end of the chain: $\overset{+\,+}{C}-\!\!-\overset{-\,-}{C}-\!\!-\overset{+\,+}{C}-\!\!-\overset{-\,-}{C}-\!\!-\overset{+\,+}{C}$. I shall also show in a later paper that halogen atoms at the ends of an open carbon chain are of opposite polarity just as are the halogen atoms on carbon atoms 1 and 4 of the benzene nucleus in *p*-dichlorobenzene.

In conclusion, it may be said that criticisms of a hypothesis should be and are welcomed because they serve to develop either its merits or demerits. The electronic hypothesis of positive and negative valences, while comparatively new, is a rapidly growing conception as is evidenced by the articles of the authors noted above who have presented many significant applications, interpretations, and deductions. The present series of papers relating chiefly to the constitution of benzene and its derivatives, has interpreted many hitherto unexplained phenomena. The fact that electronic formulas, in many instances, have proven to be of greater significance than the ordinary structural formulas lends support to the idea that the electronic conception of positive and negative valences may become not only a significant but possibly a necessary adjunct to the structure theory. This however, must depend upon the extent of its applications and experimental verifications, and upon the part that is played by just criticisms in bringing to light the relative merits and demerits of its applications.

CINCINNATI, O.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SYRACUSE UNIVERSITY.]

A METHOD FOR THE SEPARATION AND IDENTIFICATION OF CERTAIN HOMOLOGOUS α-DIKETONES.

BY J. M. JOHLIN.

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The author has made the observation that diacetyl occurs in considerable quantities in pyroligneous acid, and generally in smaller amounts in the distillate resulting from the destructive distillation of carbohydrates, such as pure cellulose, cane sugar, glucose, and lactose.

The fact that nickel readily precipitates as the salt of dimethylglyoxime was adapted for the precipitation of diacetyl with nickel chloride and hydroxylamine-hydrochloride. Repeated preliminary tests with synthetically prepared diacetyl showed that one part of diacetyl in one hundred thousand parts of water still gives a decided precipitate of the nickel salt of dimethylglyoxime when a few drops each of solutions of nickel chloride, hydroxylamine-hydrochloride and ammonium hydroxide are added. Although diacetyl itself is very volatile it is evident that, after adding the reagent necessary for its precipitation, concentration to any necessary extent can be effected without further loss.

Dimethylglyoxime, which can be prepared in a very pure state and accurately weighed, was found by repeated determinations to be quantitatively precipitated from solution when the proper amounts of sodium acetate, nickel chloride and ammonium hydroxide were added.

	Wt. of dioxime taken. G.	Wt. of nickel salt precipitated. G.	Wt. of dioxime found. G.	Loss. %.
1	0.1012	0.1259	0.1012	0.00
2	0.1001	0.1244	0.1000	0.10
3	0.1003	0.1243	0.0999	0.39

Since the nickel salt of dimethylglyoxime is practically insoluble in water, it should be possible to precipitate any of its three components quantitatively, using the other two as reagents. As diacetyl always occurs in acid solution, and since hydrochloric acid is one of the products of the reaction when it is precipitated in the form of the nickel salt of its dioxime, an exactly neutral solution is difficult to obtain. The solubility of the nickel salt in acid solution depends upon its dissociation into the nickel salt of the acid present and into dimethylglyoxime. This dissociation is less with acetic acid than with any of the mineral acids. Sodium acetate then not only sets free acetic acid in place of hydrochloric, but also furnishes a common acetate ion. That the addition of sodium acetate lessens the solubility of the nickel salt of the dioxime in dilute acetic acid solutions was shown experimentally. Though the amount of nickel salt dissolved by a solution of one part of acetic acid in fifty thousand parts of water is small, it is sufficiently large to be visibly reprecipitated when minute quantities of sodium acetate are added. Ammonium hydroxide when carefully added is more effective than sodium acetate in aiding complete precipitation. An excess of ammonium hydroxide must be avoided since it also dissolves small amounts of the nickel salt of the dioxime. The presence of ammonium chloride is necessary to prevent the precipitation of nickel hydroxide.

This method applied to the quantitative determination of diacetyl in pyroligneous acid gave results which made it evident that other homologous diketones were present, thus giving rise to the necessity of a qualitative scheme for their separation and identification.

The possibility of identifying these diketones occurring in so small amounts in the presence of each other depends upon a detailed knowledge of the properties of their dioximes and of the nickel salts of these.

The dioxime of diacetyl, that of its higher homolog acetylpropionyl, and that of its lower homolog methylglyoxal, a keto-aldehyde, were prepared according to the method of Diels[1] and Jost as modified by Gandarin[2] for the preparation of dimethylglyoxime. In each case the proportionate amounts of methyl ethylketone, of diethylketone, and of acetone were oxidized with iso-amylnitrite to the isonitroso compound and after

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[1] *Ber.*, 35, 3290 (1902).

[2] *J. prakt. Chem.*, 77, 414 (1908).

adding hydroxylamine hydrochloride extracted with ether in the form of the dioximes. From the dioximes their respective nickel salts were prepared.

All three dioximes readily sublime when heated and can, by resubliming, be separated from other nonvolatile matter. According to their solubility in hot and cold water the two higher homologs can readily be freed from the lowest by recrystallizing them from water.

The *nickel salt*[1] *of dimethylglyoxime is practically insoluble in both hot* and cold water. That of the higher homolog is very sparingly soluble even in hot water. That of the lower homolog is slightly soluble in cold water and sufficiently soluble in hot water to make possible its recrystallization from large amounts of this solvent.

Dilute ammonium hydroxide very readily dissolves the nickel salt of the lowest homolog, while the nickel salt of dimethylglyoxime is but sparingly soluble even in stronger solutions of ammonia. Ether which has been thoroughly dried dissolves the nickel salt of methylethylglyoxime, while that of dimethylglyoxime is practically insoluble and that of methylglyoxime but sparingly soluble in the same solvent.

The insolubility of the nickel salts of the dioximes of the diketones in neutral solutions, then, makes it possible to precipitate them completely even where they occur in minute quantities. The physical properties of the nickel salts and of the free dioximes give further evidence that it is possible to separate them from each other, to recover the free dioxime from each salt individually, to purify it, and by means of its melting point to identify the diketone of which it is a derivative.

A known mixture containing 0.1 g. each of nickel methylglyoxime, of nickel dimethylglyoxime, and of nickel methylethylglyoxime was used to test the efficiency of such an analysis. The amounts of these nickel salts taken represent, respectively, 0.056 g. of methylglyoxal, 0.061 g. of diacetyl, and 0.064 g. of acetylpropionyl.

The mixture was first subjected to an extraction with ether dried over sodium. It required but two extractions with 200 cc. of dried ether to completely remove all of the nickel salt of methylethylglyoxime, along with traces of the nickel salt of methylglyoxime. The ether extract was concentrated to about 50 cc. and then thoroughly shaken with an equal volume of 5% sulfuric acid until the yellow color of the ether extract and precipitated nickel salt had entirely disappeared. The ether layer now contained all of the methylethylglyoxime and traces of methylglyoxime, while the acid layer contained all of the nickel in the form of its sulfate. After separating the two layers the ether was evaporated and the methyl-

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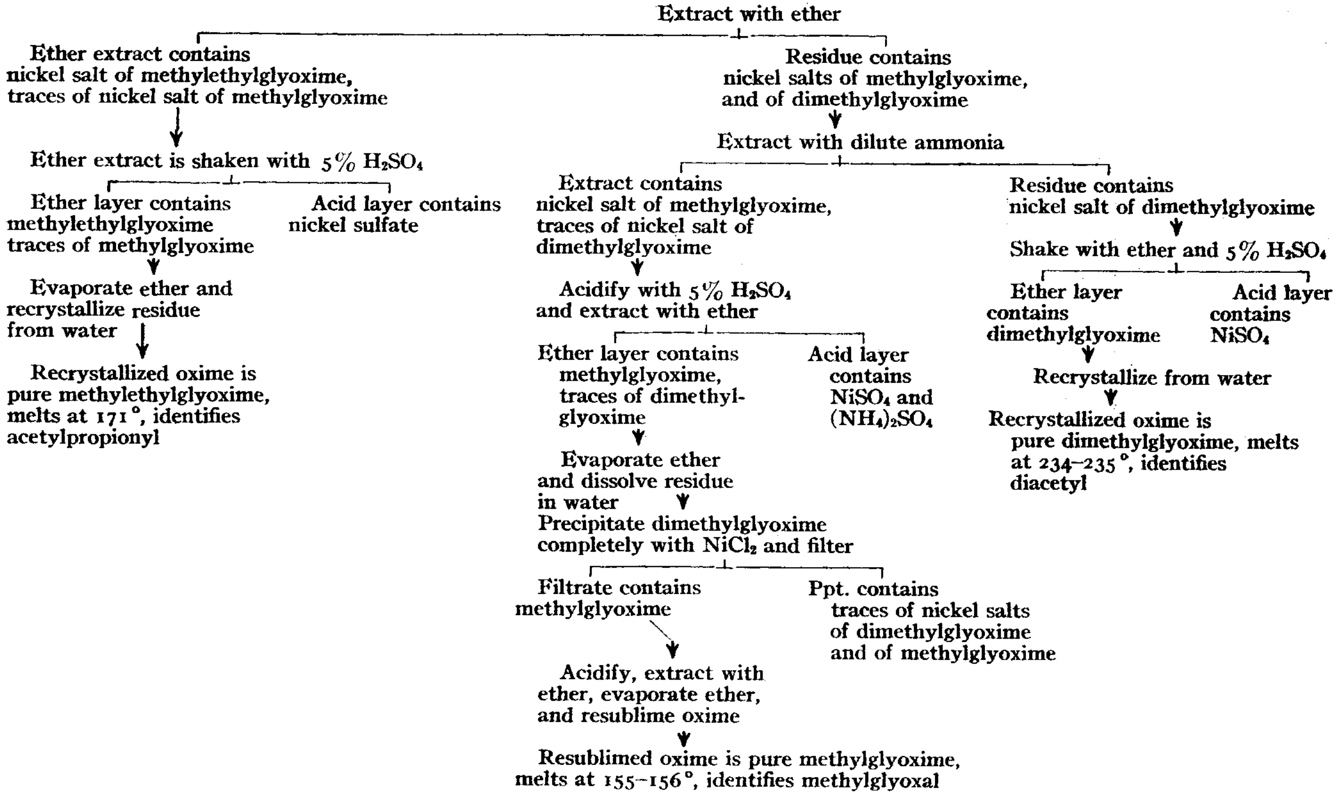
[1] Sufficient detail regarding the physical properties of these nickel salts is in some instances not supplied by Tschugaeff. In other instances, where the Russian literature was not available, abstracts of the original articles were too brief to mention physical properties at all.

MIXTURE CONTAINS THE NICKEL SALTS OF

Methylglyoxime. Dimethylglyoxime. Methylethylglyoxime.



Extract with ether

Ether extract contains nickel salt of methylethylglyoxime, traces of nickel salt of methylglyoxime

Ether extract is shaken with 5% H_2SO_4

Ether layer contains methylethylglyoxime traces of methylglyoxime

Acid layer contains nickel sulfate

Evaporate ether and recrystallize residue from water

Recrystallized oxime is pure methylethylglyoxime, melts at 171°, identifies acetylpropionyl

Residue contains nickel salts of methylglyoxime, and of dimethylglyoxime

Extract with dilute ammonia

Extract contains nickel salt of methylglyoxime, traces of nickel salt of dimethylglyoxime

Acidify with 5% H_2SO_4 and extract with ether

Ether layer contains methylglyoxime, traces of dimethylglyoxime

Acid layer contains $NiSO_4$ and $(NH_4)_2SO_4$

Evaporate ether and dissolve residue in water

Precipitate dimethylglyoxime completely with $NiCl_2$ and filter

Filtrate contains methylglyoxime

Ppt. contains traces of nickel salts of dimethylglyoxime and of methylglyoxime

Acidify, extract with ether, evaporate ether, and resublime oxime

Resublimed oxime is pure methylglyoxime, melts at 155–156°, identifies methylglyoxal

Residue contains nickel salt of dimethylglyoxime

Shake with ether and 5% H_2SO_4

Ether layer contains dimethylglyoxime

Acid layer contains $NiSO_4$

Recrystallize from water

Recrystallized oxime is pure dimethylglyoxime, melts at 234–235°, identifies diacetyl ethylglyoxime purified by recrystallization from a small amount of water. The material thus recovered was found to melt[1] sharply at 171.°

The residue of nickel salts left by the ether extraction was now thoroughly shaken with dilute ammonium hydroxide. After filtering, the filtrate was acidified with dilute sulfuric acid to a point where any precipitated nickel salt of methylglyoxime redissolved and the solution instead of having a golden yellow color had become colorless. The mixture was now extracted with ether. The methylglyoxime obtained from the ether extract was freed from traces of dimethylglyoxime by redissolving both in water containing a few drops of dilute ammonium hydroxide and adding to this solution a few drops of very dilute nickel chloride. Since the nickel salt of dimethylglyoxime is practically insoluble in so dilute a solution of ammonia, traces of it would thus be precipitated and can be removed by filtration. This procedure was continued until there was sufficient indication that all of the dimethylglyoxime had been removed. The complete removal of dimethylglyoxime is shown by the appearance of the precipitation of the scarlet modification of the nickel salt of methylglyoxime which readily changes over into the more stable yellow modification, and further by the appearance of a yellowish solution due to the solubility of nickel methylglyoxime in ammonia solutions. The solution was again made just acid with dilute sulfuric acid and the methylglyoxime extracted with ether and resublimed. The resublimed dioxime thus recovered melted[1] at 155-156°.

The residue containing the nickel salt of dimethylglyoxime left by the ammonia extraction was thoroughly shaken with 50 cc. of 5% sulfuric acid and an equal volume of ether. The ether layer containing the free dioxime was evaporated and the dioxime recrystallized from water. The substance thus recovered and purified was found to melt[1] at 234-235°

The accompanying diagram graphically outlines the course of the analysis which isolates from a mixture containing minute quantities of the insoluble nickel salts of the dioximes of these α-diketones, the pure dioximes whose melting point identifies each homolog.

THE SEPARATION OF ETHANE AND ETHYLENE BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES.[2]

By G. A. Burrell and I. W. Robertson.

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This paper shows some experiments made by the authors, at the Pittsburgh Experiment Station of the Bureau of Mines, in separating ethane and ethylene by fractional distillation in a vacuum at low temperatures. In previous communications there was shown the separation of gases

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[1] Cf. Glyoxime, Beilstein, *Organische Chemie*.

[2] Published by permission of the Director of the Bureau of Mines.