# XCVIII.—*The Quantitative Estimation of Mixtures of Isomeric Unsaturated Compounds. Part III. A Review of the Iodometric Methods and a New Bromometric Method.*

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The methods for the analysis of mixtures of three-carbon tautomerides given in the earlier papers of this series (J., 1927, 355, 2565) have now been in use for some four years, during which time information has accumulated on their relative values and on their modification to suit abnormal cases.

The original iodometric method for acids (Linstead and May, J., 1927, 2565) has been very successful for the monobasic series. In using it, the most accurate results are obtained by acidification of the reaction mixture before back-titration. The extrapolation method given in the same paper, which was originally intended for use when the βγ-isomerides were not obtainable in a state of purity, has been but little used owing to the development of the partial esterification process, which enables these substances to be purified without much difficulty. The high reactivity of the βγ-acids towards iodine diminishes with the entry of negative groups into the acid molecule to such an extent that iodometric methods lose much of their value for dibasic and aromatic unsaturated acids. In such cases halogen in a more active form has to be supplied and the present paper gives an example of the use of bromine for dibasic acids. When the second negative group is not directly attached to the three-carbon system, however, the original method is applicable.

All αβ-acids so far examined have iodine additions of 0—1% by the standard method. This provides a most valuable test for the purity of αβ-acids, particularly those liquid at room temperature. Additions greater than 1% indicate the presence of isomeric impurity, which is readily removable by esterification. Additions to βγ-monobasic acids vary from 50—100% according to structure, the highest being given by γγ-dialkyl acids, and the purity of these acids if liquid can best be checked by the constancy of the iodine addition of the acid prepared or purified by different methods.

In a few series the iodine addition of the βγ-isomeride has been found to vary with temperature: with $\Delta^{\beta}$-*n*-hexenoic acid this variation amounts to as much as 1·5% per degree (Boxer and Linstead, following paper). For these acids it is necessary to carry out the iodometric analyses in a room maintained at a constant temperature.

The original iodometric method for the analysis of mixtures of neutral substances has needed variation only in regard to the time of reaction for all the unsaturated esters and ketones so far investigated. Working with nitriles and substances of the glutaconic series containing two or more negative groups, it has been found necessary to increase the usual concentration of the reagents in order to obtain sufficient addition to the βγ-isomeride in a convenient time. With neutral substances, the temperature variation is generally inappreciable.

*Estimation of Mixtures of Itaconic and Mesaconic Acids.*—The addition of iodine to both these acids under the standard conditions was negligible, whereas that of bromine in most solvents was too rapid for convenient measurement. Piutti and Calcagni (*Gazzetta*, 1910, **40**, 577) and Biilmann (*Rec. trav. chim.*, 1916, **36**, 313) have shown that the addition of bromine in *N*/100-aqueous solution is more rapid to itaconic than to mesaconic acid, but direct application of this method was found to be difficult on account of the speed of both reactions and the ready loss of bromine vapour.

These difficulties were overcome by the use of an *N*/20-solution of bromine in concentrated aqueous potassium bromide (400 g. KBr to 1 litre), in which the salt both stabilised the solution and reduced the rate of addition just as potassium iodide reduces that of iodine addition (Linstead and May, *loc. cit.*). Analyses were carried out as follows :

The bromine solution was contained in a vessel fitted with a syphon tube to enable transference to the burette without loss of bromine. This solution was standardised before use, and from time to time during every set of analyses. For this purpose 25 c.c. quantities were run from the burette into 10 c.c. of distilled water in stoppered bottles. After being kept for 10 minutes in the dark, the solutions were treated with 10 c.c. of 10% aqueous potassium iodide and the liberated iodine was titrated with $N/20$-thiosulphate. 10 C.c. of exactly $M/15$-solutions of the pure acids or their mixtures were then pipetted into stoppered bottles and treated with an exactly equivalent amount of the bromine solution [calculated from $J$ (amount required in c.c.) $= 100/3t_{25}N$, where $t_{25}$ is the thiosulphate titration of 25 c.c. of the bromine and $N$ is the normality of the thiosulphate]. The procedure for the reaction and the back titration followed that for the blank reactions already given. No further addition occurred after the introduction of the potassium iodide and the solution could be left at this stage for some time without change in titre. The amount of addition to the pure acids varied with temperature :

| | | | | | |
|---|---|---|---|---|---|
| Temperature .................... | 16·8° | 17·1° | 20·0° | 21·0° | 23·2° |
| % Addition to mesaconic acid | 37·3 | 37·5 | 41·8 | 42·7 | 45·9 |
| % Addition to itaconic acid ... | 67·3 | 67·7 | 71·7 | 72·5 | 75·7 |

The temperature coefficient in each reaction is obviously the same and it was only necessary, therefore, to obtain a full reference curve for the addition to mixtures of known composition for one temperature and to apply a simple correction to additions taken at other temperatures. In practice the reference curve was taken at 16·8° :

| | | | | | | |
|---|---|---|---|---|---|---|
| % Mesaconic acid ... | 100 | 80 | 60 | 40 | 20 | 0 |
| % Addition ........... | 37·3 | 43·3 | 49·5 | 55·9 | 62·2 | 67·3 |

To ensure the accuracy of the temperature correction, when unknown mixtures were subsequently analysed at other temperatures, experiments were also carried out on the two pure acids and mixtures of known composition.

No variation in the temperature of the room was allowed to occur during a set of analyses and titrations carried out on the same day showed perfect agreement. Further, analyses of the same mixture at different temperatures gave figures which after correction agreed to within 0·3% addition.

The end-points are extremely clear and the rate of addition appears to be independent of the lighting. The figures obtained for the compositions of mixtures are accurate to ± 1% and agree with those determined by actual isolation of the itaconic acid (see following paper, Table V).

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