412. *The Constitution of Dimeric Keten.*

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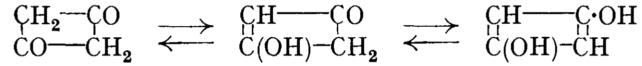
Certain dimeric ketens are capable of reacting both as ketones and as enols. For the simplest member, discovered by Chick and Wilsmore (J., 1908, **93**, 946; 1910, **97**, 1978), the following equilibria should be considered : *



Diketone (A). Keto-enol (B.) Dienol (C).

In this paper an attempt is made to determine the constitution of dimeric keten, *i.e.*, to determine which of the forms A, B, or C predominates in a possible equilibrium, by comparing the observed dipole moment, molecular refractivity, and heat of formation with calculated values. Further, the Raman spectra of the pure liquid compound and of its solution in carbon tetrachloride were examined in order to see whether the solvent exerts an influence on the constitution.

Dipole Moment.—The dipole moment of dimeric keten has been estimated as 3·15 at

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* Staudinger, *Ber.*, 1909, **42**, 4912; 1920, **53**, 1085; *Helv. Chim. Acta*, 1924, **7**, 1; Dieckmann and Wittmann, *Ber.*, 1922, **55**, 3331. The hypothesis that certain dimeric ketens, including the one here investigated, should be regarded as molecular compounds (cf. Schroeter, *Ber.*, 1916, **49**, 26, 97; 1920, **53**, 1917) will not be discussed, as we agree with Staudinger and Dieckmann (*loc. cit.*) that the arguments by which this view has been supported are unconvincing. Lardy (*J. Chim. physique*, 1924, **21**, 281) attempted to use the ultra-violet absorption spectrum of dimeric keten to disprove Schroeter's hypothesis and to decide between the three formulæ (A), (B), and (C). We do not, however, think that from his results any such conclusion can be derived.

25° in benzene solution and 3·30 in carbon tetrachloride solution (Debye units are used throughout). That of the dienolic form (C) can be calculated for three extreme cases. (1) For the symmetrical *trans*-position of the hydroxyl groups, which, on account of the electrostatic repulsion of the dipole, might be the most stable configuration, the resultant moment is zero. (2) For the *cis*-position (Fig. 1), a total moment of 3·2 is obtained if the moment of the hydroxyl group is taken as 1·7; for the position of maximum possible resultant moment, requiring some valency deflexion (shown by a broken line), a total moment of 3·4 is calculated. The *cis*- might be more stable than the *trans*-position if the London dispersion effect overbalances the electrostatic repulsion (cf. the relative stability of *cis*- and *trans*-dichloroethylene; Stuart, *Physikal. Z.*, 1931, **32**, 793). (3) If it is assumed that the potential minimum of the preferred configuration is so flat that almost free rotation of the two hydroxyl groups is possible at 25°, then the resultant moment will lie between 0 and 3·3. An exact calculation could be carried out by using Fuchs's formula (*Z. physikal. Chem.*, 1931, *B*, **14**, 339).

The moment of the keto-enol form (B) is calculated as 2·7 (Fig. 2) by assuming a moment of 2·75 for the carbonyl bond and 1·7 for the hydroxyl group. For the other configuration (drawn in broken lines) a moment of 3·2 is obtained.

FIG. 1.

Dipole moment of dienolic form (C) *of dimeric keten in the* cis-*configuration.*

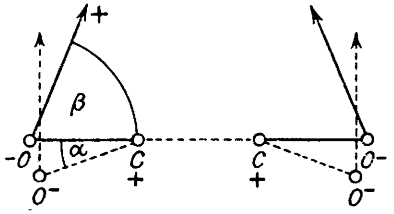

FIG. 2.

Dipole moment of keto-enol form (B) *of dimeric keten.*

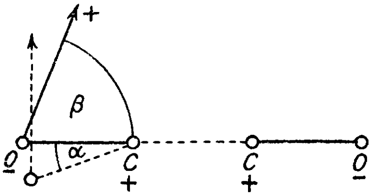

FIG. 1.—Direction of bond moments according to Eucken and Meyer (*Physikal. Z.*, 1929, **30**, 397); C–O–H angle 110°; therefore $\beta = 72°$. For C–O and O–H bond moments, see Wolf and Fuchs (Freudenberg, " Stereochemie," p. 262). The resultant moment of the *cis*-configuration is maximum if the assumption is made that $\alpha = 18°$.

FIG. 2.—For direction and value of bond moments, see Eucken and Meyer, Wolf and Fuchs (*locc. cit.*); angle $\beta = 72°$. The resultant moment of the keto-enol form is maximum if, as above, the assumption is made that $\alpha = 18°$.

It is conceivable that the group moments in dimeric keten differ considerably from those employed; *e.g.*, if the moment of the carbonyl bond is taken as 3·0, as in *cyclo*pentanone (cf. Freudenberg, " Stereochemie," 1933, p. 793), and that of the hydroxyl group as 1·8 (arbitrarily assumed), then a total moment of 3·0 is obtained for the position drawn in full lines in Fig. 2. Another reason for caution in accepting the above calculated values is that a possible influence of the resonance energy due to the two conjugated double bonds (cf. Sutton, *Trans. Faraday Soc.*, 1934, **30**, 785) has been neglected and that the moment of the C–H bond was assumed to be zero.

The figures given do, however, show that the experimentally observed dipole moment is compatible with the keto-enol form (B). For the dienolic form (C) the observed moment would seem rather high, for the assumption of a rigid *cis*-configuration is hardly probable; the possibility of form (C) cannot, however, be regarded as excluded by the dipole-moment measurements. The symmetrical diketo-form (A), on the other hand, is incompatible with the observed moment. This conclusion is supported by the fact that the 1 : 1 : 3 : 3-tetramethyl*cyclo*butanedione, for which an enolic form is impossible, has a dipole moment experimentally indistinguishable from zero (cf. table, p. 1754).

Molecular Refractivity.—Chick and Wilsmore (*loc. cit.*, 1910) found $[R_L]_D = 20{\cdot}14$ for dimeric keten, and calculated the following values: 18·78 for (A); 19·72 for (B); 20·66 for (C). The molecular refractions have now been recalculated from Eisenlohr's atomic and bond refractions ("Spektroskopie organischer Verbindungen," Stuttgart, 1912); further, it was taken into account that *cyclo*butane derivatives are always characterised by a certain exaltation *EM* of the molecular refraction (cf. Oestling, quoted by Freudenberg, *op. cit.*, p. 794); *e.g.*, the EM_D value for *cyclo*butanone is 0·49 (Eisenlohr and Oestling, *locc. cit.*), and that for 1 : 1 : 3 : 3-tetraethyl*cyclo*butanedione is 0·50 (v. Auwers, *Ber.*, 1918, **51**, 1126). It is therefore justifiable to take an *EM* value of 0·50 for the calculation of the molecular refraction of the form (A), giving 18·99. The great discrepancy between this and the observed value is, like the observed dipole moment, evidence against the diketo-form (A).

With the same allowance for exaltation, the values for (B) and (C) become 20·16 and 21·32 respectively. Too much importance should not be attached to the good agreement between the observed and the calculated value in the case of (B), for it is not known whether a double bond in a *cyclo*butane ring conjugated with another double band raises the *EM* value still further, or whether, as in *cyclo*pentadiene (cf. v. Auwers, *Ber.*, 1912, **45**, 3077), it depresses the molecular refraction.

Heat of Combustion.—The heat of combustion of dimeric keten is 447·1 kg.-cals./mol. in the liquid and 456 ± 2 kg.-cals./mol. in the gaseous state (heat of vaporisation according to Trouton). The heat of formation from C^{5s},* H, and O is accordingly 1081 kg.-cals. (cf. this vol., p. 829). For the additive calculation of the heat of formation, Pauling and Sherman's bond energies (*J. Chem. Physics*, 1933, **1**, 615) were used; only for the carbonyl bond was a different value taken, *viz.*, 183 kg.-cals. (this vol., p. 839). The calculated heats of formation are: (A) = 1101; (B) = 1075; (C) = 1049 kg.-cals.

The observed heat of formation is larger by 32 kg.-cals. than that calculated for (C). Such a difference cannot be ascribed to resonance-energy effects, as shown by theoretical considerations (cf. Pauling and Sherman, *loc. cit.*, p. 682) as well as by comparison of observed and calculated heats of formation of other compounds containing two conjugated double bonds (this vol., p. 830). The heat of combustion, therefore, excludes the dienolic form (C), but is compatible with both (A) and (B). The resonance energy corresponding to the two conjugated double bonds in (B) would increase the heat of formation, while the ring strain due to the *cyclo*butane ring would reduce it. As no exact values for these factors are available, no decision can be made between these two forms from the thermochemical data.

Raman Spectrum.—The Raman spectra of the pure liquid dimeric keten and of a solution in carbon tetrachloride are compared in the following table, the observed displacements being given in cm.$^{-1}$; the figures in parentheses are the visually estimated intensities.

Raman spectra of dimeric keten in the pure state and in carbon tetrachloride solution (20°).

Pure liquid	334(1)	450(2)	532(2)	613(¼)	674(8)	865(1)	984(1)	1104(2)	1185(¼)
Solution *	—	—	530(½)	604(1)	675(6)	860(½)	989(½)	1102(1)	1193(½)
Pure liquid	1270(¼)	1374(3)	1547(¼)	1721(½)	1888(2)	1933(3)	2962(3)	3019(3)	3127(1)
Solution	1281(¼)	1372(3)	1560(½)	1730(½)	1895(2)	1952(1)	2939(3)	3023(3)	3124(1)

* Solutions were made up of equal volumes of CCl_4 and dimeric keten.

In the solution, the lines 334 and 450 cm.$^{-1}$ could not be observed with certainty owing to the proximity of carbon tetrachloride lines. All the other lines in the two rows of the table agree within the experimental error, with the exception of those at 1933 and 1952 cm.$^{-1}$ and at 2962 and 2939 cm.$^{-1}$; but here, too, the difference is so small that it can be ascribed to the influence of the molecular force fields of the solvent.

Dissolution of the dimeric keten in carbon tetrachloride does not have any great effect on the constitution, otherwise the agreement between the Raman spectra given in the table would not be so good. It is therefore justifiable to collate observations in carbon tetrachloride solution (dipole moment) with those on the pure liquid (molecular refraction, heat of combustion) without taking into account possible constitutional changes.

EXPERIMENTAL.

Dimeric keten, prepared according to Ott, Schroeter, and Packendorff (*J. pr. Chem.*, 1931, **130**, 177), was fractionally distilled in a stream of dry air, the middle fraction (b. p. 68—72°/100

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* C^{5s} is the name of the electronic state of quadrivalent carbon.

mm.) being dried over sodium sulphate and refractionated in an all-glass apparatus immediately before use. The following b. p.'s were observed : 38·5°/23 mm., 50·5°/41·0 mm., 70·0°/100 mm.; m. p. — 8° to — 7°.

1 : 1 : 3 : 3-Tetramethyl*cyclo*butanedione was prepared from Kahlbaum's dimethylmalonic acid (m. p. 193°) (Staudinger, *Helv. Chim. Acta*, **1925**, **8**, 310), the anhydride of which was dried until of constant weight (m. p. about 120°). The dione was repeatedly recrystallised from pentane; m. p. 114—115°.

The dielectric constants and densities at 25° of solutions of dimeric keten and the tetramethyl compound were measured by methods previously described or cited (Le Fèvre, Le Fèvre, and Robertson, this vol., p. 480), and from the results the total polarisations at infinite dilution were calculated. These figures combined with the molecular refractivity (D line) give the moments, μ, which are given, together with the essential data, in the tables. The effect of making an allowance of *ca.* 10% in $[R_L]_D$ for the atomic polarisation is shown by the second values of $_0P$ and μ. The headings of the tables have the usual significance (Le Fèvre, Le Fèvre, and Robertson, *loc. cit.*).

Dipole moments of dimeric keten.

Solvent.	$_TP$.	$[R_L]_D$.	$1{\cdot}1[R_L]_D$.	$_0P$.	$\mu . 10^{18}$.
C_6H_6 *	226·3	20·1	22·1	206·2, 204·2	3·16, 3·15
CCl_4 *	245·7	20·1	22·1	225·6, 223·6	3·30, 3·30

Molecular polarisation of dimeric keten.

In benzene at 25°.

$f_1 . 10^6$	0	32453	55391	68498	92564
$M_1f_1 + M_2f_2$	78	78·1947	78·3323	78·4110	78·5554
ϵ	2·2725	2·7158	3·0943	3·3322	3·7327
d	0·87370	0·87931	0·88363	0·88551	0·89049
$P_1f_1 + P_2f_2$	26·5894	32·3554	36·4439	38·7230	42·0513
P_2f_2	26·5894	25·7265	25·1166	24·7681	24·1282
P_1f_1	—	6·6289	11·3273	13·9549	17·9231
P_1 (c.c.)	—	204·3	204·5	203·7	193·6

Extrapolated P_1 for $f_1 = 0$: 226·3 c.c.

In carbon tetrachloride at 25°.

$f_1 . 10^6$	0	25001	38707	49982	66579
$M_1f_1 + M_2f_2$	154	152·2500	151·2906	150·5013	149·3394
ϵ	2·2270	2·5623	2·7465	2·8857	3·1099
d	1·58549	1·57473	1·56889	1·56416	1·55709
$P_1f_1 + P_2f_2$	28·1948	33·1079	35·4825	37·1368	39·6014
P_2f_2	28·1948	27·4899	27·1035	26·7856	26·3176
P_1f_1	—	5·6180	8·3790	10·3512	18·2838
P_1 (c.c.)	—	224·7	216·5	207·1	199·5

Extrapolated P_1 for $f_1 = 0$: 245·7 c.c.

* Carefully dried and redistilled before use.

*Molecular polarisation of tetramethyl*cyclo*butanedione in carbon tetrachloride at* 25°.

$f_1 . 10^6$	0	4170	6788
$M_1f_1 + M_2f_2$	154	153·9416	153·9048
ϵ	2·227	2·227	2·228
d	1·58549	1·58137	1·57868
$P_1f_1 + P_2f_2$	28·1948	28·2576	28·3153
P_2f_2	28·1948	28·0786	28·0034
P_1f_1	—	0·1790	0·3119
P_1 (c.c.)	—	42·9	45·9

Only a small quantity of the tetramethyl*cyclo*butanedione was available for examination. It follows, from the fact that the observed total polarisation (*i.e.*, 43—46 c.c.) lies close to the $[R_L]_D$ + 10% value (*i.e.*, 41·3 c.c.), that the moment of the compound is, as might be expected, undetectably small. For the calculation of the molecular refractivity, v. Auwers's *EM* value (*loc. cit.*) for tetraethyl*cyclo*butanedione was used.

The heat of combustion of dimeric keten (at 20°) was determined in the apparatus already described (this vol., p. 829). The substance was weighed out in glass bulbs which were sealed with vaselin.

Heat of combustion of dimeric keten.

Dimeric keten, g.	Vaselin, g.	Δ*t* (obs.).	Δ*t* (corr.).	Heat of combustion (cals.). Total.	Corr.	Cals./g. (const. vol.).
0·39115	0·12900	1·2590°	1·2585°	3531·7	1449·4	5323·5
0·41560	0·10605	1·2155	1·2160	3412·3	1200·6	5318·0
0·49500	0·09730	1·3340	1·3330	3740·7	1106·9	5321·0
					Mean	5321·0 ± 1·5

The Raman spectra given in the first table were obtained by using essentially the experimental arrangement described by Angus and Leckie (*Proc. Roy. Soc.*, 1935, **149**, 327), but with a much smaller tube (2·5 c.c. capacity). For Raman displacements of less than 2500 cm.$^{-1}$, the 4358 Å. mercury line was used as exciting source, and for greater displacements the 4047 Å. line. The exposure times for the pure substance were 6—15 hours, and for the solutions 8—30 hours. Four plates for each were obtained; these were in very good agreement. Unless broad lines were involved the error does not exceed ± 6 cm.$^{-1}$.

SUMMARY.

The observed dipole moment and the molecular refraction of dimeric keten are incompatible with the diketo-form (A), and the dienolic form (C) is excluded by the thermochemical data. The substance must therefore exist predominantly in the keto-enol form (B). Forms (A) or (C) could nevertheless be present in comparatively small concentrations. Dissolution of dimeric keten has no great effect on the Raman spectrum, and therefore, presumably, on the constitution.

We are indebted to Professor C. K. Ingold for his continued interest, and to Imperial Chemical Industries Ltd. for the help afforded to one of us (A. W.). The heat of combustion (last table) was determined by Dr. G. Becker in the laboratory of Professor W. A. Roth, to both of whom our thanks are due.

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