Reversal of the Sign of Charge of Activated Charcoal in an Atmosphere of Oxygen

By *N. Bach* and *A. Zimin*

Measurements of the cataphoretic velocity of activated charcoal suspensions in alkaline solutions in an atmosphere of oxygen, made by Pilojan, Kriworutschko and Bach [1], showed that the charcoal, which is charged positively in pure water, becomes negative in dilute alkaline solutions. The zero charge point varied, however, from one experiment to another, and it was not possible to fix, even when doubling the measurements with different portions from the same batch of activated charcoal, a definite concentration corresponding to the reversal of sign. This led to suppose that this reversal of the electrokinetic charge was related to an accidental formation of acid oxides on the surface of the charcoal when it was exposed to air during the experiment, and not to the reversal of sign of the thermodynamic potential, occurring at a definite OH^--ion concentration, i. e. that it was not due to the electrochemical behaviour of activated charcoal acting, as was shown by Frumkin and collaborators, as an oxygen electrode [2].

It is well known that charcoal activated at 900—1000° in a current of carbonic acid has a positive charge; its surface becomes negative, however, both with respect to adsorptive and to cataphoretic properties, as a result of surface oxide formation, if it is treated with oxygen at 300—400° C. This effect was first disco-

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[1] A. Pilojan, N. Kriworutschko u. Natalie Bach, Koll. Z., **64**, 287 (1933); this paper will be referred to hereafter as „Part 1".

[2] B. Bruns u. A. Frumkin, Z. physik. Chem., **A 141**, 141 (1929). A. Frumkin, Koll. Z., **51**, 123 (1930).

vered and studied by Kruyt and de Kadt[3], and was later the object of a number of investigations by other authors [4].

In a paper on surface oxide films published in 1936, Verwey and de Boer[5], discuss in detail the question of surface oxides on carbon. They come to the conclusion that a polar surface oxide, similar to those formed with a definite activation energy on all metals at room temperature in presence of molecular oxygen, must exist on electrokinetically negative charcoal. However, in the case of carbon it must be expected that the activation energy is much higher than in the case of metals, so that the oxide can be formed rapidly enough only much above room temperature. This is in keeping with the fact that the optimum temperature for the formation of oxides is 300—400° C.

However, Miller[6], and also N. Bach[7], observed a certain alkali adsorption on charcoal as a result of its oxidation at room temperature.

Later, King[8] and King and Lawson[9] found that when activated charcoal is heated with oxygen at room temperature, a small amount of oxalic acid is formed. In these experiments the charcoal was either heated, subsequently to the activation, to dull redness in air, or was exposed to air during its cooling to room temperature after the high temperature activation. In both cases the conditions were favourable for the formation of acid oxides between 300 and 500°. It is not clear in what relation the observed formation of oxalic acid at room temperature stands to the existence of such oxides on the surface of the charcoal.

The present investigation was undertaken to find out whether the sign of charge of charcoal is reversed when it is treated with oxygen at room temperature in the form of a dry powder, of suspension in water and of suspension in alkaline solutions.

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[3] H. R. Kruyt u. G. S. de Kadt, Koll. Z., **47**, 44 (1929); Koll. Beih., **32**, 249 (1931).

[4] M. Dubinin, Z. physik. Chem., (A) **140**, 81 (1929); B. Bruns, M. Maximova u. E. Pos, Koll. Z., **63**, 286 (1933); J. A. A. Verlinden, diss. Utrecht, 1935.

[5] E. J. W. Verwey a. J. H. de Boer, Rec. Trav. Chim. Pays-Bas, **55**, 675 (1936).

[6] E. Miller, J. Phys. Chem., **36**, 2697 (1932).

[7] N. Bach, Koll. Z., **64**, 153 (1933).

[8] A. King, J. Chem. Soc., London, **1933**, 842; **1934**, 22.

[9] A. King a. C. G. Lawson, Koll. Z., **69**, 21 (1934).

Method of investigation

According to the experimental technique used in part 1, immediately before each cataphoretic measurement, 0,1 g of activated charcoal powder were shaken in a separate flask with 25 cm³ of

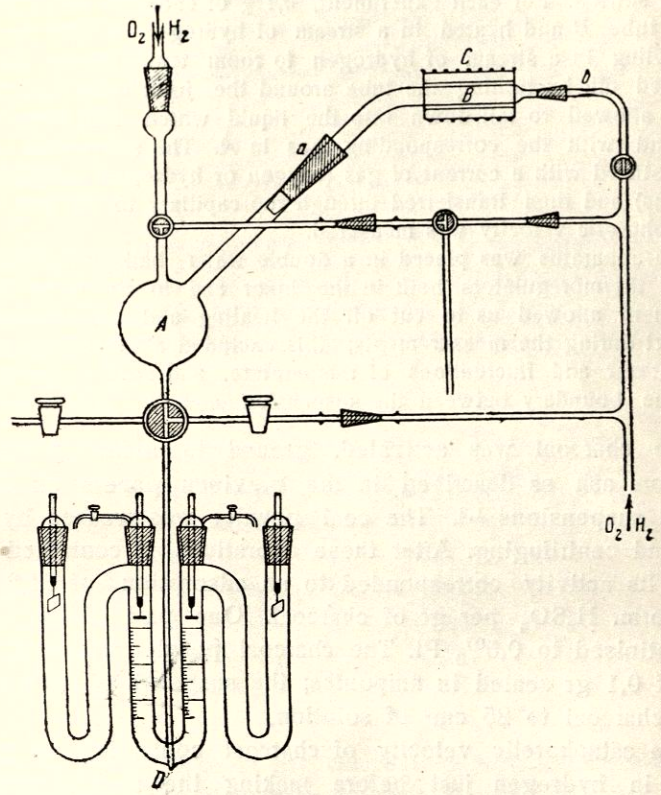

Fig. 1.

solution, and the suspension then poured into the cataphoretic apparatus. The charcoal which had been kept after its preparation sealed in ampoules in an atmosphere of hydrogen, was exposed to air when it was transferred to the flask and shaken with the liquid; it was therefore possible that surface oxides were formed during these operations. In order to have a pure and definite surface

of charcoal it is necessary to heat the coal in a stream of hydrogen immediately before each cataphoretic experiment, and to make the measurement without letting the charcoal come in contact with air.

We used the cataphoretic apparatus described in part 1, but sealed in the upper reservoir *A*, as shown in Fig. 1, a tube connected by a ground joint with the quartz tube *B* on which a small electric tube furnace *C* could be shifted. For each experiment, 0,1 g of charcoal were introduced into the tube *B* and heated in a stream of hydrogen at 900° for 30 min. After cooling in a stream of hydrogen to room temperature, the tube *B* was sealed off; by turning the tube around the joint *a* the charcoal powder was allowed to fall down into the liquid which had been saturated beforehand with the corresponding gas in *A*. The suspension was thoroughly stirred with a current of gas (oxygen or hydrogen according to the conditions) and then transferred through the capillary to the part *D* where the cataphoretic velocity was measured.

The apparatus was placed in a double water bath with heaters, stirrers and thermoregulators both in the inner and in the outer part. This arrangement allowed us to cut off the heating and the stirring in the inner part during the measurements; this excluded all vibrations produced by the stirrer and fluctuations of temperature, and gave a perfectly even and plane boundary between the suspension and the supernatant liquid.

The charcoal was activated, ground to a fine powder and freed from ash as described in the previous papers on activated charcoal suspensions [1,3]. The coal powder was washed by decantation and centrifuging. After these operations it contained 0,03% of ash. Its activity corresponded to an adsorption of 31,2 cm^3 of 0,01 norm. H_2SO_4 per gr of charcoal. One part of the charcoal was platinised to 0,5% Pt. The charcoal powder was kept in portions of 0,1 gr sealed in ampoules; the suspensions were made of 0,1 gr charcoal to 25 cm^3 of solution.

The cataphoretic velocity of charcoal containing no platinum heated in hydrogen just before making the measurement, was 2,8—2,9 μ/sec. per Volt/cm in air, whilst that of platinised charcoal in oxygen was 3,8 μ/sec. per V/cm at most. The charcoal had a positive charge.

Dry charcoal powder. 0,1 gr of charcoal powder were heated in tube *B* in a stream of hydrogen at 900°, allowed to cool in hydrogen down to room temperature, and then treated with oxygen at room temperature in the same tube. The effect of this exposure to oxygen is shown in Table 1.

These data show that not only does the treatment of dry charcoal by oxygen at room temperature leave the surface positive, but that it even increases the positive velocity. This is related with the establishment of a higher oxygen potential on charcoal.

Table 1

Time of exposure in hours	Cataphoretic velocity μ/sec. per V/cm
0	+2,5
3	+4,4
16	+3,3

Suspensions of charcoal in water. After heating in hydrogen in tube *B*, the charcoal was allowed to fall into the water contained in reservoir *A*, where the suspension was saturated with oxygen. The results of the cataphoretic measurements are given in Table 2.

Table 2

Time of exposure	Cataphoretic mobility μ/sec. per V/cm
0	+2,5
30 min.	+2,9
4 hours	+3,1
16 hours	+3,3
39 hours	+3,3

Just as in the case of dry charcoal powder, the charcoal remains positive after the treatment with oxygen, and the oxygen potential is even raised.

A prolonged treatment with oxygen of a charcoal suspension in pure water does not noticeably alter its conductivity (e. g. after 2 hours, $\varkappa$ increased from $0{,}5 \cdot 10^{-6}\ \Omega^{-1}$ to $0{,}8 \cdot 10^{-6}\ \Omega^{-1}$) so that no products of oxidation pass into solution in any marked amount.

Suspensions of charcoal in alkaline solutions. Charcoal heated in hydrogen in tube *B* was poured into alkaline solutions of different concentrations in reservoir *A* where oxygen

was bubbled through the suspensions during 6 hrs. on an average. The cataphoretic velocities of these suspensions are given in Table 3.

Table 3

Concentration of NaOH	Cataphoretic velocity μ/sec. per V/cm
0	+ 3,3
0,00005 norm.	+ 2,3
0,0001 „	+ 1,7
0,00015 „	+ 1,6
0,00022 „	+ 1,0
0,0003 „	+ 1,1
0,0006 „	+ 0,9
0,003 „	— 1,54
0,015 „	— 1,7

We may see a marked reversal of sign at a concentration of about 0,001 norm., i. e. about the same concentration at which the reversal of sign was observed in part 1. The experimental technique

Table 4

Concentration of NaOH	Cataphoretic velocity μ/sec. per V/cm
0	+ 2,5
0,0001	+ 2,1
0,0002	+ 1,7
0,0005	+ 0 (slight positive charge)
0,002	0
0,005	0
0,001	0
0,016	0

made it quite possible for surface oxides to be formed during the bubbling of oxygen through the suspensions. In order to find out the causes of the reversal of the sign of charge, it is necessary to

eliminate all possibility of oxidation during the cataphoretic experiment.

We made use of the property of pure activated non-platinised charcoal: keeping an oxygen potential in an atmosphere of hydrogen, even after being treated with hydrogen at 1000°, as was shown by Frumkin and Bruns[2]. It could be proved in part 1 that a cor-

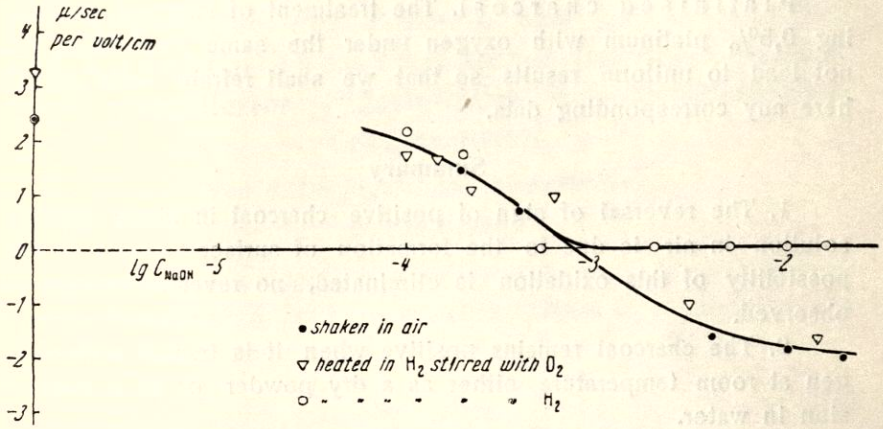

Fig. 2.

responding positive electrokinetic charge is observed under these conditions on charcoal suspensions.

The experiments were carried out exactly as described above, except that after letting the charcoal fall into the alkaline solution, the suspension was stirred with a current of hydrogen instead of with that of oxygen.

The cataphoretic velocities are given in Table 4.

In this case the charcoal remains positive. The data in Fig. 2 are those of Tables 3 and 4 and, for comparison, of a run taken from part 1. At low concentrations all the points correspond to one curve, although the cataphoretic velocity of positive non-platinised charcoal should be higher in oxygen than in hydrogen, since its thermodynamic potential is more positive in the first case [2]. This means that in the positive part of the curve, too, the charge of the charcoal is lowered as a result of the formation of acid oxides.

It can be seen that if the possibility of oxidation with molecular oxygen is really excluded, no reversal of sign is observed. This proves definitely that the reversal of sign observed when the old technique was used, was connected with the formation of acid surface oxides on the charcoal and not with the discharge of OH^--ions on the charcoal. It is of interest to note that the oxide formation is much favoured by the presence of alkali.

Platinised charcoal. The treatment of charcoal containing 0,5% platinum with oxygen under the same conditions did not lead to uniform results so that we shall refrain from giving here any corresponding data.

Summary

1. The reversal of sign of positive charcoal in dilute alkaline solution in air is due to the formation of surface oxides. If the possibility of this oxidation is eliminated, no reversal of sign is observed.

2. The charcoal remains positive when it is treated with oxygen at room temperature either as a dry powder or as a suspension in water.

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