

either lithium or sodium chloride, more nearly coincides with the effect of initial concentration.

According to the predictions of Eyring,¹² provided the ionic mechanism persists, the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide should proceed more rapidly in alcohol-benzene mixtures than in pure alcohol. It is evident from Fig. 1 that in methyl alcohol-benzene mixtures the rate constant decreases with increasing mole fraction benzene, but does not appear to approach zero in pure benzene. This indicates that an ion-pair reaction comes into play in alcohol-benzene mixtures in addition to the ionic reaction. The ion-pair reaction requires a much higher activation energy than the ionic reaction, since there is involved a separation of the ion-pair against a strong electrostatic attraction.

It appears, then, that the etherification reactions studied here are capable of proceeding by two distinct mechanisms depending on the nature of the solvent. In solvents of high dielectric constant the reactions are ionic, in solvents of very low dielectric constant an ion-pair mechanism predominates, while in solvents of moderate dielectric constant both mechanisms are involved, and the

measured rate constant depends on the fraction of total reaction occurring by each mechanism.

Summary

1. The rates of reaction of *n*-butyl bromide with the sodium salts of phenol, thiophenol and *n*-butyl mercaptan have been determined under comparable conditions, and activation energies have been determined with both methyl and ethyl alcohols as solvents.

2. The order of reactivity with *n*-butyl bromide was found to be $\text{BuSNa} > \text{PhSNa} > \text{PhONa}$.

3. Rate constants were found to decrease with increasing initial concentration of reactants.

4. Neutral salts were found to exert an effect similar in sign and magnitude to the initial concentration effect.

5. The order of reactivity of sodium *n*-butyl mercaptide with *n*-butyl bromide in different solvents, other factors being comparable, was found to be $\text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{OH} > \text{C}_6\text{H}_6$.

6. A mechanism for the reactions is postulated and discussed in the light of the experimental data and certain theoretical considerations.

EMORY UNIVERSITY, GA. RECEIVED AUGUST 29, 1941

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Kinetics of Hydrogen Consumption, Oxygen Elimination and Liquefaction in Coal Hydrogenation. Nature of the Catalytic Reactions¹

BY H. H. STORCH, C. O. HAWK, AND W. E. O'NEILL

In previous papers of this series^{2,3,4} on coal hydrogenation in the presence of a stannous sulfide catalyst, the rates of change of readily measurable quantities (namely: hydrogen absorbed, oxygen removal as water and carbon oxides, and solubility in benzene) were determined. The temperature coefficient of the rate of hydrogen absorption was relatively low, and the rate appeared to be independent of those of oxygen elimination and liquefaction. It was assumed, therefore, that the slow step in the hydrogen consumption was the diffusion of hydrogen through a liquid film on the

catalyst surface. As will be shown below, additional data and a more careful analysis show that the nature of the rate-determining step varies with the temperature.

From the earlier work² on the rates of oxygen removal and of liquefaction at various temperatures in the presence of a stannous sulfide catalyst, four stages in the coal-hydrogenation process could be discerned, namely:

(a) Solution or extraction of the coal. This is practically the only process occurring at a moderate, measurable rate below 370°. Its temperature coefficient is about 1.2/15°, and the slow step is probably a depolymerization of the coal by solvation.

(b) A primary decomposition of the coal at temperatures above 370° involving the rapid elimination of about 60% of the oxygen of the

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) H. H. Storch, C. H. Fisher, A. Eisner and L. Clarke, *Ind. Eng. Chem.*, **32**, 346-53 (1940).

(3) C. H. Fisher, G. C. Sprunk, A. Eisner, L. Clarke, M. L. Fein and H. H. Storch, *Fuel*, **19**, 13-16, 51-55, 67-69 (1940).

(4) C. H. Fisher, A. Eisner, L. Clarke, M. L. Fein and H. H. Storch, *ibid.*, **20**, 5-13 (1941).

coal as water and carbon dioxide. This reaction has a temperature coefficient of about $3.0/15^\circ$ and is probably non-catalytic.

(c) A reaction with a considerably lower temperature coefficient than that of (b) is responsible for the slower elimination of the remaining 40% of the oxygen. It was suggested that this reaction might be a catalytic process.

(d) Condensation of the dissolved primary coal decomposition products to form molecules more stable than the original coal. This process becomes important at temperatures beyond 400° and results in an apparent decrease in rate with increasing temperature for the later stages of the liquefaction and oxygen-elimination reactions. Above 440° this process results in coke formation, even in the presence of 180 atmospheres of hydrogen.

To obtain some information concerning the nature of the catalytic reactions involved in coal hydrogenation, a series of experiments was performed with one bituminous coal at various temperatures and contact times, in the presence and absence of a catalyst. To avoid possible catalytic effects of the autoclave walls, Pyrex glass liners similar to those described by the British Fuel Research Laboratory⁵ were used in all but one of the experiments described below. A detailed description of the hydrogenation equipment and method has been published.^{4,6} The coal sample (50 g.), 65 g. of tetrahydronaphthalene, and 0.5 g. of stannous sulfide were placed in the Pyrex glass liner of the 1200-cc. stainless steel bomb. In several special tests naphthalene was used as the vehicle, iodoform as the catalyst, and nitrogen or natural gas in place of hydrogen. Air was removed from the bomb by flushing with hydrogen, and hydrogen was then added until the pressure at 20° was 1000 pounds per square inch, 70.3 kg. per sq. cm. The rotating bomb and its contents were heated to reaction temperature in about one and one-half hours. Experiments of six hours duration or less were completed with only one charging of the bomb with hydrogen. Nine-, twelve- and fifteen-hour experiments were made, respectively, in two reaction periods of four and one-half, six and seven and one-half hours each. At the end of the first period, the bomb was cooled to room temperature and the gases were discharged through dilute sulfuric acid, sodium hydroxide and a wet test meter, after which fresh hydrogen was introduced to 1000 pounds per square inch at 20° for the second period. Small samples of the bomb gases were collected for Orsat analysis.

The liquid and solid products were transferred to a 250-cc. centrifuge bottle and centrifuged. The centrifuge residue was washed six times with acetone at room temperature. The centrifuged oil and the first three acetone washings were distilled through a well-insulated, indented, 6-inch column to 220° . The distillate collected at 150

to 220° , chiefly tetrahydronaphthalene, was analyzed for tar acids, bases, olefins, and aromatics. The distillation residues, which were black, semisolid pitches, were analyzed for ash, carbon, hydrogen, nitrogen, sulfur, and oxygen (by difference).

The amount of oxygen not removed by hydrogenation was calculated from the oxygen content of the coal, pitch, and residue. Reacted or eliminated oxygen was defined as that removed as water, carbon dioxide, carbon monoxide, and phenols and carboxylic acids boiling below 220° . As most of the eliminated oxygen of the coal was converted into water and carbon dioxide, similar results would have been obtained by considering the oxygen in phenols and carboxylic acids (boiling below 220°) as inert and unremoved by hydrogenation. The amount of oxygen removed by cracking during distillation of the centrifuged oil is believed to be comparatively small.

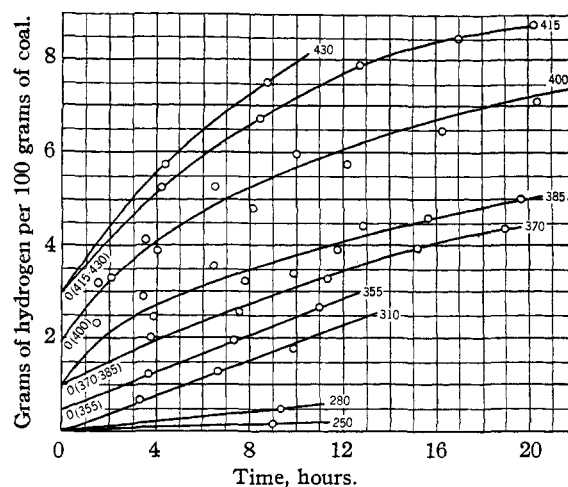


Fig. 1.—Rate of hydrogen absorption in presence of stannous sulfide catalyst. Note that point of zero absorption is shifted to make each curve distinct.

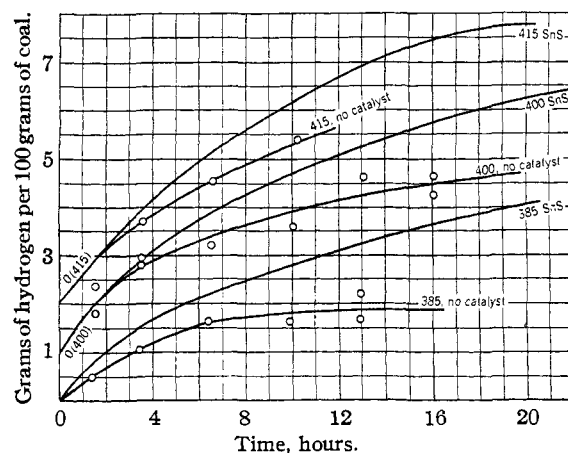


Fig. 2.—Rates of hydrogen absorption, influence of catalyst. Note that point of zero absorption is shifted on ordinate to make each pair of curves distinct.

An outline of the general features of the coal-hydrogenation reactions may be obtained from studying the data of

(5) British Fuel Research Board Report for the Year Ended March 31, 1937. H. M. S. Office, London, 1937, pp. 149-151.

(6) C. H. Fisher and A. Eisner, *Ind. Eng. Chem.*, **29**, 1371-1376 (1937).

TABLE I

BATCH HYDROGENATION OF PITTSBURGH BED COAL TO DETERMINE EFFECT OF VEHICLE, CATALYST, ETC.
 Temperature, 400°; initial pressure, 1000 lb. per square inch when bomb is cold; contact time, 1 hour in all tests.

Test no.	Coal, g.	Vehicle		Gas	Catalyst		Oxygen eliminated G. per 100 g. of coal	Hydrogen used g. of coal	Liquefaction wt. % of coal
		Grams	Formula		Grams	Formula			
H-26	50	65	C ₁₀ H ₈ ^a	Hydrogen	None		0.76	0.86	32.4
H-28	50	65	C ₁₀ H ₈	Nat. gas	None		0.00	..	13.8
H-29	50	65	C ₁₀ H ₈	Nitrogen	None		0.00	..	14.9
H-41	20	100	C ₁₀ H ₁₂ ^b	Nitrogen	None		2.45	..	67.2
H-40	20	100	C ₁₀ H ₁₂	Hydrogen	None		2.50	1.85	67.5
H-24	50	65	C ₁₀ H ₈	Hydrogen	0.075	CHI ₃	1.06	1.20	36.4
H-25-A	50	65	C ₁₀ H ₁₂	Hydrogen	.075	CHI ₃	2.46	0.90	54.1
H-6	50	65	C ₁₀ H ₁₂	Hydrogen	None		2.88	.83	60.2
H-27-A	100	100	C ₁₀ H ₁₂	Hydrogen	None		2.50	.72	64.3
H-30	50	65	C ₁₀ H ₁₂	Nitrogen	.5	SnS	1.96	..	43.1
H-31	50	65	C ₁₀ H ₁₂	Nitrogen	None		2.26	..	48.1
H-32-A	20	100	C ₁₀ H ₁₂	Hydrogen	.5	SnS	2.85	2.55	75.6
H-33	50	65	C ₁₀ H ₁₂	Hydrogen	.5	SnS	3.06	1.54	64.0

^a C₁₀H₈ = naphthalene. ^b C₁₀H₁₂ = tetrahydronaphthalene.

Table I. In all of the experiments of this table the contact time was one hour and the temperature 400°. As may be seen from Fig. 2 (discussion of this is given in a later section), the effects of catalysts at 400° and one hour reaction time are well within the limits of reproducibility of the experiments. Hence comparisons involving only two experiments, one with and one without catalyst, have doubtful significance unless substantiated by other evidence. A comparison of experiment H-26, in which naphthalene was used as vehicle, with H-28 and H-29, where the same conditions prevailed except that nitrogen and natural gas were substituted for hydrogen in H-29 and H-28 (Table I), respectively, shows clearly that hydrogen is essential for primary coal liquefaction and elimination of oxygen at 400°. The degree of liquefaction in H-26 was more than double that in H-28 and H-29, and virtually no oxygen was eliminated in the latter tests, whereas about 10% of the total coal oxygen was removed in H-26. A comparison of H-26 with H-41, in which an excess of tetrahydronaphthalene was used and nitrogen replaced hydrogen, shows that the degree of liquefaction and oxygen elimination in H-41 was 2 to 3 times as great as in H-26. It is therefore probable that one of the slow steps in coal hydrogenation in the absence of a catalyst is the formation of hydroaromatic compounds which serve as hydrogen carriers. It is necessary for this argument to call attention to the fact that the amount of hydrogen present in H-26 (about 5.7 g.) greatly exceeded that necessary (about 2 g.) for complete liquefaction and oxygen elimination.

The comparison of H-26 with H-41 is of special interest in connection with the data of Pott and Broche,⁷ which show that virtually complete liquefaction of bituminous coals may be obtained when they are heated at 390 to 410° with an equal weight of tetrahydronaphthalene-phenol-naphthalene, 2:1:2, solvent under the pressure of the solvent vapors, that is, with no added hy-

drogen or other gas. It is apparent from the discussion given above that tetrahydronaphthalene is the most essential constituent of this solvent, and that its efficacy as a liquefaction agent is related, at least in part, to its ability to transfer hydrogen to the coal substance. Further comparison of experiment H-26 with H-41 shows that naphthalene plus hydrogen gas is a much poorer liquefaction agent than tetrahydronaphthalene without hydrogen. Indeed, in the presence of an excess of tetrahydronaphthalene, the degree of liquefaction and of oxygen removal is about the same with nitrogen (experiment H-41) as with hydrogen (H-40). As may be expected from the discussion given above, both in the presence and absence of catalysts and in a hydrogen atmosphere a much larger degree of liquefaction is obtained when tetrahydronaphthalene is present than when naphthalene is the vehicle; compare H-24 with H-25A, and H-26 with H-6. The results of H-24 and H-25A also show that in the presence of iodoform as a catalyst, more hydrogen is consumed per 100 g. of coal when naphthalene is the vehicle than when tetrahydronaphthalene is used. When no catalyst is employed (compare H-26 with H-27A, and H-6), about the same amounts of hydrogen are consumed with either naphthalene or tetrahydronaphthalene as vehicles. At 400°, in the absence of a catalyst, the rate of hydrogenation of naphthalene is very slow.⁸ This fact, considered along with the experiments of Table I, indicates that one of the most important functions of the catalyst in coal-hydrogenation reactions is to

(7) A. Pott, H. Broche, H. Nedelmann, H. Schmitz and W. Sheer, *Gleichenf.* **69**, 903-912 (1933).

(8) C. O. Hawk, *Ind. Eng. Chem.* **12**, 76-93 (1933).

accelerate the rate of formation of hydroaromatic compounds which served as hydrogen carriers.

Comparison of H-30 with H-31 shows that at 400°, in the presence of nitrogen with tetrahydronaphthalene as vehicle, the presence of 1% stannous sulfide (as in H-30) does not affect the degree of liquefaction and oxygen elimination, which are, respectively: 43.1% and 1.96 g. per 100 g. of coal for H-30 and 48.1% and 2.26 g. for H-31. The differences between these values are within the limits of reproducibility (see Figs. 3 and 4) of the experiments. These results indicate that the oxygen elimination and liquefaction reactions in the presence of tetrahydronaphthalene are non-catalytic. Additional support for this conclusion is obtained by comparing the liquefaction and oxygen-elimination data of experiments in the presence of hydrogen with tetrahydronaphthalene as vehicle and various amounts of stannous sulfide given in Table I. These are abstracted in Table II to facilitate the comparisons.

TABLE II

EFFECT OF CATALYST IN PRESENCE OF HYDROGEN AND TETRAHYDRONAPHTHALENE AT 400° AND ONE HOUR CONTACT TIME

Experiment number	H-6	H-27A	H-40	H-33	H-32A
SnS (per cent. of coal)	None	None	None	1.0	2.5
Ratio coal/vehicle	0.77	1.00	0.20	0.77	0.2
Liquefaction (% of coal)	60.2	64.3	67.5	64.0	75.6
Oxygen elimination, g./100 g. coal	2.88	2.50	2.50	3.06	2.85
Hydrogen absorption, g./100 g. coal	0.83	0.72	1.85	1.54	2.55

It is apparent that there is little, if any, trend in the oxygen-elimination data with per cent. of stannous sulfide or with the coal/vehicle ratio. The differences between the data are scattered and close to the limits of reproducibility of the experiments (see Fig. 3, data for 400° and one hour contact time). There appears to be a small trend in the liquefaction data indicating a somewhat higher degree of liquefaction with larger amounts of catalyst and vehicle. Although some of the differences in the liquefaction data are well within the limits of reproducibility of the experiments (see Fig. 4, data one hour contact time at 400°), the trend toward higher values with increasing amounts of tetrahydronaphthalene and of catalyst is quite apparent. The conclusions reached above upon the basis of the data of experiments H-30 and H-31, where nitrogen and tetrahydronaphthalene were used, are therefore confirmed so far as concerns the absence of appreciable effect of catalyst on oxygen-elimination rates at 400°, but

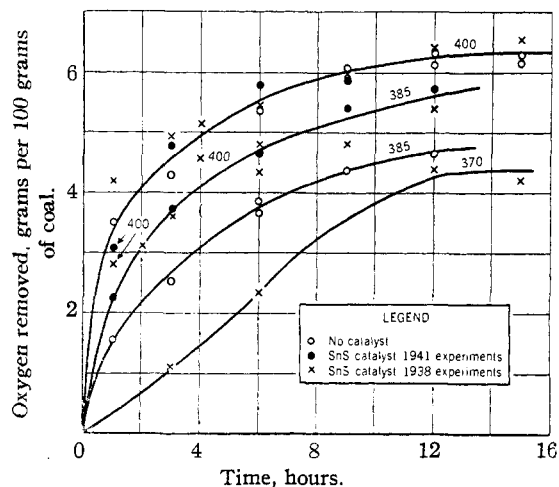


Fig. 3.—Rate of oxygen elimination, effect of catalyst.

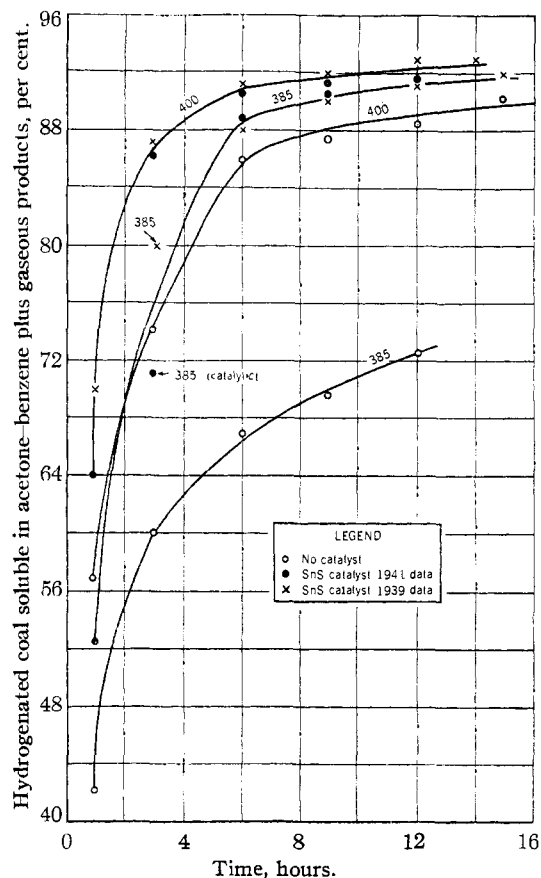


Fig. 4.—Rate of liquefaction, effect of catalyst.

there is a small effect of catalyst on the liquefaction rates. These conclusions are substantiated further by the data of Figs. 3 and 4, which will be discussed below. The order of magnitude of the effect of increasing amounts of catalyst on the liquefaction rate, derived from the data of Table II, is about the same as that found by Warren,

Bowles and Gilmore,⁹ who used stannous oxide at 445°.

The data of Table II on hydrogen absorption during one hour at 400° show a trend with coal/vehicle ratio, and a very definite increase with increased amounts of catalyst. This increased consumption of hydrogen when a catalyst is present is confirmed by the data of Fig. 2, at 385, 400 and 415°, respectively; these are discussed in a later section of this paper.

Experiment H-27A was done with a new bomb whose walls had not been in contact with stannous sulfide or any other catalytic material. A comparison of H-27A with H-40 and H-6 of Table II shows that the autoclave walls, when free from tin or other catalytic material, have no apparent accelerating effect on coal-hydrogenation reactions. This experiment confirms similar data obtained in the British Fuel Research Laboratory.⁵

All of the rate data on hydrogen absorption in the presence of 1% stannous sulfide are presented in Fig. 1. The time at reaction temperature has been corrected for the preheating periods; this correction was calculated by using the temperature coefficients: 1.25/15° for temperatures above 385°, 1.02/15° in the range 300° to 385°, and 1.5/15° for temperatures below 300°. The correction calculated for a heating rate of 2° per minute to 385° is fifty-six minutes; for the same heating rate to 430, 415, 400, 370, 355, 310, 280, and 250°, the corrections are 84, 75, 65, 48.5, 41, 18.5, 6, and 1 minutes, respectively. The heating rate for the previously published data^{2,6} was 2° per minute; the bomb was cooled and refilled with hydrogen every three hours. The heating rate for the data of the present paper was 4° per minute; the bomb was cooled and refilled with hydrogen at the end of 4.5, 6, or 7.5 hours for nine-, twelve-, or fifteen-hour heating periods, respectively.

Three peculiarities of the curves of Fig. 1 should be noted, namely: (a) The temperature coefficient for the first hour at reaction temperatures increases sharply between 370 and 385° from a value of about 1.0/15° below 370° to about 3.0/15°. Above 385° this coefficient again decreases markedly to a value of about 1.0/15°. The large coefficient in the 370–385° region is of the same order of magnitude (about 3.0/15°) as

those² for oxygen elimination and coal liquefaction during the first hour of the reaction. However, the latter coefficients were persistently high (between 2.5 and 3.0) for two 15° temperature intervals beyond 400°, whereas that for hydrogen absorption during the first hour of reaction decreases sharply beyond 400°.

(b) The change in the temperature coefficients with temperature for reaction times beyond the first hour for temperatures below 385° indicates a transition from a chemical reaction as the slow step for temperatures below about 300° to a diffusion process as the rate-determining step between 300° and 385°.

(c) Temperature coefficients for temperatures above 385° are low (about 1.25/15°) although higher than those for the 300–385° region. The shape of the curves above 385° is also different from those below this temperature. The latter, after the first hour of reaction, are approximately straight lines, indicating zero order with respect to the material reacting with the hydrogen (the concentration of hydrogen is approximately constant because of the periodic refilling). The shape of the curves above 385° indicates that two opposing reactions are taking place or that the reaction is of first or second order. The former explanation is substantiated by the maximum in the curve of the hydrogen content of the pitches plotted against temperature given in a previous publication.²

These peculiarities may be explained if one assumes that the following processes occur during coal hydrogenation: (a) Diffusion of hydrogen through liquid films on the surface of the catalyst, and on the surface of the coal. The latter surface probably persists for several hours at temperatures below about 370°, but has only a short life period (minutes) at temperatures above 385°. (b) Hydrogenation of unsaturated groups in the original coal structure. (c) Primary decomposition of the coal. (d) Hydrogenation of unsaturated groups in the primary decomposition products. (e) Secondary decomposition of the coal involving reaction between oxygen groups in the coal substance and a hydrogen carrier. (f) Dehydrogenation of the products of (e) due to thermal instability.

At temperatures below about 300°, the slowest or rate-determining step in the hydrogen absorption process is the rate of reaction of hydrogen with the unsaturated groups in the original coal

(9) T. E. Warren, K. W. Bowles and R. E. Gilmore, *Ind. Eng. Chem., Anal. Ed.*, **11**, 415-419 (1939).

structure and unsaturated groups resulting from dehydration. This reaction is accelerated by catalysts such as tin compounds. Above 300° the rate of this chemical reaction surpasses that of the diffusion of hydrogen through a liquid film on the surfaces of the coal and catalyst, and hence such diffusion is the slowest step between 300 and 370°. Above 370°, rapid depolymerization and solvation of the coal occur. This depolymerization reaction is essentially a primary decomposition of the coal, and is characterized by the large temperature coefficient observed in the first hour of reaction in the 370–385° interval. The reaction with hydrogen carriers or with each other of the unsaturated fragments from the decomposition is faster than the primary decomposition of the coal, and hence the latter is the rate-determining step. As was shown in the discussion of the data of Table II, there is a small effect of catalysts on the liquefaction rate during the first hour of reaction at 400°, and Fig. 4 shows a larger effect at 385°. Figure 2 shows similar effects of catalyst on the hydrogen consumption rate during the first hour. These catalytic effects are concerned with a secondary reaction, namely, the repolymerization of the fragments from the primary non-catalytic decomposition of the coal. In the presence of stannous sulfide the rate of hydrogenation of these fragments is faster than their repolymerization rate, and hence somewhat larger liquefaction and hydrogen consumption rates are obtained. The large temperature coefficient of the primary reaction is apparently unaffected by the catalysis of the secondary reactions.

The catalysis of the secondary reactions is relatively much larger at 385° than at higher temperatures, as may be observed from the data of Figs. 2, 3 and 4. This is particularly pronounced for hydrogen consumption during the first few hours at 385° (Fig. 2), whereas at 400° and 415° the slopes of the catalytic and the non-catalytic curves for the first hour do not differ greatly. The increased catalytic effect at 385° is probably due to the slow rate of non-catalytic regeneration of the hydrogen carrier at this temperature, whereas at 400° and higher temperatures this rate almost equals that of the reaction of the carrier with the primary decomposition product.

Above 385°, after the first hour of reaction, secondary decomposition of the depolymerized coal

is one of the rate-determining steps in the hydrogen absorption process. As shown in the discussion of the data of Tables I and II, this secondary decomposition is probably a non-catalytic reaction between oxygen groups of the primary decomposition products of the coal and a reactive hydroaromatic such as hexahydronaphthalene. The formation of the reactive hydroaromatic is accelerated by a stannous sulfide catalyst. Concomitant with this oxygen-removal reaction, there is a dehydrogenation of the coal-hydrogenation products (pitches) due to thermal instability. Because of these opposing reactions, the temperature coefficients for hydrogen consumption rates above 385° (see Fig. 1) are somewhat low for a chemical reaction. They are 1.5 to 1.25 per 15° for the first few hours of the reaction beyond the first hour, and tend toward negative values for the longer reaction times.

Data on the rates of oxygen elimination are presented in Fig. 3. The temperature coefficients for the early part of the oxygen elimination and liquefaction (Fig. 4) reactions are about 3.0/15°, and therefore the time correction for preheating is very small. For the latter part of these reactions, the temperature coefficients are much smaller, but the rate is slow enough so that even a fairly large time correction for preheating would only slightly change the position of the curves. For these reasons, no time correction was made for Figs. 3 and 4. The effect of 1% stannous sulfide is appreciable at 385° in accelerating the oxygen-elimination rate; but at 400° this effect is within the limits of reproducibility of the experiments. The catalytic effect at 385° may be explained by assuming that the rate of non-catalytic regeneration of the hydrogen carrier is smaller than the rate of reaction of this carrier with an oxygen group in the primary decomposition products of the coal; and that, between 385 and 400°, the former rate surpasses the latter. This argument presupposes that the oxygen elimination reaction is non-catalytic; this was shown to be very probable in the discussion given above of the data of experiments H-30 and H-31 and of Table I.

The effect of a catalyst on the rates of liquefaction (measured by the amount of residue insoluble in acetone-benzene) shown in Fig. 4 is qualitatively the same as the effect on the rate of oxygen elimination. The effect at 385° is quite large and that at 400° much smaller. It is, therefore, quite probable that oxygen elimination and coal

liquefaction are accomplished simultaneously, in the same chemical reaction. It has been postulated by Erasmus¹⁰ that coal is a polymer consisting mainly of relatively small aromatic and hydroaromatic units of about ten carbon atoms each, some of which are linked through linear, and some through cyclic-ether-oxygen, bonds. Such a structure would explain the close relationship between reduction of molecular weight and oxygen elimination, as well as the existence of two types of oxygen groups in the coal structure, as was postulated by Fisher and Eisner⁶ before Erasmus' book¹⁰ was published.

The authors wish to acknowledge the help given by the members of the coal-analysis section, and of the experimental coal-hydrogenation plant of the Central Experiment Station of the Bureau of Mines.

Summary

An analysis is made of data on the effect of a stannous sulfide catalyst on the rate of change of

(10) P. Erasmus, "Über die Bildung und den chemischen Bau der Kohlen," Ferdinand Enke, Stuttgart, 1938, 90 pp.

readily measurable quantities in the hydrogenation of a bituminous coal in a small autoclave. The results show that the rate-determining step for the hydrogen absorption varies with temperature. Below 300° it is apparently a chemical reaction between a hydrogen carrier and unsaturated groups in the coal; between 300 and 370° diffusion of hydrogen through a liquid film on the surface of the coal and catalyst is the slowest step; above 370° the rate-determining step is a chemical reaction between a hydroaromatic and the oxygen and unsaturated groups in the products of the primary decomposition of the coal. The chief function of the catalyst is to increase the rate of regeneration of a hydrogen carrier, which is a hydroaromatic compound such as hexahydronaphthalene. The reactions of the hydrogen carrier with oxygen and unsaturated groups are largely non-catalytic. The effects of the catalyst on the rate of oxygen elimination and on that of liquefaction are very similar, and it is probable that both processes are intimately associated in one reaction or group of reactions.

PITTSBURGH, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Mutarotation of Glucose in Water-Methanol Mixtures¹

BY HAROLD E. DYAS AND DOUGLAS G. HILL

The rate of the mutarotation of glucose has been studied extensively in water solution, both when catalyzed by the solvent, and when catalyzed by strong or weak acids and bases at various temperatures.² In solvents other than water, measurements have usually been made at one temperature only, and only a few catalysts have been used.³ It should be of interest, therefore, to measure the rate in various water-methanol mixtures, and to determine the temperature coefficients both for the solvent-catalyzed and for the acid-catalyzed reaction.

(1) This paper is in part taken from a thesis submitted by H. E. Dyas to the Graduate School of Arts and Sciences of Duke University, Durham, North Carolina, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

(2) Hudson, *THIS JOURNAL*, **32**, 889 (1910); Osaka, *Z. Physik. Chem.*, **35**, 661 (1900); Lawry and Smith, *J. Chem. Soc.*, 2539 (1927); Kuhn and Jacob, *Z. Physik. Chem.*, **113**, 389 (1924); Brønsted and Guggenheim, *THIS JOURNAL*, **49**, 2554 (1927); Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A176**, 352 (1940); Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, **37**, 289 (1941); and many others.

(3) Worley and Andrews, *J. Phys. Chem.*, **31**, 742 (1927); Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1733 (1927).

Particular interest attaches to this reaction in view of the statement of Nelson and Beegle⁴ that the equilibrium in this reversible isomerization is not changed by temperature. This statement has been accepted recently by Kendrew and Moelwyn-Hughes² in a paper appearing while the work was in process, although their data would seem to us to point strongly against its truth. If it were true, the entire free energy change of the reaction would necessarily be an entropy change, and the determination of the free energies and entropies of activation should be particularly interesting. Our work, however, seems to show definitely that the equilibrium constant does change with temperature, albeit in a rather unusual manner. The temperature coefficients of both the rates and the equilibrium constants will be shown to exhibit parallel anomalies which will need to be considered in any mechanism proposed for this reaction.

(4) Nelson and Beegle, *THIS JOURNAL*, **41**, 559 (1916).