CCXXII.—*The Catalytic Decomposition of Solutions of Sodium Hypochlorite by Finely Divided Metallic Oxides.*

By EUGEN CHIRNOAGA.

THE present paper is chiefly concerned with a study of the velocity of decomposition of aqueous solutions of sodium hypochlorite in the presence of cobalt peroxide, nickel peroxide, and mixtures of these peroxides with one another and with an inactive oxide (aluminium oxide). At the commencement of this work no systematic study of the kinetics of this catalytic reaction had been carried out, but during its progress a paper dealing with the action

of cobalt peroxide was published by Howell (*Proc. Roy. Soc.*, 1923, **104**, *A*, 134).

It will be shown that in general the reaction (evolution of oxygen) follows the equation $-dc/dt = k_1 c^{1 n}$ or, in integrated form,

$$\{c_0^{(n-1)/n} - c_t^{(n-1)/n}\}n/(n-1) = k_1 t$$

where c_0 = concentration of hypochlorite at zero time, c_t = concentration at time t, and k_1 and n are constants. In certain cases, it is found that the constant n does not differ appreciably from unity, so that the course of the reaction then follows the unimolecular law

$$-dc/dt = kc, \text{ or } \log c_0/c_t = kt.$$

It is probable that the hypochlorite ions are adsorbed on the surface of the catalyst particles, the velocity of reaction being determined by the decomposition of the adsorbed ions, whilst the more rapid process of adsorption keeps the surface layer in adsorption equilibrium with the bulk of the solution. If A = surface of the catalyst, and α = amount of adsorbed hypochlorite, then, if the adsorption can be represented by Freundlich's empirical equation, $\alpha = KAC^{1/n}$, and putting x = volume of oxygen evolved at time t, the velocity of decomposition is

$$dx/dt = k'KAc^{1/n}$$

if the adsorbed ions decompose according to the reaction $ClO' = Cl' + O$. Thus $k_1 = k'KA$. It will be shown that for very considerable variations of A, k_1 is proportional to A.

Preparation of Hypochlorite Solution.

The solution was prepared by passing purified chlorine very slowly into an ice-cold solution of approximately $2N$-sodium hydroxide (prepared from metallic sodium). The course of the reaction was followed by withdrawing from time to time 2 c.c. of the solution, decomposing the hypochlorite by neutral hydrogen peroxide solution and testing with phenolphthalein. The passage of chlorine was stopped when no pink coloration was obtained. In this manner, 4 litres of the hypochlorite–chloride solution were obtained, the operation lasting about 3 days. Titration with $N/10$-sodium arsenite showed that the solution contained 72·26 g. of sodium hypochlorite per litre. Together with the 34·4 g. of chlorine in this hypochlorite, there are produced also 34·4 g. of chlorine as chloride, so that, if no chlorate were formed, the solution would contain 68·8 g. of chlorine per litre. Direct determination (by means of silver nitrate) of chlorine as hypochlorite and chloride gave 69·0 g. per litre. It will be seen, therefore, that the prepared solution contained practically no chlorate. The approximately M-solution of sodium

hypochlorite prepared in this manner proved to possess very considerable stability, retaining 67% of its initial strength after 14 months at laboratory temperature.

Apparatus and Method of Measurement.

The hypochlorite solution and the catalyst (in the form of an aqueous suspension) were mixed in a glass vessel (immersed in a water thermostat at constant temperature) provided with a revolving glass stirrer (operating through a gas-tight mercury seal) and a side tube connected to a gas-collecting burette. The solutions or suspensions and the distilled water were brought to the thermostat temperature before mixing and were saturated with oxygen. In every case, the volume of the reacting fluid was adjusted to 100 c.c. by the addition, if necessary, of distilled water. The volume of oxygen in c.c. evolved from 100 c.c. of solution at any time t (expressed in minutes) from the starting of the reaction was reduced to standard conditions and is denoted by x in the tables which follow. The hypochlorite concentration at any moment (c_0 or c_t) is expressed in terms of equivalent c.c. of oxygen (reduced to standard conditions) per 100 c.c. of solution.* Thus $x = c_0 - c_t$.

Cobalt Peroxide as Catalyst.

A solution of cobalt chloride was precipitated by an equivalent amount of sodium hydroxide, and the calculated amount of sodium hypochlorite solution added. After the precipitate had settled, the clear liquid was decanted and the precipitate treated with another equal portion of sodium hypochlorite. This operation was repeated three times. The black precipitate was filtered on a Büchner funnel and washed until the filtrate was free from chloride and only very slightly alkaline. In other preparations, filtration was avoided in order to prevent agglomeration of the particles, and the washing was effected by numerous decantations. The peroxide was used in the form of an aqueous suspension, which was, however, not stable, most of the peroxide particles settling out after a time. Hence reproducible results could be obtained only by mixing the contents of the storage vessel immediately before use, although after a considerable time the catalyst showed signs of " ageing " (as shown by change of k, k_1, and n).

The cobalt peroxide catalysts prepared in this manner gave, up to 80—90% decomposition, fairly constant values for the unimolecular velocity coefficient k, or for the coefficient k_1 when

---

* In the experiments described, it was found that at least 90% of the hypochlorite was converted into chloride and oxygen. Hence the subsidiary reaction giving chloride and chlorate has been neglected.

$1/n = 0.9$. The following results show that the velocity of the reaction was independent of the speed of stirring over a wide range.

TABLE I.

Temp. $= 25°$.   Catalyst $= 0.0193$ g. cobalt peroxide per l. $c_0 = 29.22$;
$1/n = 0.9$.

	350 revs. per min.				1750 revs. per min.		
t.	x.	$k \times 10^4$.	$k_1 \times 10^4$.	t.	x.	$k \times 10^4$.	$k_1 \times 10^4$.
14	1·93	21	65	13	1·83	22	69
32	4·27	21	66	32	4·32	22	69
47	6·18	22	68	47	6·06	21	68
72	8·94	22	69	67	8·26	21	67
92	11·11	23	71	92	10·77	22	68
122	13·79	23	70	117	13·02	22	68
142	15·50	23	71	157	16·09	22	68
172	17·50	23	71	244	20·83	22	67
262	21·87	23	69	272	22·02	22	67
297	23·01	23	68	353	24·34	22	65
437	25·45	20	60	432	25·58	21	61

In all the later experiments, the speed of the stirrer was noted and kept at a value lying between the above limits. If the reaction mixtures are not stirred there occurs a measurable evolution of oxygen, although the rate of decomposition is much slower. Thus in an experiment conducted under otherwise precisely the same conditions as in Table I, but without stirring, a constant value for k_1 equal to 0.9×10^{-4} was obtained by putting $1/n = 3.38$, whilst the value of k diminished as the reaction proceeded.

A number of experiments were carried out to determine the relation between the velocity coefficient and a, the amount of the catalyst. In Table II, this amount is expressed as c.c. of catalyst suspension (containing 1·928 g. of catalyst per litre) used in the 100 c.c. of reaction fluid.

TABLE II.

$c_0 = 19.48$.   Temp. $= 25°$. $1/n = 0.9$.

a	2·5	5·0	7·5	12·5	20·0
$k_1 \times 10^4$	19	39	58	98	180
$10^5 \times k_1/a$	76	78	77	78	90

It will be seen that k_1 is proportional to a over a considerable range, although when a exceeds a certain value k_1/a begins to increase.

Another series of experiments was made to determine how the velocity varied with the initial concentration of hypochlorite. As these experiments gave in each individual case fair constancy for the velocity coefficient k (as shown by the example in Table III), these values have been collected for comparison in Table IV.

TABLE III.

Catalyst = 0·01928 g. cobalt peroxide per l. Temp. = 25°. c_0 = 48·7.

$t.$	$x.$	$k \times 10^5.$	$t.$	$x.$	$k \times 10^5.$	$t.$	$x.$	$k \times 10^5.$
13	2·895	205	54	10·45	194	280	34·97	196
25	5·34	201	116	19·40	190	373	39·72	197
37	7·63	200	156	24·22	192	428	41·71	197

TABLE IV.

Temp. = 25°. Catalyst = 0·01928 g. cobalt peroxide per l.

c_0	9·74	19·48	29·22	38·96	48·70
$k \times 10^5$	360	250	195	192	194

It will be seen that as the initial hypochlorite concentration (c_0) increases, the velocity coefficient at first decreases and then becomes constant.

Experiments were carried out under similar conditions to determine the value of the temperature coefficient. The results are shown in Table V.

TABLE V.

Temp.	25°	30°	35°	40°
$k \times 10^5$	220	326	540	796

From these results it follows that $k_{35}/k_{25} = 2·45$ and $k_{40}/k_{30} = 2·40$. Howell (loc. cit.) found in the same temperature region $k_{t+10}/k_t = 2·37$. These values show that the velocity of the reaction is determined by a chemical action at the adsorbing surface and not by a process of diffusion from the solution to the surface.

After the experiments just described had been carried out, using two samples of cobalt peroxide suspension prepared as described on p. 1695, another preparation was made in which the peroxide was constantly washed by decantation until no alkalinity could be detected in the wash water. This operation required 4 months, thus showing how difficult it is to remove adsorbed alkali. This cobalt peroxide suspension was much more "concentrated" and, weight for weight, more catalytically active than those used previously. The latter result might perhaps have been expected, since Howell had shown that free alkali reduces the velocity of the reaction. Experiments with this new catalyst did not give constant values for the velocity coefficient k, whereas with suitable values for $1/n$ the velocity coefficient k_1 showed a satisfactory degree of constancy over a wide range of decomposition, as may be seen from the results given in Table VI.

In Table VII are collected the mean values of k_1 for constant catalyst concentration and different initial values of the hypochlorite concentration.

<div align="center">TABLE VI.</div>

Temp. $= 25°$. Catalyst conc. $= 0\cdot211$ g. per l. $c_0 = 41\cdot48$. $1/n = 0\cdot72$.

t.	c_t.	$k_1 \times 10^4$.	t.	c_t.	$k_1 \times 10^4$.	t.	c_t.	$k_1 \times 10^4$.
6	39·16	274	45	26·12	274	152	6·30	273
12	36·98	268	77	17·81	277	182	4·01	270
22	33·45	270	92	14·76	277	232	1·97	251
33	29·87	274	114	11·01	276			

<div align="center">TABLE VII.</div>

<div align="center">Temp. $= 25°$.   Catalyst $= 0\cdot211$ g./litre. $1/n = 0\cdot72$.</div>

c_0	20·74	31·11	41·48	52·39	62·89	80·99	149·36
$k_1 \times 10^4$	264	273	272	263	277	285	286

It will be seen that there is not much variation of k_1 with initial hypochlorite concentration (compare the results given in Table IV).

Experiments with Mixtures of Aluminium Oxide and Cobalt Peroxide.—From a solution containing known amounts of cobalt and aluminium chlorides the mixed hydroxides (oxide gels) were precipitated by ammonia, washed, and treated three times with sodium hypochlorite solution. The precipitate was then washed by decantation until the wash water was only slightly alkaline. In this way aqueous suspensions could be prepared containing the same weight of cobalt peroxide per unit volume associated with various weights of aluminium oxide. Comparative experiments were then carried out with all other conditions the same (*i.e.*, temperature, initial hypochlorite concentration, and weight of cobalt peroxide per unit volume), the only variant being the percentage by weight of aluminium oxide in the mixed catalyst. As the value of $1/n$ was found to vary with the composition of the catalyst, the values of k corresponding in each case to the same fraction of hypochlorite decomposed are given in Table VIII.

<div align="center">TABLE VIII.</div>

$Al_2O_3\%$	0	13	26	39
$k \times 10^5$	200	210	260	225

Special experiments showed that aluminium oxide gel alone had no measurable catalytic action on the decomposition of hypochlorite. It is interesting to observe from the above results that the aluminium oxide shows a " promoter " action, which seems to reach a maximum between 26 and 39%.

<div align="center">*Nickel Peroxide as Catalyst.*</div>

The nickel catalysts were prepared in the same manner as those of cobalt. None of these catalysts gave constant values for k, but in all cases, by using a suitable value for $1/n$, the course of the

decomposition (up to at least 85% of the total reaction) could be well represented by the equation $dx/dt = k_1 c^{1/n}$. In general, the values of $1/n$ varied within the range 0·40—0·50, which shows the wide divergence of the results from those corresponding to the equation $dx/dt = kc$. Otherwise, the results were very similar to those obtained with cobalt peroxide. Table IX shows how k_1 varied with the amount of catalyst present. This amount (a) is expressed as the number of c.c. of a nickel peroxide suspension (containing 1·62 g. per litre) present in 100 c.c. of the reaction mixture.

TABLE IX.

Temp. = 25°. $c_0 = 26·85$. $1/n = 0·5$.

a	5	10	15	20
$k_1 \times 10^4$	220	445	680	964
$10^4 \times k_1/a$	43	44	45	48

A typical experiment is shown in detail in Table X.

TABLE X.

Temp. = 25°. $c_0 = 26·85$. $a = 5$. $1/n = 0·50$.

t.	c_t.	$k_1 \times 10^3$.	t.	c_t.	$k_1 \times 10^3$.	t.	c_t.	$k_1 \times 10^3$.
0	26·85	—	74	19·07	22	285	5·32	22
18	24·68	24	114	15·45	22	320	3·78	20
30	22·45	23	154	12·39	22	375	2·69	19

Some special experiments were made with the nickel peroxide catalyst to ascertain whether increasing amounts of sodium chloride had any effect on the velocity coefficient. The amount of sodium chloride added (*i.e.*, over and above that already present with the hypochlorite) is expressed in terms of c.c. of a N-sodium chloride solution contained in 100 c.c. of the reaction mixture. The results given in Table XI show that the additional sodium chloride has no effect.

TABLE XI.

Temp. = 25°. $c_0 = 26·85$. $1/n = 0·57$.   Catalyst = 0·32 g. per l.

Additional NaCl	0	2	6	10	20	60
$k_1 \times 10^3$	120	120	120	118	120	120

We may perhaps conclude from these results that chlorine ions are not strongly adsorbed on the surface of the catalyst. Howell showed in the case of cobalt peroxide that hydroxyl ions have a marked effect in diminishing the velocity of the reaction. The following results show that a similar effect obtains when nickel peroxide is used.

The concentrations of sodium hydroxide given in Table XII are simply calculated from the number of c.c. of a $N/1$-solution added in making up the 100 c.c. of reaction mixture, so that the lower

TABLE XII.

Temp. $= 25°$. $c_0 = 25.71$.   Catalyst $= 0.32$ g. per l.

NaOH conc.	$1/n$.	$k_1 \times 10^4$.	NaOH conc.	$1/n$.	$k_1 \times 10^4$
0	0·45	870	$N/100$	0·65	190
$N/1000$	0·53	485	$N/66.6$	0·65	170
$N/500$	0·58	360	$N/50$	0·65	160
$N/200$	0·59	280			

values may not correspond accurately to sodium hydroxide concentrations. A possible explanation of these results is that hydroxyl ions may be strongly adsorbed on the surface of the catalyst and thus diminish the surface available for the adsorption of hypochlorite ions. It has been pointed out previously that it is very difficult to wash these peroxide catalysts free from adsorbed alkali. It might also be supposed that the substance which is adsorbed by the catalyst is not hypochlorite ion but undissociated hypochlorous acid set free by the hydrolysis of the hypochlorite, the primary catalysed reaction being $HClO = H^+ + Cl^- + O$. If this were true, the addition of sodium hydroxide would decrease the hydrolysis of the hypochlorite and so diminish the velocity of the reaction. If $\log k_1$ be plotted against $\log [NaOH]$, the points obtained lie fairly well on the straight line $\log k_1 = const. - 0.35 \log [NaOH]$, so that $k_1 = const./[NaOH]^{0.35}$. Assuming the adsorption of hypochlorous acid to follow Freundlich's equation and the velocity of the reaction to be determined by the decomposition of the adsorbed molecules, we should have $dx/dt = k[HClO]^{1/n}$. From the simplest ionic theory of hydrolysis, $[HClO] = k_w[ClO']/k_a[OH'] = K[NaClO]/[NaOH]$ approximately, so that the velocity would be given by the equation

$$dx/dt = k'[NaClO]^{1/m}/[NaOH]^{1/m}.$$

This gives for k_1 (the measured velocity coefficient) the equation $k_1 = k'/[NaOH]^{1/m}$, and from the above result $1/m = 0.35$. Although these considerations give for the relationship between k_1 and $[NaOH]$ an equation which is of the same type as that found experimentally, the exponent of $[NaClO]$ which represents the experimentally found reaction velocities has the (average) value 0.61, and not 0.35. It is not possible, therefore, from this simple theory to obtain quantitative support for the view that the primary catalysed reaction is the decomposition of adsorbed molecules of $HClO$.

The temperature coefficient of the reaction as catalysed by nickel peroxide can be calculated from the data given in Table XIII,

TABLE XIII.

$c_0 = 25.00$.   Catalyst $= 0.08$ g. per l. $1/n = 0.47$.

Temp.	25°	30°	35°	40°	45°	50°
$k_1 \times 10^3$	23	35	55	83	128	196

whence $k_{35}/k_{25} = 2·39$, $k_{40}/k_{30} = 2·37$, $k_{45}/k_{35} = 2·33$, $k_{50}/k_{40} = 2·36$, the mean value being $2·36$.

Experiments with Mixtures of Nickel Peroxide and Aluminium Oxide.—These experiments were carried out in the manner described for the parallel case of cobalt peroxide. Table XIV shows how the *initial* values of k vary with the percentage of aluminium oxide in the mixed catalyst, the amount of nickel peroxide present per unit volume ($0·16$ g. per litre), the temperature, and the initial concentration of hypochlorite being the same in every case.

TABLE XIV.

% Al_2O_3	0	8·5	17·0	34·0	68·0
$k \times 10^5$	400	1620	700	150	15

It will be seen that as the percentage of aluminium oxide increases there is at first a very marked " promoter " action, followed later by an equally marked " depressor " action. The latter effect is probably due to the nickel peroxide particles becoming " enveloped " by the aluminium oxide gel.

Mixtures of Cobalt Peroxide and Nickel Peroxide as Catalysts.

The two hydroxides were precipitated together from solution by sodium hydroxide, the precipitate treated four times with sodium hypochlorite solution, and then washed by decantation until the wash water contained no chloride and had only a very slight alkaline reaction. The experiments were so arranged that the reaction mixtures contained equal total weights of the suspended precipitate per unit volume, the composition of the catalyst varying, however, from experiment to experiment. As in other similar cases, the temperature ($25°$) and the initial concentration of hypochlorite ($20·9$) were the same in every case. The values of k correspond to the initial period of the decomposition.

TABLE XV.

% Ni_2O_3	0	1	10	30	50	90	100
$k \times 10^4$	20	20	65	87	74	65	50

It will be observed that the mixed catalyst is more active, weight for weight, than either singly, the maximum activity occurring in the region of 30% of nickel peroxide.

Other Oxides as Catalysts.

Copper hydroxide (copper oxide gel) was precipitated by sodium hydroxide from aqueous solution, and washed repeatedly by decantation until as free as possible from adsorbed alkali and salts.

Suspensions of this material were employed as catalyst. The following table shows the results obtained in two experiments.

TABLE XVI.

Temp. $= 25°$. Catalyst in A $= 0.736$ g. CuO per l. Catalyst in B $= 1.472$ g. per l. $c_0 = 24.18$.

	A.			B.	
$t.$	$x.$	$k \times 10^5.$	$t.$	$x.$	$k \times 10^5.$
18	1.04	103	10	1.18	217
43	2.38	101	20	2.25	212
67	3.67	103	50	5.33	216
97	5.05	101	90	8.69	215
127	6.48	103	145	12.12	208
232	10.61	103	175	13.57	204
292	12.33	101	270	16.80	191
352	13.65	97	325	17.88	180
382	14.26	96	355	18.28	172
412	14.82	95	385	18.59	165
456	15.48	92	445	19.05	151

It will be seen that the value of k falls in each case with the progress of the reaction, although there is no very marked change until about 50% decomposition has been reached. The value of k is roughly proportional to the amount of catalyst present per unit volume. The results show that the catalytic effect of copper oxide is small compared with that of cobalt or nickel peroxide.

The catalytic activities of precipitated ferric oxide, manganese peroxide and mercuric oxide gels were much too small to be measurable by the foregoing method, so the following rough method of comparison was adopted.

Into each of three small Erlenmeyer flasks 20 c.c. of the respective oxide gel suspensions were introduced together with 3 c.c. of the stock hypochlorite solution. The initial hypochlorite concentration was $0.0847N$ in each case. After 74 days at room temperature, the undecomposed hypochlorite was determined by titration. The results are shown in Table XVII.

TABLE XVII.

Catalyst.	% NaOCl decomposed.
Ferric oxide (1.95 g. per l.)	71.7
Manganese dioxide (0.524 g. per l.)	55.3
Mercuric oxide	27.0

During the same period the (undiluted) stock hypochlorite solution had decomposed to the extent of 13%. In order of decreasing catalytic activity, the oxides (oxide gels) investigated may be arranged as follows : Nickel > cobalt > copper > iron > manganese > mercury, although it must be noted that the particular nature (age,

surface, etc.) of the catalyst preparation plays a large part in each case.

Apparent Auto-decomposition of Sodium Hypochlorite Solution.

Throughout all the experiments described, the same stock hypochlorite solution was employed. Its strength was determined from time to time by titration and found slowly to diminish. The following table shows the course of this decomposition. The unit of time is one day and the value of c_t is expressed in c.c. of equivalent oxygen (reduced to standard conditions) per 1 c.c. of solution. The temperature was the ordinary laboratory temperature ($15°$—$20°$).

TABLE XVIII.

$t.$	$c_t.$	$k \times 10^5.$	$t.$	$c_t.$	$k \times 10^5.$	$t.$	$c_t.$	$k \times 10^5$
0	10·860	—	269	9·352	25	345	8·568	29
105	10·008	34	296	9·128	25	355	8·700(?)	31
160	9·856	26	317	8·960	26	362	8·344	32
187	9·744	25	330	8·792	28	375	8·064	34
230	9·520	24	341	8·624	29	442	7·280	40

It is of interest to observe that up to 317 days the velocity of decomposition follows closely the simple unimolecular law, although Giordani (*Rend. Accad. Sci. Fis. Nat. Napoli*, 1924, iii, **30**, 107) found the reaction to be of the second order. From 317 to 442 days the coefficient k shows a slow but steady rise.