RESEARCHES ON CHEMICAL CHANGES UNDER A STRONG ELECTRIC FIELD.

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Introduction. Many reports on the studies of the chemical changes and equilibria between different gasses due to high tension electric discharges such as silent-, brush-, point-, spark-, and arc discharge, etc. are found in every periodical of that part. But those studies between gases and liquids are rare, and the results are divergent. In this experiment a new method was devised to apply extremely strong electric field to the reacting substances both safely and efficiently.

Principles and Methods. When a small gas bubble (dielectric constant $=\epsilon_g$) was placed in a dielectric liquid, which is under the action of uniform electric force E_l, the force on the bubble is given by the equation

$$E_g = \frac{3}{2+\frac{\epsilon_g}{\epsilon_l}} E_l$$

It is general that $\epsilon_g/\epsilon_l < 1$, therefore the force acting on the gas bubble is stronger than that on the surrounding dielectric liquid, or, when a certain electric potential is applied between the electrodes, the force acting on the gas bubble must be stronger than that when the whole dielectric is a gas. As the dielectric strength of a liquid is generally stronger than that of a gas, it is able to generate a corona discharge in a gas in this way without causing any breaking down of the materials.

Now, let the distance between the two parallel electrodes be L, the potential difference of the electrodes V, and the space be filled with a gas ($\epsilon_a=1$), then the electric displacement is

$$D = \frac{V}{4\pi L},$$

and the electric force

$$E_a = 4\pi \frac{D}{\epsilon_a} = \frac{V}{L},$$

Divide the space between the two electrodes into several layers (a, b, c, etc.) of thickness l_a, l_b, l_c, etc., and fill the each layer with different dielectric material of dielectric constant ϵ_a, ϵ_b, ϵ_c, etc. respectively, then the force in (a) becomes

$$E_a = 4\pi \frac{D'}{\epsilon_a} = \frac{V}{l_a + \frac{l_b}{\epsilon_b} + \frac{l_c}{\epsilon_c} + \ldots}$$

Comparing E_a and E_a' we have

$$E_a' = E_a \frac{L}{l_a + \frac{l_b}{\epsilon_b} + \frac{l_c}{\epsilon_c} + \ldots}$$

If $\epsilon_b > 1$, $\epsilon_c > 1, \ldots\ldots$, then $E_a' > E_a$.

This indicates that, selecting proper materials, the force on a special layer (here a gas) is able to make stronger than usual. It is also able to increase the electric strength of the layer in this way, and we can safely raise the applied voltage to a higher value than usual.

In this experiment, several reaction vessels were devised, but the concentric cylindrical tubes, consisting of layers of glass wall and dielectric liquids, showed to be the most convenient for the purpose. The innermost tube and outermost glass vessel, containing electrolyte solution, play the rôle of the electrodes. The reaction vessel is made of four concentric tubes A, B, C and D. The innermost tube A, containing an electrolyte solution, is used as the inner electrode. The second tube B, surrounding A, gives a passage to the reacting gases. The third tube C, surrounding B, contains the reacting liquids through which the reacting gas is bubbled up. The outermost protective tube D contains dielectric liquids such as liquid paraffine, nitrobenzene or some oils. The cylinder D is placed in water, in which the outer electrode is put.

If there are no liquids in C- and D-tube of this apparatus, the corona discharge in B will occur only when the electric force (in KV.) on the surface of A reaches the following value:

$$E = 30 + \frac{9}{\sqrt{r}} \quad (r\text{: radius of A in cm.})$$

In this experiment the applied voltage was 40–60 KV. and the reaction tubes were made of proper sizes to produce corona discharge in B, which activates the reacting gas in it. When the corona sets in, the value of ϵ of that part becomes very great and the whole voltage distributes mainly between C and D. It is evident that the distribution of the force is inversely proportional to ϵ_c and ϵ_d.

The gas, formerly activated in this way, then comes into C and mixes with the liquid in it. Here the gas, being still acted by the strong electric force, which is very irregular in C, becomes very fine particles in some cases and readily reacts with the surrounding liquid. When it is observed in the dark, every particle has pale light and some of them are scintillating. This dispersion of the gas will partly be due to the heterogeneous distribution of the electric force and partly due to the change of surface tension of the liquid film enclosing the gas bubbles. The dispersion of the gas bubbles will also be affected by the dielectric constant, viscosity and temperature of the dielectrics. In this experiment it was observed in the cases of unsaturated oils, and not in the cases of nitrobenzene and acetic acid.

Experimental Results. The cases studied in this experiment are:

1. reduction of nitrobenzene, methylene blue and benzaldehyde,
2. hydrogenation of oleic acid, silkworm pupa oil, cod-liver oil, fish oil, soy-bean oil and olive oil with hydrogen,
3. ozonisation of oleic acid and olive oil with oxygen,
4. chlorination of acetic acid with chlorine,
5. reaction of nitrogen and hydrogen to ammonia in oleic acid,
6. also the effect of temperature and that of the presence of metallic powder (catalyser) on the hydrogenation of oils.

The results are summarized in Table 1. The products were chemically tested in some cases (iodine value and solubilities, etc.), and physically in other cases (refractive indices, microscopic study, etc.) The rate of reduction was calculated by measuring the change of iodine value. The index of refraction ($n_D^{25°}$) was also measured in most cases. From these results it will not be too much to say that this is not only a new method of hydrogenation and ozonization of some organic dielectrics, but also a new method of ammonia synthesis by electric discharge. The effect of temperature elevation or addition of metallic powders such as Cu, Al, Fe (till 100°C.) is not eminent in this method, but the presence of reduced Ni is somewhat effective, especially when the temperature was elevated up to 100–120°C. These effects were studied in cases of hydrogenation of oils, but the details will be omitted here.

The following interest phenomenon has, however, to be mentioned, which was observed when the electric force was applied on the reacting system of oil and hydrogen in the tube with the metallic catalyser of Cu or Al powder. The metallic powders arrange themselves under the electric field along the wall of the glass cylinder in beautiful figures very much like the common cypress leaves. In the case of Fe powder, the figure was quite different, a ring of scintillating zone of Fe powder was observed in the upper part of the reaction tube. The width of the zone was seemed to grow inversely with the elevation of applied voltage. The appearance, growth and extinction of these dust figures are very interesting, and it will give some suggestion to experimental crystal-physics.

Table 1.

No. of Exp.		Substance	Gas	Time in hours	Amount of reduction	Reduction per hour	Results
I	a	Nitrobenzene	H_2	25			Change of colour, formation of a resinous and cryst. matter, pale yellow rhombic needle (probably azoxybenzene)
	b	Methylene blue (chloroform)	,,	5			No appreciable change
	c	Benzaldehyde	,,	29			Change was not determined
	d	Silkworm pupa oil	,,	36.5	12.7%	0.35%	Discoloration, red to white, formation of white turbidity
	e	Cod-liver oil	,,	68.5	29.9%	0.44	Increase of viscosity, formation of semitransparent solid
	f	Fish oil	,,	ca. 60	19.4	0.35	Discoloration, crystalline ppts.
	h	Olive oil	,,	26.5	8.9	0.34	Reduction prod. of 5 kinds
	i	Oleic acid	,,	39.5	21.2	0.54	Formation of stearic acid
	i′	,,	,,	48	16.3	0.34	
II	a	Aniline	O_2	15	n_D^{25} 1.58328 →	1.58304	No appreciable change
	b	Oleic acid	O_2	24	1.46034 →	1.46510	Formation of ozonide, increase of viscosity and odour
	c	Olive oil	O_2	7			Ozonized
III	a	Oleic acid	N_2	17			No change
	b	,,	$2H_2+N_2$	1.5			Some change occurred but undetermined. Formation of NH_3
IV	a	Acetic acid	Cl_2	2.5			No appreciable change
V	a	Soy-bean oil	H_2	0.5			Undetermined, 180°C.
	b	Oleic acid	,,	24	8.8	0.37	100–200°C.

In order to explain whether the chief cause of activation of the reaction is the strong electric force or the ultraviolet light produced thereby in the gas bubbles in the reaction tube, some experiments were carried out by means of an ultraviolet light generator (Acme's Sun Light), and it was verified that the ultraviolet light had also the effect of the like but the quantitative comparison has been a matter of very difficult.

Summary.

1. A new method was devised to apply extremely strong electric force to gases and dielectric liquids, and accelerate their reactions.

2. Using this method, many reactions between gases and liquids under the action of strong electric force were studied. Thereby the effect of temperature elevation and presence of metallic powders (catalyser) were also studied.

3. In connecting with the electric discharge some interesting phenomena were observed.

The most part of this experiment was carried out about four years ago (1925-26) as the graduation thesis of the Tokyo Imperial University, Faculty of Science, under the guidance of Dr. Y. Yamaguti, to whom the author expresses his best thanks. This sort of experiments should be continued by the author, but his condition is now to give up his hope for some time, and he has been obliged to write the report still on its middle way.

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