ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH.

IX. THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

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The behaviours of the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been elucidated,(1) but the rôle played by water contained in the earth has been left untouched. It has now been found that water exerts a distinct promoting action in that catalysis. Several neutral substances containing oxygen in their molecules such as methyl and ethyl alcohols, acetone, and ether have also proved to be promotors similar to water, and those which contain nitrogen such as ammonia, methylamine, acetonitrile, and amyl nitrite behave as strong poisons, while acidic substances such as hydrogen chloride and acetic acid are quite weak poisons. Chloroform, carbon tetrachloride, chlorobenzene and many hydrocarbons have been found indifferent to the catalytic action.

The acid earth used almost exclusively in the present experiment is that which has been designated earth F in the previous papers, and its catalytic activity on naphthalene measured by the yield of the resinous matter under the " standard condition " is, as stated in the previous paper,(2) 2.23. This value was taken as the standard for the comparison of the activity throughout the present experiment, unless specially mentioned.

The Action of Water. With the rise in the drying temperature of the acid earth its catalytic activity decreases rapidly, the liberation of water from the earth being observed simultaneously as shown in Fig. 1 and Table 1.(3)

The experiments were carried out under the " standard condition " in the determinations of the activities except that the samples were dried at respective temperatures for one hour. The amounts of water set free were estimated after the constant weights were obtained at respective temperatures.

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* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

(2) Loc. cit.

(3) 97 Per cent. or more of the ignition loss is due to the liberation of water. Kobayashi, Yamamoto, and Bito, *J. Soc. Chem. Ind. Japan*, **32** (1929), 998.

Table 1.

Temp. of drying	To 50°	50–120°	120–200°	200–250°	250–300°	300–500°	Above 500°
Water set free (%)	3.33	3.73	0.76	0.62	0.27	1.03	3.97

The decrease in the catalytic activity of the earth shown in Fig. 1 may not be ascribed only to the effect of the heat treatment, since water may play some rôle in the catalysis. In order to ascertain whether water influences the catalysis or not, it is necessary to procure the specimens of the earth containing the different amount of water with the same heat treatment. The earth dried at 300° adsorbs water vapour rapidly when brought into contact with the saturated vapour at room temperature and when the moist earth thus obtained is dried again at 120° it liberates almost all the water adsorbed, but a small fraction of it is always held by the earth even after the drying is continued for about 10 hours until the weight of the earth becomes constant. The water retained at the end of this treatment will be hereafter called, for convenience' sake, "retained water".

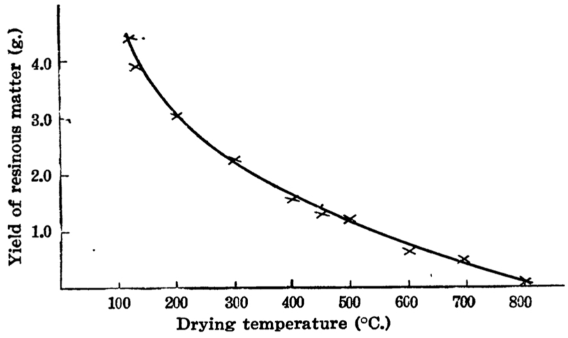

Fig. 1.

The amount of the retained water is a function of the total amount adsorbed as shown in Fig. 2. Thus several samples of the earth with different water content after the same heat treatment are obtainable, and it will be safely stated that if their catalytic activities under the same condition differ from one another it may be entirely ascribed to the difference of the amount of water contained in them.

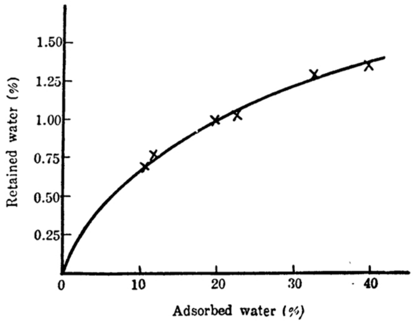

Fig. 2.

The relation between the amount of the retained water and the catalytic activity is shown in Table 2, which indicates that the larger the former is the greater the latter, in other words, the retained water exerts a decided promoting action in the catalysis.

Table 2.

Time of adsorption (days)	0	10 (hrs.)	1	7	13	21	33
Water adsorbed (%)	0	5.16	9.42	22.8	26.3	32.9	38.9
Water retained (%)	0	0.66	1.06	1.35	1.47	1.69	1.87
Yield of resinous matter (g.)	2.23	2.49	2.75	3.08	3.08	3.42	3.59
Increase in resinous matter (g.)	—	0.26	0.52	0.85	0.85	1.19	1.36

Though about 10 hours are required to get the constant weight when the moist earth is dried at any temperature, about 98 per cent. or more of the total water to be liberated is set free within 2 hours. The amount of the retained water after 5 hours' drying are plotted in Fig. 2 and those after 2 hours' drying are tabulated in Table 2, and in all the experiments described below the duration of drying was fixed at 2 hours.

The catalytic activities of the earth treated at 500° and 800° are also promoted by the retained water as shown in Table 3.

Table 3.

Temperature of pre-treatment	500°				800°	
Time of adsorption (days)	0	2	2(4)	16	0	18
Water adsorbed (%)	0	9.01	15.1	22.2	0	9.0
Water retained (%)	0	0.26	0.39	0.55	0	0.2
Yield of resinous matter (g.)	1.20	1.66	1.95	2.06	0.11	0.17
Increase in resinous matter (g.)	—	0.46	0.75	0.86	—	0.06

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(4) Owing to the differences of temperature and vapour pressure, the different values of adsorbed water are obtained after equal time of adsorption.

If a represents the yield of the resinous matter produced by the earth and b the increase in the yield caused by the retained water, then a quantity $(b/a) \times 100$ may be designated "degree of promotion". The degrees of promotion calculated from the data given in Table 2 and 3 are plotted against the amounts of the retained water expressed in millimols as shown in Fig. 3.

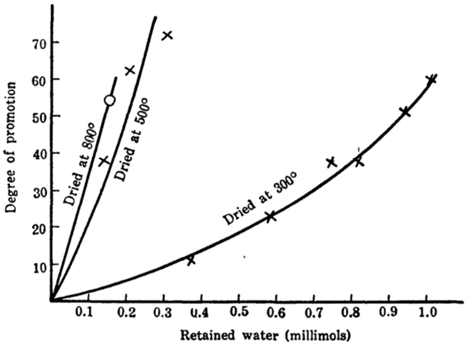

Fig. 3.

The water simply adsorbed by the dry earth as well as that added in the reaction tube in liquid state also promotes the reaction, but their promotive powers fall far behind that of the retained water as will be seen in Table 4.

Table 4.

Kind of water	Retained	Adsorbed	Added	Retained	Added
Amount of water (%)	1.70	1.99	1.93	1.87	5.14
Yield of resinous matter (g.)	3.38	2.31	2.31	3.59	2.87
Increase in resinous matter (g.)	1.15	0.08	0.08	1.36	0.45

Now, when the desorption of water from the moist earth takes place, the molecules of water stored in large capillaries in liquid state or those localized on the upper layers of the adsorbed film would be liberated first, and those held directly on the bare surface would remain to the very last, representing the retained water above designated. The data given in Table 4 seem to show that it is these water molecules adsorbed directly—therefore the most firmly held—on the surface that promote the catalysis but not those more loosely adsorbed or those simply present in the reaction system.

If, in the course of the adsorption, the monomolecular film of water is formed on the whole surface before there occurs the formation of any polymolecular film, the amount of the retained water would represent the total amount of the water adsorbed in the early stage of the adsorption and the former would become independent of the latter if once the whole surface is covered. As a matter of fact, however, this is not the case. As will be suggested in next communication, the amount of water needed to cover the whole surface of the dry earth represents about 2.5 per cent. of the weight of the earth on the assumption of a packed monomolecular layer. Fig. 2 and Table 2 show that the proportionality between the amount of retained water and the total amount adsorbed extends far above this limiting value. It would appear therefore that the formation of the polymolecular layers as well as capillary condensation commences long before the whole surface is covered with a monomolecular layer. Hoover and Rideal⁽⁵⁾ came to the same conclusion from a different view point in the case of the adsorption of ethyl alcohol on thoria.

The Actions of Oxygen-containing Neutral Substances other than Water. Methyl and ethyl alcohols, acetone, and ether were examined and all of them were found to promote the reaction to a marked degree. All materials were cautiously purified by appropriate methods. The adsorption of vapours was carried out in a desiccator at saturated vapour pressures and the retained amounts were determined by the same method as the above-mentioned. As in the case of water, the amount of each retained substance was found to be a function of the total amount adsorbed. The plots of degrees of promotion against the retained amounts expressed in millimols of the respective substances are shown in Fig. 4.

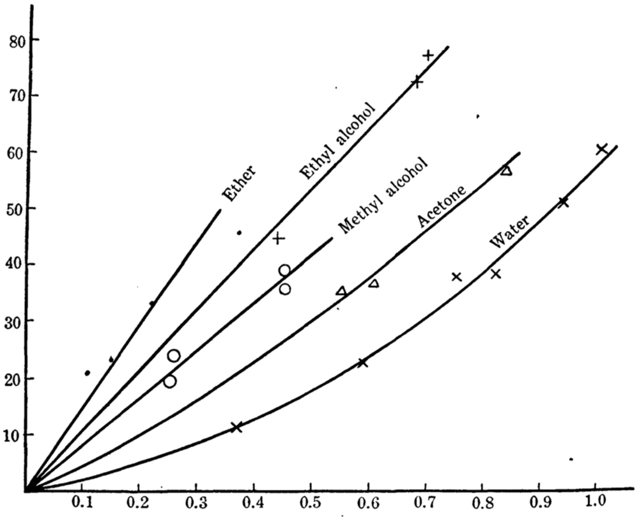

Fig. 4.

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(5) *J. Am. Chem. Soc.*, **49** (1927), 122.

The order of magnitudes of the degrees of promotion corresponding to the same millimols of the retained substances can be easily given from Fig. 4 as follows:—

Ether > ethyl alcohol > methyl alcohol > acetone > water.

Gurwich(6) has studied the heats of adsorption of various organic liquids when brought into contact with Fuller's earth(7) as well as the dispersive powers which were measured by the percentage of Fuller's earth remaining in suspension in those liquids after shaken up with them. The results of his determinations(8) are given in the second and third columns of Table 5.

Table 5.

Substance	Heat of adsorption	Dispersive power (%)	Dielectric const. (18°)	Surface tension (20°)(9)	Solubility of naphthalene (0°)(10)
Ether	10.7	0.90	4.36	16.49	large
Ethyl alcohol	17.2	—	20.8	22.03	0.0209
Methyl alcohol	21.8	1.60	31.5	23.02	0.0087
Acetone	27.3	1.72	21.5 (20°)	23.35 (16.8°)	—
Water	30.2	2.85	81.1	70.60	0.0000

The order of the magnitudes of both the heats of adsorption and dispersive powers determined by Gurwich is exactly reverse to the order of the degrees of promotion observed by the present author. The regularity of this relation is very striking. It is also noticed that the solubility of naphthalene, the dielectric constant, and the surface tension of the liquids go either parallel or reverse to the degree of promotion as shown in Table 5.

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(6) *J. Russ. Phys. Chem. Soc.*, **47** (1915), 805.

(7) Japanese acid earth is in many respects similar to Fuller's earth, and it is generally accepted that the former is a species of the latter.

(8) Cited from Langmuir's paper. *J. Am. Chem. Soc.*, **39** (1917), 1898.

(9) This column represents the surface tensions expressed in dynes per cm. in the atmospheres of the saturated vapours of the respective substances.

(10) The solubility of naphthalene is expressed in mols per mol of the respective solvent. The solubility in acetone is not found in literature, so far as the author knows.

As will be fully discussed in next communication, the catalytic action of Japanese acid earth on naphthalene may be considered to be brought about by the three component catalyst consisting of Al_2O_3, SiO_2, and water, and when molecules of naphthalene are adsorbed on the catalytically active centres formed by these three components they are activated so as to produce β,β'-dinaphthyl. When the earth is heated to 300° the liberation of water from some of these active centres takes place rendering them incapable of participating in the catalysis. They will, however, recover their ability if water molecules are again put in their original positions. This recovery of catalytic activity is accomplished by the retained water when the earth is brought into contact with water vapour, giving rise to the observed promotion of the activity. Moreover, the molecules of water to form the active centres are replaceable by those of neutral substances such as alcohols, acetone, and ether, and the similar promoting action is effected by them.

The degree of promotion depends therefore upon both the number of the active centres thus recovered and the number of molecules of naphthalene to be activated on each of these new centres, in other words, upon the number and the intensity or the mean life of new active centres.

Table 5 shows that, the greater is the degree of promotion the smaller the heat of adsorption and the dispersive power and the larger the solubility of naphthalene. The heats of adsorption and the dispersive powers would be considered as measures of the molecular affinities between these various liquids and the acid earth, while the solubilities of naphthalene as measures of the molecular affinities between these liquids and naphthalene. The author is inclined to believe that the former is connected with the number of the active centres to be recovered and the latter with the intensity or the mean life of these centres to activate the molecules of naphthalene adsorbed on them, that is, the larger the molecular affinity between the vapour and the acid earth the more difficult becomes the formation of the active centres, and the larger the molecular affinity between the vapour and naphthalene the stronger is the intensity or the longer is the mean life of the active centres. Dielectric constant and surface tension are in close connection with the molecular structure and the orientation of molecules on the surface of liquids respectively, and it may be anticipated that these quantities would bear some relationship with the catalytic activity.

It is tempting to go on studying how Al_2O_3, SiO_2, and oxygen-containing neutral substances must be configurated in order to form the active centres and how molecules of naphthalene must be oriented on them in order to be activated, and further study on these lines is expected to be carried out in near future.

The Action of Hydrogen Chloride, Acetic Acid, and Ethyl Acetate. The acidic substances such as hydrogen chloride and acetic acid (and most probably hydrogen sulphide, too) are quite weak poisons to the catalytic action. Their total amounts adsorbed are fairly small compared with the neutral substances. Table 6 shows the results of experiments on these substances as well as ethyl acetate.

Table 6.

Substance	Hydrogen chloride		Acetic acid	Ethyl acetate
Amount adsorbed (%)	2.23	—	5.96	20.03
Amount retained (%)	0.33	1.21 (added)	5.58	4.20
Amount retained (millimol)	0.09	0.33	0.93	0.48
Yield of resinous matter (g.)	2.25	2.01	2.01	2.44
Decrease in yield (g.)	0	0.22	0.22	0.21 (increase)
Decrease in yield (%)	0	10	10	10 (increase)

Ethyl acetate is a neutral substance and moreover values of both the heat of adsorption and dispersive power determined by Gurwich lie between those of methyl alcohol and ether; therefore it seems very reasonable that it would make a promotor as strong as the alcohol at least. The fact is, however, that it proved to be a very weak promotor as will be seen from Table 6. This may be explained by the experiment by Dr. Inoue(11) that ethyl acetate is decomposed by the catalytic action of Japanese acid earth giving acetic acid, the poison to the reaction.

The Actions of Nitrogen-containing Substances. Ammonia and methylamine are the most strong poisons, while acetonitrile and amyl nitrite are milder in their poisoning actions as shown in Table 7.

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(11) *J. Soc. Chem. Ind. Japan*, **28** (1925), 598.

Table 7.

Substance	Ammonia	Methylamnie	Acetonitrile	Amyl nitrite
Amount adsorbed (%)	5.49	5.66	27.06	61.05
Amount retained (%)	0.84	4.45	3.08	16.02
Amount retained (millimol)	0.49	1.43	0.75	1.36
Yield of resinous matter (g.)	0	0	0.28	0.23
Decrease in yield (g.)	2.23	2.23	1.95	2.00
Decrease in yield (%)	100	100	88	90

The Actions of Hydrocarbons, Chlorine-containing Neutral Substances, and Thiophene. It should be noted that the retained amounts of these substances are in general very small unless the adsorbed substance is decomposed by the catalytic action of the earth at room temperature as in the case of alicyclic unsaturated hydrocarbons. Benzene, toluene, cyclohexane, cyclohexene, and methylcyclohexenes were examined and all of them were found to be indifferent to the reaction. It does not matter whether these substances were retained, adsorbed or added or entirely absent. The yield of the resinous matter was always equal within the experimental error. Chlorobenzene behaves similarly. Chloroform and carbon tetrachloride are also indifferent as long as their amounts are small, but if they are added in relatively large quantities the yield of the resinous matter is decreased to some extent, the evolution of hydrogen chloride being observed simultaneously. It appears therefore that they are non-poisonous in themselves, and their apparent poisoning action is to be ascribed to hydrogen chloride produced by the catalytic action of the earth.

The experiments hitherto carried out with thiophene are not sufficient to draw any decided conclusion thereby. It may be only mentioned here that when thiophene is added in fairly large quantity the slight poisoning effect is observed, accompanied by the evolution of hydrogen sulphide.

Summary.

(1) The catalytic action of Japanese acid earth on naphthalene is greatly promoted when it contains the "retained water", designated temporarily by the present author.

(2) The molecules of the "retained water" may be replaced by those of several other neutral substances containing oxygen in their molecules, the catalytic activity of the earth being thereby raised to a greater or smaller extent according to the nature of the substance.

(3) The term "degree of promotion" has been introduced, and the relation between the degree of promotion and molecular affinity has been discussed.

(4) The nitrogen-containing substances such as ammonia, methylamine, acetonitrile, and amyl nitrite have been found to be strong poisons to the catalysis, while the acidic substances such as hydrogen chloride and acetic acid have proved to be quite weak poisons.

(5) Chloroform, carbon tetrachloride, chlorobenzene, and many hydrocarbons have been found indifferent to the catalytic action.

The author wishes to express his cordial thanks to Dr. Inoue for his interest and encouragement taken in this study.

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