Reactivity of Coke. I.
Absolute Reaction Rates of the Carbon Dioxide-Carbon Reaction

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The reactivity of coke is very important in industry and so the reactions of carbon dioxide with charcoal and pure graphite have been extensively studied.[1-4] The mechanism of this reaction is at present considered as follows:

$CO_2+C\longrightarrow CO+[CO]$ surface oxide (1)
$[CO]\longrightarrow CO$ (2)

The reaction (1) of the surface oxide for-

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1) W. E. J. Broom and M. W. Travers, *Proc. Roy Soc.*, (London) **135A**, 512 (1932).

2) J. Gadsby, E. J. Long, P. Sleightholm and K. W. Sykes, *Proc. Roy Soc.*, (London) **A193**, 357 (1948).

3) I. Langmuir, *J. Am. Chem. Soc.*, **37**, 1154 (1915).

4) A. F. Semechkova and D. A. Frank-Kamenetzky, *Acta Physico. Chim.* (U.R.S.S.), **12**, 829 (1940).

mation is very rapid and only about 0.5 % of sites on the total carbon surface seem to take part in the reaction (1). Desorption of 「CO」 is the rate-determining step.

In a recent paper, Bonner and Turkevich[5] discussed the carbon dioxide-carbon reaction using C^{14} as a tracer and supported the above mechanism.

More recently, Reif[6] discussed the mechanism of this reaction theoretically and Gulbransen and Andrew[7] questioned the surface oxide formation from their results using a sensitive microbalance. Gulbransen and Andrew,[7] Wynne-Jones and his coworkers[8] emphasized the effects of metal oxide impurities on the reaction rate of carbon dioxide with pure graphite.

In the present paper, the surface areas of eight carbons were determined by the adsorption of ammonia at 0°C by the B.E.T. method and, using these values, the absolute reaction rates of the carbon dioxide-carbon reactions were obtained and discussed from the absolute reaction rates theory.

Apparatus, Materials and Procedure

The apparatus is shown in Fig. 1. A is a reaction tube of quartz, F, a mercury reservoir, B, a gas burette and $L_1 \sim L_9$, vacuum cocks. A was kept at 0°C with the surface area determination and regulated at a constant temperature in the range from 850° to 978°C within ±1°C with the reaction rate measurement.

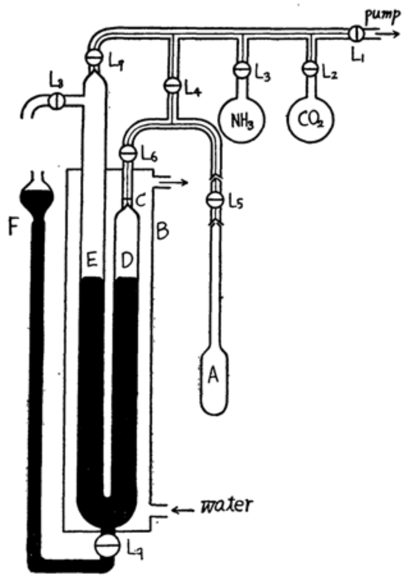

Fig. 1—Apparatus

Eight carbons as shown in Table I were used and their particle size is 10∼20 mesh except for fine acetylene black and carbon for spectroscopic analysis. All carbons were previously treated with 6N-hydrochloric acid for about 40 hrs. and then washed by boiling distilled water during about 200 hrs. Analytical results and the density of all carbons using carbon tetrachloride at the end of all the experiments are shown in TABLE I.

TABLE I*

Sample	Moisture %	Ash %	Density g./cc.
Coke I	0.87	12.95	1.92
Coke II	2.03	11.18	1.79
Coke III	0.17	12.90	1.89
Pitch coke	0.30	2.32	1.90
Oil coke	0.17	0.39	2.00
Charcoal	4.82	0.70	1.27
Carbon for spectroscopic analysis	0.10	trace	2.25
Acetylene black	0.30	0.10	2.27

Ammonia was prepared by the thermal decomposition of 28% aqueous ammonia, dehydration by calcium oxide, potassium hydroxide and metallic sodium and lastly vacuum distillation at dry-ice temperature.

Carbon dioxide was prepared by the thermal decomposition of sodium bicarbonate and dehydration by both calcium chloride and phosphorus pentoxide.

Method for Determination of Surface Area.—The surface areas of carbon samples were determined using the adsorption of ammonia at 0°C following the simple B.E.T. method.[9,10]

The carbons were previously evacuated at 1100°C for 12∼15 hrs. until 10^{-4} mmHg to eliminate some surface oxide and residual volatile matters. The adsorption of ammonia vapor was determined volumetrically at a series of P/Po values between 0.05 and 0.3. The B.E.T. plots of $P/v(Po\text{-}P)$ vs. P/Po were made and V_m and C in the B.E.T. equation were calculated.

$$P/v(Po-P)=\frac{1}{V_mC}+\frac{C-1}{V_mC}P/Po \qquad (3)$$

Where, V_m is the volume of monomolecular adsorption, C is a constant and approximately equal to $\exp(E_1-E_L)/RT$ where E_1 is the heat of adsorption of the first adsorption layer and E_L is the heat of liquefaction. P is the equilibrium pressure, Po, the saturation pressure, and v, the volume of gas adsorbed. From the value of V_m, the total surface area of the sample, S, can be calculated by the following equation, using the average

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[5] F. Bonner and J. Turkevich, *J. Am. Chem. Soc.*, **73**, 561 (1951).

[6] A. E. Reif, *J. Phys. Chem.*, **56**, 785 (1952).

[7] E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, **44**, 1048 (1952).

[8] W. F. K. Wynne-Jones, H. E. Blayden and H. Marsh, *Brenn. Chem.*, **33**, 238 (1952).

* Samples were heated at 1100°C in vacua before surface area and reaction rates measurements and so subjected to vacuum treatment at 1100°C for about 20—60 hrs. in all.

[9] S. Brunauer, P. H. Emmett and E. Teller, *J. Am Chem. Soc.*, **60**, 309 (1938).

[10] S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, ibid., **62**, 1723 (1940).

surface area per molecule of ammonia of 12.9×10^{-16} sq. cm. and then the specific surface area, *A*, of the sample can also be obtained,

$$S=(12.9\times10^{-16}\times V_m\times6.02\times10^{23})/22400\times10^4,\ m^2 \quad (4)$$

Method for Determination of Reaction Rates. After the surface area measurement, the sample was heated and the adsorbed ammonia was thoroughly desorbed. Carbon dioxide was introduced into the reaction tube A in Fig. 1 after regulating the temperature of the sample at a constant temperature in the range from 850° to 978°C and the increase of total pressure against time at constant volume was measured by cathetometer and the reaction rates of the system of carbon dioxide and carbons were determined.

After the reaction rate measurement was over and before the next surface area determination or the next reaction rate measurement, the sample was again evacuated at 1100°C for 3∼15 hrs. until 10^{-4} to 10^{-5} mmHg to evaporate the surface oxide considered to be formed by the former reaction with carbon dioxide. The absolute reaction rates were obtained from the reaction rates measurement and the surface area determination.

Results and Discussion

(I) Surface Areas of Carbons. The B.E.T. plots of $P/v(Po-P)$ vs. P/Po are shown in Fig. 2 and monomolecular adsorption volume V_m, total surface area S, specific surface area *A*, B.E.T. constant *C* and the difference of the heat of adsorption of the first layer and the heat of liquefaction E_1-E_L are summarized in Table II. The surface areas and the weights of the coke I were determined before and after the reaction rate measurement with carbon dioxide as shown in No. 5-2, No. 5-3 and No. 5-4 in Table II and their differences were found to be so small that after the experiment with charcoal, No. 6 in Table II, the surface area determination was made at once and from these surface area values and kinetic data, the absolute reaction rates for various temperatures were obtained.

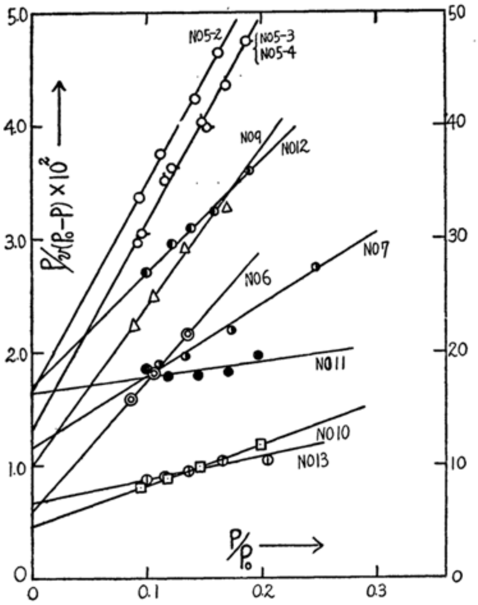

Fig. 2.—B.E.T. plots
Ordinate; left-hand, No. 5, No. 6, No. 9 and No. 12
right-hand, No. 7, No. 10, No. 11 and No. 13

The largest specific surface area of the samples investigated was 399 m²/g of charcoal and the smallest, 0.41 m²/g of oil coke and their ratio was about 10^3. If charcoal and acetylene black were excepted, the ratio of

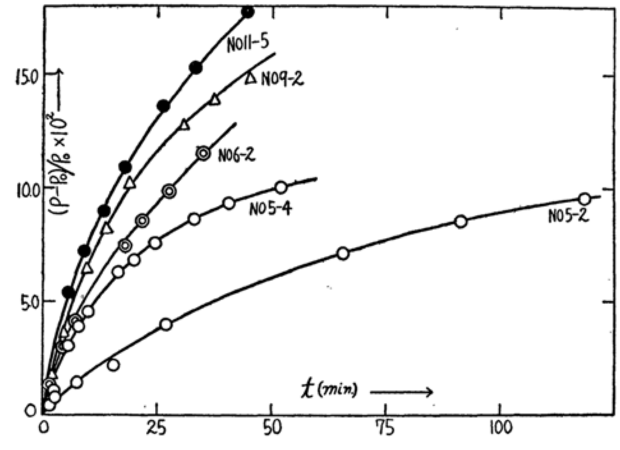

Fig. 3.—Relation between increase of total pressure and time
● acetylene black at 1230°K
△ coke II at 1173°K
◎ charcoal at 1173°K
○ coke I at 1173°K and 1223°K

TABLE II

Sample	Experimental number No.	Vacuum pretreatament at 1100°C hr.	Sample weights g	V_m cc	S m²	A m²/g	C	$E_1-{}_lE$ cal/mol	Reaction temperature K	Number of moles of CO_2	Po mmHg	Slope	$1/2.303Po$	K	Ka_{obs} molecules cm^{-2} sec^{-1}	$Ka_{calc.}$ molecules cm^{-2} sec^{-1}
Coke I	5—2	15	8.0879	5.01	17.8	2.20	12.1	1360	1173	4.727×10^{-4}	784.0	5.44×10^{-4}	5.53×10^{-4}	0.0902	3.18×10^{9}	2.21×10^{9}
	5—3	15	8.0749	5.02	17.9	2.22	15.4	1490	1123	4.124 〃	665.4	6.47 〃	6.52 〃	0.00765	2.79×10^{8}	3.36×10^{8}
	5—4	15	8.0658	5.03	17.9	2.22	15.4	1490	1223	4.301 〃	719.0	5.98 〃	6.03 〃	0.298	1.08×10^{10}	1.30×10^{10}
	5—5	15	8.0590						1223	4.514 〃	752.0	5.73 〃	5.76 〃	0.311	1.11×10^{10}	1.30×10^{10}
Charcoal	6—1	15	0.0735	8.25	29.3	399.0	20.2	1640	1123	3.877 〃	573.0	7.18 〃	7.56 〃	0.0633	1.56×10^{9}	8.43×10^{8}
	6—2	3							1173	3.262 〃	495.0	8.45 〃	8.75 〃	0.342	8.19×10^{9}	5.06×10^{9}
	6—3	3							1223	4.664 〃	718.5	5.33 〃	6.04 〃	2.22	5.31×10^{10}	3.28×10^{10}
Oil coke	7—1	15	11.6119	1.34	4.76	0.41	6.43	1020	1223	4.157 〃	727.0	5.37 〃	5.97 〃	2.21	2.87×10^{11}	3.64×10^{11}
	7—2	10							1173	5.538 〃	635.0	6.65 〃	6.54 〃	0.220	4.10×10^{10}	7.32×10^{10}
	7—3	10							1123	4.493 〃	764.5	5.66 〃	5.66 〃	0.060	7.75×10^{9}	1.33×10^{10}
	7—4	10							1173	4.083 〃	700.1	6.07 〃	6.20 〃	0.393	5.04×10^{10}	7.32×10^{10}
	7—5	10							1223	3.649 〃	645.0	6.27 〃	6.72 〃	1.55	1.99×10^{11}	3.64×10^{11}
Coke II	9—2	15	6.9295	6.66	23.7	3.42	15.0	1480	1173	3.542 〃	562.0	7.55 〃	7.71 〃	0.492	1.19×10^{10}	1.30×10^{10}
	9—4	5							1223	4.415 〃	755.0	5.57 〃	5.75 〃	2.09	6.19×10^{10}	7.30×10^{10}
	9—5	5							1123	3.433 〃	535.0	8.25 〃	8.11 〃	0.0616	1.86×10^{9}	2.12×10^{9}
	9—7	5							1223	4.232 〃	703.0	5.90 〃	6.19 〃	1.94	5.70×10^{10}	7.30×10^{10}
	9—9	5							1223	4.254 〃	702.0	6.25 〃	6.18 〃	2.10	6.29×10^{10}	7.30×10^{10}
Coke III	10—1	15	10.1108	2.42	8.6	0.85	9.21	1210	1123	4.341 〃	700.0	5.95 〃	6.20 〃	0.0903	7.13×10^{9}	1.33×10^{10}
	10—2	10							1153	3.668 〃	600.0	6.80 〃	7.24 〃	0.360	2.86×10^{10}	3.70×10^{10}
	10—3	5							1183	3.946 〃	650.5	6.66 〃	6.69 〃	0.780	6.20×10^{10}	1.09×10^{11}
	10—5	5							1223	4.202 〃	713.0	5.88 〃	6.09 〃	2.23	1.76×10^{11}	3.82×10^{11}
Acetylene black	11—1	12	0.2309	3.36	12.0	52.0	1.81	326	1172	3.653 〃	552.2	7.58 〃	7.87 〃	0.089	6.07×10^{9}	5.55×10^{9}
	11—2	3							1212	4.768 〃	734.0	5.49 〃	5.91 〃	0.379	2.13×10^{10}	2.28×10^{10}
	11—3	3							1251	4.140 〃	642.0	6.60 〃	6.78 〃	1.18	6.58×10^{10}	7.46×10^{10}
	11—4	3							1193	4.148 〃	630.0	6.64 〃	6.88 〃	0.151	8.20×10^{9}	1.15×10^{10}
	11—5	3							1230	4.361 〃	675.0	6.16 〃	6.43 〃	0.870	4.85×10^{10}	3.95×10^{10}
	11—6	3							1216	4.906 〃	753.0	5.58 〃	5.76 〃	0.417	2.33×10^{10}	2.57×10^{10}
Pitch coke	12—1	15	12.2474	8.49	30.2	2.46	6.93	1055	1213	5.170 〃	681.0	6.21 〃	6.37 〃	0.366	1.00×10^{10}	0.91×10^{10}
	12—2	3							1252	3.544 〃	613.0	6.82 〃	7.07 〃	1.41	3.13×10^{10}	3.24×10^{10}
	12—3	3							1172	4.596 〃	774.0	5.58 〃	5.61 〃	0.117	2.58×10^{9}	1.97×10^{9}
	12—4	3							1143	3.839 〃	644.0	6.73 〃	6.74 〃	0.0296	6.58×10^{8}	7.30×10^{8}
Carbon for spectroscopic Analysis	13—1	12	9.0180	3.76	13.8	1.49	3.86	736	1223	3.722 〃	621.0	6.53 〃	6.99 〃	0.687	3.44×10^{10}	3.26×10^{10}
	13—2	3							1224	4.186 〃	691.0	5.86 〃	6.29 〃	1.15	5.76×10^{10}	6.62×10^{10}
	13—3	3							1192	3.930 〃	643.0	6.55 〃	6.75 〃	0.237	1.18×10^{10}	1.13×10^{10}
	13—4	3							1142	4.245 〃	680.0	6.33 〃	6.38 〃	0.0376	1.92×10^{9}	1.83×10^{9}

the largest specific surface area of cokes to the smallest was about 8.

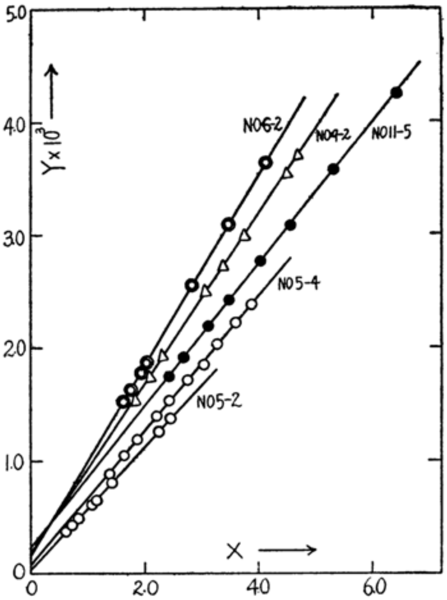

Fig. 4.—Relation between Y and X
○ coke I at 1173°K and 1223°K
● acetylene black at 1230°K
△ coke II at 1173°K
◎ charcoal at 1173°K

(II) Reaction Rates of Carbons with Carbon Dioxide. Typical examples of the increase of the total pressure P against time t at constant temperature and volume are illustrated in Fig. 3. Po is the initial pressure. As time passes. the increase of the total pressure becomes smaller. It has been interpreted that this decrease was due to the retardation effect of the adsorption of carbon monoxide formed by the reaction of carbon dioxide with carbon; but more recently, Reif concluded that it was due to the reversible reaction of the reaction (1).

In the present paper, assuming that

a) the reaction (1) is rapid and always in equilibrium and the concentration of surface oxide is negligibly small compared with total active centers on the carbon surface,

b) the reaction (2) is the rate-determining step,

the following experimental equation is easily obtained,

$$dP/dt = K\ P_{co_2}/P_{co} \qquad (5)$$

where P is the total pressure, t, the time, K, a rate constant and Pco_2 and Pco denote the partial pressure of carbon dioxide and carbon monoxide respectively. From the assumption (a), there are the following approximate relations,

$$Pco_2 = 2Po - P, \qquad Pco = 2(P - Po) \qquad (6)$$

Integrating Eq. (5) under the initial condition that P is equal to Po at $t=0$ using the relation of Eq. (6), the following equation is obtained,

$$Y = K/4.606\ Po + X/2.303\ Po \qquad (7)$$

where Y is equal to $1/t \log Po/(2Po-P)$ and X equals $(P-Po)/t$. There must be a linear relation between Y and X from Eq. (7). The examples of these relations using experimental data in Fig. 3 are indicated in Fig. 4. Very good straight lines are obtained and $1/2.303Po$ must give the slope of these straight lines from Eq. (7). The comparison between the slope obtained from the figures and calculated values of $1/2.303Po$ are indicated in Table II and their differences are only a small percentage. Accordingly, Eq. (5) may satisfactorily represent the experimental data. The value of Y at $X=0$ is $K/4.606Po$ and then the rate constant, K, can be obtained. K represents the reaction rate when Pco_2/Pco equals unity. The number of molecules which react per sq. cm. per second at $Pco_2/Pco=1$, K_a, can be calculated by the following equation from K and the total surface area S,

$$K_a = a\ K\frac{273}{760}\ \frac{1}{60}\ \frac{6.02\times10^{23}}{22400}\ \frac{1}{S\times10^4} \qquad (8)$$

where, *a is* a constant determined by the volume of the reaction tube, the sample weight, the density of carbon and etc., and other figures are conversion factors.

K and $Ka_{obs.}$ are summarized in Table II. The plots of log Ka vs. $1/T$ are illustrated in Fig. 5 and Ka may by expressed in the form of

TABLE III

Sample	$A_{obs.}$ molecules cm^{-2} sec^{-1}	$A_{calc.}$ molecules cm^{-2} sec^{-1}	E, Kcal/mol
Oil coke	3.39×10^{27}	5.57×10^{27}	91
Coke III	〃	〃	〃
Coke II	5.12×10^{27}	〃	95
Charcoal	$8.9\ \times10^{27}$	〃	97
Acetylene black	5.62×10^{27}	〃	〃
Carbon for spectroscopic analysis	〃	〃	〃
Pitch coke	5.75×10^{27}	〃	99
Coke I	〃	〃	〃

$$Ka = A\exp(-E/RT) \qquad (9)$$

whe A and E are respectively the frequency factor and the observed activation energy. A and E obtained by the least squares are shown in Table III.

The values of A and E of oil coke, acetylene black and pitch coke coincide with those of coke III, carbon for spectroscopic analysis and coke I respectively.

The activation energy becomes smaller as the straight lines in Fig. 5 go upwards. It is very interesting that the line of charcoal does not deviate so much from those of coke II and carbon for spectroscopic analysis in Fig. 5 and that acetylene black and carbon for spectroscopic analysis fall exactly on the same line. Generally speaking, the ratio of the maximum value of Ka to minimum at the same temperature is about 16—20 for various carbons and is very small compared with the ratio of the largest specific surface area to the smallest, that is, 10^3, but among various cokes, except for charcoal and acetylene black, the difference of Ka is much greater than that of the speific surface area.

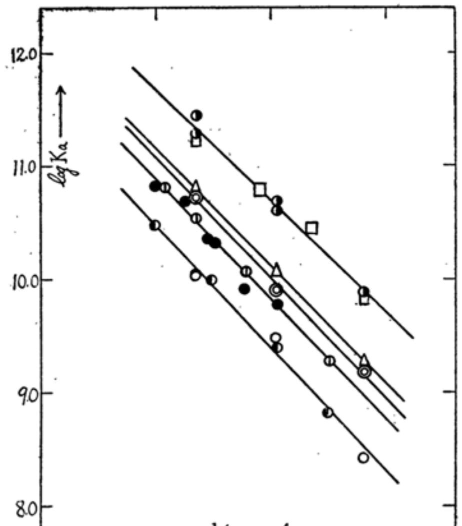

Fig. 5. Relation between log Ka and $1/T$

◑ Oil coke
□ coke III
△ coke II
◎ charcoal
● acetylene black
⦶ Carbon for spectroscopic analysis
◐ Pitch coke
○ coke I

The systematic relations between the crystallographic structure of carbons and the values of Ka were not observed as shown in Fig. 5. This might be masked by the catalytic effects of impurities. From the above experimental results, it may be concluded that the difference of the specific reaction rates of pure amorphous carbon and pure graphite will be small and for carbons containing some impurities, the catalytic effects of the ash in carbons on the reaction rates may be much greater than that of the crystallographic structure of carbons that is, the degree of graphitization of carbons, and the difference of the observed activation energies may be due to the difference of the catalytic action of some impurities in carbons. These conclusions may be properly understood from various experimental facts that even small quantities of metallic oxide impurities usually play a very important part on the catalytic reactions. For example, Wynne-Jones and his co-workers[8)] indicated that the addition of 0.1—0.02 per cent of sodium carbonates or elemental iron greatly affects the reactivity of pure graphite. In a recent paper, Parravano[11)] indicated the change of the activation energies with the addition of some metallic oxide to nickel oxide in the reduction of nickel oxide by hydrogen. The activation energy of pure nickel oxide was 26.4 Kcal/mol, and with the addition of 1 mole per cent of alumina and 0.5 mole per cent of tungsten oxide, they became 35.2 Kcal/mol and 9.2 Kcal/mol respectively.

(III) A Theoretical Consideration of the Reaction Rates. The reaction mechanism of this system may be assumed as already mentioned and the absolute reaction rate theory[12)] may be applied to this mechanism as follows,

$$\begin{array}{ccccccc} CO_2 & + & C & \rightleftarrows & CO & + & [CO] \\ P_{co_2} & & C_s & & P_{co} & & C_a \end{array} \quad \text{surface oxide} \qquad (1')$$

$$\begin{array}{ccccc} [CO] & \rightleftarrows & [CO]^{\neq} & \longrightarrow & CO \\ C_a & & C_a^{\neq} & & \end{array} \qquad (2')$$

The absolute reaction rates can be obtained from the following equation,

$$v = kT/h \cdot C_a \cdot f_a^{\neq}/f_a \exp(-E_1/RT) \qquad (10)$$

where k, R,and h are universal constants, Ca, the concentration of the surface oxide, $f_a^{\neq}/f_a$, the ratio of the partition functions of the activated state and the surface oxide, E_1, surface activation energy and T, the temperature.

From the assumption (a) already stated, there is the following relation,

$$\frac{C_a}{C_S} = \frac{P_{co_2}}{P_{co}} \cdot \frac{f_{co}}{f_{co_2}} \cdot \frac{f_a}{f_s} \exp(-E_2/RT) \qquad (11)$$

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11) G. Parravano, *J. Am. Chem. Soc.*, **74**, 1194 (1952).

12) S. Glasstone, K. J. Laidler and H. Eyring: "The Theory of Rate Process," p. 369 (1941).

where, C_S is the concentration of the bare sites, P_{co_2} and P_{co}, the partial pressure of carbon dioxide and carbon monoxide, f denotes the partition functions of each species and E_2, the heat of reaction of the reaction (1′). From the assumption (a) C_s is also nearly equal to L, the concentration of the total active centers. When Eq. (11) is substituted for Ca in Eq. (10) using the relation of $C_s \fallingdotseq L$, some equations can be obtained as follows,

$$v = kT/h \cdot L \cdot P_{co_2}/P_{co} \cdot f_{co}/_{co_2} \cdot f_a^{\ddagger}/f_s$$
$$\exp\{-(E_1+E_2)/RT\} \equiv Ka\ P_{co_2}/P_{co} \qquad (12)$$

$$\text{where } Ka = kT/h \cdot L \cdot f_{co_2}/f_{co} \cdot f_a^{\ddagger}/f_s \qquad (13)$$
$$\exp\{-(E_1+E_2)/RT\} \equiv A\exp(-E/RT)$$

$$\text{here } A = kT/h \cdot L \cdot f_{co}/f_{co_2} \cdot f_a^{\ddagger}/f_s \qquad (14)$$

$$E = E_1 + E_2 \qquad (15)$$

Eq. (12) is identical with the experimental reaction rate equation (5). A can be calculated from Eq. (14) and the calculated value using $L=10^{15}$, $f_a^{\ddagger}/f_s=1$ and $T=1173$°K as the mean of the experimental temperatures is 5.57×10^{27} molecules cm^{-2} sec^{-1}. The calculated value of A is in satisfactory agreement with the observed values in Table 3. Ka can also be calculated from Eq. (13) using the activation energies obtained experimentally. $Ka_{calc.}$ for each temperature are tabulated in Table 2. The agreement of the calculated values with the observed is also very excellent. Accordingly, the mechanism presented in this paper may be interpreted by the absolute reaction rate theory.

Summary

The absolute reaction rates of carbon dioxide with eight carbons have been obtained from the surface area measurement by the B.E.T. method using ammonia adsorption at 0°C and the reaction rate measurement.

The activation energies ranged from 91 Kcal/mol of oil coke and coke III to 99 Kcal/mol of coke I and pitch coke.

The reaction mechanism that the reaction of the formation of surface oxide is rapid and always in equilibrium and the concentration of the surface oxide is negligibly small compared with total active centers and the rate-determining step is the desorption of surface oxide can be interpreted by the theory of absolute reaction rates.

It may be concluded that the difference of the activation energies will be due to catalytic effects of some impurities in carbons, and that the difference of the absolute reaction rates due only to the difference of the crystallographic structure of pure carbons without the catalytic effects of impurities will be small.

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