0.06	Readsorption + direct addition (syringe)	0.027

studies (9, 11) indicated that the amount of water remaining on the black was 0.035 mmoles. The rate constant decreased by a factor of 7. An additional 0.06 mmoles of water was added by syringe while the reaction was in progress, and the rate decreased further by a factor of 3. Thus, the initial portion of water added back had a much greater effect than the larger second portion. A plausible explanation for these results is that there is a range of catalytic activity for the active sites and that the more active sites are preferentially poisoned. This conclusion is incorporated in the site model presented below.

The 2-methyl-1-pentene \rightleftharpoons 2-methyl-2-pentene isomerization was also carried out over deuterated catalysts. Since the molar ratio of olefin to exchangeable hydrogen was 250/1 in typical runs, the level of deuteration of olefin would have been extremely low for complete equilibration. Therefore, deuterium analyses of product and, in some cases, reactant were carried out at low conversions. The results obtained at 7.4% conversion are given in Table 2. The retention of over 80% of the deuterium by the black indicates that only a fraction of the exchangeable acidic groups are catalytically active. A conversion of 7.4% corresponds to formation of 3.1 mmoles of 2-methyl-2-pentene. Only 1.73 mEq of exchangeable deuterium were present in this run (11). Thus, if the sites were of uniform activity, one would expect a very high percentage of the deuterium to be removed by the reversible

isomerization. At lower temperatures a smaller fraction of exchangeable hydrogen was removed during isomerization. Thus, it appears that fewer exchangeable sites are catalytically active at lower temperatures. The fact that deuterium is found in the olefins is, of course, consistent with the direct protonation mechanism proposed above.

Equation 8, which relates the empirical rate constants to the proposed mechanism, suggests a study of the dependence of the empirical rate constant, k_f , on the amount of black in the olefin-black slurry. In the elementary reactions (1) through (3), S represents active sites, and in Eq. (8), S represents the concentration of free active sites. It is clear that the concentration of free sites will be related to the amount of black in the slurry and to the number of sites occupied by olefin and by water. In this study the ratio of black to olefin has been expressed as milligrams of black per milliliter of olefin, and for convenience is referred to as a concentration. Furthermore, it is assumed that the surface area per gram is constant for a given black and that all of the surface is available to the reactants and poison. The latter assumption would fail if the primary carbon black particles formed aggregates that were not penetrable by reactants.

If k is defined as $k = k_1k_2/(k_{-1} + k_2)$, Eq. (8) can be written as

$$k_f = kS. \quad (9)$$

By conservation

$$S_0 = S + PS + I, \quad (10)$$

where S_0 is the initial concentration of active sites and is assumed to be proportional to the initial black concentration. If it is assumed that I is negligible, Eq. (10) reduces to $S_0 = S + PS$. Thus, Eq. (9) can be written as

$$k_f = k(S_0 - PS). \quad (11)$$

The validity of the assumption ($I \ll S_0$ and PS) is supported by the observation that at 7.4% conversion over deuterated catalyst only 19% of the sites have lost deuterium. By analogy to solution reac-

TABLE 2
DEUTERIUM UPTAKE BY REACTANT AND PRODUCT
AT 7.4% CONVERSION AND 20°C OVER
DEUTERATED CARBON BLACK

	% d_1	% d_2
Deuterium incorporation		
2-Methyl-2-pentene (product)	4.6	0.2
2-Methyl-1-pentene (reactant)	0.5	—
Deuterium distribution (%)		
Product	Reactant	Black
9	10	81

tions it appears reasonable to assume that the surface concentration of a reactive intermediate such as an adsorbed carboonium ion would be relatively small.

The dependence of k_f on S_0 was investigated by adding the same amount of olefin from a single batch to different amounts of degassed black. The main source of water is residual water in the partially dried olefin. Since the same amount of olefin was used, P_0 , the initial concentration of poison was constant for the series of runs. If K for reaction 1 were so large that the reverse reaction could be neglected, PS would be essentially equal to P_0 and therefore constant for a given batch of olefin. In this case, a plot of k_f versus S_0 would be linear with a slope of k and an intercept of $(-kPS)$. Such plots were not linear indicating that PS varied. This result supports the equilibrium assumption for reaction (1).

Equation (11) would still be useful for testing the dependence of k_f on black concentration if PS could be determined. An expression for PS can be obtained by combining Eq. (10) with the conservation equation

$$P_0 = P + PS, \quad (12)$$

and the equilibrium expression for reaction (1)

$$K = \frac{PS}{(P)(S)}. \quad (13)$$

Solution of the resulting quadratic yields

$$PS = \frac{(1/K) + P_0 + S_0 - \{[(1/K) + P_0 + S_0]^2 - 4P_0S_0\}^{1/2}}{2}. \quad (14)$$

Substitution of Eq. (14) into Eq. (11) yields an expression for the dependence of k_f on K , P_0 , and S_0 . However, since the resulting equation does not submit readily to simplification, it is difficult to visualize the form of dependence. In order to obtain a graphical representation, K and P_0 values within the ranges of the current study were chosen and substituted into Eq. (14); PS was then calculated for a range of S_0 . Next k_f values over the range of S_0 were obtained from Eq. (11), and $\log k_f$ was

plotted vs $\log S_0$ with the results shown in Figs. 2 and 3. Since the mechanism that gives rise to the two families of calculated curves in Figs. 2 and 3 is a simple and perhaps a common mechanism for liquid-solid systems, it is felt that other studies of rate dependence on catalyst concentration may conform to the current analysis. Thus, plots such as Figs. 2 and 3 may serve to identify competitive inhibition in reversible systems and yield some idea of the magnitudes of K and P_0 .

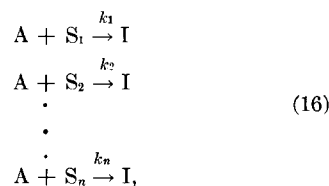
Figure 3 is of particular interest because one might reasonably guess that the dependence of a catalytic rate constant on catalyst concentration would be of the form

$$k_{\text{cat}} = k'[\text{catalyst}]^x, \quad (15)$$

where x is the apparent order with respect to catalyst. Equation (15) predicts that a plot of $\log k_{\text{cat}}$ versus $\log [\text{catalyst}]$ should yield a straight line with a slope equal to x .

In Fig. 3, the $P_0 = 0$ line is an example of this situation with $n = 1$. Equation (11) reduces to Eq. (15) when $P_0 = 0$ because in the absence of poison, PS also equals zero. However, if a competitive inhibitor is present as in this study the log-log plot still yields a reasonably straight line but the observed order is larger than unity and not related in an obvious way to the elementary steps of the mechanism.

The catalyst poisoning results and deuterium incorporation study indicate that there is a range of site activity. The dependence of k_f on S_0 indicated in Eqs. (11) and (14) does not take the distribution of site activity into account. In order to consider heterogeneity of active sites, we assume a series of sites S_i with a corresponding set of rate constants, k_i . The forward part of reaction (2) can then be written:



where n is the total number of sites avail-

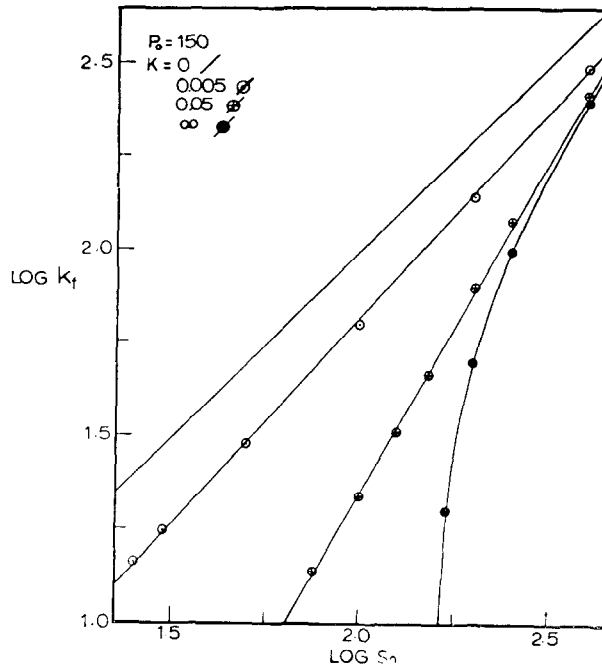


FIG. 2. Family of curves generated by the mechanism with P_0 constant and variable values for the equilibrium constant for competitive inhibition.

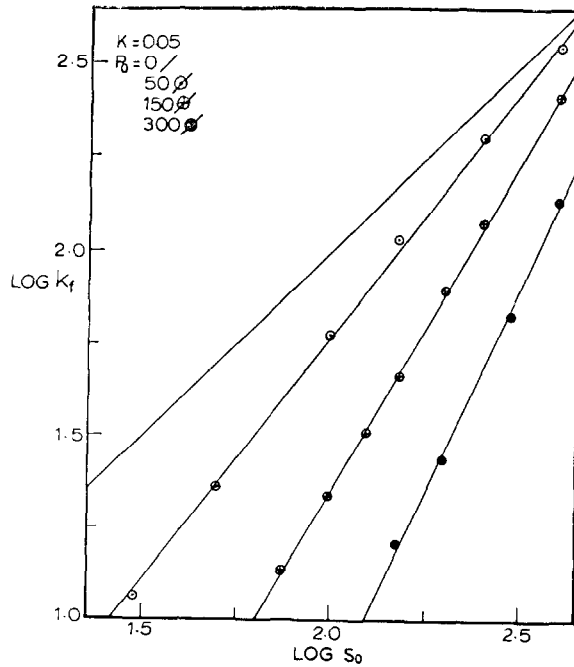


FIG. 3. Family of curves generated by the mechanism with a single value for the equilibrium constant and variable levels of catalyst poison.

able under a given set of reaction conditions. Since consideration of the reverse reaction does not affect the conclusions, it is omitted for simplicity. The rate of disappearance of A is given by

$$-\frac{dA}{dt} = k_1AS_1 + k_2AS_2 \cdots k_nAS_n \quad (17)$$

$$-\frac{dA}{dt} = A \sum_{i=1}^n k_iS_i.$$

The empirical forward rate constant can be identified in Eq. (17) as

$$k_f = \sum_{i=1}^n k_iS_i. \quad (18)$$

Since the variation in activity is likely to be continuous rather than discrete, the summation in Eq. (18) can be replaced by an integral

$$k_f = \int kS(k)dk, \quad (19)$$

where $S(k)$ is a distribution function indicating the number of sites having k values in the range k to $(k + dk)$.

Some distribution function must be assumed in order to evaluate k_f from Eq. (19). An exponential function proved to give a satisfactory fit to the data, and such a function is also advantageous for the sake of mathematical simplicity. Thus, the function selected was

$$S(k)/S_0 = a \exp(-ak) \quad 0 < k < \infty, \quad (20)$$

where a represents a normalization factor. Substitution into Eq. (19) gives

$$k_f = S_0 \int_0^{\infty} ak \exp(-ak)dk, \quad (21)$$

where the limits indicated assume no poisoning. Integration yields

$$k_f = S_0/a. \quad (22)$$

If the more active sites are preferentially poisoned, as suggested by the poisoning results, and k' is the rate constant for the least active poisoned site, Eq. (20) can be integrated to yield PS:

$$PS = S_0 \int_{k'}^{\infty} a \exp(-ak)dk, \quad (23)$$

$$PS = S_0 \exp(-ak').$$

The rate constant, k_f , will be given by the integral over all sites which are not poisoned:

$$k_f = S_0 \int_0^{k'} ak \exp(-ak)dk,$$

$$k_f = (S_0/a)[1 - (ak' + 1) \exp(-ak')]. \quad (24)$$

Equation (24) can be converted to a useful form by eliminating k' using Eq. (23):

$$k_f = a^{-1}[S_0 - PS - PS \ln(S_0/PS)]. \quad (25)$$

Reasonable values of K and P_0 were assumed and k_f was calculated from Eqs. (14) and (25) for a series of S_0 values in the concentration range used in this study. Log k_f versus log S_0 plots for the generated data and the experimental data could then be compared. At constant temperature, K is a constant, and for a given batch of olefin P_0 is constant. In Fig. 4 the log-log plots are presented for data collected at the same temperature for two different batches of olefin. Either experimental line taken separately could be fitted by any number of combinations of K and P_0 . However, since these runs were made at the same temperature, both data sets must be correlated with a single assumed K if the mechanism and site model are consistent with the data. A computer search was made to see if the experimental slopes of 1.30 and 1.48 (solid lines) could be obtained with a single value of K . The best fit was obtained with $K = 1/221$. In

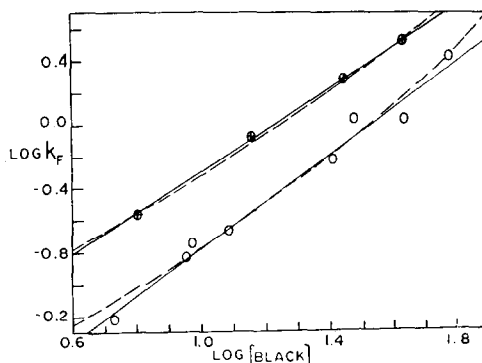


FIG. 4. Rate dependence on black concentration at 52.5°C; (---) generated by mechanism and heterogeneous site model. (O) Molecular sieve dried olefin; (⊕) calcium hydride dried olefin.

the faster run using calcium hydride dried olefin, the broken line was generated with $P_0 = 135$. In the slower molecular sieve dried run, the best fit was obtained with $P_0 = 358$. Although there is substantial scatter in the slower run, Fig. 4 indicates that the model and mechanism are consistent with the data. The K and P_0 values are in arbitrary units relative to S_0 which ranged from 70 to 800.

It is also possible to test the model using a constant P_0 and a variable K . This can be done by determining k_f as a function of S_0 at two temperatures with olefin taken from a single batch so that P_0 is constant. Since reaction (1) is undoubtedly exothermic, K will decrease with increasing temperature. According to the site model and mechanism, the slope of a $\log k_f$ versus $\log S_0$ plot will decrease when K decreases (see Fig. 2). Figure 5 is the log-log plot for black dependence runs at 0 and 19°C using a single batch of sodium dried olefin. The slope is smaller at 19°C as predicted. Lines were fitted by the method of least squares.

Since the exponential distribution function indicated in Eq. (19) was selected

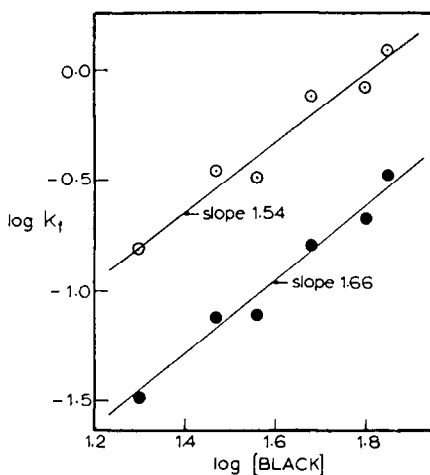


FIG. 5. Rate dependence on black concentration with sodium dried olefin over black partially poisoned by readsorption; (O) at 19.1°C, (●) at 0.0°C.

rather arbitrarily, several other simple functions were considered briefly. For given K and P_0 values, the slope and amount of curvature of the $\log k_f$ versus $\log S_0$ plots varied somewhat with the function selected, but the variations were not extensive over the concentration range used in this study. It is doubtful that the data are precise enough or cover a sufficient range of S_0 to distinguish between the functions on the basis of fit.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This study was also partially supported by a research grant from Cabot Corporation.

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