

THE CATALYTIC ACTION OF  $Al^{+++}$  IONS IN  
REDUCTION-OXIDATION SYSTEMS

A. Krause

Roczniki Chemii 28 (1954) 3-11

(From Polish)

25X1



August 1955

## THE CATALYTIC ACTION OF $Al^{+++}$ IONS IN REDUCTION-OXIDATION SYSTEMS

A. Krause

Roczniki Chemii 28 (1954) 3-11

(From Polish)

$Al^{+++}$  ions are practically inactive in the reaction of the decomposition of  $H_2O_2$  and in the reaction of the peroxidative oxidation of various organic substrates. In conjunction with other micro-elements and suitable carrier substances, however, the activity of the  $Al^{+++}$  ions may be strong and the specific action of this element is then important.

The advantageous influence of  $Al^{+++}$  as catalytic agent of certain organic reactions has long been known. The Friedel and Crafts reactions, inter alia, are good examples of this. As is well known, the course of these reactions depends upon the presence of  $AlCl_3$ .

With regard to bio-catalytic systems, the action of  $Al^{+++}$  ions was investigated first of all by plant physiologists and soil experts [1]\*. According to the opinion of the experts,  $Al^{+++}$  ions even in very low concentrations, exert on the whole a harmful influence on the growth of many plants, especially in an acid environment. It appears, however, that there are exceptions to this rule, as is shown by the investigations of Znamienski [2] who originally observed the advantageous action of the element by accident in a variety of wheat (*Triticum pseudohostianum*).

In the reduction-oxidation systems investigated in recent years in this Institute [3], the  $Al^{+++}$  ion behaves fundamentally in an inert manner. It does not decompose  $H_2O_2$  or intervene in reactions for the removal of oxygen on oxidised substrates. Nevertheless, the fact does not justify the assertion that  $Al^{+++}$  ions are altogether deprived of any influence on catalytic actions of this type. In the article "On the sociology of chemical elements" [3,4], we have endeavoured to explain that it is impossible to predict the catalytic properties of any element or ion, as long as we do not know its position in the group of other elements, in the sphere of which the said element, as a catalytic agent, may have an entirely different form from that which it has as a separate individual. It had therefore to be assumed that in association with complex catalysts, the  $Al^{+++}$  ion would be able to act as an inhibiting agent or as promoter, according to the prevailing experimental conditions in relation to a given catalytic reaction taking place with a suitable substrate. In fact, in the course of our investigations on catalysis and catalysts, we found characteristic examples of complex catalysts exhibiting the two-fold behaviour of  $Al^{+++}$  ions in reduction-oxidation systems. The results of these investigations are given in the following account.

### 1. $Al^{+++}$ IONS AS INHIBITING AGENT

When investigating the various systems of complex catalysts we had the opportunity of repeatedly confirming the fact that  $Al^{+++}$  ions in many cases exercise an inhibiting action in the decomposition of  $H_2O_2$  at a temperature of  $37^\circ$ . As catalyst supporters or carriers for the  $Al^{+++}$  ions, we used the following complex gels which were prepared by careful mixing and air drying.

- (1) Mixed gel of aluminium, chromium and iron hydroxides precipitated at a temperature of  $20^\circ$  by addition of a small amount of ammonia to an aqueous solution containing  $AlCl_3 + CrCl_3 + Fe(NO_3)_3$  in the atomic proportions  $Al:Cr:Fe = 1:1:1$ . The water content of the air-dried gel was 44.4%  $H_2O$ .

\* For references, see end.

- 2 -

- (2) Mixed gel of copper + lead + iron hydroxides of a light-brown colour, precipitated at a temperature of 20° by sodium hydroxide (free from  $O_2$ ) in stoichiometric proportions from a mixed aqueous solution of  $Cu(NO_3)_2 + Pb(NO_3)_2 + Fe(NO_3)_3$  in the atomic proportions  $Cu:Pb:Fe = 1:1:1$ . The air-dried gel contained about 21.8%  $H_2O$ .
- (3) Mixed gel of magnesium + copper + iron hydroxides obtained by precipitation from an aqueous solution of  $MgCl_2 + CuSO_4 + FeCl_3$  (atomic proportions  $Mg:Cu:Fe = 0.3:0.3:1$ ) by adding NaOH in small amounts at a temperature of 20°. The air-dried gel contained about 38.5%  $H_2O$ .
- (4) Gel of cobalt ferrocyanide prepared at a temperature of 20° from an aqueous solution of  $Na_4[Fe(CN)_6] + Cu(NO_3)_2$  in stoichiometric proportions,  $NH_4Cl$  being used as coagulant. The air-dried preparation contained about 12%  $H_2O$ .

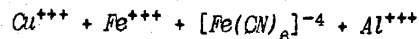
All the preparations 1 to 4 decomposed  $H_2O_2$  vigorously at a temperature of 37°. The  $Al^{+++}$  ion adsorbed on the surface of these catalysts was a paralysing agent in all the experiments, sometimes very active. In an experiment of a mixed catalyst (5 mg) of copper, magnesium and iron hydroxides, the activity of the  $Al^{+++}$  ions was still perceptible in a density of  $10^6$  g in 201 ml of  $H_2O_2$  solution, i.e. in a dilution of 1:200 millions. The results of these experiments are shown in Tables 1, 2 and 3\*.

In the course of these investigations, we also found simple catalysts exhibiting susceptibility to the poisoning action of  $Al^{+++}$  ions. According to Wolski's investigations [5], the catalytic activity of copper oxide (10 mg) undergoes a considerable diminution in the presence of 1 mg of  $Al^{+++}$ . The air-dried copper oxide contained 4.3%  $H_2O$  and was obtained in the wet method by preparing a gel of  $Cu(OH)_2$  in an alkaline solution (1 n NaOH). The results obtained are shown in Table 4.

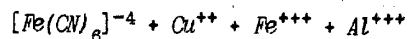
## II. $Al^{+++}$ ION AS PROMOTER

In passing to the action of  $Al^{+++}$  ions as an activating agent, it must be stated that in general this element is found less frequently in the role of promoter than as a inhibitor. When investigating the efficiency of different catalysts and carriers in reduction-oxidation systems in the presence of certain substrates, we found that copper oxide, of which we have already spoken is activated by  $Al^{+++}$ , when it is a matter of the oxidation of indigo-carmin by means of  $H_2O_2$  (Table 4).

Nevertheless, the  $Al^{+++}$  may likewise be an activator in the reaction of the catalytic decomposition of  $H_2O_2$ . A good example of this is the complex catalyst of a gel of copper-iron ferrocyanide, investigated recently [6]. The efficiency of this catalyst is increased considerably under the influence of  $Al^{+++}$ , as is shown by the figures given in Table 5. We have investigated the so-called catalytic mutation [7], the influence of which is sufficiently clearly marked. The order in which the separate components of the catalyst are added during its preparation is not immaterial. The most advantageous combination, as follows from Table 5, is the following order:



On the other hand, the order



was less advantageous.

The above figures show that the  $Al^{+++}$  acted in these systems as an efficient activator, especially in relatively high concentrations ( $10^{-2}$  g and  $10^{-3}$  g  $Al^{+++}$ ). This action disappeared on reducing the concentration to  $10^{-5}$  g  $Al^{+++}$  in 200 ml of  $H_2O_2$ .

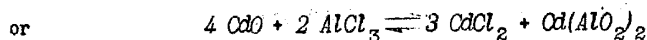
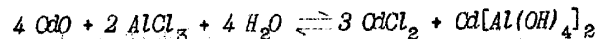
If the complex catalyst investigated is used in the system  $HCOOH/H_2O_2$ , there occurs an intense acceleration of the oxidation reaction of the formic acid at a temperature of 37°, as shown by our previous investigations [8]. The addition of  $Al^{+++}$  ions was not without influence in this case also, since it produced - it is true in different degrees - a slight inhibition of the oxidation reaction of formic acid, depending on the mutation employed (see above). On comparing the figures given in Tables 5 and 6, one is struck above all by the fact that the strongest inhibiting action of the  $Al^{+++}$  ion in the peroxidative reaction is found in the combination of the catalyst ( $Cu^{+++} + Fe^{+++} + [Fe(CN)_6]^{-4}$ ) in connection with which the  $Al^{+++}$  ion

\* For Tables, see end.

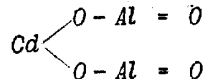
- 3 -

was the most efficient catalytic promoter in the reaction of the decomposition of  $H_2O_2$  (Table 5). Generally speaking, the position is similar to that obtaining in the case of the catalyst  $Cu/Al^{+++}$ , although in the converse relation, since in these conditions, the  $Al^{+++}$  ion was distinguished as a peroxidative activator, being simultaneously a catalytic inhibitor.

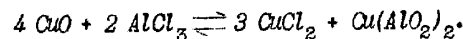
The catalytic action of  $Al^{+++}$  ions in reduction-oxidation systems is thus twofold and to a high degree specific. Since a similar phenomenon - although not in such a striking form - has been considered by us in the case of other ions (for example  $Co^{+++}$ ) [8], the conjecture arises that a certain rule is involved here, from which there may also be exceptions. Recently, Winowski [9], when investigating  $CdO$  as a carrier, found that the  $Al^{+++}$  ion also produced a diminution in the decomposition of  $H_2O_2$  and of the peroxidative oxidation of indigo carmine, from which it would be necessary to infer that, due to the partial exchange of both components, a relatively durable (stable and inactive) complex compound (cadmium hydroxy-aluminate or cadmium aluminate) is formed, resulting in the blocking of the active centres on the surface of the cadmium oxide:



The structural formula of this compound would be written as follows:

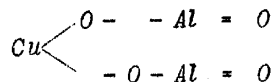


It is unquestionable that copper oxide is also subject to such an exchange with  $Al^{+++}$ :

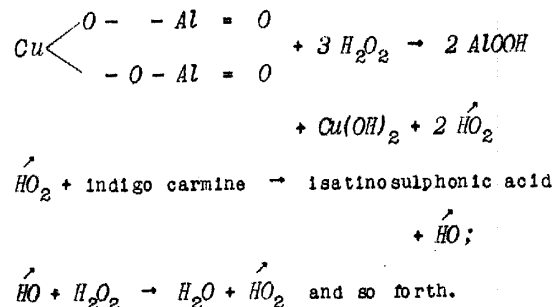


Nevertheless, the structural (diagrammatic) formula of copper hydroxy-aluminate or copper aluminate must be given in a different way, distinguishing its peculiar structure, which would be expressed by an increased peroxidative activity of this compound, taking into account its simultaneous inactivity in the decomposition of  $H_2O_2$ .

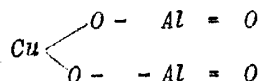
The structural formula



satisfies this requirement, because as a result of the action of  $H_2O_2$  only  $HO_2$  radicals will be the cause of the oxidation (dehydrogenation) of the organic substrate:



On the other hand, it does not seem that the structural formula



is correct, since in the reaction with  $2 H_2O_2$ , the radicals  $HO$  and  $HO_2$  would attack simultaneously, of which especially the former may initiate an uninterrupted chain of reactions of the decomposition of  $H_2O_2$ , which would not be consistent with the passivity of the catalyst  $CuO/Al^{+++}$  with regard to the oxidation of hydrogen peroxide.

REFERENCES

- [1] K. SCHARRER. Biochemie der Spurenelemente. Berlin, 1944.
- [2] J. ZNAMIENSKI. Bull. jard. bot. U.S.S.R., 26 (1927) 631.
- [3] A. KRAUSE. Investigations on Catalysts - in the collective work "Catalysis and Catalysts", PWT, Warsaw, 1952.
- [4] A. KRAUSE. Bull. Soc. des amis Sc. et Lettres de Poznan, 12 (1953) 43.
- [5] W. WOLSKI. Thesis for Doctorate, Poznan, 1951 (unpublished).
- [6] A. KRAUSE and St. ZIELINSKI. Roczniki Chem., 27 (1953) 327.
- [7] A. KRAUSE. Compt. rend. mens. acad. polon. Cl. math. nat., No. 5 - 10, (1951) 57.
- [8] A. KRAUSE. Compt. rend. mens. loc. cit. (1951) 60.
- [9] Z. WINOWSKI. Unpublished results.

- 5 -

TABLE 1

Inhibiting action of  $Al^{+++}$  ions in the decomposition of  $H_2O_2$  at a temperature of  $37^\circ$ .  
 200 ml  $H_2O_2$  (about 0.3%) +  $10^{-3}$  g  $Al^{+++}$  in 1 ml + carrier I = aluminium + chromium + iron hydroxides or carrier II = cobalt ferrocyanide.

10 ml solution =  $a_0$  ml 0.1 n  $KMnO_4$ .

| Time min. | 0.1 g I | 0.1 g I + $10^{-3}$ g $Al^{+++}$ | 0.1 g II | 0.1 g II + $10^{-3}$ g $Al^{+++}$ | $10^{-3}$ g $Al^{+++}$ |      | Blank test |      |
|-----------|---------|----------------------------------|----------|-----------------------------------|------------------------|------|------------|------|
|           |         |                                  |          |                                   |                        |      |            |      |
| $a_0$     | 17.6    | 17.6                             | 16.2     | 16.2                              | 17.6                   | 16.2 | 17.6       | 16.2 |
| 30        | 17.0    | 17.1                             | 15.2     | 15.7                              | .                      | .    | .          | .    |
| 60        | 16.1    | 16.5                             | 14.3     | 15.2                              | .                      | .    | .          | .    |
| 120       | 13.9    | 15.0                             | 12.5     | 13.9                              | .                      | .    | .          | .    |
| 180       | 11.4    | 12.5                             | 10.6     | 12.2                              | .                      | .    | .          | .    |
| 240       | 9.3     | 10.6                             | 9.0      | 11.3                              | .                      | .    | .          | .    |
| 300       | 7.4     | 8.8                              | 7.8      | 10.2                              | 16.3                   | 15.7 | 17.6       | 15.7 |

NOTE: The  $Al^{+++}$  ions used in the form of aqueous solutions of  $AlCl_3$  for carrier I or  $Al_2(SO_4)_3$  for carrier II.

TABLE 2

Inhibiting action of  $Al^{+++}$  ions in the decomposition of  $H_2O_2$  at a temperature of  $37^\circ$ .  
 200 ml  $H_2O_2$  (about 0.3%) + 1 ml  $Al^{+++}$  (in the concentration as below) + carrier (c): copper + lead + iron hydroxides (5 mg).

10 ml solution =  $a_0$  ml 0.1 n  $KMnO_4$ .

| Time min. | Alone (c) | (c) + $10^{-3}$ g $Al^{+++}$ | (c) + $10^{-4}$ g $Al^{+++}$ | (c) + $10^{-5}$ g $Al^{+++}$ | Blank test |      |
|-----------|-----------|------------------------------|------------------------------|------------------------------|------------|------|
|           |           |                              |                              |                              |            |      |
| $a_0$     | 19.0      | 19.0                         | 19.0                         | 19.0                         | 19.0       | 19.0 |
| 60        | 15.3      | 16.0                         | 15.9                         | 15.1                         | .          | .    |
| 120       | 10.3      | 14.5                         | 13.0                         | 10.8                         | .          | .    |
| 240       | 4.4       | 11.5                         | 6.8                          | 4.8                          | .          | .    |
| 300       | 2.1       | 10.0                         | 4.5                          | 2.4                          | 18.6       | 18.6 |

NOTE: The  $Al^{+++}$  ions used in the form of an aqueous solution of  $Al_2(SO_4)_3$ .

TABLE 3

Inhibiting action of  $Al^{+++}$  ions in the decomposition of  $H_2O_2$  at a temperature of  $37^\circ$ .  
 Carrier (c): copper + magnesium + iron hydroxides (5 mg). Further details as in Table 2.

| Time min. | Alone (c) | (c) + $10^{-3}$ g $Al^{+++}$ | (c) + $10^{-4}$ g $Al^{+++}$ | (c) + $10^{-5}$ g $Al^{+++}$ | (c) + $10^{-6}$ g $Al^{+++}$ | (c) + $10^{-7}$ g $Al^{+++}$ |
|-----------|-----------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
|           |           |                              |                              |                              |                              |                              |
| 60        | 14.8      | 16.1                         | 15.8                         | 15.4                         | 15.2                         | 15.0                         |
| 120       | 11.2      | 14.9                         | 14.4                         | 13.1                         | 12.8                         | 12.0                         |
| 240       | 5.1       | 12.2                         | 10.4                         | 6.6                          | 6.5                          | 5.1                          |
| 300       | 3.2       | 11.0                         | 8.5                          | 4.1                          | 4.1                          | 3.1                          |

NOTE: The  $Al^{+++}$  ions used in the form of an aqueous solution of  $Al_2(SO_4)_3$ .

- 8 -

TABLE 4

Catalyst  $\text{CuO} + \text{Al}^{+++}$  in the decomposition of  $\text{H}_2\text{O}_2$  (I), in the peroxidative oxidation of indigo-carmin (II) at a temperature of  $37^\circ$ .

I. 10 mg  $\text{CuO} + 1$  mg  $\text{Al}^{+++}$  in 1 ml + 150 ml  $\text{H}_2\text{O}_2$  ( $\approx 3\%$ ): 10 ml solution =  $a_0$  ml n  $\text{KMnO}_4$ .

II. 1 mg  $\text{CuO} + 1$  mg  $\text{Al}^{+++}$  in 1 ml + 30 ml indigo-carmin (= 10.8 mg dy) + 150 ml  $\text{H}_2\text{O}_2$  ( $\approx 3\%$ ).

The concentration of the dye given below in grams per litre was indicated by colorimetry (Visomat).

| Time min.         | I    |                         |                   |            | Time min. | II    |                         |                   |            |
|-------------------|------|-------------------------|-------------------|------------|-----------|-------|-------------------------|-------------------|------------|
|                   | CuO  | CuO + $\text{Al}^{+++}$ | $\text{Al}^{+++}$ | Blank test |           | CuO   | CuO + $\text{Al}^{+++}$ | $\text{Al}^{+++}$ | Blank test |
| $a_0 \rightarrow$ | 19.7 | 19.7                    | 19.7              | 19.7       | 0         | 0.060 | 0.060                   | 0.060             | 0.060      |
| 30                | 18.0 | 19.4                    | 18.9              | 19.7       | 15        | 0.055 | 0.044                   | 0.053             | .          |
| 60                | 18.1 | 19.3                    | 18.9              | 19.6       | 30        | 0.045 | 0.027                   | 0.048             | .          |
| 90                | 13.4 | 19.0                    | 18.9              | 19.6       | 45        | 0.034 | 0.015                   | 0.042             | .          |
| 180               | 43   | 17.8                    | 18.8              | 19.4       | 60        | 0.028 | -                       | 0.035             | 0.060      |

NOTE: The  $\text{Al}^{+++}$  ions were used in the form of an aqueous solution of  $\text{AlCl}_3$ .

TABLE 6

Inhibiting influence of  $\text{Al}^{+++}$  ions (in the concentration as below in 1 ml) in the peroxidative oxidation of formic acid at a temperature of  $37^\circ$  in the presence of the basic catalyst (I) =  $[\text{Fe}(\text{CN})_6]^{-4} + \text{Cu}^{++} + \text{Fe}^{+++}$  or (II) =  $\text{Cu}^{++} + \text{Fe}^{+++} + [\text{Fe}(\text{CN})_6]^{-4}$  (cf. Table 5) + 100 ml  $\text{H}_2\text{O}_2$  ( $\approx 0.6\%$ ) + 100 ml 0.1 n  $\text{HCOOH}$ .

10 ml of solution =  $a_0$  ml 0.02 n  $\text{NaOH}$ .

| Time min.         | I Without $\text{Al}^{+++}$ | I + $10^{-2}$ g $\text{Al}^{+++}$ | I + $10^{-3}$ g $\text{Al}^{+++}$ | I + $10^{-2}$ g $\text{Al}^{+++}$ | II + $10^{-2}$ g $\text{Al}^{+++}$ | $10^{-2}$ g $\text{Al}^{+++}$ | $\text{H}_2\text{O}_2 + \text{HCOOH}$ without catalyst (blank test) |
|-------------------|-----------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|-------------------------------|---|
| $a_0 \rightarrow$ | 24.9                        | 24.9                              | 24.9                              | 24.9                              | 24.9                               | 24.9                          | 24.9  |
| 40                | 17.5                        | 19.3                              | 18.0                              | 17.6                              | 19.5                               | .                             | .   |
| 80                | 6.6                         | 9.7                               | 8.0                               | 6.9                               | 11.7                               | .                             | .   |
| 120               | 2.8                         | 5.7                               | 4.1                               | 3.2                               | 6.8                                | .                             | .   |
| 140               | 2.1                         | 5.0                               | 3.0                               | 2.9                               | 5.7                                | 24.4                          | 24.3  |

TABLE 5

Catalytic mutation in the decomposition of  $H_2O_2$  at a temperature of  $37^\circ$ . Complex catalyst (I) prepared in the order  $[Fe(CN)_6]^{-4} + Cu^{+++} + Fe^{+++}$  (ions per 1 mg in 1 ml) +  $Al^{+++}$  m 1 ml (in the proportions given below) + 200 ml  $H_2O_2$  ( $\approx 3\%$ ). Catalyst (II) prepared in the order  $Cu^{+++} + Fe^{+++} + [Fe(CN)_6]^{-4} + Al^{+++}$ . 10 ml of solution =  $Q_0$  ml 0.1 n  $KMnO_4$ .

| Time<br>min. | (I)                   |                            |                            |                            |                            | (II)                  |                            |                            |                            |                            | $10^{-2}g$<br>$Al^{+++}$ | $H_2O_2$<br>without<br>catalyst<br>(blank test) |      |
|--------------|-----------------------|----------------------------|----------------------------|----------------------------|----------------------------|-----------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|---|------|
|              | Without<br>$Al^{+++}$ | $+ 10^{-2}g$<br>$Al^{+++}$ | $+ 10^{-3}g$<br>$Al^{+++}$ | $+ 10^{-4}g$<br>$Al^{+++}$ | $+ 10^{-5}g$<br>$Al^{+++}$ | Without<br>$Al^{+++}$ | $+ 10^{-2}g$<br>$Al^{+++}$ | $+ 10^{-3}g$<br>$Al^{+++}$ | $+ 10^{-4}g$<br>$Al^{+++}$ | $+ 10^{-5}g$<br>$Al^{+++}$ |                          |   |      |
| $Q_0$        | 16.3                  | 16.3                       | 16.3                       | 16.3                       | 16.3                       | 16.3                  | 16.3                       | 16.3                       | 16.3                       | 16.3                       | 16.3                     | 16.3  | 16.3 |
| 60           | 13.1                  | 12.4                       | 12.5                       | 12.8                       | 13.0                       | 13.0                  | 12.8                       | 12.8                       | 13.1                       | 13.1                       | 16.2                     | 16.3  | 16.3 |
| 120          | 11.8                  | 8.5                        | 9.7                        | 11.4                       | 11.8                       | 10.9                  | 8.5                        | 9.8                        | 11.0                       | 11.0                       | 16.0                     | 16.1  | 16.1 |
| 240          | 9.6                   | 3.2                        | 5.6                        | 8.7                        | 9.2                        | 8.4                   | 2.3                        | 5.6                        | 7.7                        | 8.0                        | 15.8                     | 16.0  | 16.0 |
| 300          | 8.9                   | 2.0                        | 4.1                        | 7.2                        | 8.6                        | 7.3                   | 1.1                        | 3.9                        | 6.1                        | 6.8                        | 15.7                     | 15.8  | 15.8 |

NOTE: The above ions were used in the form of aqueous solutions of  $K_4[Fe(CN)_6]$ ,  $CuSO_4$ ,  $Fe(NO_3)_3$ ,  $Al_2(SO_4)_3$ . All the agents were of maximum purity (Merck, pro anal.).