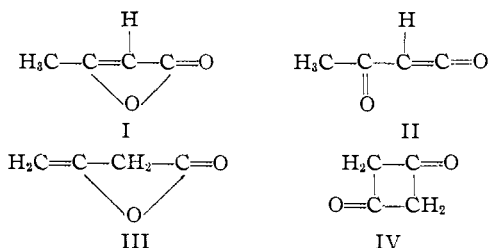


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND OF NORTHWESTERN UNIVERSITY]

## The Structure of Diketene from Spectroscopic Evidence

BY M. CALVIN, THEODORE T. MAGEL\* AND C. D. HURD

Although the dimer of ketene has been known for over thirty years its structure is still uncertain, even though it has recently become a commercial product. During this time four different formulas have been proposed on the basis of both chemical and physical evidence.<sup>1,2</sup>



The present investigation was undertaken in the hope that a consideration of the absorption spectrum of diketene might make possible a distinction among these formulas or at least supply new information concerning the structure of the ketene dimer.

### Experimental Part

**Diketene.**—A sample of diketene was generously furnished by Dr. R. W. McNamee of the Carbide and Carbon Chemicals Corporation. This material was distilled at reduced pressure (b. p. 43° at 28 mm.) and sealed in a glass tube. After standing at room temperature for about three days during shipment from Evanston to Berkeley the sample had acquired a deep orange color. It was transferred to a high vacuum sublimation apparatus consisting simply of a double armed tube which could be connected to the vacuum system. The material was sublimed from one side at the melting point of diketene  $\sim -7^\circ$  into the other arm at the temperature of liquid air. After about 80% of the material had come over, the white sublimate was transferred to another sublimation vessel and the process repeated. The sublimate was warmed until all the material had melted to a water-white liquid. It was then cooled again until about half the material was frozen and the supernatant liquid poured back into the arm from which it had been sublimed. The remaining solid was melted and a sample pipetted out into a volumetric flask containing the trimethylpentane solvent.

**2,2,4-Trimethylpentane.**—This paraffin hydrocarbon was washed with fuming sulfuric acid and distilled from

metallic sodium. It showed no absorption down to 2400 Å.

**$\beta$ -Butyrolactone.**—A sample of  $\beta$ -butyrolactone was supplied to us by Mr. T. R. Simonson, who prepared it by the procedure of Johansson<sup>3</sup> and had a b. p. of 42° at 5 mm. pressure.

**Vinyl Acetate.**—A sample of Eastman Kodak Co. vinyl acetate was subjected to the same treatment as the diketene.

**Dehydroacetic Acid.**—A sample of well crystallized Kahlbaum material was used.

**Absorption Measurements.**—The absorption spectra were obtained photographically by the methods already described.<sup>4</sup>

### Results

In Fig. 1 are shown the absorption spectra obtained for diketene and for vinyl acetate, together with those of mesityl oxide and ethyl  $\beta$ -ethoxycrotonate taken from the article of Ramart-Lucas.<sup>5</sup> The absorption spectrum obtained for  $\beta$ -butyrolactone is shown in Fig. 2 together with those of acetone and ethyl acetate. In Fig. 3 is given the absorption spectrum obtained for dehydroacetic acid. Since this shows a band in approximately the same region as that of the diketene but with approximately  $10^4$  times the intensity, the diketene spectrum is plotted in the same figure and both of them are  $\epsilon$  vs.  $\lambda$  plots instead of  $\log \epsilon$  vs.  $\lambda$  plots as in Figs. 1 and 2. If the observed spectrum of the diketene in the region of 3130 were due to a small amount (1 part in  $\sim 10^4$ ) of dehydroacetic acid the two curves shown in Fig. 3 should be capable of superposition by merely adjusting the ordinate axis. This is clearly not the case.

There is one other possible source of the 3130 band of diketene, and this is ketene itself. If ketene were in equilibrium with its dimer and the observed band in diketene were due to this amount of ketene in the equilibrium, it is possible to say, from a comparison of the observed  $\epsilon$  values with those known to be due to ketene, that a twenty-fold dilution of the diketene solution should produce an apparent increase in the  $\epsilon$  value of about three to fourfold. This is actually not true, the

(3) Johansson, *Lunds Universitets Årsskrift*, N. F. part 2, **12**, No. 8 (1916).

(4) M. Calvin and R. E. Buckles, *THIS JOURNAL*, **62**, 3324 (1940).

(5) P. Ramart-Lucas, Tome 11, Fascicule 1 of Grignard's "Traité de Chimie Organique," Massou et Cie., Paris, 1936.

\* Abraham Rosenberg Research Fellow 1940-1941.

(1) A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940); Angus, Leckie, LePèvrè, LePèvrè and Wassermann, *J. Chem. Soc.*, 1751 (1935).

(2) C. D. Hurd and J. W. Williams, *THIS JOURNAL*, **58**, 962 (1936); Hurd and Roe, *ibid.*, **61**, 3355 (1939); Hurd and Abernethy, *ibid.*, **62**, 1147 (1940).

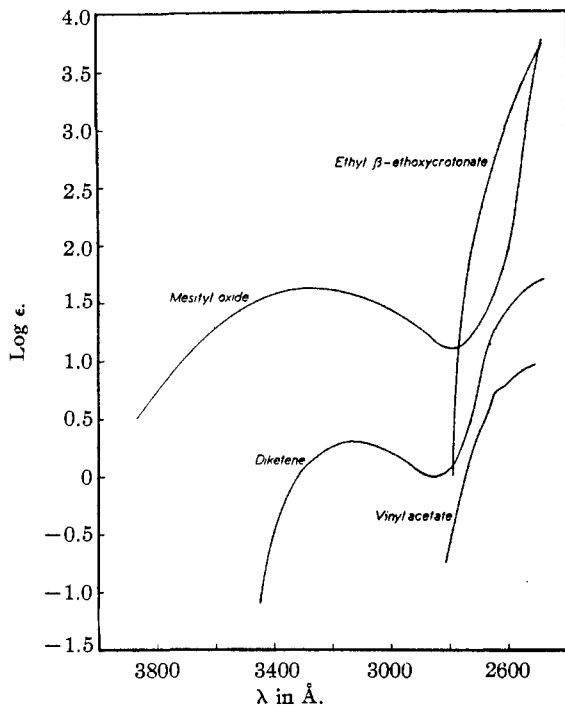


Fig. 1.—Diketene, 0.1305 *M*, in 2,2,4-trimethylpentane in 1-cm. cell; vinyl acetate, 0.12 *M*, in 2,2,4-trimethylpentane in 1-cm. cell.

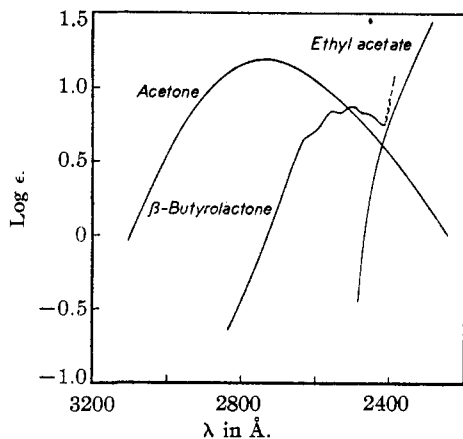


Fig. 2.— $\beta$ -Butyrolactone, 0.1227 *M*, in 2,2,4-trimethylpentane in 1-cm. cell.

$\epsilon$  value remaining constant to within the experimental error, over the twenty-fold dilution. The absence of such a rapid reversible equilibrium,  $2 \text{ Ketene} \rightleftharpoons \text{Diketene}$ , is entirely in accord with the known chemical properties of the substances involved.

### Discussion

The detailed arguments on the basis of pre-existing evidence have been presented elsewhere<sup>1-2</sup>

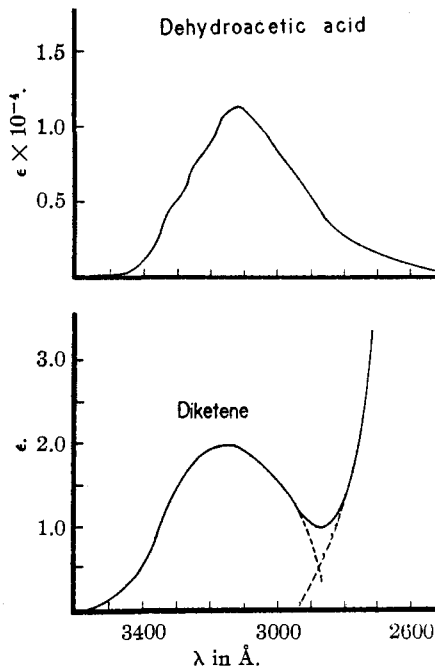


Fig. 3.—Dehydroacetic acid,  $4.52 \times 10^{-5}$  *M*, in 2,2,4-trimethylpentane in 1-cm. cell.

and will be drawn upon here only insofar as they may affect our present conclusions.

A comparison of the diketene curve (Fig. 1) with that of cyclobutanone<sup>6</sup> immediately eliminates the cyclobutanedione formula (IV), or its enols, in concordance with the chemical evidence. The diketene band at 3130 Å. is much too small and somewhat too far into the violet to correspond to the 100% enol form and the ketone band at 2800 Å. is totally lacking, eliminating the possibility of an equilibrium between keto and enol forms.

The band at 3130 indicates the presence in the structure of at least one pair of closely associated double bonds, one of them<sup>7</sup> being  $\text{C}=\text{O}$ . This type of spectrum is typified by the one of mesityl oxide shown in Fig. 1. The spectra of acrolein, crotonaldehyde, etc., are similar. There was, however, the possibility that the lactone oxygen of formula III might be enough of a conductor<sup>7</sup> to provide the conjugation necessary for the appearance of such a band. The absorption spectrum of vinyl acetate, given in Fig. 1, shows that this is not so, since it has the appearance of an ordinary ester. This is a confirmation of the lack of any

(6) G. Förster, R. Skrabal and J. Wagner, *Z. Elektrochem.*, **43**, 290 (1937).

(7) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939); G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 155.

abnormality in the heat of hydrogenation of vinyl acetate.<sup>8</sup> Thus formula III is eliminated.

In order to predict the type of absorption spectrum one might expect from a molecule having the structure of acetylketene (II) it is necessary to examine somewhat more closely the structure and absorption of ketene itself. The long wave absorption of this substance,<sup>9</sup> in hexane solution, is an absorption band having a maximum at *ca.* 3200–3300 Å. at which point the molar absorption has a value around  $\epsilon = 15$ . This absorption can be attributed to the excitation of oscillations between the extreme structures (Va) and (Vb).



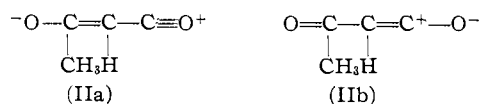
Form Va is, of course, the ordinary polar form which contributes in all carbonyl compounds. Form Vb, however, is characteristic of ketene and there is evidence that it contributes appreciably even in the ground electronic state of the molecule. The dimensions of this molecule have been determined by Beach and Stevenson<sup>10</sup> using the method of electron diffraction and they give 1.17 Å. for the C–O distance and 1.35 Å. for the C–C distance. These are, respectively, considerably shorter and somewhat longer than the normal distances for the corresponding bonds (1.24 Å. for C=O and 1.33 for C=C) and the authors attribute these differences to the contribution of (Vb) to the ground electronic state of the molecule. A measurement of the dipole moment of ketene would be very illuminating in this connection. We, therefore, attribute the first absorption band of ketene to an excitation of oscillations between the extreme forms (Va) and (Vb), *i. e.*, the first excited state of ketene contains a higher contribution of these forms than the ground state. Thus, the weakly amphoteric auxochromes such as alkyl groups (compare the absorption of the paramethyl derivatives of nitrobenzene and aniline) will shift the band somewhat toward the red, as is the case in diethylketene.<sup>9</sup> The introduction of the acetyl group, however, should produce a large shift toward the red together with an increase in intensity. This is based on empirical grounds (compare acetone and diacetyl) as well as for theoretical reasons. The acetyl group,

(8) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 275.

(9) P. Ramart-Lucas, Tome II, fascicule 1 of Grignard's "Traité de Chimie Organique," Masson et Cie., Paris, 1936, Fig. 27, page 104.

(10) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

because of its electron attracting property, will not only enhance the contribution of (Vb) in the ketene part of the molecule, but will introduce a number of new forms, one of the most important (with respect to color at least) of which is (IIa)



The excitation of oscillations between the extreme forms (IIa) and (IIb) should produce an absorption clear into the visible, and a compound having the acetylketene structure should be yellow to orange which, of course, diketene is not.

We are thus left with  $\beta$ -crotonolactone (I) and it remains to be seen if the observed absorption can be reconciled with this structure. The compound most nearly analogous to  $\beta$ -crotonolactone for which the absorption spectrum is available is ethyl  $\beta$ -ethoxycrotonate, whose spectrum is shown in Fig. 1. The 3200 Å. band, characteristic of the conjugated system C=C–C=O is lacking. This we attribute to the fact that the C=O in the crotonic ester is not a simple carbonyl but part of a carboxyl, and it is so completely taken up in the ester resonance  $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O}^- \end{array}$ , that it cannot participate in the resonance system  $\begin{array}{c} \text{C}=\text{C}-\text{C}=\text{O} \\ | \quad | \\ \text{OR} \quad \text{OR} \end{array}, \text{C}^+-\text{C}=\text{C}-\text{O}^-$ .<sup>11</sup> This

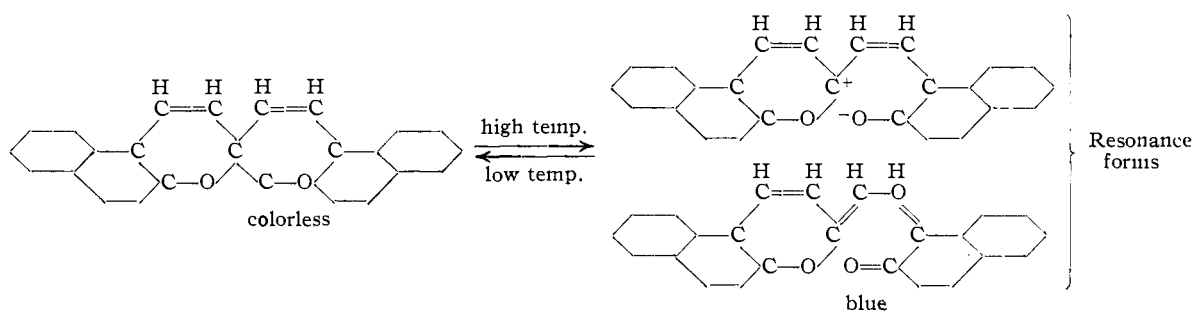
same condition accounts for the non-appearance of carbonyl absorption ( $\sim 2800$  Å.) in esters, which may be seen in Fig. 2 from a comparison of acetone with ethyl acetate. If, however, the ester resonance could in some manner be reduced, the C=O should begin to show more of the carbonyl properties. Such a reduction in the interaction of the two oxygen atoms of an ester group may be effected by displacing them from that configuration most favorable to the contribution of the forms  $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OR} \end{array}, \begin{array}{c} \text{O}^- \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O}^+\text{R} \end{array}$ . This distortion must occur in  $\beta$ -butyrolactone, and a weak band appears at  $\sim 2600$  Å. (see Fig. 2) which is attributable to the increased carbonyl character of the C=O in the lactone. The band is, however, of shorter wave length and weaker intensity than that of a true carbonyl as exemplified by acetone in Fig. 2. The absorption of cyclobutanone is much the same as that of acetone with respect to position and in-

(11) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, pp. 235, 172.

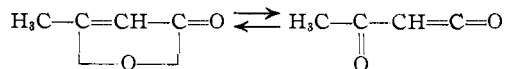
tensity, but it shows vibrational structure due to the rigidity of the ring. This vibrational structure also appears in the  $\beta$ -butyrolactone.

The absorption of diketene bears the same relationship to that of ethyl  $\beta$ -ethoxycrotonate and mesityl oxide as the absorption of  $\beta$ -butyrolactone bears to that of ethyl acetate and acetone. This is compatible only with the  $\beta$ -crotonolactone formula for diketene. There is, however, a lack of vibrational structure which one might expect in the absorption of a ring compound. This we attribute to the extreme ease with which the ring in  $\beta$ -crotonolactone is opened especially in the excited state.

Of all the known reactions of diketene only two



seem more or less definitely to require apparently mutually exclusive structures for the substance. These are (1) the ozonolysis leading to pyruvic aldehyde requiring the acetylketene form on the basis of the usual Harries mechanism and (2) the hydrogenation leading to  $\beta$ -butyrolactone requiring the  $\beta$ -crotonolactone form. It is therefore of interest to make an estimate of the free energy for the isomerization



From the bond energies, resonance energies, and

strain energies (in both the four membered ring and the ketene structure) it appears that  $\Delta H$  is approximately  $-5$  to  $-8$  kcal./mole (in favor of the lactone form). The entropy difference must, however, be in the opposite direction being smaller for the ring compound by about 12 units (cyclopropane  $\rightarrow$  propylene,  $\Delta S \simeq 7$ ; cyclohexane  $\rightarrow$  hexene,  $\Delta S \simeq 20$ ). We thus arrive at  $\Delta F \simeq -1$  to  $-5$  kcal./mole (in favor of the lactone). If the equilibrium is relatively rapid and reversible, with the ozonization fast for the acetylketene while the hydrogenation is fast for the lactone, the apparent difficulty is resolved. A somewhat similar rapid reversible equilibrium has been described<sup>12</sup> for the compound

### Summary

1. The absorption spectra of diketene,  $\beta$ -butyrolactone, vinyl acetate, and dehydroacetic acid, all in 2,2,4-trimethylpentane solution, have been measured.
2. On the basis of these measurements it is decided that the  $\beta$ -crotonolactone formula for diketene is most probable, together with the condition of extremely easy transformation into the isomeric acetylketene form.

BERKELEY, CALIFORNIA  
EVANSTON, ILLINOIS

RECEIVED MAY 12, 1941

(12) W. Dilthey and R. Wizinger, *Ber.*, **59**, 1856 (1926).