[CONTRIBUTION FROM THE BROOKHAVEN NATIONAL LABORATORY]

Study of the Carbon Dioxide–Carbon Reaction Using C^{14} as a Tracer[1]

BY FRANCIS BONNER[2a] AND JOHN TURKEVICH[2b]

Radiocarbon C^{14} has been used to study the reaction between carbon dioxide, carbon monoxide and charcoal using a recycling system with continuous monitoring of the radioactivity of the gaseous components of the system. Radiochemical measurements were correlated with changes of composition of the gas and with pressure measurements. The data obtained were interpreted in terms of a mechanism which postulates a rapid reaction of the carbon dioxide with the surface to give an oxygenated surface and a radioactive carbon monoxide and a subsequent slow two-stage unimolecular decomposition of the oxygenated surface into non-radioactive carbon monoxide and charcoal.

The study of the reaction of carbon dioxide and charcoal to produce carbon monoxide is of great interest, not only from the point of view of establishing the mechanism of this very simple chemical transformation, but also because of its importance in combustion, water gas production, and the gasification of solid fuels. It has been previously studied by a number of investigators[3-8]:

The latter workers, refs. 7 and 8, have made an extensive investigation of the kinetics of the reaction in both flow and static systems. In the following investigation radioactive C^{14} isotope was used to study the mechanism of the reaction.

Apparatus

The apparatus employed in this investigation is shown in Fig. 1. It consisted of four parts: one for the preparation of radioactive CO_2 (ABC), one for the introduction of inactive gases (HIJ), one for the circulation of active CO_2 over charcoal (DEFG) and, finally, a pumping system (KLMNO).

Charcoal pellets were suspended in a quartz 1″ diameter reaction tube E by a quartz grill (made of $^1/_{16}$″ rod). Additional support for the charcoal pellets was attained by placing a thin layer of Refrasil quartz fiber material on the grill. A chromel–alumel thermocouple dipped just below the surface of the charcoal bed. The quartz tube was heated by means of a standard tube furnace 8″ long and with inside diameter 1.25″, which was operated through a constant voltage transformer and maintained the temperature constant to within a few degrees.

G was a Victoreen (Model VG-10) bell-jar counter with a 3.4 mg./cm.^{2} mica window attached with Apiezon W wax to a glass holder. Since the counter was filled with approximately 10 cm. of ethanol–argon counting mixture, the window was flexed concave downward upon evacuation and gas-filling of this portion of the system had to be carried out slowly to avoid breakage of the window.

Experimental Procedure

Active CO_2 was prepared according to the method of Zwiebel, Turkevich and Miller.[9] C^{14} containing $BaCO_3$ was obtained from the Isotopes Branch, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. It had been assayed at 10 μc. per mg.

The volumes of the various components of the system were determined by expansion of helium from a bulb of known volume placed in the position normally occupied by the CO_2 generator tube. This determination was made for the purpose of calculating initial pressures of CO_2 in the reaction system.

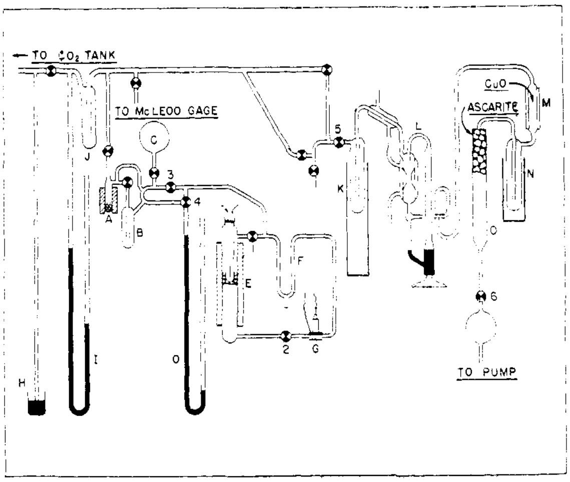

Fig. 1.—Apparatus.

3.5 g. of standard coconut char, obtained from Princeton University, were loaded in the quartz tube. Pumping schedules involved pumping the charcoal from about 15 to 45 hours at 850° before each run. While the authors realize that such a pumping schedule does not result in a thoroughly clean carbon surface,[10] they feel that it is thoroughly adequate to assure reproducibility, and that it is a necessary compromise both from the standpoint of time, and of wear and tear on the quartz vessel at temperatures over 1000°.

Because of the extreme softness of the C^{14} radiation, the window thickness reduced the counting efficiency by a factor greater than two. Background counts could be made only with the system evacuated or filled with inactive gas, and ranged from 29 to 38 counts per minute. The background count was reduced to its initial value within a few minutes of removal of active gas from the system. Self-absorption corrections were determined by measuring the counts per minute of radioactive CO_2 as a function of pressure from a few mm. to 760 mm. (Fig. 2). The low pressure portion of the curve gave a good straight line and deviations from this line at higher pressures were assumed to be due to self-absorption of the β particles within the gas. These deviations were used to construct a self-absorption correction curve for CO_2. A similar curve for CO was obtained from the CO_2 self-absorption curve by multiplying deviations from linearity by e^{μ} where μ is the ratio of the molecular weights of the two compounds. A rough estimate indicated the over-all efficiency to be 1 to 2%. The performance of the counter was checked before and after each run by placing a 5 μg. source of aged radium at a standard position near the counter.

Procedure

After outgassing the charcoal and the reaction system, radioactive CO_2 was allowed to enter the system to the right of stopcocks 1 and 2, and measurements were made of the gas pressure and radioactivity. When these had reached a steady value, the run was begun by opening the stopcocks

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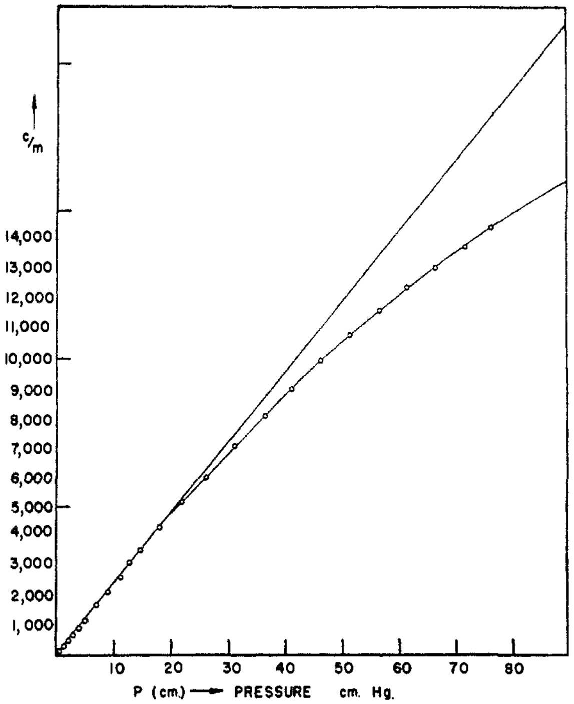

Fig. 2.—Counting rate *vs.* pressure.

1 and 2, allowing the CO_2 to expand over the charcoal and to flow around the reaction system by thermal convection. This thermal convection was not the rate determining step since the conversion of CO_2 to CO took place within 4 minutes from the time of introduction of the gas into the thermal syphon, and most processes involved changes in pressure and radioactivity over a period of at least a half hour. The CO_2 content of the gas was determined by condensing it in liquid air. The runs lasted from 18 to 50 hours.

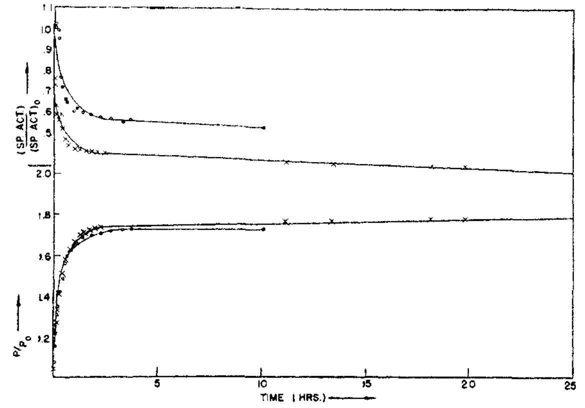

Fig. 3.—Change of pressure and activity with time at 735°: O, run no. 6 at initial pressure of 330 mm.; X, run no. 7 at initial pressure of 180 mm.

Results

At the relatively low temperature of 500°, there is no pressure change nor any change in the number of counts per minute in the gas for intervals up to 25 hours. This is interpreted to indicate that there is no exchange between the carbon dioxide and either the carbon of the surface or any adsorbed carbon monoxide or any adsorbed carbon dioxide remaining on the surface from previous pumping-off procedures. Condensation of the carbon dioxide in liquid air after overnight treatment at 500° showed several per cent. of a non-condensable gas whose specific activity was never less than that of the original carbon dioxide. This suggests the reaction

$$CO_2 + \text{charcoal} = CO + \text{oxygenated charcoal}$$

with the carbon dioxide molecules approaching the surface depositing their oxygen on the surface, and the reactant molecules coming off as the product molecules of CO. This point of view has been suggested by previous workers.[3-9] The results presented also exclude the possibility that one carbon dioxide molecule is adsorbed and a carbon monoxide molecule involving another carbon atom is desorbed. Furthermore, if the process of adsorption of carbon dioxide is to be considered as a dissociative process on the surface, then only one carbon–oxygen bond is dissociated.

Typical results at the higher temperatures are illustrated in Figs. 4 and 5. In these graphs, the ratio of the pressure to the initial pressure and also the ratio of the specific activity to initial specific activity are plotted against time for two temperatures, 735 and 848°, and for two pressures at each temperature. Runs 6 and 9 were made with an initial pressure of about 330 mm., while runs 7 and 10 were made at 180 mm. It is seen that the process is directly proportional to the initial pressure at these two temperatures. Furthermore, it was found by condensation of the gases that over 95% of the

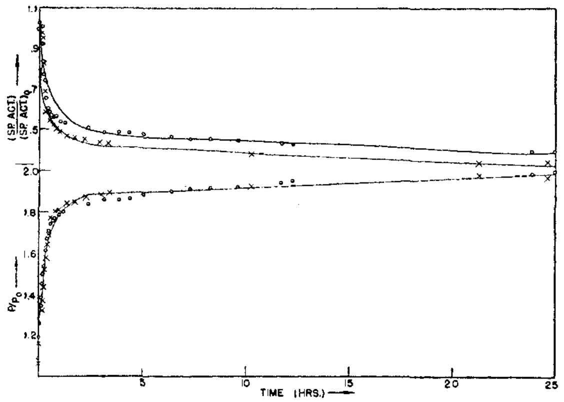

Fig. 4.—Change of pressure and activity with time at 848°: O, run no. 9 at initial pressure of 330 mm.; X, run no. 10 at initial pressure of 180 mm.

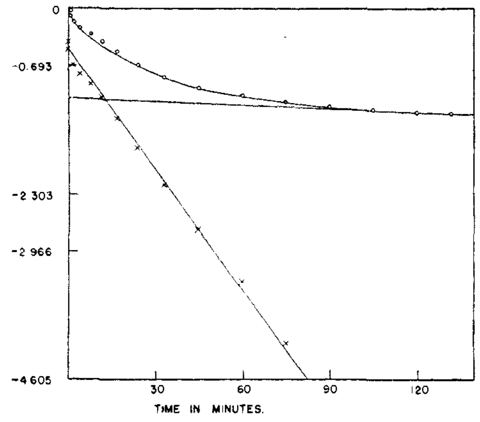

Fig. 5.—Breakdown of run no. 6 at 735° into a sum of two exponentials.

carbon dioxide was converted into carbon monoxide within at most 4 minutes from the start of the reaction, with no increase in pressure. The process can therefore be visualized as taking place in two stages. In the first stage the carbon dioxide after approaching the surface, leaves the surface as carbon monoxide, dropping its oxygen and forming an oxygenated charcoal surface. This process is very rapid at 700–848° (95% of CO_2 converted to CO within 4 minutes). The specific activity of the carbon monoxide is the same as that of the carbon dioxide introduced. The second process is the decomposition of the oxygenated surface with the desorption of the surface oxygen as carbon monoxide, removing at the same time carbon from the charcoal. This slow process involves an increase in pressure and a decrease in the specific activity of the carbon monoxide. Inasmuch as the surface contains varying but finite amounts of oxygen, we are led to a kinetic expression of the type

$$dP/dt = k(2P_0 - P),$$

where P_0 is the initial pressure, P the pressure at time t, and k the specific rate constant. This kinetic expression expressed the fact that the rate of increase in pressure is proportional to the amount of oxygen left on the surface in the first rapid process. On integration, and using the condition that at time $t = 0$ the pressure is P_0, we get

$$\ln (2 - P/P_0) = -kt$$

When, however, $\ln (2 - P/P_0)$ is plotted against time, we do not get a straight line, but a curve, which can be resolved into two straight lines (Fig. 6, giving the following as an analytical expression for the pressure change

$$P = P_0(2 - a_1e^{-b_1t} - a_2e^{-b_2t})$$

This suggests that there are at least two different types of oxygenated charcoal sites possibly associated with edges and faces of the small graphite crystals in the charcoal. Table I gives the experimental values for the constants a_1, a_2, b_1 and b_2 at three different temperatures. It is seen that the value of a_1 increases from 0.60 at 735° to 0.78 at 848° with the corresponding drop in the contribution of the second type of surface a_2. The value of the unimolecular constant b_1 is an order of magnitude greater than that of b_2. When the logarithms of these constants are plotted against the reciprocal of absolute temperature an activation energy of 8 kcal. is obtained for the first type of surface, and 21 kcal. for the second type of surface.

TABLE I

Run	Temp., °C.	a_1	a_2	b_1	b_1^*	b_2	b_2^*
5	735	0.60	0.34	0.045	...	0.00348	....
6	735	.60	.36	.058	...	.00122	....
7	735	.62	.34	.051	0.049	.00167	5.8×10^{-4}
8	758	.67	.25	.056	.052	.00105	6.6×10^{-4}
9	848	.77	.23	.079	.056	.00246	2.1×10^{-3}
10	848	.78	.21	.071	.066	.00357	2×10^{-3}

Radioactivity studies were based on the measurement of the ratio of the specific activity to the initial specific activity as a function of time. Some qualitative conclusion must be stated. Except in the case of one run, (6) the specific activity obtained on letting the gas into the reaction chamber was what one would calculate from the volume expansion, indicating little exchange with adsorbed carbon dioxide or carbon monoxide. Furthermore, if one molecule of radioactive carbon dioxide gives two molecules of carbon monoxide, involving one inactive carbon atom from the charcoal surface, one would expect the final ratio of specific activities to be equal to 0.5. The observed value is closer to 0.4, showing that some exchange takes place during the course of decomposition of the oxygenated charcoal surface. On the other hand, no exchange is observed if one keeps radioactive carbon monoxide in contact with the charcoal for a long interval of time after a run. This is interpreted to mean that the exchange between the radioactive carbon monoxide and the charcoal is confined to a small number of sites on the charcoal surface, and that at the end of the run these are equilibrated with the gas phase. Further experiments are being carried out to study the interaction of radioactive carbon monoxide and charcoal. If the process of interaction of radioactive carbon dioxide with charcoal is visualized as a rapid oxygenation of the charcoal surface, followed by a unimolecular decomposition of the surface, then there should be a quantitative relationship between the rate of increase in pressure and the drop in specific activity. An analysis of the specific activity data, using considerations of a similar nature to those used in the discussion of the pressure increase, gives the following equation for the change in specific activity A with time

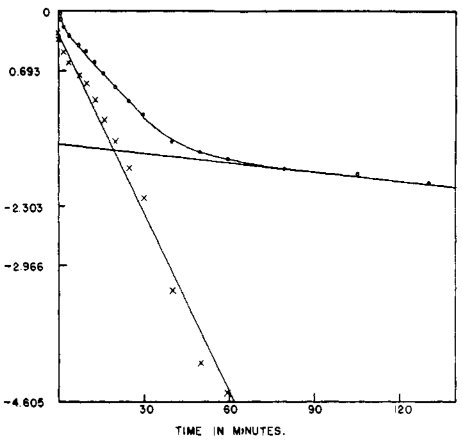

Fig. 6.—Breakdown of run no. 9 at 848° into a sum of two exponentials.

$$A = A_0(0.4 + 0.5e^{-b_1^*t} + 0.1e^{-b_2^*t})$$

where A_0 is the initial specific activity of the CO_2 gas. Examination of Table I shows that the coefficients b_1^* and b_2^* are of the same order of magnitude as those obtained from pressure studies.

To check whether there was any active carbon retained on the charcoal surface, an old charcoal sample which had been previously used for runs with radioactive carbon dioxide was pumped for 43 hours at 848° and treated with inactive carbon dioxide. In this case, both the pressure and the specific activity increased, showing that active carbon was present on the surface. Elementary considerations gave the following relationship between the specific activity at time t, A and the final activity A_∞

$$(A - A_\infty)/A_\infty = 0.72e^{-4\times 10^{2}t} + 0.28e^{-2\times 10^{-3}t}$$

The coefficients obtained are similar in magnitude to those obtained from both pressure studies and studies with radioactive carbon dioxide, and indicate that the exchange takes place at sites which are involved in the interaction of carbon dioxide and charcoal.

The results presented are in agreement with the mechanism proposed by earlier workers (3–9) who assumed that the first step was $CO_2 + C \rightarrow CO +$ an oxygenated surface, followed by a slow decomposition of this oxygenated surface to give a second molecule of CO. Under the conditions of the present investigation characterized by the rapid circulation of the CO_2 past the charcoal granules, the first step was very rapid. Consequently, we did not measure either the activation energy of this step nor the inhibiting effect of carbon monoxide. The activation energy for the second step was found to be much lower than that found by the previous workers. However, these workers were not able to separate out experimentally into two distinct stages the process of interaction of carbon dioxide with charcoal. Further work is being carried out at the laboratory on the use of isotopic tracers in the study of the interaction of carbon dioxide, carbon monoxide, steam and charcoal.

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Mechanism Studies of the Fischer–Tropsch Synthesis. The Addition of Radioactive Alcohol

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To help elucidate the mechanism of Fischer–Tropsch synthesis, methyl-labeled and methylene-labeled radioactive ethyl alcohol have been added to a 1:1 carbon monoxide–hydrogen synthesis gas being passed at 1 atm. pressure over an iron catalyst at about 230°. Measurement of the radioactivity of the hydrocarbon products shows negligibly small activity for all methane formed and an approximately constant activity of 2150 ± 100 counts per minute per cc. S.T.P. for the C_5 to C_{10} hydrocarbons. The C_2, C_3 and C_4 hydrocarbons have activities of about 1825, 1850 and 2000 counts per minute per cc. Degradation experiments on the C_3 hydrocarbons show that about 90% of the added carbon atoms are attached to the α-carbon atom of the alcohol adsorption complex whereas 10% are attached to the β-carbon. These results suggest that either ethyl alcohol or some surface complex formed by the adsorption of ethyl alcohol behaves like an intermediate in hydrocarbon synthesis over iron Fischer–Tropsch catalysts and that at least the first of the added carbon atoms attaches itself principally to the α-carbon atom of the surface complex.

The mechanism of the Fischer–Tropsch synthesis has been the subject of much speculation and experiment since the reaction was first discovered by Fischer and Tropsch in 1926. The original authors endeavored to explain the reaction by proposing[1] that metallic carbides are formed as intermediate products, and that these are reduced by the hydrogen present to form methylene groups which polymerize to give the higher hydrocarbons. The carbide theory, however, was criticized by Elvins and Nash[2] because it did not explain the formation of oxygenated compounds which are found in the synthesis product along with the hydrocarbons. They proposed the other principal mechanism for the synthesis that has thus far been advanced by suggesting that some C–H–O complex on the catalyst surface was the more likely intermediate.

The proposal of Elvins and Nash that carbon–hydrogen–oxygen complexes on the catalyst surface were the true intermediates in the Fischer–Tropsch hydrocarbon synthesis has received considerable indirect support in recent years. Storch and his group at the U. S. Bureau of Mines[3] have called attention to the similarity between the synol process which produces alcohols and the Fischer–Tropsch hydrocarbon synthesis. A. W. Weitkamp,[4] in a very thorough investigation of the products of an operating Fischer–Tropsch unit, has shown that the plot of per cent. branched chain aliphatic hydrocarbons against carbon number (length of chain) gives the same curve as is obtained by plotting the per cent. branched chain alcohols against their carbon number. He pointed out that this strongly suggests that the same mechanism operates in both the formation of alcohols and hydrocarbons.

It occurred to us that speculation relative to the mechanism of hydrocarbon synthesis would be on a much sounder basis if one could trace in the reaction products the disposition of certain simple oxygen-containing organic molecules added to the synthesis gas. In view of the availability of both methyl-labeled and methylene-labeled radioactive ethyl alcohol and in view of the suggestion frequently made that the alcohols may well be intermediate products, we have selected this compound for our first attempt to elucidate the nature of the intermediate complex that may be important in hydrocarbon synthesis.

If ethyl alcohol is either an intermediate or if it becomes modified slightly upon adsorption on the catalyst surface to form an intermediate, one might logically expect in these tracer experiments to find a constant molar radioactivity in all of the hydrocarbon products having three or more carbon atoms. On the other hand, if the alcohol is not an intermediate but is simply degraded to CH_2 groups on the surface or to carbon monoxide, one might expect to find the radioactive carbon distributed as a constant fraction of the carbon atoms in the prod-

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