Regeneration of Activated Carbon

Part I: Thermal Decomposition of Adsorbed Sodium Dodecylbenzene Sulfonate

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Equilibrium adsorption isotherms and rates of thermal decomposition were measured for sodium dodecyl-benzene sulfonate (DBS) adsorbed on powdered activation carbon. The rate data were obtained in a thermal gravimetric apparatus operated both at constant temperature (522 to 666 K) and with a constant rate of temperature increase from 298 to 1023 K.

About 50% of the adsorbed material could be removed at temperatures up to 748 K and only a small amount of the remaining 50% could be eliminated by further heating to 1,023 K. The residual adsorbate at 1,023 K was considerably greater than could be accounted for by inorganic materials such as Na_2SO_4.

The kinetics of the decomposition up to 748 K could be explained by a two-reaction sequence, either parallel or consecutive reactions. Rates of decomposition were slower than found in earlier studies (Chihara et al., 1981) with adsorbed sucrose, and the kinetic steps were different. With sucrose, considerable decomposition occurred between 298 and 428 K. While with DBS, no decomposition was observed in this temperature range. Above 400 K, it was possible to explain the kinetics of decomposition in the case of sucrose by a single step forming residual carbon and volatile products, while with DBS, a two-reaction sequence was required.

SCOPE

Regeneration of activated carbon normally requires drying of the spent carbon at temperatures up to 378 K, followed by heating and gasification at temperatures up to 1,073 K. The gasification process with an oxidizing gas is usually necessary to retain most of the original adsorption capacity. A large fraction of the deposited material can be removed by thermal decomposition prior to gasification (oxidation). For an adsorbate such as sucrose with no inorganic residue, nearly all of the adsorbed material is volatilized by heating alone. With more refractory materials such as DBS, heating to 1,073 K leaves significant carbonaceous material in addition to the inorganic residue.

For design of regenerators, rate equations are necessary for both thermal decomposition and gasification. In a prior study (Chihara et al., 1981), kinetics were measured for these two processes with carbon containing adsorbed sucrose. For this easily decomposed adsorbate, the overall thermal decomposition process could be explained by separate, single, rate-controlling steps, the first for 298 K $< T <$ 428 K and the second occuring at 428 $< T <$ 773 K. The objective of the current work was to measure rates of thermal decomposition and gasification for a refractory adsorbate, and DBS was considered to be representative of such components found in wastewaters.

First, equilibrium isotherms were measured at 303 and 308 K. Then thermal decomposition data were obtained in a TGA apparatus operated at constant temperatures up to 666 K and with a constant rate of temperature rise up to 1,023 K, all at atmospheric pressure in a stream of helium. These results are reported in Part I. In Part II rates of gasification of residual adsorbed material are reported and analyzed.

CONCLUSIONS AND SIGNIFICANCE

Equilibrium isotherms for DBS on BPL activated carbon (bituminous coal base) indicate capacities of 0.28 to 0.60 kg adsorbed per kg of activated carbon over a range of solution concentrations (aqueous) from 20 to 9,000 ppm. These capacities are more than twice those for sucrose on the same carbon.

No thermal decomposition was observed below about 490 K for DBS, while for sucrose more than 30% of the adsorbed material was removed by heating to 428 K. Then all except for a few percent of the original weight of adsorbed sucrose could be removed by further heating to 773 K. In contrast, thermal decomposition of DBS in the range of 490 to 748 K reduced the adsorbed material by only about 50%. Rate data for sucrose could be explained by single decomposition reactions giving volatile and adsorbed products. For DBS in the 490 to 748 K range, two rate-determining reactions were required. Either consecutive or parallel reactions could explain the data and both lead to the same final equations for the weight change. Hence, it was not possible to discriminate between the two reaction schemes. The activation energies for the two reactions were 1.09×10^5 and 2.0×10^5 J/mol.

The remaining 50% of the original adsorbed material decomposed slowly at temperatures above 748 K, and most of it remained on the carbon at 1,023 K in TGA experiments with rates of temperature rise of 0.1 and 0.3 K/s. Since probably not more than 20% of the original adsorbate could remain as inorganic material, these results suggest that considerable carbonaceous residue remains on the carbon at 1,023 K. Gasification

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by oxidation is necessary if the residual material is to be removed at temperatures below 1,023 K. Kinetics of steam regeneration and recovery of adsorption capacity are presented in Part II.

The use of activated carbon for purification of wastewaters is growing, and economic considerations require regeneration. Rate data are necessary for careful design of regeneration equipment. Such information is meager, particularly for powdered carbon. Suzuki et al. (1978) studied rates of thermal regeneration of spent, powdered carbon loaded with different single adsorbates. From their results adsorbates were grouped into three types according to their rates of decomposition. DBS was in the more refractory group. Hernandez and Harriott (1976) investigated the low-temperature gasification with oxygen of sodium dodecylbenzene sulfonate on activated carbon. They employed fluidized beds and measured the effectiveness of regeneration by determining the adsorption capacity at various times during the regeneration process.

Large differences in regeneration rates for different adsorbates were found by Suzuki et al. (1978). Therefore, detailed kinetic information is needed for a variety of contaminants to design regeneration processes for different wastewaters. Polysaccharides are thermally decomposed and gasified at a relatively high rate. Chihara and colleagues (1981) measured the kinetics of thermal decomposition and gasification (with steam) of sucrose as a representative of the polysaccharide class of adsorbates. While nearly all the adsorbate could be removed by thermal decomposition, complete regeneration to the adsorption capacity of the virgin carbon required oxidation of the residual carbon. This oxidation step with steam obeyed the rate equation proposed (Walker et al., 1959) for oxidation of many types of carbon.

More refractory, aromatic-type contaminants also are found in many wastewaters. The objective of the research reported here is to obtain rate data for sodium dodecylbenzene sulfonate (DBS) as a model contaminant of the more refractory type. After thermal decomposition to 1,073 K, Suzuki et al. (1978) found that about 50 wt. % of the original DBS remained on the activated carbon. A part of this residue is probably inorganic material such as sodium sulfate. A study of DBS is interesting because a significant amount of inorganic salt could catalyze the final gasification step of the regeneration process.

EXPERIMENTAL

The experimental work consisted of two parts: 1) preparation of activated carbon samples saturated with DBS and determination of adsorption isotherms; and 2) thermal regeneration experiments in the TGA apparatus.

Sample Preparation and Adsorption Measurements

A coal-based activated carbon (type BPL, Pittsburgh Activated Carbon Co.) was used. This virgin carbon was from the same batch that was used by Chihara et al. (1981) in studying regeneration with sucrose as the adsorbate. The carbon had a broad pore-size distribution, a reported ash cotent of 8 wt. % and surface area (by nitrogen adsorption) of 7.2×10^5 m^2/kg. Other properties were tabulated by Chihara (1981). The original 4 × 8 mesh particles were first crushed, sieved, and the 48 to 65 mesh material used for most of the experiments. Pretreatment consisted of boiling in deionized water to remove fines and drying in an oven at 393 K for 24 hours.

Sodium dodecylbenzene sulfonate (analytical grade, Pfaltz and Bauer, Inc.) was dissolved in deionized water, and known weights of carbon particles were added to flasks containing different known concentrations of the DBS solution. The flasks were placed in a constant-temperature (303 and 308 K) shaking device for four days. Preliminary tests indicated that equilibrium was attained in about two days. A Beckman Total Organic Carbon Analyzer was used to measure the concentration of the solution at equilibrium. The DBS-loaded particles were reclaimed by filtration and dried by one of two methods:

A. Vacuum drying at 298 K for 5.5 hours

B. Drying in an oven in air at atmospheric pressure and 393 to 413 K for five days

The amounts of DBS adsorbed was determined from the weight of the samples before adsorption and after drying. These results were compared with the amounts adsorbed as obtained from the concentrations of the solutions before and after impregnation. The equilibrium data covered DBS concentrations in the solutions from 20 to 9,000 ppm and adsorbed concentrations up to about 0.60 kg/(kg of virgin carbon).

TGA Experiments

A Perkin Elmer, Model TGS-2 (with System 4 microprocessor controller) was used to measure the weight vs. time data for thermal decomposition. The modifications made by Chihara et al. (1981) and the flow rates used in that study were employed here. Details of the modified apparatus, operating conditions, and a flow diagram are given in the Chihara paper.

A carbon sample containing DBS with a weight of the order of 2×10^{-6} kg was placed in the platinum pan and heated. In one set of experiments the temperature was increased to 1,023 K at constant rates of 0.1 to 0.3 K/s. In the second experiments the temperature was rapidly increased to one of five temperatures (522 to 666 K) and then held at constant temperature.

In thermal decomposition experiments it is important to eliminate, as far as possible, oxygen from the gas flow to reduce the rapid oxidation of carbon as adsorbate. A high-purity helium (99.995%) was employed as a carrier gas and care taken to reduce leaks. The effect of oxygen was tested by measuring the weight change when a sample of virgin carbon was heated to 1,023 K at a rate of 0.1 K/s. During the first heating of the sample, a small weight loss, less than 2%, was observed. During subsequent heating cycles the weight loss was negligible. The initial weight loss was presumably due to desorption of residual material on the activated carbon. In the subsequent kinetic analysis of the data, the sample weight has been corrected for this small change in mass of virgin carbon.

Several other preliminary experiments were carried out to ensure that the weight vs. time data were a measure of intrinsic kinetics rather than the combined effect of intrinsic kinetics and transport processes. These experiments are described later.

ADSORPTION ISOTHERMS

The adsorption equilibrium results obtained from solution concentrations are shown by the open points in Figure 1. There is not a significant difference between the 303 and 308 K data points. The solid points represent the results obtained from weighing the carbon samples, and these coincide reasonably well with the hollow points. The agreement between the data from drying at 298 and at 393–413 K indicate that adsorbed DBS does not desorb appre-

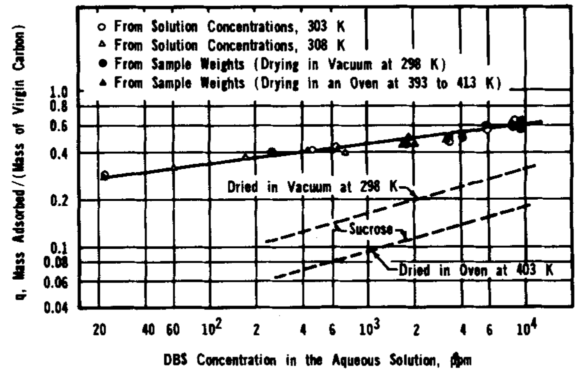

Figure 1. Adsorption equilibrium isotherms.

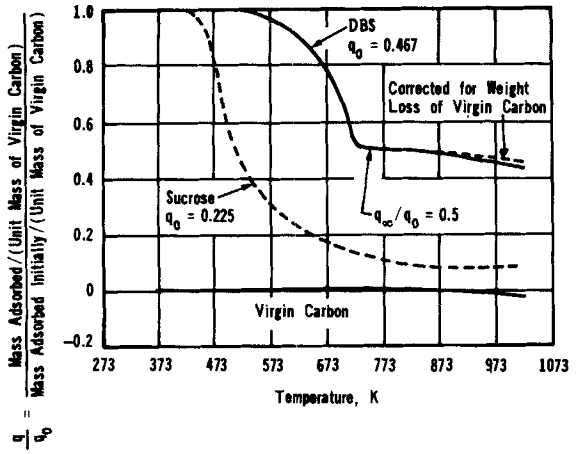

Figure 2. Typical TGA data for DBS samples and for virgin carbon (heating rate = 0.1 K/s).

ciably when heated to 413 K. This is in contrast to the earlier data (Chihara et al., 1981), for sucrose which are shown by the dashed lines in Figure 1. Not only is the adsorption capacity lower for sucrose but considerable desorption occurs when the samples are heated from 298 to 403 K.

PRELIMINARY ANALYSIS

Typical TGA data are shown in Figure 2. The amount adsorbed is expressed as q/q_o, where q is the remaining mass adsorbed per unit mass of virgin carbon and q_o is the initial value of q before heating begins. Only a little more than 50% ($q/q_o \sim 0.45$) of the DBS is desorbed by heating to 1,023 K. Part of the large residue remaining on the carbon is presumably due to the non-volatile sodium and sulfur. If the thermal decomposition were represented by the overall reaction

$$2\,CH_3(CH_2)_9CH(C_6H_5SO_3Na)CH_3(s) \rightarrow Na_2SO_4(s) + SO_2(g) + \text{volatile products},$$

about 20% of the weight of the initially-adsorbed DBS would remain as Na_2SO_4. Since Figure 2 shows 45% remains, complete desorption of the carbonaceous material is not achieved by heating to 1,023 K.

The prior results for sucrose, shown by the dashed curve in Figure 2, are strikingly different. The different shapes for DBS and sucrose suggest different kinetics. Also, for sucrose the desorption is more nearly complete; a value of q/q_o of 0.08 at 1,023 K was found by Chihara et al. (1981).

Transport Considerations

To test whether the data represented intrinsic kinetics, three types of preliminary experiments were carried out. First, TGA curves were measured for helium flow rates of 3.4×10^{-7} and 6.7×10^{-7} m^3/s (at 298 K, 1 atm). These two curves were not measurably different. Next, TGA curves were determined for one and for three layers of carbon particles in the pan. Again the curves were essentially the same. When a reacting gas mixture is introduced, for example, helium plus steam, the rate of reaction has been found (Chihara et al., 1981) to decrease with the number of layers. This mass-transfer effect was not observed when only helium was in the gas stream. Finally, a TGA curve was measured with particles with an average radius of 8.5×10^{-4} m. This is 6.8 times as large as the average radius for the 48 to 65 mesh fraction used for the kinetic studies. No distinction could be drawn between the curves for the two sizes, suggesting that intraparticle transport was not affecting the data for these particle sizes.

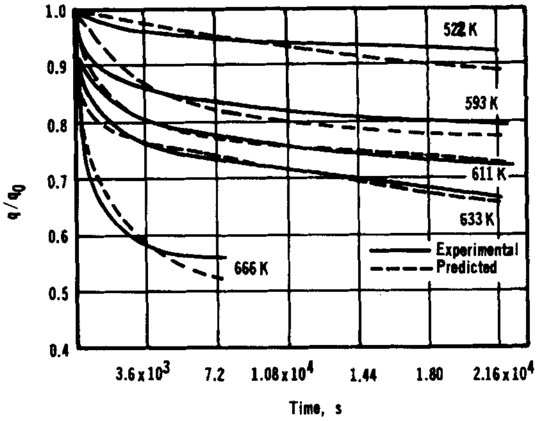

Figure 3. Experimental and predicted weight vs. time data at constant temperature.

DECOMPOSITION KINETICS

The DBS curve in Figure 2 shows that the major decomposition process starts at about 490 K and is nearly complete at 748 K. A second, small loss in weight occurs when the temperature is further increased to 1,023 K. We will interpret these results by a two-process decomposition. In the first process, most of the products are volatile but adsorbed intermediate remains. In the second process, this intermediate partially decomposes, slowly, on further heating, but a considerable residue remains at 1,023 K.

Kinetics of the First Process (490 < T < 748)

Figure 3 shows the data obtained by rapid heating (160 K/s) followed by a constant temperature within the range where the first decomposition occurs. The concentrations of products in the effluent helium were too low to measure quantitatively. However, gas chromatographs indicated at least two volatile products containing sulfur and hydrocarbons. We have found that the weight vs. time data can be explained by two reaction schemes. If the decomposition products are grouped into single volatile and adsorbed products, the first scheme is represented in an overall way by two *consecutive* reactions:

$$\overline{D} \xrightarrow{k_1} s\overline{S}(\text{Ads.}) + i\overline{I}(s) + G_1(g) \tag{1}$$

$$\overline{S}(\text{Ads.}) \xrightarrow{k_2} G_2(g) \tag{2}$$

where $\overline{I}(s)$ is a stable (up to 748 K) adsorbed intermediate and $\overline{S}$(Ads.) is a less-refractory absorbed species that desorbs according to the second reaction. The shape of the curves for DBS ($\overline{D}$) up to 723 K in Figures 2 and 3 could not be explained by a single reaction such as Eq. 1. If the decomposition and desorption (of $\overline{S}$) steps are first order, the following rate equations may be written:

$$\frac{dq_D}{dt} = -k_1 q_D \tag{3}$$

$$\frac{dq_s}{dt} = s k_1 q_D - k_2 q_s \tag{4}$$

$$\frac{dq_I}{dt} = i k_1 q_D \tag{5}$$

with initial condition

$$q_D = q_o; \quad q_s = q_I = 0; \quad \text{at } t = 0 \tag{6}$$

Integration of Eqs. 3–5 with Eq. 6 yields

$$\frac{q_D}{q_o} = \exp(-k_1 t) \tag{7}$$

$$\frac{q_s}{q_o} = \frac{s k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{8}$$

$$\frac{q_I}{q_o} = i[1 - \exp(-k_1 t)] \tag{9}$$

Since the total amount adsorbed, q, is given by

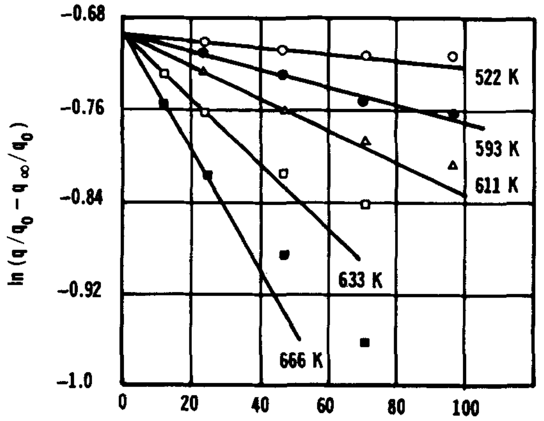

Figure 4. Data for initial rates for first process (490 < T < 748 K).

$$q = q_D + q_s + q_I \tag{10}$$

Equations 7–9 give

$$\frac{q}{q_o} = i + \left(1 - i + \frac{sk_1}{k_2 - k_1}\right)\exp(-k_1t) - \frac{sk_1}{k_2 - k_1}\exp(-k_2t) \tag{11}$$

Let q_∞ be the final value for the amount adsorbed at the end of the first process (i.e., at 723 K in Figure 2). Then q_∞/q_o is obtained from Eq. 11 by setting $t = \infty$. In terms of q_∞/q_o this equation becomes

$$\frac{q}{q_o} - \frac{q_\infty}{q_o} = \alpha_1 \exp(-k_1t) + \alpha_2 \exp(-k_2t) \tag{12}$$

$$\left.\begin{aligned} \alpha_1 &= 1 - i - \frac{sk_1}{k_1 - k_2} \\ \alpha_2 &= \frac{sk_1}{k_1 - k_2} \\ q_\infty &= iq_o \end{aligned}\right\} \tag{13}$$

In the second scheme it is supposed that adsorbed *DBS* consists of two different species, $\bar{D}_1$ and $\bar{D}_2$, and that these species each decompose according to the *parallel* reactions:

$$\bar{D}_1 \xrightarrow{k_1'} i_1\bar{I}_1(\text{Ads}) + G_1'(g) \tag{14}$$

$$\bar{D}_2 \xrightarrow{k_2'} i_2\bar{I}_2(\text{Ads}) + G_2'(g) \tag{15}$$

First-order rate equations may be written for these reactions, giving differential equations analgous to Eqs. 3–5. If these equations are solved in exactly the same way as Eqs. 3–5 were solved, the final expression for q/q_o is

$$\frac{q}{q_o} - \frac{q_\infty}{q_o} = \beta_1 \exp(-k_1't) + \beta_2 \exp(-k_2') \tag{16}$$

where

$$\left.\begin{aligned} \beta_1 &= a(1 - i_1) \\ \beta_2 &= b(1 - i_2) \end{aligned}\right\} \tag{17}$$

and the initial amounts of $\bar{D}_1$ and $\bar{D}_2$ are related to q_o by

$$\left.\begin{aligned} (q_{D_1})_o &= aq_o \\ (q_{D_2})_o &= bq_o \end{aligned}\right\} \tag{18}$$

Equations 12 and 16 are of the same form, but α_1 and α_2 are functions of ratios of rate constants while β_1 and β_2 are not. Our experimental data consisted of q/q_o as shown in Figures 2 and 3. This overall information was insufficient to discriminate between the two schemes. In fact, if α_1 and α_2 are treated as constants, numerical analysis of the experimental q/q_o vs. time data will lead to the same values of the rate constants k_1 and k_2.

The analysis procedure used is first to determine approximate values for k_1 from the data in Figure 3 during the initial time period. At low times the second step (Eq. 2) is neglected. Figure 4 shows the low-time data of Figure 3 plotted according to the first term on the right side of Eq. 12. Straight lines are obtained up to decompositions of about 6%. This suggests that from 0 to 6% decomposition the weight loss is the first term of reactions 1, while above 6% the influence of reaction 2 is significant. In preparing Figure 4, q_∞/q_o is taken equal to 0.5 in agreement with the TGA data shown in Figure 2. The k_1 values obtained from the slope of the lines in Figure 4 are displayed in an Arrhenius plot (by the open points) in Figure 5. The straight line through the points for these preliminary values of k_1 can be written

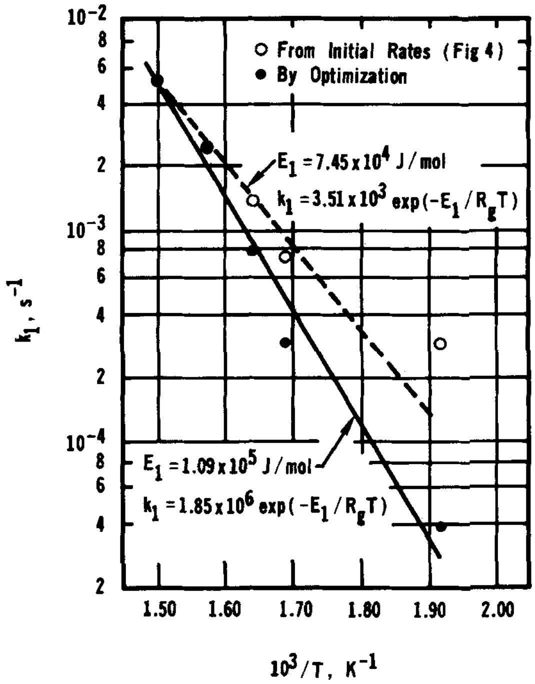

Figure 5. Arrhenius plot for Eq. 1 of first process (490 < T < 748 K).

$$k_1 = 3.51 \times 10^3 \exp(-7.45 \times 10^4/R_gT) \tag{19}$$

At $t = 0$, Eq. 12 reduces to

$$\alpha_1 + \alpha_2 = 1 - \frac{q_\infty}{q_o} = 1 - 0.5 = 0.5, \tag{20}$$

and a similar equation would be applicable for $\beta_1 + \beta_2$, according to Eq. 16. Hence, Eq. 12 or 16 with β replacing α, may be written

$$\frac{q}{q_o} - \frac{q_\infty}{q_o} - \alpha_1 \exp(-k_1t) = (0.5 - \alpha_1)\exp(-k_2t) \tag{21}$$

This equation shows that a plot of the left side vs. t on semilog paper should be a straight line for the proper value of α_1. The slope and the intercept of the line give k_2 and a check on the assumed value of α_1. If the α values are assumed to be constant, the results for $\alpha_1 = 0.2$ are shown in Figure 6 for the data given in Figure 3. The data for the three intermediate temperatures give intercepts of about 0.3, in agreement with $\alpha_1 = 0.2$ and Eq. 20. Figure 7 is an Arrhenius plot of the resultant k_2 values, and the equation of the line is

$$k_2 = 1.7 \times 10^{12} \exp(-2.0 \times 10^5/R_gT) \tag{22}$$

The reasons for the deviations in Figure 6 for $T = 666$ K are not clear. Perhaps the desorption of $\bar{S}$ according to Eq. 2 occurs at this relatively high temperature even at low time values so that the reaction scheme is invalid at 666 K. Interestingly, the slope of the low-time section of this line for this temperature in Figure 6 gives a value of k_2 that is consistent with the results

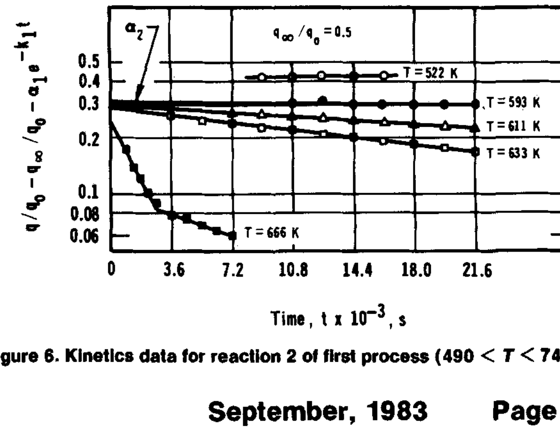

Figure 6. Kinetics data for reaction 2 of first process (490 < T < 748 K).

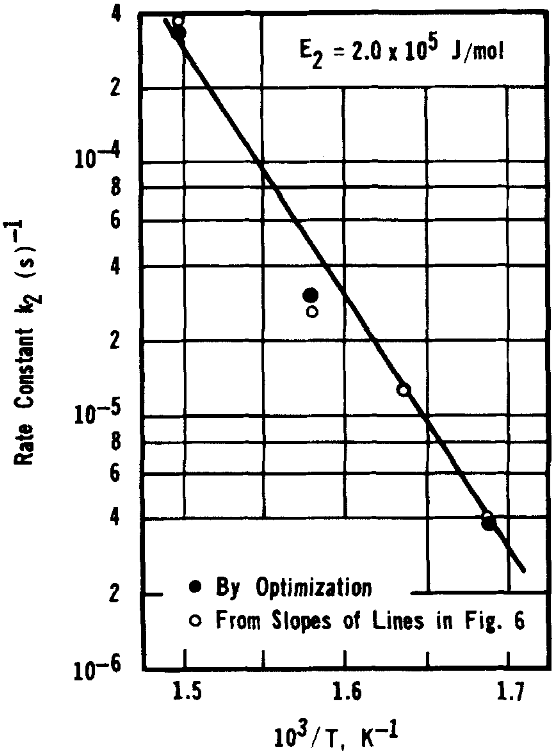

Figure 7. Arrhenius plot for reaction 2 of first process (490 < T < 748 K).

for other temperatures in Figure 7. The data for T = 522 K do not fit the model, but the total extent of decomposition was but 7%. Hence, small errors in the data leads to large errors in this line in Figure 6.

Revised values of k_1 and k_2 were obtained by minimizing the sum of the squares of the deviations between the experimental points in Figure 3 and the predicted q/q_o from Eq. 12, using chosen values of k_1 and k_2. The optimization procedure for each temperature was initiated by using the preliminary values of k_1 and k_2 given by Eqs. 19 and 22. The revised results give essentially the same values for k_2, but the expression for k_1 becomes

$$k_1 = 1.85 \times 10^6 \exp(-1.09 \times 10^5/R_gT) \tag{23}$$

The dotted lines in Figure 3 show the predicted results by Eq. 12, using Eqs. 22 and 23 for k_1 and k_2 and $\alpha_1 = 0.2$. The agreement is reasonably good for all the temperatures and over the whole decomposition range, although significant deviations occur at some conditions. This is not surprising since Eqs. 1 and 2, or 14 and 15, are gross simplifications of what must be a complex process. Better agreement could be obtained with more elaborate mechanisms. However, such mechanisms would be based upon more conjecture and lead to rate equations that might be too complex for use in design.

As mentioned, α_1 and α_2 were taken to be constant, independent of temperature. From Eqs. 13 this means that the ratio k_1/k_2 has been assumed to be independant of temperature. If, instead, the parallel mechanism of Eqs. 14 and 15 were employed, this assumption is not necessary. This is because β_1 and β_2 in Eq. 16 are not functions of the rate constants, as shown by Eq. 17. Using Eqs. 22 and 23 gives values of k_1/k_2 that change considerably with temperature. However, the change in α values caused by the variation in k_1/k_2 is not significant. Firm conclusions cannot be drawn about such a complex process from only overall weight vs. time data.

The reaction schemes considered for the thermal decomposition of adsorbed DBS, that is, Eqs. 1 and 2, or 14 and 15, are different from the schemes suggested by the data for the decomposition of adsorbed sucrose, Chihara et al. (1981). First, it was necessary to account for the low-temperature (T < 428 K) decompositions for sucrose, and this was interpreted by a one-step reaction of the form of Eq. 1. Then the high-temperature (T > 428 K) decomposition could be explained by another single-step reaction of the form of Eq. 1. It was not possible to represent the decomposition of DBS, which only occurred above 490 K, by a single-reaction mechanism.

Predicted TGA Curves

To check the suitability of Eqs. 12 or 16 we can compare experimental TGA curves up to 748 K with those predicted from the constant-temperature data (Figure 3).

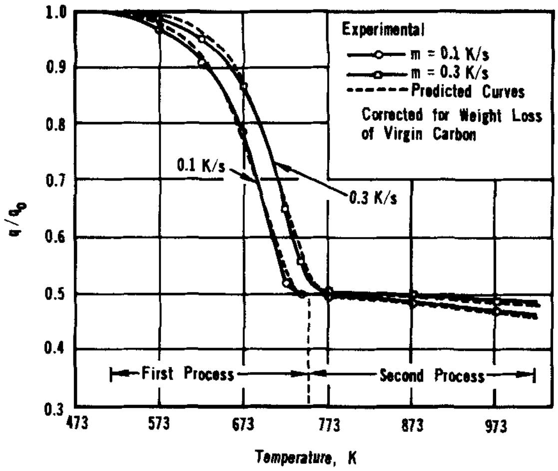

Figure 8. Experimental and predicated TGA curves.

The derivative of Eq. 12 with respect to time, along with the equation for a constant heating rate, m,

$$m = \frac{dT}{dt} \tag{24}$$

gives

$$\frac{d\left(\frac{q}{q_o} - \frac{q_\infty}{q_o}\right)}{dT} = \frac{\alpha_1}{m} k_1 \exp(-k_1t) + \frac{\alpha_2}{m} k_2 \exp(-k_2t) \tag{25}$$

The initial condition is

$$q/q_o = 1.0, \quad \text{at } t = 0 \tag{26}$$

Equation 25, with Eq. 26, can be integrated numerically with k_1, k_2, α_1, α_2 obtained from the constant temperature data, that is, from Eqs. 22 and 23 and $\alpha_1 = 0.2$, $\alpha_2 = 0.3$. The predicted q/q_o vs. temperature curves so obtained are shown in Figure 8 by the dashed lines for two heating rates, m. The agreement with the experimental curves is good, except in the low-temperature region. It is concluded that the simple, two-reaction sequence of Eqs. 1 and 2, or 14 and 15 can explain the high-temperature TGA results, even though the actual decomposition process must be more complex.

Kinetics of the Second Process (T > 748 K)

Figures 2 and 8 indicate that there is but a slight decomposition, at temperatures above 748 K, of the sizeable deposit remaining at that temperature. Thus thermal decomposition at temperatures of 1,023 K cannot reduce significantly the final 50% ($q_\infty/q_o = 0.5$) of the residue left at 748 K. Only a part of this residue is inorganic.

Since the decrease in weight in the second process is so small, it is difficult to draw conclusions about the reactions involved. The thermal cracking model of Suzuki et al. (1978) fits the data and is used here. In this model it is proposed that the adsorbed intermediates, $\bar{I}(s)$ in Equation (1) or $\bar{I}_1$ and $\bar{I}_2$ in Eqs. 14 and 15, decompose into residual carbon and volatile components according to a first-order cracking reaction

$$\bar{I} \xrightarrow{k_3} g'G'(g) + c\bar{C}(s) \tag{27}$$

The results, obtained by this model, from TGA data for three heating rates are shown in Table 1. The three activation energies are in good agreement. The $(k_3)_o$ values cover a wider range, but this is a sensitive parameter. It should be emphasized that the small weight change observed for this second process means that the kinetic results are only approximate.

TABLE 1. KINETIC PARAMETERS FOR HIGH-TEMPERATURE (SECOND PROCESS) DECOMPOSITION

m, K/s	$q_{\infty h}/q_{oh}$	$E_3 \times 10^{-4}$ J/mol	$(k_3)_o$, s^{-1}
0.1	0.92	5.78	1.9
0.2	0.91	5.95	4.6
0.3	0.93	6.12	8.7

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NOTATION

a = fraction of total DBS absorbed as $\overline{D}_1$
b = fraction of total DBS adsorbed as $\overline{D}_2$
$\overline{C}$ = residual adsorbed material
$\overline{D},\overline{D}_1,\overline{D}_2$ = adsorbed forms of sodium dodecylbenzene sulfonate
E_1 = activation energy of decomposition of DBS to intermediate, J/mol
E_2 = activation energy of desorption for Eq. 2, J/mol
E_3 = activation energy of decomposition of intermediate to adsorbed residual material, J/mol
G_1,G_2,G',G'_1,G'_2 = gaseous products
$\overline{I},\overline{I}_1,\overline{I}_2$ = intermediate products retained on the carbon
k_1 = first-order rate constant for decomposition of DBS to intermediate, 1/s
k'_1 = first-order rate constant for Eq. 14
$(k_1)_o$ = preexponential factor for k_1, s^{-1}
k_2 = first-order rate constant for desorption step of adsorbed reactive solid, s^{-1}
k'_2 = first-order rate constant for Eq. 15, s^{-1}
$(k_2)_o$ = preexponential factor of Arrhenius equation for k_2, s^{-1}
k_3 = first-order rate constant for decomposition of intermediate to adsorbed residual material, s^{-1}
$(k_3)_o$ = preexponential factor of Arrhenius equation for k_3, s^{-1}
m = constant heating rate, K/s
q = mass adsorbed per unit mass of initial virgin carbon
q_o = mass adsorbed initially (time = 0) per unit mass of initial virgin carbon; q_{oh} = mass adsorbed at beginning of second process
q_∞ = mass adsorbed at infinite time (per unit mass of initial virgin carbon) for first process; $q_{\infty h}$ = mass adsorbed at 1,023 K for second process
R_g = gas constant, J/(mol)(K)
$\overline{S}$ = adsorbed product of decomposition
T = temperature, K
t = time, s

Greek Letters

α_1,α_2 = coefficients defined by Eq. 13
β_1, β_2 = coefficients defined by Eq. 17

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Part II: Gasification Kinetics with Steam

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The kinetics of the reaction between steam and thermally-regenerated activated carbon containing DBS residue was studied at 973 to 1,062 K and atmospheric pressure. The results fit a Langmuir-Hinshelwood rate equation originally developed for the oxidation of other types of carbon with steam. The rates of reaction were relatively high. Auxiliary experiments with added Na_2SO_4 indicated that the non-volatile inorganic residue from DBS has a catalytic effect.

Readsorption measurements on regenerated samples demonstrated that thermal regeneration alone resulted in considerable loss (35%) in adsorption capacity but that thermal regeneration followed by steam gasification could completely restore the adsorption capacity for DBS on the remaining virgin carbon.

SCOPE

The results of Part I showed that about half of the original adsorbate remained on the activated carbon after thermal regeneration to 748 K. Furthermore, little of this residue from DBS (sodium dodecylbenzene sulfonate) was removed by heating to 1,023 K. Accordingly, oxidation is necessary in order to gasify the carbonaceous residue and restore the adsorption capacity of the carbon. Because of the nonvolatile inorganic content of DBS, there may be a buildup of material on the carbon even after gasification. This buildup will depend on the amount of

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