

**478.** *Keto-Enol Ratios in Solutions of Ethyl Acetoacetate.  
Infra-red Spectroscopic Indications.*

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The spectrum of ethyl acetoacetate has been studied in the 3- $\mu$ . and 6- $\mu$ . regions in relation to the effects of solvent and concentration. Optical density measurements, at the wave-length of maximum absorption due to the C=C linkage, are reconcilable with Meyer's results by the "bromine-titration" method. Estimates are made of the ketone : enol proportions of the ester in ethylene dibromide and pyridine.

IN relation to dielectric-polarisation measurements already presented (Le Fèvre and Welsh, this vol., p. 1909), a consideration of the infra-red spectrum of ethyl acetoacetate became of obvious interest. It is well known that hydroxyl groups and olefinic double bonds, both characteristic of enols, usually cause absorption from 2.7 to 3  $\mu$ . and at about 6  $\mu$ ., respectively (Thompson, *J.*, 1948, 328). The "free-hydroxyl" bands should therefore occur at a region likely to be transparent for the keto-structure, Me·CO·CH<sub>2</sub>·CO<sub>2</sub>Et. The possibility thus existed that enol : ketone ratios could be determined by direct spectral measurement of the enol content of a given equilibrium.

The principles underlying this have been discussed before (Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755, 767; Fox and Martin, *Trans. Faraday Soc.*, 1940, **36**, 902; Thompson and Sutherland, *ibid.*, 1945, **41**, 199). If the optical density ( $d_\lambda$ ) at a wave-length  $\lambda$  is taken as  $\log 100/(100-A)$ , where  $A = \% \text{ absorption}$ , then for a mixture  $d_\lambda$  is often equal to  $(c_E \cdot e_E + c_K \cdot e_K) \times \text{cell length}$  ( $c$  refers to the molar concentrations,  $e$  to the extinction coefficients of the solutes, and subscripts E and K to the enol and ketone, respectively). Use of a wave-length for which, say,  $e_K = 0$ , gives  $d_\lambda = c_E \cdot e_E$ .

Preliminary observations on ethyl acetoacetate in the 2.5—3- $\mu$ . region, made with a Hilger D209 spectrograph and quartz prism, have been mentioned by Hukins and Le Fèvre (this vol., p. 898). Absorptions were reported at 2.70 and 2.89—2.90  $\mu$ . The former, it was thought, might have been due to traces of water (compare Fox and Martin, *loc. cit.*, on benzyl alcohol, and Davies, *Trans. Faraday Soc.*, 1940, **36**, 333, on chloral hydrate), and the latter to *cis*-hydroxyl (compare Davies, *loc. cit.*; Wulf *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 2287; Rodebush *et al.*, *ibid.*, 1947, **69**, 770). However, the ester showed no marked absorption at 3.1—3.2  $\mu$ . (as do simple alcohols and phenols, or salicylaldehyde) where evidence of intra- and inter-molecular H bonding is to be expected (cf. Fox and Martin, *loc. cit.*; Thompson, *loc. cit.*; Hukins and Le Fèvre, *loc. cit.*).

Previous investigations, of both the infra-red and Raman spectra of ethyl acetoacetate, are on record. Bawn (*J.*, 1932, 1189) had found absorption at 2.9  $\mu$ . but had associated it with the C=O group. Barnes and co-workers [*Ind. Eng. Chem. (Anal.)*, 1943, **15**, 659; "Infra-red Spectroscopy," Reinhold, 1944] include a curve for this ester, between the limits 5 and 10  $\mu$ ., among their compilations of spectra. It shows a great reduction of transmission between 1700 and 1800  $\text{cm}^{-1}$  and a lesser one between 1600 and 1700  $\text{cm}^{-1}$ . The second feature is present also with the esters of fumaric and maleic acids, but not with those of succinic acid, whilst the first is common to all esters. The weaker absorption cited seems therefore to indicate the presence of a C=C linkage. Kohlrausch and Dadiou (*Ber.*, 1930, **63**, 1657; Kohlrausch, "Der Smekal-Raman Effekt," Springer, 1931; *J. Opt. Soc. Amer.*, 1931, **21**, 286; cf. Hibben, "The Raman Effect," Chem. Catalog Co., 1939) have reported the Raman spectrum of ethyl acetoacetate and identified certain shifts with C=O and C=C linkages, although the band at 3380  $\text{cm}^{-1}$  (hydroxyl, 2.96  $\mu$ .) seems to have been very faint (it was not detected by Venkateswaran and Bhagavantam, *Indian J. Physics*, 1930, **5**, 129).

The present paper therefore deals with two questions: (a) are the OH and C=C absorptions found in the positions and forms to be expected and, if so, (b) can their intensities be related to the enol : ketone ratios determined by other methods?

#### EXPERIMENTAL.

Materials were dried and purified as described by Le Fèvre and Welsh (*loc. cit.*). The spectroscopical examinations were carried out with the Perkin Elmer recording instrument in the Division of Industrial Chemistry, Melbourne (whose hospitality we gratefully acknowledge).

Results are indicated in the figures.

Figs. 1—3 cover the region where hydroxyl frequencies should be displayed, and Figs. 4 and 5 that where C=C and C=O bands are expected. Concentrations are indicated as  $v/v\%$ .

#### DISCUSSION.

It will be noted that the curves in carbon tetrachloride reveal an absorption at about 3370  $\text{cm}^{-1}$  (*i.e.*, 2.97  $\mu$ .). In carbon disulphide this appeared at approximately 3420  $\text{cm}^{-1}$  (*i.e.*, 2.92  $\mu$ .). With the lithium fluoride prisms, the corresponding point was registered rather weakly at *ca.* 3480 (*i.e.*, 2.87  $\mu$ .). Hukins and Le Fèvre using a quartz prism recorded it as 3450—3460  $\text{cm}^{-1}$  (*i.e.*, between 2.89 and 2.90  $\mu$ .). The absence of *two* absorptions having the relative positions and magnitudes usually reported for OH seems therefore to be established. The single band noted might, of course, represent that normally expected on the long-wave side of, and close to, the "monomeric" hydroxyl band (Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419, and other references above). If such were the case, we must infer that there is no "free hydroxyl" in the enol form. Yet, in salicylaldehyde (where internal chelation is indicated by evidence of various kinds, Sidgwick and Callow, *J.*, 1924, **125**, 527, and which, like enolic ethyl acetoacetate, contains the structural unit HO—C=C—C=O) the "monomeric" peak is clear at 2.76  $\mu$ .—almost the figure given for it by Fox and Martin—notwithstanding the particularly strong and extensive "association" absorption that continues on from this point right into the C—H region (Hukins and Le Fèvre, *loc. cit.*). Because of the last contrast, and in spite of the obvious suggestion provided by the discussion of Buswell, Rodebush, and

Whitney (*J. Amer. Chem. Soc.*, 1947, **69**, 770) on the infra-red spectra of certain vinyl alcohols stabilised against tautomeric rearrangement by steric hindrance from substituent groups, we hesitate to relate the absorptions observed by us to a *cis*-enolic structure of ethyl acetoacetate. The possibility that they might be weak overtones or combinations of the  $C=C$  fundamental

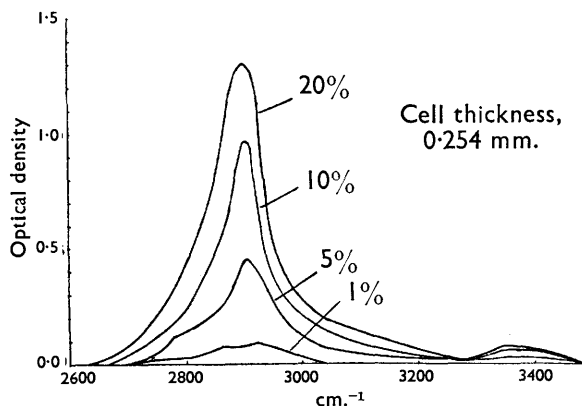


FIG. 1. Solution in  $CCl_4$  (NaCl prism).

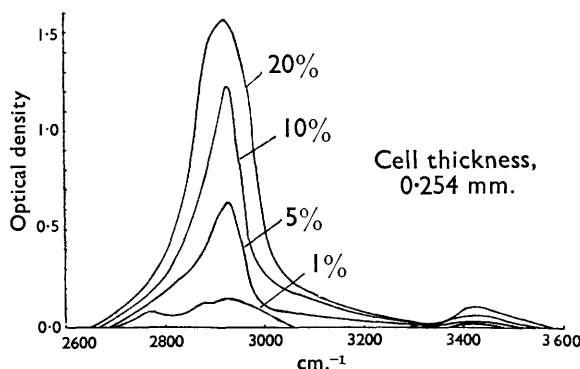


FIG. 2. Solution in  $CS_2$  (NaCl prism).

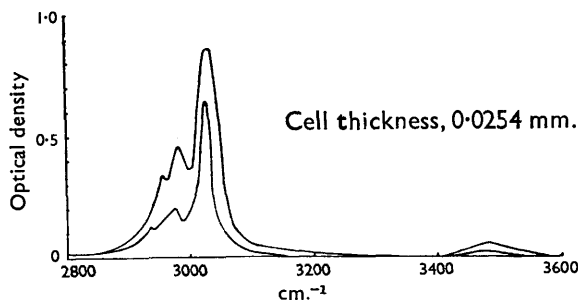


FIG. 3. Upper curve: pure ester. Lower curve: solution (20%) in  $CS_2$  (LiF prism).

cannot be definitely eliminated at this stage (compare Thompson and Whiffen, *J.*, 1946, 1005, on a similar problem with dimeric keten).

The peaks shown in the neighbourhood of  $3000\text{ cm}^{-1}$  in Figs. 1—3, and by Hukins and Le Fèvre, are obviously from C-H stretching modes (Thompson, *loc. cit.*) and require no comment.

When we turn to the  $6\ \mu$ . region (Figs. 4 and 5), absorption is seen to occur at almost the same wave-lengths in either carbon tetrachloride or carbon disulphide, that at  $1640\text{ cm}^{-1}$  being weaker

than that at  $1730\text{ cm.}^{-1}$ . The agreement with the diagram of Barnes *et al.* (*loc. cit.*) is satisfactory. For the reason given before, we identify the  $1640\text{-cm.}^{-1}$  maxima with the  $\text{C}=\text{C}$  linkage, and those at  $1730\text{ cm.}^{-1}$  with superimposed carbonyl and carboxy-frequencies. Raman spectra (see above) confirm this, since all esters give displacements which are similar to those of ketones, whilst that of the olefinic double bond is distinct at  $1645\text{ cm.}^{-1}$  (Dadiou and Kohlrausch, *Monatsh.*, 1930, 55, 201).

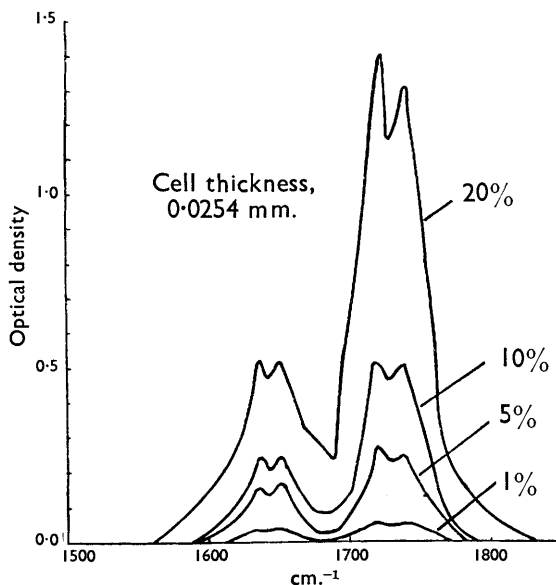


FIG. 4. Solution in  $\text{CCl}_4$  (NaCl prism).

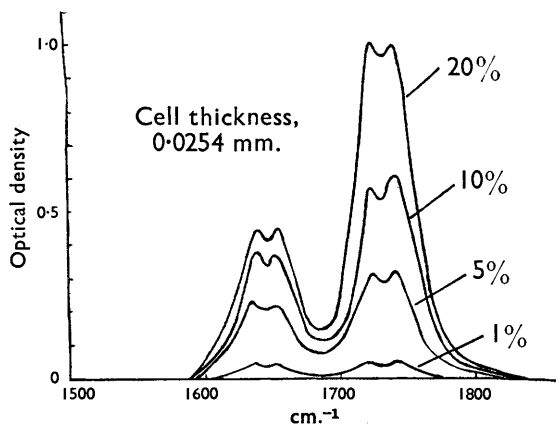


FIG. 5. Solution in  $\text{CS}_2$  (NaCl prism).

For our attempts at quantitative analysis, owing to the poor resolution of the  $3400\text{ cm.}^{-1}$  bands by the sodium chloride or lithium fluoride prisms, we have used the wave-lengths of maximum  $\text{C}=\text{C}$  absorption. It is relevant to mention that we think the twin peaks of Figs. 4 and 5 may be adventitious and due to the fact that it was necessary to secure a pen record for the absorption by the cell plus solvent above that for the cell plus solution on the same paper, and to use as zero reference the straight line joining the initial and final points with the shutter closed. Our experience was, unfortunately, that two "blank" curves could not be matched in this way, departures being correlated roughly with the amount of water-vapour absorption, and tending—

in the final %-transmission graph—to produce small peaks where none should occur. Accordingly, in what follows we have taken mean values of the highest optical densities and in all cases the average of a number of determinations.

We have followed a procedure parallel to that adopted with the apparent-dipole-moment data (Le Fèvre and Welsh, *loc. cit.*) and plotted the observed optical densities for the 1650-cm.<sup>-1</sup> band against the enol concentrations in g.-mols. per litre in the various solutions (cf. Figs. 4 and 5). The last information was deduced from the "bromine-titration" experiments of Meyer and Kappelmeier (*Ber.*, 1911, **44**, 2718; 1912, **45**, 2852). Our solutions were made up by volume and expressed as weight fractions by assuming that the volume of the solution was the sum of the volumes of the components. This approximation was tested on data obtained in the polarisation work, from which it was evident that weight fractions could be thus calculated with the accuracy of reading of an enol-%— $w_1$  graph from Meyer and Kappelmeier's results. The fact that Fig. 6 smoothly represents our present findings provides further support for the correctness of the earlier (chemical) keto-enol analyses.

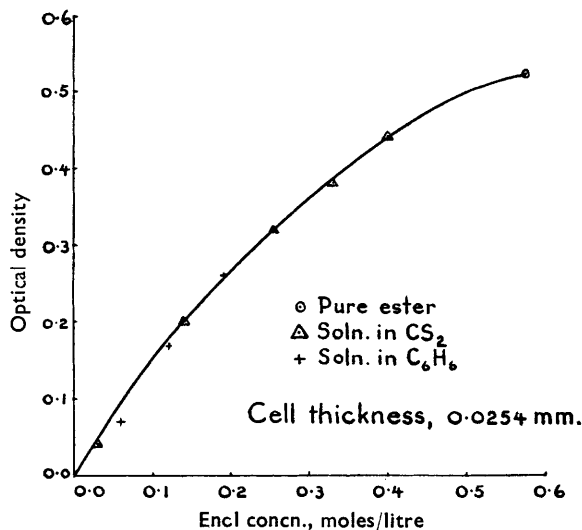


FIG. 6.

With the aid of Fig. 6, an interpretation of the optical densities of the ethylene dibromide and pyridine solutions may be attempted. The ratios  $K$  (= enol-concentration/ketone-concentration) against concentrations of total ester obtained are then :

Ethylene dibromide	Concn. (g.-mols./l.)	2.62	1.57	0.786	0.650	0.393
	$K^*$	0.13	0.12	0.10	0.08 <sub>5</sub>	0.08
Pyridine	Concn. (g.-mols./l.)	1.54	0.77			
	$K^*$	0.05	0.05			

\* At room temperature, *i.e.*, *ca.* 18°.

The equilibrium position in pyridine is of interest since in our previous paper we left open the possibility that this solvent might induce a high enol-% by intermolecular H-bonding;  $C_5H_5N \dots H \dots O-CMe \cdot CH \cdot CO_2Et$ . This evidently does not occur; presumably therefore the polarity of the medium ( $\mu_{C_5H_5N} = 2.1D$ ;  $\epsilon = ca. 12.4$ ) is still the determining influence (cf. Le Fèvre and Welsh, *loc. cit.*).

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