[CONTRIBUTION FROM SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

Studies of the Fischer–Tropsch Synthesis. XIV. Hägg Iron Carbide as Catalysts[1]

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Reduced, fused-iron catalysts were converted to Hägg iron carbide by treatment with either carbon nonoxide or $1H_2 + 4$ CO gas, and these carbided catalysts were tested in the Fischer–Tropsch synthesis with $1H_2 + 1CO$ gas at pressures varying from 7.8 to 21.4 atmospheres. Carbides prepared with either of the gases had essentially the same activity and selectivity. The initial activities of catalysts converted to Hägg carbide were higher than those of corresponding reduced catalysts. At 7.8, 11.1 and 14.5 atm., the activity of the carbided catalysts was either constant or increased slowly with time. At 21.4 atm., the activity of the carbide decreased rapidly with time. Although the products from carbides had a higher average molecular weight than those from reduced catalysts, it appears that these differences may largely be attributed to variations in operating temperature and not to any major change in the selectivity of the catalyst. There was no drastic change in the selectivity as observed when reduced catalysts are converted to nitrides. The carbides oxidized during synthesis, the rate of oxidation increasing with operating pressure. In most experiments, the total carbon content increased initially and then either remained constant or decreased. The observed composition changes may be explained by two processes: (a) the reaction of water vapor with carbide to produce in one case magnetite and elemental carbon and in the other magnetite and methane; and (b) the reaction of hydrogen with carbidic or elemental carbon to form methane.

The postulate that metal carbides are active catalysts and/or intermediates in the Fischer–Tropsch synthesis[2a,b] has prompted a large amount of research. Recently, carbides of cobalt[3] and nickel[4] were shown to have relatively low activity compared with the metal. Studies with carbides prepared from $C^{14}O$ demonstrated that neither iron nor cobalt carbides could be regarded as intermediates unless only a minute portion of the catalyst surface was effective in the synthesis.[5] Nitrides and carbonitrides of iron were active catalysts in the synthesis and produced high yields of oxygenated molecules.[6,7] German documents[8] indicated that the higher carbides of iron were active catalysts, frequently more active than similar non-carburized catalysts; however, the results are not as conclusive as may be desired.

Hofer,[9] *et al.*, and Jack[10] have characterized two low temperature carbides of approximate composition Fe_2C: The hexagonal close-packed (ϵ) and the Hägg or percarbide (χ). These carbides are produced under certain conditions in the synthesis with, or pretreatment of, Fischer–Tropsch catalysts; however, cementite (Fe_3C) is not produced under normal synthesis or pretreatment conditions. Ekstrom and Adcock[11] found a carbide of approximate composition FeC in an iron catalyst used in the fluidized synthesis.

Bureau of Mines studies[12] of composition changes of a reduced iron catalyst in the Fischer–Tropsch synthesis have shown that the iron of the fresh catalyst was partly converted to Hägg carbide. Simultaneously, but at a lower rate, magnetite was produced, apparently largely at the expense of reduced iron. The magnetite content increased rapidly initially and more slowly as the synthesis proceeded. Under comparable conditions, nitrided iron catalysts oxidized at a lower rate than reduced catalysts, and carbon replaced nitrogen to produce carbonitrides of iron.[6,7,13] McCartney,[14] *et al.*, have examined by electron diffraction a variety of reduced, carbided and nitrided iron catalysts after use in the synthesis. Although some of these results were difficult to interpret, they demonstrated that nitrides and, in some instances, carbides oxidized less rapidly than reduced catalysts.

The present paper describes synthesis tests of fused-iron catalysts in which the iron was largely converted to Hägg carbide. The activities, selectivities and composition changes of carbided catalysts and reduced catalysts during synthesis with $1H_2 + 1CO$ gas are compared.

Experimental

Preparation, Composition and Reduction of Catalysts.—The fused-iron oxide catalysts employed in these studies were prepared by standard electrical fusion methods,[15,16] and 6- to 8-mesh particles were used. Previous papers have described synthesis tests[13,17] and surface area and pore volume studies.[18,19] The composition of these catalysts is given in Table I.

Preparation of Hägg Carbide.—Fused catalysts were reduced in hydrogen (space velocity[20] about 2,500 hr.$^{-1}$) at

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(1) Article not copyrighted.

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(7) J. F. Shultz, B. Seligman, L. Shaw and R. B. Anderson, *Ind. Eng. Chem.*, **44**, 397 (1952); R. B. Anderson, in "Advances in Catalysis V," Academic Press, Inc., New York, N. Y., 1953, p. 355.

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(17) R. B. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

(18) W. K. Hall, W. H. Tarn and R. B. Anderson, THIS JOURNAL, **72**, 5436 (1950).

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(20) Space velocity = volumes of gas (S.T.P.) per volume of catalyst space per hour.

TABLE I

PROMOTER CONCENTRATIONS IN CATALYSTS (PARTS PER 100 PARTS IRON BY WEIGHT)

Catalyst	D-3001	D-3008
Al_2O_3	..	2.83
Cr_2O_3	1.21	..
K_2O	0.85	1.39
MgO	6.8	..
SiO_2	0.9	0.28

TABLE II

PRETREATMENT OF CATALYSTS

(Unless otherwise noted catalyst is D3001.)

	Reduction in hydrogen[a]				Carburization[a,b]				
Test	Temp., °C.	Space velocity, $hr.^{-1}$	Time, hr.	Extent of reduction, %	Gas	Temp., range, °C.	Total time, hr.	Atom ratio, C/Fe	Phases from X-ray diffraction[c]
X152	450	1000	43	90.2	None	......	..	..	α
X289	400–525[d]	8000	72	97.5	CO	227–350[e]	18	0.56	$\chi M \alpha$
X294	500	2500	24	96.6	CO	150–350[e]	18	.58	$\chi \alpha$
X320	500	2080	24	97.7	CO	150–350[e]	48	.56	χM
X323	500	1780	41	96.8	$1H_2 + 4CO$	200–275[f]	48	.43	$\chi \alpha$
X325	500	2330	43	97.2	$1H_2 + 4CO$	200–275[f]	48	.42	χM
X339	500	2490	40	98.2	$1H_2 + 4CO$	200–275[f]	48	.42	χ
X342	500	1990	24	97.2	CO	150–350[e]	18	.43	$\chi \alpha$
X394	500	2100	24	99.5	CO	150–350[e]	29	.53	χ
X399	500	2860	40	97.9	CO	150–350[e]	18	.46	$\chi \alpha$
X408	500	2370	24	98.6	CO	150–350[e]	20	.50	χ
X417	500	2450	24	98.7	CO	150–350[e]	18	.46	χ
X428	500	2240	26	97.9	CO	160–320[e]	19	.52	χ
X515	500	1180	24	97.8	None	......	..	..	α
X380[g]	400–525[d]	6950	48	100	None	......	..	..	α
X416[g]	400–525[d]	2450	56	100	CO	150–350[e]	13	.42	$\chi \alpha$

[a] Both pretreatment steps at atmospheric pressure. [b] Space velocity of CO or $1H_2 + 4CO$ about 100 $hr.^{-1}$. [c] Phases from X-ray diffraction in order of decreasing intensity of pattern: χ = Hägg carbide, α = α-iron, and M = magnetite. [d] Twenty-four hours at 400°, 24 hours at 450°, 12 hours at 500° and 12 hours at 550°. [e] Temperature increased as required to maintain CO_2 content of exit gas at about 20%. [f] Twelve hours at 200°, 12 hours at 250° and 24 hours at 275°. [g] Catalyst D3008 employed in these tests.

450 or 500° or according to a temperature schedule typical of that used in ammonia synthesis. The reduction was done in a tilting aluminum-bronze block furnace,[6] and the reduced catalyst was handled in carbon dioxide by an appropriate method that precluded oxidation of the catalyst by either air or carbon dioxide.[6]

Conversion of the reduced catalyst to Hägg carbide was accomplished in the tilting reactor. With pure carbon monoxide (space velocity = 100 $hr.^{-1}$), the carbiding temperature was increased progressively from 150 to 350°, as required to maintain the carbon dioxide content of the exit gas at about 20%.[19] Approximately 20 hours was required to deposit carbon corresponding to the formula Fe_2C (atom ratio C/Fe = 0.5) with Hägg carbide being the predominant phase detected by X-ray diffraction or thermomagnetic analysis. This carbiding procedure is particularly advantageous for the preparation of Hägg carbide. Because the rate of carburization is maintained low and approximately constant, the possibility of the following two side reactions occurring is minimized: (a) deposition of elemental carbon due to rapid carburization and (b) oxidation of elemental iron or carbide by excessively large concentrations of carbon dioxide resulting from high conversion of carbon monoxide. Carburization of freshly reduced catalysts at 325–350° would produce cementite, elemental carbon and magnetite, in addition to Hägg carbide. In the carbiding schedule the catalyst is largely converted to Hägg carbide by the time that these temperatures are reached, and apparently only Hägg carbide is formed under these conditions.

In carburization with $1H_2 + 4CO$ gas, the temperature was increased stepwise: 12 hours at 200°, 12 hours at 250° and 12 hours at 275°. This procedure similarly minimizes the possibilities of over-heating and oxidation due to excessively high rates of carburization, and usually satisfactory samples of Hägg carbide without excessive amounts of elemental carbon or magnetite may be prepared in this way. The reduction and carburization conditions used in the pretreatment of fused catalysts are given in Table II.

Synthesis Tests and Analytical Methods.—The catalyst testing apparatus and methods have been described previously.[8,13,17,21] The pretreated catalysts were transferred in carbon dioxide to the synthesis reactor. $1H_2 + 1CO$ gas was passed over the catalyst, the pressure increased to the desired value, and the reactor temperature increased rapidly to 200°. Then the temperature was increased at about 7° per hour until apparent contractions (CO_2-free) of about 65% were observed. Thereafter the temperature was varied by small increments to maintain the contraction at this value. In special experiments, the temperature was maintained constant, and the contraction was held at the desired value by adjusting the flow. $1H_2 + 1CO$ gas was used in all synthesis tests.

Catalyst tests were continued except for recovery of products at intervals of one week. Gaseous components were analyzed by a Consolidated mass spectrometer. Liquid and solid hydrocarbons, including dissolved oxygenated molecules, were fractionated by a simple 1-plate distillation and the lower boiling fractions analyzed for functional groups by infrared spectrometry.[13] Usually these characterizations of liquid and solid "hydrocarbons" were made on composite samples of products from 3 to 6 weeks of testing. Average activities, A_{Fe} (defined as cc. of synthesis gas converted per gram of iron per hour at 240°, when the flow is adjusted to give an apparent contraction of 65%) were determined by an empirical rate equation[21b] from weekly averages of space velocity, contraction and temperature.

In most cases the catalyst was analyzed after pretreatment and at the end of the synthesis test. In several experiments the catalyst was sampled at frequent intervals by discharging the entire charge into heptane, removing 3–5 cc., and then returning the remaining portion to the reactor.[12] As a precaution, the synthesis temperature was lowered about 10° for a brief period after sampling, because the catalyst, due to partial extraction of high molecular weight hydrocarbons with heptane, was very active in the initial 2 or 3 hours. After a thorough extraction with boiling toluene, the catalyst samples were subjected to one or more of the following analyses.

(a) Chemical analyses for iron and carbon by conventional methods. From these data and the ratio of promoters

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(21) (a) A. Krieg, A. P. Dudash and R. B. Anderson, *Ind. Eng. Chem.*, **41**, 1508 (1949); (b) R. B. Anderson, B. Seligman, J. F. Shultz, R. Kelly and M. A. Elliott, *ibid.*, **44**, 391 (1952).

to iron an estimate of oxygen content by difference was made.

(b) Powder X-ray diffraction.

(c) Electron diffraction of thoroughly extracted samples. These results have been described separately.[14]

(d) Thermomagnetic analyses.[22]

(e) Chemical analyses for the amount of carbon dioxide liberated upon treatment of the sample with sulfuric acid. These data are required to determine the magnitude of carbonate formation either as siderite or promoter carbonates.[6]

In the experiments described in the present paper, catalyst analyses were chiefly made by methods (a), (b) and (e).

Experimental Data

Activity and Selectivity.—Data for the activity of reduced and reduced-and-carbided fused iron catalysis as a function of time are presented in Figs. 1–4. Figures 1 and 2 compare activities of catalysts at operating pressures of 7.8 and 21.4 atmospheres (absolute), respectively. Figure 3 shows the activities as a function of operating pressure, and Fig. 4 compares activities of catalysts under different conditions of operation. In these figures the activity was corrected to a standard synthesis condition (240° and 65% conversion) by use of an empirical rate equation.[21b] The activities were computed from average weekly synthesis conditions. The logarithmic time scale was employed to include data of experiments of long duration without excessively compressing the initial periods of synthesis.

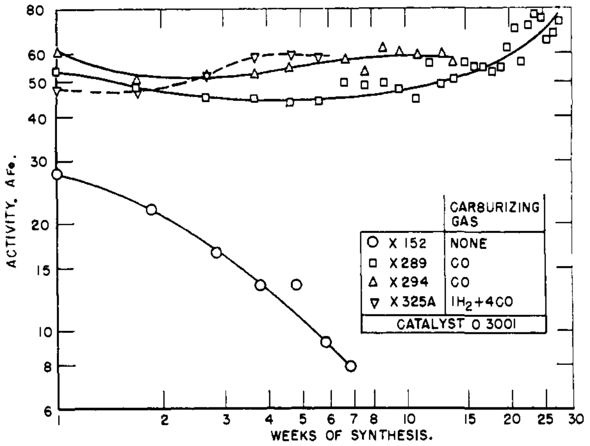

Fig. 1.—Activity of reduced and carbided catalysts as a function of time for synthesis with $1H_2 + 1CO$ gas at 7.8 atm.

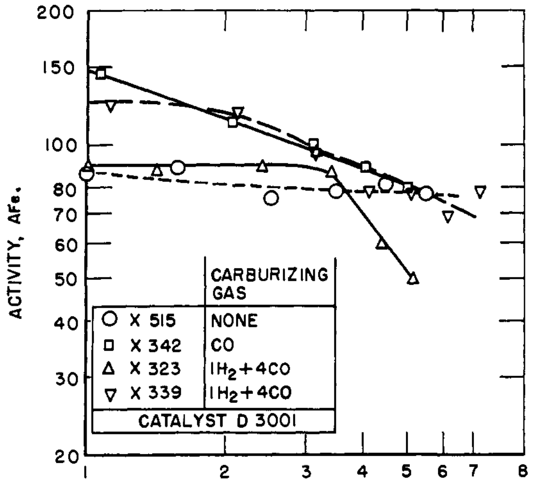

Fig. 2.—Activity of reduced and carbided catalysts as a function of time for synthesis at 21.4 atm.

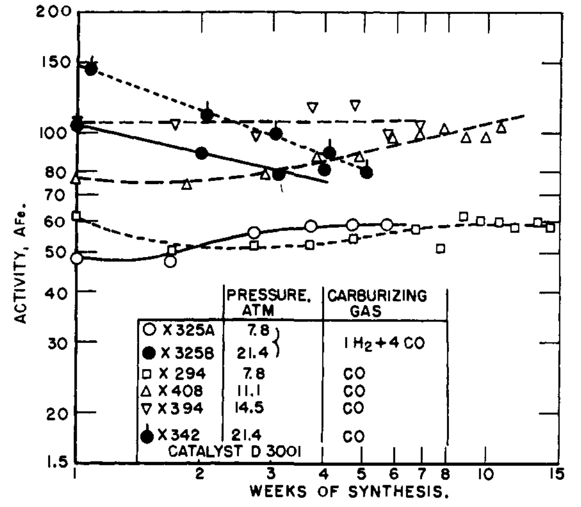

Fig. 3.—Activity-time plots for carbided catalysts at various operating pressures.

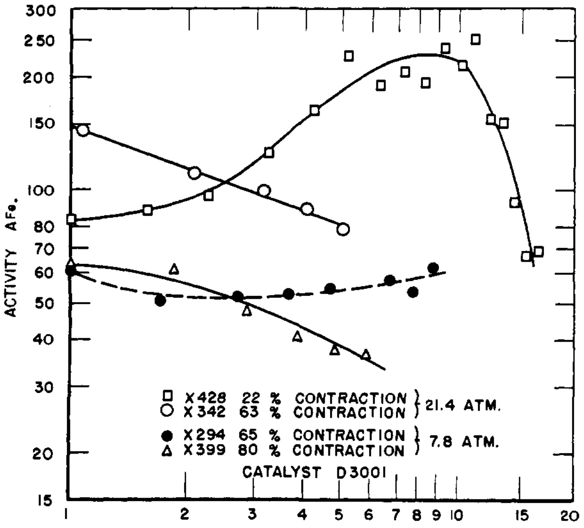

Fig. 4.—Variation of activity with time at different contractions.

Figure 5 compares product distribution data from tests of both reduced and reduced-and-carbided catalysts at 7.8 and 21.4 atm. corresponding to activity data in Figs. 1 and 2. Figure 6 demonstrates the effect of operating pressure on selectivity of carbided catalysts (activities in Fig. 3).

The selectivity plots present the distribution of total hydrocarbons, in weight per cent., including oxygenated molecules dissolved in the condensed hydrocarbon phases, "water-soluble oxygenated molecules being excluded." Gaseous hydrocarbons and distillation fractions of condensed "hydrocarbons" are shown. Numbers designated with (=) in gaseous hydrocarbon block indicate percentages of olefins, and for the distillation fractions, Br is bromine number, OH weight % hy-

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(22) L. J. E. Hofer and E. M. Cohn, *Anal. Chem.*, **22**, 907 (1950).

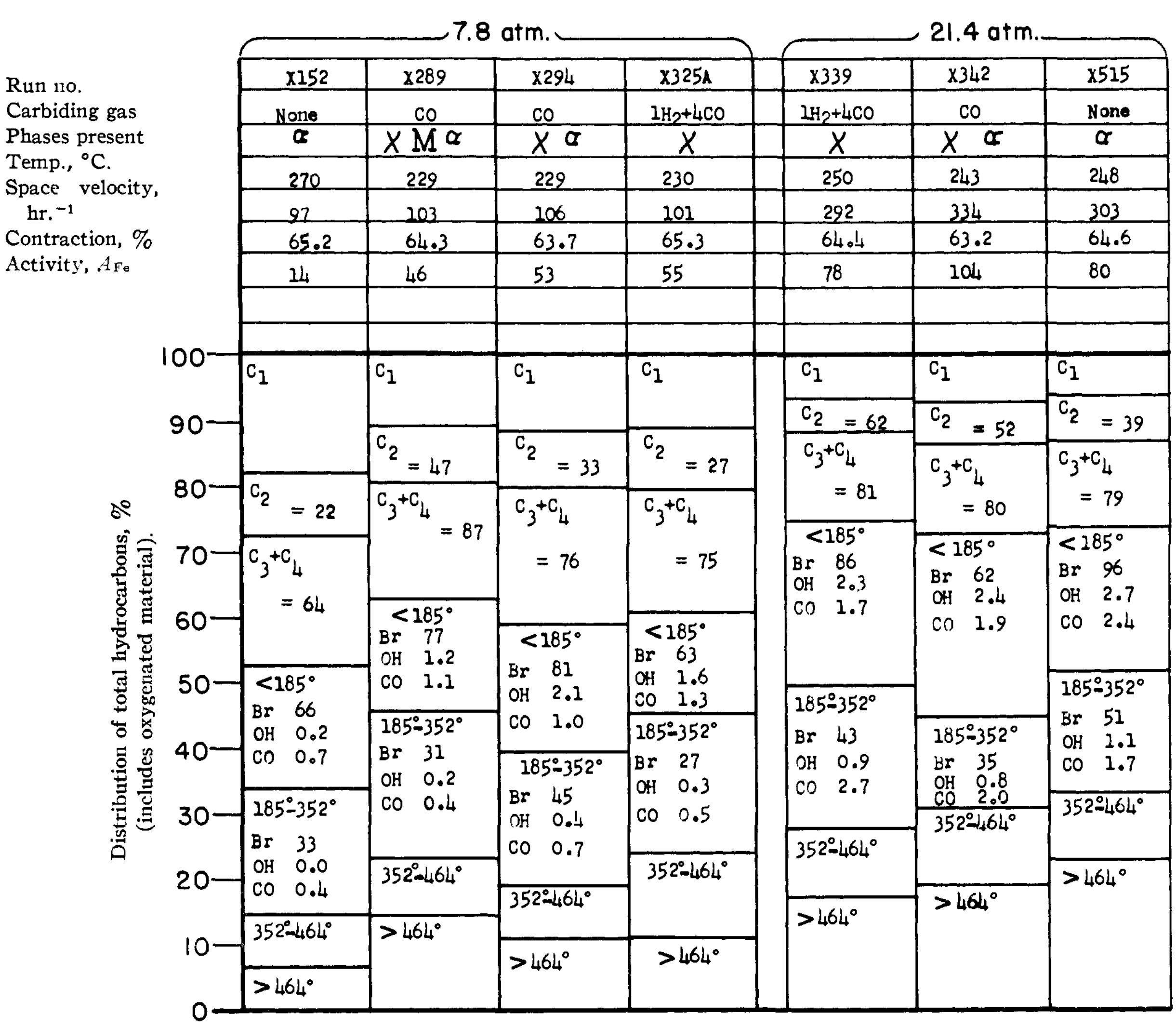

Fig. 5.—Product composition of reduced and carbided catalyst D3001 with $1H_2$ + 1CO gas at 7.8 and 21.4 atm. Symbols representing phases are defined in Tables II and IV.

droxyl group, and CO weight % carbonyl group as aldehyde, ketones and acids. The relative usage[23] of H_2 and CO is given in Table III.

Catalysts containing principally Hägg carbide have greater initial activities than reduced catalysts. At 7.8 atm. the activity of the carbides remained essentially constant or increased slowly, whereas the activity of the reduced catalysts[24] decreased to 1/3 of its initial value in seven weeks of synthesis (Fig. 1). At 21.4 atm. the activity of carbides decreased rapidly with time, but the reduced catalysts had essentially constant activity (Fig. 2). At both synthesis pressures, samples prepared by carburization either with carbon monoxide or $1H_2$ + 4CO gas had essentially the same activity. The large differences in the activity–time trends for

TABLE III

USAGE RATIOS (H_2:CO) FOR TESTS OF FUSED CATALYSTS WITH $1H_2$ + 1CO GAS

Tests[a]	Carbiding gas	Pressure, atm. (abs.)	Average Contraction, %	Usage ratio, H_2/CO
X152	None	7.8	65	0.72
X289	CO	7.8	64	.81
X294	CO	7.8	64	.75
X399	CO	7.8	80	.75
X325A	$1H_2$ + 4CO	7.8	65	.87
X325B		21.4	64	.88
X408	CO	11.1	63	.83
X417	CO	11.1	62	.78
X394	CO	14.5	64	.84
X342	CO	21.4	63	.79
X323	$1H_2$ + 4CO	21.4	64	.85
X339	$1H_2$ + 4CO	21.4	64	.83
X428	CO	21.4	22	1.46
X515	None	21.4	65	0.76
X380	None	21.4	65	.67
X416	CO	21.4	62	.80

[a] All tests with catalyst D3001 except X380 and X416 in which D3008 was used.

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(23) In the literature of the Fischer–Tropsch synthesis the relative consumption of H_2 + CO is termed "usage ratio," which is defined as moles of H_2 consumed divided by moles of CO consumed.

(24) In test X-194, described in references 8 and 12, the activity remained essentially constant in the synthesis at 7.8 atm. However, in a similar test (X-168 in reference 8) the activity decreased in the same manner as shown in Fig. 1. In both tests, Hägg carbide was produced to some extent in the synthesis. The higher content of Hägg carbide in X-194, resulting from a variation in the induction procedure, may possibly explain the constant activity observed in this test.

reduced and carbided catalysts at 7.8 and 21.4 atm. led to tests of carbides at intermediate pressures. At 7.8, 11.1 and 14.5 atm., the activity of carbides was constant or increased slowly with time (Fig. 3). The initial activities increased approximately linearly with operating pressure. In test X325 the catalyst was tested at 7.8 atm. for six weeks (Figs. 1 and 3), and the activity increased slightly with time. In the seventh week the operating pressure was increased to 21.4 atm. The activity was greater at the higher pressure, but it decreased in a manner typical of catalysts tested entirely at 21.4 atm.

At a given pressure the distribution of products from catalysts converted to Hägg carbide by treatment either with carbon monoxide or $1H_2 + 4CO$ gas were about the same as shown in Fig. 5. The average molecular weight of products from carbided catalysts was slightly higher than those from corresponding reduced catalysts; however, the difference in product distribution can be largely attributed to the differences in operating temperature. The average molecular weight increased with synthesis pressure, in the range 7.8 to 21.4 atm., as shown in Figs. 5 and 6. In all cases the amount of oxygenated molecules in the oil phase from carbided catalysts was low, and not significantly different from products of reduced catalysts. The carbided catalysts had somewhat higher usage ratios (H_2:CO) than corresponding reduced preparations (Table III). The high usage ratio in test X428 resulted chiefly from operation at low conversion. The selectivity of carbided catalysts with respect to the production of hydrocarbons and oxygenated molecules was about the same as the selectivity of reduced catalysts.

In tests at 7.8, 11.1 and 14.5 atm. the activity remained essentially constant, and tests as long as 25 weeks were possible since catalyst disintegration was not severe. At 21.4 atm., however, the activity of carbided catalysts decreased rapidly, and catalyst deterioration caused plugging of the reactor and related difficulties after only a few weeks of synthesis.

Figure 4 demonstrates the influence of conversion on activity of carbides at 21.4 atm. In contrast to the rapid decline of activity and catalyst disintegration at 65% contraction, the activity of a carbide at low conversions, 22% (test X428), increased more than threefold in the first 12 weeks, and then decreased to about the initial value by the 16th week. Apparently the improved operability in test X428 results from the lower concentration of reaction products, especially water, in the gas stream. Figure 4 also compares tests at 7.8 atm. in which the apparent contraction was maintained at 65% (test X294) and 80% (X399). The activity of the catalyst operated at the higher conversion decreased with time, whereas the activity increased at the lower conversion.

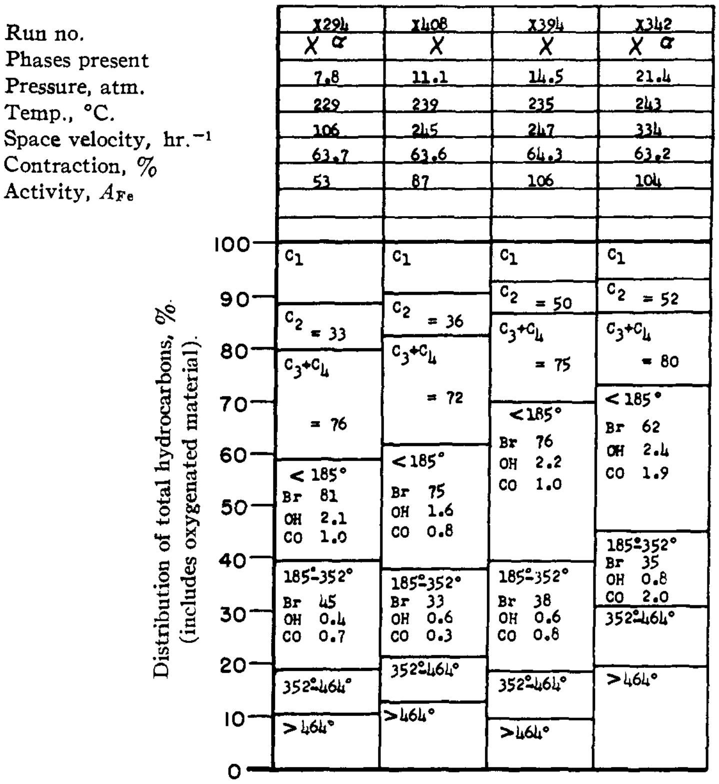

Fig. 6.—Product composition of carbided catalyst D3001 as a function of operating pressure. Symbols representing phases are defined in Tables II and IV.

Another fused-iron catalyst (D3008, promoted with alumina and alkali) was tested with $1H_2 + 1CO$ gas at 21.4 atm. in both the reduced and carbided states. The initial activity of the carbide was higher than that of the reduced catalyst, but the activity of carbided catalyst decreased rapidly with time as observed for catalyst D3001. Activities of the reduced and the carbided samples were:

Duration of synthesis, wk.	Activity, A_{Fe} Reduced (X380)	Hägg carbide (X416)
1	108	157
2	95	110
3	85	
4	73	
5	67	
6	59	

The particles of the sample converted to Hägg carbide deteriorated rapidly so that the converter tube plugged during the third week of synthesis.

Composition and Phase Changes.—The changes in composition of catalysts in the tests described in the previous section were followed as a function of time. Figures 7–11 present phases identified by X-ray diffraction and changes in carbon and oxygen contents from chemical analyses for tests at 7.8–21.4 atm. Data from chemical analyses are presented as atom ratios C/Fe and O/Fe. Since X-ray analyses indicated that α-iron was present in only minor amounts, an estimate of the content of Hägg carbide was made assuming that the iron of the catalyst is present as either Fe_3O_4 or Fe_2C.

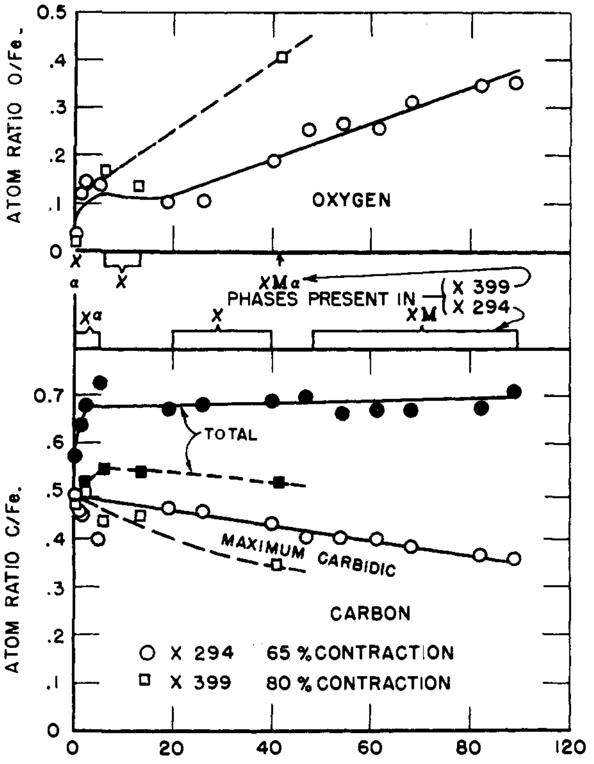

Fig. 7.—Composition changes carbided catalyst D3001 in synthesis with $1H_2 + 1CO$ gas at 7.8 atm. Symbols representing phases are defined in Tables II and IV.

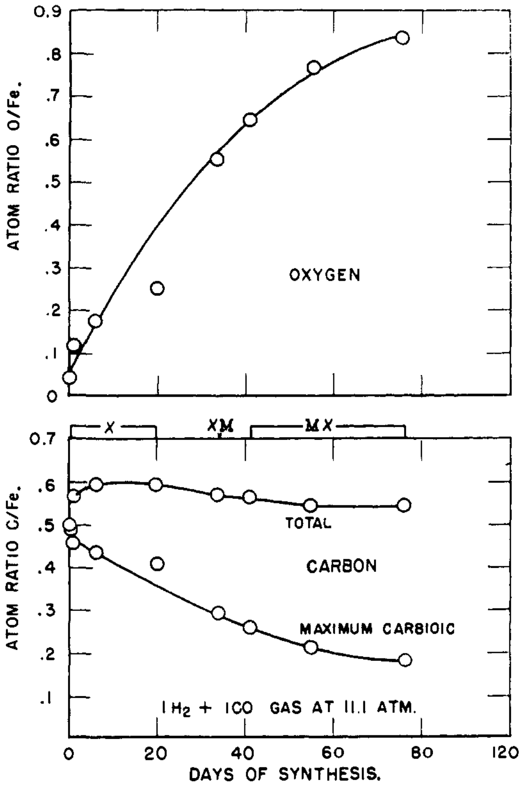

Fig. 8.—Composition changes of carbided catalyst D3001 in the synthesis with $1H_2 + 1CO$ gas at 11.1 atm. test X 408. Symbols representing phases are defined in Tables II and IV.

This value, expressed as atom ratio C/Fe, represents the maximum amount of carbide. A further complication of this simple approximation is the presence of carbonates in the samples. Analyses for carbon dioxide and iron were made on the final samples of each series. These data and the corrections to the atom ratios of total carbon, carbidic carbon, and oxygen to iron, assuming that carbon dioxide was present as magnesium carbonate, are given in Table IV. The corrected

TABLE IV

COMPOSITION CHANGES OF CATALYSTS SHOWING CARBONATE CONTENT

Test X-	Operating pressure, atm.	Time, days	CO_2,[a] %	Atom or mole ratios[b] Total C/Fe	Maximum carbidic C/Fe	O/Fe	CO_2/Fe	Phases from X-ray analysis[c]
289	7.8	194	3.52	0.673	0.289	0.564	0.063	χM
				(.610)	(.336)	(.438)		
408	11.1	76	4.15	.546	.185	.840	.077	Mχ
				(.469)	(.243)	(.686)		
394	14.5	20	..	.630	.191	.824	...	MχS
		48	5.27	.536	.036	1.235	.105	MχS
				(.431)	(.119)	(1.023)		
320	21.4	21	6.32	.493	.030	1.254	.125	Mα
				(.368)	(.123)	(1.004)		
323	21.4	39	5.45	.504	.284	0.574	.095	Mα
				(.409)	(.356)	(.384)		
325	7.8, 21.4	70	5.66	.392	.055	1.186	.109	Mα
				(.255)	(.137)	(0.968)		
339	21.4	57	7.70	.347	0	1.58	.159	MS
				(.188)	(.026)	(1.26)		
342	21.4	37	5.31	.487	0	1.47	.110	MαS
				(.377)	(.029)	(1.26)		
416	21.4	16	0.46	.265	.134	.975	.008	Mα

[a] Weight % CO_2 on extracted sample; iron was also determined on this sample. [b] Values in parentheses are corrected for carbon and oxygen as carbon dioxide assuming that it is present as $MgCO_3$. [c] Phase presented in order of decreasing intensity of diffraction pattern: χ = Hägg carbide, M = magnetite, α = α-iron, and S = carbonate as $MgCO_3$ or $FeCO_3$.

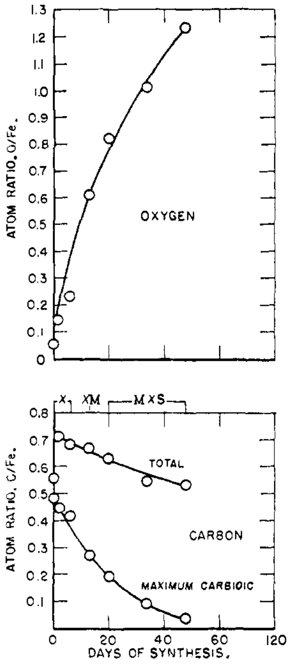

Fig. 9. — Composition changes of carbided catalyst D3001 in the synthesis with $1H_2 + 1CO$ gas at 14.5 atm. (test X 394). Symbols representing phase are defined in Tables II and IV.

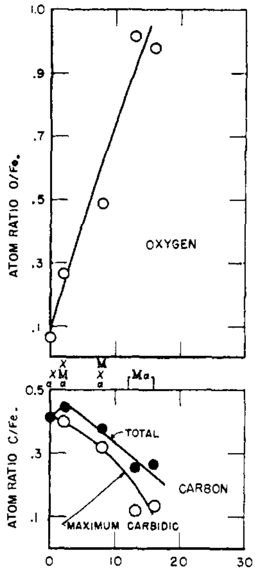

Fig. 11.—Composition changes of carbided catalyst D3008 in synthesis with $1H_2 + 1CO$ gas at 21.4 atm. (test X 416). Symbols representing phases are defined in Tables II and IV.

values were used for only the data of tests X320 and X342 in Fig. 10. Uncorrected data used in other figures show the trend of composition changes satisfactorily.

The data of Figs. 7–11 may be summarized as follows: 1. The atom ratio O/Fe increased during synthesis, approaching the value for magnetite, *viz.*, 1.33 in tests at 14.5 and 21.4 atm. The rate of oxidation increased with operating pressure.

2. The atom ratio total C/Fe increased rapidly in the first 5 days of synthesis, and then either remained constant or decreased. At 7.8 atm. the total C/Fe remained essentially constant after the initial increase, but from 11.1–21.4 atm. the atom ratio total C/Fe decreased with time. In the initial period the total C/Fe increased from about 0.5–0.6 to 0.7.

3. Although the values for maximum carbidic carbon are only approximations, they showed the same trends as the phases from X-ray diffraction. As the synthesis proceeded, X-ray diffraction lines of magnetite appeared. The lines of magnetite increased in intensity and those of Hägg carbide decreased. In tests at 14.5 and 21.4 atm., the magnetite lines eventually became the prominent pattern, and in some experiments at 21.4 atm. the lines of Hägg carbide disappeared. In tests at 21.4 atm. lines of α-iron were found in the used catalysts.

4. At 21.4 atm. the rate of oxidation and the rate of removal of carbon was greatly decreased by operation at low conversions (about 25% in test X428 compared with 65% in X320 and X342). It should be noted that the amount of synthesis gas converted per unit time was greater in test X428 at the lower conversion. Similarly in tests at 7.8 atm., a catalyst operated at about 80% conversion (X399) oxidized more rapidly than the sample tested at 65% conversion (X294).

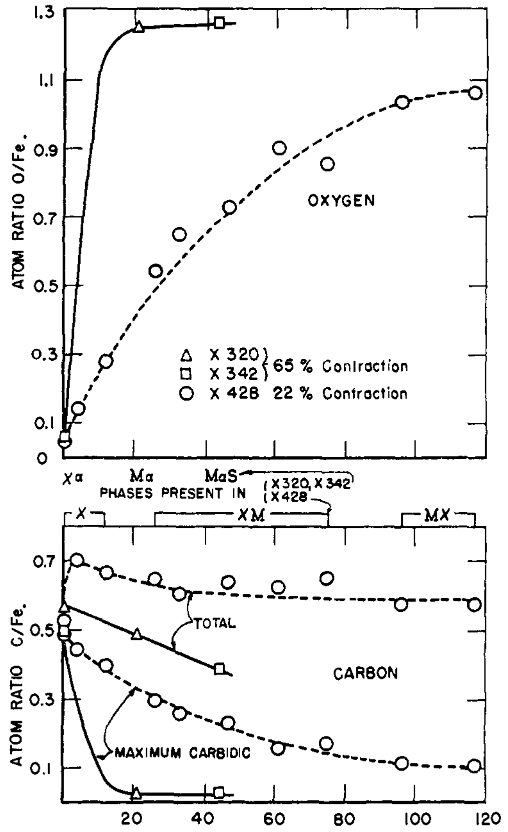

Fig. 10.—Composition changes of carbided catalyst D3001 in the synthesis with $1H_2 + 1CO$ gas at 21.4 atm. Symbols representing phases are defined in Tables II and IV.

5. In tests at 7.8 to 14.5 atm. the catalyst retained sufficient mechanical stability to permit long periods of synthesis without plugging of the reactor tube even in experiments in which the catalyst was repeatedly removed from the reactor for sampling. The stability of the sample in the test at 14.5 atm. was very good in view of the high degree of oxidation in this test. With Hägg carbide at 21.4 atm. and high conversions, particle deterioration and plugging of the reactor terminated most of the tests in 2 to 4 weeks. Sampling was difficult because the catalyst was caked in the reactor; therefore, the analytical data shown in Fig. 10 are from two separate tests that were terminated after 3 and 6 weeks of synthesis.

6. With catalyst D3001 the carbon dioxide content increased with operating pressure. In a few experiments at 14.5 and 21.4 atm. diffraction lines corresponding to $MgCO_3$ or $FeCO_3$ were found. These phases are isomorphous and cannot be distinguished by the diffraction data. However, it seems likely that most of the carbon dioxide is present as magnesium carbonate since sizable amounts of carbon dioxide were found in catalysts containing magnesia as promoter, and only small

amounts in preparations promoted with alumina or zirconia.[6] Furthermore, the ratio CO_2/Fe exceeded the value of 0.10, corresponding to complete conversion of magnesia and potassium oxide to carbonates, by significant amounts in only two samples.

7. In a 21.4-atm. test of fused catalyst D3008 (Fe_3O_4–Al_2O_3–K_2O) converted to Hägg carbide (Fig. 11), both oxidation and particle deterioration proceeded rapidly, and the reactor plugged during the third week of synthesis. The X-ray diffraction pattern of α-iron was found in all samples.

8. The carbide of Eckstrom and Adcock,[11] the hexagonal carbide, and cementite were not found in any of the catalysts after pretreatment or use in synthesis.

Discussion

Fused catalysts converted to Hägg carbide have about the same selectivity as the corresponding reduced samples. The only significant difference was the higher usage ratios, H_2/CO, observed for the carbided samples. Available data[21b] indicate that the principal primary synthesis reaction has a usage ratio of about 2, and this value is decreased by the water–gas shift reaction. Thus, the magnitude of usage ratio may largely depend upon the rate of the water–gas reaction, and if this reaction scheme is correct, it may be inferred that carbides are somewhat less active catalysts for this step. Data of Koelbel[25] showing that the water–gas shift reaction ($1H_2O + 1CO$ at 240° and 1 atm.) proceeds more slowly on carbided than on reduced catalysts are consistent with these results.

In the synthesis with catalysts converted to Hägg carbide, the total carbon content increased in the first few days of testing. The initial increase in carbon content may result from two processes: (a) the formation of magnesium carbonate in catalyst D3001, and (b) conversion of residual α-iron in the fresh catalyst to Hägg carbide. In experiments at 7.8 atm. diffraction lines of α-iron in the fresh catalyst disappeared during this period of synthesis. Usually the initial increase in carbon exceeded by only a small amount the value corresponding to complete conversion of promoters to carbonates. After the initial increase, the carbon content either remained constant or decreased slowly. The estimated values for maximum carbidic carbon decreased more rapidly than total carbon due to the formation of magnetite. The oxygen content of the catalyst increased continuously during the synthesis, and catalyst deterioration in the moderate temperature range, 200–260°, is probably due to structural changes accompanying oxidation rather than to carbon deposition.

The observed composition changes must result from a number of competitive reactions, some limited by kinetic and others by thermodynamic factors. Under most synthesis conditions the ratio, CO_2/CO, is sufficiently low to reduce magnetite, and to produce carbide or elemental carbon. Furthermore, carbides or elemental carbon can be produced by reactions of carbon monoxide and hydrogen. On the other hand the ratio of H_2O/H_2 is usually sufficiently large to oxidize iron and carbides; the carbides may be oxidized according to the equations

$$3Fe_2C + 8H_2O \longrightarrow 2Fe_3O_4 + 3C + 8H_2 \quad (1)$$

$$3Fe_2C + 8H_2O \longrightarrow 2Fe_3O_4 + 3CH_4 + 2H_2 \quad (2)$$

Also, the ratio $CH_4/(H_2)^2$ is low enough to permit the hydrogenation of carbides or elemental carbon to methane. Removal of elemental carbon as carbon monoxide by water or carbon dioxide is not thermodynamically possible. On this basis the component responsible for the oxidation and possibly the removal of carbon appears to be water vapor reacting according to equations 1 and 2. The thermodynamic tendency for equation 2 as well as for hydrogenation of elemental and carbidic carbon increases with operating pressure, which may account for the progressive decrease of total carbon and the presence of α-iron in samples from tests at the higher operating pressures. Typical data for partial pressures of H_2, CO, H_2O, CO_2 and CH_4 and significant ratios of these concentrations in the exit gas are given in Table V. These data represent the maximum values for products and minimum values for reactants as observed in the *main gas stream* in synthesis tests. In all experiments the ratio (H_2O/H_2) is large enough for the oxidation of iron or carbide. It appears that oxidation by water is possible at all conversions above about 5%. The ratio (CO_2/CO) exceeds that required for oxidation only in the test at conversions of about 80%. In all cases the ratio $CH_4/(H_2)^2$ is sufficiently low to permit the hydrogenation of carbides and elemental carbon.

On this basis the increased rate of oxidation and removal of carbon at the higher operating pressures and larger conversions must be related to the influence of the higher partial pressures of products, principally water vapor.

In the Fischer–Tropsch synthesis with porous catalysts the partial pressures of oxidizing components of the gas stream may represent only minimum values of these molecules in contact with the catalyst surface, for the gas in the pores very likely contains considerably greater concentrations of product molecules. Each pore may act like a long reactor and possibly the gas entering a pore continues to react until hydrocarbons and iron oxide are formed. Within the pores, these processes as well as synthesis, are impeded by the large amount of wax (liquid at synthesis temperature) adsorbed on the catalyst.

In the initial period, catalysts converted to Hägg carbide are more active than reduced catalysts at all synthesis pressures. Thus, the presence of Hägg carbide, as well as other interstitial phases of iron, nitrides and carbonitrides,[13] increases the catalytic activity. In the case of nitrides and carbonitrides the activity data are difficult to interpret, because the enhanced activity may result from either an increase in the "intrinsic" activity or an increase in the accessible surface due to the lower-molecular-weight product from the nitride or carbonitride synthesis. Since the present carbided catalysts have essentially the same selectivity as reduced preparations, the relative accessi-

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(25) H. Koelbel and F. Engelhardt, *Erdoel and Kohle*, **2**, 52 (1949).

TABLE V

PARTIAL PRESSURES OF SIGNIFICANT PRODUCTS IN EXIT GAS FROM TYPICAL EXPERIMENTS

Test	Operating pressure, atm.	Apparent contraction, %	Partial pressures, atm.[a]					Ratios of partial pressures[b]		
			H_2	CO	H_2O	CO_2	CH_4	$\frac{H_2O}{H_2}$	$\frac{CO_2}{CO}$	$\frac{CH_4}{(H_2)^2}$
294	7.8	65	2.94	1.66	0.93	1.97	0.29	0.316	1.19	0.033
399	7.8	80	2.39	0.33	1.90	2.61	.56	.795	7.91	.098
342	21.4	65	7.98	5.24	2.10	5.42	.65	.263	1.03	.010
428	21.4	22	9.44	9.96	1.08	0.75	.17	.115	.007	.0019

[a] Other gaseous components are present in minor amounts and are not included. Water is determined by difference and these values are slightly high. [b] Thermodynamic data: the oxidation of iron to magnetite at 250° requires H_2O/H_2 and CO_2/CO in excess of 0.025 and 2.2, respectively.[8] Hydrogenation of graphite to methane requires $CH_4/(H_2)^2$ less than 1200. The free energy of formation of Hägg carbide at 250° is +3.7 kcal./mole.[26] Thus, oxidation or hydrogenation of the carbide should have a greater thermodynamic tendency than corresponding reactions with iron or graphite, respectively.

bility of the catalyst surface, as determined by product distribution, should be approximately equal for the reduced and the carbided catalyst. Surface areas of reduced, carbided or nitrided catalysts before synthesis are approximately equal.[19]

At pressures of 7.8–14.5 atm., the activity of carbides remained constant or increased with time, but at 21.4 atm. the activity of carbides decreased rapidly. Although the rapid decrease in activity at 21.4 atm. is probably related to the rapid oxidation and simultaneous destruction of the carbide and modification of the physical structure of the catalyst, the explanation is not simple. For example, the carbided catalyst used at 14.5 atm. had a constant activity even when more than 80% of the iron had been converted to magnetite. Similarly, although the reduced catalysts oxidize less rapidly at 7.8 atm. than at 21.4 atm., the activities at the lower pressure usually decrease with time (X152, Fig. 1) but remain essentially constant at the higher pressure (X515, Fig. 2). Thus, other factors, such as changes in physical structure accompanying oxidation, are probably important in determining catalytic activity. The activities of nitrided iron catalysts, which oxidize at a slower rate than corresponding reduced catalysts, remain essentially constant for long periods of synthesis.[18]

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BRUCETON, PA.

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(26) L. C. Browning, T. W. DeWitt and P. H. Emmett, THIS JOURNAL, **72**, 4211 (1950).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE CATHOLIC UNIVERSITY OF AMERICA]

Activation Energies of Reactions of Methyl Radicals with Organic Molecules[1]

BY FRANCIS OWEN RICE AND ROBERT E. VARNERIN

RECEIVED JULY 19, 1954

We have decomposed 50-50 mixtures of two organic compounds one of which is fully deuterated and have determined initial values of the ratio $[CH_4]/[CH_3D]$ or $[CD_3H]/[CD_4]$ (depending on which compound was more stable) at different temperatures. We have assumed that these ratios give the relative speeds of reaction of either CH_3 or CD_3 with the respective compound. For example $[CH_4]/[CH_3D]$ would be the relative speeds of the two reactions, $CH_3 + RCH_3 \rightarrow CH_4 + RCH_2$ and $CH_3 + R'CD_3 \rightarrow CH_3D + R'CD_2$ where RCH_3 and $R'CD_3$ are the two organic compounds. The relative activation energies were determined by plotting the logarithm of the ratio against $1/T$. Our results are in good agreement with published measurements made in a much lower range of temperature.

In some recent work[2] in this Laboratory, we studied the thermal decomposition of mixtures of organic compounds in which one was the ordinary compound and the other was fully deuterated. For example when 50-50 mixtures of CH_3CHO and C_2D_6 are heated to about 500°, the products are methane and carbon monoxide, showing that the ethane suffers no perceptible decomposition into ethylene and hydrogen. However, the methane formed is not pure CH_4 but a mixture of CH_4 and most of the deuterated methanes. If one measures the ratio $[CH_4]/[CH_3D]$ for different fractional decompositions one can determine by extrapolation the ratio at the beginning of the reaction. Under proper conditions, such measurements give the relative speeds of two known elementary reactions at a given temperature; by varying the temperature, the difference of the activation energies of the two reactions may be obtained.

If we decompose a 50-50 mixture of two organic compounds, RCH_3 and $R'CD_3$ (R' being fully deuterated), the initial value of the ratio $[CH_4]/[CH_3D]$ may be assumed to be the relative rates of the two elementary reactions

$$CH_3 + RCH_3 \longrightarrow CH_4 + RCH_2 \text{ and}$$
$$CH_3 + R'CD_3 \longrightarrow CH_3 + R'CD_2,$$

providing that CH_3 is a chain radical. The ratio $[CH_4]/[CH_3D]$ can be conveniently measured if

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(2) F. O. Rice and R. E. Varnerin, THIS JOURNAL, **76**, 324, 2629 (1954).