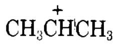
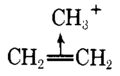
$CH_3CH_2CH_2^+$

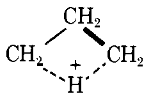
3


$CH_3\overset{+}{C}HCH_3$

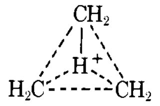
4


$CH_2\overset{\overset{CH_3^+}{\uparrow}}{=\!=}CH_2$

5



6



7

that the only other stable $C_3H_7^+$ species is one of the protonated cyclopropanes (**5–7**). Moreover the relative energies of the three ions (Table I) are in essentially perfect agreement with our calculations, assuming that the stable form of protonated cyclopropane is **6**. All available calculations (Table I) agree with simple MO arguments in ruling out **7** as a candidate. The only other evidence comes from studies of the reactions of cyclopropanes with acid in solution.[14] These have been held to indicate that protonation of cyclopropane leads to **6** rather than **5**. However, the scrambling of hydrogen atoms under these conditions implies that **5** and **6** cannot differ much in energy; we predict the activation energy of the scrambling reaction to be ≤ 6 kcal/mol.[15]

MINDO/2′ calculations[16] (see Table I) had correctly predicted **4** and **6** to be the only stable $C_3H_7^+$ species; however, they incorrectly predicted **6** to lie below **4** instead of above. Apparently the small residual tendency of MINDO/2′ to overestimate the stabilities of nonclassical ions relative to classical ions has been overcome in MINDO/3.

Table I also shows the results of ab initio SCF calculations by Pople et al. using STO-3G,[17] 4-31G,[17] and 6-31G*[18] basis sets. It will be seen these make a rather poor showing. The first two[17] incorrectly predict a distorted *n*-propyl cation (**3**) to be more stable than *any* of the protonated cyclopropanes, and, while the most recent calculations[18] make **5** and **6** marginally more stable than **3**, the difference is still less than that observed and this small improvement is achieved only at the expense of a worse estimate of the difference between **3** and **4**. Moreover none of these methods can give estimates of the heats of formation of the various species—only their relative energies.

The fact that so little improvement was achieved by passing from 4-31G to 6-31G* is particularly disturbing. It certainly seems to suggest that the ab initio SCF approach tends to *underestimate* the stabilities of nonclassical structures relative to those of classical isomers. As pointed out above, this seems also to have been the case for $C_2H_7^+$, and other examples could be cited.[19]

Part of the error here may have been due to the use of assumed (STO-3G) geometries in the 4-31G and 6-31G* calculations.[17,18] It is unfortunately expensive to calculate geometries using large basis sets. This difficulty does not arise in the case of MINDO/3 where calculations for much larger systems, with complete geometry optimization, are trivial. Since the results are apparently also more accurate than those given by the best available ab initio methods, this would seem to be the method of choice at present for the study of "nonclassical" carbonium ions.[23]

References and Notes

(1) This work was reported at the 23rd National Organic Symposium of the American Chemical Society, Tallahassee, Fla., June 1963, and at the South West Regional Meeting of the American Chemical Society, El Paso, Texas, Dec 1963.

(2) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

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(6) All the geometries reported here were found by minimizing the energy with respect to *all* geometrical variables, no assumptions of any kind being made—except in the case of unstable species (e.g., *n*-Pr$^+$; see below) where specific geometrical constraints had to be imposed to prevent rearrangement to more stable species.

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(12) In the case of **3** (*n*-Pr$^+$), that the CCC bond angle is the same as in propane; in the case of **5**, that the carbon atoms form an isosceles triangle; in the case of **6**, that the molecule has C_{3v} symmetry.

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(15) Since the *potential* surface is rather complicated, we are *not* sure that there may not be a path of lower energy than the one we found, which corresponded to a barrier of 6.0 kcal/mol.

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(19) See, e.g., recent publications[20,21] concerning the Hoffmann[22] structure for $(CH)_5^+$.

(20) M. J. S. Dewar and R. C. Haddon, *J. Am. Chem. Soc.*, **95**, 5836 (1973).

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(23) Since this manuscript was submitted, Dr. W. Thiel has found an additional minimum on the potential surface for $C_2H_7^+$, similar to **2** but with the methyl groups staggered instead of eclipsed. The calculated heat of formation (211.8 kcal/mol), while less than that for **2**, is still greater by 7 kcal/mol than that for **1**. The central CH and CC distances are 1.25 and 1.67 Å, respectively, compared with 1.22 and 1.76 Å for **2**.

(24) Robert A. Welch Postdoctoral Fellow.

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Evidence for Ion Pairing of Carbanions in Methanol

Sir:

A recent communication by Hogen-Esch,[1] described an elegant spectral investigation of the solution environment of fluoradenide salts. No evidence was found for ion pairing in methanol or ethanol. This observation seriously damages the only simple explanation of the mysterious cation dependent effects which have been observed when methoxide salts have been employed to measure the kinetic and equilibrium acidities of carbon acids in methanol.[2] As methoxide-methanol is one of the most common media for carbanion studies and is a prototype in its class of polar, protic solvents, a knowledge of its capacity to solvate and separate ions is of crucial importance. We have therefore extended the work of Hogen-Esch[1] and wish to report the first direct evidence for carbanion ion pairing in methanol.

Reaction between fluoradene and potassium methoxide or lithium methoxide in methanol gave solutions with spectral characteristics identical with those attributed by Hogen-Esch to hydrogen bonded, free fluoradenide ions. (See Figure 1.) To our surprise, however, the use of tetramethylammonium methoxide gave an altered spectrum in which the broad absorption at ca. 536 nm was replaced by two distinct maxima at 516 and 549 nm. (See Figure 1.)

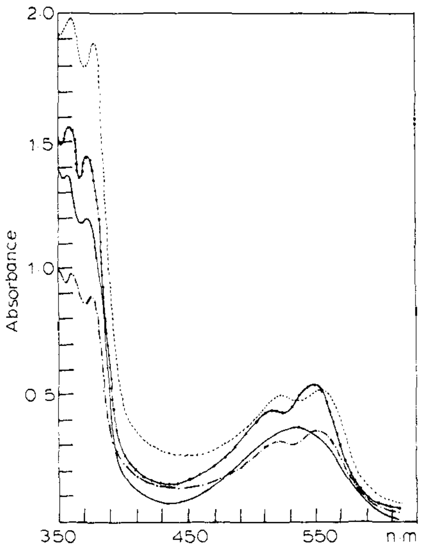

Figure 1. Absorption spectra for fluoradenide ions in methanol at 30°: (—) FD-KOMe (7.2 × 10^{-4} *M*, 0.143 *N*); (–•–•–•–) FD-Me_4NOMe (3.5 × 10^{-4} *M*, 0.045 *N*); (– – – –) FD-KOMe-18-crown-6 (2.9 × 10^{-4} *M*, 0.087 *N*, 0.462 *M*); (• – • –) FD-Me_4NOMe-18-crown-6 (2.3 × 10^{-4} *M*, 0.077 *N*, 0.231 *M*) FD = fluoradene.

This spectrum is very similar to the spectra attributed to contact ion pairs of fluoradenide ion in THF and THP.[1] No detectable change in the spectrum was observed as [Me_4NOMe] was varied from 0.40 to 0.01 *M*.[3]

We also found that addition of 18-crown-6 to the potassium methoxide solutions produced an ion-pair spectrum. This spectrum showed maxima at 520 and 554 nm. The double maximum was still present when the concentration of potassium methoxide was made greater than that of crown ether but a gradual transition to a broad, single maximum was observed as the potassium methoxide concentration was increased. At high concentrations of potassium methoxide, the spectrum became indistinguishable from that observed in the absence of crown ether. Apparently the crown ether complexed ion pair and the species responsible for the broad maximum are sufficiently comparable in stability that the position of equilibrium can be driven toward the latter by increasing [KOMe]. Either of the following equilibria would explain this result

$$FD^-K^+CE + K^+ \rightleftharpoons FD^-K^+ + K^+CE$$

$$FD^-K^+CE + MeO^- \rightleftharpoons FD^- + MeO^-K^+CE$$

where FD^- = fluoradene anion, CE = crown ether, and methanol of solvation is omitted.

Both in this study and in the previous work, it has been found that no spectral changes occur as the concentration of alkali metal methoxide in methanol is changed (in the absence of crown ether). Moreover, both lithium and potassium methoxides produce the same spectrum. While we concede that these results suggest that the lithium, sodium, and potassium salts of fluoradene exist as free ions in methanol, we find it difficult to understand why a carbanion which exhibits a preference for ion pairing with tetramethylammonium ion and crown ether-complexed potassium ions would not also form ion pairs with methanol-solvated lithium, sodium, and potassium ions.

Ion pairing of alkali metal salts in methanol is marginal at the concentrations appropriate to conductance studies but can be observed.[4] It seems likely that most ion pairs are solvent separated in methanol[4b,5] and may be regarded as having the general formula $R^-M^+(MeOH)_n$. It is possible that this situation obtains for lithium, sodium, and potassium fluoradenides. If the number of methanol molecules was large, the cation and anion could be sufficiently insulated to render the spectral properties of the anion insensitive to the nature of the cation. It is interesting in this regard to note that addition of crown ether alters the tetramethylammonium ion pair and the new spectrum is identical with the crown ether-complexed potassium ion pair.

When nitrobenzene is added to solutions of fluoradenide ions in methanol, the fluoradenide ion is destroyed by a one-electron transfer process as evidenced by the precipitation of bifluoradene and by the appearance of nitrobenzenide ion (ESR). Interestingly, the rate of this process is much slower for solutions containing tetraalkylammonium or crown ether-complexed potassium ion pairs than for the uncomplexed potassium salt. When potassium methoxide is used to produce the fluoradenide ion, the rate increases markedly with increasing [KOMe] whereas it is independent of [Me_4NOMe] when this base is employed. The electron-transfer process is believed to be reversible and we are unprepared to present a detailed kinetic analysis at this time. It is clear, however, that the effective rate of the electron transfer process is quite sensitive to the type of ion pairs present. A similar effect had been reported[2f] for the reaction of 9-methoxyfluorene with nitrobenzene and methoxide salts. In that system the protonation rate of the carbanion was a factor in determining the overall rate. This complication can be disregarded in the case of fluoradene, because the anion concentration is directly monitored.

Acknowledgment. We wish to thank the National Science Foundation for a Grant GP-42837X supporting the work.

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(3) A referee has suggested that the observed spectrum might be due to an ion aggregate such as $FD^-M^+MeO^-$. We cannot rule out this possibility but the lack of spectral change over a wide range of concentrations makes it seem improbable. Either the spectral characteristics of the anion would have to be insensitive to aggregation changes or a particular state of aggregation would have to be favored over all others. It is worth mentioning that when [Me_4NOMe] was lowered to 0.0036 *M*, minor spectral changes were observed. Background absorption from the high fluoradene concentrations required prevented us from going to lower base concentration where we would expect to observe the free ion.

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Conversions of Alcohols to Halides by Homolytic Reactions

Sir:

Preparation of alkyl halides from hindered or rearrangement-prone primary and secondary alcohols is difficult. Reagents such as HX, PX_3, PX_5, and SOX_2 often yield other products or halides resulting from hydride shifts[1] (eq 1) and alkyl rearrangements (eq 2).[2] Circumvention of the diffi-