1-Methyl-7-methoxy-7,12-dihydropleiadene. One-half gram of 1-methyl-7(12H)-pleiadenone[25] and 0.55 g of lithium aluminum hydride were dissolved in 25 ml of ether and stirred for 14 hr. Acid hydrolysis and conventional work-up produced the crude carbinol (infrared showed O–H stretching and no carbonyl absorption), which was dissolved in acidified methanol and refluxed overnight, as in the preparation of II. After chromatography over alumina, the methyl ether was obtained as crystals, mp 61.5–63° (from ethanol–water), in *ca.* 35–40% yield (0.218 g).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.59; H, 6.62.

7-Methyl-7,12-dihydropleiadene and 7-Methyl-7,12-dihydropleiadene-7-*d*. Methyl 8-benzyl-1-naphthoate was prepared from the reaction of 8-benzyl-1-naphthoic acid[3] with diazomethane in ether in quantitative yield. An ester group was confirmed by a carbonyl band in the infrared spectrum at 1730 cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.56; H, 5.16.

The ester was converted to 8-benzyl-1-acetylnaphthalene by inversion addition of ethereal methyllithium (slightly over 1 mole) to the ester in ether solvent. A conventional work-up gave the ketone as an uncrystallizable oil which was characterized by infrared spectroscopy, $\nu_{>=O}$ 1686 cm^{-1}.

The ketone from the preceding step was reduced by excess lithium aluminum hydride (or lithium aluminum deuteride) in ether to give 8-benzyl-1-(α-hydroxyethyl)naphthalene which again was characterized by infrared spectroscopy (no carbonyl absorption) as the correct reduction product.

The above oil was cyclized with acetic acid containing a drop of sulfuric acid on the steam bath for 2 hr. Dilution with ice water and ether extraction, followed by washing and drying, gave 7-methyl-7,12-dihydropleiadene, mp 104–105° (from ethanol).

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.27; H, 6.60.

7,12-Dihydro-7-acetoxy-12-methylpleiadene. To a suspension of 0.456 g (12 mmoles) of lithium aluminum hydride in 50 ml of anhydrous ether was added a solution of 1.796 g (6.85 mmoles) of 12-methyl-7(12H)-pleiadenone dissolved in 50 ml of dry tetrahydrofuran. The reaction mixture was stirred for 14 hr at room temperature and then hydrolyzed with water and 10% sodium hydroxide solution. The solid inorganic salts were filtered and washed with ether. The ether filtrates were combined, washed with water, dried over sodium sulfate, and concentrated to give a white solid. Recrystallization from ethanol–water gave 1.2 g of white, feathery crystals of the alcohol, mp 182–184°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.70; H, 6.18. Found: C, 87.51; H, 6.32.

The procedure used to prepare the acetate was the same as that used for the preparation of 7-acetoxy-7,12-dihydropleiadene. From 110 mg of 7-hydroxy-12-methyl-7,12-dihydropleiadene was obtained 35 mg of product, mp 141–143°, after two recrystallizations from petroleum ether (bp 60–110°). The infrared spectrum showed acetate carbonyl at 5.73 μ.

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.40; H, 6.00. Found: C, 83.85; H, 6.21.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work. Also, we are especially indebted to Professor D. J. Pasto of Notre Dame University for performing the spin decoupling nmr experiments and aiding in their interpretation.

The Electronic Spectra of Carbonium Ions in Strongly Acidic Solutions[1]

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Contribution from the Department of Chemistry, Western Reserve University, Cleveland, Ohio, and The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts. *Received December 10, 1965*

Abstract: The ultraviolet and visible absorption spectra of a number of alkyl-, cycloalkyl-, aryl-, alkynylcarbonium ions, and of hydroxy- and oxocarbonium ions, the structures of which have been established by nmr spectroscopy, are reported in fluorosulfonic acid–antimony pentafluoride and concentrated sulfuric acid (oleum) solutions, generally at low temperatures. Alkylcarbonium ions are shown to exhibit *no* ultraviolet absorption above 210 mμ. Aryl-, cyclopropyl-, and alkynylcarbonium ions show characteristic ultraviolet absorption spectra. Alkyloxocarbonium ions show no ultraviolet absorption maxima above 210 mμ, whereas aryloxocarbonium ions absorb in the characteristic aryl-conjugated regions. The ultraviolet spectra of a number of protonated ketones (hydroxycarbonium ions) were also obtained and compared to the related carbonium ions.

The literature on the ultraviolet spectra of carbonium ions is extensive, but contains much uncertainty. This uncertainty has its origin in the lack of stability of carbonium ions in relatively weak acid solutions, and that the spectra were measured at room temperature. It is the purpose of this paper to report ultraviolet spectra of carbonium ions, all of which have been directly observed by nmr spectroscopy in the same acid–solvent systems and at the same temperatures at which the ultraviolet spectra were obtained. The development of extremely strong acid systems[2] has made it possible to prepare stable species and observe the spectra of carbonium ions of practically every structural class. Since low temperatures are necessary to retain the structural integrity of many of the carbonium ions, the spectra of these species were taken at −60°.

Results

A. Alkylcarbonium Ions. (a) Introduction. The ultraviolet spectra of many alkylcarbonium ions have been reported over the years, most notably by Symons and co-workers,[3-5] but these reports were questioned

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[1] Stable Carbonium Ions. XXI. Part XX: G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362 (1966).

[2] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **85**, 1328 (1963).

[3] J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959).

[4] J. Rosenbaum and M. C. R. Symons, *ibid.*, 1 (1961).

[5] J. Rosenbaum, M. Rosenbaum, and M. C. R. Symons, *Mol. Phys.*, 3, 205 (1960).

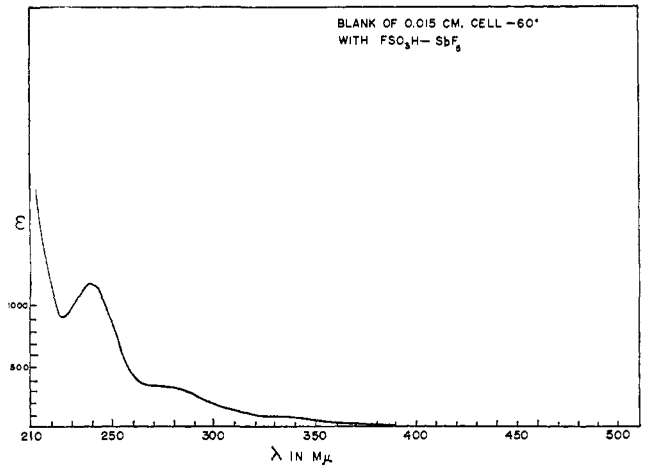

Figure 1.

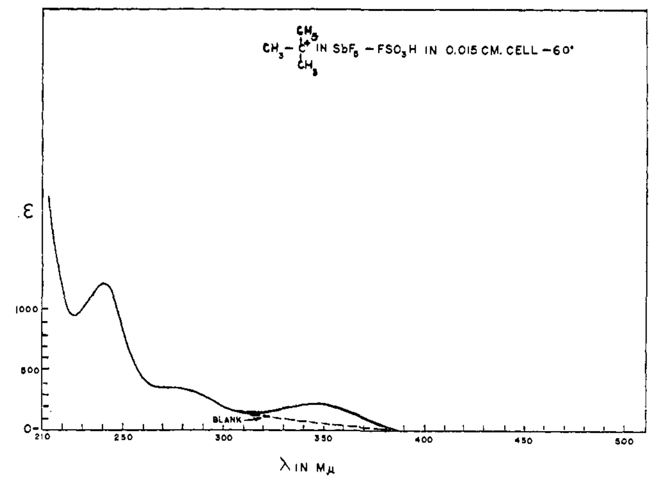

Figure 2.

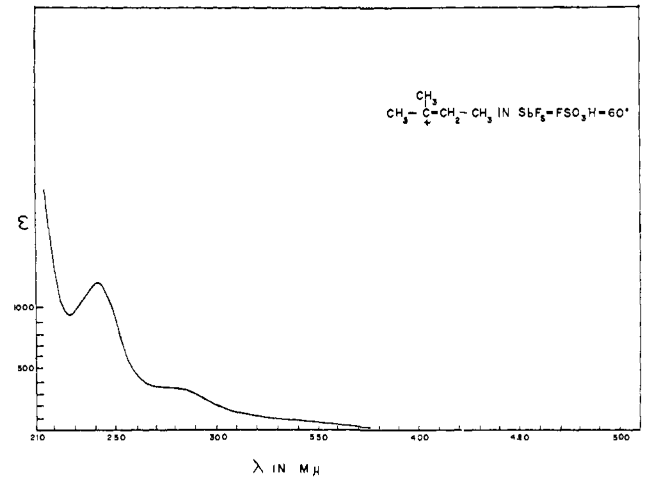

Figure 3.

by subsequent investigators. The observation of the ultraviolet spectra of stable alkylcarbonium ions in acidic solutions has been made possible in the work of Olah, *et al.*, who obtained alkyl cations as stable species in SbF_5 solution.[2,6] Once it was demonstrated that isopropyl, *t*-butyl, *t*-amyl cation, etc. were stable species in these solvents, ultraviolet studies were performed. The ultraviolet studies showed only a weak (ϵ 500 or less) absorption in the 300-mμ region. It was suggested that the weak absorption maxima were either due to secondary cyclized allylic ions or to a forbidden transition, but excluded the possibility of a high intensity transition in the 290-mμ region, as claimed previously.[3,5,7–10] The question whether alkyl cations can absorb in the 300-mμ region was left, however, still open for question. The spectral measurements reported here establish that alkyl cations have no absorption maxima at wavelengths >220 mμ. In the absence of formal charge delocalization, simple MO theory does not predict an absorption maximum above 220 mμ for simple alkyl cations. An attempt to explain absorptions reported for alkyl cations[3–5] considered that, as a result of extensive hyperconjugation, the charge was delocalized in a quasi-π system which would produce a relatively long wavelength charge-transfer-type transition.[11] Apparently, this treatment overemphasizes hyperconjugation in alkyl cations.

Matsen and co-workers noted that an absorption band was rapidly formed (295–310 mμ) by adding olefins to sulfuric acid and attributed this band to the corresponding alkyl cations.[7] They also noticed SO_2 in these systems (SO_2 absorbs in this range). However, after a reexamination of the systems Matsen retracted this view[8] and attributed the absorption band to products arising from oxidation processes. Russian workers reported that a series of tertiary alcohols formed an absorption band in sulfuric acid in the 300-mμ region[9] and assigned this band to the corresponding alkyl cations.[10] Recently Rosenbaum and Symons reported that[3,4] a series of alcohols and olefins in concentrated sulfuric acid gave ultraviolet absorption maxima at 292 ± 2 mμ with large extinction coefficients (log $\epsilon = 3.5$ to 4). According to their data the absorption maxima were formed by first-order kinetics; but a recent reinvestigation showed that the formation proceeds with second-order kinetics.[12]

(b) Results and Discussion. It has been shown by Olah and co-workers that tertiary alkyl cations such as the *t*-butyl as well as *t*-amyl, *t*-heptyl, and related cations are quantitatively generated from their corresponding alcohols in FSO_3H-SbF_5 at $-60°$.[13a] We have now measured the ultraviolet spectra of each of these ions under these same conditions at concentrations from 10^{-3} to above 10^{-1} *M*. It was found that these tertiary alkyl cations have no ultraviolet absorption above 210 mμ, comparing the spectra with those of solvent blanks under identical conditions (Figures 1–4). The trace absorption in the solution of the *t*-butyl cation is in all probability not due to a forbidden

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(6) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(7) F. A. Matsen, J. Gonzalez-Vidal, W. H. Harwood, and E. Kohn, Abstracts of Papers, 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, 1955, p 21.

(8) J. Gonzalez-Vidal, E. Kohn, and F. A. Matsen, *J. Chem. Phys.*, **25**, 181 (1956).

(9) V. F. Lavrushin, N. N. Verkhouod, and P. K. Monchan, *Dokl. Akad. Nauk SSSR*, **105**, 723 (1955); *Chem. Abstr.*, **50**, 11256*h* (1956).

(10) V. F. Lavrushin and N. N. Verkhouod, *Dokl. Akad. Nauk SSSR*, **115**, 312 (1957), *Chem. Abstr.*, **52**, 6251*e* (1958).

(11) S. F. Mason, *Quart. Rev.* (London), **15**, 339 (1961).

(12) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, **86**, 1745 (1964).

(13) (a) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965); (b) R. Waack and M. A. Doran, *ibid.*, **85**, 1651 (1963).

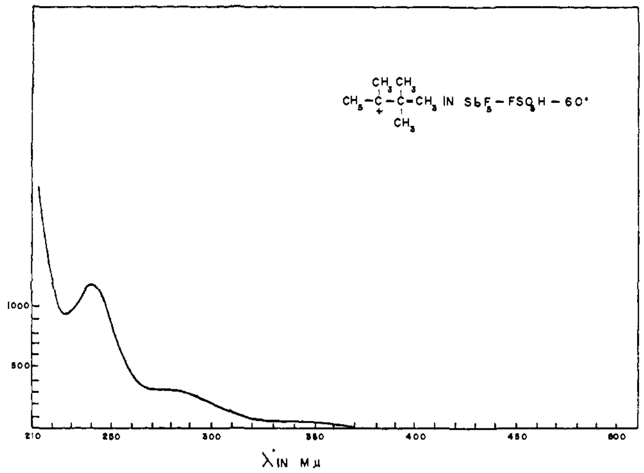


Figure 4.

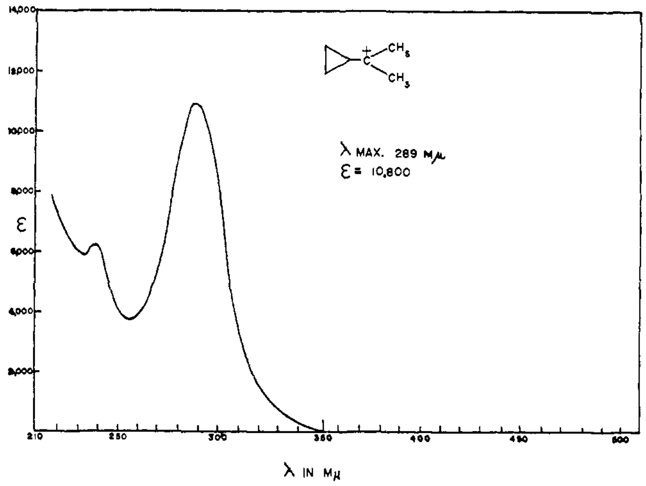
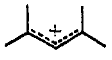


Figure 5.

transition of the *t*-butyl cation itself, since the position and extinction coefficient of this very weak band varied from experiment to experiment. It is most likely due to traces of polymeric impurities. The previously observed band at 293 mμ (ε 500) in SbF_5 solutions of $(CH_3)_3CF$ and related halides at room temperature must now be considered to have been due to trace impurities since no absorption was observed in the 290–300-mμ region for any of the tertiary alkyl cations examined in present work. Thus it can now be concluded that alkylcarbonium ions, like protonated alkyl ketones[40] and trialkylboranes[41] (see subsequent discussion), have no ultraviolet absorption maximum above 210 mμ. The lack of discrete absorption maxima for alkyl cations above 210 mμ is in agreement with the spectral findings for the analogous negative ions, *i.e.*, alkyllithium compounds.[13b]

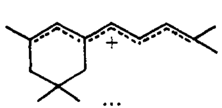
B. Cycloalkylcarbonium Ions. Cycloalkylcarbonium ions like the 1-methylcyclopentyl cation[14] show no ultraviolet absorption above 210 mμ. The 2-norbornyl cation, previously observed in SbF_5–SO_2 and FSO_3H–SbF_5 solvent systems,[15] also shows no ultraviolet absorption maximum above 210 mμ.

Cyclopropylcarbonium ions represent an interesting class of stable carbonium ions in FSO_3H–SbF_5. Though simple alkylcarbonium ions have no ultraviolet absorption above 210 mμ, cyclopropylcarbonium ions do. The cyclopropyl ring delocalizes positive charge while conjugating with the vacant p orbital in the ion.[16] In this respect it resembles a double bond, and the λ_{max} of the cyclopropyldimethylcarbonium ions supports this view (Figure 5). Its 289-mμ absorption is in the region where allylic cations absorb, and the observed extinction coefficient is equal to that of a large variety of allylic cations. These ions have been observed by nmr spectroscopy in SbF_5–SO_2–FSO_3H solutions by Pittman and Olah.[16] Data of the ultraviolet spectra of three cyclopropylcarbonium ions are shown in Table I. The striking feature of these data is the fact that successive cyclopropyl substitution does not lead to successively longer wavelength absorption. When an allylic cation (*i.e.*, i, λ_{max} 305 mμ)[17] is compared to a dienylic cation (*i.e.*, ii, λ_{max} 397 mμ),[18] one sees a large increase in the λ_{max}. Another substantial increase in λ_{max} is found by adding another double bond to form a trienylic cation (*i.e.*, iii, λ_{max} 470 mμ).[19] However, the substituted trivinyl cation, where there is cross conjugation, behaves as a dienylic cation and not a trienylic cation (*i.e.*, iv, λ_{max} 402 mμ).[20] On this basis one might expect that the dicyclopropylcarbonium ion would have a λ_{max} at a longer wavelength than the cyclopropyldimethylcarbonium ion.

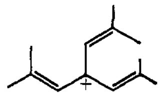


i

ii

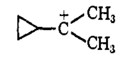
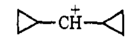
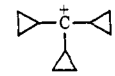


iii



iv

Table I. Ultraviolet Absorption of Cyclopropylcarbonium Ions

Ion	λ_{max}, mμ	ε
	289	10,800
	273	12,200
	270	22,600

It was of interest to establish whether the FSO_3H–SbF_5 solvent system causes any appreciable shifts of the ultraviolet absorption maxima compared with other acidic solvents, as sulfuric acid. In the case of the tricyclopropylcarbonium ion it was possible to demonstrate that there is no appreciable change in the absorption maximum in the FSO_3H–SbF_5 solvent systems used in the present investigation and concentrated

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(14) George A. Olah, unpublished results.

(15) P. von R. Schleyer, R. C. Fort, Jr., W. W. Watts, M. S. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 4195 (1964).

(16) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(17) N. C. Deno, M. J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2998 (1963).

(18) N. C. Deno and C. U. Pittman, Jr., *ibid.*, **86**, 1871 (1964).

(19) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965).

(20) T. S. Sorensen, private communication.

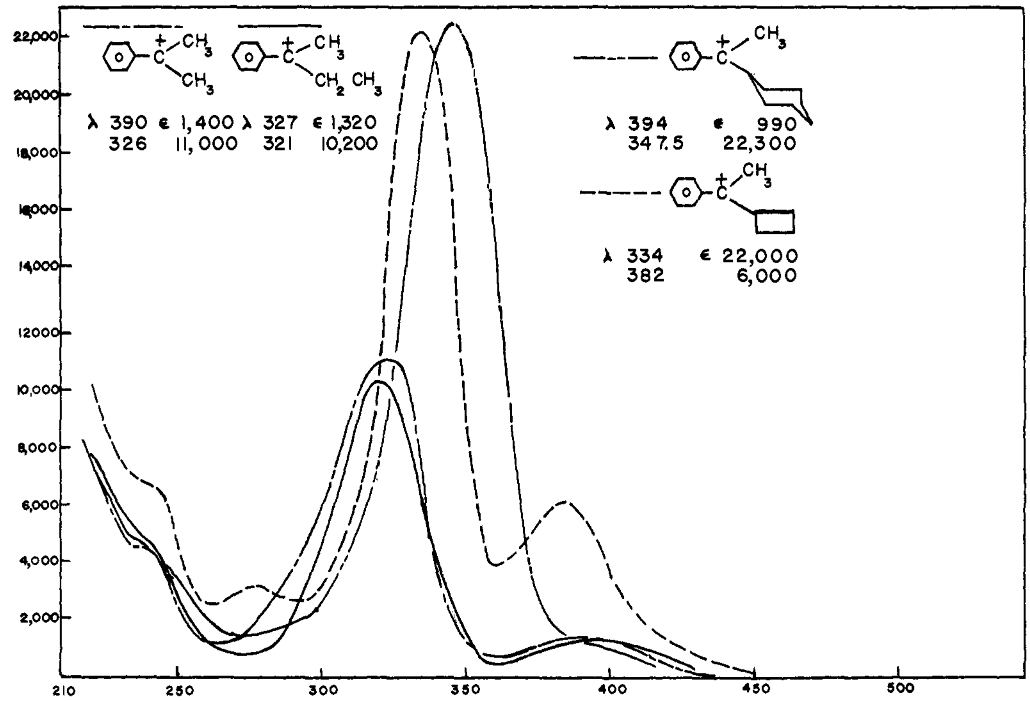
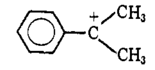
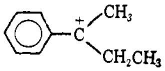
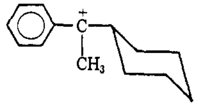
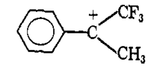
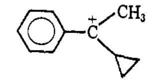
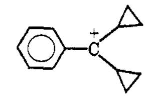
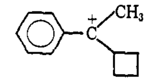
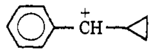


Figure 6.

sulfuric acid used in previous work.[21] In both systems the tricyclopropylcarbonium ion absorbs at 270 mμ.

Table II. Ultraviolet Absorption of Monophenylcarbonium Ions

Ion	λ_{max}, mμ	ε
	390 326	1,400 11,000
	397 321	1,320 10,200
	394 347.5	990 22,300
	347	3,400
	316 404	15,200 2,140
	340 322 285	12,600 12,500 16,600
	382 334	6,000 22,000
	343	18,000 (slowly decays at −50°)

C. Arylcarbonium Ions. Three surveys of the ultraviolet and visible spectra of monoarylcarbonium ions have appeared.[3,22,23] It has, however, been recently pointed out that much of the early data need revision[24] and some of the data have been retracted.

We have now investigated the ultraviolet absorption of a series of monoarylcarbonium ions. Representative spectra are shown in Figure 6. The data are tabulated in Table II. Each of these ions has been previously conclusively demonstrated to exist in these solutions as stable species by nmr spectroscopy.[25-28]

Monophenylcarbonium ions, with the exception of cyclopropylphenyl- and phenylmethyltrifluoromethylcarbonium ions, exhibit two absorption maxima. There is a strong maximum at shorter wavelength and a weak one at longer wavelength. The phenylmethylethylcarbonium ion for instance exhibits maxima at 397 mμ (ε 1320) and 321 mμ (ε 10,200). The maxima were found to be the same over a 50-fold concentration range and over a 80° temperature range (−50 to +30°).

Our results sharply contrast with previous measurements of the spectra of monoarylcarbonium ions.[3,23] Where previous reports assigned extinction coefficients below 1000 to monoarylcarbonium ions,[23] polymeric species must have actually been observed. Grace and Symons[3] report ions I–IV are formed from their corresponding alcohols and olefins in 100% H_2SO_4. However, the reported λ_{max} for I–IV (435, 390, 327, 405, respectively) do not agree with our results. It has recently been demonstrated that ions II and III are not stable in 100% H_2SO_4 and acidity level of ~30% oleum must be used to stabilize II. Ion I cannot be formed even in SO_2–SbF_5–FSO_3H at −60°. Since the protonating power of this acid is at least 10^4 greater than

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[21] N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

[22] N. C. Deno, P. T. Groues, J. J. Jaruzelski, and M. N. Lugasch, *ibid.*, **82**, 4719 (1960).

[23] J. F. A. Williams, *Tetrahedron*, **18**, 1487 (1962).

[24] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 178 (1964).

[25] G. A. Olah, *J. Am. Chem. Soc.*, **86**, 932 (1964).

[26] D. G. Farnum, *ibid.*, **86**, 934 (1964).

[27] G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 3507 (1965).

[28] G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 3509 (1965).

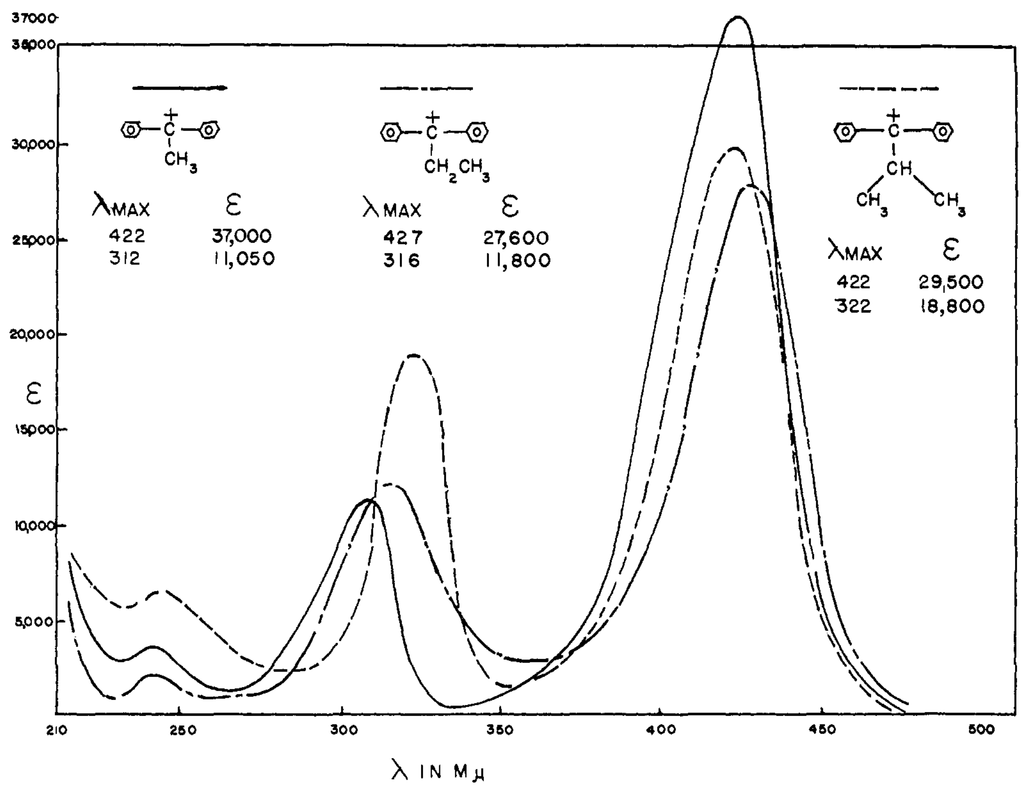
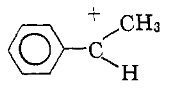
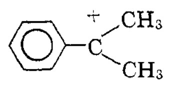
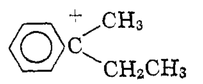


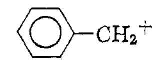
Figure 7.

100% H_2SO_4, the species absorbing at 435 observed in 100% H_2SO_4 is considered to be a dimeric or a polymeric species. Previous attempts to generate I in H_2SO_4 and oleum systems have repeatedly failed. Several


I


II

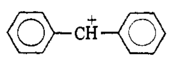
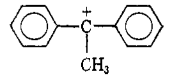
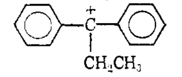
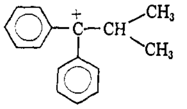
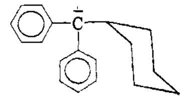
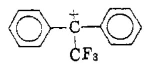
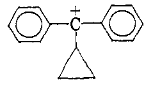
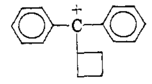
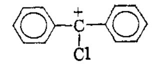
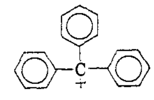

III


IV

attempts to generate IV in SbF_5-FSO_3H-SO_2 at low temperatures have also failed, making it extremely unlikely that it could exist over long periods in 100% H_2SO_4.

Table III summarizes data of the ultraviolet absorption of nine diphenylcarbonium ions and for the sake of comparison that of the well-known triphenylcarbonium ion. Representative spectra are shown in Figure 7. Each of these ions has conclusively been shown to be quantitatively generated from the corresponding alcohols in SbF_5-FSO_3H.[25,27,29] The diphenyl- and triphenylcarbonium ions have been extensively studied previously by Gold,[30] Deno,[31] and Evans[32a] and their co-workers by ultraviolet spectroscopy in H_2SO_4 solutions, and by Leftin and Hall by absorption on silica-alumina.[32b] Our findings agree very closely with these previous studies and illustrate that in the SbF_5-FSO_3H solvent at ~ −60° there is no significant change of the positions of maximum absorption compared with the

Table III. Ultraviolet Absorption of Diphenylcarbonium Ions in FSO_3H-SbF_5 Solution

Ion	λ_{max}, mμ	ε
	440 292	38,000 2,900
	422 312	37,000 11,050
	427 316	27,600 11,800
	422 322	29,500 18,800
	427 338	36,100 17,100
	485 331	21,500 4,300
	435 358 319	30,100 8,360 10,350
	388 335	6,750 22,900
	434 334 291	24,900 25,400 13,000
	403 429	38,700 38,700

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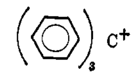
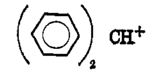
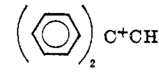
(29) G. A. Olah and C. U. Pittman, Jr., unpublished.

(30) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(31) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955); N. C. Deno, P. J. Grovoes, and G. Saines, *ibid.*, 81, 5790 (1959).

(32) (a) A. G. Evans, *et al.*, *J. Chem. Soc.*, 1824 (1954); 104 (1957); (b) H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, 66, 1457 (1962).

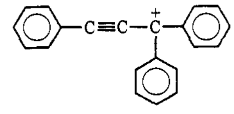
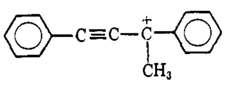
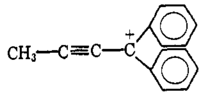
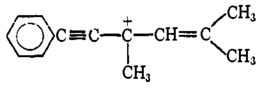
Table IV. Comparison of Ultraviolet Absorption of Arylcarbonium Ions in Different Solvents

Class	Ion	Solvent	λ_{max}, mμ	Ref
Triaryl		FSO_3H–SbF_5	403, 429	Present work
		Concd H_2SO_4	404, 431	31
		BBr_4^- salt in H_2SO_4	405, 432	33
		Cl^- in CH_3NO_2	405, 430	35
Diaryl		FSO_3H–SbF_5	440	Present work
		Concd H_2SO_4	440	31
		$SbCl_6^-$ salt in CH_2Cl_2–$SbCl_5$	451	34
Diarylalkyl		FSO_3H–SbF_5	422, 312	Present work
		Concd H_2SO_4	322, 312	30

absorption maxima previously observed in sulfuric acid solutions at room temperature.

Table IV compares the ultraviolet absorption data of representative arylcarbonium ions in different solvents. This suggests that there is no appreciable contribution of charge-transfer phenomenon between the ions and solvent in strongly acidic media.

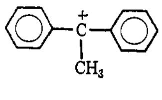
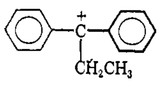
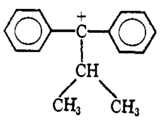
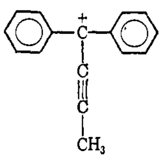
Table V. Ultraviolet Absorption of Alkynylcarbonium Ions

Ion	λ_{max}, mμ	ϵ
	504 449	36,900 26,600
	493 406 334	36,900 2,400 2,500
	452 420 372	16,000 Shoulder 16,300
	461 389 312	28,200 17,900 13,200

D. Alkynylcarbonium Ions. Table V tabulates the ultraviolet spectra of four alkynyl cations observed in FSO_3H-SbF_5 solvent at −65°. These ions have been demonstrated to be stable in FSO_3H-SbF_5 by nmr spectroscopy.[36]

The diphenylpropynylcarbonium ion may be compared to the series of diphenylcarbonium ions given in Table VI. Addition of CH_3—C≡C– to the diphenyl system results in a shift of λ_{max} to longer wavelength. Apparently the chromophore $C_6H_5\overset{+}{C}C_6H_5$ is not as effective as $CH_3C{\equiv}C\overset{+}{C}C_6H_5$. The suggestion that when more than two conjugated groups are attached to the central carbon, *i.e.*, $(C_6H_5)_2CHLi$ *vs.* $(C_6H_5)_3CLi$,[13b] the chromophore consists of only two of the groups with the third acting as a cross-conjugating electron donor or acceptor, is supported by the data of Table VI. The shift to shorter wavelength of the diphenylmethylcarbonium ion absorption maxima as a result of alkyl substitution is probably in part due to the effect of steric crowding on the planarity of the chromophore, but it is also in the direction expected based on the inductive effect of an alkyl substituent on the transition energy of an odd alternate ion.[37] In such molecules the effect of an alkyl substituent on transition energy varies with the position of substitution.

Table VI. Comparison of the Ultraviolet Absorption of Diphenylcarbonium Ions

				
λ_{max}, mμ	422	427	422	462
	312	316	322	420
				372

E. Oxocarbonium Ions (Acyl Cations). Stable alkyl-, aryl-, and cyclopropyloxocarbonium ions were obtained from the corresponding acyl fluorides and Lewis acid fluorides, like antimony pentafluoride.[6] They can also be quantitatively generated by dissolving the corresponding carboxylic acid into 30% oleum.[38,39] Nmr spectra were used to verify the existence of each of these acyl cations. The ultraviolet spectra of 13 alkyl-, alkenyl-, cyclopropyl-, and aryloxocarbonium ions in 33% oleum are summarized in Table VII. Figure 8 shows representatives of the spectra.

Alkyloxocarbonium ions, as the acetyl and propionyl cations, have no ultraviolet absorption above 210 mμ. Though the cyclopropyl ring conjugates strongly with the charged carbon ion in carbonium ions,[30] the cyclopropyloxocarbonium ion does not absorb above 220 mμ in the ultraviolet. The crotonyl cation does not absorb above 235 mμ. It can be seen by comparison of the data in Tables I, II, and VII that oxocarbonium ions absorb at lower wavelengths than the related carbonium ions.

F. Protonated Ketones (Hydroxycarbonium Ions). Protonated ketones can be considered as hydroxycarbonium ions $R\overset{+}{C}(OH)R$ and in the past have been used as models for the corresponding carbonium ions. The ultraviolet absorption of protonated ketones

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(33) K. M. Harmon and A. B. Harmon, *J. Am. Chem. Soc.*, **83**, 865 (1961).

(34) J. Holmes and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

(35) A. G. Evans, *et al.*, *Trans. Faraday Soc.*, **47**, 711 (1951).

(36) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965).

(37) R. Waack and M. A. Doran, *J. Phys. Chem.*, **68**, 1148 (1964).

(38) N. C. Deno, M. J. Wisotsky, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **86**, 4370 (1964).

(39) C. U. Pittman, Jr., and G. A. Olah, unpublished results; N. Friedman, Ph.D. Thesis, Pennsylvania State University, 1965.

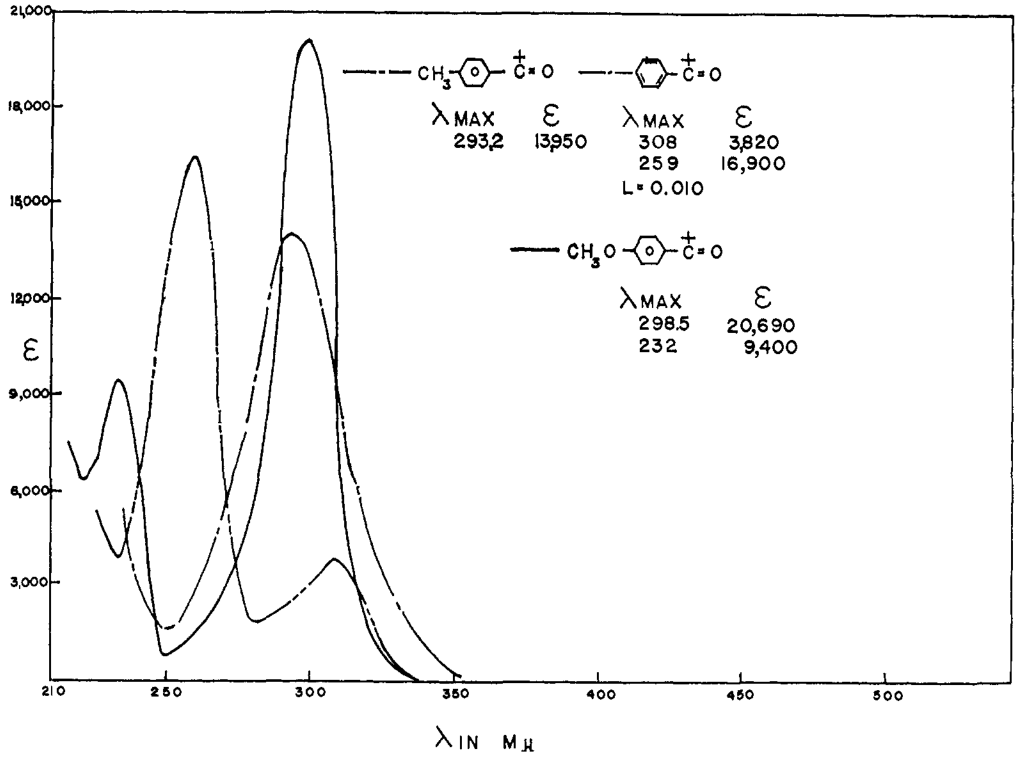
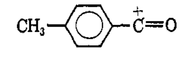
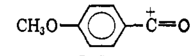
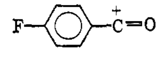
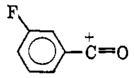
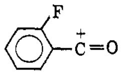
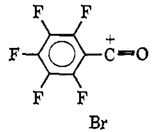
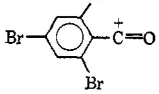
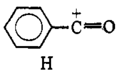
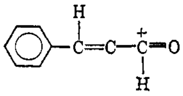


Figure 8.

might therefore be analogous to that of the corresponding ion.

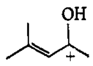
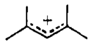
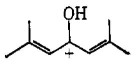
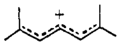
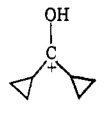
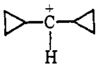
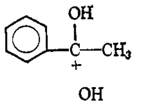
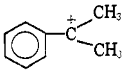
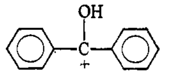
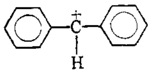
Table VII. Ultraviolet Absorption of Oxocarbonium (Acylium) Ions

Ion	λ_{max}, mμ	ε
$CH_3-\overset{+}{C}=O$	<215	
$CH_3CH_2\overset{+}{C}=O$	<215	
$CH_3-CH=CH-\overset{+}{C}=O$	<235	
	<220	
	293.2	13,950
	298.5 232	20,690 9,400
	294 269.5	3,130 16,600
	317 262	2,970 14,200
	297 249	1,580 12,300
	309 258	2,220 14,150
	371 314.5	7,700 28,800
	308 259	3,700 16,900
	326.5	29,600

Campbell and Edward[40] showed that protonated aliphatic ketones (dimethyl, methyl ethyl, and methyl isopropyl ketones), as well as aliphatic cyclic ketones, do not absorb above 200 mμ, in agreement with our findings for alkyl cations. Other possible alkylcarbonium ion models such as the isoelectronic trialkylboranes[41] and $(CH_3O)_3C^+$[42] also do not absorb above 220 mμ.

The spectra of several protonated ketones and the related carbonium ions determined in our present work in FSO_3H-SbF_5 are compared in Table VIII.

Table VIII. Comparison of Ultraviolet Absorption of Protonated Ketones (Hydroxycarbonium Ions) with Carbonium Ions

Protonated ketone	λ_{max}, mμ	Log ε	Carbonium ions	λ_{max} mμ	Log ε
	284			305	4.03
	340 277	4.33 3.79		397	4.00
	235	4.12		273	4.09
	296 335	4.27 3.33		326 390	4.05 3.15
	344 291	4.89 3.06		440 292	4.58 3.46

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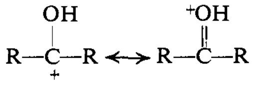
(40) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960).

(41) A. G. Davies, D. G. Hase, and L. F. Larkworthy, *Chem. Ind.* (London), 1519 (1959).

(42) R. W. Taft, personal communication of unpublished results.

Comparison of the data shows that protonated ketones absorb at lower wavelengths than the corresponding carbonium ion. This comparison appears to be general and should be of predictive value. It could be interpreted as demonstrating the greater charge delocalization in carbonium ions over protonated ketones. In protonated ketones, resonance forms a and b are both important, and thus the hydroxycarbonium ions form a is only a partial contributor.



$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{+}{C}}-R \longleftrightarrow R-\overset{\overset{\displaystyle {}^{+}OH}{\|}}{C}-R$$

a b

Comparison of Spectra of Carbonium Ions and Their Corresponding Carbanions. Both Hückel and self-consistent field molecular orbital treatments predict, to a first approximation, that the transition energies for the anion and cation of an even or odd alternate hydrocarbon should be similar.[13b,32,43,44] A comparison of the new spectral data reported here for carbonium ions with that reported for the corresponding organolithium compounds further supports this prediction.[13b,32,43,44] Previously one outstanding lack of correspondence was the absorption of monoarylcarbonium ions and carbanions. It was shown in the present investigation that spectra of monoarylcarbonium ions when taken at low temperature are in reasonable agreement with those of the corresponding carbanions.

Having reliable data for the absorption of carbonium ions to compare with that of carbanions illustrates a second generality which is consistent with MO calculations. In general the strong absorption maximum of the electron-deficient cation is at shorter wavelength than that of the corresponding electron-rich carbanion. This is the relative magnitude of transition energies that would be expected on the basis of the effect of the charge on the effective electronegativities of the carbon cores.[13b] Using the ω technique[45] to compensate for the effect of charge on the effective electronegativities of the carbon cores, it is found that excess negative charge causes the bonding orbitals to be raised relative to the antibonding orbitals. Positive charge has the opposite effect; thus the direction of the difference in absorption maxima of cations and anions is also that expected on the basis of molecular orbital considerations.

The absorption spectra of the alkyldiphenylmethyllithium species are very sensitive to solvent in solvents of low dielectric constant,[43] but in solvent of higher dielectric constant, which solvate the lithium cation to give strongly solvated ion pairs, the spectra of the carbanions also show no change in the position of maximum absorption with changes in solvent. The lack of solvent dependence in the carbonium ion spectra indicates carbonium ions are so strongly solvated that there is little interaction between the cation and its anion.

Experimental Section

The preparation of the solutions of the stable carbonium ions discussed in this paper have all been described previously. Solutions of from 1 to 10^{-3} M have been used. In general, concentrations of 10^{-1} to 10^{-2} M were prepared. All spectra were run in short path length (0.2–0.015 cm) quartz absorption cells on a Cary 14 recording spectrometer. The cell compartment of the spectrometer was fitted with a variable temperature control unit cooled by a flow of nitrogen. A detailed description of this unit is being published elsewhere.[45] *

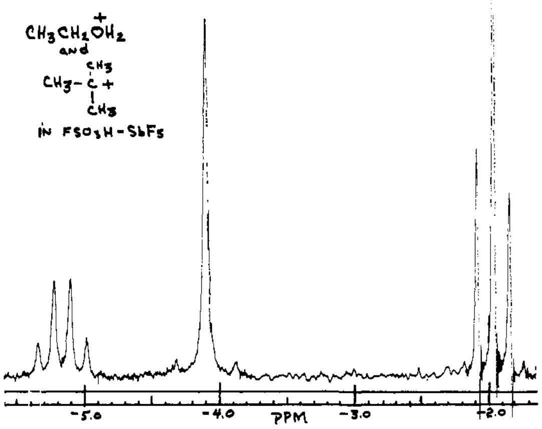


Figure 9.

Blank runs of each of the three acid systems used in the cell were first recorded. Concentrated H_2SO_4 and 30% oleum gave only a trace of end absorption at 210–220 mμ. The blank spectrum of FSO_3H-SbF_5 at −60° is given in Figure 1. Such blanks were run several times and shown to be reproducible.

Samples were prepared by accurately weighing ~0.01 to 0.04 g of the precursor alcohols (ketones, acids) on an analytical balance and then dissolving them in 0.5 ml of ethanol cooled to −78°. In a separate flask a 10% SbF_5–90% FSO_3H solution of measured volume (between 10 and 15 ml) was cooled to −78°. Then the ethanol solution of the precursor was added to the acid solution with rapid stirring. Samples were then introduced directly into the quartz cells which were precooled. In this manner the spectra of the carbonium ions were taken at low temperatures without being exposed to temperatures above −50°. A blank of ethanol (10^{-1} M) in SbF_5-FSO_3H exhibited no absorption maximum above 210 mμ. The ethanol dilution technique was also applied to samples run in concentrated H_2SO_4 and 30% oleum at room temperature.

By using small cell path lengths (*i.e.*, 0.2 cm or less) solutions of fairly high concentrations could be used. Spectra were reproducible and showed no change in the wavelength of maximum absorption or extinction coefficient varying the concentration from 10^{-3} to 1 M.

The spectra were immediately recorded and in all cases but one did not change with time. This was expected from previous nmr studies showing that the representative alcohols and ketones are immediately and quantitatively converted to carbonium ions. The one spectrum which did change with time was *p*-toluic acid in 30% oleum at room temperature. A slow growth of the absorption maximum of the *p*-toluoyl cation was found to match the known rate of formation of the *p*-toluoyl cation from previous nmr studies.[46]

Ethanol is frequently used as a solvent for dissolving carbonium ion precursors in strong acids since protonated ethanol has no ultraviolet absorption above 210 mμ. In order to unequivocally demonstrate that protonated ethanol does not interact with carbonium ions, nmr studies were performed. An example is the nmr spectrum of a solution of ethanol and *t*-butyl alcohol in SbF_5-FSO_3H at −60° (Figure 9). The spectrum shows clearly that the single sharp band of the *t*-butyl cation at −4.10 ppm coexists with the methyl triplet at −2.04 ppm and the methylene quartet at −5.23 ppm. Neat ethanol contains a triplet for the methyl protons at −1.83 ppm and the methylene octet at −3.20 ppm. The large downfield shift of the methylene protons and the moderate downfield shift of the methyl protons of ethanol in FSO_3H-SbF_5 indicate ethanol is protonated.

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[43] R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963).

[44] N. H. Velthorst and G. J. Hoijtink, *J. Am. Chem. Soc.*, **87**, 4529 (1965).

[45] R. Waack, M. Doran, and P. E. Stevenson, *ibid.*, in press.

[46] C. U. Pittman, Jr., unpublished results.