[Contribution from the Chemical Laboratory of Wellesley College]

THE STUDY OF THE MOLECULAR CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS BY THE ABSORPTION OF LIGHT

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The original aim of this work was to determine the molecular structure of acetylacetone and diacetyl monoxime by a study of their absorption curves, and a comparison of their curves with those of certain derivatives of known constitution.

The absorption of the following substances was investigated in the ultraviolet region of the spectrum: acetylacetone, the dioxime of acetylacetone, acetylacetone monoxime anhydride, and copper acetylacetone; diacetyl monoxime, dimethylglyoxime anhydride and the copper salt of dimethylglyoxime. The visible absorption of the two copper compounds was also investigated. In every case the solvent was 95% alcohol.

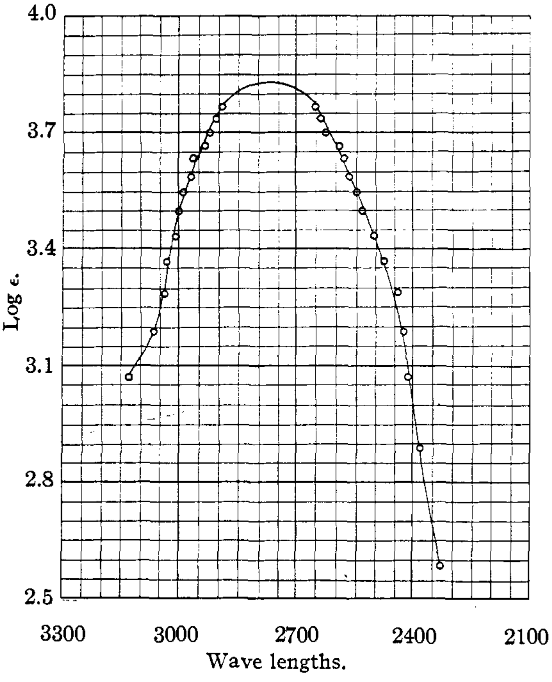

Fig. 1.—Acetylacetone in alcohol.

The apparatus used for the determinations in the ultraviolet region of the spectrum included a Hilger sector photometer and a Hilger quartz spectrograph; in the visible region, a Nutting photometer and a Hilger wave-length spectrometer. A spark between iron electrodes was used as a source of light in the former, and a 12-volt, 3-ampere, 36-watt Mazda lamp in the latter. The light was passed simultaneously through the solvent and solution, and then through the photometer and spectrometer. The amount of light passing through the solution was kept constant, while that passing through the solvent was varied by varying the size of the sector opening in the sector photometer, or by varying the angle of the nicol prism in the Nutting photometer. Observations were made by means of a photographic plate in the ultraviolet, and by the eye of the observer in the visible region. The molar absorption coefficient (ϵ) was calculated from the relation $I = I_0.10^{-\epsilon cd}$, I/I_0 being the ratio between the intensities of the light through the solution and through the solvent, c the molar concentration and d the thickness of layer of solvent and solution. The data are plotted as curves, using the logarithms (to the base 10) of the molar coefficient of absorption as ordinates, and the wave lengths in Ångström units as abscissas. The method is in such general use that further descriptive details seem unnecessary.

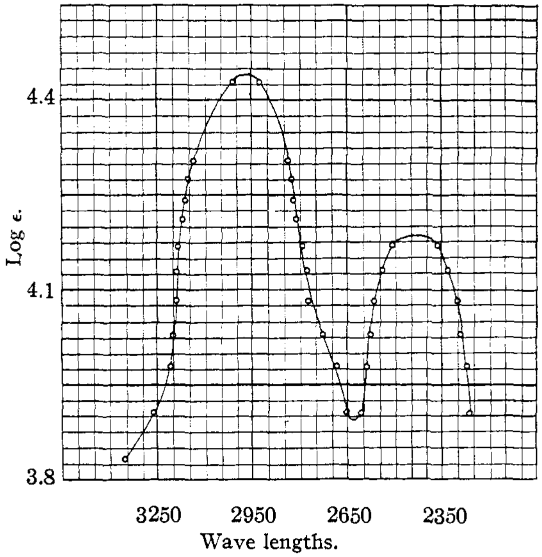

Fig. 2.—Copper acetylacetonate in alcohol.

The substances used were purified to the proper melting points or boiling points or, if these constants seemed doubtful or were not known, purification was continued until the light absorption remained constant.

Acetylacetone has already been studied by Grossmann,[1] and the results found here differ slightly because of a difference in solvent. Copper acetylacetonate has also been examined both in the ultraviolet and in the

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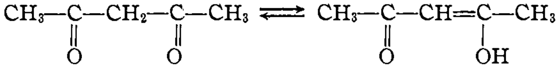
[1] Grossmann, *Z. physik. Chem.*, **109**, 305 (1924).

visible region by French and Lowry,[2] and the work was repeated here for the purpose of checking the new instruments.

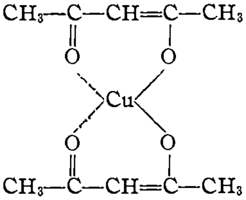
Acetylacetone may undergo keto-enol tautomerism in the following way.



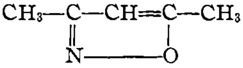
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CH_3$$

I II

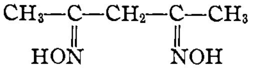
To determine in which form acetylacetone exists in alcoholic solution its absorption was compared with certain derivatives in which either one or the other of the above chain formations is stable. Copper acetylacetonate (III) and acetylacetone monoxime anhydride (IV) have the structure of the enol form (II), while the dioxime (V) probably has the keto form (I).



III



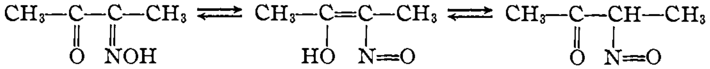
IV



$$CH_3-\underset{\underset{HON}{\|}}{C}-CH_2-\underset{\underset{NOH}{\|}}{C}-CH_3$$

V

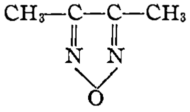
Diacetylmonoxime may have the following forms.



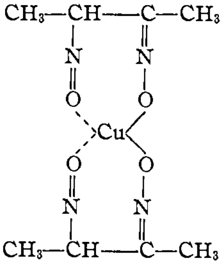
$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{HO}{|}}{C}=\underset{\underset{N=O}{|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{N=O}{|}}{CH}-CH_3$$

VI VII VIII

Its curve was compared with those of dimethylglyoxime anhydride (IX), whose chain would have the structure of the first form of diacetylmonoxime, and with copper dimethylglyoxime (X), which would identify the third form as far as the straight chain is concerned.



IX



X

Acetylacetone[3] was examined in a 0.00004 *M* solution in 95% alcohol. It showed a band with a maximum at $\lambda = 2770$; $\log \epsilon = 3.84$. Its copper salt was examined, in the ultraviolet, in a 0.000025 *M* solution and in a

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[2] French and Lowry, *Proc. Roy. Soc.*, **106**, 489 (1924).

[3] See Table I for summary of all curves, and Fig. 1 for curve of acetylacetone.

1/350 *M* solution in the visible region. It exhibited two bands in the ultraviolet: one at $\lambda = 2970$, $\log \epsilon = 4.44$, and the other at $\lambda = 2433$, $\log \epsilon = 4.19$. In the visible region it showed a band at $\lambda = 6400$, $\log \epsilon = 1.72$, and a minimum, to which it owes its blue color, at $\lambda = 4680$, $\log \epsilon = 0.83$. Acetylacetone monoxime anhydride was examined in 0.01, 0.001 and 0.0001 *M* solutions. It showed only continuous absorption, with the suggestion of a band just beyond the shortest observable wave lengths. Acetylacetone dioxime was examined in 0.001 and 0.0001 *M* solutions and showed only continuous absorption. The curve obtained was almost a straight line, with no hint of a maximum unless far out in the extreme ultraviolet region.

The maximum in the case of the larger band of the copper salt of acetylacetone is considerably higher than that of acetylacetone itself. The copper salt must have the chain formation of the enol form. The dioxime shows no band at all, and it must be similar to the keto form. Therefore, the acetylacetone probably contains some enol form, to give rise to the band, but it is not all in the enol form or its maximum would be considerably higher, as it is in the copper compound. This is in accord with the results found by Grossmann,[1,4] who concluded that acetylacetone was an equilibrium mixture of the keto and enol forms, and that the band is due to the enol form. He found that the height of the band varied with the solvent used. On measuring the per cent. of enol in the different solvents by bromine titration, he found that the height of the band varied with the per cent. of enol present. In pure alcohol he found a maximum at $\lambda = 2725$, $\epsilon = 10{,}500$, $\log \epsilon = 4.03$, and in pure water at $\lambda = 2770$, $\epsilon = 1900$, $\log \epsilon = 3.28$. Assuming the per cent. of enol in alcoholic solution (measured by bromine

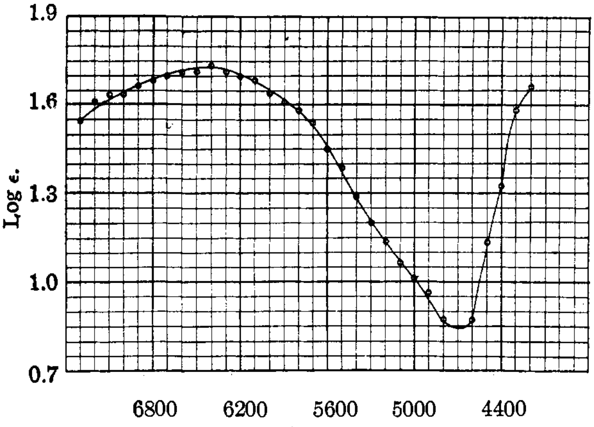

Fig. 3.—Copper acetylacetonate in alcohol (visible).

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[4] Compare Morton and Rosney, *J. Chem. Soc.*, **1926**, 706.

titration) to be 84, he calculated the percentages in the other cases from the proportionality between the absorption coefficient and the enol content. For water he calculated 15%, while bromine titration gave 20%. Using that same principle in the present case the per cent. of enol has been calculated and found to be about 55.7, a value midway between Grossmann's values for pure alcohol and pure water. Since the solvent in this case was 95% alcohol, the value of the enol content is entirely logical.

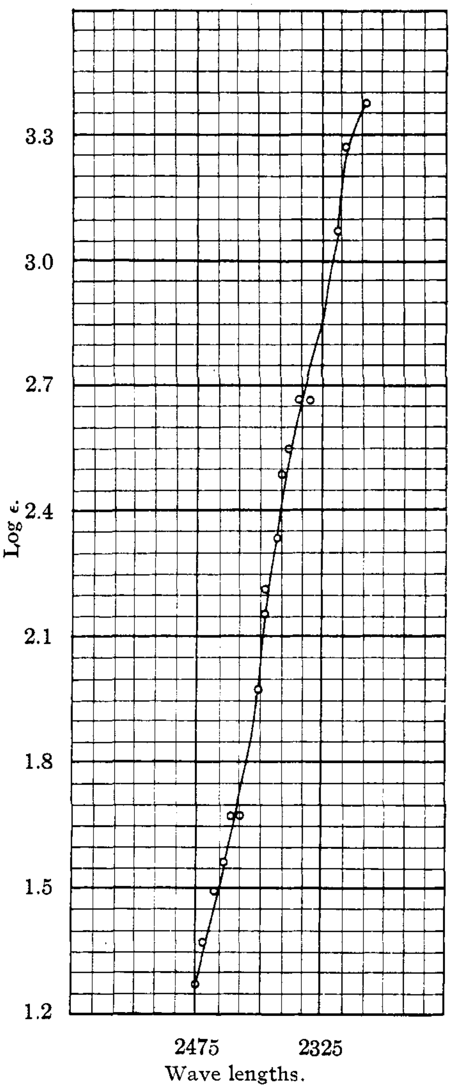
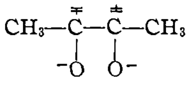


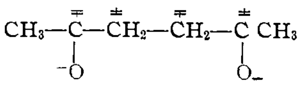
Fig. 4.—Acetylacetone monoxime anhydride in alcohol.

The copper compound of acetylacetone was examined by French and Lowry,[2] who concluded that the band in the visible region is due to the coördinated copper, and that the presence of the copper influences the rest of the molecule by shifting the maximum toward the red. It has also brought a second band, not mentioned by French and Lowry, into the ultraviolet region from the shorter wave lengths. There are several reasons for supposing a second band to exist in the case of acetylacetone itself. When Bielecki and Henri[5] examined diacetyl and acetonylacetone, they found not only maxima but also minima and then increasing absorption, as if toward second maxima. These two compounds have crossed polari-



$\mathrm{CH_3}-\underset{\substack{|\\ {}^-\mathrm{O}}}{\overset{\mp}{\mathrm{C}}}-\underset{\substack{|\\ \mathrm{O}^-}}{\overset{\pm}{\mathrm{C}}}-\mathrm{CH_3}$

and



$\mathrm{CH_3}-\underset{\substack{|\\ {}^-\mathrm{O}}}{\overset{\mp}{\mathrm{C}}}-\overset{\pm}{\mathrm{CH_2}}-\overset{\mp}{\mathrm{CH_2}}-\underset{\substack{|\\ \mathrm{O}^-}}{\overset{\pm}{\mathrm{C}}}\ \mathrm{CH_3}$

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[5] Bielecki and Henri, *Ber.*, **46**, 3640 (1913).

ties and would, according to Lowry and French,[6] have bands nearer the red than the corresponding bands of the uncrossed compounds. Bielecki and Henri[7] found a single maximum in the curves for acetone, diethylketone and methylethylketone, while for dipropyl, ethylpropyl and methylhexyl ketones they found also minima and increasing absorption again. It is well known that addition of alkyl groups tends to shift the absorption toward the red. The conclusion here drawn is that three different influences have shifted the absorption toward the red: coördinated copper, crossed polarities and increasing molecular weights, and that the crossed polarities and increasing molecular weights have shifted the absorption so that the minimum between the two maxima is measurable, while the coördinated copper has succeeded in shifting the absorption so far that the second maximum has become observable.

The monoxime anhydride of acetylacetone has the chain formation of the enol form. Its curve seems to promise a maximum just beyond the wave lengths which can be investigated, while the dioxime, though traced to the same point, shows no sign of the flattening indicating the approach to a maximum. In both cases the presence of the nitrogen has shifted any possible maximum toward the shorter wave lengths.

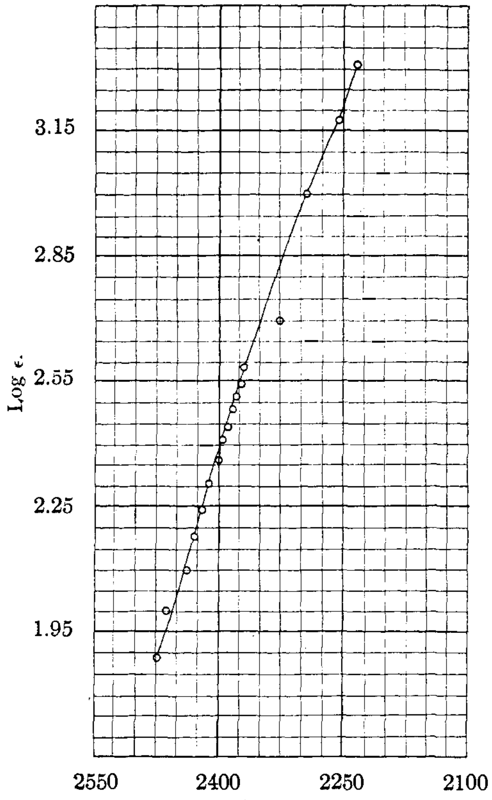

Fig. 5.—Acetylacetone dioxime in alcohol.

Diacetyl monoxime was examined in 0.00025 and 0.000025 *M* solutions, and showed only continuous absorption. Copper dimethylglyoxime was examined in a 0.001 *M* solution in the visible and in 0.0001, 0.00002 and 0.00001 *M* solutions in the ultraviolet region. The visible spectrum showed a minimum at about λ = 7350, log ε = 1.37, to which the dark red-brown

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[6] Lowry and French, *J. Chem. Soc.*, **125**, 1927 (1924).

[7] Ref. 5, p. 3638.

color of the solution is due. The rest of the curve showed only continuous absorption throughout the ultraviolet, with a break in the continuity when the concentration was changed, between 2560 and 2900 Å. The slope of the curve also changed abruptly on dilution, as if the solvent in some way affected the constitution of the molecule. Dimethylglyoxime anhydride showed, on examination of 0.02, .0.002, 0.0002 and 0.00002 *M* solutions, nothing but exceedingly steep continuous absorption. The increase of log ϵ = from 0.67 to 2.85 took place in the interval from $\lambda = 2409$ to $\lambda = 2280$, or 129 Å.

If the curves of diacetyl monoxime, dimethylglyoxime anhydride and the copper compound of dimethylglyoxime are compared, it is evident that the anhydride and the copper salt are most unlike, while the parent substance, diacetyl monoxime, in form and amount of absorption, comes between the other two. Therefore, on our former basis of judgment we should conclude that the monoxime has neither the form $CH_3COC(=NOH)CH_3$, similar to dimethylglyoxime anhydride, nor the form $CH_3CH(NO)COCH_3$, as in the copper compound, but is an equilibrium mixture of the two. Actually, the curves have so little in common that one hesitates to dispose of the question in that simple manner. Other compounds should be examined in which, if possible, there were no disturbing influences such as the coördinated copper or the ring structure of the anhydride, and which held in stable form the possible chain formations of diacetyl monoxime. A very good substance for this comparison would be methyl nitroso-*iso*propyl ketone, $CH_3COC(NO).(CH_3)_2$, which has no possibility of forming an isonitroso or oxime compound, and would therefore identify the first form of diacetyl monoxime.

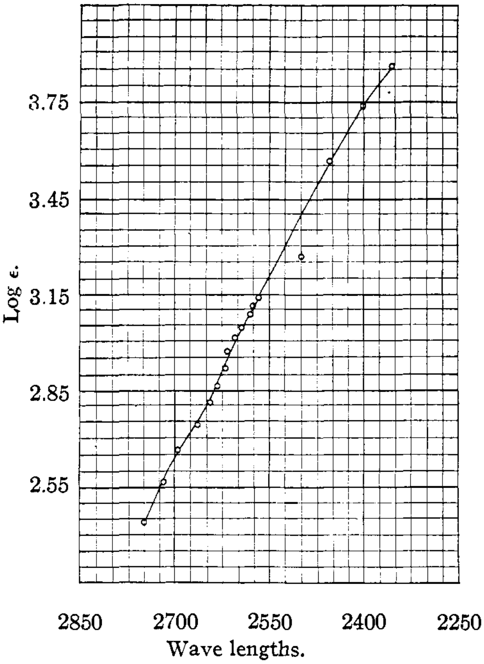


Fig. 6.—Diacetyl monoxime in alcohol.

Since there is no maximum in the curve of diacetyl monoxime, probably the compound represented by Formula VII does not exist, for the enol group present in that form would ordinarily give a band at about 2700 Å.

TABLE I

COMPARISON OF ABSORPTION

Substance	Maximum	Minimum	Wave lengths for values of log ε			
			Log ε = 1.5	Log ε = 2.5	Log ε = 3.5	Log ε = 4.0
Acetylacetone	Log ε = 3.84		..	2310	3000	..
	λ = 2770			2310	2535	
Copper acetylacetonate	Log ε = 1.72					
	λ = 6400	Log ε = 0.83				
	....	λ = 4680		Between	Between	3210
	Log ε = 4.44		5660	4200	4200	2710
	λ = 2970	....		and	and	2280
	....	Log ε = 3.89	4340	3400	3400	2580
	Log ε = 4.19	λ = 2625				
	λ = 2433					
Acetylacetone dioxime	Continuous		..	2380	..	..
Acetylacetone monoxime anhydride	Continuous		2460	2375	..	..
Diacetyl monoxime	Continuous		..	2732	2475	..
Copper dimethylglyoxime		Log ε = 1.37	7520			
	Infra-red	λ = 7350	7270	5200	3275	2450
Dimethylglyoxime anhydride	Continuous		2355	2302	..	..

If a certain value of log ε (3.5) be chosen on the curves for diacetyl monoxime and the copper salt of dimethylglyoxime (Table I), the influence of the coordinated copper can be seen by comparing the wave lengths. There is a displacement of about 800 Å., from 2475 Å. to 3280 Å., while at log ε = 3.9, which is beyond the discontinuity in the copper curve, the displacement is only about 175 Å. On the curve of the anhydride these two points would be far out in the ultraviolet, if reached at all.

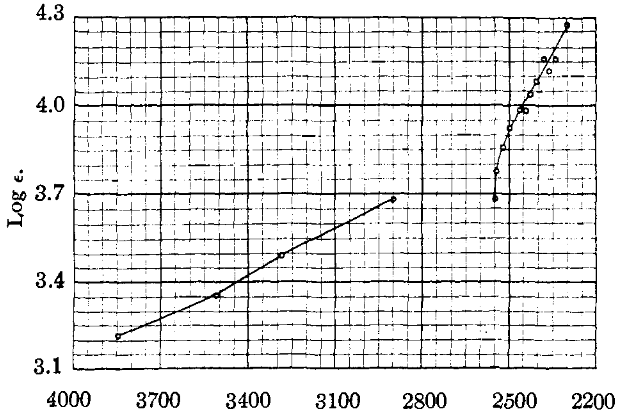


Fig. 7.—Copper dimethylglyoxime in alcohol.

On comparing the visible absorption of the two copper compounds, a displacement of the minimum from λ = 4680 in the copper acetylacetonate to λ = 7350 in the copper dimethylglyoxime is seen, while the maximum has been shifted from the visible red (λ = 6400), to the infra-red. The copper acetylacetonate has a ring of six atoms (XI), and has no crossed polarities, while copper dimethylglyoxime (XII) has an unstable ring of seven atoms, and has crossed polarities. The crossed polarities would be expected to shift the absorption toward the longer wave lengths, as is the case.

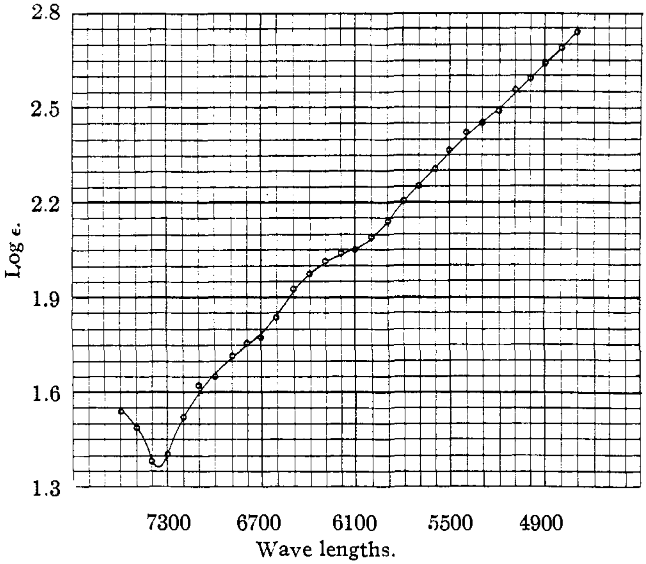
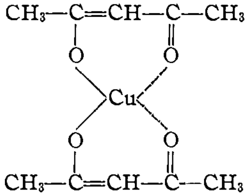
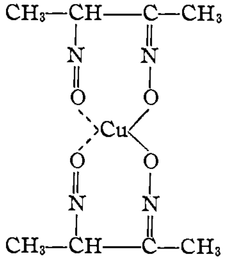


Fig. 8.—Copper dimethylglyoxime in alcohol (visible).



XI



XII

Summary

1. The absorption curves are given for alcoholic solutions of acetylacetone, copper acetylacetonate, acetylacetone monoxime anhydride, acetylacetone dioxime; diacetyl monoxime, copper salt of diacetyl dioxime,

and diacetyl dioxime anhydride in the ultraviolet, and for the two copper compounds in the visible region.

2. The conclusion is drawn that acetylacetone in 95% alcohol solution is an equilibrium mixture of the keto and enol forms, the per cent. of the enol form being midway between that found by Grossmann for solutions in pure alcohol and pure water.

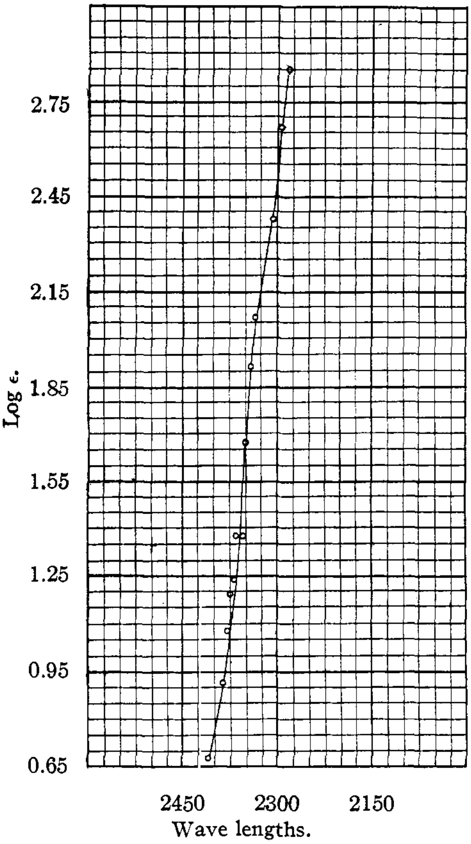


Fig. 9.—Dimethylglyoxime anhydride in alcohol.

3. A tentative conclusion is drawn that diacetyl monoxime is also an equilibrium mixture.

4. Incidentally, certain influences of coördination and of crossed polarity are noted. Studies along these lines are being continued.

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