

157. *The Infra-red Spectra and Structure of Tautomeric Compounds.*

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It has long been known that there exists a relationship between absorption spectra in the infra-red and chemical constitution. Coblenz (*Pub. Carnegie Inst.*, No. 35, 1905; 65, 1906; 97, 1908), from his classical work on liquids, concluded that certain persistent bands found in a series of homologous compounds could be ascribed to some particular groupings or linkages present in the molecule. It is now possible from the extensive researches of Lecomte, Henri, Bonino and Ellis, and others (see Schaefer and Matossi, "Das Ultrarote Spectrum," Berlin, 1930, p. 266, etc.) to refer a particular absorption band to a single linkage in the molecule. Thus the characteristic vibrations of the ground states of C—H, C=O, C≡N, C—OH, N—H, S—H linkages in organic molecules have all been recognised.

Conversely, from a knowledge of the infra-red spectrum it should be possible to determine the linkages or groupings present in the molecule. For instance, Ross (*Proc. Roy. Soc.*, 1926, A, **113**, 208), from an investigation of the infra-red spectrum of pyrone, concluded that the molecule consisted of a benzenoid group together with a hydroxyl group. The method, however, owing to difficulty of technique, does not appear to be suitable for use as a routine method in organic chemistry as desired by Ross. The use of the Raman spectrum appears to be less difficult and more accurate.

In the present investigation it was proposed to follow the enol-keto change of tautomeric compounds by observation of the change of intensity of the hydroxyl bands.

The infra-red studies of Weniger (*Physical Rev.*, 1910, **31**, 388), Bonino (*Gazzetta*, 1923, **53**, 575), Sappenfield (*Physical Rev.*, 1929, **33**, 37), and others indicate that the corresponding bands at 0.923, 1.55, 3.00, 6.90 μ in the spectra of the alcohols are assignable to the C—OH linkage. In the same way, the carbonyl group of the aliphatic ketones is characterised by bands at 1.9, 2.9, and 5.9 μ . A compound existing in both forms would therefore be expected to show both series of bands.

Investigations now carried out with 80% enolised acetylacetone have proved, however, that the characteristic hydroxyl bands are absent from the spectrum. Other similar tautomeric compounds have been investigated, and in no case have the hydroxyl bands been detected, although the carbonyl bands were observed in all cases.

E X P E R I M E N T A L.

Apparatus.—The work was carried out in a basement room fitted with heavy slate benches on brick pillars. The spectrometer, filament, mirrors, and other equipment were housed in a large wooden box blackened on the inside. The galvanometer was situated in a large dark room and mounted on a heavy concrete pillar sunk into the ground. The assemblage was such that all controls could be operated by a single observer seated at the end of the dark room. In order to ensure rigidity, the spectrometer, mirrors, etc., were clamped to the slate bench.

Spectrometer. The spectrometer was a large standard Hilger instrument with wave-length drum calibrated for a 60° rock-salt prism. It was enclosed in a heavily lagged draught-free box. The drum was rotated by means of a long rod suitably attached to a low-g geared wheel making contact with a large cog soldered to the end of the drum. The drum readings were observed by means of a telescope.

Source of radiation. The source of radiation was a Nernst filament mounted on a heavy stand; it was enclosed in an asbestos housing fitted with a metal shutter, and was usually operated at 0.8 amp. and 100 volts, constant current being maintained by using two 100-volt batteries alternately.

Thermopile and galvanometer. A 20-junction bismuth-silver thermopile as supplied by Hilger was employed. It was enclosed in an air-tight casing (which could be evacuated) fitted with a rock-salt window. The galvanometer was of the Downing type and was generally used at a sensitivity of about 10^{-10} amp. per mm. deflexion at 1.5 metres. Electromagnetic disturbances were appreciable, and, as the galvanometer could not be shielded satisfactorily, accurate work had to be carried out at night, when the galvanometer was quite steady.

Absorption cells. Rock-salt cells of various thicknesses were used. They were made according to the method of Ross (*loc. cit.*), freshly cleaved rock-salt plates being put together exactly as before cleavage. The cell holder consisted of a large brass plate in which two identical square holes had been cut. The cells were held in front of these holes by adjustable screws, allowing movement in two planes. The holder moved on two heavy vertical runners screwed into the slate bench and was worked by means of a crank. It was brought into line with the spectrometer slit by means of suitable stops.

Setting of Spectrometer.—The spectrometer was first set visually by the sodium D line 0.5893μ , and finally on the carbon dioxide emission band at 4.44μ . Prominent bands of the solvents

employed were used as a check. The accuracy with which any sharp band could be repeated was 0.02μ .

Purification of Liquids.—Acetylacetone was carefully distilled, dried, and fractionated in a vacuum. Benzoylacetone was twice crystallised from ether; m. p. 61° . Kahlbaum's 100% acetic acid was dried and distilled; b. p. 118° .

Ethyl acetoacetate and methylacetoacetate were dried and distilled at 15 mm., and redistilled just before use.

Acetone was purified by the method of Shipsey and Werner (J., 1913, **103**, 125); b. p. 56° .

A sample of alcohol which had been specially purified for velocity measurements was used.

Kahlbaum's carbon tetrachloride was dried over calcium chloride and distilled; b. p. 77° .

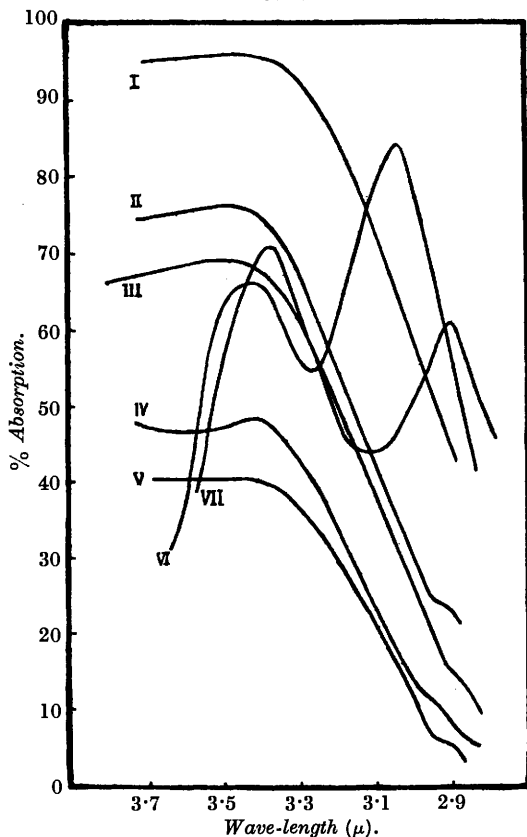
Procedure.—The cell was first balanced with the blank over the whole region of spectrum and was then filled with the liquid to be investigated without removal from the cell holder. The method of observation was that described by Robertson, Fox, and Hiscocks (*Proc. Roy. Soc.*, 1928, **120**, 128, 149), readings being taken at intervals of 0.02μ , except with very broad bands for which the intervals were 0.04μ . The slit width used was $0.007''$ from 2 to 4.5μ and $0.010''$ from 4.5 to 6.5μ . The average galvanometer deflexion was 30 cm.

Results.

Acetylacetone.—The region around 3.0μ was investigated with cells of various thickness. With a cell of liquid thickness 0.05 mm., the absorption was over 90% and the band at 3.4μ was very broad. To avoid the use of thinner cells, which were difficult to fill, a solution of acetylacetone in carbon tetrachloride was employed, since this solvent shows no prominent absorption band below 6.0μ . The band characteristic of the hydroxyl group at 3.0μ was in no case observed, and, moreover, the broad C—H band at 3.4μ could not be resolved even with very dilute solutions or with thin films of the pure liquid of the order of 0.001 mm. in thickness. Such films were obtained by pressing a drop of liquid between two freshly cleaved rock-salt plates, the open edge of the cell being protected by strips of mica attached with Lepage's fish glue, or by pressing copper strips against the sides on placing in the cell holder. Such cells were never employed for more than $\frac{1}{2}$ hour. The results showing a range of absorption of 60—10% at 3.0μ are summarised in Fig. 1. For comparison purposes the spectra of ethyl alcohol in carbon tetrachloride and pure acetone between 2.9 and 3.5μ are also shown. The absorption curve of the alcohol shows clearly the separation of the 3.00μ hydroxyl band and the CH band at 3.41μ . The ketone

band of the acetone at $2.90\ \mu$ is also easily resolvable. A complete spectrum of pure acetylacetone from $2.5\text{--}9.0\ \mu$ is given in Fig. 2. Very thin films of liquid were used, the breaks in the curve denoting changes of cell. The bands at 8.12 , 5.82 , and $2.90\ \mu$ are identified

FIG. 1.



- I. Pure acetylacetone.
 II. 50% Solution of acetylacetone in CCl_4 .
 III. 25% " " " " " "
 IV. 10% Solution of benzoylacetone in " CCl_4 .
 V. 5% " " acetylacetone " "
 VI. 10% " " ethyl alcohol " "
 VII. Pure acetone: cell thickness, about $0.05\ \text{mm}$.

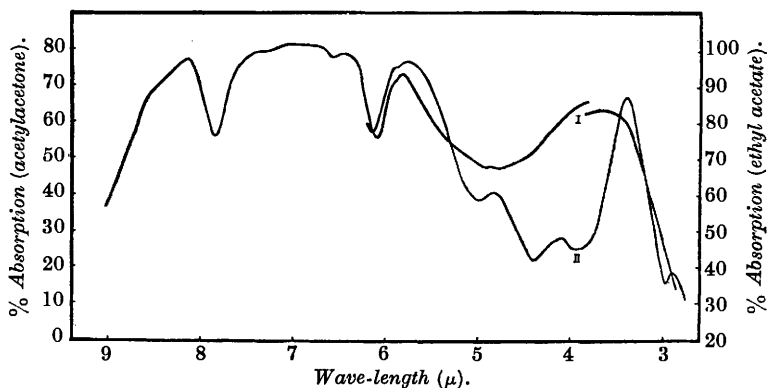
with the carbonyl group. Wide regions of absorption extending from $3.4\text{--}3.8\ \mu$ and $6.7\text{--}7.4\ \mu$ are very noticeable in the neighbourhood of the C—H vibration bands. Owing to the complete transparency of thin cells below $2.8\ \mu$, this region was not studied. Ellis (*J. Amer. Chem. Soc.*, 1929, **51**, 1384) has investigated acetylacetone

below 3.0μ , using cells 40 mm. thick. The bands found are assignable to the C—H and C=O linkage, no evidence for the presence of the hydroxyl band at 1.55μ being obtained.

Ethyl Acetoacetate and Methylacetoacetate.—These esters were investigated in the region $2.9\text{--}6.2 \mu$. The percentages of enolic compound in the equilibrium mixture of these compounds at room temperature, as determined by the bromine-titration method of Meyer (*Ber.*, 1911, **44**, 2718; 1912, **45**, 2852), are shown below :

Liquid.	Enol, %.	Liquid.	Enol, %.
Ethyl acetoacetate	7.7	Acetylacetone	80.5
Ethyl methylacetoacetate	4.0	Benzoylacetone	98.0

FIG. 2.



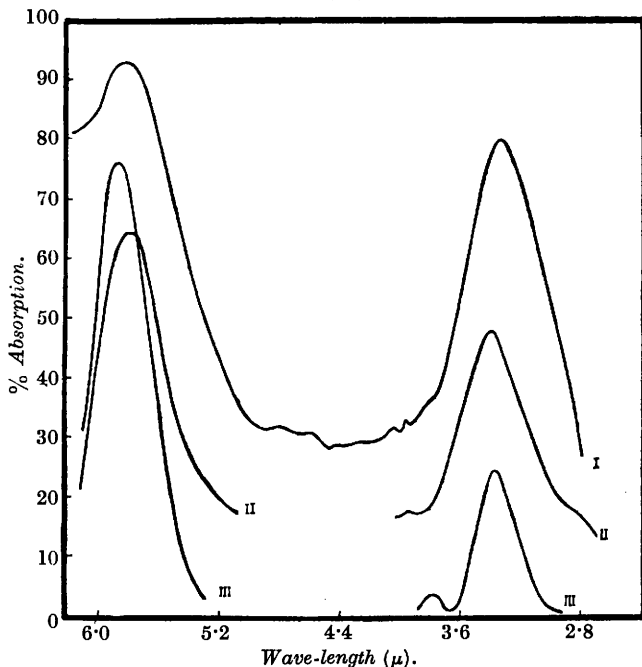
- I. *Acetylacetone* : thin films about 0.002 mm. in thickness.
 II. *Ethyl acetate* : cell thickness 0.05 mm.

The spectra are shown in Fig. 3. The bands at 3.38μ were much sharper than in the case of acetylacetone. This may result from the lower enol content of the mixture and will be referred to later. As in the case of acetylacetone, no band at 3.0μ was observed with either of these compounds. The intense bands at 5.88μ in acetoacetic ester and at 5.82μ in its methyl derivative arise from the vibration of the carbonyl group. A spectrum of ethyl acetate, taken for purposes of comparison, is shown in Fig. 2.

Benzoylacetone.—The presence or absence of the hydroxyl bands in tautomerides should be capable of demonstration by an examination of the pure enolic constituent. This was not possible in the liquid phase at room temperature, since the change from the enol form to the equilibrium mixture is rapid and highly catalysed. Solid forms of tautomeric compounds, however, consist entirely of one or other of the isomerides and attempts were made to obtain a spectrum of the solid form. Benzoylacetone in the solid phase is

completely enolised : thin films of it were prepared by warming rock-salt plates in an oven, melting the solid small crystals between them, and cooling the whole in a vacuum, or by crystallisation from dilute solution in benzene or carbon tetrachloride. The spectral bands, however, showed very broad maxima and were unsatisfactory since the thin crystalline film scatters most of the incident

FIG. 3.



- I. Ethyl acetoacetate : cell thickness 0.10 mm.
 III. " " thin film.
 II. Ethyl methylacetoacetate : thin film.

radiation, the maximum variation in absorption over the range 2.8—3.5 μ being only 10%. The band at 3.4 μ showed a broad maximum and it was not possible to resolve any band in the region of 3.0 μ .

A solution of benzoylacetone in carbon tetrachloride (highly enolised) showed the same absorption characteristics as acetylacetone, *viz.*, a broad C—H band at 3.4 μ , C=O band at 2.90 μ , and no hydroxyl band at 3.0 μ .

Acetic Acid.—It is well known that the carbonyl group in the carboxyl radical has not the normal ketonic properties. The absorption spectra of the acids, however, show the characteristic

carbonyl bands at 1.9, 2.9, and 5.8 μ , as found in the aldehydes and ketones (Ellis, *loc. cit.*). It therefore became of interest to examine the spectra of the carboxylic acids for the presence of the hydroxyl bands. The spectrum of acetic acid showed no indication of these bands, although the ketonic and C—H bands were readily detected. Sappenfield (*loc. cit.*) recently pointed out that the hydroxyl bands at 1.55 μ and 3.00 μ do not occur in the spectrum of butyric acid, and concluded that the hydroxyl groups of acids and alcohols are quite different chemically and that this causes loss of confidence in the simple bond theory. The conclusion of Smith and Boord (*J. Amer. Chem. Soc.*, 1926, **48**, 1512), that the band at 5.8 μ in acetic acid is due to the hydroxyl group, has been shown to be incorrect by Ellis and others (*loc. cit.*).

Raman Spectrum of Acetoacetic Ester.—The Raman spectrum of acetoacetic ester has been recorded by Kohlrausch and Dadiou (*Ber.*, 1930, **63**, 1657; Kohlrausch, "Smekel-Raman Effekt," Berlin, 1931; *J. Opt. Soc. Amer.*, May, 1931). The frequency differences 1706—1726 (wave numbers) are identified with the C=O bindings as occurring in ketones and esters respectively. The Raman line at 1600 cm.^{-1} is characteristic of the carbon double bond, and the authors remark "that in spite of the fact that the freshly distilled ester contains only 20% of the enol isomer the C=C linkage gives a very intense line." This provides conclusive evidence for the existence of more than one form of molecule in the tautomeric liquid. On the other hand, the authors state that the hydroxyl band at 3380 cm.^{-1} is present although very faint—it is not shown in their diagram. This line was not found by Venkateswaran and Bhagavantam (*Indian J. Physics*, 1930, **5**, 129). The appearance of this frequency corresponding to the 3.0 μ infra-red band is surprising, especially in view of the fact that it is not observed in the alcohols other than methyl alcohol. The intensity of the line is not sufficiently great to indicate the presence of the hydroxyl binding in the enol form and may have resulted from impurities present in the original liquid.

Discussion of Results.

The conclusion derived from the foregoing results is that the normal hydroxyl vibration existing in the alcohols is not present in the infra-red spectra of the enolic forms of certain tautomeric compounds. This may result from one of two causes: (a) the hydroxyl group is not present in the enolic isomeride, (b) the hydroxyl linkage is present in the molecule but the influence of the neighbouring —C=C— group causes a displacement of the characteristic band.

In view of the second possibility, since the hydroxyl group in the enolic compound $\cdot\text{C}(\text{OH})\cdot\text{C}$ is similar to that in a secondary or tertiary alcohol, with modification by the adjacent double bond, it would be of interest to see how the C—OH linking in the alcohols is altered by change of the groups attached to the carbon atom. Weniger (*loc. cit.*) studied the spectra of the homologous series of alcohols methyl to octyl from 1 to 10 μ , and found that the characteristic hydroxyl bands are only slightly shifted by increase in the length of the carbon chain. He also showed that, with the exception of a few feeble bands, the isomerides of propyl and amyl alcohol were very similar to the normal alcohols. Similar results were obtained by Lecomte ("Le Spectra Infra-Rouge," Paris, 1928) for butyl and isobutyl alcohol. In the case of the secondary and tertiary alcohols containing the linkage $>\text{CH}\cdot\text{OH}$ and $\geq\text{C}\cdot\text{OH}$ respectively, Weniger found that the hydroxyl bands at 1.55, 3.0, 6.9, and 7.3 μ were identical with those of the primary alcohols, but above 8.0 μ marked differences in spectra were observed. If the absorption in this region can be correlated, the 9.6 μ band of the primary alcohols is shifted to 9.1 μ in the secondary and 8.6 μ in the tertiary alcohols. The 3.0 μ band, then, is not changed either by increasing the length of the carbon chain or by substitution of the hydrogen atoms attached to the carbon linked to the hydroxyl group.

The studies of Bonino (*loc. cit.*) on the carbon-hydrogen linkage have shown that the band at 3.4 μ is displaced only slightly in a series of hydrocarbons, and is not appreciably altered by substitution of the hydrogen attached to the CH linking by hydroxyl or halogen: he has summarised the data (*Trans. Faraday Soc.*, 1929, 25, 876). On the other hand, a considerable displacement is observed when the carbon of the C—H grouping is linked to a double bond. For instance, the 3.39 μ band in ethane is moved to 3.28 μ in ethylene, the corresponding band in benzene being at 3.25 μ . Bonino concludes that there are two types of C—H linkage—that in saturated hydrocarbons and that (C=CHR) in an aromatic nucleus or in unsaturated hydrocarbons. This is confirmed by Raman spectra investigations by Kohlrausch (*loc. cit.*).

Unfortunately, the corresponding data for alcohols are lacking, but a double bond adjacent to the hydroxyl group will no doubt have an important influence on the C·OH vibration. It has been noticed that the C—H band in the highly enolised substances benzoyl- and acetyl-acetone is very broad. It might, therefore, be suggested that the 3.0 μ hydroxyl band is moved under the influence of the double bond to the region of the 3.4 μ band, although such a large shift seems highly improbable. Alternatively, the broad band may be due to the presence of the two types of C—H vibration already

discussed, it being assumed that the enol form contains a double bond. This question can only be settled by investigations with high dispersion such as are used in the study of gases.

On the other hand, it is well known that the hydrogen in tautomeric compounds is mobile or very loosely held. The absence of the hydroxyl vibration or the shifting of the band may be due to this cause. Andrews (*Physical Rev.*, 1930, **36**, 531) has shown that the forces under which groups with fixed mass vibrate may be considered as acting along lines associated with the chemical valency bonds. These forces can be characterised by two force constants due to (1) stretching and (2) bending of the bond. This has been recently demonstrated by Andrews with models and explains certain results in Raman spectra. From a study of the formaldehyde bands in the ultra-violet, Herzberg (*Trans. Faraday Soc.*, 1931, **27**, 378) concludes that the hydrogen vibration in formaldehyde is of this type and executes both a longitudinal and transverse vibration. Similar results were predicted by Dennison (*Astrophys. J.*, 1925, **62**, 84) for the methane molecule. He calculated that the force between the hydrogen atoms was greater than between the carbon and hydrogen. The remarkable mobility of the hydrogen atom of the enol form points to the existence of a transverse as well as a longitudinal vibration of the hydrogen of the C—OH group, and further, the force between it and the adjacent hydrogen (or maybe, the carbon) is such that there is a probability of the hydrogen atom jumping across to the second carbon. Polanyi and Wigner (*Z. physikal. Chem.*, 1928, Haber Festband, 439) have calculated this probability by a consideration of elastic waves set up in the molecule. On this picture of a tautomeric compound, the hydrogen atom may be considered as loosely held to both the carbonyl and the C—H linkage, with a certain probability of its being in one of the positions. The carboxyl group would then consist of two apparent carbonyl groups with a hydrogen oscillating between them.

Summary.

The infra-red spectra of a number of tautomeric liquids have been determined between 2.8 and 6.3 μ . It has been demonstrated that these compounds do not show the hydroxyl bands to be expected from their chemical structures.

Similarly, the hydroxyl bands are absent from the spectrum of the carboxyl grouping, although the carbonyl bands are prominent. It is suggested that this may be due either to a shifting of the characteristic hydroxyl bands under the influence of the neighbouring double bond, or to the presence of some abnormal vibration of the hydrogen atom of the supposed hydroxyl group.

In conclusion, the author wishes to express his thanks to Prof. W. E. Garner for his constant interest and advice during the course of this investigation, and to the Department of Scientific and Industrial Research for a maintenance grant.

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