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Microwave Spectrum of CH2DCH : CH2; Equilibrium Conformation of Propylene

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ism. These shifts were measured at a resonance frequency of 30 Mc/sec, and some were verified at 40 Mc/sec.†

If it is assumed that polarization of the fluoride ion by the solvent occurs principally through hydrogen bonding, most of the results can be understood qualitatively. Decreased hydrogen bonding results in less polarization and therefore increased shielding of the nucleus.[1] The results indicate that methanol molecules, which readily replace water molecules around the fluoride ion, form weaker hydrogen bonds, while formamide bonds to fluoride ion even more strongly than does water. The temperature effect can also be understood in these terms. The measurements must in part reflect the steric limitations of the larger organic molecules in replacing water molecules around the ion. The fluoride ion is, of course, exceptional because of its small size and high charge density and there is much evidence for very strong interaction with the solvent. The results may perhaps be viewed in terms of Gurney's[2] recent ideas concerning order and disorder in the region of dissolved ions, fluoride being a strong "order-producing" ion. From this point of view we are seeking to correlate the observed chemical shifts with entropy and viscosity data.

SA point out that if the fluoride ion is more polarized by the potassium ion than by the water dipoles, ion association would result in a shift to lower field. On the other hand Connick and Poulson[3] have found that AlF^{++} and AlF_2^+ give resonances in higher field than aqueous fluoride ion. Possibly, then, the shifts to higher field which we have observed when the concentration of KF is very high could also be due to ion association. This hypothesis is consistent with the comparatively greater concentration effect found for methanol solutions. However, the difficulty of separating the effect of direct polarization by positive ions from other effects prevalent in concentrated solutions is acute and we have as yet no unambiguous evidence for ion pair formation. One might argue that for very concentrated solutions in the immediate vicinity of the fluorine there is no real difference between the breaking of hydrogen bonds by positive ions and momentary association. In any case, except in solutions of high viscosity, we have not observed any significant line width changes, indicating that exchange of the fluoride ion between its different states is rapid.

We have also made a preliminary study of the fluorine resonance in solutions of CF_3CO_2K, CF_3SO_3Na, and KPF_6. Addition of methanol again results in increased shielding but the shifts are very much smaller. Studies of the Cl^{35} resonance at 3 Mc/sec in solutions of NaCl in different solvents show there is little or no chemical shift, though in some instances we have observed considerable line broadening. Full details of all the results will be submitted for publication at a later date.

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[1] J. N. Shoolery and B. J. Alder, J. Chem. Phys. 23, 805 (1955), hereafter referred to as SA.

† We wish to thank Dr. Byron Murphey and Dr. George Tiers of the Central Research Department, Minnesota Mining and Manufacturing Company, for the measurements at 40 Mc/sec.

[2] R. W. Gurney, *Ionic Processes in Solution* (New York, 1953), p. 250.

[3] R. E. Connick and R. E. Poulson, J. Am. Chem. Soc. 79, 5153 (1957).

Microwave Spectrum of $CH_2DCH:CH_2$; Equilibrium Conformation of Propylene†

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The first requirement for a theory of the forces hindering internal rotation is that the theory should correctly predict which of the possible conformations of a molecule corresponds to the potential minimum. The staggered conformation has been established as the stable one for ethane, methyl silane, and some halogenated derivatives; and recently it has been shown that in acetaldehyde, acetyl fluoride, and acetyl chloride the oxygen atom of the acetyl group is eclipsed by one of the methyl hydrogens.[1] We report an analogous result for propylene: one of the methyl hydrogens is eclipsed with respect to the double bond, so that the other two methyl hydrogens are staggered by the hydrogen of the CH group (conformation I of Fig. 1).

Lide and Mann[2] studied the microwave spectrum of normal propylene and determined the barrier height (1980 cal/mole). The moments of inertia of $CH_3CH:CH_2$ do not depend on the equilibrium angle of internal rota-

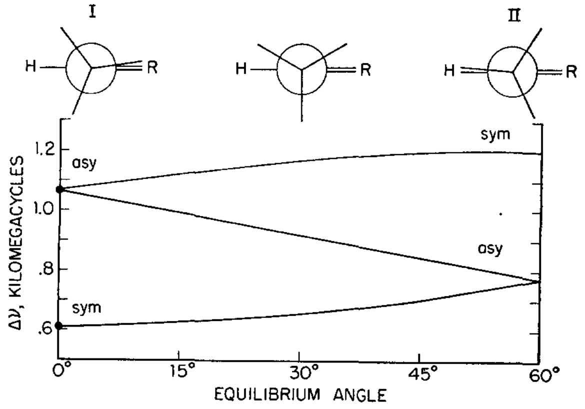

FIG. 1. Isotopic shift of the $0_{00}-1_{01}$ transition for different rotational isomers *versus* assumed equilibrium angle of internal rotation. The circles indicate the observed lines. The projections shown are Newman[5] diagrams; *R* denotes the CH_2 group.

TABLE I. Observed spectra (Mc/sec).[a]

Rotational transition[b]	*sym*-$CH_2DCH:CH_2$	*asy*-$CH_2DCH:CH_2$
$0_{00}-1_{01}$	16 832.90	16 377.15
$1_{11}-2_{12}$	32 364.62	31 813.22
$1_{01}-2_{02}$	33 626.22	32 735.40
$1_{10}-2_{11}$	34 966.65	33 694.55

[a] ±0.15 Mc/sec.
[b] Ground vibrational state.

tion, since CH_3 is a symmetric top. For $CH_2DCH:CH_2$, however, rotational isomers occur and give distinct spectra. Tunnel effect splittings of the 0→1 and 1→2 parallel transitions in $CH_2DCH:CH_2$ must be very small, as is clear from the spectrum of normal propylene. Consequently, the isotopic frequency shifts, $\Delta\nu=\nu(CH_3)-\nu(CH_2D)$, for these transitions can be predicted from the usual rigid rotor formulas. The predicted spectra are quite sensitive to the value assumed for the equilibrium angle, as illustrated in Fig. 1. In general, three rotational isomers of the CH_2D species could appear. However, if either I or II represents the equilibrium conformation, only two distinct rotational isomers will be observed: one which has a plane of symmetry containing the D atom (*sym*-isomer), and one which has no plane of symmetry (*asy*-isomer).

A sample of $CH_2DCH:CH_2$ was prepared by reacting allyl chloride with D_2O in the presence of zinc dust and excess acetic anhydride.[3] Table I lists the observed frequencies. Only parallel transitions are available because the perpendicular component of the dipole moment is extremely small.[2] Within the accuracy of measurement, the frequencies fit rigid rotor spectra; the derived constants[4] are given in Table II. Characteristic Stark patterns also confirm the line assignments. Two isomers are observed, and the spectra are in excellent agreement with the initial predictions based on conformation I. Furthermore, the fact that the relation $I_a+I_b-I_c=I(CH_3)$ is satisfied for the species assigned as *sym*-I shows that it has a plane of symmetry containing the D atom; this is by itself conclusive proof that I is the equilibrium conformation.

Dauben and Pitzer[5] have concluded from arguments based on thermal data that I corresponds to the equilibrium conformation of the methyl groups in *cis*- and *trans*-2-butene. Accordingly, they correctly predicted the conformation in propylene to be I. However, the van der Waals model for internal barriers recently developed by Mason and Kreevoy,[6] which has been able to account for about half of the observed barrier height in a number of molecules, proves to be qualitatively inadequate for propylene: this model predicts conformation II to be 0.5 kcal more stable than I,[7] whereas actually I is 1.98 kcal more stable than II.

TABLE II. Rotational constants and principal moments of inertia.

	sym-$CH_2DCH:CH_2$	*asy*-$CH_2DCH:CH_2$
A	40 615±200 Mc	44 085±500
B	9066.92 ±0.15	8658.80 ±0.15
C	7765.90 ±0.15	7718.14 ±0.15
I_a	12.447±0.061 amu A²	11.467±0.129
I_b	55.756±0.001	58.384±0.001
I_c	65.096±0.001	65.499±0.001
$I_a+I_b-I_c$	3.106±0.062	4.352±0.130

We wish to thank Professor E. Bright Wilson, Jr., for his interest and encouragement. We are indebted to Dr. L. C. Leitch of the National Research Council, Ottawa, Canada, for advice concerning the preparation of $CH_2DCH:CH_2$.

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‡ National Science Foundation Predoctoral Fellow, 1955–1957.

[1] For a summary of microwave determinations of barrier heights and equilibrium conformations, and literature references, see E. B. Wilson, Jr. [Proc. Natl. Acad. Sci. U. S. **43**, 816 (1957)].

[2] D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. **27**, 868 (1957).

[3] This is a modified form of the synthesis used by C. D. Hurd and J. L. Azorlosa [J. Am. Chem. Soc. **73**, 33 (1951)].

[4] The data of Table II are not sufficiently independent of that for normal propylene to be useful for structural calculations. Likewise, although an isotopic shift of the Stark effect is observable, the principal axis components of the dipole moment differ from those of the normal species by only about 0.01 *D*, which is not enough to permit the orientation of the dipole moment to be determined.

[5] W. G. Dauben and K. S. Pitzer, "Conformational Analysis," in *Steric Effects in Organic Chemistry*, edited by M. S. Newman (John Wiley and Sons, Inc., New York, 1956), Chap. 1, p. 59.

[6] E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc. **77**, 5808 (1955); **79**, 485 (1957).

[7] Professor Kreevoy has kindly confirmed this.

Comments and Errata

Line Shape in the OH $^2\pi-^2\Sigma$ Transition

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THE presently available information on the widths and shapes of the lines in the ultraviolet $^2\pi-^2\Sigma$ bands of OH come from the work of Oldenberg and Rieke[1] (referred to as OR) in which the *f* numbers (later corrected[2]) were determined. At 1473°K and in one atmosphere of $2H_2O+O_2$ the OH lines in absorption were found to have a Lorentz shape and a width of 0.58 cm^{-1}, as compared to the Doppler width of 0.21 cm^{-1}. The integrated absorption coefficients of 17 lines in the O−O band were found not to fall in the theoretical ratios[3] and were corrected by extrapolation to zero absorption. The correction factor was as high as two for the strongest line.

Although this extrapolation is probably justified for the purpose of finding the true integrated absorption coefficients, it leads to an inconsistency which adversely affects the use of the line absorption method[4] for