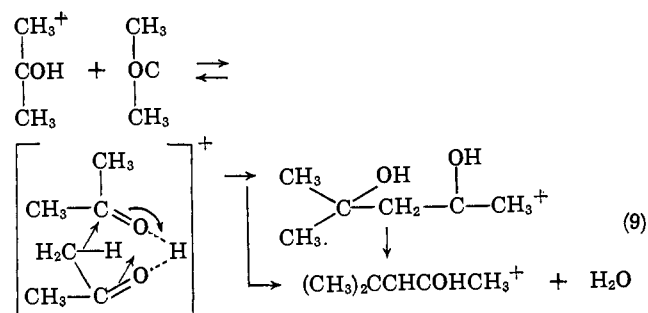


gen migration to give the isomeric protonated diacetone alcohol which contains C-C bonds. The protonated mesityl oxide may be formed from dehydration of protonated diacetone alcohol or the complex.



Since the relative concentration of protonated acetone passes through a maximum with increasing pressure in a manner similar to that indicated for the protonated molecules in Figures 1-3, it must react rapidly.

It seems unlikely that rate constants for any ionic reaction will be much larger than 10^{-9} cc./molecule sec. so the neutral reactant must be the most abundant species, acetone in the ketone not enol form. It is, of course, not possible to say that the enol form of acetone is absent under these conditions for the formation of small amounts of protonated diacetone alcohol or protonated mesityl oxide; however, this alternative provides a plausible mechanism for condensation without the necessity of invoking reaction with a minor component.

Other product ions are formed, methylated and acetylated acetone being the most abundant, but the reactions forming these ions cannot be clearly established, so no further treatment will be given.

Acknowledgment. The author is very grateful to Mr. W. C. Gieger for performing these experiments with his accustomed competence, and to Drs. F. H. Field and W. H. Starnes for helpful discussions.

Field Gradient and Magnetic Shielding at the Deuteron (Proton) in Ketene

W. H. Flygare¹ and V. W. Weiss

Contribution from the William A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. Received June 1, 1965

The microwave spectra of D_2C_2O has been observed under high resolution in order to determine the deuterium quadrupole coupling constants. Line half-widths at half-heights of 20 kc. were obtained. The results in the principal inertial axis system are $X_{aa} = -10 \pm 8$, $X_{bb} = 64 \pm 8$, and $X_{cc} = -54 \pm 8$ kc. Assuming axial bond symmetry and coincidence of the principal inertial and principal field-gradient axis systems gives the quadrupole coupling constant along the C-H bond of $X_{aa} = 120 \pm 12$ kc. compared to the much larger value of 171 kc. along the C-H bond in formaldehyde. The field gradient at the deuteron and diamagnetic shielding at the proton are calculated using normalized hybrid functions. The calculated electronic field gradients agree well with the experimental quantities. The calculated diamagnetic shielding and experimental total average shielding are used to predict the paramagnetic shielding and the functional dependence of the three proton spin-rotation constants. The predicted average paramagnetic shielding at the proton is $\sigma^p = -80.4 \times 10^{-6}$. The predicted value of the sum of spin-rotation constants is $M_{bb} + M_{cc} = 5.0$ kc.

I. Introduction

This paper is a discussion of the high-resolution microwave spectra of D_2C_2O leading to the deuteron quadrupole coupling constants. The resultant field gradients are also calculated using the hybrid orbital

method and the field gradient matrix elements given before for formaldehyde.

Previous work in this laboratory has involved the investigation of the electronic structure of the formaldehyde molecule. The field gradients at the deuteron² and the field gradients and spin-rotation interactions³ at ^{17}O , and the molecular magnetic moments,⁴ which lead to the diamagnetic susceptibility in formaldehyde, have been investigated. We have also calculated the three independent deuteron field gradients, the diamagnetic shielding at the proton, the two independent oxygen field gradients and the diamagnetic susceptibility⁵ in formaldehyde. The LCAO-SCF functions in formaldehyde gave reasonably poor agreement with experiment. A set of normalized hybrid orbitals were constructed and will be presented in a forthcoming paper which give much better agreement with experiment.

Therefore, one of the main reasons for studying the field gradients and magnetic shielding in ketene is to attempt an application of the hybrid orbitals similar to those proposed for formaldehyde. The hybrids and ionic character in the various regions in the ketene molecule will be quite different from those in the formaldehyde molecule and will therefore provide a good test of the method. It is also relevant to attempt a transfer of the molecular integrals used in calculating

(2) W. H. Flygare, *J. Chem. Phys.*, **41**, 206 (1964).

(3) W. H. Flygare and J. T. Lowe, *ibid.*, **43**, (1965); *Proc. Natl. Acad. Sci. U. S.*, **53**, 576 (1965).

(4) W. H. Flygare, *J. Chem. Phys.*, **42**, 1563 (1965).

(5) D. Eisenberg, J. M. Pochan, and W. H. Flygare, *ibid.*, **43** (1965).

(1) Alfred P. Sloan Fellow.

the field gradients and diamagnetic shielding in formaldehyde to the ketene molecule.

The average magnetic shielding at the proton in ketene is also measured. The diamagnetic shielding is calculated with the hybrid orbitals leading to a prediction of the paramagnetic shielding at the proton in ketene. An estimate of the proton spin-rotation interaction is also given and the possible observation of this interaction with high-resolution microwave spectroscopy is also discussed.

II. Experimental Section

Synthesis. Ketene and ketene- d_2 were synthesized by passing acetone and acetone- d_6 over a glowing wire at about 700°. The ketene formed was purified by fractional distillation in a vacuum line.

Chemical Shift. The chemical shift of ketene was measured in diethyl ether at $-65 \pm 2^\circ$ using tetramethylsilane as an external standard. Ketene was transferred into degassed dimethyl ether until a 40% solution was obtained. The sample was sealed in a 4-mm. Pyrex tube which was placed in a standard 5-mm. n.m.r. tube with tetramethylsilane between the two tubes. A correction in chemical shift was made for the external standard and for the 4-mm. tube.

Since acetone was the precursor to the ketene, a control sample of ether and acetone was run. From this it was concluded that no acetone was in the ketene sample. The spectrum was also checked for the possibility of the ketene dimer, acetic acid, and acetic anhydride; no peaks were observed which coincided with the known spectra.⁸ The proton resonance in ketene occurred at a τ value of 7.4 p.p.m. Upon a several-day warm-up of the sample, the diketene spectra⁹ appeared and the ketene spectra vanished. Our value of $\tau = 7.4$ p.p.m. agrees well with a recent value¹⁰ of about 7.6 p.p.m. obtained concurrently with our work. We will use an average value of $\sigma_{\text{TMS}} - \sigma_{\text{H}_2\text{C}_2\text{O}} = 2.5 \times 10^{-6}$ for the chemical shift of the proton in ketene.

Microwave Spectrometer. The design of the high-resolution microwave spectrometer has been described previously,² and no new features were employed in this work.

III. Microwave Spectra and Analysis

Rotational Energy Levels. The energy levels of $\text{D}_2\text{C}_2\text{O}$ can be calculated from the matrix elements given by Posener.¹¹ The general analysis of $\text{D}_2\text{C}_2\text{O}$ type spectra has been discussed by Flygare² in relation to D_2CO , and those results are summarized here. As the deuterium nucleus has a spin of 1, the nuclear spin states in $\text{D}_2\text{C}_2\text{O}$ are $I = 0, 1, 2$. The I values of 0 and 2 are symmetric spin states and the $I = 1$ state is antisymmetric. As all the rotational transitions studied here in $\text{D}_2\text{C}_2\text{O}$ are a dipole odd-even to odd-odd ($J_{\text{oe}} \rightarrow J_{\text{oo}}$) K transitions, the rotational states are antisymmetric with respect to the exchange of the

deuterium nuclei. Thus, only the $I = 1$ nuclear states will be present in $\text{D}_2\text{C}_2\text{O}$ as the total wave function must be symmetric with respect to exchange of the deuterium nuclei. As the $I = 0$ and $I = 2$ states are not present in the energy systems studied here, the off-diagonal elements in the quadrupole perturbation go to zero giving expression 1 for the energy levels involved in the a dipole $J_{\text{oe}} \rightarrow J_{\text{oo}}$ transitions. The derivation

$$E = E_{\text{rr}} - \frac{4f(IJF)}{J(J+1)} \sum_g X_{gg} \langle P_g^2 \rangle \quad (1)$$

of this expression is evident from eq. 2 of ref. 2. E_{rr} is the rigid rotor energy and $f(IJF)$ is Casimir's function which is conveniently tabulated for a large number of I, J , and F values.¹² X_{gg} values, where $g = a, b$, and c are the principal inertial axes, are the quadrupole coupling constants for each deuteron in $\text{D}_2\text{C}_2\text{O}$. $\langle P_g^2 \rangle$ is the average value of the square of the g th component of the rotational angular momentum over the rotational state. All microwave spectra to be discussed here were adequately explained with eq. 1, and no additional effects were observed owing to deuteron spin-rotation interactions (which are expected to be small).

Relative intensities for the transitions studied here are simply taken from the tables of the $I = 1$ single nucleus coupling case in Townes and Schawlow.¹²

Microwave Spectra and Analysis of Data. The microwave spectra of several isotopic species of ketene have been observed before^{6,13} including the $\text{D}_2\text{C}_2\text{O}$ molecule. No work has been reported on the deuterium quadrupole coupling, however. The $K = 1$ series transitions of $\text{D}_2\text{C}_2\text{O}$ were observed for our analysis as these transitions exhibit the largest nuclear quadrupole perturbation. The observed transitions are listed in Table I where all transitions are observed here for the first time except the $5_{15} \rightarrow 5_{14}$ which was observed by Johnson and Strandberg.⁶ The spectra reported here were all taken at Dry Ice temperatures under high-resolution conditions. Line widths were very narrow where half-widths at half-heights of 20 kc. were achieved, even up to the Ku band ($7_{17} \rightarrow 7_{16}$ at 15,905 Mc.). The spectra look like normal $I = 1$ spectra (where only $\Delta F = 0$ transitions were observed) with the two $\Delta F = 0, F = J + 1$, and $J - 1$ transitions being unresolved and to a lower frequency than the weaker $\Delta F = 0, F = J$ transition. Thus, all transitions appeared as a broader line (unresolved $F = J + 1$ and $F = J - 1$ transitions) down frequency and a narrower weaker line ($F = J$ transition) at a higher frequency. The frequencies between these lines are given in Table I. The resolution of the highest frequency transition which is the $7_{17} \rightarrow 7_{16}$ at 15,905 Mc. is shown in Figure 1. The markers are every 5 kc. The analysis of the spectra was straightforward using eq. 1 where the values of $\langle P_a^2 \rangle$, $\langle P_b^2 \rangle$, and $\langle P_c^2 \rangle$ were calculated on the computer using the values of B and C given by Johnson and Strandberg and the value of A calculated from the structure of ketene shown in Figure 2. The values of $\langle P_g^2 \rangle$ are not very sensitive to changes in structure, however, as ketene is

(6) H. R. Johnson and M. W. P. Strandberg, *J. Chem. Phys.*, **20**, 697 (1952).

(7) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(9) A. R. Bader, H. S. Gutowsky, G. A. Williams, and P. E. Yankwich, *J. Am. Chem. Soc.*, **78**, 2385 (1956).

(10) E. L. Alfred, D. M. Grant, and W. Goodett, *ibid.*, **87**, 673 (1965).

(11) D. W. Posener, *Australian J. Phys.*, **11**, 1 (1958).

(12) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(13) A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15**, 542 (1959).

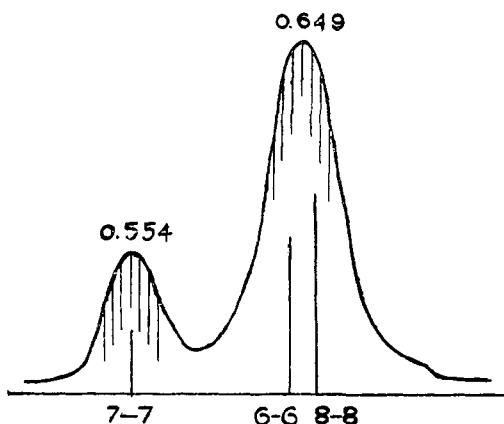


Figure 1. The $7_{17} \rightarrow 7_{18}$ transition in D_2C_2O at 15,905.29 Mc. The higher frequency peak is the least intense, and the numbers indicate the $\Delta F = 0$ transitions. The markers are every 5 kc.

very close to a prolate symmetric top. Unfortunately the experimentally observed $\Delta F = 0$ splittings in Table I are only sensitive to the value of $X_{bb} - X_{cc}$. The values of $X_{bb} - X_{cc}$ is also given in the table for each transition giving an average value of $X_{bb} - X_{cc} = 118$ kc. After assigning the value of $X_{bb} - X_{cc}$, the values of ν_0 were interpolated and are also given in Table I. As the frequencies are multiplets of $B - C$, these values are also given yielding an average $B - C = 568.08 \pm 0.05$ Mc. which agrees well with Johnson and Strandberg's value of 568.14 ± 0.1 Mc.

Table I. $K = 1$ Series Spectra Observed in $D_2C_2O^a$

Transition	Splitting, kc.	$X_{bb} - X_{cc}$, kc.	ν_0	$B - C$
$3_{13} \rightarrow 3_{12}$	83 ± 5	117	$3,048.75 \pm 0.05$	568.12
$4_{14} \rightarrow 4_{13}$	81 ± 5	111	$5,681.12 \pm 0.05$	568.11
$5_{15} \rightarrow 5_{14}$	88 ± 5	118	$8,521.23 \pm 0.05$	568.08
$6_{16} \rightarrow 6_{15}$	91 ± 2	119	$11,929.34 \pm 0.05$	568.06
$7_{17} \rightarrow 7_{16}$	95 ± 4	123	$15,905.29 \pm 0.05$	586.05
	Average	118 kc.		568.08 ± 0.05

^a The column headed by Splitting is the frequency between the unresolved $\Delta F = 0$, $F = J + 1$, and $F = J - 1$ and the $\Delta F = 0$, $F = J$ transitions. The values of $(X_{bb} - X_{cc})$ give the experimental splittings.

In order to obtain information concerning X_{aa} , we attempted to resolve the $0_{00} \rightarrow 1_{01}$ transition in D_2C_2O at $17,673.3 \pm 0.1$ Mc. which will be split into a triplet with the splitting being directly dependent on X_{aa} . A partial resolution was achieved which gives an approximate value of X_{aa} . The result is $X_{aa} = -10 \pm 8$ kc. Using Laplace's equation, the resultant values of the quadrupole coupling constants are $X_{aa} = -10 \pm 8$, $X_{bb} = 64 \pm 8$, and $X_{cc} = -54 \pm 8$ kc. If we now assume the principal field-gradient tensor coincides with the C-H axis shown in Figure 2, and further assume the C-H bond is axially symmetric, we can obtain the quadrupole coupling constant along the C-H bond of $X_{\text{bond}} = 120 \pm 12$ kc. This value is considerably smaller than the corresponding value in formaldehyde² of $X_{\text{bond}} = 171 \pm 3$ kc.

IV. Calculations

Consider the single determinant molecular wave function for a molecule

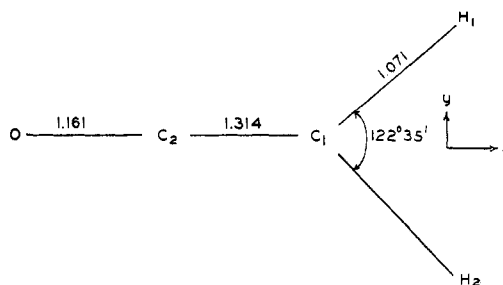


Figure 2. The structure of ketene.

$$\psi = \det|\psi_1\alpha(1)\psi_1\beta(2)\dots\psi_{n/2}\beta(n)| \quad (2)$$

where ψ_i 's are the doubly occupied molecular orbitals (MO's) and n is the number of electrons in the molecule. If each of the doubly occupied molecular orbitals is mutually orthonormal, the average value of any one electron operator, Q , is

$$Q_{av} = 2 \sum_{i=1}^{n/2} \int \psi_i^* [Q] \psi_i d\tau \quad (3)$$

If we now approximate the MO's, ψ_i , by a linear combination of atomic orbitals (LCAO), where X_j are the atomic Slater-type orbitals (STO's)

$$\psi_i = \sum_j X_j A_{ji} \quad (4)$$

eq. 3 becomes

$$Q_{av} = 2 \sum_{i=1}^{n/2} \sum_{j,k} A_{ji}^* A_{ki} \int X_j^* [Q] X_k d\tau \quad (5)$$

where the sums over j and k are over all functions in the STO basis set in eq. 4. In the Roothaan¹⁴ procedure, the coefficients A_{ji} in eq. 5 are determined by the variation principal and the self-consistent-field (SCF) method. As the energy is used as the criterion for minimization, the Roothaan SCF functions do not always give good calculated values for one-electron properties. Thus, as it is an extremely difficult task to compute SCF functions and the results do not always predict accurately one-electron molecular properties, it is necessary to investigate other methods of obtaining the LCAO coefficients in eq. 4 and 5. A forthcoming paper will show that a simple set of coefficients relating to the hybridization and ionic character in formaldehyde gives a better description of several observables including three independent deuteron field gradients, two oxygen field gradients, and the proton diamagnetic shielding. Correspondingly, as the SCF coefficients have not been determined for the LCAO-MO in ketene, we will compute the field gradient and diamagnetic shielding with a similar set of hybrid orbitals.

Figure 2 gives the axis system used in this calculation. The 11 doubly occupied LCAO-MO's in the 22-electron ketene molecule can be written as

$$\begin{aligned} \phi_1 &= 1S_0 \\ \phi_2 &= 1Sc_2 \\ \phi_3 &= 1Sc_1 \end{aligned}$$

(14) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

$$\begin{aligned}
\phi_4 &= a_1 \left\{ a_2(\text{Sc}_1) + \sqrt{1/2 - a_2^2}(\text{Pzc}_1) + \frac{1}{\sqrt{2}}(\text{Pyc}_1) \right\} + \\
&\quad \sqrt{1 - a_1^2}(\text{H}_1) \\
\phi_5 &= a_1 \left\{ a_2(\text{Sc}_1) + \sqrt{1/2 - a_2^2}(\text{Pzc}_1) - \frac{1}{\sqrt{2}}(\text{Pyc}_1) \right\} + \\
&\quad \sqrt{1 - a_1^2}(\text{H}_2) \\
\phi_6 &= a_3 \left\{ \sqrt{1 - 2a_2^2}(\text{Sc}_1) - \sqrt{2}a_2(\text{Pzc}_1) \right\} + \\
&\quad \sqrt{1 - a_3^2} \left\{ \frac{1}{\sqrt{2}}(\text{Sc}_2) + \sqrt{\frac{1}{2}}(\text{Pzc}_2) \right\} \\
\phi_7 &= a_4(\text{Pxc}_1) + \sqrt{1 - a_4^2}(\text{Pxc}_2) \\
\phi_8 &= a_5(\text{Py}_0) + \sqrt{1 - a_5^2}(\text{Pyc}_2) \\
\phi_9 &= a_6 \left\{ \sqrt{1 - 2a_7^2}(\text{So}) + \sqrt{2}a_7(\text{Pzo}) \right\} + \\
&\quad \sqrt{1 - a_6^2} \left\{ \frac{1}{\sqrt{2}}(\text{Sc}_2) - \sqrt{\frac{1}{2}}(\text{Pzc}_2) \right\} \\
\phi_{10} &= a_7(\text{So}) - \sqrt{1/2 - a_4^2}(\text{Pzo}) + \frac{1}{\sqrt{2}}(\text{Px}_0) \\
\phi_{11} &= a_7(\text{So}) - \sqrt{1/2 - a_4^2}(\text{Pzo}) - \frac{1}{\sqrt{2}}(\text{Px}_0)
\end{aligned} \tag{6}$$

The atomic orbitals in the LCAO-MO's in eq. 6 are the usual STO except the hydrogen functions which have the larger orbital exponent of 1.2. These choice of AO's are identical with those of Foster and Boys¹⁵ in the case of formaldehyde. ϕ_1 , ϕ_2 , and ϕ_3 are the inner 1s orbitals on the heavy atoms which will not participate to a large extent in the bonding. ϕ_4 and ϕ_5 are the C₁-H equivalent bonds with a_1^2 being the relative C₁-H ionic character and a_2 the C₁ hybrid parameter. The angle between the C₁-H equivalent C₁ hybrid orbitals is

$$\cos \theta_{45} = -\frac{a_2^2}{1 - a_2^2} \tag{7}$$

ϕ_6 is the C₁-C₂ σ bond, where a_3 is related to the relative electron concentration in the bond. Note that the C₂ contribution to the σ bond is pure sp. ϕ_7 is the C₁-C₂ π bond perpendicular to the molecular plane with a_4 related to the electron distribution in this bond. ϕ_8 is the C₂-O π bond in the molecular plane. ϕ_9 is the C₂-O σ bond, and ϕ_{10} and ϕ_{11} are the oxygen lone pairs.

As eq. 5 requires the LCAO-MO functions to be orthonormal, we must orthonormalize the functions in eq. 6 before computing the average values of the observables. We have used the symmetric orthogonalization technique here which gives the following result when substituted into eq. 5.

$$Q_{\text{av}} = 2 \sum_{i=1}^{n/2} \sum_{j,k} \sum_{m,n} [S^\phi]_{im}^{-1/2} A_{mj} A_{nk} [S^\phi]_{ik}^{-1/2} \times \int X_j^* [Q] X_k d\tau \tag{8}$$

where $[S^\phi]^{-1/2}$ is the inverse square root of the overlap matrix in the ϕ basis in eq. 6. In order to reduce the calculation to the region of the molecule containing the C-H bonds, we will further approximate our calculation by assuming all integrals in eq. 8 which involve oxygen atomic orbitals just cancel the oxygen nuclear

(15) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960).

contribution to the field gradient. Our previous work in computing one-electron properties at the proton and deuteron in formaldehyde indicate this approximation will be quite good. Thus, we now need the actual values of the integrals, $\int X_j^* [Q] X_k d\tau$, involving the field gradient and diamagnetic shielding operators and the H₁, H₂, C₁, and C₂ STO's in ketene. As the structures of the C=CH₂ fragment in ketene and the O=CH₂ molecule are similar, we have used the formaldehyde two- and three-center integrals in our calculation.

Electronic Field Gradient. The quadrupole coupling constant along the C-H bond in ketene was determined to be 118 kc. Using the most recent value¹⁶ for the deuteron quadrupole moment of 2.1796×10^{-27} cm.² gives the bond-axis field gradient a value of 0.183 in atomic units (e/a_0^3). The experimental data and the nuclear contribution to the field gradients are given in Table II. The calculation of the electronic contribution to the field gradient using only the C=CD₂ fragment of ketene was straightforward with the use of eq. 6 and 8 as discussed previously. The field-gradient integrals were taken from the forthcoming formaldehyde work. The choice of the hybridization and ionic parameters in eq. 6 are given in Table III. a_1 , a_5 , and a_8 were chosen to be similar to the best hybrid and ionic parameters in the equivalent formaldehyde functions. a_3 was chosen to shift electrons toward the oxygen, and a_4 in the C₁-C₂ π bond was chosen to give equal electron density on each carbon. The value of a_2 which determines the C-H hybrid angle was chosen to conform to the slightly larger than tetrahedral experimental result. Owing to the approximate nature of this calculation, we did not attempt to minimize the difference between the calculated and experimental field gradients by variation of a_i . The results in Table II are, however, in reasonable agreement with experiment.

Table II. Deuteron Field Gradients in Ketene^a

Nuclear field gradients	$q_{\beta\beta}$	$q_{\beta\alpha}$	$q_{\alpha\alpha}$
O
C ₂	0.002	0.142	0.108
C ₁	-0.720	0.000	1.440
H ₂ (D)	-0.007	-0.026	0.209
Total nuclear	-0.725	+0.116	1.577
Experimental	-0.092	0.0	0.183
Exptl. electronic field gradient	+0.633	-0.116	-1.394
Calcd. electronic field gradient	0.58	-0.18	-1.32

^a The α axis is along the C-H bond and the β axis is perpendicular to α in the molecular plane. The experimental field gradients perpendicular to the C-H bond are assumed equal. The oxygen nuclear contribution to the deuteron field gradient is assumed to be canceled by the eight electrons associated with this atom. All units are in (e/a_0^3). The calculated values are with the parameters in Table III, the equations in text, and the formaldehyde matrix elements.

Magnetic Shielding at the Proton. The experimental value of the proton chemical shift relative to tetramethylsilane is

$$\sigma_{\text{TMS}} - \sigma_{\text{OC}_2\text{H}_2} = 2.5 \times 10^{-6} \tag{9}$$

(16) H. Narumi and T. Wantanabe, *Bull. Am. Phys. Soc.*, **9**, 11 (1964).

Table III. The Choice of Hybridization and Ionic Parameters in Eq. 6 to Compute the Field Gradient at the Deuteron and Diamagnetic Shielding at the Proton in Ketene^a

$a_1 = 0.860$	$a_4 = 0.707$
$a_2 = 0.580$	$a_5 = 0.820$
$a_3 = 0.650$	$a_6 = 0.920$
$\theta_{45} = 120^\circ 30'$	

^a a_1 , a_5 , and a_6 are the same parameters used in the best hybrid orbitals in formaldehyde.

As the proton shielding in H_2 is known to be $\sigma_{H_2} = 26.6 \times 10^{-6}$, it is necessary to refer the shielding at the proton in ketene to the shielding in H_2 in order to obtain the absolute shielding in ketene. By using⁸ $\sigma_{TMS} - \sigma_{H_2} = 8.6 \times 10^{-6}$, we can obtain the absolute shielding at the proton in ketene which is

$$\sigma_{OC_2H_2} = 32.6 \times 10^{-6} \quad (10)$$

The total average shielding can be described by a sum of a diamagnetic and paramagnetic contribution.¹⁷ The paramagnetic contribution is proportional to the spin-rotation constants,¹⁸ however, giving

$$\sigma_{OC_2H_2} = \sigma^d + \sigma^p = 32.6 \times 10^{-6} = \frac{e^2}{3mc^2} \left\langle \psi^0 \left| \sum_i \frac{1}{r_i} \right| \psi^0 \right\rangle + \frac{e^2}{6mc^2} \left\{ \frac{hc}{2eu_{NH}} \left(\frac{M^{H_{aa}}}{A} + \frac{M^{H_{bb}}}{B} + \frac{M^{H_{cc}}}{C} \right) - 2 \sum_l' Z_l r_l^{-1} \right\} \quad (11)$$

where $\sigma^d = (e^2/3mc^2) \langle \psi^0 | \sum_i r_i | \psi^0 \rangle$ is the diamagnetic shielding depending on the ground-state molecular electronic wave function ψ^0 . e , m , and c are the electronic charge, electronic mass, and speed of light, respectively. h , u_N , and g_H are Planck's constant, the nuclear magneton, and g value of the proton. The $M^{H_{gg}}$ are the proton spin-rotation constants, and A , B , and C are the rotational constants. The sum over l is over all nuclei except the proton at which the chemical shift is determined, and Z_l is the atomic number of the l th nucleus. r_{Hl} is the distance from the proton to the l th nucleus. The rotational constants in ketene are $A = 284 \times 10^9$, $B = 9.1 \times 10^9$, and $C = 8.5 \times 10^9$ c.p.s. The unknowns in eq. 11 are σ^d , $M^{H_{aa}}$, $M^{H_{bb}}$, and $M^{H_{cc}}$. Thus, if the spin-rotation constants were known, the absolute value of the diamagnetic shielding could be obtained. As the spin-rotation constants are not available, however, we will compute the value of the diamagnetic shielding and predict the spin-rotation constants prior to their experiment determination. Using eq. 8 and the methods discussed above, we should be able to compute a fairly good value of σ^d for the proton in ketene. Using the diamagnetic shielding integrals from formaldehyde and the hybrid orbitals defined by eq. 6 and Table III of this paper give a value of the calculated diamagnetic shielding of

$$\sigma_{H_2C_2O}^d = 113 \times 10^{-6} \quad (12)$$

which is slightly larger than the value in formaldehyde. This result gives the calculated paramagnetic shielding of

$$\sigma_{H_2C_2O}^p = -80.4 \times 10^{-6} \quad (13)$$

(17) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **90**, 232 (1953).

(18) W. H. Flygare, *J. Chem. Phys.*, **41**, 793 (1964).

Using the structure in Figure 2 and eq. 11 gives

$$\sigma_{H_2C_2O}^p = 58.1 \times 10^{-6} \left(\frac{M_{aa}}{284 \times 10^9} + \frac{M_{bb}}{9.1 \times 10^9} + \frac{M_{cc}}{8.5 \times 10^9} \right) - 113 \times 10^{-6} \quad (14)$$

where the spin-rotation constants are in units of c.p.s. It is clear from eq. 14 and analogy with the spin-rotation constants in formaldehyde² of $M^{H_{aa}} = -15.2 \times 10^9$, $M^{H_{bb}} = 1.5 \times 10^9$, and $M^{H_{cc}} = 6.7 \times 10^9$ c.p.s., that the $M^{H_{aa}}/A$ term will be smaller than the sum of the M_{bb}/B and M_{cc}/C terms. Thus, assuming M_{aa}/A can be ignored and also recognizing that $B \approx C \approx 8.8 \times 10^9$ in ketene, we can write eq. 14 as $M_{bb} + M_{cc} \approx 5.0 \times 10^9$ c.p.s., which is smaller than the corresponding value in formaldehyde. This very small value of $M_{bb} + M_{cc}$ in ketene explains why Cox, Thomas, and Sheridan¹³ could not observe the spin-rotation interaction in ketene by studying transitions up to $J = 14$ (their stated line widths were 100 kc.). As the $K = 1$ series of rotational transitions in ketene is sensitive to $M_{bb} + M_{cc}$ and insensitive to M_{aa} , they would have had to go to much higher J values in order to have observed a perturbation larger than their line width. We have also failed to observe the perturbations due to this value of $M_{bb} + M_{cc}$, but our line widths are also too large to make a study feasible at this time. Increased resolution will make the observation of the proton spin-rotation interaction in ketene possible, however.

V. Discussion

The field gradient at the deuteron in ketene is considerably smaller than the corresponding value in formaldehyde. The field gradient at the deuteron can be thought of as arising primarily from the positive charge on the carbon atom which has been partially shielded by the electrons surrounding the nucleus. In ketene the dipole moment of 1.45 D.⁶ is considerably smaller than the value of 2.3 D.¹⁹ in formaldehyde. Thus, one would expect a larger negative charge on the carbon atom (near the protons) in ketene than in formaldehyde. This would increase the electronic field gradient and decrease the resultant quadrupole coupling constant along the C-H bond. Such a trend is reflected in both our experimental and calculated field gradients.

On the other hand, a recent correlation of C-H force constants and deuteron field gradients in diatomic species by Salem²⁰ has shown a striking regularity where the C-H force constant, k , is computed from

$$k = eq \quad (15)$$

where e is the electronic charge and q is the field gradient. Applying this relation to formaldehyde and the experimental value of² $q = 8.45 \times 10^{14}$ e.s.u. cm.⁻³ along the C-H bond gives a calculated C-H stretching force constant of $k = 4.1 \times 10^5$ dynes cm. which is in excellent agreement with the experimental value from infrared data of²¹ $k = 4.2 \times 10^5$ dynes cm. As the C-H force constant in ketene has increased to $5.3 \times$

(19) R. B. Lawrence and M. W. P. Strandberg, *Phys. Rev.*, **83**, 363 (1951).

(20) L. Salem, *J. Chem. Phys.*, **38**, 1227 (1963).

(21) E. S. Ebers and H. H. Nielsen, *ibid.*, **6**, 310 (1938).

10^5 dynes cm.,^{22,23} the above analogy would predict an increased field gradient at the deuteron in ketene relative to formaldehyde. The opposite trend is observed by our work which indicates that eq. 15 is not valid for the nonlinear polyatomic molecules such as formaldehyde or ketene. It is also possible, however, that the assignment of the low C-H force constant in formaldehyde is in error. Salem's²⁰ calculated force constants for linear molecules using eq. 15 are all smaller than the actual force constants which agrees with our results in ketene. Formaldehyde would therefore require a larger force constant to bring it in accord with the present results.

- (22) S. Sundaran and F. F. Cleveland, *J. Chem. Phys.*, **32**, 1554 (1960).
(23) C. B. Moore and G. C. Pimentel, *ibid.*, **38**, 2816 (1963).

The chemical shielding in ketene is also interesting as the experimental average shielding is the largest methylene shift measured.⁸ The large methylene proton shielding in ketene arises from both a large diamagnetic and relatively small paramagnetic contribution. Our results show that ketene has a slightly larger diamagnetic term than formaldehyde but a considerably smaller paramagnetic term leading to a small proton spin-rotation interaction in ketene.

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A Study of the Benzyl Free Radical and Substituted Benzyl Free Radicals

Joe E. Hodgkins and E. Dennis Megarity

Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas. Received July 12, 1965

The spectra of a series of substituted benzyl free radicals have been taken and the shifts from the unsubstituted radical have been measured. These shifts have been correlated with $\Delta\sigma$, a reaction constant. Substituent effects on α -substituted benzyl radicals have also been measured. These are unusual in that delocalization decreases with an increase in the stability of the radical. The benzyl radical itself seems to form primarily through vibronic excitation involving a C-H stretching mode of the methyl group of toluene. The extinction coefficient of the benzyl radical has been measured by a method that has not been used previously.

Introduction

In the late 1950's Porter, *et al.*,¹⁻⁶ conducted intensive research on the benzyl ($C_6H_5CH\cdot$) and other related radicals. These workers were successful in obtaining the spectrum of the benzyl radical in gas and solution phases and also in solid EPA. Porter and Strachan¹ established the assignment of $3187 \pm 5 \text{ \AA}$. to the benzyl radical by obtaining the spectrum of the intermediate from a number of different but reasonable precursors. This wave length assignment to the benzyl radical gains support from the theoretical calculations of Dewar, Longuet-Higgins, and Pople.^{7,8} These researchers predicted a value of 2965 \AA . in the gas phase, and Bingle⁹ predicted a long wave length band at 4580

\AA . Porter and Wright³ obtained the benzyl radical in gas phase and recorded the principal absorption band at 3053 \AA . The longer wave length band was obtained by Porter and Strachan,⁵ who assigned a value of 4527 \AA . to the radical in matrix at 77°K . These results are in reasonably good agreement with the calculated values.

A number of substituted toluenes were photolyzed by Porter, *et al.*^{1,2} The bands due to the transients were assumed to be result of substituted benzyl radicals because their band shapes were identical with that of the radical obtained from toluene and because the bands disappeared upon warming the matrix.

The purpose of this study was to obtain the spectra of a number of substituted benzyl radicals in hopes to measure the degree of stabilization afforded by the substituents by ultraviolet absorption spectra. In addition, we were interested in determining the extinction coefficient of the benzyl radical and in assigning the particular energy of ultraviolet radiation which was leading to formation of the radical.

Results and Discussion

Table I indicates the benzyl and substituted benzyl radicals formed by photolysis at 77°K . with their assigned wave lengths. While most of the substituted radicals show a wave length shift to the red in comparison to benzyl, the halogen-substituted radicals show either no stabilization¹⁰ or, in the case of fluorine, a marked destabilization. The relative ease of photolysis, as determined by photolysis times necessary to

- (1) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).
(2) I. Norman and G. Porter, *Proc. Roy. Soc. (London)*, **A230**, 399 (1955).
(3) G. Porter and F. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).
(4) G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957).
(5) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).
(6) G. Porter, Special Publication No. 9, The Chemical Society, London, 1958, p. 139.
(7) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc. (London)*, **A67**, 795 (1954).
(8) H. C. Longuet-Higgins and J. A. Pople, *ibid.*, **A68**, 591 (1955).

- (9) W. Bingle, *Z. Naturforsch.*, **10a**, 462 (1955).

(10) A shift to slightly longer wave lengths of the same transition is normally considered to be stabilization, especially when the compounds differ only slightly in structure. The transitions involved in substituted aromatic compounds are considered to be perturbations of the normal benzenoid transitions.