together with the necessity for oxygen in the reaction, indicates that species III is a photoöxidation product of the thiazine dyes in which the methyl substituents were removed resulting in the formation of thionine. It is known that methylene blue may be demethylated by non-photochemical oxidation in alkali to give dyes with fewer methyl substituents.[5]

TABLE I

ABSORPTION MAXIMA OF PHOTO-PRODUCTS

	Wave length of absorption max.	
Dye	Free dye	Photo-product with PMA
Thionine	599	607
Azure C (monomethylthionine)	616	607
Azure A (u-dimethylthionine)	620	608
Azure B (trimethylthionine)	652	605
Methylene blue (tetramethylthionine)	665	606

The highly specific nature of the polymer required for the reaction implies that the polyacrylic acids serve as substrates for a very special type of dye binding. In the dye–polymer complex the transition from the ground to the first electronic excited state does not differ from that of the free dye since the absorption spectra are virtually identical. Transitions from the first electronically excited state to other states must, however, be profoundly affected by the complexation with the specific polymers. It appears that the spatial arrangement of the carboxyl groups on the polyacrylic acids is particularly suited to complex with the thiazines *via* their amino groups to distort the electron configuration of the excited dye molecules. This arrangement does not exist for any of the other polymeric acids which were tested nor for the dibasic acids studied.

There are two distinct photochemical processes involved in the light induced spectral shift of the complexed thiazine dyes. The first process to give species II does not require oxygen. It is possible that the absorption of light by the original dye imparts a certain electron configuration which enables the dye molecule to be bound to the substrate in a manner which allows it to be readily photoöxidized to give species III. This first process does not require oxygen and probably does not involve long-lived states. On the other hand, the second process involves long-lived states because very small amounts of KI or *p*-phenylenediamine retard the reaction. From the observed retardation we estimate, using the Stern–Vollmer expression and the calculated diffusion controlled encounter frequency in solution,[6] that the lifetime of the excited species which reacts with oxygen to be about 10^{-5} sec. By analogy with other dyes whose rate of photochemical conversion is influenced by O_2, KI and *p*-phenylenediamine, we propose that this long-lived excited state is a triplet state. It has been shown with triphenylmethane dyes[3] that binding can encourage triplet formation. Here, however, it appears that a specific substrate is required and that the binding takes place only after the dye is excited. The low quantum yield observed is probably accounted for in terms of internal conversion to the ground state which are competitive to transitions to the long-lived state.

[5] H. J. Conn, "Biological Stains," 5th Ed., Biotech Publications, Geneva, N. Y., 1946.

[6] G. Oster and A. H. Adelman, THIS JOURNAL, **78**, 913 (1956).

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[CONTRIBUTION FROM THE MELLON INSTITUTE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Diketene: Infrared Spectrum and Structure. II[1]

BY FOIL A. MILLER AND GERALD L. CARLSON

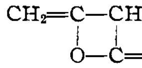
RECEIVED MARCH 16, 1957

Earlier temperature-dependence measurements on the infrared spectrum of diketene vapor by Miller and Koch have been repeated, and have been found to be incorrect. There is no evidence from the vapor spectrum for an equilibrium between two forms. Furthermore the spectrum of the solid, the liquid and the vapor are essentially the same. It follows that diketene in all its states exists predominantly or entirely in a single form, which other X-ray and nuclear magnetic resonance spectra studies have shown to be the 3-buteno-β-lactone structure. It appears that the five strong bands in the double bond stretching region, long a stumbling block to understanding the structure, are due to two fundamentals and three combination tones.

Introduction

Some time ago Miller and Koch[2] studied the infrared spectrum of diketene vapor as a function of temperature between 30 and 180°. They found reversible changes which were attributed to the existence of two forms of diketene in equilibrium. This conclusion helped explain the presence of five strong bands in the region 1650–1950 cm.$^{-1}$, and was attractive for understanding the welter of other conflicting evidence concerning the structure of diketene.

Since then an X-ray diffraction study by Katz and Lipscomb[3] has shown that crystalline diketene has the 3-buteno-β-lactone structure



$$\begin{array}{l} CH_2{=}C{-}CH_2 \\ \qquad\;\, | \quad\;\; | \\ \qquad\;\, O{-}C{=}O \end{array}$$

3-buteno-β-lactone

This was confirmed by a nuclear magnetic resonance spectra study of crystalline diketene by Ford and

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[1] (a) From a thesis submitted by G. L. Carlson in partial fulfillment of the requirements for the degree of Master of Science at the University of Pittsburgh. (b) This work was supported in part by a grant from the National Science Foundation.

[2] F. A. Miller and S. D. Koch, Jr., THIS JOURNAL, **70**, 1890 (1948).

[3] L. Katz and W. N. Lipscomb, *Acta Cryst.*, **5**, 313 (1952).

Richards,[4] which demonstrated that the protons occur only in CH_2 groups. More recently Bader, Gutowsky, Williams and Yankwich,[5] also using nuclear magnetic resonance, concluded that this same form is the only significant one existing in the liquid between 25 and 120°.

Because these results for solid and liquid directly contradict the earlier conclusions drawn for the vapor, it was deemed desirable to repeat the earlier work to see whether it was in error or whether the vapor really does have a different composition from the liquid and solid. This has been done, and the finding is that the earlier infrared work was in error. There is no temperature dependence to indicate an equilibrium between two forms.

Experimental

Commercial diketene (obtained from the Carbide and Carbon Chemicals Company through the courtesy of R. C. Miller of Mellon Institute) was distilled at reduced pressure (b.p. 43.5° at 48 mm.). It was then further purified by fractional crystallization. Because this appears to have been an especially effective method, the procedure will be described. Diketene melts at $-7°$. A cold-bath was prepared from a 1:1 solution of sodium thiosulfate in water, and cooled with Dry Ice until slushy. The sample was immersed in this slush, and stored in a Dewar flask in a cold room at $-5°$. In about 24 hr. large crystals of diketene had formed. Cooling was allowed to proceed until about half of the sample had crystallized. The remaining liquid was decanted, and the pure sample was stored at $-5°$ under nitrogen until used; n^{20}_{D} 1.4376.

A Perkin-Elmer model 112 infrared spectrometer (single beam, double pass) was used with a NaCl prism, and with a slit servo accessory to approximately level out the 100% line. The instrument was completely flushed with dry, CO_2-free air, and the range 700–4000 cm.$^{-1}$ was covered.

The spectrum of the solid was obtained in a low temperature cell, similar to one described by Lord, McDonald and Miller,[6] which had a conventional vapor-tight liquid cell about 0.05 mm. thick attached to the Housekeeper seal. The liquid sample was slowly solidified in this cell by adding Dry Ice slush to the coolant reservoir. After the spectrum of the solid had been obtained, the sample was melted and the liquid spectrum was measured in the same cell.

The system for handling and heating the vapor was similar to that used by Miller and Koch,[2] but a considerable improvement was made in the manner of sealing the windows onto the cell. The ends of the 5-cm. long Pyrex cell body were flanged and ground flat. Rocksalt windows were clamped against the flanges with metal rings and tie rods. A very satisfactory grease was compounded of 10% extremely fine silica (Monsanto's Santocel 54) and 90% Dow-Corning No. 200 silicone oil. This grease, used on both the flanged surfaces and the stopcocks, gave a vacuum-tight system at temperatures up to at least 250°. Because the windows are not attached to the glass with a rigid seal, but are merely pressed against the flanges, there is no problem with differential expansion.

In this work the temperature of the vapor was varied between 40 and 180°. A sample pressure of 19 mm., measured at 40°, was used. There was no evidence of any decomposition of the sample after hours of heating. Another grease, compounded from lithium stearate (10 g.) and No. 60 lubricating oil (40 g.),[7] caused sample decomposition at temperatures as low as 100°. Carbon dioxide was a product, but there was no ketene, allene nor methylacetylene.

Results and Discussion

The infrared frequencies agree well with the earlier results of Whiffen and Thompson[8] and Miller and Koch[2] and references cited by them. Whiffen and Thompson's spectrum shows the 1130 band to be considerably more intense than 1106, whereas our finding is that it is only slightly more so. This is certainly due to an impurity in their sample, for the spectrum of our crude material matched theirs in this region, whereas purification diminished the 1130 cm.$^{-1}$ band.

Our spectra for the liquid and for the solid were essentially the same, as shown in Table I. The cell (0.05 mm.) was far too thick for some of the bands, which makes it impossible to locate their maxima accurately. This also is the reason why only two bands are reported in the double bond region; the four strong bands have merged into two very broad ones. The significant finding is that the liquid and solid spectra are essentially the same. This reinforces the conclusion of Bader, Gutowsky, Williams and Yankwich[4] that diketene has the same single structure in the liquid as in the solid.

The spectrum of the vapor at room temperature already has been shown to be essentially identical with that of the liquid.[2] It must therefore be concluded that it too consists of a single form of diketene.

TABLE I

INFRARED FREQUENCIES (IN CM.$^{-1}$) OF SOLID AND LIQUID DIKETENE

(solid, *ca.* $-40°$; liquid, *ca.* 25°)

Solid	Liquid	I^a	Solid	Liquid	I^a
812	810	vs	1520	1517	w
862–884[b]	832–884[b,c]	vs	..	1538	w
959	960	s	1555	1555	w
1024	984–1017[b,d]	vs	1572	..	m
1060	1050	m	1704[b]	1704[b,e]	vs
1115	1100	m	1847 [b]	1875[b,e]	vs
1143	1130	w	1886		
1173	..	w	1946	1957	sh
1196	1193	m	2030	2010	m
1247	1237	vs	2079	2073	m
1365	1374	s	2222	2213	w
1396	1391		2348	2337	m
1416	1408		3020	..	m
1458	1463	m	3065	3075	
1474			3181	3163	

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder. [b] Too intense to measure accurately in 0.05 mm. cell. [c] Thinner sample gives band at 870 with shoulder at 840. [d] Thinner sample gives band at 1011. [e] See Table II.

The earlier evidence for an equilibrium between several forms—the change of the vapor spectrum with temperature—could not be repeated. A careful comparison of the spectrum at 40° with that at 180° over the range 700–4000 cm.$^{-1}$ showed no significant differences, but only the expected flattening and broadening of the bands at higher temperature. An especially careful study was made of the regions where Miller and Koch had noted marked changes, and no such changes were observed. There was no band at 1797, at 1133 nor at 1185 cm.$^{-1}$. It has already been mentioned that much of the 1133 cm.$^{-1}$ intensity could have been due to an impurity. None of the other effects were duplicated. It is con-

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(4) P. T. Ford and R. E. Richards, *Disc. Faraday Soc.*, **19**, 193 (1955).

(5) A. R. Bader, H. S. Gutowsky, G. A. Williams and P. E. Yankwich, THIS JOURNAL, **78**, 2385 (1956).

(6) R. C. Lord, R. S. McDonald and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).

(7) I. E. Puddington, THIS JOURNAL, **65**, 990 (1943).

(8) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

TABLE II

EXPLANATION OF THE INTENSE BANDS IN THE DOUBLE BOND REGION

Vapor			CCl_4 soln.[b]			Liquid[b]	
Cm.$^{-1}$		Assignment	Cm.$^{-1}$	I	Assignment	Cm.$^{-1}$	
1676	s	2 × 838 = 1676	1675	s	2 × 840 = 1680	1689	vs, broad
		803 + 887 = 1690			804 + 875 = 1679		
		670(R) + 1007 = 1677			670(R) + 1006 = 1676		
1720	vs	C=C stretch	1708	vs	C=C stretch		
1776	m	2 × 887 = 1774	1752	s	2 × 875 = 1750	1744	m
1875	s	887 + 1007 = 1894[a]	1867	s	875 + 1006 = 1881[a]	1864	vs
1922	vs	C=O stretch	1900	vs	C=O stretch	1897	vs

R = Raman frequency. [a] Fermi resonance with C=O stretch. [b] Frequencies measured with CaF_2 prism.

cluded that the earlier work was incorrect, and that diketene exists in the 3-buteno-β-lactone form only.

An attempt was made to explain the temperature-induced changes observed by Miller and Koch. Their raw curves were re-examined, and there is no doubt that changes were clearly indicated. One possibility is that some component of the glyptal seal distilled into the cell at high temperature and condensed out at low temperature, even though a blank run was made to test this possibility. Since it is known that phthalic anhydride can be distilled out of glyptal, its vapor spectrum was determined. A glyptal resin (General Electric Company's No. 1202) also was examined by placing a sample at the bottom of the evacuated gas cell and heating to 200°. Neither material accounted for the earlier observations, and we are at a loss to explain them.

There is still the problem of accounting for the five strong bands in the 1650–1950 cm.$^{-1}$ region on the basis of the single 3-buteno-β-lactone structure. This structure would be expected to have only two fundamentals there. One is the carbonyl stretching frequency, which will be abnormally high because of being external to a 4-membered lactone, and which we can guess will be about 1830 cm.$^{-1}$.[9] The other is the olefinic stretching frequency, which also will be abnormally high because of being exocyclic to a four-membered ring.[9] We would predict it to be about 1720 cm.$^{-1}$. Actually the C=O frequency must be the band at 1900 in solution (1922 in the vapor) while the C=C stretch must be 1708 in solution (1720 in the vapor) (see Table II.) The intensity of the latter is remarkably high for an olefinic stretch.

The remaining three strong bands are then presumably to be explained as combination tones, in spite of their considerable intensity. Table II shows that this can be done as far as the frequencies are concerned, although it is still hard to understand their high intensity. It will be noted that in the pure liquid there are only four bands. The double bond frequency appears to be lower than its value of 1708 in the solution, and it apparently merges with the 1675 band to give a single very broad band at 1689.

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[9] R. C. Lord and F. A. Miller, *App. Spectros.*, **10**, 115 (1956).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Hydrogen Peroxide–Olefin Reactions in the Vapor Phase

BY E. R. BELL, W. E. VAUGHAN AND FREDERICK F. RUST

RECEIVED MARCH 2, 1957

Hydrogen peroxide has been decomposed in the presence of ethylene, propylene and isobutylene at temperatures between 435 and 630°. The products are traceable to an initial attack by hydroxy radical involving either addition to the double bond or abstraction of a hydrogen atom from the olefin. As a consequence of the latter process diallyl and dimethallyl are major products from propylene and isobutylene, respectively. Many other compounds must originate from radical association reactions. Much fragmentation of the olefins seems to have had its genesis in the initial addition of a hydroxy radical to the olefin double bond. In cases where the carbon skeleton has been retained, hydrogenation and dehydrogenation processes can be significant. Reaction steps which logically interpret the data have been proposed.

Introduction

Hydrogen peroxide has a thermal stability much greater than that of the organic peroxides and for this reason its significance to combustion phenomena in temperature regions beyond the cool flame zone is substantially greater. Moreover, this stability suggests that hydrogen peroxide may have useful properties as a high temperature reactant.

Its thermal decomposition is apparently a complex of both heterogeneous and homogeneous processes. McLane[1] has reported that the decomposition in nitrogen begins to be essentially homogeneous only above 470° in reactors whose walls have been treated with boric acid. Although the reaction showed first-order kinetics in the temperature range 470–540°, the activation energy increased from 40 kcal. in a reactor whose surface to volume ratio was 7 cm.$^{-1}$ to 50 kcal. in one with a ratio of 3 cm.$^{-1}$. (A boric acid-coated reactor of surface-volume ratio 0.4 cm.$^{-1}$ has been chosen for these studies.)

The near coincidence of this high activation energy with the O–O bond strength in hydrogen perox-

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[1] C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).