A NOTE ON THE DETERMINATION OF RESACETOPHENONE BY KOPPESCHAAR'S METHOD

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Received November 10, 1950

THERE is a large volume of literature[1,2,3] on the quantitative bromination of phenols and phenolic compounds. Phenol itself is readily and quantitatively tri-brominated but substituted phenols frequently yield erratic results. The chief factors involved are: (*a*) nature and position of substituent, (*b*) amount of bromine added in excess, (*c*) temperature, and (*d*) acid concentration. No universal bromination procedure could therefore be laid down for the estimation of phenolic compounds. The titration of resacetophenone with standard bromate-bromide mixture in presence of mineral acid (Koppeschaar's method) was now investigated and the results reported. The ketone was dissolved in acetic acid and the titrations performed in an all-glass apparatus designed to prevent loss of bromine.

Brominations were carried out at laboratory temperature (ca. 30° C.) with varying amounts of bromate-bromide mixture added initially. The acid concentration employed was approximately 1 N in all the experiments. The excess of bromate was determined by adding potassium iodide and titrating the liberated iodine with standard sodium thiosulphate using starch as indicator. The volume of bromate used up was calculated in the usual manner. The results are given in Table I.

The results presented in Table I show that the bromate used up does not depend on the amount of ketone alone but also on the magnitude of the excess bromate used initially. Consequently reproducible results could not be obtained in a direct titration by Koppeschaar's method. However, on plotting the total volume of bromate solution initially added against the actual excess in each experiment (determined iodometrically) a linear relationship was observed.

By extrapolation to zero excess, the bromate equivalents of the ketone in solution were obtained. These values corresponded to di-bromination. Typical results obtained are given in Table II.

TABLE I

Resacetophenone taken (gm.)	Bromate (c.c.)	
	Initially added	Used up
0·0226	5·0	1·82
	10·0	7·01
	15·0	8·43
	20·0	9·61
	25·0	10·55
0·0452	10·0	4·5
	20·0	7·3
	30·0	8·9
0·1130	30·0	24·4
	33·5	30·2
	35·9	32·3
	40·0	33·3
	49·7	37·2
	80·0	48·2
	100·0	56·9

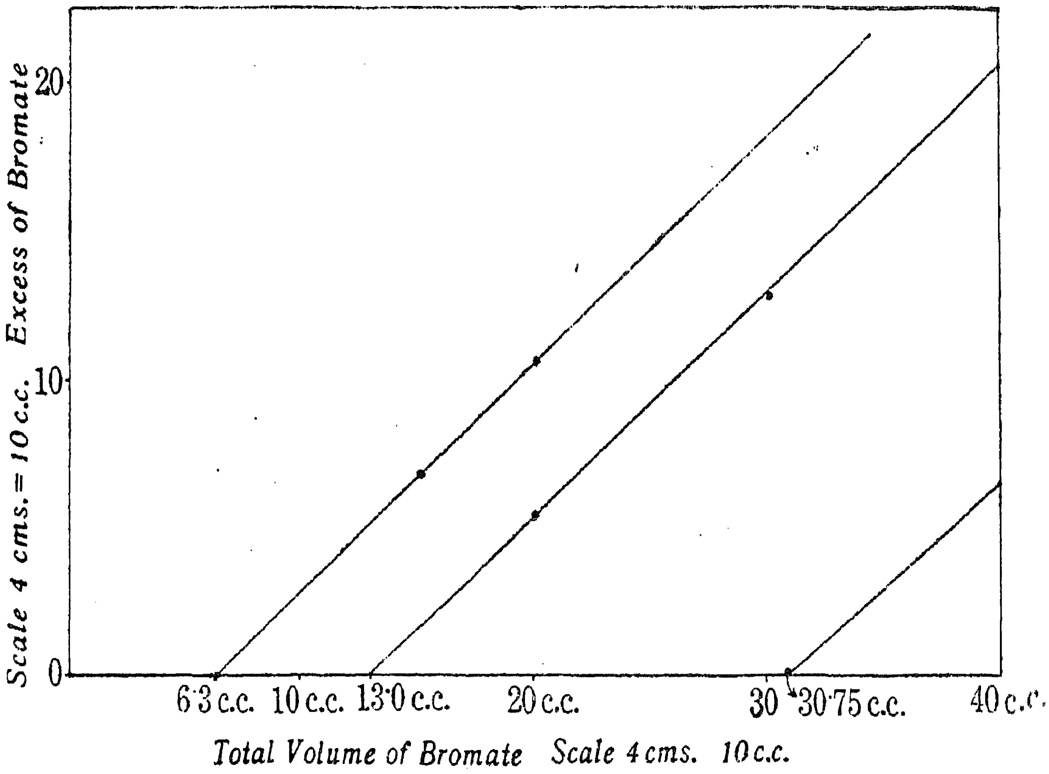
TABLE II

Resacetophenone (gm.)

Taken	Found	Error (%)
0·0226	0·0233	3·1
0·0452	0·0482	6·7
0·1130	0·1140	0·9

In evaluating the magnitude of the error, it should be noted that the graphical method involves a certain amount of approximation of the figures depending on the scale used. It is estimated, therefore, that the maximum error is of the order of 5%.

It is to be noted that the bromination is a slow and progressive reaction which goes beyond di- and tri-bromination stage. The solution becomes prematurely yellow with quantities of bromate even slightly less than the theoretical quantity required for di-bromination. At this stage the solution liberates iodine from potassium iodide indicating the presence of free bromine. It is therefore not possible to secure accurate values even for di-bromination by adding a slight excess of bromate and brominating for 10 15 minutes. The extrapolation method alone yields satisfactory results.



On brominating with a large excess, it was found that a fourth bromi atom entered the molecule by replacing either one of the hydroxyls or t nuclear acetyl group. By analogy with the behaviour of saligenin, salicyl acid and aldehyde it may be inferred that it is the nuclear acetyl and not t phenolic group that is replaced. During later stages of bromination t insoluble bromo compound goes into solution.

SUMMARY

Quantitative studies on the bromination of resacetophenone show that the reaction was slow and progressive and its magnitude depend primarily on the amount of bromate initially added in excess of the theoretic equivalent so that reproducible results could not be obtained directly Koppeschaar's method. However, on plotting the volume of broma initially added against the excess found by titration, a linear graph w obtained which on extrapolation to zero excess gave the value of broma equivalent to di-bromination of the ketone present in solution. The es mated maximum error involved was of the order of 5%.

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