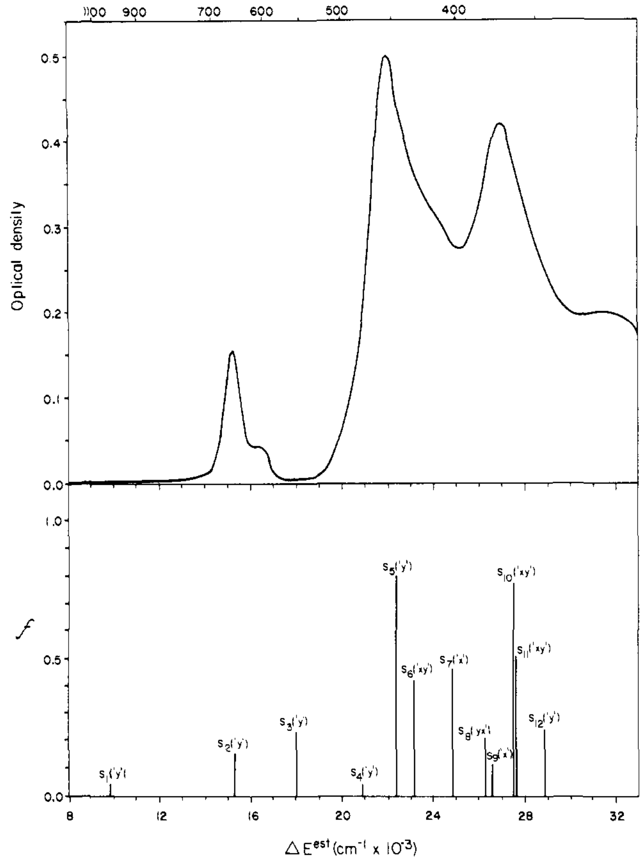

Figure 2. Comparison of the experimental spectrum of III (see Figure 1) in acetone (top) with calculated transition energies, oscillator strengths, and polarizations of EtChl *a* enol (bottom). Transition energies are estimates from the equation given in footnote 16; *f* represents the oscillator strength; approximate polarization directions are given in parentheses. "x" and "y" indicate transitions polarized predominately along the *x* and *y* axes, respectively, of Figure 1. "xy" and "yx" refer to transitions of intermediate polarization which exhibit slightly more *x*- or *y*-polarized character, respectively. The experimental spectrum was obtained from M. Wasielewski of Argonne National Laboratory.

putational details have been described previously in studies of EtChl *a* (keto form)[12] and related systems.[13-16]

A number of molecules possess the same characteristic π-electron system as Chl *a* enol, including those in Figure 1 as well as "peripheral" magnesium complexes of pheophorbide *a*[17] and cyclopheophorbide *a* enols.[18] The electronic absorption spectra of III shown in Figure 2 is generally typical of these systems, as is the absence of observed fluorescence. The moderately low intensity absorption at about 15 200 cm^{-1} appears to be analogous to the more intense Q_y absorption at about the same energy in Chl *a*, but this is not the case. In Chl *a*, Q_y is firmly established as the $S_1 \leftarrow S_0$ absorption. In EtChl *a* enol, however, the calculated results shown in Figure 2 place $S_1 \leftarrow S_0$ at 9922 cm^{-1}, with an oscillator strength $f = 0.04$, while the 15 200 cm^{-1} absorption is due to $S_2 \leftarrow S_0$ ($f = 0.15$).[19] Therefore, the $S_1 \leftarrow S_0$ transition in II and III is apparently not observed due to the near-forbidden character of the transition. However, there is evidence of weak absorption near 750 nm observed in pheophorbide *a* enols.[3] The absence of observed fluorescence in these systems is also consistent with the predicted low $S_1 \leftarrow S_0$ emission probability and would be observed in the 9000–12 000 cm^{-1} region, not at ca. 15000 cm^{-1} as in Chl *a*.

Examination of the ground- and excited-state electronic charge distributions reveals several other relevant points. First, the electronic states of EtChl *a* enol are much more polar than those of EtChl *a*, as shown by the data in Table I. In particular, there is extensive charge reorganization associated with the $S_1 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions, which likely results in broad absorption bands. In this regard, we feel that the $S_3 \leftarrow S_0$ transition, which appears somewhat out of place in Figure 2, most likely appears as a broad band at the onset of the Soret absorption. The high intensity and split profile of the Soret band appears well represented by intense transitions to states S_5–S_7 and S_{10}–S_{11}. The polar nature of the computed electronic states of the enol (particularly, S_1 and S_3) also suggests that the absorption spectrum should be more easily influenced by solvent and environmental effects than in EtChl *a*, and there is some experimental evidence to support this.[3]

The estimated locations of the three lowest lying triplet states, T_1–T_3, are given in Table I. Unlike EtChl *a*, where S_1 and T_3 were predicted to be degenerate,[12] there is no low-lying triplet state in EtChl *a* enol within 2000 cm^{-1} of S_1, a feature which suggests that intersystem crossing might be more difficult in EtChl *a* enol than in EtChl *a*, and this is no doubt related to the difficulty of forming triplet states in these molecules.[5]

Acknowledgment. This work was supported by the Division of Chemical Sciences of the United States Department of Energy.

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(19) Oscillator strengths are obtained directly from CI wave functions using $f = {}^2/_3\ \Delta D|\mu|^2$, where μ and ΔE are the calculated transition dipole and transition energy, respectively, in atomic units.

A Primary Carbon-13 Equilibrium Isotope Effect. ^{13}C NMR Spectrum of 2,3-Dimethyl-2-[2-^{13}C]butylium Ion

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Among the many ^{13}C and ^{14}C kinetic isotope effects reported, few have involved formation of carbonium ions.[1] One might expect that solvolysis of isotopic carbon compounds would be slower since bonds are broken. However, the remaining bonds to the cationic carbon would be expected to become *stiffer*, producing an opposing effect and making the result difficult to predict. *Equilibrium* isotope effects would give a clearer indication, since they are independent of the transition state. The difficulty with coventional methods for measuring these isotope effects is that they are expected to be extremely small. We have recently reported a new NMR technique capable for measuring small isotope effects on equilibria with high accuracy.[2]

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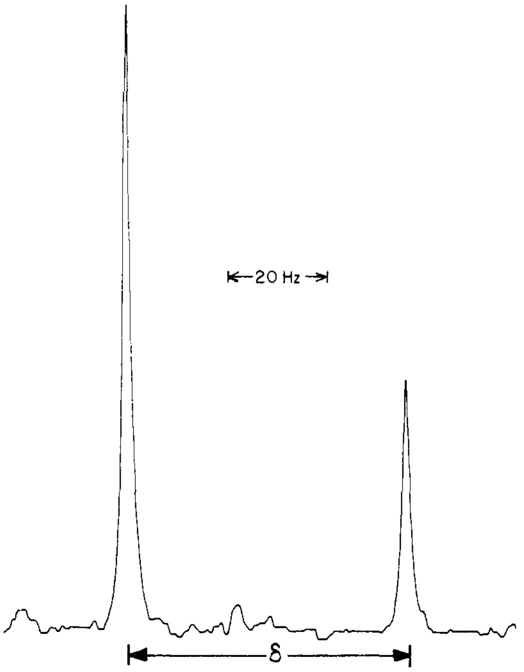
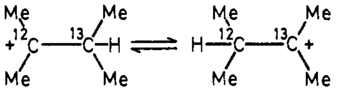
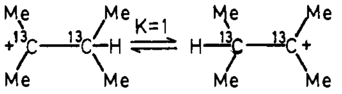


Figure 1. ^{13}C NMR spectrum of central carbons of mixture of I and II at −73 °C (δ 56.9 Hz).

The 2,3-dimethyl-2-[2-^{13}C]butylium ion (I) is suitable for study. However, since only the ^{13}C gives an NMR peak, only a slight shift would result from a small isotope effect, and without a *reference* peak we could not measure this shift. The *dilabeled* species (II) provides the necessary reference peak, since the equilibrium constant for it is exactly unity due to symmetry.



[I]



[II]

We have found that the equilibrium in I favors the positive charge on the carbon-13. Over temperatures ranging from −135 to −62 °C, we have obtained values for K from 1.0114 to 1.0197. A least-squares fit of this data to the Van't Hoff equation yielded $\Delta H = -6.0 \pm 0.2$ cal/mol and $\Delta S = -0.056 \pm 0.001$ cal/(mol deg), where the uncertainties are standard deviations.

By measuring the difference in chemical shift δ between the carbonium–methine carbon averaged peaks for I and II, the equilibrium constant could be determined by the equation $K = (\Delta + 2\delta)/(\Delta - 2\delta)$, where Δ is the chemical shift difference between the carbonium carbon and the methine carbon in the "frozen out" I. Δ has been estimated to be equal to 277 ppm for I.[3] Table I gives a listing of temperatures, δ's, and equilibrium constants for I.[9]

The ion sample was prepared by our molecular beam technique;[4] 0.07 mL of the labeled 2,3-dimethyl-2-butanol precursor was condensed with 1.0 g of SbF_5 on top of a mixture of 1.5 mL of SO_2ClF and 1.3 mL of SO_2F_2 which had been previously distilled in.

Table I

temp, °C[a]	splitting, Hz	K_{equil}[b]	temp, °C[a]	splitting, Hz	K_{equil}[b]
−62	53.5	1.0115	−106	70.6	1.0151
−67	55.2	1.0118	−111	74.2	1.0159
−73	56.9	1.0122	−113	75.7	1.0162
−77	58.8	1.0126	−117	77.0	1.0165
−84	61.5	1.0132	−121	78.9	1.0169
−89	64.0	1.0137	−125	81.3	1.0174
−90	63.5	1.0136	−129	83.5	1.0179
−95	65.9	1.0141	−130	86.5	1.0186
−101	68.4	1.0147	−133	85.9	1.0184
−104	70.3	1.0151	−135	91.8	1.0197

[a] ^{13}C NMR probe temperature measured by using the temperature dependence of the peaks of neat 2-chlorobutane.[8] [b] Obtained using Δ = 18 806 Hz.

Dilabeled 2,3-dimethyl-2-butanol, the ion precursor, was prepared as follows: A portion of 2-[2-^{13}C]propanone[5] was reduced to 2-propanol with $LiAlH_4$ and converted to isopropyl chloride.[6] The labeled isopropyl chloride was diluted with unlabeled isopropyl chloride, and the Grignard reagent was prepared in dry ether in the presence of 1,2-dibromoethane. The remaining portion of labeled acetone was added to the Grignard reagent to yield the dilabeled 2,3-dimethyl-2-butanol. The extent of labeling was determined from the intensities of the ^{13}C NMR multiplets due to the methine and carbinol carbons. It was purified by GC to yield 20 mg of labeled alcohol. This was mixed with 110 mg of unlabeled 2,3-dimethyl-2-butanol which had been purified in the same way. The resulting alcohol was then 3.5% dilabeled, 10.1% monolabeled, and 86.3% unlabeled. Therefore the peak of the monolabeled ion was predicted to be more intense than that of the dilabeled ion, allowing us to determine which peak was which and, therefore, to determine the direction of the isotope effect. This assignment was verified by heating the sample, allowing it to scramble to an equilibrium mixture of the isomeric tertiary hexyl cations. Since some of the monolabeled ion came from precursor with ^{13}C at natural abundance and the dilabeled ion was specifically enriched at the methine carbons, the mono-to-dipeak intensity ratio was expected to increase. Indeed, scrambling caused this ratio to increase from 2.4 to 9.3, showing that the assignment was correct.

If ^{13}C in the dilabeled ion produced a shift in the neighboring ^{13}C (an *intrinsic* isotope shift), an error would result. However, the ^{13}C NMR spectrum of the dilabeled 2,3-dimethyl-2-[2,3-$^{13}C_2$]butanol consists of 2 singlets for the carbon sites in the monolabeled species, each surrounded by a doublet for the dilabeled species. The average of the chemical shifts of the peaks of a doublet corresponds to the chemical shift of the enclosed singlet to within 3.7 Hz for both carbon sites. (The digital resolution of this spectrum was 1.85 Hz). Since the structure of this alcohol is similar to the carbocation, we would expect that if there are intrinsic shifts in the dilabeled ion, they would be less than 4 Hz. Another possible source of error in our values is in the estimation of Δ. A variation of ±10 ppm in Δ would lead to a variation in ΔH of only ±5%.[7]

This method does not depend on knowing the exact amount of isotope incorporation in starting materials or products, as in other methods of determining equilibrium isotope effects; however, its usefulness is limited to those molecules undergoing degenerate rearrangement reactions rapidly enough to give averaged NMR spectra.

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