THE HALOGEN ABSORPTION OF TURPENTINE.

By ETHEL M. TAYLOR.

(Read at the Meeting, November 5, 1919.)

It is well known that the iodine absorption of turpentine varies with the time of action of the iodine solution (*cf.* Archbutt, *J. Soc. Chem. Ind.*, 1902, **21**, 1439, and Worstall, *ibid.*, 1904, **23**, 302), and, although the figure obtained approximates to the ratio 4 : $C_{10}H_{16}$, there is no indication that the absorption stops at this point; indeed, all the evidence points to a main reaction in which 4 atoms of iodine are added, and a second slower action in which a further addition of iodine takes place with formation of a halogen acid, indicating substitution.

Repetition of Archbutt's experiments, extending, however, the time of action in both directions, gave results practically identical with those found by him, and, owing to the fact that finality of absorption was never obtained, did not admit of mathematical study. An attempt was made to measure the acidity produced in each case, but the variation of the result showed that a portion at least of the acidity was formed during the dilution with water during the titration.

The use of Wijs solution was therefore abandoned, and a $\frac{N}{1}$ solution of IBr_3 in chloroform adopted for the study of the action; the first series consisted in submitting 0.1 gram. of turpentine to the action of 10 c.c. of $\frac{N}{1}$ IBr_3 for varying times, with results as under :

Time.	Halogen Absorbed.	
	Calculated as Iodine.	Calculated as Bromide.
15 minutes	384.5	242.0
30 "	388.5	244.6
1 hour	407.0	256.2
2 hours	418.6	263.4
3 "	420.1	264.5
4 "	425.3	267.6
6 "	441.7	275.7
18 "	445.0	280.0
24 "	469.5	293.1

On plotting out these results on squared paper they appeared to lie approximately on a logarithmic curve, and the value for time = one minute would be very close to the theoretical value for 4I. This indicated that the first action was extremely rapid with IBr_3 in chloroform, being practically instantaneous, and that the secondary reaction was sufficiently slow to be negligible under these conditions.

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A second series was made, titrating the excess of iodine after about one minute's exposure and varying the amount of halogen added:

Halogen Added, Calculated as Bromine per Cent.	Halogen Absorbed, Calculated as Bromine per Cent.	Ratio Added to Absorbed.	Calculated.
120.2	97.6	1.231	97.5
129.5	102.6	1.262	103.5
138.8	109.4	1.269	109.5
148.0	116.7	1.268	115.5
156.2	121.4	1.278	121.5
166.5	127.7	1.305	127.5
185.0	139.4	1.327	139.5
370.0	212.1	1.745	—
925.0	237.0	3.90	—

It is seen that the absorption is nearly proportional to the amount added, with quantities of halogen insufficient to reach the ratio $4\text{Br} : \text{C}_{10}\text{H}_{16}$, and when plotted they lie very close to a straight line of which the equation is

$$\text{Br. absorbed} = 19.5 + 0.6486 (\text{Br added}),$$

while with a large excess the results are very close to the theoretical (235.3).

Incidentally this shows that the absorption does not take place in two stages, and there is no indication of a resting stage $\text{Br}_2 : \text{C}_{10}\text{H}_{16}$. The close approach of the ratio of Br added to Br absorbed to 1.333 (the ratio of IBr_3 to Br_3) during the straight line portion would appear to indicate that the halogen absorbed is bromine.

The conclusions drawn are:

1. The reaction between turpentine and halogen is

and there is no intermediate reaction.

2. This reaction can be realised with practically no secondary reaction by adding 10 c.c. $\frac{N}{1}$ IBr_3 in chloroform solution to 0.1 to 0.15 gm. turpentine dissolved in 10 c.c. chloroform, adding KI solution within one minute and titrating back immediately with thiosulphate solution.

The work was carried out in the Analytical Laboratory of Boots Pure Drug Co., Ltd., to whom my thanks are due.

[Mrs. Taylor is unfortunately prevented from continuing the work, owing to ill-health. She has sent me her notes, from which I have extracted the completed portion of her investigation.—H. D. RICHMOND.]

DISCUSSION.

Mr. ARCHBUTT remarked that the author's paper was of considerable interest, and fully confirmed his own observations. He had always regarded the test with Wijs solution as a purely empirical one, the value of which depended upon the strict observance of uniform conditions. The author's observations seemed to show that

the modified procedure which she recommended placed the halogen absorption test upon a more precise and scientific basis, and the method was well worth a trial, especially in view of the fact that some of the glacial acetic acid now offered by the dealers, even some sold as of A. R. quality, did not give a stable Wijs solution. He (Mr. Archbutt) had not yet discovered the cause of this, and it did not appear to seriously affect the determination of the iodine values of fixed oils, but it did very seriously interfere in the case of oil of turpentine.

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