165. *Induction Periods in Chemical Reactions. The Action of Phosphorous Acid on Alkali Bromate and Iodate.*

By Panchanan Neogi, Binayendra N. Sen, and Sudhamoy Mukherjee.

In continuation of our investigation on the induction period in chemical reactions (Neogi and Neogi, J., 1927, 30; Neogi and Mukherjee, *J. Indian Chem. Soc.*, 1929, **6**, 529; Neogi and Sen, *ibid.*, 1931, **8**, 725), we observed that in the reduction of bromates and iodates by phosphorous acid, a considerable time elapses before bromine or iodine appears. In the former case, the period of induction is very long, and this is probably responsible for Vitali's statement (*Boll. Chim. Farm.*, 1899, **38**, 201) that bromates (in contrast to iodates) do not react thus.

The induction period is now shown to be due to successive reactions, as in our previous work (*loc. cit.*), and we record the effect thereon of changes in conditions of concentration, temperature, and presence of additional substances, *e.g.*, alcohols, glycerol, and salts.

Experimental.

The period of induction was measured in the manner indicated in any of our previous communications (*locc. cit.*). The concentrations are given in g.-mols. per litre and are indicated by C with the appropriate subscript; T is the induction period in seconds.

Influence of Concentration.—The induction period is approximately inversely proportional to the concentration of either reagent in three of the series shown in the tables, but when the acid concentration is varied, that of the bromate remaining constant, the product of concentration and induction period increases indefinitely.

$NaIO_3$ and H_3PO_3.

$C_{H_3PO_3} = 4{\cdot}3220$. Temp., 30°.

C_{NaIO_3}.	T.	$K_1 = C_{NaIO_3} \times T$.
0·1404	6·6	0·9266
0·0702	12·3	0·8635
0·03650	24	0·8760
0·01990	43	0·8557
0·01404	64	0·8986
0·00995	84	0·8358
0·00842	102	0·8592
0·00348	242	0·8449
		Mean 0·8700

$K' = K_1 \times C_{H_3PO_3} = 3{\cdot}760$.

$KBrO_3$ and H_3PO_3.

$C_{KBrO_3} = 0{\cdot}327$. Temp., 30°.

$C_{H_3PO_3}$.	T.	$C_{H_3PO_3}$.	T.
3·98	19	1·79	68
3·58	22·7	1·51	93
3·46	24·6	1·39	104
3·26	30	1·19	125
2·98	32·8	0·995	161
2·51	41	0·716	237
2·19	49		

$NaIO_3$ and H_3PO_3.

$C_{NaIO_3} = 0{\cdot}1404$. Temp., 30°.

$C_{H_3PO_3}$.	T.	$K_2 = C_{H_3PO_3} \times T$.
4·322	6·6	28·53
2·161	12·4	26·80
1·318	20·4	26·90
1·080	26	28·08
0·6483	42	27·24
0·5931	45	26·70
0·3084	86	26·52
0·1850	145	26·82
		Mean 27·19

$K' = K_2 \times C_{NaIO_3} = 3{\cdot}817$.

$KBrO_3$ and H_3PO_3.

$C_{H_3PO_3} = 6{\cdot}13$. Temp., 29°.

C_{KBrO_3}.	T.	$K = C_{KBrO_3} \times T$.
0·259	16·5	4·27
0·219	19·4	4·25
0·186	22·8	4·24
0·159	26·8	4·26
0·133	32·0	4·26
0·113	38·3	4·33
0·0896	47·2	4·23
0·0730	59·0	4·31
0·0564	75·0	4·26
0·0365	117·0	4·27

Influence of Temperature.—The period of induction decreases with rise of temperature and the relation can be expressed by $\log T = a - bt$, where t is the temperature and a and b are constants, as shown by the following table, in which b was calculated for successive intervals from the relation $b = (\log T_1/T_2)/(t_2 - t_1)$. In the corresponding reaction with sodium iodate, b was constant at the same value, but a fell continuously from 2·352 at 30° to 1·441 at 70° ($C_{H_3PO_3} = 0{\cdot}817$; $C_{NaIO_3} = 0{\cdot}02528$).

$KBrO_3$ and H_3PO_3.

$C_{H_3PO_3} = 1{\cdot}596$; $C_{KBrO_3} = 0{\cdot}2073$.

t	30°	35°	40°	45°	50°	55°	60°	65°	70°
T	172	130	97	73	56	42	31·2	23·3	17·6
b		0·024	0·025	0·025	0·023	0·025	0·026	0·025	0·024
$a = \log T + bt$ ...	2·974	2·975	2·971	2·970	2·978	2·979	2·970	2·967	2·968

Influence of Alcohols.—A point of interest is the difference in the influence of the two isomeric propyl alcohols, the normal alcohol causing an increase and the *iso*- a decrease in the induction period. Similar differences had previously been found (*locc. cit.*) in the reactions between sodium iodate and hypophosphorous acid and between mercuric chloride and sodium bicarbonate.

Periods of induction (secs.) for additions of alcohols.

$C_{H_3PO_3} = 2{\cdot}191$; $C_{NaIO_3} = 0{\cdot}0816$; Temp. = 31°.

C.c. of alcohol added.	0.	1.	2.	4.	6.	8.
MeOH	20	22·6	25	34	38	46
EtOH	20	29	35	93	159	218
Pr$^{\alpha}$OH	20	1920	3600			
Pr$^{\beta}$OH	20	24·2	28·4	35	56	144
Bu$^{\alpha}$OH	20	262	412	680		

$C_{H_3PO_3} = 2{\cdot}39$; $C_{KBrO_3} = 0{\cdot}335$; Temp. = 25°.

MeOH, drops	0	1	2	3	4	10
T	62	23	15	11	7·5	4·2

$C_{H_3PO_3} = 1{\cdot}60$; $C_{KBrO_3} = 0{\cdot}335$; Temp. = 25°.

EtOH, drops	0	2	4	6	8	10	15	30
T	105	62	50·6	39	31	24·6	16·4	10·7
Pr$^{\alpha}$OH, c.c.	0	1	2	3	4	5	6	
T	105	151	164	181	206	235	274	

$C_{H_3PO_3} = 2{\cdot}39$; $C_{KBrO_3} = 0{\cdot}207$; Temp. = 28°.

Pr$^{\beta}$OH, drops	0	10	15	20	30	40	50	80	
T	71	44	36	30	19	13·8	9·4	0	
Bu$^{\alpha}$OH, drops	0	5	10	15	20	30	40	50	80
T	71	46	39	32·5	28·5	22	16·5	14	10

Influence of Glycerol.

$C_{H_3PO_3} = 2{\cdot}191$; $C_{NaIO_3} = 0{\cdot}0816$; Temp. = 30·8°.

Glycerol, c.c.	0	1	2	4	6	8	10
T	20	29	36	61	109	181	228

$C_{H_3PO_3} = 2{\cdot}01$; $C_{KBrO_3} = 0{\cdot}310$; Temp. = 30°.

Glycerol, drops	0	2	4	6	8	12	20	31	40
T	56	44·5	36	31	25·5	10·6	14·6	9·6	6·7

Influence of Mineral Acid.

$C_{H_3PO_3} = 2{\cdot}3991$; $C_{NaIO_3} = 0{\cdot}0306$; Temp. = 31°.

0·310N-HCl, c.c.	0	1	2	4	6	8
T	55	51	46	38	29	19

$C_{H_3PO_3} = 2{\cdot}01$; $C_{KBrO_3} = 0{\cdot}310$; Temp. = 26°.

1·080N-HCl, drops	0	1	2	3	4	5	(1 c.c.)
T	56	41	25	17·2	13·5	12·4	8·8

Influence of Sodium Thiosulphate.

$C_{H_3PO_3} = 1{\cdot}331$; $C_{NaIO_3} = 0{\cdot}01102$; Temp. = 30·8°.

$8{\cdot}556 \times 10^{-5}N$-$Na_2S_2O_3$, c.c.	0	1	2	3	4	5
T	250	22	16·4	7	3·6	0

$C_{H_3PO_3} = 2{\cdot}01$; $C_{KBrO_3} = 0{\cdot}310$; Temp. = 25°.

0·00841N-$Na_2S_2O_3$, drops	0	1	2	3	4	5	6	8
T	60	53	41	32	25	21	18	14

Influence of Sulphur Sol.

$C_{H_3PO_3} = 3{\cdot}076$; $C_{NaIO_3} = 0{\cdot}0139$; Temp. = 30°.

Sulphur sol, drops	0	4	6	8	10	15	40
T	86	73	39	17·6	10	5·2	0

$C_{H_3PO_3} = 2{\cdot}042$; $C_{KBrO_3} = 0{\cdot}0806$; Temp. = 28·6°.

Sulphur sol, c.c.	0	1	2	3	4	5
T	230	67	50	46	31	22

Influence of Salts.—The induction period is affected by anions but not by kations. For each salt, the volume of the reaction mixture was 20 c.c.

$C_{H_3PO_2} = 2{\cdot}01$; $C_{KBrO_3} = 0{\cdot}322$; Temp. = 25°

Salt.	Wt., g.	*T.*	Salt.	Wt., g.	*T.*	Salt.	Wt., g.	*T.*
(None)	—	61	KCl	0·373	2	Na_2SO_4	0·808	93
$KHC_4H_4O_6$	0·262	74	NaCl	0·292	5	KNO_3	0·505	88
$NaHC_4H_4O_6$	0·194	72	K_2SO_4	0·435	94	$NaNO_3$	0·425	87

Influence of Geometrical and Optical Isomerides.—It will be seen that fumaric acid lengthens the period, and maleic acid shortens it slightly. Both the tartaric acids cause diminution in the period but to different extents, the *d*-acid having greater influence than its antipode. Similar observation was made by Neogi and Sen (*loc. cit.*) on the influence of these isomerides on the reaction between sodium iodate and hypophosphorous acid.

$C_{H_3PO_2} = 4{\cdot}322$; $C_{NaIO_3} = 0{\cdot}01404$; Temp. = 30°.

Substance.	Weight, g.	*T.*	Substance.	Weight, g.	*T.*
(None)	—	64	*d*-Tartaric acid...........	0·0311	21
Fumaric acid	0·015	93	*l*-Tartaric acid	0·0311	49
Maleic acid	0·015	56			

Wall Effect.—In order to see if there was any wall effect in these reactions, the glass surface was increased by addition of various amounts of purified glass-wool to the reacting solutions but in no experiment was the induction period sensibly altered from its original value. The reactions thus seem to be purely homogeneous.

PRESIDENCY COLLEGE, CALCUTTA. [*Received, March 27th,* 1933.]