On the Color Reaction Between Iodine and the Basic Acetates of Some Rare Earth Elements.

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It was found by Damour[1] that basic lanthanum acetate acting with iodine shows a blue color which resembles to that produced by the familiar iodine-starch reaction. Biltz,[2] Berczeller,[3] Lottermoser and Herrmann,[4] Krüger and Tschirch,[5] etc. observed the same phenomenon.

As for the action of iodine upon the basic acetates of rare earth elements other than lanthanum, there are also some reports published.[6] Although Orlow[7] noticed the similar reaction in the case of basic praseodymium acetate, it is generally believed that the above-mentioned color reaction is specific to lanthanum.[8] But, according to the present authors' experiments, besides the basic acetate of lanthanum, those of praseodymium, neodymium and samarium take on an intense indigo color when properly treated with iodine, while those of yttrium, gadolinium and erbium remain colorless with the same treatment.

Materials. The purity of the salts of the rare earth elements used was examined by the X-ray spectroscopic method. As for lanthanum, praseodymium, neodymium, samarium and gadolinium, the amount of impurities was so small that they might be assumed for the present purposes to be sufficiently and highly pure. Compared with the above-mentioned salts, the purity of yttrium salts used was somewhat low, and that of erbium salts used was still lower. The acetates were prepared according to the method of Lottermoser and Herrmann[9] from oxides and acetic acid.

The Color Produced by the Iodine-Basic Acetate Reaction. A solu-

(1) Damour, *Compt. rend.*, 43 (1856), 976.

(2) Biltz, *Ber.*, 37 (1904), 719.

(3) Berczeller, *Biochem. Zt.*, 84 (1917), 160.

(4) Lottermoser, *Kolloid-Zt.*, 33 (1923), 271; Lottermoser u. Herrmann, *Z. physik. Chem.*, 122 (1926), 1.

(5) Krüger u. Tschirch, *Ber.*, 62 (1929), 2776; 63 (1930), 826.

(6) e.g. Damour, *op. cit.*; Behrens, *Chem. CB.*, (1902) I, 296; Orlow, *Chem-Ztg.*, 31 (1907), 45; Krüger u. Tschirch, *op. cit.*

(7) Orlow, *op. cit.*

(8) Krüger and Tschirch (*op. cit.*) described in their first report that basic praseodymium acetate showed the color reaction with iodine, but later they considered that it was due to the impureness of the materials used and, in their second report, withdrew what was stated in their former report.

(9) *op. cit.*

tion of each acetate was treated with ammonia[10] and basic acetate was precipitated. A solution of iodine and potassium iodide was added to it. Being left at room temperature for 2 or 3 days, it took on gradually a color[11] mentioned in the second column of Table 1. But when it was heated about 10 minutes by immersing the vessel in the boiling water, an indigo color developed immediately in the cases of lanthanum, praseodymium, neodymium and samarium as shown in the third column of Table 1. For comparison, the descriptions of Krüger and Tschirch,[12] which are quite different from ours in the cases of praseodymium, neodymium and samanium, are given in the fourth column of Table 1.

Table 1. The Colors of Iodine-Basic Acetates.

Elements	When left at room temperature	When heated in the boiling water	According to Krüger and Tschirch
Yttrium	Colorless	Colorless	Colorless
Lanthanum	Indigo	Indigo	Indigo
Praseodymium	Blue	Indigo	Colorless
Neodymium	Bluish violet	Indigo	Colorless
Samarium	Yellow	Indigo	Colorless
Gadolinium	Colorless	Colorless	——
Erbium	Colorless	Colorless	Colorless

The colored precipitate, after being left 2 days at room temperature and after the removal of free iodine from it, was shaken vigorously with

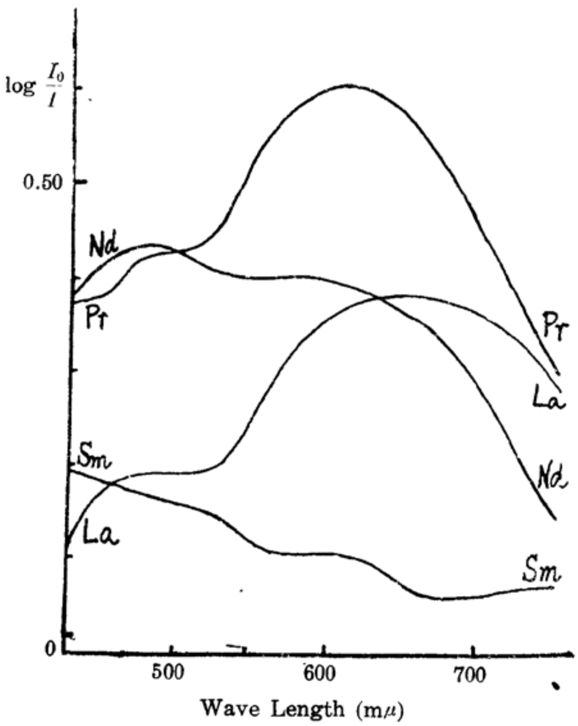

Fig. 1.

water. The water took on the same color as the precipitate. The colored solution thus formed was separated from the precipitate with the aid of a centrifuge and was examined with the Pulfrich photometer. The absorption curves obtained are given in Fig. 1, where I_0 denotes the intensity of the initial light and I, that of the light transmitted.

It is seen from the figure that the absorption maximum of lanthanum salt lies in the longest wave-length side, and those of the salts of the other elements shift to the shorter wave-length side in the order of praseodymium, neodymium and samarium. The absorption maximum of samarium salt does not appear in the visible part.

From this fact, it may be allowed to conclude that the absorption maximum of the iodine-basic acetate color shifts to the shorter wave-length side with the increase of the atomic numbers of the rare earth elements, i.e. with the decrease of the basicity of the elements. The colorlessness of the iodine-basic acetates of gadolinium, erbium and yttrium, which was shown in the experiments, may also be expected from this rule.

The Change of Color with the Lapse of Time. As Berczeller[(13)] and Lottermoser[(14)] already pointed out, the color of iodine-basic lanthanum acetate changes from reddish brown or brown to blue with the lapse of time. We studied the color change with the Pulfrich photometer. The experimental procedure was as follows.

To 1 ml. of lanthanum acetate solution[(15)] were added 0.3 ml. of 1N. ammonia and 2 ml. of 0.1N. iodine-potassium iodide solution. The mixture after being left at room temperature for a definite time mentioned in Fig. 2, was treated in the same way as already mentioned; thus the solution for the photometric measurement was prepared. The absorption curves obtained are given in Fig. 2.

From this figure, it would be seen that the absorption maximum shifts to the longer wave-length side with the lapse of time,[(17)] and that

(10) The color did not appear when a large excess of ammonia was used; so such large excess of it should be avoided. Also the insufficient quantity of it should be avoided, as such insufficient quantity caused the incomplete precipitation of basic acetate.

(11) In order to remove the yellow or brown color due to free iodine, the precipitate after the treatment was washed with water by decantation with the aid of a centrifuge. Then the color was observed.

(12) In stead of acetates, Krüger and Tschirch (*op. cit.*) used the mixture of the nitrates of the rare earth elements and sodium acetate. We also carried out the experiments with the same mixtures as theirs but, contrary to their results, we confirmed that praseodymium, neodymium and samarium showed the above mentioned color reaction.

(13) *op. cit.*

(14) *op. cit.*

(15) 1 ml. of the solution corresponds to 11.5 mg. of La_2O_3.

(16) The room temperature was between 10.4°C and 16.4°C during these experiments. Any particular attentions to keep the temperature constant were not paid.

(17) Immediately after the addition of iodine solution, the basic lanthanum acetate takes on a reddish brown color. After 1 hour, it becomes reddish violet, after 5 hours, violescent indigo and finally it takes on an indigo color.

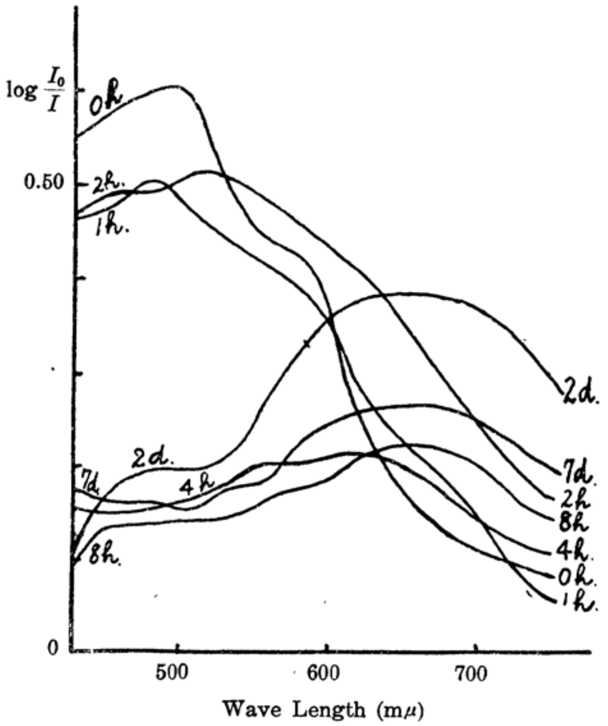

Fig. 2.

the shape of the curve after 8 hours is similar to that after 7 days, in other words, the final indigo color appears already in 8 hours and is stable at least for 7 days.

The similar results were obtained with praseodymium and neodymium, but compared with lanthanum, the color changes somewhat more slowly with these elements.

The Relation between the Concentration of Iodine and the Quantity of Sorbed Iodine. As for the relation between the concentration of iodine and the quantity of sorbed iodine, Lottermoser[18] pointed out that Freundlich's sorption isotherm holds good in the case of basic lanthanum acetate. According to our experiments, it also holds good in the cases of the basic acetates of praseodymium and neodymium.

The Mechanism of the Interference of Other Ions. As for the effect of other ions upon the color of iodine-basic lanthanum acetate, many experimental results were reported by Krüger and others.[19] According to them, the presence of other rare earth elements greatly interfered with the formation of the blue colored substance, but it is not so in our experiments with praseodyminum and neodymium. The mixture of the basic acetates of lanthnum, praseodymium and neodymium also took on an indigo color and no mutual interference was recognized. But the interfering effect of the rare earth elements which did not show the

(18) *op. cit.* (19) *op. cit.*

above-mentioned color reaction was considerable. For example, when yttrium was present in a quantity larger than 0.7:1 in the atomic ratio to lanthanum, no coloration of basic lanthanum acetate was seen.

It is also mentioned in the literature that the interfering effect of fluoride ions, sulfate ions, etc. is remarkable, while that of nitrate ions, chloride ions, etc. is not much. But no satisfactory explanation of the mechanism of the effect of these ions is hitherto given. One possible explanation by the present authors is as follows. When a lanthanum solution containing acetate ions and the interfering ions, e.g. sulfate ions, is treated with ammonia, the basic lanthanum sulfate, which shows no color reaction with iodine, precipitates in earlier stages and interferes with the action of the basic lanthanum acetate which precipitates later. On the contrary, when a lanthanum solution containing acetate ions and the non-interfering ions, e. g. nitrate ions, is treated with ammonia, the precipitation of the basic lanthanum acetate occurs before that of the basic lanthanum nitrate which shows no color reaction with iodine, and the action of basic lanthanum acetate is not greatly interfered. The results of the following experiments seem to support such an interpretation.

(1) A solution containing lanthanum acetate and ammonium sulfate was treated with an insufficient amount of ammonia. The precipitate thus formed showed no color reaction even when it was heated. But the precipitate formed with a sufficient quantity of ammonia took on an indigo color with iodine.

(2) When a solution containing a larger amount of sulfate ions was treated with a sufficient quantity of ammonia, the precipitate thus formed took on only a faint color with iodine. But, even in such a case, if a solution, after the previous removal of the precipitate which was formed with an insufficient amount of ammonia, was treated again with ammonia, the precipitate then formed showed distinctly the color reaction.

(3) When the amount of sulfate was still larger and exceeded the quantity equivalent to lanthanum, no colored precipitate was produced in spite of the presence of acetate ions in the solution. In such a case, the previous removal of the precipitate formed in earlier stages just mentioned above was of no use.

(4) The precipitate, which was formed with a small amount of ammonia from a solution containing lanthanum acetate and lanthanum nitrate, took on an indigo color with iodine. But the precipitate formed with a larger amount of ammonia was only unevenly colored with dirty violescent indigo. When the solution was treated with ammonia after the previous removal of the precipitate, which was produced with an insufficient amount of ammonia and showed the color reaction, the precipitate thus formed remained almost colorless with iodine.

(5) As already mentioned above, the basic acetate precipitate which was formed from a solution containing lanthanum acetate and a considerable quantity of yttrium acetate, did not show the color reaction with iodine. But when the method of fractional precipitation with ammonia

was applied to such a solution, the precipitate in earlier stages did not show the color reaction, while that in later stages took on an indigo color with iodine. This showed that the precipitation of basic yttrium acetate occurred before that of basic lanthanum acetate.

The above-mentioned experimental results seem to support our interpretation on the mechanism of the effect of some anions and cations. Hitherto little attention was paid by earlier authors to the quantity of ammonia used, but it is obvious from the above-mentioned experiments that the amount of ammonia added to form basic acetate precipitate plays always an important role.

Summary. (1) The color reaction between iodine and basic acetate is not, as is often believed, peculiar to lanthanum. It is shown also by praseodymium, neodymium and samarium.

(2) The absorption maximum of iodine-basic acetate shifts to shorter wave-length side with the decrease of the basicity of the rare earth elements.

(3) The color change of iodine-basic acetate with the lapse of time was studied photometrically.

(4) It was confirmed that the sorption isotherm holds good in the cases of the basic acetates of lanthanum, praseodymium and neodymium.

(5) The effect of other ions on the color reaction was discussed.

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