V.—*Period of Induction in Chemical Reactions. Interaction of Mercuric Chloride and Sodium Hydrogen Carbonate.*

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WHILST preparing certain compounds of mercury, the authors found that interaction between mercuric chloride and alkaline hydrogen carbonates does not take place at once, but that there is a distinct period of induction. The present paper deals with this particular reaction, and those with other salts are being investigated.

Standard solutions of mercuric chloride and sodium hydrogen carbonate were prepared. 10 C.c. of the sodium hydrogen carbonate solution were added as quickly as possible to 10 c.c. of the mercuric chloride solution in a 50 c.c. test-tube, which was then sharply shaken once; the interval between the moment of mixing and the first appearance of the red precipitate of oxychloride at the top of the mixture was read from a stop-watch. The moment when the last portion of the sodium hydrogen carbonate solution had been poured was taken as the moment of mixing. A lens was used to ascertain the moment when the precipitate first made its appearance at the lowest point of the meniscus, and a black background facilitated the observation. The concentrations of the reactants were varied severally and jointly, giving three sets of experiments: (1) constant concentration of mercuric chloride (Table I); (2) constant concentration of sodium hydrogen carbonate (Table II); and (3) variable concentrations of both mercuric chloride and sodium hydrogen carbonate (Tables III and IV).

The determination of the exact time when the precipitate just became detached from the lowest point of the meniscus required practice and sometimes six determinations were made with one particular mixture, the mean being taken.

TABLE I.

$C_{Hg} = 1·467$; temp. 23°.

C_{Na}.	t.	$C_{Na} \times t = K$.
2·0000	31·5	63·00
1·6666	39·5	65·80
1·4228	45·5	64·97
1·2500	50·5	63·12
1·1110	55·5	61·60
1·0000	65·0	65·00
0·9090	72·0	65·44
0·8334	81·0	67·50
0·7692	85·0	65·38
0·7142	92·0	65·70
	Mean	64·76

TABLE II.

$C_{Na} = 1·723$; temp. 23°.

C_{Hg}.	t.	$C_{Hg} \times t = K$.
1·476	41	60·51
1·2295	48	59·01
1·0548	58	61·17
0·9225	69	60·85
0·8144	78	63·95
0·7380	82	60·52
0·6708	87	58·34
0·6150	95	58·42
0·5676	102·5	58·00
0·5271	110·5	58·24
	Mean	59·90

C_{Hg} and C_{Na} represent concentrations of mercuric chloride and sodium hydrogen carbonate, respectively, in g.-mols. per 10 litres of water (10 c.c. of each solution were used in each experiment); *t* is the period of induction in seconds.

For the experiments in Tables III and IV, each reactant was diluted to 0·835, 0·71, 0·625, 0·55, 0·50, 0·45, 0·42, 0·38, and 0·36 of its original concentration (see Fig. 1), but the values of C_{Na} in Table IV are double the corresponding values in Table III, the values of C_{Hg} remaining the same.

Fig. 1.

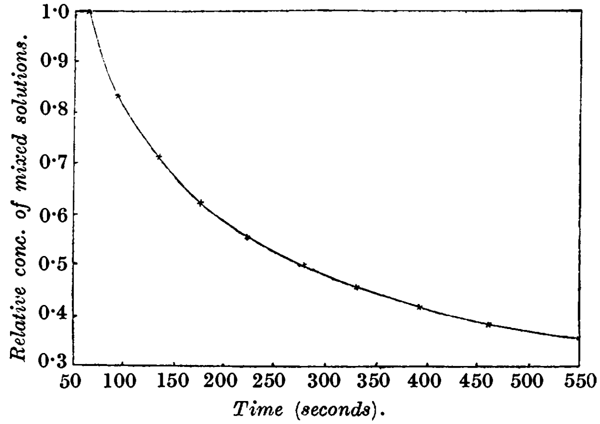


Table III.

Temp. 23°.

C_{Hg}.	C_{Na}.	*t*.	$C_{Na} . C_{Hg} . t = K$.
1·4760	1·000	65	95·94
1·2295	0·833	92	94·22
1·0547	0·7143	133	99·16
0·9225	0·625	175	100·89
0·8199	0·5555	221	100·65
0·7380	0·5000	270	99·63
0·6708	0·4545	330	104·61
0·6150	0·4167	392	104·69
0·5676	0·3846	460	100·43
0·5271	0·3571	550	103·52
			Mean 100·37

Table IV.

Temp. 23°.

C_{Na}.	*t*.	$C_{Na} . C_{Hg} . t = K$.
2·000	32	95·46
1·666	46	94·22
1·428	68	102·42
1·250	90	103·78
1·111	112	102·02
1·000	130	95·94
0·909	154	93·90
0·8334	190	97·49
0·7692	225	98·24
0·7143	250	96·63
		Mean 98·01

From Tables I—IV it will be seen that the period of induction is approximately inversely proportional to the concentration of the solutions. It was not possible to get more concordant results, as the reaction is apparently very complex (*vide infra*).

Effect of Temperature.

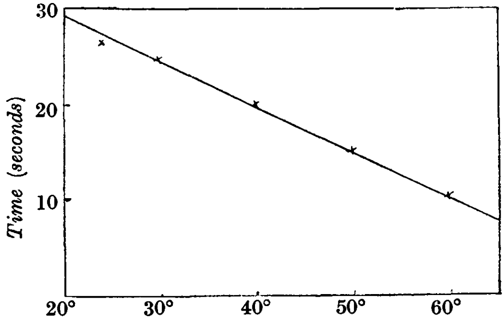
The two solutions contained in large test-tubes were kept in a glass thermostat for ½ hour, then the sodium hydrogen carbonate was immediately poured into the test-tube containing the mercuric chloride, and the period of induction read from the stop-watch. The experiment was repeated at 24°, 30°, 40°, 50°, and 60°, the concentrations of mercuric chloride and sodium hydrogen carbonate being kept constant. 10 C.c. of mercuric chloride ($C_{\mathrm{Hg}} = 1{\cdot}476$) and 10 c.c. of sodium hydrogen carbonate ($C_{\mathrm{Na}} = 2{\cdot}000$) were taken in each experiment.

TABLE V.

Temperature	24°	30°	40°	50°	60°
Period of induction (secs.) ...	31·5	26·1	20·0	15·0	10·5

The period of induction therefore diminishes, as the temperature is increased, approximately at the rate of 5 secs. for every increase of 10° (see Fig. 2).

FIG. 2.



The possible conversion of sodium hydrogen carbonate into carbonate when the temperature was raised was also studied; in addition to the two test-tubes containing mercuric chloride and sodium hydrogen carbonate, a third test-tube containing 10 c.c. of the same sodium hydrogen carbonate solution was suspended for ½ hour in the thermostat in each experiment under the same conditions of temperature. The conversion of hydrogen carbonate into carbonate was estimated with standard sulphuric acid solution by the double-indicator method :

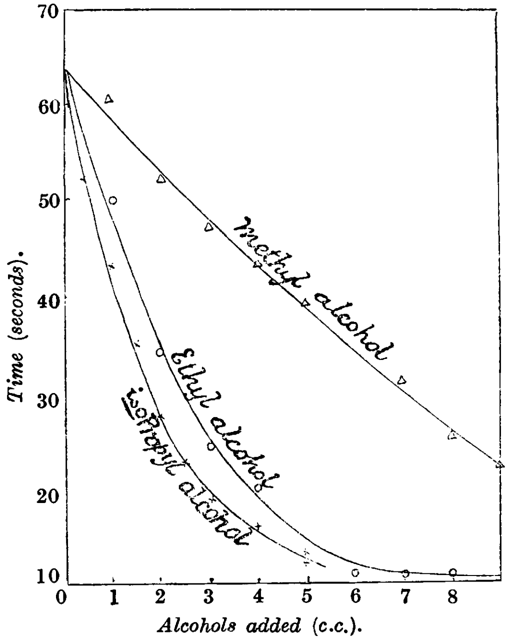
Temperature	30°	40°	50°	60°
Carbonate formed ...	0·000598	0·000653	0·000761	0·010332

The proportion of carbonate in the hydrogen carbonate increases with the rise of temperature from 30° to 60°. Sodium hydrogen carbonate solution (1 : 14) was found not to change during 24 hours at laboratory temperature.

Effect of Light.

Solutions of mercuric chloride ($C_{Hg} = 1{\cdot}476$) and sodium hydrogen carbonate ($C_{Na} = 2{\cdot}00$) were prepared in the dark-room and kept over-night. The period of induction, noted in red light on the following day, was found, after some trials in order to adjust vision in red light, to be the same as that in diffused daylight, *viz.*, 32 secs. at 22°. The reaction is therefore not photochemical.

FIG. 3.



Action of Alcohols.

The effect of alcohols and sugars on the period of induction was next studied. Methyl and ethyl alcohols progressively diminished the period of induction up to a certain limit. *iso*Propyl alcohol accelerated the reaction and hence diminished the period of induction, whereas *n*-propyl alcohol increased the period of induction so greatly that with 1·5 c.c. added to 20 c.c. of the mixture no precipitate was observed within ½ hour. In fact, *n*- and *iso*-propyl alcohols may be distinguished with the help of a dilute solution of mercuric chloride and sodium hydrogen carbonate. Glycerol caused a pronounced increase in the period of induction, but glucose, sucrose, mannitol, and dulcitol had very little effect.

The concentrations of the two solutions were kept constant ($C_{\mathrm{Hg}} = 1\cdot457$; $C_{\mathrm{Na}} = 1\cdot000$); 10 c.c. of each solution were taken each time and the amount of alcohol added was increased, the alcohol being mixed with the mercuric chloride solution and the whole being cooled to 22° before the sodium hydrogen carbonate solution was added. The effects of methyl, ethyl, and *iso*propyl alcohols are plotted in Fig. 3.

Methyl alcohol (c.c.)	0	1	2	3	4	5	6	7	8	9	10
t (secs.)	67	62	52	47	43	39	37	31	25	22	20
Ethyl alcohol (c.c.) ...	0	1	2	3	4	5	6	7	8	9	
t (secs.)	63	50	34	24	20	15	12	11	11	11	
n-Propyl alcohol (c.c.)	0	0·2	0·4	0·6	0·8	1·0	1·5	2·0			
t (secs.)	63	108	132	143	160	1100	1200	1500			
*iso*Propyl alcohol (c.c.)	0	0·5	1·0	1·5	2·0	2·5	3·0	4·0	5·0		
t (secs.)	63	52	43	35	27·5	22·5	19	16	14		

Glycerol (c.c.)	0	1	2	3
t (secs.)	63	129	165	221

Wt. of substance added.	*t* (secs.).	Wt. of substance added.	*t* (secs.).
nil.	73*	0·0884 g. mannitol	74
0·4309 g. glucose	75	0·1235 ,, ,,	75
0·2345 ,, ,,	74	0·0775 ,, dulcitol	75
0·2034 ,, sucrose	74	0·0926 ,, ,,	75·5
0·1245 ,, ,,	74		

* This mixture was not of the same concentration as the foregoing.

Salts.

For obvious reasons, the effects of acids and alkalis could not be studied, but the action of certain salts, inorganic and organic, was investigated. 5 C.c. of an *M*/10-solution of a salt and 10 c.c. each of mercuric chloride and sodium hydrogen carbonate solutions were taken in each experiment, the temperature being 25°.

TABLE VI.

Substances added.	*t* (secs.).	Substances added.	*t* (secs.).
Water (5 c.c.)	28	Na Citrate	49
NaCl	68	K Citrate	48
KCl	67	Na Oxalate	54
Na_2SO_4	27	K Oxalate	54
K_2SO_4	27	$NaNO_3$	29
Na Tartrate	24	KNO_3	29
K Tartrate	24		

Table VI shows that chlorides, citrates, and oxalates markedly lengthen the period of induction, tartrates diminish it, and sulphates and nitrates have scarcely any action; further, that anions, but not cations, influence the period of induction. This is quite in conformity with the work of Berczeller (*Int. Z. Biol.*, 1916, **2**, 444), who has shown that the effects of salts on the period of induction in the interaction of iodic and sulphurous acids are also dependent on the anions and not on the cations.

Discussion of Results.

The results given above establish the following points :

1. The period of induction is inversely proportional to the concentrations of each reactant, temperature being constant.
2. It diminishes with rise of temperature.
3. It increases with the addition of *n*-propyl alcohol, glycerol, chlorides, oxalates, and citrates, and diminishes with the addition of tartrates and of methyl, ethyl, and *iso*propyl alcohols. Nitrates, glucose, sucrose, mannitol, and dulcitol have no effect on the period of induction.

The present work agrees with Landolt's work on the action of sulphurous and iodic acids (*Ber.*, 1886, **19**, 1317) in that the period of induction in both cases is inversely proportional to the concentrations of the reactants.

The problem now is to determine the reactions which cause this period of induction. In the reaction between iodic and sulphurous acids, the separation of iodine is supposed to take place in several stages through iodous, hypoiodous, and hydriodic acids. In the case of mercuric chloride and sodium hydrogen carbonate, the intermediate reactions are obscure and complex. Under the conditions of our experiments, a red precipitate of the constitution $HgCl_2,2HgO$ is formed along with small quantities of the yellow oxychloride $HgCl_2,3HgO$. The black variety, $HgCl_2,2HgO$, is not formed until the red precipitate has been kept for some days. The formation of these oxychlorides has been reported by many workers, *e.g.*, Biltz (*Arch. Pharm.*, 1869, **190**, 202) and Thummel (*ibid.*, 1889, **27**, 589). It is evident that no carbonate is precipitated, and that carbon dioxide is evolved. Biltz thought that excess of sodium hydrogen carbonate formed a double salt, but Thummel has shown that the precipitate does not contain any mercuric carbonate, carbon dioxide being given off. We are of the opinion that the *formation of the oxychloride by the action of alkali hydrogen carbonate on mercuric chloride can never be instantaneous.* It would be more reasonable to suppose that mercuric carbonate or hydrogen carbonate is first formed and then combines with mercuric chloride in stages with the formation of oxychlorides and liberation of carbon dioxide. The work of previous workers shows that the two oxychlorides, $HgCl_2,2HgO$ (red) and $HgCl_2,3HgO$ (yellow), are precipitated, whilst the unstable $2HgCl_2,HgO$ and $HgCl_2,HgO$ are probably formed as intermediate compounds, *e.g.* :

$$Hg(HCO_3)_2 + 2HgCl_2 = 2HgCl_2,HgO \text{ (unstable) } + 2CO_2 + H_2O;$$
$$2HgCl_2,HgO + Hg(HCO_3)_2 = 2HgCl_2,2HgO \text{ (unstable) } + 2CO_2 + H_2O.$$

Since the velocity of a reaction is proportional to the amount of the reacting substances, the speed of the formation of the red oxychloride is the result of the velocities of successive reactions such as those above, and the belated appearance of the red precipitate—the period of induction—corresponds with the time required for the consecutive reactions to take place before the actual precipitation of the red compound could commence. The fact that mercuric chloride is very feebly ionised in aqueous solution accounts for the smallness of the precipitate. That it has material influence on the period of induction also will be apparent from the following considerations :

(*a*) The slight ionisation of mercuric chloride in aqueous solution does not greatly increase with further dilution, and the number of ions present in solutions in which the concentration of mercuric chloride gradually diminishes therefore becomes less and less. As the velocity of ionic reactions depends on the concentration of the ions, it is evident that with further dilution the velocities of the intermediate reactions would be retarded, and hence the period of induction would increase.

(*b*) Arrhenius and others have shown that the ionisation of mercuric chloride increases in the presence of alcohols. This would explain the relatively large precipitate with alcoholic solutions of mercuric chloride and also the decrease in the period of induction in the case of methyl and ethyl alcohols, for, with increased ionisation, the velocities of the intermediate reactions would increase and hence the period of induction would decrease.

(*c*) Since rise of temperature also increases ionisation, the period of induction would decrease owing to the increased velocities of the intermediate reactions.

The action of methyl, ethyl, and *iso*propyl alcohols in shortening the period of induction may also be due to catalytic action. Their presence hastens the rates of the intermediate reactions, for it has been shown by Thummel (*Arch. Pharm.*, 1889), **27**, 589 that alcohols readily decompose the oxydichloride to the red dioxychloride. The catalytic effect of the alcohols in this case increases with their concentrations to a certain limit. Sodium chloride inhibits the reactions owing to the formation of double salts with mercuric chloride. The action of glycerol, nitrates, citrates, tartrates, and oxalates is probably catalytic in nature.

Conclusions.

1. A distinct period of induction precedes the precipitation of the red oxychloride in the interaction between mercuric chloride and sodium hydrogen carbonate.

2 The period of induction is inversely proportional to the concentration of each reactant, the temperature of the system being constant.

3. It diminishes as the temperature is raised, evidently owing to the increased velocities of intermediate reactions. It diminishes approximately at the rate of 5 seconds for a temperature increase of 10°.

4. The period of induction is the result of several successive reactions which take place before the final appearance of the red dioxychloride of mercury.

5. It diminishes with the addition of methyl, ethyl, or *iso*propyl alcohol or of tartrates, and increases with the addition of glycerol, *n*-propyl alcohol, chlorides, citrates, and oxalates. Sugars, such as glucose and sucrose, and polyhydric alcohols, such as mannitol and dulcitol, as well as nitrates and sulphates have scarcely any effect on the period of induction. The period of induction is influenced by the anions of salts and not by the cations.

6. The reaction is not photochemical in nature.

7. The feeble ionisation of mercuric chloride in aqueous solution explains the small quantity of precipitate produced. It has material influence on the period of induction also, since, owing to the low concentrations of ions on further dilution, the velocities of the intermediate reactions would be lessened and therefore the period of induction would increase. The reverse result is obtained when the ionisation of mercuric chloride is increased by the presence of methyl and ethyl alcohols or by raising the temperature.

8. A very dilute solution of mercuric chloride and sodium hydrogen carbonate may be used to distinguish between *n*- and *iso*-propyl alcohols: with the latter the precipitate of the red oxychloride appears within a few seconds, whilst with the normal alcohol the precipitation takes much longer—even more than $\frac{1}{2}$ hour.

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