

## LI.—*The Velocity of Oxime Formation in Certain Ketones.*

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THE hindering influence produced by the introduction of various groups into ketonic compounds has been already studied by the author in the case of the additive products formed with sodium hydrogen sulphite (Trans., 1905, 87, 185), and it seemed desirable to apply a somewhat similar method to the case of oxime formation, with the view of finding whether steric hindrance was actually the chief factor in the problem. If the rates of formation of the oximes of various ketones showed the same relations to each other as those found in the case of the "bisulphite" compounds, the probability that steric hindrance played a great part in the reaction would be increased, since chemically the reactions are quite different in character.

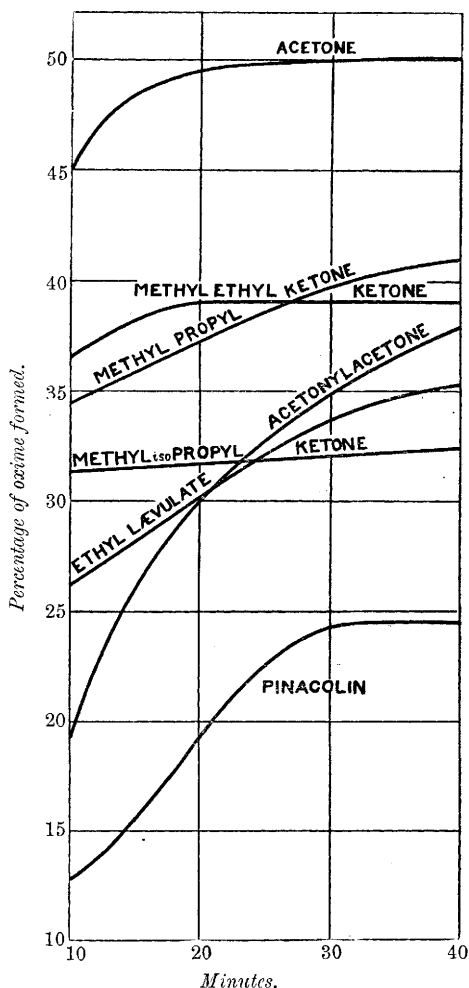
The simplest method of estimating the percentage of oxime formed in a given case seemed to be to determine the amounts of free hydroxylamine present in a solution both before and after the reaction has lasted for a fixed interval of time.

Several series of experiments were carried out before a satisfactory process was discovered. At first an indirect method was tried: a fixed excess of ferric sulphate was boiled with the oxime solution in an atmosphere of carbon dioxide, and the amount of ferrous sulphate thus formed was estimated by titration with potassium permanganate. This did not give concordant results, nor did direct titration of the unchanged hydroxylamine, either with Fehling's solution or with a solution of potassium nitrite.

In the end the following mode of estimation, adapted from a method of estimating hydroxylamine described by Meyeringh (*Ber.*, 1877, 10, 1940), was found to be the best. In order to obtain results comparable with those already found in the case of the "bisulphite" compounds,  $N/10$  aqueous solutions of the ketones were diluted with alcohol to  $N/12$ . Fifty c.c. of the ketone solution were mixed with an equal volume of  $N/12$  hydroxylamine sulphate solution, and the mixture was left in ice. Every ten minutes, 10 c.c. were withdrawn, to which were added 20 c.c. of  $N/5$  iodine solution and 20 c.c. of  $N/5$  disodium hydrogen phosphate solution; the whole was placed on a water-bath for one minute, and the excess of iodine remaining was then titrated with sodium thiosulphate in the usual way.

The rationale of the method is as follows. The ketone, in forming an oxime, uses up a certain quantity of hydroxylamine; the remaining hydroxylamine is decomposed by warming with the iodine solution, and the hydriodic acid thus produced is taken up by the sodium phosphate before it affects the oxime; the amount of iodine left unchanged is then estimated by means of the thiosulphate titration, and from it the amount of hydroxylamine employed in oxime formation can be deduced. This method was found to be sufficiently accurate, the results being concordant to within one per cent., which is sufficiently close for the purpose in view. It fails, however, when employed with aldehydes, owing to their ready oxidation; and also in the case of compounds containing the group  $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$  which react with iodine on warming.

The results obtained are shown in the table and curves. In the case of acetylacetone, twice the usual quantity of the hydroxylamine solution was used, and the results given show the percentage of oxime formed at each carbonyl group.



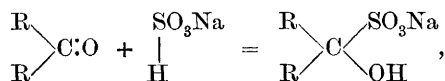
	10	20	30	40 minutes.	percentage of oxime	
Acetone .....	45.1	49.7	50.0	50.1	percentage of oxime	
Methyl ethyl ketone ...	36.6	39.2	39.2	39.2	"	"
" propyl " ...	34.7	37.3	39.9	41.2	"	"
" isopropyl ketone	31.4	31.5	32.0	32.0	"	"
Ethyl laevulate .....	26.1	30.0	33.9	35.0	"	"
Acetylacetone .....	19.0	30.0	35.0	39.0	"	"
Pinacolin .....	12.9	17.0	24.5	24.5	"	"

On the whole, the foregoing results appear to support those already obtained as to the influence of the methyl group when it is substituted for a hydrogen atom near the carbonyl group. During the first ten minutes of all the reactions, the only divergence from the relations determined in the case of the "bisulphite" compounds is to be found with ethyl lævulate, the velocity of the "bisulphite" reaction of which lay between those of methyl propyl and methyl isopropyl ketones, whilst in the foregoing table it has a lower rate of reaction than methyl isopropyl ketone. Apart from this instance, the same influences appear to govern the courses of both reactions. If the percentages of oxime formed by acetone, methyl ethyl ketone, methyl isopropyl ketone, and pinacolin at the end of twenty minutes are considered, the following numbers are obtained:

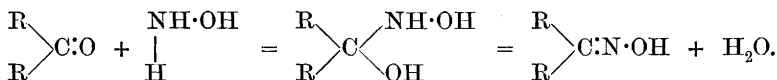
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ .....	49.7 per cent.	$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}(\text{CH}_3)_2$ .....	31.5 per cent.
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3$ .....	39.2 ,,	$\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_3$ .....	17.0 ,,

It will be noticed that the velocity of the reaction in the case of methyl ethyl ketone appears to undergo retardation after twenty minutes, causing the percentage of oxime generated at the end of a forty-minute period to fall below that produced in the case of methyl isopropyl ketone.

The reaction of oxime formation appears to be, on the whole, more rapid than the addition of sodium hydrogen sulphite to the carbonyl group; a state of equilibrium is reached more speedily. This is to be expected when we take into account the nature of the reaction and the relative masses of the groups involved. In the case of the "bisulphite" compounds it is merely a question of adding on a bulky group:



whereas in the second instance a smaller group enters, and water is immediately eliminated:



The oximes appear to be better suited than the "bisulphite" compounds for estimations of the velocity of formation of additive compounds of ketones, when many methyl groups lie in the neighbourhood of the carbonyl. The oxime method has also a great advantage over the other, since in the titration of the "bisulphite" compounds a slow inverse action takes place, which does not occur in the case of the hydroxylamine estimation. This method might

conceivably be useful in confirming the constitutions of cyclic carbonyl compounds containing many methyl groups.

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