The Effect of the Silent Electrical Discharge on the Synthesis of Monochloroacetic Acid.

By Yutaka ISOMURA.

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I. Red Phosphorus as Catalyser.

Monochloroacetic acid has been simply prepared with catalysers such as red phosphorus,(1) iodine,(1) sulphur,(2) etc., by bubbling vigorously gaseous chlorine into acetic acid in direct sun-light and its yield has never exceeded 60.6%.(3) In the present research, instead of direct sunlight, the silent electrical discharge was applied for the activation of chlorine and it was found that the discharge is so effective as to increase 15–100% of the best yield of monochloroacetic acid ever obtained.

Apparatus. The usual apparatus (Fig. 1) was improved as shown in Fig. 2, to increase the effect of the discharge. An induction coil is used (primary circuit: constant current of 3 A., 8 V.; secondary circuit: 0.25 mA., 14000 V.).

Experimental. At every run of experiments the followings have been kept the same: temperature, 100°C., 7 g. of red phosphorus, and 70 c.c. of acetic acid (99–100%), while the volume of chlorine passed

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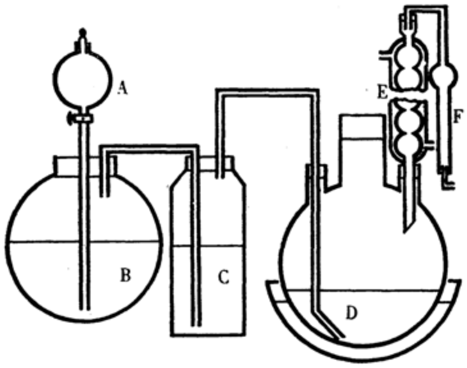
(1) H. Müller, *Ann.*, **133** (1865), 156.

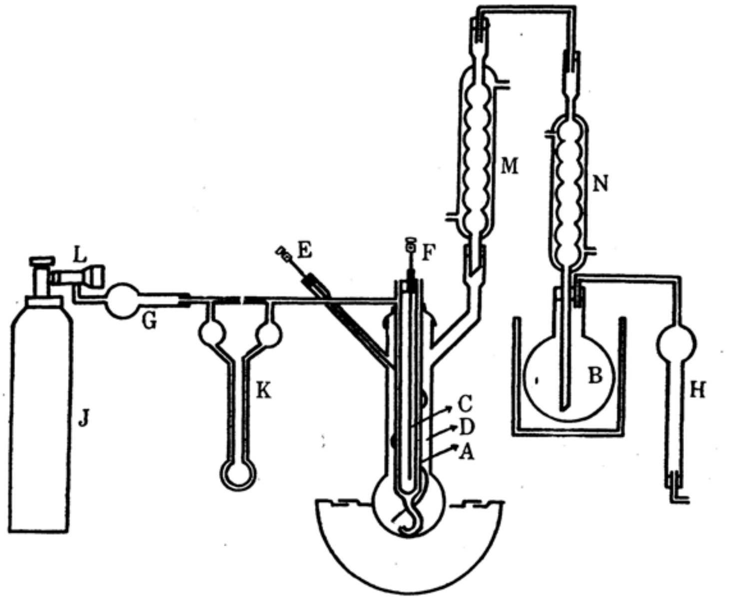
(2) Anger and Behall, *Bull. soc. chim.*, [3], **2** (1889), 145.

(3) Cohen, "Practical Organic Chemistry", 106, London (1930).



A : Conc. H_2SO_4
B : $CaOCl_2$
C : Conc. H_2SO_4
D : CH_3COOH + catalyser
E : 50 cm. Liebig Condenser
F : $CaCl_2$ tube.

Fig. 1.



A : Outside electrode.
B : CH_3COCl collector. (cooled by immersing in ice water)
C : Inner electrode in dil. H_2SO_4.
D : CH_3COOH + catalyser.
E : To the earth.
F : To the secondary circuit of the induction coil.
G, H : $CaCl_2$ tube.
J : Cl_2 bomb.
K : Cl_2 flowmeter.
L : Microdrive auxiliary valve.
M : 50 cm. Liebig condenser.
N : 40 cm. Liebig condenser.

Fig. 2.

into acetic acid in unit time and the duration of the reaction have been varied. The experimental results are shown in Table 1–3, and Fig. 3–8.

There is a linear relation between the pressure difference of chlorine in the flowmeter and the volume of chlorine bubbled into acetic acid per minute, as in shown in Fig. 3.

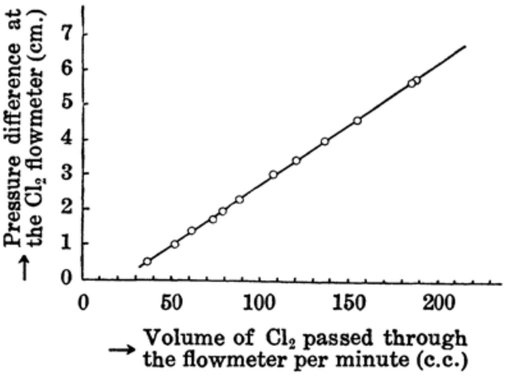


Fig. 3.

Careful observations of the reaction permit attention to the following points as to the mechanism of the reaction.

(1) An abundant quantity of acetyl chloride is formed in the reaction.

(2) The behaviour of phosphorus as catalyser is not a simple carrier of chlorine and it is often dissolved completely into the reacting system. By the quantitative analysis on the residue of the distillation, the following substance are found in the extracts by water.

$$CH_3COOH : HCl : H_3PO_4 = 1.3 : 1 : 37.5$$

(3) The equation which was formerly believed to explain the reaction being

$$CH_3COOH + Cl_2 = CH_2ClCOOH + HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (A),$$

the values $\frac{\text{Observed yield of monochloroacetic acid}}{\text{Theoretical yield by the equation (A)}} \times 100$ and $\frac{\text{Volume of chlorine calculated from the yield of monochloroacetic acid by the equation (A)}}{\text{Total chlorine bubbled into the system}} \times 100$ (for example, the yield of monochloroacetic acid by passing 222 c.c. of chlorine per minute for four hours with the discharge), are too small to explain the completion of the reaction as is shown in Table 3.

To clear up these points and to modify the former views about the mechanisms of the reaction, the following new equation is proposed by the author. The equation is made up in a simple form from many individual processes which were previously investigated by Brückner⁽⁴⁾. That is

$$2\,P + 6\,CH_3COOH + 9\,Cl_2 = 2\,CH_3COCl + 6\,HCl$$
$$+ 4\,CH_2ClCOOH + 2\,POCl_3 \quad \ldots\ldots \quad (E).$$

Judging from the values calculated by the equation (E) in the Table 1–3 and in Fig. 4–8, it will be found that the above mentioned points are cleared up by this equation. Though it may not be of an exclusive nature, it will at least indicate the principal mechanism of the reaction.

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(4) Brückner, *Z. angew. Chem.*, **50** (1928), 226.

Table 1. Acetic acid : 70 c.c. ; Duration of reaction : 2 hours ; Catalyser : red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12
Preess. diff. at the Cl_2 flowmeter (cm.)	3	3	4	4	4.5	5	5	6	6	7	7	7
Duration of electric discharge (hours)	—	2	—	2	2	—	2	—	2	—	2	2
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	12.2	12.2	15.2	15.2	16.85	18.55	18.55	21.71	22.63	25.13	25.13	25.15
Total yield of $CH_2ClCOOH$ (g.)	4	6	8	11	14	9	15	11	19	14	26	22
$\frac{CH_2ClCOOH\ \text{produced}}{CH_3COOH\ \text{taken}} \times 100$	5.55	8.17	10.85	15.0	19.1	12.2	20.5	15.0	27.2	19.1	35.5	29.9
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	3.44	5.15	6.88	9.5	12.05	7.75	12.9	9.5	17.2	12.05	22.3	18.93
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	5.18	7.78	10.35	14.18	18.2	11.62	19.5	14.18	26.0	18.2	33.7	28.5
Yield per litre of Cl_2 (g.)	0.33	0.49	0.53	0.73	0.85	0.48	0.82	0.51	0.88	0.56	1.03	0.87
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	7.78	11.66	12.2	17.14	19.7	14.46	19.17	15.3	20.82	13.2	24.52	20.74
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	17.48	26.2	28.06	38.55	44.32	25.85	43.1	34.37	46.83	29.7	55.15	46.6
CH_3COCl in the collector (g.)	2	2	2	2	2	2	3	3	3	3	4	4

Table 2. Acetic acid : 70 c.c. ; Duration of reaction : 3 hours ; Catalyser : red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12	13
Press. diff. at the Cl_2 flowmeter (cm.)	2	2	3	3	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	3	—	3	—	3	—	3	—	3	3	—	3
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	13.52	13.52	18.34	18.56	22.95	22.65	27.93	28.38	32 37	32.91	32.91	37.10	37.8
Total yield of $CH_2ClCOOH$ (g.)	10	17	18	28	25	35	34	45	40	48	49	45	54
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	13.6	23.2	24.5	38.2	34.0	47.7	46.0	61.2	53.6	65.3	66.8	61.2	73.5
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	8.6	14.7	15.4	24.1	21.5	30.1	29.2	38.7	34.4	41.3	42.1	38.7	46.6
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	12.95	22.1	23.3	36.3	32.3	45.5	44.0	58.5	52.0	62.2	63.5	58.5	70.0
Yield per litre of Cl_2 (g.)	0.74	1.25	0.99	1.51	1.09	1.55	1.22	1.58	1.24	1.46	1.49	1.21	1.43
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	17.53	29.81	23.10	35.8	25.8	36.6	23.9	37.6	29.3	34.52	35.3	28.8	33.8
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	39.3	67.06	52.35	80.46	57.83	82.4	64.9	84.5	65.9	77.8	79.4	64.7	76.2
CH_3COCl in the collector (g.)	3	3	5	?	8	8	10	8	10	10	6	4	5

Table 3. Acetic acid: 70 c.c.; Duration of reaction: 4 hours; Catalyser: red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11
Press. diff. at the Cl_2 flowmeter (cm.)	1.4	1.4	2	2	2	2	2.75	2.75	2.75	2.75	4
Duration of electric discharge (hours)	—	4	—	—	4	4	—	—	4	4	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	13.97	14.01	17.47	17.92	17.83	17.93	22.31	21.96	22.30	22.14	30.59
Total yield of $CH_2ClCOOH$ (g.)	5	12	9	12.2	19.8	18	15	17	32.3	34.3	30.5
$\frac{CH_2ClCOOH\ \text{produced}}{CH_3COOH\ \text{taken}} \times 100$	6.8	16.3	12.2	16.6	26.9	24.5	20.3	23.0	43.7	46.4	41.5
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	4.3	10.3	7.7	10.5	17.0	15.5	12.9	14.6	27.8	29.5	26.2
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	6.5	15.6	12.2	16.1	25.7	23.3	19.4	22.2	42.0	44.0	39.5
Yield per litre of Cl_2 (g.)	0.36	0.86	0.52	0.67	1.11	1.0	0.67	0.78	1.44	1.56	0.99
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	8.48	20.3	12.2	16.1	26.3	26.5	15.9	18.4	34.4	36.8	23.6
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	19.1	45.7	27.5	36.3	59.2	53.5	35.9	41.3	77.3	82.6	53.2
CH_3COCl in the collector (g.)	3	5	5	8	8	8	8	8	8	10	15

No. of experiments	12	13	14	15	16	17	18	19	20	21
Press. diff. at the Cl_2 flowmeter (cm.)	4	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	4	4	—	4	—	4	4	—	4
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	30.66	30.37	30.70	37.74	36.78	43.78	43.18	43.2	50.86	49.73
Total yield of $CH_2ClCOOH$ (g)	29	47	46	40	62	49	70	68	54	73.
$\frac{CH_2ClCOOH\ \text{produced}}{CH_3COOH\ \text{taken}} \times 100$	39.4	63.9	62.7	53.1	87.0	67.0	95.2	92.5	73.7	99.3
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	25.0	40.4	39.5	34.4	56.0	42.3	60.2	58.5	46.5	62.8
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	37.6	61.0	59.6	51.8	80.5	63.5	91.0	88.0	70.0	94.5
Yield per litre of Cl_2 (g.)	0.94	1.52	1.50	1.06	1.68	1.12	1.62	1.57	1.06	1.47
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	22.4	36.7	35.5	25.1	40.0	26.5	38.4	37.4	25.5	34.8
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	50.5	82.5	79.9	56.5	89.9	59.6	86.5	83.9	56.6	78.3
CH_3COCl in the collector (g.)	15	3	5	10	10	15	10	15	15	15

In Fig. 4–11

⊙ 2 hours' reaction with discharge

○ 2 hours' reaction without discharge

● 3 hours' reaction with discharge

◑ 3 hours' reaction without discharge

⊗ 4 hours' reaction with discharge

◒ 4 hours' reaction without discharge

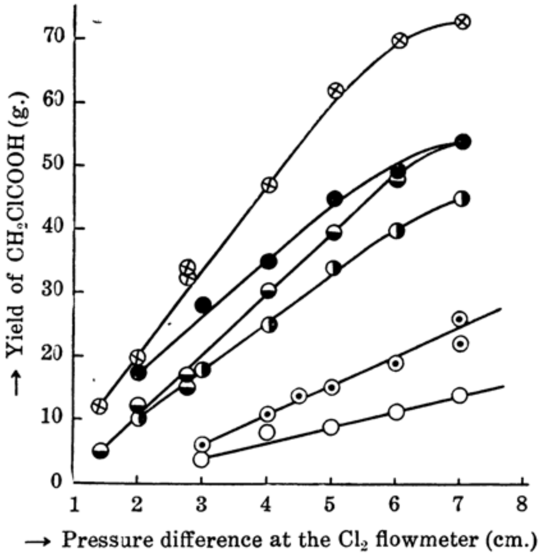

Fig. 4.

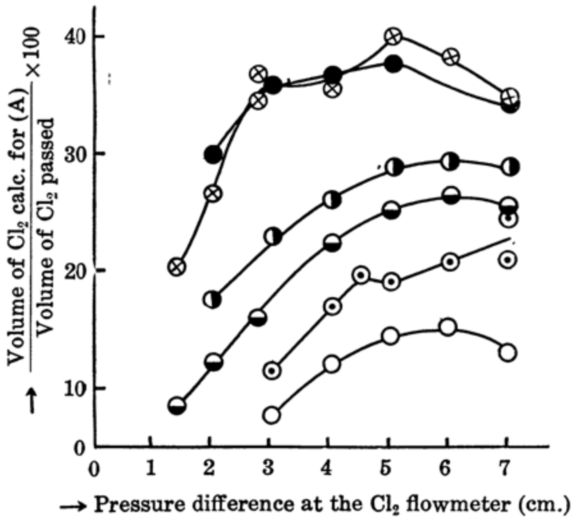

Fig. 5.

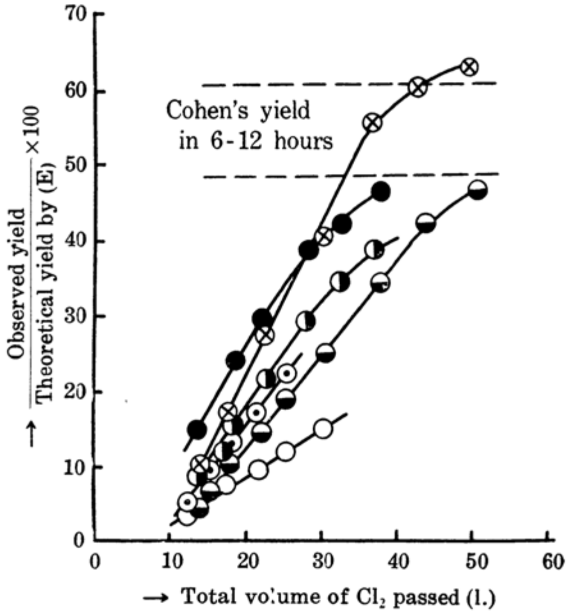

Fig. 6.

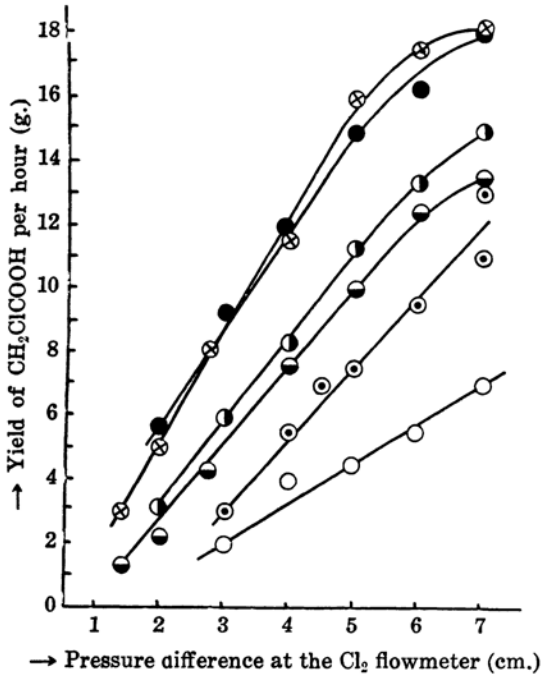

Fig. 7.

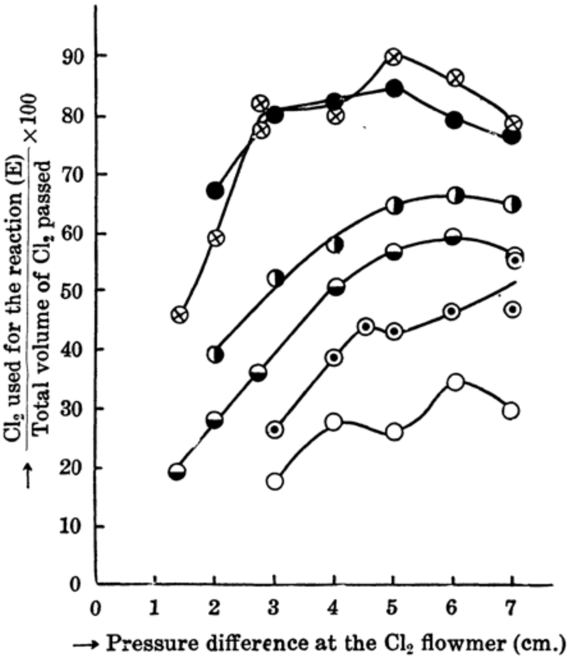

Fig. 8.

II. Iodine, Red Phosphorus, and Phosphorus Pentachloride as Catalyser.

Brückner[(4)] reported that he obtained 66% of monochloroacetic acid in four hours by using 1 g. I_2 + 2 g. P_4 + 2 g. PCl_5 as catalyser and bubbling 245 c.c. of chlorine per minute through acetic acid. This result was so amazing that even now this catalyser maintains its industrial application.

The experiments were carried out by the present author with the same catalyser in much the same way as was previously mentioned and the same results as those of Brückner were obtained. However, by using 1 g. of iodine for 70 c.c. of acetic acid, a great deal of difficulties were found to eliminate iodine vapour from every fraction of the distillation. The amount of iodine was then diminished from 1 g. to 0.2 or 0.1 g. so far as the yield of monochloroacetic acid was not affected. With the modified catalyser, that is 0.1–0.2 g. I_2 + 2 g. P_4 + 2 g. PCl_5, the experiments were carried out to see the effect of the silent electrical discharge on the synthesis of monochloroacetic acid. As the result, the yield of monochloroacetic acid was increased in a great extent and the elimination of iodine from the product was satisfactory by carrying out the distillation at 180–190°C.[(5)]

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(5) Even if 0.1 or 0.2 g. of iodine is used for 70 c.c. of acetic acid, the distillates between 180 and 190°C. have sometimes pinc tint. It is found that 0.5-1% of active charcoal is effective enough to decolourize such a small quantity of iodine in monochloroacetic acid. Iodine is completely adsorped by charcoal at the temperature between 180 and 190°C.

Table 4. Acetic acid : 70 c.c. ; Duration of reaction : 2 hours.

Catalyser	0.1 g. I_2 + 2 g. P_4 (red) + 2 g. PCl_5												1 g. I_2+2 g. P_4+2 g. PCl_5		
No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Brückner (Acetic acid : 100 c.c.)
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	3	4	4	5	5	6	6	6	7	7	5	6	7.9
Duration of electric discharge (hours)	—	2	2	—	2	—	2	—	2	2	—	2	—	2	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	12.0	11.91	11.9	15.18	14.92	17.28	17.28	21.28	21 3	21.49	24.66	25.12	17.77	21.28	29 4
Total yield of $CH_2ClCOOH$ (g.)	22	25	25	30	34	38	43	42	47	51	53	60	40	49	64
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	30.0	34 0	34.0	40.8	46.3	51.8	58.5	57.2	64.0	69.5	72 3	81.8	54 5	66.8	64
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	18.8	21.5	21.5	23.8	29.2	32.7	37.0	36 1	40 5	43.8	45.5	51.2	34.4	42.2	40.6
Yield per hour (g.)	11	12.5	12.5	15	17	19	21.5	21	23 5	25.5	26.5	30	20	24.5	32.0
Yiela per litre of Cl_2 (g.)	1.83	2.09	2.09	1.97	2.28	2.19	2.48	1.97	2.20	2.37	2.15	2.39	2.25	2.30	2.17
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	43.5	49.8	49.8	46.8	54.0	52.1	59.0	46.8	51.2	56.3	51.0	56.5	52.1	54.6	51.6
CH_3COCl in the collector (g.)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	?

Table 5. Acetic acid: 70 c.c.; Duration of reaction: 3 hours; Catalyser: 0.1 g. iodine + 2 g. red phosphorus + 2 g. phosphorus pentachloride.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	3	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	—	3	—	3	—	3	—	3	3	—	3
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	18.25	18.28	18.25	22.96	22.81	27.88	27.88	33.32	33.13	33.13	37.87	38.34
Total yield of $CH_2ClCOOH$ (g.)	44	46	49	59	62	69	77	80	85	84	80	92
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	60.0	62.8	66.8	80.5	84.5	94.0	104.6	108.5	115.6	114.0	108.5	125.0
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	37.8	39.7	42.2	50.8	53.3	59.3	66.2	68.8	73.2	72.2	68.8	79.2
Yield per hour (g.)	14.7	15.3	16.3	19.7	20.7	23.0	25.7	26.7	28.3	28.0	26.7	30.7
Yield per litre of Cl_2 (g.)	2.41	2.51	2.68	2.58	2.72	2.47	2.76	2.40	2.56	2.53	2.11	2.40
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	57.2	59.6	63.6	60.9	64.4	58.7	65.5	56.9	60.8	60.1	50.1	56.9
CH_3COCl in the collector (g.)	2	2	2	2	2	2	2	2	2	2	2	3

Table 6. Acetic acid: 70 c.c.; Duration of reaction: 4 hours; Catalyser: 0.1 g. iodine+2 g. red phosphorus+2 g. phosphorus pentachloride.

No. of experiments	1	2	3	4	5	6	Bruckner (Acetic acid: 100 c.c. $1g. I_2+2g. P_4+2g. PCl_5$)
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	4	4	5	5	7.9
Duration of electric discharge (hours)	—	4	—	4	—	4	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	24.43	24.43	30.46	30.46	36.94	36.91	58.8
Total yield of $CH_2ClCOOH$ (g.)	68	74	84	88	90	93	104
$\frac{CH_2ClCOOH\text{ produced}}{CH_3COOH\text{ taken}} \times 100$	92.6	100.6	114	119 5	122.5	126.5	104
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	58.5	63.5	72.0	75.5	77.4	80.0	66.0
Yield per hour (g.)	17	18.5	21	22	22.5	23.3	19.1
Yield per litre of Cl_2 (g.)	2.78	3.03	2.76	2.89	2.43	2.52	1.77
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	66.0	71.8	65.4	68.5	57.7	59.7	41.9
CH_3COCl in the collector (g.)	3	3	3	3	3	3	?

From the experiments the followings can be perceived.

(1) Iodine is dissolved in acetic acid as ICl or ICl_3 and thus serves for the equal distribution of chlorine in the system. By the thermal decomposition in the distillation, iodine is again set free from ICl or ICl_3 and is mixed in every distillate.

(2) The yield of acetyl chloride is far less than that of the previous experiment (only 2.5 g in four hours).

(3) Phosphorus pentachloride serves to produce acetyl chloride in adequate amount and velocity.

(4) Sometimes a part of phosphorus is dissolved, but in the majority of the experiments it maintains its initial amount, and the yield of monochloroacetic acid never fluctuates as it does otherwise by the diminution of the amount of phosphorus.

From the above mentioned facts we may conclude that the main mechanism of the reaction is expressed by the equation (A), and that the added substances take rôle of the catalyser.

Not only from the above mentioned facts, but also from the values calculated by the equation (A) as is shown in Table 4–6, and Fig. 9–11, the equation seems to be correct.

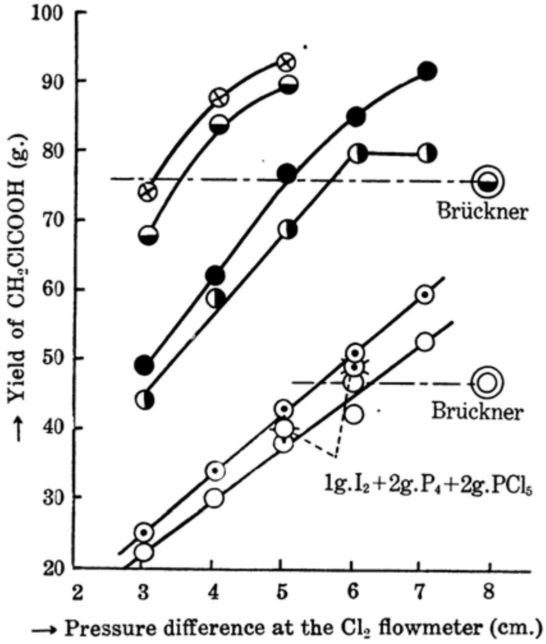

Fig 9.

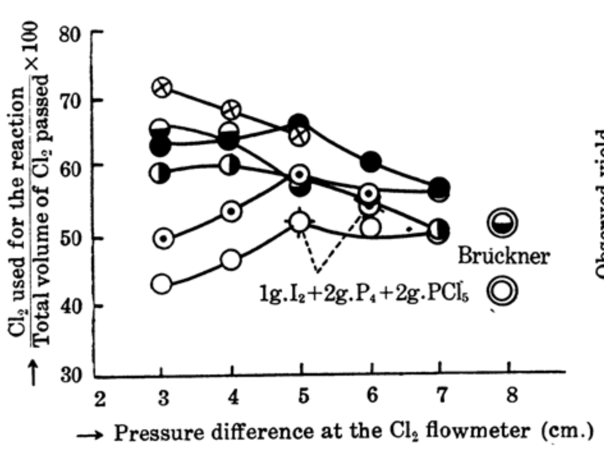

Fig. 10.

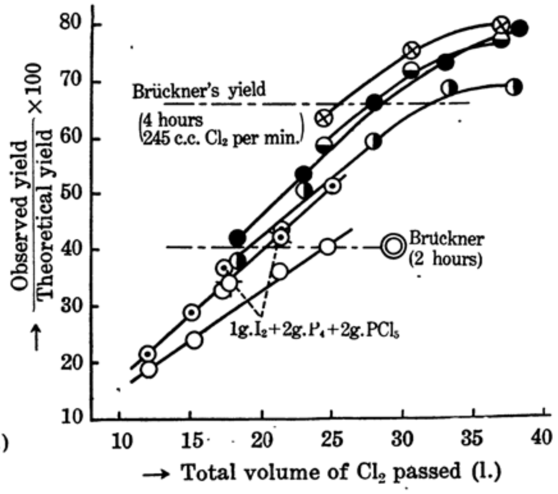

Fig. 11.

Summary.

(1) Silent electrical discharge is very effective to produce monochloroacetic acid from acetic acid and chlorine by using red phosphorus as catalyser, and it increases 15–100% of the yield of monochloroacetic acid compared with the formerly obtained results. The yield of 62.8% in four hours running is one of the best record that is attained in the experiment using red phosphorus (10%) as catalyser. A new equation (E) is proposed to clear up several questions involved in the formerly believed equation (A).

(2) The reaction between acetic acid and chlorine was carried out under the influence of the silent electrical discharge, using iodine, red phosphorus, and phosphorus pentachloride as catalyser. The reaction is expressed by the equation (A). The yields of 79.2% in the reaction for three hours discharge and 80.0%, for four hours discharge, are far better than the yield of 66% reported by Brückner. This is chiefly due to the effect of the new modified catalyser and of the silent electrical discharge.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.