Hydrocarbons from Carbide (A) V. Non-catalytic Polymerization under Elevated Pressures(1). Comparison between Ordinary and Elevated Pressure Reactions.

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In Papers (A) II to IV(2), inclusively, we have given rather in detail the results of non-catalytic direct synthesis of hydrocarbon liquids from calcium carbide under ordinary pressure, and with the valuable informations gained therefrom, we have now attempted the same synthesis but under elevated pressures. The experimental results and discussions have been already given in Japanese(1), and in this paper we shall summarize only the main features of the three original papers, including also the additional discussions which are not found in the above papers(1). The treatment of the general subject, the synthesis of hydrocarbon liquid products directly from calcium carbide, will be made as complete as possible, however, always in harmony with the reliability and completeness of our experimental results which, we must admit, are not quite satisfactory at places.

Under elevated pressures we have limited our investigations to hydrogen-carbide, carbon monoxide-carbide, and a few preliminary runs with carbon dioxide-carbide systems. What prompted us to study these systems were the following questions: (1) Would the products from the carbide contain more hydrogen when they are prepared in excess of it? (2) What would be the behaviour of nascent acetylene towards hydrogen? (3) What are the effects of carbon monoxide (and water gas) particularly on the total liquid yield? (4) What differences exist between the runs under low and elevated pressures?

Before answering these questions, it would be of advantage to touch on some of the experimental details which are necessary for understanding and appreciating the difficulty involved and for estimating the reliability to be expected of the results.

For these high pressure experiments, three one liter autoclaves, which could be only used for static experiments, had been used. As a practical means of furnishing the necessary water for the carbide reactions, aluminum hydroxide, which gave up most of its water in the temperature range, 200 to 300°C, was used. Because of these limitations, the results obtained were limited both in scope and significance.

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(1) This subject will be presented by the authors and M. Nibayashi in detail in Japanese in a series of Papers I to III, which will appear in *J. Soc. Chem. Ind., Japan*, **45** (1942). In the present paper most of the experimental details and tables will be omitted and only the high-lights of the three papers, which will henceforth be referred to as Papers I, II, and III, will be summarized.

(2) R. Negishi and O. Kamiike, this Bulletin, **17**(1942), 118; *ibid.*, **17**(1942), 44; *ibid.*, **17**(1942) to be published.

Some of the difficulties and uncertainties involved in these experiments will be mentioned briefly. First of all, heating of the autoclave had to be very carefully controlled to maintain the temperature in the range where aluminum hydroxide gave up most of its water. Since the reactions between calcium carbide and water are rapid and highly exothermic, if the release of the water is too rapid, there are apt to occur sudden "jumps" both in temperature and pressure. One example given below illustrates the "jumps" effectively. Initially, carbide grains of 2–3 mm. diameter and 100 kg/cm². of hydrogen were employed.

Exp. No.	Just before Jump		Just after Jump		C/H in Residue	Vol. % of $CH_4+C_2H_6$
	Temp. (°C.)	Press. (kg./cm².)	Temp. (°C.)	Press. (kg /cm².)		
I_A—7	260	163	433	279	19	57.6

If powdered carbide is used, the jumps are more pronounced. They take place in less than one minute. When they occur, no liquid products, but saturated gases mostly of low molecular weight, and a large amount of free carbon in the residue are formed. Jumps were prevented to a large extent by using grains and by separating the hydroxide catalyst from the carbide by charging the former in a cylinder supported at the center of the autoclave. The hydroxide catalyst thus charged will be referred to as "in cylinder".

The second difficulty encountered was in obtaining satisfactory weight and carbon balances. Needless to say, our runs under elevated pressures were less refined than those under ordinary pressure, but besides this difference in the experimental refinement, there were at least two outstanding sources of difficulty. One of them was associated with the fact that the autoclaves had to be opened and closed after each run, and small leakage was often undetected. This probably accounted for the chief uncertainty in the weight balance. Uncertainty in the residue analysis was presumably the largest factor which gave unsatisfactory results in the carbon balance.

The residue consisted of free carbon, very high polymers, unreacted carbide, carbonate, calcium oxide, and small quantities of sulfur and other compounds. We found no satisfactory method of analysis. Our method was to extract the residue with chloroform and then to react it with water to determine the unreacted carbide; then with either dilute HCl or acetic acid to determine the carbonate content. The acetate or the chloride formed was dissolved with excess of water, and after drying, the residue was subjected to elementary analysis. It was quite difficult to oxidize the residue completely, and often very severe conditions, which were not without harm to the reagents in the combustion tube, had to be employed. Evidence of incomplete combustion of the sample was often noticeable.

While our blank runs indicated that below 400°C autoclaves II and III, which were used in most of the runs of our series, were practically without any catalytic effect* for carbon monoxide and hydrogen mixtures, autoclave I was appreciably catalytic already at lower temperatures for the reduction of CO into methane and H_2O. Above 400°C the catalytic effect of each autoclave was more apparent, but the character of the reactions remained the same. When CO and H_2 were mixed with carbide alone, some hydrocarbon liquid products were obtained, but this was accounted for by the reactions:

$CO+H_2 \rightarrow$ methane and ethane + H_2O

$H_2O+CaC_2 \rightarrow CaO + C_2H_2$ Polymerize into liquid products.
(and Carbonate)

Under similar conditions similar results were obtained, and the less the catalytic effect, the more reproducible were the results. These facts indicated that most of our runs were sufficiently reliable, and most of the differences in the carbon and weight balances were due to the factors considered above. It may be inferred, therefore, that when the total weight balance does not deviate a great deal from 100%, the results are, except for the residue analysis, nearly correct, regardless of what the corresponding total carbon balance may indicate. For the comparison of the gaseous and liquid products, therefore, it is the total weight balance, and not necessarily the carbon balance, that serves as a guide as to the reliability of the data. Our temperature readings are probably good to about ±5°C and the pressure within ± 5 kg/cm^2. In our present investigations, accuracy of 5% would be as satisfactory as might be hoped for, and even an order of 10% must be considered rather satisfactory.

Discussion. The results of blank runs on the catalytic effects of the autoclaves have been reported in Paper I, and those of the systems, hydrogen-carbide and carbon oxides-carbide, have been given in Paper II. We shall not retabulate the results here, but immediately avail ourselves of answering the questions raised at the beginning of this paper. The answers will not be given in the order of the questions.

(A) Effects of Pressure and Temperature. (1) *On the Yield of Products.* Results under various total initial pressures of the runs made with hydrogen, carbon monoxide (or water gas), and carbon dioxide are given in Table 20. Most of our runs were made in the neighborhood of 100 atmospheres, since it was evident from the hydrogen system that at about this pressure, a maximum in the total liquid products (free of gases condensed and dissolved in the trap and extractable products from the solid residue) was found. The existence of this maximum may have some connection with the concentration of the acetylene available. Although the total liquid products seem to be a direct function of the total pressure, the yields of saturated gases** are rather a function of the partial pressure of hydrogen. This is to be expected. The percentage yield of liquid products based on the

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* For a more detailed description of the effect, see Ref. 1, particularly Paper I.

** Those of olefins and acetylene are small and the results are less definite.

Table 20. Effect of Pressure and Temperature on Products.

(Max. Reaction Temp. $\simeq$ 450°C.)

Exp. No.	Total Initial Press. kg./cm². at Room Temp.	Partial H_2 Press.	% Calculated on Reacted CaC_2 Carbon			Wt. (g.) Carbonate Carbon in Residue*	Note	Gas
			Methane+ Ethane Carbon	Residue Carbon	Liquid Carbon			
I_A 14	25	25	16.9	55**	23.6	$< 3.8^{Ω}$		H_2
I_A Ser. 26	50	50	29.3	27.6**	26.6	$<17^{Ω}$	"in cylinder"	
I_A Ser. 37	50	50	19.7	25.6**	28.4	$<15^{Ω}$		
I_A Ser. 16	100	100	42.0	5.8	32.8	2		
II_A Ser. 38	100	100	32.6	4.4	33.3	1.3		
I_A 1	200	200	49.5	7.3**	24.9	$< 4^{Ω}$	Calcd. on 200 grs.	
II_A 15	70	53	27.6	6.7	22.1	4.3		CO+H_2
II_A 11	70	50	25.2	13.8	22.2	9.3		
II_A Ser. 21	100	56	22.7	10.6	23.1	23.1		
I_A Ser. 51	100	∞80	26.2	21.4	36.8	25.8		CO+H_2
II_A Ser 18	70	∞55	10.1	17.2	12.6	14.4	405°C.	CO+H_2
III_A Ser. 57	180-150***	∞50	24.4	12.7	25.0	26.7	370°C.	

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* Calculated on 60 grams of reacted carbide carbon.

** Contains carbonate carbon.

Ω Contains residue carbon.

*** At 370°C.

reacted carbide carbon of the elevated pressure runs are appreciably higher than the corresponding ones of ordinary pressure. We believe that this apparent increase in the yield is due to temperature effects than to any change in the reaction mechanism. In the autoclave runs any solid products, such as the yellow powder formed at lower temperatures and heavy liquid products adsorbed on the solid, are either decomposed into liquid or distilled out at higher temperatures, e.g., 450°C. On the other hand, in the runs under ordinary pressure, any such products will remain in the residue. Support for this argument is found in the relatively small amounts of carbon in the solid residues of the runs of high as compared with those of the low pressure, as shown in Table 15 (Paper (A) IV) and Table 20. Another evidence of this can be got from the results of II_A–Ser. 18 in which the highest temperature is 405°C. There, the percentage of liquid products is very much smaller, but the residue contains about 15 g. of extractable liquid as compared with a few grams from the others at 450°C. The results of III_A–Ser. 57, which will be discussed further in detail later, illustrate the same point.

(2) *On Hydrogenation.* In Table 21 the ratios of H/C, corrected and not corrected for methanol oxygen (Paper (A) III), of the condenser condensates of the runs under low and high pressures are given. In the last row of the table, percentages of hydrogenation based on the H/C ratio of acetylene for the different gases used are shown. It is evident

Table 21. Degree of Hydrogenation of Condenser Condensates.

System	Low Pressure			Elevated Pressure		
Gas	H_2	$CO+H_2$	CO_2+H_2	H_2	$CO+H_2$	CO_2+H_2**
H/C×10 Found	1.101	1.026	1.018	1.173	1.276	1.122
H/C×10 Corrected*	0.905	0.890	0.858	0.973	1.091	0.833
% Hydrogenated based on H/C of Acetylene.	8.7	6.8	3	17.5	31.0	0

* Corrected for methanol oxygen.

** Result of one run.

that under elevated pressures, the percentages are higher. It is very much higher for $CO+H_2$ system while it is, within our experimental accuracy, about the same for CO_2+H_2 system. Furthermore, it seems that in the latter system the pressure has practically no effect. The fact that among the runs under high pressure, the degree of hydrogenation is almost independent of the pressure, within the range investigated, seems to strengthen our belief that the mechanism of the nascent acetylene polymerization is highly specific and but slightly—if at all—affected by pressure. The apparent increase in the percentages must be due to an increase in the time of contact. While in the runs under ordinary pressure it is about 20 sec, in the autoclave runs the substances remain in contact with hydrogen over 100 minutes. A particular increase in the H/C ratio for $CO+H_2$ system may be due to a slight formation of liquid product from water gas under elevated pressures. This statement appears paradoxical to what we have mentioned in Paper I that the gas itself does not form any liquid products. Since the conditions involved in the blank and present runs are quite different in such factors as the time of contact, the reaction products, it may be quite possible that a negligible amount in the blank runs could have become a bit more appreciable in the present runs, where especially any catalytic tendency will be greatly enhanced by the presence of the carbide(3). Or it may be in some way connected with the presence of the reactive hydrogen* produced by some such reaction(4) as

$$CaO + H_2O + CO = CaCO_3 + H_2, \quad (A)$$

which is a combination of

$$H_2O + CO = CO_2 + H_2 \quad \text{and}$$
$$CaO + CO_2 = CaCO_3.$$

We have seen that both of these reactions take place readily in our systems. According to Ellis(4), the first reaction, (A), so-called "lime process", takes place most readily under elevated pressures and at about

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(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15**(1941), 31.

(4) C. Ellis, "Hydrogenation of Organic Substances," 3rd Ed., 738, D. Van Nostrand Co., N. Y., (1930).

* We have seen the same sort of evidence in the runs under low pressure (2).

450–600°C. The fact that $CO+H_2$ may have reacted under elevated pressures to produce some liquid products becomes more probable, though not necessarily more conclusive, in the light of the results of III_A Ser. 57. In this run the reaction temperature was constant at 370°C, and water gas was charged 5 times at the reaction temperature to maintain the total pressure to 160–180 kg/cm^2. The time of reaction was 1600 minutes. A liquid product condensed at 370°C was over 9 g. and 25% of the total reacted carbon, assuming that all the carbon had come from the carbide.* These values represent in percent and in the absolute amount a maximum at such a low temperature. A word should be added that in this run a catalyst, which was, however, found quite inactive,** had been used, and this fact cannot be entirely over-looked in the above discussion.

(B) **Products.** (1) *Liquid.* The combined liquid products from the runs under high pressure were separated into three groups: those obtained when aluminum hydroxide was in contact with the carbide, the hydroxide "in cylinder", and those obtained with water gas mixtures. Their distillation curves and a similar one for the runs under low pressure are shown in Fig. 3. It is interesting that the curves for the runs under low pressure and the hydroxide 'in cylinder" are alike in many respects. This is probably due to the temperature effect. This is in accord with thermodynamic considerations$^{(3)}$. When the hydroxide and the carbide are separated, i.e., the hydroxide is "in cylinder", the water vapor released must diffuse through the atmosphere of the gas and the concentration of the water molecules must be uniformly distributed throughout by the time they react with the carbide. If, however, the hydroxide is in intimate contact with the carbide, the concentration of the water molecules may not be uniform, but may be larger at places, and there the temperature may be higher than the average of the system. This explanation seems

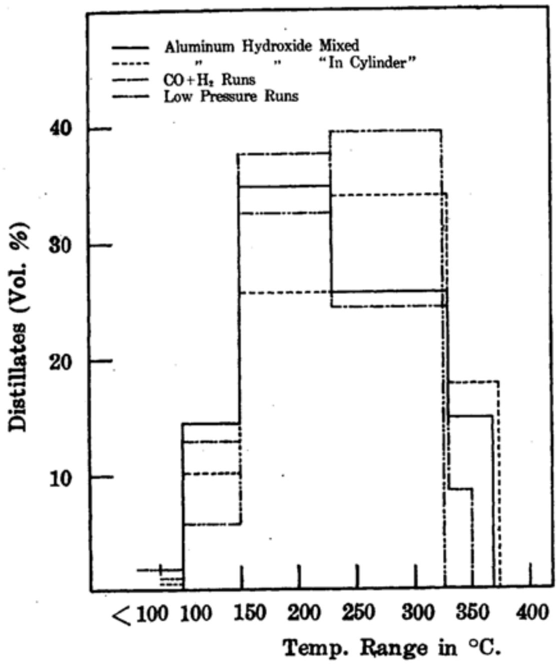

Fig. 3. Distillation Curves.

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* This assumption seems reasonable (Papers (A) III and II).

** As will be explained in one of the subsequent papers to be published elsewhere that even a slightly active catalyst may become rather active in the presence of the carbide.

to suffice for the shape of the curve for the liquid obtained when the hydroxide is in mixture with the carbide. The fact that its curve is similar to that of the water gas system may be accidental. As has been mentioned in a preceding section, CO and H_2 may have formed some liquid products which boil at lower temperatures. III_A Ser. 57 is a good example.

No detailed chemical analysis of the products has been made, but from some of the physical constants determined, they are chiefly aromatic and condensed in nature, as in the case of the runs under low pressure. From what has been said above, it seems quite probable that the main reaction of the nascent acetylene molecules under elevated pressures (under our present limited conditions) is the same as that under ordinary pressure runs, and the minor differences are ascribable to temperature and side effects, such as the formation of liquid products from the carrier gas itself, independently of the main reaction. The elementary analyses of the products are given in Tables 5, 7, and 9 in Paper II.

So far in these papers, we have reported only those runs made with aluminum hydroxide, but we have made some with zinc hydroxide as well. The results of the latter will be now given briefly. The yield of liquid products was about as satisfactory, and the products appeared more stable than those with aluminum hydroxide; their colour* did not change on standing, even over a year, and they appeared to be more hydrogenated. It seemed that zinc hydroxide had some catalytic effects⁽⁵⁾.

(2) *Gas.* The results of gas analysis of the runs are given in Tables 2, 3, 6, 9 and also in Paper II. It may be of some interest to mention that in some of the runs, especially when the total pressure of the system is low, the gaseous products** (at room temperature) found in the trap may be as high as 1/4 of the total original condensates (gaseous products condensed in trap and liquid products), as in runs II_A–13, II_A–11, and I_A Ser. 23; about 1/5 for I_A Ser. 37***. The analyses of the gases found in the trap are given in the same tables. It may be of some interest to note that their compositions are chiefly propane, butane, and olefines.

(3) *Residue.* The carbon content of the residue was small in every case when hydrogen was used and was also rather small for the other systems when that due to the carbonate carbon was taken account of. It is significant that the carbonate carbon contents are small in the hydrogen system, larger in the carbon monoxide (or water gas) system, and

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* Amber, reddish, clear, and less dark than with aluminum hydroxide.

(5) A. J. Lozovoi, *Gen. Chem.* (USSR) **1** (1931), 717. He had found that zinc oxide showed some catalytic effect in the polymerization of ordinary acetylene molecules, and it produced a liquid product at 370°C while aluminum oxide was much less catalytic and it did not reduce the ordinary temperature (500–600°C) of liquid formation.

** Condensed and dissolved in the trap cooled with alcohol-solid carbon dioxide.

*** Conditions of Runs.

Run	Gas	Total Press. kg./cm². (Room Temp.)
II_A 13	CO and H_2	37
II_A 11	,,	70
I_A Ser. 23	H_2	25
I_A Ser. 37	H_2	50

its value is, indeed, about the same as that of the carbon dioxide system when the time of contact is sufficiently long. As has been said before, the yield of liquid products increases at the expense of the carbon content in the residue. This is evident in Table 20.

(C) **Limitations of the Results.** As has already been mentioned in Paper I, the results obtained here are limited both in scope and significance because of the limitations imposed on the experimental conditions. Since aluminum hydroxide gives up most of its water at 200 to 300°C, the main reaction of the water vapor and the carbide is the formation of yellow powder(6), or a cuprene-like substance, the formation of which is influenced only slightly by the variation in the gases employed. Above 300°C the apparent formation of the liquid products is due to a sort of distillation effect which is again only a little affected by the species of the gases. On account of these factors, it is but natural that the differences owing to pressure, temperature, and species of gases are not as clearly marked as they would be if a proper choice in the apparatus has been made. Since we now possess an autoclave in which the water vapors can be made to react with the carbide under any desired temperature and pressure, we are certain that more significant results are possible.

The carbide reactions are characterized by a large evolution of the heat of reaction, and this heat must be taken away rapidly and effectively in order to obtain a maximum benefit from the use of carbide. Problems concerning the utilization of the heat of reaction will be the subject of a subsequent paper.

(D) **Couclusion.** The use of nascent acetylene to bring about more effective polymerization, and the use of the carbide as a means of promoting and accelerating many organic syntheses which otherwise would be thermodynamically improbable are new problems that have not been heretofore investigated at all, or but slightly.

Therefore, in this series of investigations it has been the intention of the authors to study these problems rather broadly, but still sufficiently in detail to obtain data which are of fundamental interest and to see further what practical possibilities are open to them.

The polymerization of nascent acetylene has been made under ordinary pressure in dynamic system and under elevated pressure in static system. The data obtained are somewhat fragmentary because of the explorative nature of the investigation, of the extensiveness of the field to be covered, and finally of the limitation imposed on the experimental conditions; but they are, nevertheless, sufficient to draw some general conclusions.

First of all, it is safe to conclude that the efficacy of the polymerization into liquid products of nascent acetylene is higher than that, even in the presence of an active catalyst, of the ordinary actylene—a manifestation of very high reactivity of nascent acetylene. For this reaction, the apparatus necessary is quite simple, and the need of a catalyst is dis-

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(6) R. Negishi, M. Nibayashi, S. Kataoka, and O. Kamiike, *J. Soc. Chem. Ind., Japan*, **45**(1942), in print.

pensed with. However, the reaction has certain limitations. The final products are almost exclusively aromatic or condensed, as shown by their high densities and boiling points, and they are too diversified to be easily separated into individual components. The course of its polymerization cannot be controlled but with difficulty because of the extreme reactivity and specificity of the reactions of nascent acetylene. It seems to the authors that the production of the paraffin series, as the main products directly from calcium carbide, is not likely unless a catalyst of high selectivity is found. The heat of reaction involving the carbide is enormous, and this factor must be well considered; otherwise, harmful rather than favorable effects of the carbide will take place.

The specificity of nascent acetylene polymerization seems uninfluenced by the presence of foreign substances. and this fact makes possible the use of carbide as a means of clarifying the mechanism of a reaction in which even a catalyst may be present, without the fear of introducing undesirable side reactions involving acetylene and the reactants of the desired reaction. However, the fact that the commercial carbide almost invariably contain sulphur and phosphorus compounds as impurities must not be overlooked when a catalyst is used.

Because of the fact that calcium carbide is a powerful deoxygenating agent by virtue of its strong affinities for water and carbon dioxide molecules, it may be used with advantage in the preparation of deoxygenated products. As an example, it can take off the oxygen from alcohols readily. Butyl alcohols may be prepared from either methanol or ethanol, or both(7), and completely deoxygenated compounds can also be formed from them. Thermodynamically, it is possible to deoxygenate practically all organic compounds, and this should be of great interest as a means of preparing such materials as olefines, unsaturated compounds, ethers, and other useful for organic syntheses.

The introduction of calcium carbide opens up the possibilities of organic syntheses enormously by virtue of its large increase in the free energy of reaction and the shift in the equilibrium owing to its great affinities for water and carbon dioxide molecules, which are not infrequently the by-products of organic reactions. By a proper choice of catalyst and experimental conditions, unlimited number of desirable substances may be synthesized.

Finally, this will conclude a series of investigations on the direct synthesis of hydrocarbons from calcium carbide. Due to circumstance, we are unable to pursue further this investigation and, with regret, we must leave many of the unsolved problems as they are. It is hoped that we shall be able to take up again this investigation from where we must leave off now.

What have been reported by us in a number of papers(1)(2) are the results of the culminating efforts of the following members, Messrs. Araki, Hayashi, Inaba, Kano, Kodama, Masunaga, Nagayoshi, Nakano, Sakon, Shimamura, and Shimono. To them our thanks are due. We are grateful to Dr. S. Hamai, Messrs. Nibayashi, Isobe, and Kataoka for their hearty co-operation.

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(7) R. Negishi, *Rev. Phys. Chem., Japan,* **15**(1941), 127; *ibid.,* **15**(1941), 171.

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Summary.

The effects on the character and yield of liquid products synthesized directly from calcium carbide under elevated pressures, of the species of gases, pressure, and temperature have been summarized. It has been found that the yield of liquid products increases with increasing total pressure of the system up to about 100 atmospheres and then decreases with further increase in the pressure.

The apparent characteristics of the products in carbon monoxide (or water gas) system seem different from the others, and an explanation for this has been given. As in the low pressure runs, carbon monoxide has rather harmful effects while, on the other hand, carbon dioxide has beneficial effects on the yield of liquid products.

There have been found slight differences in the yields and the properties of the products under elevated and ordinary pressures, and these differences have been explained as due rather to the effects of the time of contact and temperature than to any change in the mechanism of the polymerization reaction.

The limitations and the significance of the synthesis of hydrocarbon liquids directly from calcium carbide and several unique properties of the carbide which may be useful in organic syntheses have been pointed out and discussed.

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