ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE ALDRICH CHEMICAL CO. INC., AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Proton Magnetic Resonance Spectrum and Structure of Diketene[1]

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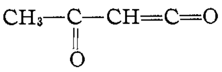
The proton magnetic resonance spectrum of diketene in the liquid state has been investigated under high resolution at temperatures between 25 and 170°. The results show that the liquid up to 120° is in the 3-buteno-β-lactone form, with no evidence of any other kind of molecule. At higher temperatures, irreversible changes occur in diketene.

Introduction

The definitive X-ray study by Katz and Lipscomb[2] has established that the structure of diketene in the solid state is the 3-buteno-β-lactone form, V. This has been confirmed by Ford and Richards[3] who observed the broad proton magnetic resonance absorption line shape in the solid. However, the vibrational spectra[4,5] of diketene in the liquid and vapor phases as well as in solution suggest that diketene may be an equilibrium mixture of V and the 2-buteno-β-lactone form, IV, or perhaps the 1,3-cyclobutadione form, III. The main spectroscopic argument favoring a mixture[4] is the appearance of five strong bands in the double bond stretching region (1500 to 2000 cm.$^{-1}$), while each of the postulated forms, I to V, would have at most two fundamentals in this region. In addition, Miller and Koch[5] found that the spectrum of diketene vapor changes at temperatures between 30 and 180° in a manner suggesting a reversible equilibrium of two (or more) forms.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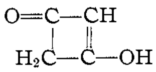
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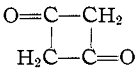
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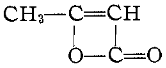
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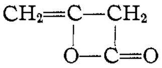
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The kind of structural problem presented by liquid diketene lends itself very readily to investigation by high resolution nuclear magnetic resonance techniques,[6,7] and indeed our results for diketene serve as an excellent example of one of the main advantages in certain types of problems of the NMR techniques over more conventional methods. To a first approximation, the number and relative intensities of the components in the NMR spectrum of a liquid sample are given simply by the number of non-equivalent structural sites and by the fraction of the nuclei in each type of site. The different components result from the influence of the electronic environment of a given nuclear species on the position of its magnetic resonance; this influence produces "chemical shifts" in the resonance position, which in general are different for different structural sites.[6] The absorption intensities, on the other hand, are directly proportional to the concentrations of the nuclei.

In this manner, the proton resonance of diketene is predicted to have two main components with relative intensities of 3:1, if the molecular structure is I; if II, 2:1:1; III, 4; IV, 3:1; and V, 2:2. A mixture would, of course, give a composite spectrum. This relative simplicity contrasts with the vibrational spectra, where some of the absorption in the double bond region could be overtones or combination bands. Accordingly, we undertook a high resolution proton magnetic resonance study to establish the structure of liquid diketene.

Experimental

The commercially available diketene was redistilled.[8] Three fractions were taken at a reduced pressure of 91.4 mm.: (1) b.p. 63–68.4°, (2) b.p. 68.4–69.4°, and (3) b.p. 69.4–69.5°. The proton spectra were recorded as a function of applied magnetic field at a fixed frequency of 17.735 Mc. using an improved version[9] of the high resolution spectrometer described earlier.[6,10] The volume of sample in the rf coil was about 0.02 ml. The spectra of all three fractions were observed. Representative spectra are reproduced in Figs. 1–3. The abscissa is in δ-units, defined as $10^5(H_r - H_c)/H_r$ where H_r is the magnetic field applied for resonance in a reference sample of H_2O and H_c that applied to the diketene.

The room temperature spectrum under moderate resolution of fraction (2) is given in Fig. 1; it is identical with that of fraction (3). The chemical shifts of the two resonance components found were measured as δ-values of −0.13 ± 0.02 and −0.06 ± 0.02. Under higher resolution each of the two components exhibits fine structure, as shown in Fig. 2. The b.p. of fraction (1) demonstrates that it is impure and in fact its proton spectrum has a weak impurity line at −0.33, a position characteristic[6] of CH_3 groups, which

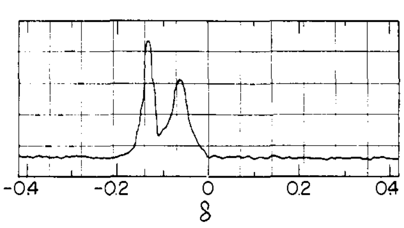

Fig. 1.—The proton magnetic resonance absorption spectrum of pure liquid diketene at room temperature. The absorption was plotted at a fixed frequency of 17.735 Mc. as a function of applied magnetic field. The total field sweep is 35 milligauss, sweep time, 12 sec.

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[1] This research was supported in part by the U. S. Office of Naval Research and by a grant-in-aid from E. I. du Pont de Nemours and Co.

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

[3] P. T. Ford and R. E. Richards, *Disc. Faraday Soc.*, **19**, 230 (1955).

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

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

[6] L. H. Meyer, A. Saika and H. S. Gutowsky, *ibid.*, **75**, 4567 (1953).

[7] H. S. Gutowsky, *Disc. Faraday Soc.*, **19**, 187, 248 (1955).

[8] We are indebted to Mr. H. E. Knipmeyer for the distillation.

[9] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **24**, in press (1956).

[10] H. S. Gutowsky, L. H. Meyer and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

most likely is from either acetic acid originally added to stabilize the diketene or else from acetic anhydride, a common impurity.[4] On standing at room temperature the samples became somewhat discolored due to polymerization of the diketene, but the room temperature spectra of fractions (2) and (3) did not appear to change.

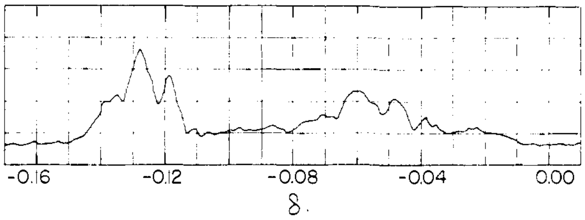

Fig. 2.—The proton magnetic resonance absorption spectrum of pure liquid diketene at room temperature under higher resolution than the spectrum in Fig. 1. The total sweep is 7.1 milligauss; sweep time, 18 sec.

The spectrum of a sample taken from fraction (2) was observed at temperatures up to 170°. A new line started to appear at 120° at a δ of -0.31 ± 0.02. This line increased in intensity and apparent complexity at higher temperatures, at the expense of the two original components, and a weak line developed at a δ of $+0.07$. However, the effects were irreversible and the new absorption remained in the spectrum when the sample was cooled to room temperature, as shown by the spectrum reproduced in Fig. 3. After the cycle, the sample was badly discolored suggesting extensive polymerization.

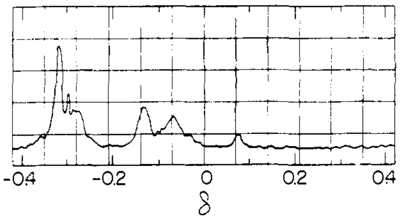

Fig. 3.—The proton magnetic resonance absorption spectrum at room temperature of a sample of liquid diketene which had been heated to 170°; otherwise same as Fig. 1.

Discussion

Structure V, the 3-buteno-β-lactone form, is the only one for which two main proton resonance components of equal intensity are predicted. The observed room temperature spectrum, in Fig. 1, has only two main components. They are of somewhat different peak intensity but the more intense line is sharper so the areas are essentially equal which is the proper criterion to use. Moreover, the -0.06 line is close to the region in which vinyl groups absorb[6] while the -0.13 line compares favorably in position with the resonance of $-CH_2-$groups in small heterocyclic compounds.[11] Therefore, as concluded in an earlier report of preliminary results,[7] this simple but powerful argument proves that liquid diketene has the 3-buteno-β-lactone structure, V.

There is still the question of whether any of the other forms is present to a small extent, perhaps with absorption overlapping that of V or else too weak to detect. Structures I and III contain a CH_3 group whose proton resonance would be in the region[6] -0.42 to -0.30, where no absorption was observed in pure diketene. This component would be the strongest one for either of the structures, and the sensitivity of our measurements is such that certainly no more than 3 to 5% of I or III could be present without our having detected it.

Forms II and III have $-CH_2-$ groups for which the proton resonance positions would be close to or overlap that of the $-CH_2-$ group in the 3-buteno-β-lactone. However, the spectrum in Fig. 2, under higher resolution than in Fig. 1, reveals no structure attributable to either II or III. Indeed, the fine structure observed supports the assignment of components and the structural conclusions already drawn. Most of this fine structure arises from the indirect coupling, *via* the bonding electrons, of the proton spins.[12] If the coupling of each proton in the $-CH_2-$ group was the same to each proton in the $CH_2{=}C$ group, and small compared to the chemical shift between the two groups, each of the two chemically shifted resonances would be a triplet.

The two $-CH_2-$ group protons are entirely equivalent since they are symmetrically disposed on either side of the plane which contains the rest of the molecule. And the resonance centered at -0.13, assigned to the $-CH_2-$ group, does appear to be a triplet. However, the resonance at -0.06 is more complex; but this is expected because the two protons in the vinyl group are not quite equivalent; they are in the plane of the "molecular skeleton" and one is *cis* and the other *trans* to the lactone ring. The resulting very small chemical shift spreads the vinyl group triplet into two overlapping triplets, more or less as observed. The actual situation is somewhat more complicated than just described because (a) the two vinyl group protons have different coupling constants with the $-CH_2-$ group protons, (b) the coupling constants are comparable to the chemical shifts,[13,14] and (c) the coupling between the protons in the vinyl group produces observable effects. Without going into the details, it appears on theoretical grounds[15] that the $-CH_2-$ group resonance would have a maximum of 8 components, while the $CH_2{=}C$ group would have two overlapping sets each of 8 components. Under higher resolution than given in Fig. 3, the $-CH_2-$ group resonance does appear to have 4 components, each a doublet. Structure III, if present, would have a single absorption line in this region; but all lines observed are accounted for. So unless the absorption from III is obscured by that from V, none of form III is present. This places an upper limit of about 5% on III.

One might argue that the observed spectrum has really three main chemically shifted components of relative intensities 2:1:1, and that the sample was therefore II. But this would require that the broad absorption at -0.06 be assigned to the $-CH{=}C$ and $C{=}C-OH$ groups and the absorption at -0.13 to the $-CH_2-$ group. However, $-CH{=}C$ groups are known[6] to absorb at $+0.05$ to $+0.15$ and the $C{=}C-OH$ group would be expected near phenols at about $+0.20$, so diketene cannot be II.

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(11) H. S. Gutowsky, R. L. Rutledge, S. Searles and M. Tamres, This Journal, **76**, 4242 (1954).

(12) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(13) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

(14) M. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc.* (*London*), **A226**, 490 (1954).

(15) H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

The absence of any detectable absorption in these regions as well as in the vicinity of the $-CH_2-$ group resonance at -0.13 places an upper limit of 5 to 10% on the presence of form II.

As to the spectra at higher temperatures, we did not detect any reversible changes. There is, of course, the possibility that the large irreversible changes shown in Fig. 3 could have obscured a small reversible effect. Moreover, the temperature dependence of the infrared spectrum was observed[5] in the vapor phase where intermolecular reaction would be slower than for the liquid used in our experiments. So we cannot prove the absence of a small percentage of another form in equilibrium with V at temperatures above 120°. But this appears to us to be rather unlikely. For one thing, the arguments of Miller and Koch[5] supporting an equilibrium mixture imply comparable percentages of at least two forms at room temperature; and we have shown this definitely not to be the case. The changes with temperature reported[5] in the relative intensities of the infrared bands in the double bond region are comparable to those found at room temperature upon changing solvents.[4] Both observations can be ascribed to a dependency of the infrared transitions probabilities on molecular environment. A last point is that the new infrared bands found[5] at 180° could be spurious. New bands were also found at 100° upon heating the sample but disappeared or decreased in intensity upon further heating or upon heating to 180° and then cooling to 100° again. There is no assurance that the new bands found at 180° might not also have changed upon such treatment.

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[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH & DEVELOPMENT CENTER]

Spectroscopic Studies on Dyes. I. The Association of Indigo Dyes in the Solid Phase[1]

BY JULIUS WEINSTEIN AND GEORGE M. WYMAN

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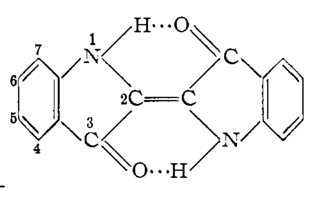
The visible spectra of indigo and seven of its alkyl- and halogen-substituted derivatives were determined in the solid phase as pellets in potassium bromide and also as aqueous suspensions. The first absorption band of indigo was found to exhibit a strong bathochromic shift when the solid spectrum was compared with that obtained in solution. The introduction of methyl or chlorine substituents in the 4- and 7-positions was found to decrease the magnitude of this shift. No such shift was observed in 5,5',7,7'-tetrabromoindigo. On the basis of these observations it was concluded that, in the solid state, indigo dyes are associated, probably by means of hydrogen-bonding. Bulky substituents in the 4,4'- or 7,7'-positions prevent the close approach of the -CO- and -NH- groups of neighboring molecules and thus interfere with the formation of molecular aggregates. A study of the infrared spectra of these dyes in the -CO- and -NH- stretching regions also supports this explanation. The absorption spectra of cellophane and gelatin films dyed with indigo indicate that under these conditions indigo is also present in the associated form.

Introduction

The problem of the structure and the configuration of indigo has intrigued organic chemists since Baeyer's classic work on the synthesis and constitution of this dye.[2] This has resulted in a large number of frequently conflicting reports in the literature on the subject.[3] There appears to be general agreement that indigo (I) is the *trans* isomer, preferentially stabilized by intramolecular hydrogen-bonding (which is only possible in the *trans* configuration), as had first been suggested by Scholl.[4] This was recently confirmed by spectrophotometric techniques when it was observed that, in contrast to thioindigo dyes,[5] indigo dyes in solutions in organic solvents do not undergo photochemical *trans-cis* isomerization.[6] In addition, the same authors also found evidence for hydrogen-bonding in indigo in the solid phase from a study of its infrared spectrum.



During a study of the effect of solvents on the spectrum of indigo, Sheppard and Newsome determined the visible spectrum of a solid film of this dye sublimed on glass.[7] They found that the absorption band occurs at considerably longer wave lengths in the solid phase than in solutions in organic solvents. This bathochromic shift is readily seen from the curves in Fig. 1. Since this unusually large shift in the position of the absorption band suggests the occurrence of structural changes, it was decided to undertake a study of the spectra of indigo and some of its derivatives in the solid phase in the hope of obtaining a better understanding of this phenomenon.[8]

Experimental

(a) **Dyes.**—4,4'-Dichloro-5,5'-dibromoindigo and 7,7'-dimethylindigo were research samples provided through

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[1] Presented before the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

[2] A. v. Baeyer, *Ber.*, **16**, 2204 (1883).

[3] (a) T. Posner, *ibid.*, **59B**, 1799 (1926); (b) R. Pummerer and H. Fiesselmann, *Ann.*, **544**, 206 (1940); (c) G. Heller, *Ber.*, **77B**, 163 (1944); (d) J. v. Alphen, *Rec. Trav. Chim.*, **60**, 138 (1941).

[4] *Cf.* W. Madelung and O. Wilhelmi, *Ber.*, **57**, 237 (1924).

[5] (a) G. M. Wyman and W. R. Brode, THIS JOURNAL, **73**, 1487 (1951); (b) W. R. Brode and G. M. Wyman, *J. Research Natl. Bur. Standards*, **47**, 170 (1951).

[6] W. R. Brode, E. G. Pearson and G. M. Wyman, THIS JOURNAL, **76**, 1054 (1954).

[7] S. E. Sheppard and P. T. Newsome, *ibid.*, **64**, 2937 (1942).

[8] Shortly after the results of the present investigation were first reported it came to our attention that a study of the X-ray diffraction pattern of indigo disclosed that in the solid phase indigo exists in the *trans* configuration with association between neighboring dye molecules, probably by means of hydrogen bonding (*cf.* Helene v. Eller, *Compt. rend.*, **239**, 975 (1954)).