# *Studies on Solid Carbons. II. The Gas-phase Oxidation of Solid Carbons*[*]

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The heterogeneous reaction between solid carbon and oxidizing gas is important from both the theoretical and industrial standpoints. In the past, several studies[1-7] have been made of this problem, but there still remain many points unresolved.

It is well known, regarding the oxidation of carbon, that the reactivity diminishes in accordance with the degree of graphitization[8]. The reactivity would be expected to depend primarily upon the physical fine structure (i. e., surface area, micro-pore volume and micro-pore radius) in a case of the same order of graphitization. It appears to be of interest, therefore, to find some correlation between the reaction rate and the surface properties of carbon.

The present work was carried out in order to investigate the gas-phase oxidation with nitrogen dioxide, using five typical carbons which differ in material and in manufacturing method, and also to investigate the characteristics of the rate of reaction under various conditions. The particle shapes and the degrees of the graphitization of carbon samples were observed with an electron microscope and X-ray diffraction. The physical fine surface structure of the composing particles was determined by means of the adsorption and desorption of gas at a low temperature.

## Experimental

**Apparatus and Procedure.** — The reaction apparatus is illustrated in Fig. 1. The reaction vessel H was a modification of that of Takeuchi[9]. The volume of the vessel H up to tap $K_4$ and $K_5$ is 123 cc. The carbon sample (2.0 g.) was kept in the vessel H. After it was evacuated under about $10^{-5}$ mmHg at 200°C for several hours, the temperature was lowered to 150°C (reaction temperature). The temperature of the electric furnace E, which contains H, was controlled ($\pm 1$°C) automatically. A MacLeod gauge B was used for the measurement of the low pressure. $J_2$ is a reservoir of hydrogen gas used for the "$H_2$-treatment" of the carbon sample. $NO_2$ gas was taken from the gas reservoir $J_1$ into the space between the taps $K_1$, $K_2$, $K_3$, $K_5$, $K_7$ and $K_8$, space with a volume of 277 cc. (not including the volume of the manometer C). The gas was introduced in H by opening $K_5$ to start the reaction. F is a photo-cell attached closely to H and connected to a micro-ammeter. The intensity of incident light from lamp G was kept constant. The variations of transmittance accompanying the reaction were followed by the photo-cell. The relation between the transmittance and the $NO_2$ concentration at the temperature range of 120 to 170°C is shown by a curve in Fig. 2. The reaction rate was obtained from this curve. A Bourdon gauge D was used to follow the changes in total pressure.

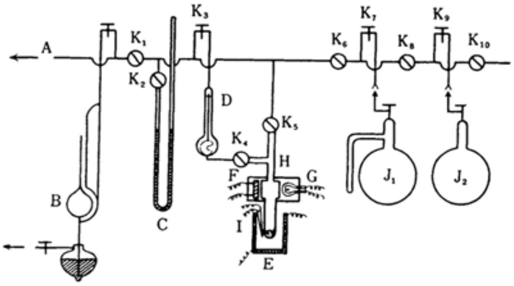

Fig. 1. Apparatus for the reaction between carbons and $NO_2$.

The surface areas, the micro-pore volumes and the mean micro-pore radii were obtained from

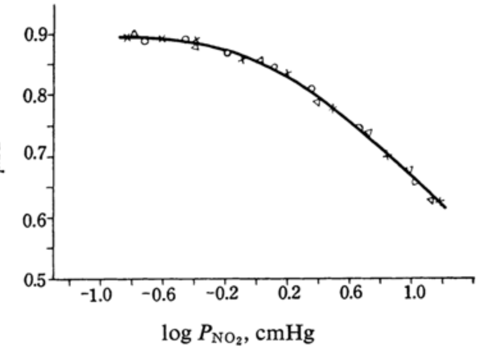

Fig. 2. Calibration curve.
△, 120°C; ○, 150°C; ×, 170°C

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[1] J. D. Lambert, *Trans. Faraday Soc.*, **32**, 452 (1936).

[2] W. K. Lewis, E. R. Gilliland and H. Hipkin, *Ind. Eng. Chem.*, **45**, 1697 (1953).

[3] P. L. Walker, Jr., R. J. Foresti, Jr. and C. C. Wright, ibid., **45**, 1703 (1953).

[4] H. Watts, *Trans. Faraday Soc.*, **53**, 93 (1957).

[5] C. N. Spalaris, *J. Phys. Chem.*, **60**, 1480 (1956).

[6] A. Turuizumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 266 (1958).

[7] R. N. Smith, J. Swinehart and D. Lesnini, *J. Phys. Chem.*, **63**, 544 (1959).

[8] E. g., W. R. Smith and M. H. Polley, ibid., **60**, 689 (1959).

[9] T. Takeuchi, *Catalyst*, **7**, 67 (1951).

TABLE I. CHARACTERISTICS OF SAMPLE CARBONS

| | Kind of carbons | | | | |
|---|---|---|---|---|---|
| | Philblack-I ($C_1$) | Miike-carbon ($C_2$) | Artificial graphite ($C_3$) | Petroleum coke | |
| | | | | A, ($C_4$) | B, ($C_5$) |
| Appearance | Spherical particle, ca. 0.5 mm.$\phi$ | Fine powder, ca. 100-mesh | Scalelike particle, ca. 0.5 mm.$\phi$ | Fine powder, ca. 200-mesh | Spongelike particle, ca. 2.0 mm.$\phi$ |
| Row material | Petroleum modified | Coal gas | Coal coke | — | — |
| Manufacture method | Imperfect combustion | Thermal decomposition | — | — | — |
| Degree of agglomeration | Large | Small | — | — | — |
| Particle diameter (m$\mu$) | 29.8 | 320.0 | — | — | — |
| Surface area (m$^2$/g.) | 101.0 | 9.4 | — | — | — |

| Fine structure | ($C_1$) | | ($C_2$) | | ($C_3$) | ($C_4$) | | ($C_5$) |
|---|---|---|---|---|---|---|---|---|
| | $C_{orig}$ | $C_{re}$ | $C_{orig}$ | $C_{re}$ | $C_{orig}$ | $C_{orig}$ | $C_{re}$ | $C_{orig}$ and $C_{re}$ |
| B. E. T. area (m$^2$/g.) | 104.0 | 108.0 | 15.2 | 12.2 | 2.1 | 10.8 | 8.3 | 0.9 |
| Micro-pore volume (cc./g.) | 0.07 | 0.06 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | — |
| Mean micro-pore radius (Å) | 13.5 | 12.1 | 26.8 | 32.8 | 133.4 | 26.0 | 33.8 | — |

adsorption and desorption-isotherms of nitrogen at the temperature of liquid nitrogen (−195°C). The B. E. T. method was applied to the adsorption isotherms to determine the surface areas of the carbon samples assuming 16.1 Å$^2$ as the cross-sectional area of nitrogen, and Kelvin's equation was adopted for the desorption isotherms to determine the micro-pore volumes and the mean micro-pore radii.

The particle shapes of the carbons were observed with an electron microscope (Type JEM-5G, made by the Japan Electron Optics Laboratory Co., Ltd.). The specimens were prepared by dispersing the carbons in alcohol by an ultrasonic wave apparatus (cycle: 7000 kc.; time: 2 min.) and by scooping them on collodion film supported on a copper mesh.

The degrees of crystallization by X-ray diffraction were measured with a "Geigerflex" made by the Rigaku Denki Co., using Cu(Ni)$K_\alpha$ radiation on the specimens packed in an aluminum case after the carbons had been pulverized with a merter.

**Materials.**—Five carbons produced commercially (Philblack-I ($C_1$), Miike carbon ($C_2$), artificial graphite ($C_3$), petroleum coke-A ($C_4$) and petroleum coke-B ($C_5$)) were used, whereas sample $C_4$ was powder of 200-mesh which had been prepared by the pulverization of sample $C_5$. The physical properties of these carbons are listed in Table I. Before use, these carbons were washed in boiling water for about one hour and were then dried in the atmosphere.

The "$H_2$-treatment" of carbon was performed under about 50 cmHg of hydrogen at 500°C for about 30 min. after it had been washed by boiling water. Before use, the temperature of the reaction vessel was lowered to 200°C; the procedure subsequently followed was as mentioned above*.

The treatment of carbon by benzoyl peroxide was performed by Ōkita's method[10].

The following procedure was adopted to regenerate the sample: after the reaction had stopped, the oxidized sample was washed with boiling water for about one hour**.

The nitrogen dioxide gas was prepared by heating of "extra pure grade" lead nitrate (supplied by Wako Junyaku Co., Ltd.) at 470°C. It was purified by vacuum distillation and stored in reservoir $J_1$.

The nitrogen gas used in the adsorption experiment was of a high purity (99.98%), having been supplied by Nissan Kagaku Co., Ltd.

## Results

The values of the surface area and of the physical fine structure are shown in Table I, and the results of observation with the electron microscope are shown in Table I and Fig. 3. The sign "$C_{orig}$" in line 8 of the table denotes the sample washed in boiling water, and the "$C_{re}$" denotes the sample regenerated by

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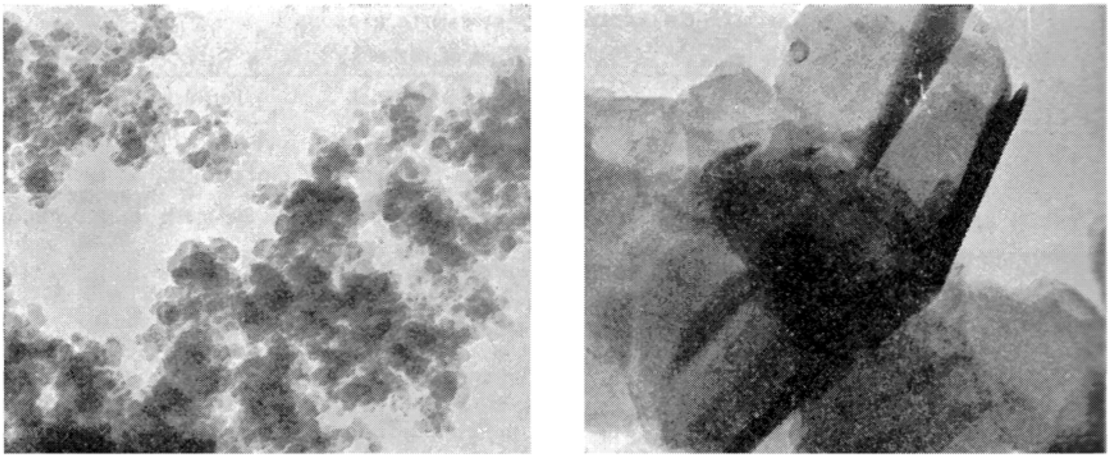
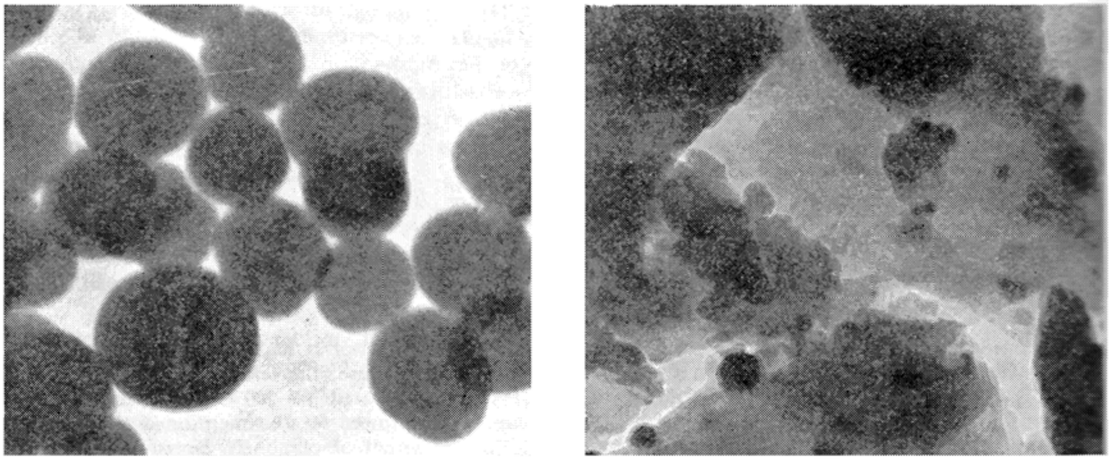
* The hydrogen contents found by elementary analysis of the sample were 0.56% after the "$H_2$-treatment" and 0.30% for the original sample.

[10] K. Ōkita et al., *J. Japan. Rubber Soc.*, 30, 661 (1957).

** During this treatment, much dregs-state material rose to the surface of the boiling water.



Sample $C_1$ Sample $C_3$



Sample $C_2$ Sample $C_4$

Fig. 3. Electron micrographs of sample carbons (×54000).

washing with boiling water after it had been used for the reaction with nitrogen dioxide. The electron microscopic areas of samples $C_1$ and $C_2$, calculated by assuming 2.0 as their density, are shown in line 7 of the table. The area of sample $C_1$ coincides with that given by the B. E. T. method, but the area of sample $C_2$ is smaller by about 40% than the B. E. T. area. From this fact, it can be surmised that the surface of the particles composing $C_1$ is comparatively smooth. On the other hand, the discrepancy in the areas of sample $C_2$ found in the two methods can be attributed to the existence of a roughness which could not be recognized with the electron microscope. In Fig. 3, it is also clear that both the samples, $C_1$ and $C_2$, are composed of spherical particles of inherent diameters, and that the diameter of $C_2$ is about 10 times larger than that of sample $C_1$. The particles of sample $C_2$ are more dispersed than those of sample $C_1$, which agglomerate to form secondary particles. Consequently, the physical fine structure of sample $C_1$ (Table I, lines 10 and 11) is formed of particles which have a smooth surface, while that of $C_2$ exists on the surface of a composing particle itself. Sample $C_3$ is composed of irregular thin films, while $C_4$ is composed of irregular thin films and small spherical particles. Therefore, the roughness in the surfaces can not be estimated as it was in the cases of $C_1$ and $C_2$. The electron micrographs suggest also that the degree of graphitization of sample $C_3$ is higher than those of $C_1$ and $C_2$, and that that of sample $C_4$ is between $C_3$ and $C_1$ or $C_2$, because it is composed of films similar to those found in $C_3$ and of particles similar to those found in $C_1$ or $C_2$.

X-ray diffraction patterns of sample carbons are shown in Fig. 4. The results show that the degrees of graphitization of samples $C_1$ and $C_2$ are quite low and indicate the characteristics of typical carbon black. The patterns of both samples, $C_3$ and $C_4$, indicate that their degrees of graphitization are quite high compared with $C_1$ and $C_2$ and that that of $C_3$ is higher than that of $C_4$. These facts support the conclusion obtained from the results of the electron microscopic observation.

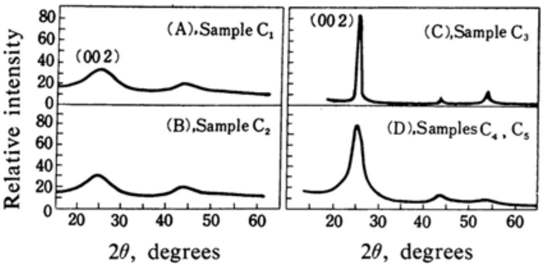


Fig. 4. X-Ray diffraction patterns of sample carbons.
(A) and (B); Cu(Ni)$K_\alpha$, 35 kV., 15 mA., 32-0.8-4 sec., $2^1/_2°-2^1/_2°-0.2$ mm., 1°−1 cm./min. (C); Cu(Ni)$K_\alpha$, 30 kV., 10 mA., 64-1-4 sec., 1°−1°−0.1 mm., 1°−1 cm./min. (D); Cu(Ni)$K_\alpha$, 30 kV., 15 mA., 8-1-4 sec., 1°−1°−0.1 mm., 1°−1 cm./min.

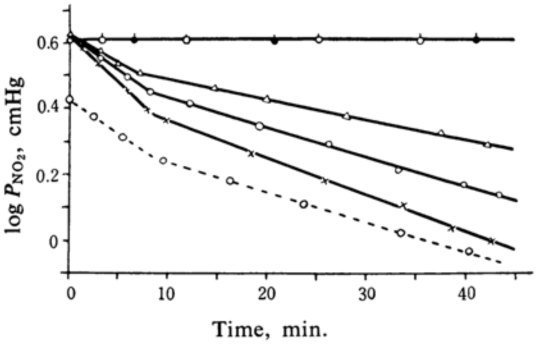


Fig. 5. Changes of $NO_2$ pressure with time on carbons (per 2 g.) at 150°C. ×, $C_1$; ○, $C_2$; ⫯, $C_3$; △, $C_4$; ●, $C_5$; --○--, $C_2$ (at 170°C)

The results of oxidation, which was carried out at 150°C with 4.2 cmHg of initial pressure of nitrogen dioxide, are shown in Fig. 5. The figure shows that the relation of the logarithm of pressure against time can be expressed by bent straight lines which are steep in the the initial stage. The rates of the consumption of nitrogen dioxide obtained from the lines are shown in Table II, where $K_1$ and $K_2$ denote the rate constants per unit gram and area respectively. It is noteworthy that the ratio of the rate in the initial stage ($k_1$) to that in the second stage ($k_s$) can be given in the range 2.0 to 3.0 for every carbon.

Figure 6 shows the results of the experiments carried out to ascertain the reaction order of

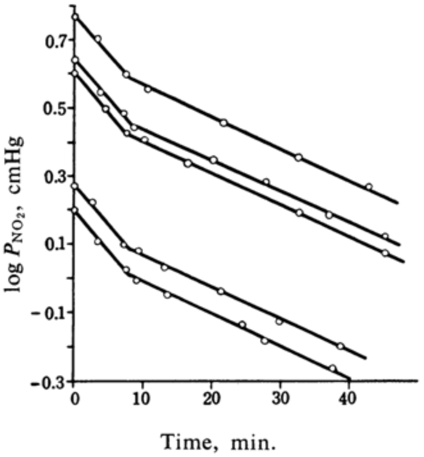


Fig. 6. Effect of initial pressure of $NO_2$ for the rate of reaction of carbon. Sample carbon: $C_2$; Reaction temperature: 150°C.

TABLE II. DATA OF THE REACTION BETWEEN CARBONS AND NITROGEN DIOXIDE

| Kind of carbon | | Rate constant $K_1$ ($g^{-1}\cdot sec^{-1}$) Initial $k_1\times10^4$ | $K_1$ ($g^{-1}\cdot sec^{-1}$) Second $k_s\times10^4$ | $K_2$, $cm^{-2}\cdot sec^{-1}$ Initial $k_1\times10^9$ | $K_2$, $cm^{-2}\cdot sec^{-1}$ Second $k_s\times10^9$ |
|---|---|---|---|---|---|
| $C_1$ | $C_{orig}$ | 5.56 | 1.89 | 0.53 | 0.18 |
| | $C_{re}$ | 5.29 | 2.00 | 0.49 | 0.19 |
| | $C_{no\text{-}re}$* | 1.57 | 1.03 | — | — |
| $C_2$ | $C_{orig}$ | 3.84 | 1.74 | 2.53 | 1.14 |
| | $C_{re}$ | 2.00 | 0.89 | 1.64 | 0.73 |
| | $C_{no\text{-}re}$* | 0.93 | 0.93 | — | — |
| $C_3$ | $C_{orig}$ and $C_{re}$ | — | — | — | — |
| $C_4$ | $C_{orig}$ | 3.15 | 1.32 | 2.92 | 1.22 |
| | $C_{re}$ | 1.68 | 0.69 | 2.02 | 0.83 |
| | $C_{no\text{-}re}$* | 0.50 | 0.50 | — | — |
| $C_5$ | $C_{orig}$ and $C_{re}$ | — | — | — | — |

* Sign $C_{no\text{-}re}$ denotes the sample which was outgassed for several hours at 200°C after sample $C_{orig}$ had been oxidized by nitrogen dioxide.

nitrogen dioxide by using sample $C_2$ under various initial pressures. From the results shown in Figs. 5 and 6, reaction order could be determined to be first. Unexpectedly, in spite of the change of the pressure of nitrogen dioxide in the reaction, no change at all in total pressure was recognized. Figure 5 shows that either the sample $C_3$ of the highest degree of graphitization or $C_5$ of a little higher degree did not react with a measurable rate.

It is of particular interest that the pulverization of carbon markedly increased the reaction rate. By pulverization, the rate of $C_5$ (i. e., that of $C_4$) became as fast as that of $C_2$. In the cases of $C_1$ and $C_2$, no remarkable difference in the rate $K_1$ could be found, though a difference exists in their surface areas. Accordingly, the rate $K_2$ of sample $C_2$ becomes greater than that of $C_1$.

The exeriment on sample $C_2$ at the higher temperature, i. e., 170°C, was carried out to learn the activation energies at the initial and second stages of the reaction. However, no detectable change in the rate could be found. This fact indicates that the activation energies in both stages are very small ($< 3$ kcal.*), giving thus no difference between the two.

When pre-treated with hydrogen and benzoyl peroxide, the reaction rate of nitrogen dioxide the B. E. T. areas and the electron micrographs showed no detectable change in any sample.

Tables I, II and Fig. 7 show the results of the reaction carried out to observe the effect of the regeneration upon the surface structure and the reaction rate of the carbons. In Table II, it can be found that the rate $K_1$ of the regenerated sample $C_1$ became markedly greater than that of the not regenerated sample and that it is almost the same as that of fresh carbon. In the cases of $C_2$ and $C_4$, the rates also became greater than that of not regenerated samples, while their rates in the initial and second stages of the reaction are about half of those of the fresh carbons. In Table I, it can be found that the change in fine structure of the regenerated sample $C_1$ is very small, but both samples $C_2$ and $C_4$ indicate a decrease in B. E. T. areas and an increase in mean micro-pore radii. Those facts suggest that the roughness of the composing particles of $C_2$ and $C_4$ were diminished to some extent by the regeneration. However, these hypotheses could not be verified by the electron micrographs.

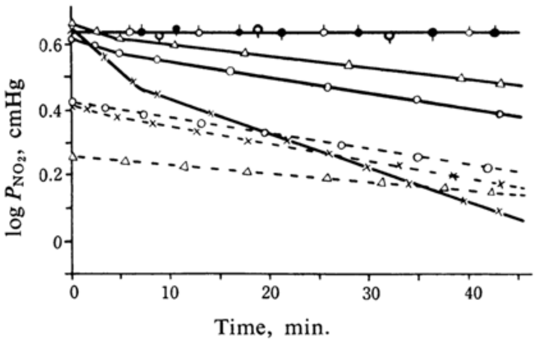


Fig. 7. Changes of $NO_2$ pressure with time on carbons (per 2 g.) regenerated and not regenerated at 150°C.

—×—; $C_1$ regenerated
—○—; $C_2$ regenerated
—ȯ—; $C_3$ regenerated
—●—; $C_4$ regenerated
—△—; $C_4$ regenerated
--×--; $C_1$ not regenerated
--○--; $C_2$ not regenerated
♀ ; $C_3$ not regenerated
--△--; $C_4$ not regenerated
● ; $C_5$ not regenerated

## Discussion

The rate of oxidation of carbons can be considered simply to be controlled by the following factors: the degree of graphitization, the physical fine and/or the chemical structures of the surface, though these factors can not be discussed separately.

The well-graphitized carbons, $C_3$ and $C_5$, possessed different X-ray diffraction patterns, as is shown in Fig. 4. However, no difference was found in the oxidizing reaction with nitrogen dioxide. This indicates that the progress of graphitization prevents the oxidation by nitrogen dioxide. The samples which are composed from amorphous carbon, i. e., $C_1$ and $C_2$ reacted with nitrogen dioxide quickly, but their $K_2$ rates differed markedly from each other. It can be noticed that the micro-pore volume of sample $C_2$, which reacted with nitrogen dioxide more rapidly than $C_1$, is smaller than that of $C_1$, and that the mean micro-pore radius is greater than that of $C_1$. If the micropore radius is small, the wall of the capillary will be a much more difficult location for the reaction than a free surface. Therefore, the difference in rates found in the two samples ($C_1$, $C_2$) can be attributed to a defference in their physical fine structures. Whether or not the rate of oxidation is affected by the diffusion of gas can be confirmed by plotting the concentration of nitrogen dioxide against square root of time[11]. Figure 8 shows that the relationships are represented by convex curves in the initial stage of the reaction, but, by straight lines in the second stage. This indicates that the rate of the reaction was controlled by the

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* The value was estimated by the experimental error.

[11] R. M. Barrer and D. W. Riley, *J. Chem. Soc.*, **1948**, 133.

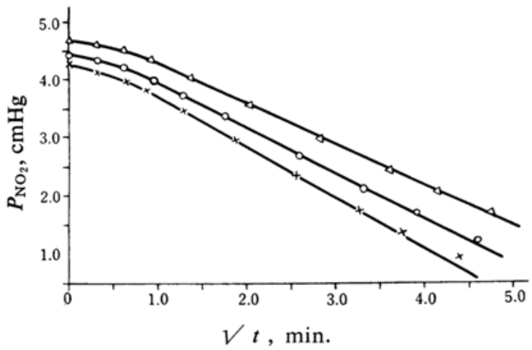

Fig. 8. Changes of $NO_2$ pressure with square root of time on carbons (per 2 g.) at 150°C. × : $C_1$ ; ○ : $C_2$ ; △ : $C_4$.

diffusion of gas except in the short initial stage. We can conclude by referring Fig. 5 to Fig. 8 that rate $k_1$ in Table II concerns only the chemical reaction and that it is the rate of the reaction on the free surface of carbons.

The sites of different reactivities can be considered to exist on the surface of carbon as has been believed in the field of physico-chemical studies on solid surfaces.

To explain exactly the differences in rates $k_1$ which were not controlled by diffusion, more information about the physical and chemical properties of the free surface, e. g., geometrical arrangement and functional group on the surface, will be required. It is very difficult, however, to make clear the properties mentioned above because of the complexity and the instability of the carbon surface. However, the adaptation of the results in the following two studies can be ascribed to the relation between the rate of reaction and the nature of the surface.

The number of edge atoms in $C_5$ must be increased by pulverization. The increase in the reaction rate in $C_4$ should correlate with the increase in edge atoms because the edge atoms of microcrystalline of carbons may be considered to be more susceptible to chemical attack than the atoms in the center of the basal plane. Such a view accords with that of Long and Sykes[12], who studied the oxidation of carbon with steam.

Recently, Smith and his co-workers[7] have reported that the oxidation of carbon by nitrogen monoxide was greatly retarded by pretreatment with hydrogen at 1000°C for 15 min. In this study, the oxidation of carbon was not affected by hydrogen. In both reactions, the adsorption of oxidizer (nitrogen dioxide or nitrogen monoxide) occurs on carbon prior to oxidation. In this case, the number of sites to be occupied by the oxidizer would be decreased by the occupation of pre-treated hydrogen. Accordingly, the rate of oxidation is expected to decrease. The result of the reaction with nitrogen monoxide reveals either that the hydrogen on carbons is not readily attacked by the adsorbed nitrogen monoxide or that the reaction products (or groups) of hydrogen and oxygen given by nitrogen monoxide have a nature which is hard to distinguish from the carbon. However, in the case of nitrogen dioxide the result indicated that because of the nature of the strong oxidizer, the hydrogen was readily released into the gas-phase after it had been attacked by nitrogen dioxide.

In short, the oxidation of carbon by nitrogen dioxide is greatly affected by the physical fine structure but not by the chemical structure of the carbon surface.

## Summary

The gas-phase oxidation of five sorts of carbons with nitrogen dioxide has been measured under a pressure range from 2.4 to 9.0 cmHg at 150°C by a static method, in order to determine, primarily, the relation between the reaction rate and the physical properties of carbons (B. E. T. area, degree of graphitization, particle shape, micro-pore volume and mean micro-pore radius).

The rate of consumption of nitrogen dioxide has been determined photometrically.

The well-graphitized carbons did not react with nitrogen dioxide, while the rate curves obtained on the amorphous carbons showed as bent straight lines, the inclination of which is steep at the initial stage, followed by a slow second stage. The activation energy in the reaction is very small ($<3$ kcal.).

The explanation of the results is as follows: the consumption of nitrogen dioxide in the initial stage relates mainly to chemical reaction on the free surface of the carbon, and the rate is controlled by the free surface area and the concentration of the edge atoms of the surface. The rate of the second stage relates to the diffusion process the micro-pore of carbon particles, and it is controlled by the physical fine structure of the surface.

The author wishes to express his gratitude to Professor Toyosaburo Takeuchi for his cordial guidance and discussion on this study.

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[12] F. J. Long and K. W. Sykes, *Proc. Roy. Soc.*, **A 193**, 377 (1948).