Diketene: Infrared Spectrum and Structure

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The structure of the ketene dimer, $(CH_2=C=O)_2$, has been in question ever since its discovery in 1908. Five possible forms have been seriously considered at various times:

CH₃—C—CH=C=O
   |
   O

I
Acetylketene

CH₂=C—CH₂
     | |
     O—C=O

II
Vinylaceto-β-lactone

CH₃—C=CH
    | |
    O—C=O

III
β-Crotonolactone

O=C—CH₂
    | |
   H₂C—C=O

IV
Cyclobutanedione-1,3

HOC=CH
   | |
 H₂C—C=O

V
Mono-enol of IV
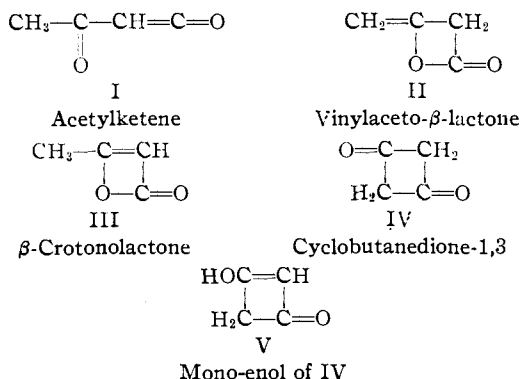
The present status of the problem has been well summarized by Boese[1] and by Hanford and Sauer.[2] Chemical reactions appear to have been of little help in elucidating the structure, for some indicate one form and some another. It is very difficult to evaluate such evidence critically because of the considerable possibility of rearrangements. Since the problem is to establish the structure of the ground electronic state of diketene, it seems undesirable to argue from evidence that involves also an unknown activated state. One is therefore inclined to discount such evidence and to rely on physical measurements made only on the ground state if possible. These, however, have also led to contradictions. The non-zero dipole moment[3,4] eliminates the possibility that the structure may be symmetrical form IV alone. The Raman spectrum has been obtained for the liquid,[5,6,7] and the infrared spectrum for both liquid and solutions.[8] The absence of any O-H stretching frequency eliminates V, and the many coincidences between the Raman and infrared spectra eliminate again the existence of form IV alone. A further decision between the remaining forms I, II, and III has not yet been made from the data. It is noteworthy that five

(1) Boese, Ind. Eng. Chem., 32, 16 (1940).

(2) Hanford and Sauer, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 127 ff.

(3) Oesper and Smyth, THIS JOURNAL, 64, 768 (1942).

(4) Hurdis and Smyth, ibid., 65, 89 (1943).

(5) Angus, Leckie, LeFevre, LeFévre and Wassermann, J. Chem. Soc., 1751 (1935).

(6) Kohlrausch and Skrabal, Proc. Indian Acad. Sci., 8A, 424 (1938).

(7) Taufen and Murray, THIS JOURNAL, 67, 754 (1945).

(8) Whiffen and Thompson, J. Chem. Soc., 1005 (1946).

strong bands are found in the double bond stretching region (1500–2000 cm.$^{-1}$), whereas each of the postulated forms would have only two fundamentals there. (Form I may be an exception, with only one band in this region. The ketene group in this molecule probably would give one band above this range and one below it.) The remaining three (or four) bands must then be explained either as combination tones, or as due to the presence of more than one form. The ultraviolet absorption maximum at 3130 A ($\epsilon = 2$) would seem to favor III.[9] (This too involves an upper electronic state, however.) Electron diffraction studies are said to be compatible with II or III, incompatible with I and IV.[10] Unfortunately none of these data provide unambiguous proof for any one of the possible structures. Because of this it has been suggested several times[2,8] that there may be two (or more) forms in equilibrium.

It occurred to us that the existence of such an equilibrium, Form A $\rightleftarrows$ Form B, might possibly be demonstrated by measuring the infrared spectrum as a function of temperature. The van't Hoff equation, $d \ln K/dT = \Delta H/RT^2$, indicates that if ΔH is sufficiently large the equilibrium constant will change appreciably with temperature. The resulting alteration in the composition of the equilibrium mixture may then be evidenced in the infrared spectrum. Conversely, however, a spectrum which changes with temperature does not indicate the existence of an equilibrium unless other temperature effects are excluded. Two such effects come to mind immediately. (a) An irreversible chemical change. This possibility can be eliminated if the changes in the spectrum are found to be reversed when the sample is brought back to its original temperature. (b) Altered population of the energy levels in accordance with the Boltzmann factor. For a moderate rise in temperature the increased population of the higher vibrational levels will increase the intensity of difference bands, but should not appreciably affect the relative intensities of fundamentals. Hence a very few weak bands may become markedly intensified at higher temperatures, but they should be calculable as difference tones. The effect of increased temperature on the rotational fine structure is one of broadening and flattening the rotational branches. If the width of a vibration–rotation band of an asymmetric rotator is defined as the separation of points on the

(9) Calvin, Magel and Hurd, THIS JOURNAL, 63, 2174 (1941).

(10) Private communication from Bauer, Bregman and Wrightson to Hanford and Sauer, as reported in reference 2, p. 218, footnote. See also Abstracts of Papers, 109th meeting of American Chemical Society, April, 1946.

band envelope where the intensity has a given value, then the width of the band is proportional to the square root of the absolute temperature.[11] Thus in going from 30 to 180° the band width will increase by a factor of about 1.2. This should not be a confusing effect, as we shall be looking for more marked changes in the spectrum.

Experimental

Diketene was prepared by the dimerization of ketene according to the method of Williams and Krynitsky.[12,13] The spectrum was measured from 3 to 15 μ with a Model 12-B Perkin–Elmer infrared spectrometer equipped with rocksalt optics, a General Motors breaker-type amplifier, and a Brown recorder. A 5-cm. Pyrex cell was used for the vapor. The rocksalt windows were sealed on with glyptal resin, which was found to hold well at temperatures up to 180° if one heats or cools rather slowly to avoid cracking the seal. The cell was heated in a small oven consisting of a sheet metal cylinder closed with endplates of transite that were held together by four tie rods. A window was cut in each piece of transite and closed by clamping over it a polished rocksalt plate. A suitably insulated electrical heating element was wrapped around the metal cylinder. The cell was connected by glass tubing to an external sample reservoir immersed in a water bath. The connecting tube had a small U-type mercury manometer sealed to it so that pressures in the range 0–20 mm. could be read. The primary purpose of the manometer was to indicate any failure in the glyptal seals. The connecting tube and manometer were wrapped with a spiral of resistance wire and heated electrically to a temperature sufficiently high so that no condensation occurred in them. In this manner the reservoir was made the coolest part of the system. The pressure of the vapor was thus determined by the temperature of the liquid reservoir, whereas the temperature of the vapor in the beam was determined by that of the oven.

Spectra were measured at vapor temperatures of approximately 30, 60, 100, 140 and 180°. Experimental conditions for the various determinations were

No.	Temp. of reservoir, °C.	Temp. of cell, °C.
1	28	60
2	29	100 ± 2
3	34	141 ± 2
4	35	182 ± 1
5	< −50	183 ± 2
6	29	102 ± 3
7	28	31 ± 1
8	< −50	30

In runs 5 and 8 the vapor was condensed into the liquid reservoir by cooling with a Dry Ice-bath. These runs thus served as blanks to give the transmission through the empty cell, and to demonstrate that no deposit had formed on the windows. After completion of run 5 vapor was readmitted to the cell at 180°, the cell was slowly cooled to 100°, and the spectrum was remeasured at this temperature. The apparatus was then allowed to stand overnight to reach temperature equilibrium with the room, and run 7 was made with the vapor at 31°. The cell then stood overnight again while the sample reservoir was cooled with a Dry Ice-bath, and blank run 8 was made. It was necessary to wait this long because it was found during blank runs 5 and 8 that about 3 mm. of residual

(11) Badger and Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938); see also Avery and Ellis, *ibid.*, **10**, 10 (1942).

(12) Williams and Krynitsky, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 64.

(13) We are indebted to Mr. J. L. Anderson of the Organic Manufactures program of this Department for preparation of one of the two samples used.

permanent gas was present in the system. This impeded the diffusion of vapor back into the reservoir. We believe that this gas was air which degassed from the system during heating, for it gave no infrared absorption.

Another experiment was performed for the purpose of locating very weak bands. In this case a dish of liquid diketene was placed within the smaller or source housing of the spectrometer. This provided a path length of 40 cm. at a vapor pressure of about 13 mm.

Finally, the spectra of solutions of diketene in carbon tetrachloride and carbon disulfide were obtained to get a comparison between our samples and those used by Whiffen and Thompson.

Results

In brief, the spectrum was found to change markedly with temperature, and these changes were reversed on cooling.

Table I summarizes our results at 30°, and gives for comparison the data reported by Whiffen and Thompson[8] for the pure liquid and for solutions. The agreement is reasonably satisfactory. We observed the same change in the relative intensities of certain bands in the 1700–1900 cm.$^{-1}$ region upon change of solvent that was noted by these authors. Our bands in the 3000 cm.$^{-1}$ region are accurate to only about ±15 cm.$^{-1}$ because of poor dispersion, but the spectrum was scanned to 3600 cm.$^{-1}$ to confirm the absence of hydroxyl groups in the vapor. It is noteworthy that the very intense band of ketene monomer at 2153 cm.$^{-1}$ is not present in any of our spectra at any temperature.

It is necessary to point out at this time that the intensities reported in this paper are only qualitatively correct for the following two reasons. First, our procedure was to record a radiation curve through an empty cell, and then to use this in calculating transmission for all the other determinations. (Run 8 was used for this purpose.) Many of the experimental conditions varied slightly from run to run—amplifier gain, energy output from the globar, atmospheric water vapor in the air path, and so on—so the runs are not strictly comparable. Secondly, the concentration of the vapor molecules in the beam was not quite the same at the various temperatures. Assuming an ideal gas, the concentration is proportional to P/T. We hoped to measure the pressure with the little manometer, and to adjust it by changing the temperature of the reservoir in such a manner as to keep P/T constant for the vapor. However, because of the permanent gas alluded to earlier, there was an error in all the pressure measurements. Since the vapor pressure was of the order of 15 mm., a 3 mm. error was relatively large. Hence the amount of sample in the beam was not the same for the various runs. For these two reasons it is evident that we will not be justified in comparing absolute intensities. Nevertheless a comparison of the relative intensities of two bands in one spectrum with the relative intensities of the same two bands in another spectrum will be meaningful. In this connection it should be remembered that the intensity of a band is to be measured by the area under the band envelope

TABLE I

THE INFRARED SPECTRUM OF DIKETENE

Whiffen and Thompson[8] (liq., soln.)		This work (solution)		This work (vapor, 30°)	
Cm.$^{-1}$	I^a	Cm.$^{-1}$	I^a	Cm.$^{-1}$	I^a
805	s	804	s	796 803 811	m
846	s	840	s	838	m
868	s	875	vs	879 887 893	vs
893	?	893	vw		
914	?	914	vw		
946	?				
957	m	958	vw		
986					
1009	s	1006	vs	1001 1013	s
1055	w				
1106	m	1095	w		
1130	m	1125	m	1130	w
				1209	b
1194	m	1199	w	1220	vw
1239	s	1238	s	1237	m
				1250	w
		1288	w	1292	w
1375	m	1367	m	1371	m
1393	m	1392	m		
1417	m	1411	m		
1685	s	1675	s	1676	s
1705	s	1709	vs	1720	vs
1745	s	1750	s	1776	m
1865	s	1869	s	1875	s
1895	s	1899	vs	1922	vs
		1960	vw	1970	vw
2010	w	2007	w	2012	w
2040	w				
2110	w	2112	vw	2124	w
2230	w				
2420	vw				
2480	vw				
2560	w				
2660	vw				
2710	w				
				2846	b
				2923	w
2970	m	2999	vw		
3010	m			3007	b
3082	w				
3370	w				
3620	w				

^{a} vs = very strong, s = strong, m = medium, w = weak, vw = very weak. ^{b} Observed only for the 40 cm. absorbing path described in the text.

rather than by the position of maximum absorption, because a band will flatten and broaden as the temperature increases.

Figure 1 compares the two 100° spectra (runs 2 and 6). Although the two curves are not quantitatively identical, the general agreement is good except for the two bands at 1133 and 1838 cm.$^{-1}$.

The first of these will be discussed later. The second is apparently due to some extraneous material such as the glyptal lacquer because it is most intense in the first run, weaker in the second, and missing in all the others. The two spectra are sufficiently similar to indicate that reversibility is established.

Figure 2 compares the spectrum at 60° with that at 180° (runs 1 and 4). Examination will reveal several significant differences. Consider first the region 1600–1820 cm.$^{-1}$, which contains the four bands at 1676, 1720, 1776, and 1797 cm.$^{-1}$. At 60°, 1720 is much the strongest, 1776 is very slightly more intense than 1676, and 1797 is completely missing. At 180° the intensity is in the order 1776 ≅ 1720 > 1676, and 1797 has appeared. Figure 3B shows that these changes occur gradually as the temperature is increased. A comparison of 1676 and 1776, for example, shows that the intensity of the 1776 cm.$^{-1}$ band changes from less than that of 1676 at 30° to much more at 180°. The changes are reversible, as indicated by the rerun at 100°, and by the fact that the 30° run (which was made last of all) fits the general trend. This group of four bands thus shows a very definite and reversible change with temperature. The 1797 cm.$^{-1}$ band cannot be explained as any reasonable difference tone.

Similar changes are found in the 1100–1300 cm.$^{-1}$ region, as shown in Fig. 3A. The band at 1133 cm.$^{-1}$ is most intense in the first spectrum measured (60°), and is completely gone at 180°. On cooling back to 100° it reappears, but not as intensely as in the first 100° run. On further cooling to 30° it is still present, but with rather low intensity. Hence this band seems to indicate an irreversible change. Since there is little other evidence for irreversibility in the spectrum, one might attribute the band to some impurity. It is reported by Whiffen and Thompson, but by none of the Raman investigators. On the other hand it does reappear, even though weakly, at the lower temperatures. We have no explanation for the behavior. The band at about 1185 cm.$^{-1}$ comes in as temperature increases and goes out again on cooling. It may be the difference tones 1683 − 504(R) = 1179 and 1722 − 531(R) = 1181 (R = Raman band). On the other hand, the 1237-1250 doublet shows the converse behavior, disappearing as the temperature increases. Another band at 1292 cm.$^{-1}$ is present only at the lower temperatures. This band is not reported in any earlier work, and so it may be due to an impurity. Other characteristic changes in the spectrum are noticeable too. For example, as the temperature increases, the intensity of the 1919 cm.$^{-1}$ band relative to that of the 1676–1720–1776 group becomes markedly less. This change is also reversible with temperature.

There can be no doubt, then, that there are real changes in the spectrum as the temperature is increased. We feel that they cannot be due to
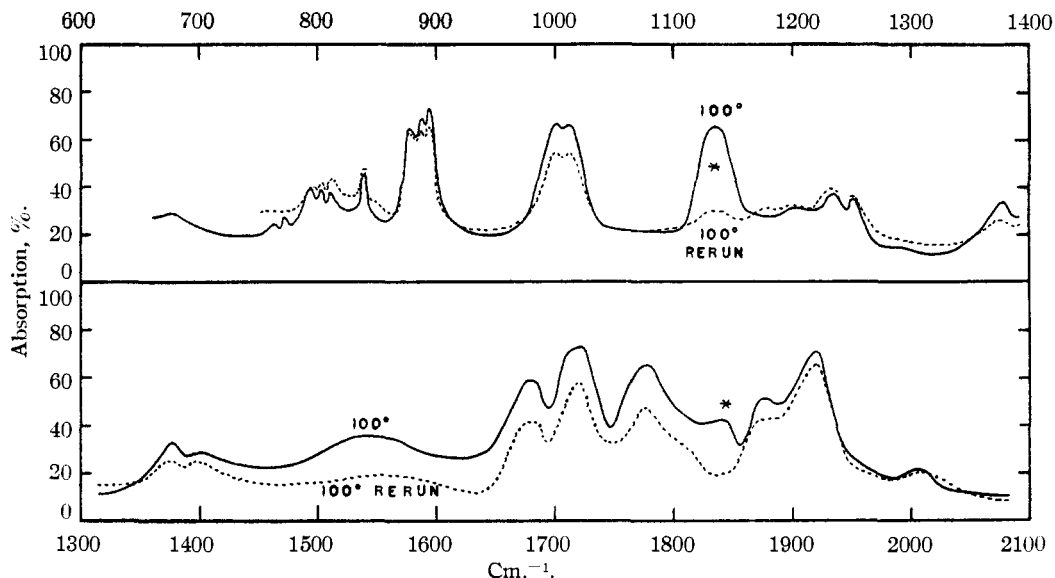
Fig. 1.—Infrared spectrum of diketene vapor at 100° (runs 2 and 6). Bands marked with an asterisk are of questionable origin. See discussion in text.

an irreversible chemical reaction because the original features of the spectrum are recovered on cooling. (The 1133 cm.$^{-1}$ band is an exception to this.) Also the changes are much too marked to be attributed entirely to changes in the population of the vibrational and rotational levels. Hence we feel that the results indicate the existence of an equilibrium between two forms of diketene which co-exist at room temperature.

Discussion

If one accepts the existence of such an equilibrium, it becomes much easier to understand the anomalous behavior of diketene which has been so puzzling heretofore. For example, one chemical reaction may proceed through one form, and another reaction through the other form. It is also now reasonable to find five strong bands in the double bond stretching region. Four (or three) fundamentals are to be expected, leaving only one (or two) to be explained as a combination tone.

The question as to which forms comprise the equilibrium mixture now presents itself. The spectroscopic evidence has been thoroughly discussed by Whiffen and Thompson.[8] We feel that
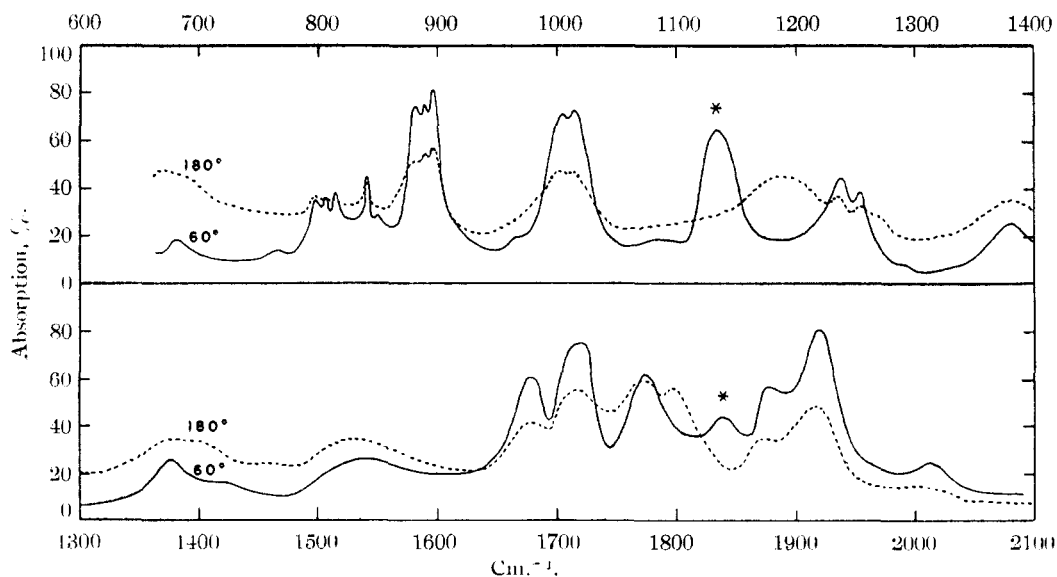

Fig. 2.—Infrared spectrum of diketene vapor at 60° and 180° (runs 1 and 4). Bands marked with an asterisk are of questionable origin. See discussion in text.
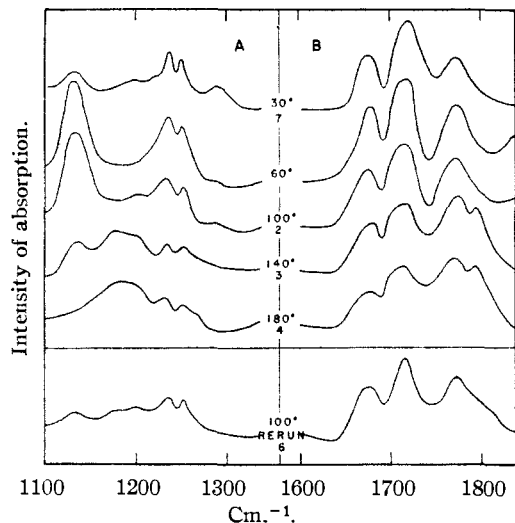
Fig. 3.—Detailed comparison of selected bands at the various temperatures. The curves have been displaced vertically.

their reason for eliminating the acetylketene structure (I)—the lack of a ketene group band near 2150 cm.$^{-1}$—is very compelling. It is our opinion that if as much as 2–4% of the material were in Form I, a band would have been observed in the region 2100–2200 cm.$^{-1}$. This elimination of Form I receives further support from the electron diffraction results cited earlier.[10] Forms II and III seem to be adequate to explain all the observations on diketene—chemical reactions, electron diffraction, ultraviolet absorption, vibrational spectrum, dipole moment. There remains the possibility that Form IV (cyclobutanedione-1,3) may be one of the components of the mixture. It has been amply proved that this structure alone cannot represent diketene, but it is not so easy to prove that it is not present in the equilibrium mixture. However, if there are only two components, it seems probable that they would be II and III rather than either one of these with IV. The conversion between II and III is accomplished by transfer of a proton and the shift of a double bond. Changes of this type are fairly common. On the other hand the conversion of IV into either II or III involves breaking and reforming the four-membered ring, and one would expect the activation energy to be higher for this process than for the former one. Some chemical evidence can also be adduced to support the elimination of IV. It has been shown that diketene does not react with sodium metal, with acetyl chloride, nor with phenyl isocyanate.[14] These reagents are sensitive to the presence of hydroxyl groups, and so it is apparent that diketene contains neither hydroxyl groups nor a potential enolic structure. Judging by analogy with other compounds, Form IV would be expected to enolize sufficiently to show some reaction with these reagents. The fact that no such reaction has been detected indicates that Form IV is not present. This argument is not by itself convincing, because of its speculative nature, but it does add some support to the conclusion reached above.

To summarize, then, it seems that diketene is probably an equilibrium mixture of Forms II and III (vinylaceto-β-lactone and β-crotonolactone).

We have been unable to decide which form is favored by increasing the temperature. One can say, however, that certain of the vibrational bands belong to the high temperature form and certain others to the low temperature form. One thus has an experimental method for following the separation of the two forms.

Summary

1. The infrared spectrum of diketene vapor has been measured at five temperatures ranging from 30 to 180°.

2. The spectrum changes with temperature in such a manner as to indicate an equilibrium mixture of two (or more) kinds of molecules.

3. The equilibrium is probably between two of the three structures: vinylaceto-β-lactone, β-crotonolactone, and cyclobutanedione-1,3. The first two seem most likely; they are capable of accounting for all the experimental observations on diketene.

(14) Chick and Wilsmore, J. Chem. Soc., **97**, 1981 (1910); Hurd and Williams, THIS JOURNAL, **58**, 964 (1936).