TABLE IX (*continued*)

$$F_{22} = K + 2F_O + \frac{1}{4}F_1s\left(4R^2 + 4Rr + \frac{7}{10}r^2\right)$$

$$F_{23} = -\frac{1}{2\sqrt{2}}F_1rs\left(2R^2 + \frac{9}{10}Rr - \frac{1}{5}r^2\right)$$

$$F_{33} = \frac{2}{3}\left(H + \frac{13}{40}F\right)r^2 + H_1 + \frac{1}{20}F_1s\left(R^2 + r^2 + \frac{35}{2}Rr\right)$$

A_{2u}, B_{2u}, E

$$F_{11} = K_1 - \frac{1}{20}F + \frac{1}{2}F_1s\left(4R^2 + 4Rr + \frac{7}{10}r^2\right)$$

$$F_{12} = \frac{\sqrt{3}}{4}Rs\left[F_1r(2r + R) - \frac{1}{10}F_1R(2R + r)\right]$$

$$F_{22} = H_1Rr + \frac{1}{4}Rrs\left[3F_1Rr + \frac{1}{10}F_1(2R + r)(2r + R)\right]$$

B_{1g}

$$F_{11} = F_{11}^{A_{1g}}$$

$$F_{12} = F_{12}^{A_{1g}}$$

$$F_{22} = K - \frac{1}{5}F_O + \frac{1}{2}F_1s\left(4R^2 + 4rR + \frac{7}{10}r^2\right)$$

B_{2g}

$$F_{11} = \left(H_O + \frac{11}{20}F_O\right)R^2$$

E_u

$$F_{11} = K_1 + \frac{3}{2}F + \frac{1}{4}F_1s\left(4r^2 + 4Rr + \frac{7}{10}R^2\right)$$

$$F_{12} = F_{12}^{A_{1g}} \qquad F_{13} = F_{13}^{A_{1g}}$$

$$F_{14} = F_{34} = O$$

$$F_{22} = K + \frac{9}{10}F_O + \frac{1}{2}s\left[(2R + r)^2F_1 - \frac{3}{10}r^2F_1\right]$$

$$F_{23} = F_{23}^{A_{1g}} \qquad F_{33} = F_{33}^{A_{1g}} \qquad F_{24} = \frac{9}{20}F_OR$$

$$F_{44} = \left(H_O + \frac{11}{20}F_O\right)R^2$$

The symmetry coördinates for the in-plane modes are given in Table VIII. Using these symmetry coordinates, the secular equation was set up according to the procedure of Wilson.[19] The *G* and *F*-matrices are calculated as shown in Table IX. An Urey–Bradley type field[20] was used to express the potential energy. The values of the force constants which give the best fit with the observed infrared and Raman frequencies are given in Table X.

TABLE X

FORCE CONSTANTS OF $[Pt(NO_2)_4]^{2-}$ ION (10^5 DYNE/CM.)

Str.	Bend.	Repulsive
K(Pt–N) = 3.40	H(O–N–O) = 0.15	F(O....O) = 3.0
K_1(N–O) = 7.30	H_1(Pt–N–O) = 0.08	F_0(N....N) = 0.2
	H_0(N–Pt–N) = 0.04	F_1(Pt....O) = 0.03

Using these values of the force constants, the calculations have been made according to the usual procedure,[19] and the results are shown in Table II.

OSAKA, JAPAN

[19] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[20] T. Shimanouchi, *ibid.*, **17**, 245, 734, 848 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proton Resonance Spectra and Structures of Mercury(II)–Olefin Addition Compounds

BY F. A. COTTON AND J. R. LETO

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The proton resonance spectra of methyl ethyl ether, $CH_3OCH_2CH_2HgOCOCH_3$ and $HOCH_2CH_2HgOH$ are reported. The first two were measured in CCl_4 solution and the measured chemical shifts extrapolated to infinite dilution. The last compound was measured in basic D_2O and shifts again extrapolated to infinite dilution. The results conclusively support the above structures for the mercury compounds on the basis of observed area ratios and spin–spin hyperfine structure. The relative chemical shifts of the several types of methyl and methylene groups are in general accord with expectation from previous studies.

Introduction

As part of a broad study of the nuclear resonance spectra and structures of the addition compounds formed by various metals with alkenes and alkynes, we have investigated the proton resonance spectra of two simple but typical olefin adducts of mercury (II) salts, *viz.*, $CH_3COOHgCH_2CH_2OCH_3$ and $HOCH_2CH_2HgOH$. Aside from its intrinsic interest, this study serves a purpose in our over-all program of providing data on olefin–metal complexes for which there is good evidence that addition of HgX_2 across the double bond to give a carbon–mercury(II) σ-bond has occurred.[1] It is found that, conversely, the proton resonance spec-

[1] For comprehensive discussion of this point see G. F. Wright. *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957), and J. Chatt. *Chem. Revs.*, **48**, 7 (1951).

tra provide conclusive proof of the structures of these compounds independent of any inferences from their chemical behavior.

Experimental

The measurements were made with a Varian model 4300 B high resolution n.m.r. spectrometer with super stabilizer at a frequency of 40 mc. and magnetic field of 9350 gauss. Samples were contained in cylindrical glass tubes having o.d. 5 mm. and i.d. 3 mm. These tubes were filled to a depth of about 6 cm. and were rotated at a speed of 500–900 r.p.m. within the crossed coil system of the probe by means of air pressure. When capillary references were used, the column of reference material was about 0.75 mm. in diameter and at least as tall as the main body of the solution.

Materials. 1. **β-Hydroxyethylmercury(II) Chloride.**—The method of Hoffman and Sand[2] was used with modification. A solution of 15 g. of mercuric nitrate in 300 cc. of water (to which 5 cc. of glacial acetic acid had been added) was saturated at 0° with ethylene gas from a tank (Matheson, C.P.). With the ethylene bubbling continuously through the solution, 0.75 *M* NaOH was added dropwise from a buret until the appearance of a yellow-white precipitate of basic mercuric nitrate. The addition of base was then stopped until the basic salt had completely redissolved on further addition of ethylene. When the solution had cleared, more base was added and the process repeated. Finally, when further addition of base caused no yellow precipitate, the *p*H of the solution was about 11. From this point the preparation proceeded according to the method of reference 2. The material is light sensitive and was stored in a brown bottle; yield 80%, m.p. 153–155°.

2. **β-Methoxyethylmercury(II) acetate** was prepared according to the method of Schoeller and Schrauth.[3] The congealed mass of white crystals obtained in this procedure was purified by melting the solid at 45° under petroleum ether, decanting the extract and chilling it to −70° by immersion in a CO_2–acetone-bath. Scratching the side of the flask vigorously caused the precipitation of the flaky white product, which was centrifuged in the cold and collected. This process was repeated as often as needed to extract all of the white mass. The product was recrystallized from petroleum ether as above, and stored under nitrogen. The last traces of petroleum ether were removed from the product by melting *in vacuo;* yield 85%, m.p. 42°.

Caution should be exercised in the preparation, purification and handling of this material, since the solid raises blisters on the skin, and the petroleum ether solutions are rapidly absorbed into the skin where first degree burns and blistering result at the affected site. The oily material appears to "creep" on glass, and it is possible that it also penetrates surgical rubber gloves.

3. **Methyl Ethyl Ether.**—The method of preparation favored in the literature is the Williamson synthesis, employing $NaOCH_3$ and C_2H_5I in methanol solution. However, for convenient preparation in the quantities desired, another method which gave better results than the Williamson synthesis was that of Norton and Prescott,[4] in which an equimolar mixture of methyl and ethyl alcohols is treated at 140° with concd. sulfuric acid in the usual manner for continuous etherification. A two-foot packed column was used to reflux the unreacted alcohols, the dimethyl ether (b.p. −23°) was allowed to escape, and the diethyl and methyl ethyl ethers were removed as they formed and condensed by an ice-water condenser and brine slush-bath in series. This distillate was held at 5° while the product was fractionally distilled from the diethyl ether through another packed column and the distillate condensed onto clean sodium metal to remove unreacted alcohols. Finally the purified ether was distilled at 10° once more into a trap cooled with CO_2–acetone; b.p. 10–12°.

Preparation of Solutions. 1. **β-Hydroxyethylmercury(II) Chloride and KOH.**—β-Hydroxyethylmercury(II) chloride is insoluble in all common media, but reacts with base in aqueous solution to give the double base $HO-Hg-CH_2CH_2-OH$ which is extremely soluble. Solutions in D_2O were used to avoid interference by an intense solvent line. A solution 1 *M* in this mercury compound was prepared by dissolving 0.2811 g. per cc. of 1 *M* KOH in D_2O. This solution, along with solutions 0.5 and 0.25 *M* (prepared by dilution of the 1 *M* solution with micropipets) were placed in sample tubes along with the water reference capillary and sealed off.

2. **β-Methoxyethylmercury(II) Acetate.**—Samples 1, 0.5 and 0.25 *M* in CCl_4 were prepared by dissolving the solid in freshly distilled solvent, inserting the water capillary, and sealing off.

3. **Methyl Ethyl Ether.**—The low boiling point and ease of peroxide formation for this ether necessitated an arrangement for preparing the solutions and filling the sample tubes on a vacuum line. A benzene capillary was used in this case to avoid fracture of the capillary by expansion on freezing during the distillations. By sealing the sample tube onto the vacuum line at the proper angle, the capillary could be kept above the level of the frozen distillate, and tapped down into the main body of the sample just before sealing off. In this way, two solutions of the ether in CCl_4 were prepared, 50 and 10% by weight.

Measurements.—Solutions of the mercury compounds were studied at room temperature, and the spectra of the ether solutions were taken quickly upon solutions warming from 0 to about 15°. Spectra were recorded in most cases on a Sanborn recorder, while in cases where intensity or area ratios were desired a Brown recorder, because of the larger size of the trace, was found convenient. Two methods of calibration generally were used. In the first method the 70.5 c.p.s. difference between the proton resonance of capillary water and benzene was recorded at the same sweep rate and chart speed as the sample spectrum. The separation in mm. between reference and other resonance is then converted to c.p.s. In the second method, an audio frequency signal was used to produce a side band on the observed resonances at a frequency whose difference from the central resonance frequency corresponded to the frequency of the signal from the audio oscillator. Thus an internal calibration with each spectrum could be obtained. Frequency differences in c.p.s. are referred to as − or + from water, depending on whether the proton is more shielded or less shielded than the protons of water. All results are extrapolated to infinite dilution. Plots of shift *vs.* concentration were linear and quite flat. Differences between shifts at 1 *M* and 0 concentration were never more than 3–4%.

Results

1. **Methyl Ethyl Ether.**—The spectrum (Fig. 1) consists of three lines, a triplet centered at −154 c.p.s. with 7 c.p.s. splitting, a singlet at −65 c.p.s., and the components of a quartet centered at −42 c.p.s. The spectrum of this compound is used as a reference in assigning proton resonances of methyl, methylene and methoxy protons in the mercury derivatives. The triplet at −154 c.p.s. is assigned to the CH_3 protons of the ethyl group, split by spin–spin coupling with the two adjacent methylene protons. The singlet at −65 c.p.s. is assigned to the protons in the CH_3O grouping, while the quartet at −42 c.p.s. (which appears as a partially resolved shoulder on the 65 c.p.s. line with accompanying fine structure) is due to the protons of the $-CH_2O$ grouping, the structure of the predicted quartet being lost in the strong 65 c.p.s. resonance. The splitting between the only two resolvable lines of the quartet is 7 c.p.s. The ratio of total area under the triplet to the total area under the combined singlet and quartet is 121:204, or nearly 3:5. This corresponds to the number of protons involved in $CH_3/(CH_3O + CH_2)$. These measured shifts in the ether, −154, −65 and −42 c.p.s., may be compared with the corresponding average shifts of −168, −64 and −68 c.p.s. as given for the same types of proton by Gutowsky.[5]

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[2] K. H. Hoffman and J. Sand, *Ber.*, **33**, 1340 (1900).

[3] W. Schoeller, W. Schrauth and W. Essers, *ibid.*, **46**, 2864 (1913).

[4] L. M. Norton and C. O. Prescott, *Am. Chem. J.*, **6**, 244 (1885).

[5] L. H. Meyers, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

2. β-Methoxyethylmercury(II) Acetate.—The spectrum of this compound (Fig. 1) consists of two singlets at −112 and −56 c.p.s., and two triplets, centered at −105 and −44 c.p.s., each with splitting of 7 c.p.s. As can be seen from the figure, the spectrum is highly symmetrical, and the measured area ratio of the absorptions at 30–60 and 90–120 c.p.s. is 1:1. The assignment of the −112 c.p.s. line to the CH_3 protons of the acetate is unambiguous. The −56 c.p.s. singlet corresponds to the CH_3O protons, while the −44 c.p.s. triplet is assigned to the resonance of the CH_2O protons, split by spin-coupling with the adjacent CH_2 group. The triplet at −105 c.p.s. is thus assigned by default to the CH_2–Hg protons. This value is not unreasonable when compared with the −97 c.p.s. shift of the CH_2–Pb protons in tetraethyllead.[6]

3. β-Hydroxyethylmercury(II) Hydroxide.—The spectrum of this compound consists of three lines, two triplets centered at −110 and −32 c.p.s., respectively, each with 8 c.p.s. splitting, and a singlet at +5 c.p.s. Because of unusually good resolution on this compound, we were able to resolve the weak shoulder on the center line of each triplet. This shoulder may also be resolved, *e. g.*, in ethanol. The assignment of the two triplets in this compound follows closely the assignment in the acetate compound, with the −110 c.p.s. resonance corresponding to the CH_2–Hg protons and the −32 c.p.s. resonance to the CH_2O protons. The OH proton gives rise to the singlet at +5 c.p.s.

The very small positive shift of the OH protons was measured in two ways. In the first method, a capillary of pure water was used to measure the shift of OH^- protons in a 1 *M* solution of KOH in D_2O. The same shift was obtained with a 1 *M* solution of the mercury compound in this KOH solution. Using the method of slow sweep, and recording beats to determine the period, the frequency difference was found to be 5.1 c.p.s. In the second method, a toluene capillary was used with the 1 *M* solution of the mercury salt, and the measured frequency difference between the phenyl protons and the OH protons was compared with the known frequency difference between the phenyl protons and water protons. These data are summarized in Table I.

TABLE I

CHEMICAL SHIFT OF PROTONS ON VARIOUS FUNCTIONAL GROUPS

Ether, $CH_3OCH_2CH_3$; acetate, $CH_3OCH_2CH_2HgOCOCH_3$; base, $HOCH_2CH_2HgOH$

Functional group	Average shift (c.p.s. from H_2O, 40 mc.) (Gutowsky)	Compound	Shift in compound (c.p.s. from H_2O)
$CH_3\overset{\vert}{\underset{\vert}{C}}-$	−168	Ether	−154
$CH_3\overset{\overset{O}{\Vert}}{C}-$	−132	Acetate	−112
CH_3O-	− 64	Ether	− 65
		Acetate	− 56
CCH_2O-	− 68	Ether	− 42
		Acetate	− 44
		Base	− 32
$-CH_2HgO$	...[a]	Acetate	−105
	...	Base	−110

[a]–CH_2Pb shift in tetraethyllead = −97 c.p.s.

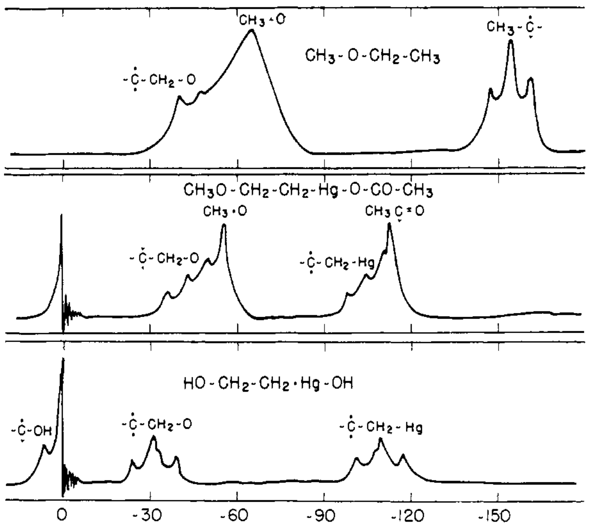

Fig. 1.—Proton resonance spectra of methyl ethyl ether (top), β-methoxyethylmercury(II) acetate (middle) and β-hydroxyethylmercury(II) acetate (bottom).

Two features of the spectrum of $HOCH_2CH_2HgOH$ require further comment.[7] The appearance of shoulders on the central components of the triplets is puzzling since their positions are the reverse of what would be expected for second-order splittings. Professor J. S. Waugh of this department has informed us that the observed positions would be correct only in the unlikely event that spin-lattice relaxation of the nuclear singlet states is more rapid than that of the triplets. However, he has calculated that in this range of J/δ, second-order structure should be more prominently resolved in the outer lines than in the central lines of the triplets. Hence the observed shoulders cannot be explained in this way, and we cannot suggest any other explanation.

The intensity of the peak due to exchangeable protons in the $HOCH_2CH_2HgOH$ appears in Fig. 1 to be too low relative to the peaks due to the methylene protons. More accurate intensity measurements were attempted using a Brown recorder. These were not entirely unambiguous because the peak was considerably overlapped by the absorption of the capillary water. We estimate from the Brown recorder records that the intensity ratio of OH to either of the CH_2 resonances is about 3:4. It is well known[1] that in the preparation of materials such as $HOCH_2CH_2HgCl$ the corresponding ethers also may be obtained. Analyses of our material indicate that we had a mixture of the alcohol and the ether $(HOHgCH_2CH_2)_2O$. Upon standing in the basic solution in which it was dissolved for the n.m.r. measurements, further conversion of alcohol to ether may have occurred. The 3:4 intensity ratio, intermediate between 1:2 for the

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[6] E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

[7] We acknowledge the suggestion of the referee that we discuss these points in more detail than we originally had done.

pure ether and 1:1 for the pure alcohol, thus can be explained.

The comparison of the present data with the average values reported by Gutowsky is generally good. The deviations that exist are probably due largely to medium effects since Gutowsky examined mainly pure organic liquids while our data are—for two of the compounds—for infinitely dilute solutions in the "spherical" solvent[8] CCl_4.

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(8) A. A. Bothner-By and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF SYRACUSE UNIVERSITY AND BROOKHAVEN NATIONAL LABORATORY]

The Absorption Spectra and Decay Kinetics of the Metastable States of Chlorophyll A and B[1]

BY HENRY LINSCHITZ[2] AND KYOSTI SARKANEN

RECEIVED APRIL 7, 1958

Using flash-illumination apparatus with improved time-resolution, the absorption spectra and decay kinetics of the metastable states of chlorophyll A and B have been studied in pyridine and benzene solution at 25°. The spectra are peculiarly diffuse and a measurable absorption extends beyond 7500 Å. The decay kinetics obey the following rate law: $-dC^*/dt = k_1C^* + k_2(C^*)^2 + k_3C^*C_g$ (C^* = concentration of the metastable, C_g = ground state). Values of the k's are presented and the results are discussed. The fast k_2 process does not appear to be due simply to effects of paramagnetic molecules on the triplet–singlet conversion.

Introduction

The formation of a long-lived excited state of chlorophyll and its function as the energy-storing and catalytic agent in photosensitization have been postulated for some time, on the basis of much indirect evidence. This has included data on the kinetics of sensitization, fluorescence quenching and steady-state bleaching.[3,4] Recently, direct demonstrations of this metastable state (probably the triplet) have been given by flash-excitation techniques, and preliminary estimates of its absorption spectrum and lifetime have been obtained.[5-10] It is desirable to extend the spectral data, both in wave length coverage and precision, particularly in view of recent ideas on the mechanism of energy accumulation and transfer in photosynthesis.[11,12] Moreover, the study of the kinetics of conversion of the triplet to the ground state bears directly on the general and important problem of the nature of radiationless transitions in complex molecules.

Existing kinetic data on the deactivation reactions of the metastable state are very rough. This uncertainty is due mainly to the relatively long duration of the exciting flashes which have been used so far, comparable in fluid solvents to the lifetime of the metastable state itself. The overlapping of excitation and deactivation not only greatly complicates the kinetic analysis, but with oscillographic recording of absorption changes, necessitates large scattered-light corrections over most of the decay curve, with consequent further loss of accuracy.

In this paper, we present new data on the metastable states of chlorophyll A and B, taken with apparatus providing an exciting flash of much shorter duration than those previously used. Absorption spectra have been measured over the range 3500–7500 Å. The kinetic data establish that only one metastable species of chlorophyll is present in pyridine or benzene solution, and permit the evaluation or estimation of three rate constants involved in the transition to the ground state. The improved time resolution also makes feasible the direct study of bimolecular reactions between the metastable state and added quenchers.

Experimental

1. **Apparatus.**[13]—Changes in absorption of a steady light beam, passed through the sample, were measured by a photocell and oscilloscope as function of time after excitation, the flash being triggered at a suitable interval after starting the sweep. The apparatus is shown diagrammatically in Fig. 1.

Mullard "Arditron" lamps, Type LSD-2, were used as the flash source.[14] These are short, wide tubes, with a straight 40 mm. spark gap, filled to 1 atm. with argon containing a small addition of hydrogen and, when fresh, have a breakdown potential near 11,000 volts. This permits the use of high-voltage low-capacity storage condensers to minimize flash duration and obviates the need for auxiliary spark gaps. Triggering of these high-pressure lamps is facilitated by using copper electrodes, activated by impregnation with

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[1] This work was assisted by a grant from the U. S. Atomic Energy Commission to Syracuse University (Contract No. AT-(30-1)-820), and was carried out in part while H. L. was on sabbatical leave at Brookhaven National Laboratory.

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(3) E. Rabinowitch, "Photosynthesis," Interscience Publishers, Inc., New York, N. Y., 1956, Vol. III, Chap. 35, and earlier volumes.

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(10) R. Livingston, ref. 9, p. 3.

(11) J. Franck, ref. 9, p. 142.

(12) P. L. Allen and J. Franck, *Arch. Biochem. and Biophys.*, **58**, 124 (1955).

(13) This apparatus was developed and built at the Brookhaven National Laboratory, in collaboration with Mr. Lloyd Nevala and Mr. Fred Merritt, of the Instrumentation Section. It is a pleasure to acknowledge their indispensable assistance, as well as advice from Mr. W. Higinbotham.

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