

“On the Oxidising Action of the Rays from Radium Bromide as shown by the Decomposition of Iodoform.” By W. B. HARDY, F.R.S., Caius College, Cambridge, and Miss E. G. WILLCOCK, Newnham College, Cambridge. Received July 21, 1903.

In the course of certain experiments one of us noticed that a solution of crystals of pure iodoform in chloroform rapidly became purple. The colour change is due to the liberation of iodine, and the purple solution readily gives the starch test, and is decolourised by thiosulphate. This decomposition of iodoform occurs in a variety of solvents, namely, in chloroform, benzene, carbon bisulphide, carbon tetrachloride, pyridene, amyl alcohol, and ethylic alcohol. In alcohol the change is shown only by a deepening of the original yellow tint of the solution to brown; iodine when dissolved in alcohol having a yellow-brown tint.

As the reaction itself seems not to have been described, a few words may be devoted to it before passing to the main point—namely, the influence of the rays from radium upon this chemical change.

The liberation of the iodine needs the presence of oxygen—though exceedingly minute amounts are sufficient—and some form of radiant energy. When oxygen is washed out by a stream of  $\text{CO}_2$ , or the vapour of the solvent, no change takes place; the solution of iodoform retains its faint yellow tint in full daylight.

If a minute quantity of oxygen be left behind, the colour deepens in daylight to a brownish-yellow, but iodine is not liberated—the solution will not give the starch test. That is to say, there is an intermediate stage of chemical change which is reached in presence of minute amounts of oxygen, and which falls short of the actual liberation of iodine.

If a pair of platinum electrodes be dipped in a solution which is in process of changing to purple, and a field ( $\pm 4$  volts per centimetre) be established, a heavy, oily, colourless liquid slowly drips from each electrode. The nature of this liquid has not yet been determined, but from its specific gravity probably it is methylene iodide.

In the complete absence of any radiant energy, and in presence of abundant oxygen, the solution of iodoform undergoes no change at ordinary temperatures. When heated to near the boiling point, however, the solutions change even in the dark.

Salts, when present, have a remarkable influence on the reaction, although they can hardly be said to be soluble in the reagents employed. For instance, if a solution of iodoform in benzene be divided into two parts, and to one part solid sodium chloride be added, and then both be heated, the one with the salt decomposes much more rapidly. Compared in this way, it was found that

NaCl; KCl;  $\text{KNO}_3$ ;  $\text{Pb}(\text{NO}_3)_2$ ;  $\text{Ba}(\text{NO}_3)_2$ ;  $\text{BaCl}_2$  accelerate  
 $\text{K}_2\text{SO}_4$ ;  $\text{CaCO}_3$ ;  $\text{BaSO}_4$ ;  $\text{MgCO}_3$  retard.

It is remarkable that the salts which were tried should so group themselves that those with univalent acids accelerate, those with bivalent acids retard.

The influence of salts appears to be purely a case of surface action. If the salt first be heated for a few minutes with two changes of the solvent (benzene), it entirely loses its power.\*

Probably owing to obscure catalytic action of this kind one finds that in certain apparently clean test-tubes the very sensitive solution of iodoform in chloroform changes to purple even in the dark. The catalysing power of such a tube, however, is very rapidly exhausted.

Probably also owing to catalytic action some samples of iodoform decompose when dissolved in chloroform even in complete darkness. The impurity which brings about this apparently spontaneous change can be distilled off by suspending the sample in water and boiling for a considerable time. The first distillate condenses as a red liquid, when this ceases to come over the distillate will be found to be approximately or quite stable. The impurity can be got rid of more effectively by recrystallising from ethylic alcohol.

The chemical feature on which we wish to lay most stress is that for the liberation of iodine oxygen is needed—it is in all probability due to an oxidation, and, like many oxidation processes, it is carried on, under ordinary circumstances and at ordinary temperatures, only in the presence of light.

The reaction, on the one hand, is a delicate test for the presence of oxygen, on the other, a convenient method for measuring the chemical activity of various rays. We found the trace of oxygen which remains after  $\text{CO}_2$  has been bubbled through the chloroform, and over the iodoform for one hour, sufficient to produce a decisive change of tint.

The beautiful purple colour which the liberated iodine makes in solvents other than alcohol, lends itself readily to measurements which may be made by choosing some solution of iodine in chloroform as a standard colour and matching the fluids under examination with it.

The reaction, when once started, continues for a time in absolute darkness and then ceases. Thus, if light be allowed to play upon a tube so as to produce, say, a faint purple tint, and the tube then be removed to the dark, the faint purple tint will deepen to a certain extent. On renewed exposure to light the action recommences.

\* According to Würster ('Ber. d. Deut. Chem. Gesellschaft,' vol. 19, p. 3201), finely powdered bodies in general occlude "active" oxygen. The two carbonates, however, were the most finely powdered of the salts used.

*Action of the Radiations from Radium.*

We used 5 milligrammes of pure radium bromide, supplied by Buchler & Co., of Brunswick, and we found that a solution of iodoform in chloroform was turned deep purple by simply resting the test-tube containing it on a plate of mica covering the radium salt. That is to say, the active rays penetrate mica and glass.

They also penetrate cardboard. Tubes containing a solution of iodoform in chloroform were enclosed in a box of black cardboard, and they remained unchanged for 60 hours. On placing the box over the radium salt the tubes became purple in about 10 minutes.

For the following reasons we believe that the active rays from radium are entirely different from the active rays of light.

The active rays of sunlight are completely arrested by an opaque layer of lamp-black deposited over a test-tube, by black cardboard, by aluminium, or, in short, by any substance opaque to visible light rays. The active radium rays traverse lamp-black, black cloth, or cardboard, and aluminium sheet 1 mm. thick, without any measurable loss.

An ordinary yellow gas-light was found to emit active rays in quantity sufficient to change iodoform dissolved in chloroform at 1 foot distant in a few minutes, even when the test-tube was jacketed with water in order to prevent any heating. There is, therefore, no reason to believe that the activity associated with light is different from the ordinary chemical activity of light.

The radium rays which produce the change were identified by measuring the effect of screens upon the time necessary to produce a standard depth of purple in 1 c.c. of a standard solution of iodoform in chloroform.

A comparison of radium unscreened and screened so as completely to intercept the  $\alpha$  rays, failed to show any action on the part of these rays.

Attention was then turned to the more penetrating  $\beta$  and  $\gamma$  rays. A corked test-tube was suspended at a constant distance from the radium (approximately 3 mm.), the same test-tube being used throughout. 1 c.c. of the standard solution was used for each measurement. In these measurements the wall of the test-tube was always present as a screen.

Time necessary to read the standard colour—

	Minutes.			Means.
	13	12	13	
1. Radium uncovered .....	13	12	13	12.6
2. Thin screen of mica.....	11	12.5	12	11.8
3.     "     "     and sheet of writing paper ..	12	—	—	12.0
4. Glass, $\pm$ 0.5 mm. ....	15	14.5	14.5	14.8
5. Aluminium, $\pm$ 1 mm. thick .....	15.5	15.5	15.5	15.5
6. Lead plate, $\pm$ 2 mm. thick .....	between 200—250			225.0
7.* Four lead plates, each $\pm$ 2 mm. thick .....	less than 1000			<1000

\* In this case the distance between the radium and the solution was, of course, increased in order to make room for the screens.

Professor Rutherford was good enough roughly to measure the stopping power of the screens actually used. Nos. 2, 3, 4, and 5 stopped all the  $\alpha$  rays. No. 6 stopped 80 per cent. of the  $\beta$  rays, and allowed the  $\gamma$  rays to pass. No. 7 stopped practically all the  $\beta$  rays, and allowed only  $\gamma$  rays to pass.

The obvious conclusion from these figures is that the action is mainly due to the  $\beta$  rays—that is to say, to the stream of negative electrons. On the other hand, the fact that action is not arrested by as many as four of the lead screens makes it certain that the very penetrating  $\gamma$  rays also are chemically active.

As the  $\gamma$  rays are said to be the same as the Röntgen rays—that is to say, ethereal pulses—the action of the latter was tried by exposing tubes of iodoform dissolved in chloroform, which were enclosed in light-tight cardboard boxes. The Röntgen rays were found to be active, the solutions were purple at the end of 15 minutes.

An exact comparison of the relative activity of light, radium rays and Röntgen rays cannot be attempted, but the experiments prove that light is the most active. The difference appears to be very great. The profound and often lethal physiological action of radium rays must therefore, for the present, be looked upon as being due to their power of penetration rather than to the fact that they exert any novel or very intense action. They reach parts which are shielded by a cuticle very impervious to light waves. Viewed in this way the pigmentation of the human skin found in tropical races, and in those exposed to sunlight, may be regarded as an increased protection to the internal structures which acts by increasing the opacity of the epidermis.

One of us has already shown that the  $\alpha$  rays profoundly modify the *physical* state of colloidal solutions.\* If the colloid particles be electrically negative, the  $\alpha$  rays act as coagulants; if the colloid particles be electrically positive they act as solvents, that is to say, the rays decrease the average size of the particles.

As a provisional basis for investigating the physiological action of radium rays we may therefore regard the  $\alpha$  rays as altering the physical state of the living matter, the  $\beta$  and  $\gamma$  rays as altering the chemical processes, especially perhaps the oxidation processes of the tissues.

It may be well to mention briefly the instances of chemical decomposition produced by radium rays which have been described up to the present.

Berthelot† gives the following cases. Iodic acid is decomposed with liberation of iodine by rays from radium and by light. Unlike the liberation of iodine from iodoform the change proceeds very slowly, free iodine being present only after 14 days' exposure. Nitric acid

\* 'Journal of Physiology,' vol. 29, 1903, p. xxix.

† 'Comptes Rendus,' vol. 133, 1901, p. 659.

forms nitrous fumes when acted upon by the radium rays or by light.

Becquerel\* mentions the case of mercuric chloride which in presence of oxalic acid is decomposed by light rays, and by radium rays.

“Experiments in Radioactivity, and the Production of Helium from Radium.” By Sir WILLIAM RAMSAY, K.C.B., F.R.S., and FREDERICK SODDY, M.A. Received July 28, 1903.

1. *Experiments on the Radioactivity of the Inert Gases of the Atmosphere.*

Of recent years many investigations have been made by Elster and Geitel, Wilson, Strutt, Rutherford, Cooke, Allen, and others on the spontaneous ionisation of the gases of the atmosphere and on the excited radioactivity obtainable from it. It became of interest to ascertain whether the inert monatomic gases of the atmosphere bear any share in these phenomena. For this purpose a small electroscope contained in a glass tube of about 20 c.c. capacity, covered in the interior with tin-foil, was employed. After charging, the apparatus if exhausted retained its charge for thirty-six hours without diminution. Admission of air caused a slow discharge. In similar experiments with helium, neon, argon, krypton, and xenon, the last mixed with oxygen, the rate of discharge was proportional to the density and pressure of the gas. This shows that the gases have no special radioactivity of their own, and accords with the explanation already advanced by these investigators that the discharging power of the air is caused by extraneous radioactivity.

Experiments were also made with the dregs left after liquefied air had nearly entirely evaporated, and again with the same result; no increase in discharging power is produced by concentration of a possible radioactive constituent of the atmosphere.

2. *Experiments on the Nature of the Radioactive Emanation from Radium.*

The word emanation originally used by Boyle (“substantial emanations from the celestial bodies”) was resuscitated by Rutherford to designate definite substances of a gaseous nature continuously produced from other substances. The term was also used by Russell (“emanation from hydrogen peroxide”) in much the same sense. If the adjective “radioactive” be added, the phenomenon of Rutherford is distinguished from the phenomena observed by Russell.

\* *Ibid.*, vol. 133, 1901, p. 709.