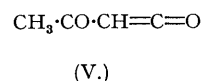
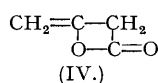
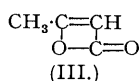
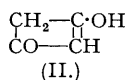
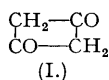


217. The Structure of Dimeric Keten : Infra-red Measurements.

By D. H. WHIFFEN and H. W. THOMPSON.

The infra-red spectrum of dimeric keten has been measured between 2 and 15 μ and correlated with the Raman spectrum. The results have been considered in relation to the different possible structures which have been suggested for this compound. Although an unambiguous decision cannot be made, some of the structures which are plausible on other grounds can be excluded, and it seems that the substance must have one of two possible lactone formulæ or be a mixture of them.

ALTHOUGH the dimer of keten is now an important synthetic reagent, its structure is still in doubt. Five possible formulæ, viz., (I)—(V), have been suggested. Formula (I) was favoured by Rice and Roberts (*J. Amer. Chem. Soc.*, 1943, **65**, 1677) from results on the pyrolysis of diketen and examination of the products by experiments

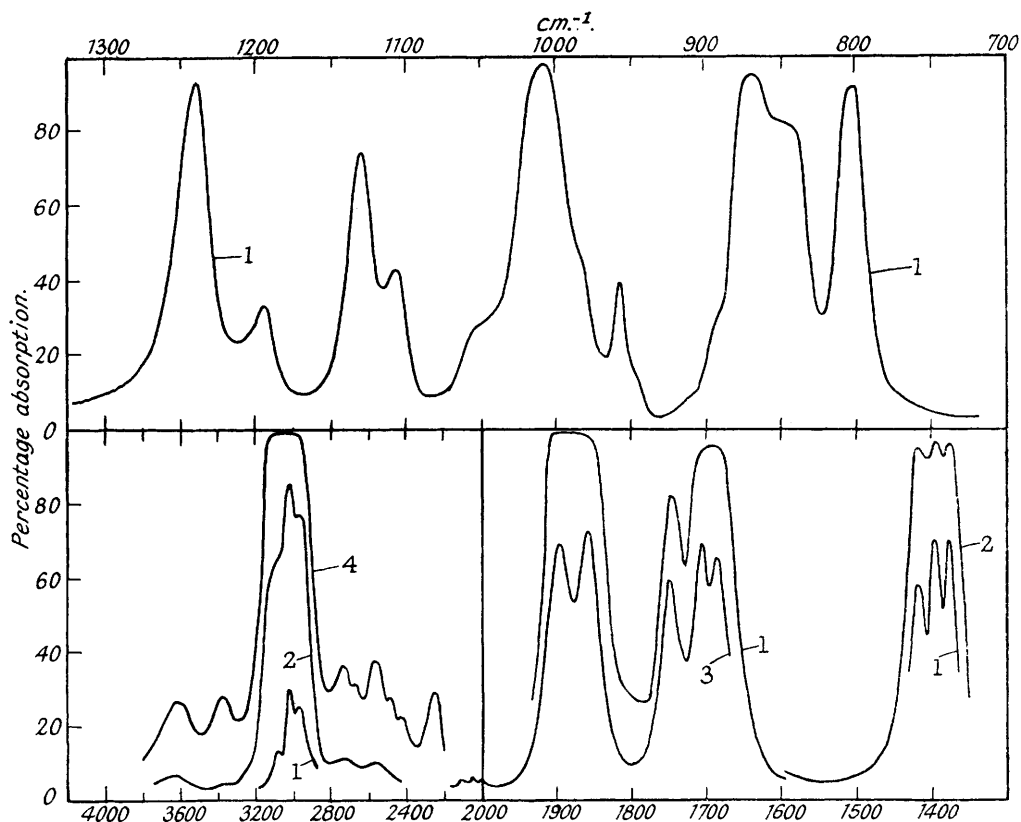


on the "take-up" of metallic mirrors. Staudinger and Beretza (*Ber.*, 1909, **42**, 4908) and more recently Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann (*J.*, 1935, 1751) preferred formula (II), the last group of workers pointing out that the measured dipole moment is incompatible with (I), and that thermochemical data exclude a di-enolic form. From other pyrolytic experiments Hurd and his collaborators (*J. Amer. Chem. Soc.*, 1936, **58**, 962; 1939, **61**, 3355; 1940, **62**, 1147; 1941, **63**, 2174) have suggested that (III) or (V) must be the

correct formula. On the other hand, Boese (*Ind. Eng. Chem.*, 1940, **32**, 16) found that β -butyrolactone is formed by the catalytic reduction of dimeric keten, and argued that the formula must be (IV). Perhaps the only certain deduction from all these observations is that keten dimer cannot be exclusively (I).

The Raman spectrum was measured earlier by Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann (*loc. cit.*) both for the liquid and for solutions in carbon tetrachloride. Dr. Wassermann recently suggested to us that the infra-red absorption spectrum might throw further light on the problem, and kindly supplied us with two samples of the dimer. We have therefore measured the spectrum both of the liquid and of solutions in carbon disulphide, carbon tetrachloride, and chloroform, between 2 and 14 μ , using a single-beam recording spectrometer of high resolving power with rock-salt prism, and over the range 5—8 μ using a similar double-beam recording instrument. The great value of the latter instrument lies in its ability to obviate troubles due to the absorption by atmospheric water vapour near 6 μ ; it will be described in detail elsewhere.

In the meantime the Raman spectrum has been re-measured by Taufen and Murray (*J. Amer. Chem. Soc.*, 1945, **67**, 754), who conclude that formulæ (I), (II), and (III) are impossible. Our present infra-red measurements, whilst also leading to no clear decision, serve to supplement the Raman spectra.



The dimeric keten was redistilled before use. Several samples were measured and gave the same spectrum. The absence of any of the strong bands of acetic anhydride showed that this possible impurity was absent; similarly no keten monomer could be detected, the spectrum of this substance having been measured also (Drayton and Thompson, to be published shortly).

The spectrum of the liquid is shown in the figure, and the positions of the absorption bands are listed in the table, together with the observed Raman intervals.

It may be noted that the relative intensity of the two infra-red bands at 1865 and 1895 appears to alter in different solvents. In carbon tetrachloride that at 1895 is the stronger, but in chloroform that at 1865. Similarly the bands at 1685 and 1705 vary in relative intensity in different solvents, and also shift slightly in wave-length.

Kohlrausch and Skrabal (*Proc. Ind. Acad. Sci.*, 1938, **8**, A, 424) have pointed out that the number of Raman intervals observed is greater than could arise if the molecule had the symmetrical structure (I). Another similar argument now strengthens this conclusion, since formula (I) has a centre of symmetry, and in this event there should be no "coincidences" between the active fundamentals, overtones or combination in the Raman spectrum on the one hand and the infra-red spectrum on the other. Inspection of the table shows that many such coincidences occur. This argument would lose its force if molecular distortion in the liquid led to a breakdown of the selection rules, but this does not seem to be so since the spectra of solutions in carbon

Positions of bands, in cm^{-1} .

Infra-red.	Raman.			Infra-red.	Raman.		
	T. and M.	K. and S.	A, L, F, F, and W.		T. and M.	K. and S.	A, L, F, F, and W.
—	154 (44)	149 (4)	—	1417 m.	—	—	—
—	324 (8)	324 (2)	334	—	—	—	1547
—	444 (15)	438 (3)	450	1685 s.	1689 (10b)	1686 (1b)	—
—	504 (7)	501 (1)	—	1705 s.	—	—	1721
—	531 (20)	523 (3)	532	1745 s.	1760 (w)	—	—
—	—	—	613	—	1791 (w)	—	—
—	670 (100)	671 (8)	674	1865 s.	1859 (20)	1856 (3)	—
805 s.	803 (3)	800 (0)	—	1895 s.	1896 (14)	1891 (2)	1888
846 s.	840 (6)	844 (1)	—	—	—	—	1933
868 s.	870 (9)	864 (2)	865	2010 w.	—	—	—
893 ?	—	—	—	2040 w.	—	—	—
914 ?	—	—	—	2110 w.	—	—	—
946 ?	—	—	—	2230 w.	—	—	—
957 m.	951 (3)	951 (0)	—	2420 v.w.	—	—	—
986 w.	986 (10)	984 (2)	984	2480 v.w.	—	—	—
1009 s.	1017 (4)	1016 (1)	—	2560 w.	—	—	—
1055 w.	—	—	—	2660 v.w.	—	—	—
1106 m.	1104 (1)	1099 (1)	1104	2710 w.	—	—	—
1130 m.	—	—	—	2970 m.	2958 (61)	2966 (10b)	2962
1194 m.	—	—	1185	3010 m.	3019 (43)	3019 (10b)	3019
1239 s.	—	—	—	3082 w.	3072 w	—	—
—	—	—	1270	—	3127 (15)	3131 (4b)	3127
—	—	1313 (0)	—	—	—	3213 (1)	—
1375 m.	1374 (20)	1373 (3)	1374	3370 w.	—	—	—
1393 m.	—	—	—	3620 w.	—	—	—

disulphide are not appreciably different from that of the pure liquid. Thus there is evidence of all kinds against formula (I).

The infra-red spectrum provides definite evidence against formula (II). This structure has an enolic OH group, which should give rise to a band in the region of 3μ , displaced to a greater or less extent from the normal position near 3600 cm^{-1} towards lower frequencies in consequence of molecular association. Dimeric keten has no band in this region which could indicate either the unassociated or the associated form, and it may be noted that the same argument applies to the Raman spectrum. The very weak bands in the infra-red spectrum

in this region are much more reasonably interpreted as overtones and combinations. We have measured for purposes of comparison the absorption of *cyclopentanol* as a liquid and also dissolved in carbon tetrachloride, and have found as expected the strong "association" band characteristic of the OH group. The concentration and

path length were chosen so as to compare appropriately with those used in measuring the spectrum of dimeric keten and it is clear that no significant amount of hydroxylic structure can be present. We have also measured the spectrum of the enolic substance (VI) which shows the OH band.

A decision between the remaining three formulæ is more difficult. The problem can be approached in three ways, by considering (1) the bands near 3000 cm^{-1} , (2) the bands between 1500 and 2200 cm^{-1} , and (3) the bands in the region below 1500 cm^{-1} . The main bands in the region of 3000 cm^{-1} will be connected with stretching vibrations of C-H bonds, which have slightly different frequencies according to the particular structure of which the C-H bond forms a part. Intense infra-red bands between 1500 and 2200 cm^{-1} are usually attributed to vibrations which are largely controlled by the stretching of double bonds such as C=C, C=O, or C=N. The bands at frequencies below 1500 cm^{-1} are connected with vibrations of the skeleton, and are less easily correlated with specifically localised motions.

As regards (2), the region of the double-bond absorption, dimeric keten shows five fairly intense bands. Three of these, at 1685 , 1865 , and 1895 cm^{-1} , have Raman analogues at 1689 , 1859 , and 1896 , and a fourth at 1745 may be connected with the Raman interval 1760 . We may now consider what frequencies would be expected in this region for each of the formulæ (III), (IV), and (V). Formulæ (III) and (IV) each have two double bonds, and will be expected to have two corresponding infra-red bands. Structure (V) has three double bonds, which will give three bands due to the stretching modes, but in the system $>\text{C}=\text{C}=\text{O}$, as with allene, $>\text{C}=\text{C}=\text{CH}_2$, one of the double-bond frequencies will lie lower, owing to interaction, and the other will be raised. In allene (Thompson and Harris, *Trans. Faraday Soc.*, 1944, **40**, 295) the two frequencies are 1069 and 1965 cm^{-1} respectively, in keten at about 1130 and 2160 , and in diphenylketen the higher frequency is at about 2130 cm^{-1} . It is unlikely that the presence of the additional carbonyl group in dimeric keten if represented by (V) will raise the lower frequency just referred to by an amount sufficient to bring it above 1500 cm^{-1} .

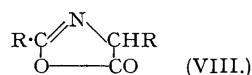
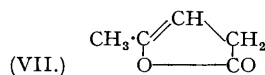
If therefore three or more of the five observed infra-red bands of dimeric keten in the range 1500 — 2000 cm^{-1} are due to double-bond fundamentals, no single formula is sufficient. We cannot decide whether three or more of the five bands are, in fact, due to fundamentals. They might be combinations, for example: $1865 \approx (1009 + 846)$ or $(1009 + 868)$, and $1895 \approx (1239 + 670)$. None of the three structures involved has symmetry characteristics which might enable us to apply selection rules for the infra-red and Raman spectra.

Hence the only further step possible is to compare the observed spectrum with those of other compounds

having a related structure. As regards (V), the acetylketen structure, it has already been stated that keten and diphenylketen have bands at 2160 and 2130 cm^{-1} , and a frequency of about 2150 seems characteristic of the keten skeleton. The only question is whether the presence of the additional carbonyl group in the acetyl group, conjugated with the $\text{C}=\text{C}$ linkage, can modify the frequencies of the $\text{>C}=\text{C}=\text{O}$ skeleton so as to bring that at about 2150 down to 1895 or 1865. Although this effect is unpredictable, it does not seem likely. In mesityl oxide, $(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, where the frequencies due to $\text{C}=\text{C}$ and $\text{C}=\text{O}$ are about 1625 and 1690, the conjugation has not much affected the "normal" values for those bonds. Hence the observed spectrum of dimeric keten seems against the presence of structure (V).

We therefore have to consider whether (III) or (IV), or a mixture of these, would give the spectrum found. Few compounds which are similar in structure to (III) or (IV) have been measured. The spectra of unsaturated compounds, ketones, and esters have shown that the stretching frequencies of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds can vary over wider limits than was previously supposed. It will become clear from the arguments given below that a clear decision between (III) and (IV) is impossible, and that a mixture of the two structures might satisfactorily explain the observed bands.

In saturated cyclic ketones the frequency of the carbonyl group depends upon the strain in the ring; thus in *cyclohexanone*, *cyclopentanone*, and *cyclobutanone* it lies at about 1710, 1740, and 1775 cm^{-1} . The infra-red spectra of 5-membered lactones (Richards, to be published shortly) usually show a band due to the carbonyl group between 1740 and 1800 cm^{-1} , and when a $\text{C}=\text{C}$ link is included in the ring, the carbonyl frequency tends to lie at the higher end of this range. Thus, the lactone (VII) has the $\text{C}=\text{C}$ frequency at 1675 cm^{-1} and the



$\text{C}=\text{O}$ frequency at 1800 cm^{-1} . Similarly in simple oxazolones of the type (VIII), the carbonyl frequency lies at about 1800 cm^{-1} . On passing from the 5- to the 4-membered ring as in (III) or (IV) the carbonyl frequency might be expected to rise slightly, but conjugation with the internal double bond as in (III) may diminish it. With dimeric keten, one of the bands at 1745, 1859, 1896 will be attributable to the $\text{C}=\text{O}$ group. A decision between (III) and (IV) is clearly impossible.

As regards the $\text{C}=\text{C}$ bond frequency, Taufen and Murray have drawn attention to the absence of a band between 1600 and 1640 cm^{-1} in the Raman spectrum which might have been attributed to this bond in a ring. Similarly there is no band in the range in the infra-red spectrum. In some 5-membered unsaturated lactones, however, such as (VII) (above), this frequency is as high as 1675 cm^{-1} . Dimeric keten has a band at 1685. However, the decrease in the size of the ring in (III), as well as the conjugation, may be expected to lower this frequency somewhat. Hence formula (III) seems unlikely. If the correct formula is (IV), we might interpret the bands at 1745 or 1865, and 1685 as being due to the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ stretching vibrations, and those at 1705, 1865, or 1745, 1895, and 1791 (Raman) as combinations.

This ambiguity between structures (III) and (IV), as well as the large number of strong bands in the "double bond" region, raises the question whether there are in reality two forms present. The close agreement between the spectra of different samples of dimeric keten, and the fairly close correspondence between the infra-red spectrum and the Raman spectrum measured by several independent laboratories, are against this hypothesis, unless the two forms are in equilibrium with each other. That some of the bands change in relative intensity with change of solvent is also noteworthy in this connexion. A change of the polar properties of the solvent might affect the band intensities with a single species, but if there were preferential interaction of some kind with one form of a pair, a similar result might be found.

As regards the region around 3μ , the infra-red bands of dimeric keten at about 3010 and 3082 are paralleled by the Raman intervals 3019, 3072. The other infra-red band at about 2970 may be the analogue of the Raman interval 2960. Formulæ (III) and (IV) will each have four $\text{C}-\text{H}$ stretching modes. Now $\text{C}-\text{H}$ stretching vibration frequencies differ in magnitude according to the remainder of the molecule (Fox and Martin, *Proc. Roy. Soc.*, 1940, 175, A, 208; Barnes *et al.*, *Ind. Eng. Chem. Anal.*, 1943, 15, 659), but a useful generalisation is that for $\text{C}-\text{H}$ bonds contiguous to an unsaturation, the frequencies are above 3000 cm^{-1} , whilst in saturated compounds they are usually below 3000. In this respect the results probably favour (IV) rather than (III). The frequency at 3082 cannot be due to a vibration of the CH_3 group, is not likely to be due to the >CH group, but would agree with the group $=\text{CH}_2$. Moreover, the presence of the CH_3 group should give rise to a band between 2800 and 2900, and none is found. Hence the evidence seems to favour (IV).

As regards the bands below 1500 cm^{-1} , we might expect to find a band near 1375 due to the symmetrical deformation of the CH_3 group, as found with many hydrocarbons, although it is now known that this band can be displaced considerably in some molecules as a result of neighbouring influences in the molecule. There is indeed a band at 1375 with dimeric keten, the low intensity of which may not be surprising if judged against those of the bands due to the more polar linkages. However, the methyl group should also give rise to a band in the region 1440—1460 cm^{-1} , but none is found above 1417. In this connexion a suitable analogue to (III) might be methyl acetate (Thompson and Torkington, *J.*, 1945, 644). The observed spectrum seems therefore again to favour (IV) rather than (III), in which case the bunch of bands near 1400 cm^{-1} might be due to deformations of the group $=\text{CH}_2$ and the ring methylene group. Olefins containing the group $=\text{CH}_2$ give rise to an intense band near 890 cm^{-1} due to a deformational mode (Thompson and Torkington, *Proc. Roy. Soc.*,

1945, 184, A, 13), which is somewhat displaced in non-hydrocarbon molecules. The strong band at 868 cm.^{-1} with dimeric keten might be connected with this mode.

To summarise, therefore, the spectrum of dimeric keten suggests that it has the structure (III) or (IV), or is a mixture of both, and while much of the argument is tentative, the balance may favour formula (IV).

We are grateful to the Department of Scientific and Industrial Research for a Research Assistantship, and to the Government Grant Committee of the Royal Society for financial help in the purchase of apparatus. Our thanks are also due to Dr. Wassermann for suggesting the problem and for the gift of dimeric keten.

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