dimethylbutane,; the tertiary:primary hydrogen reactivity ratio was then determined by glpc analysis of the colorless solution which resulted (Table III).

N-Tritylpentanoamide. The procedure used is related to that for the synthesis of tritylamides.[26] A mixture of 8.3 g (0.1 mole) of Eastman valeronitrile, 12.0 g (0.046 mole) of Matheson triphenylcarbinol, 4.9 g (0.05 mole) of concentrated H_2SO_4, and 15 ml of dioxane was heated at 60° for 3 hr, cooled, and poured into 300 ml of ice-cold water. The precipitated solid was collected, boiled with hexane, and recrystallized twice from ethanol–water to give 5.4 g (32%) of N-tritylpentanoamide, mp 184.5–185.5°. The yield was even less when acetic acid or dibutyl ether was used as solvent.

Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.64; H, 7.33; N, 4.25.

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(26) J. A. Sanguigni and R. Levine, *J. Med. Chem.*, 7, 573 (1964).

The Spectral Properties of Alkoxymethyl Cations[1]

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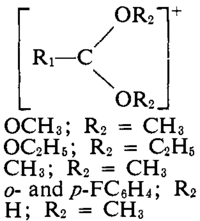
Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania. *Received February 11, 1966*

Abstract: The results of the first detailed nmr, infrared, and ultraviolet spectroscopic investigations of alkoxymethyl cations (alkoxycarbonium ions) are reported. These ions were studied as Meerwein fluoroborate salts or as generated in acid solutions from corresponding ortho esters or ketals. All of the results are consistent with near-coplanar structures for $(CH_3O)_3C^+$ (C_{3h} point group indicated), $(CH_3O)_2CCH_3^+$, and $(CH_3O)_2CH^+$, which may be regarded as resonance hybrids (C^+—$OCH_3 \leftrightarrow >C{=}O^+CH_3$). The $COCH_3$ bond is estimated to have 0.2–0.3 π bond order. An energy of activation for restricted rotation about this bond of 11 ± 4 kcal/mole has been obtained for $(CH_3O)_2CCH_3^+$. The proton nmr shielding of OCH_3 is shifted to lower fields by about 1.8 ppm on formation of the methoxymethyl cation from ortho ester or ketal. The precise value of this shift depends upon solvent and upon R_1 and R_2 of $CH_3OCR_1R_2^+$, as expected by considerations of delocalization of positive charge to oxygen. This investigation accords with earlier mass spectroscopic appearance potential studies and the results of Meerwein's alkoxy exchange reactions which indicate very large stabilization energies for alkoxymethyl cations. In spite of this high thermodynamic stability it has been noted that alkoxymethyl cations may be rapidly discharged by the following two general reactions: (a) $ROCR_1R_2^+ + H_2O \rightarrow O{=}CR_1R_2 + ROH + H^+$ and (b) $ROCR_1R_2^+ + N^\nu \rightarrow O{=}CR_1R_2 + RN^{\nu+1}$ (where N is a nucleophile of charge ν).

Alkoxymethyl cations have recently been found to possess large gaseous stabilization energies relative to the methyl cation.[3,4] For example, the stabilization energy of $CH_3OCH_2^+$ is 68 kcal compared to 35 kcal[3] for $CH_3CH_2^+$ and that for both $(CH_3O)_2CH^+$ and $(CH_3O)_3C^+$ is 92 kcal[4] compared to 74 kcal[5] for $(CH_3)_3C^+$.

The finding of large stabilization energy was in particular anticipated by the excellent investigations of Meerwein and his associates:[6] the fluoroborate salts of a number of alkoxymethyl cations were prepared and isolated; the transfer of OR between carbonium ions was established as a general reaction; the methoxy transfer reaction between equimolar methyl orthocarbonate and the trityl (triphenylmethyl) cation was shown to proceed with essentially complete formation of $^+C(OCH_3)_3$ ($(C_6H_5)_3C^+ + C(OCH_3)_4 \rightarrow C(OCH_3)_3^+ + (C_6H_5)_3COCH_3$), dramatically illustrating that the familiar trityl cation possesses less stabilization energy.

These facts based upon observations in both the vapor and condensed phases provide supporting explanation for the mechanistic evidence[7] that alkoxymethyl cations are formed as reaction intermediates in acid-catalyzed hydrolysis of acetals, ketals, and ortho esters without nucleophilic assistance. Supporting physical properties or structural evidence has been lacking for this interesting class of organic cation. In this study we have determined the ultraviolet, infrared, and nuclear magnetic resonance spectra for a representative series of alkoxymethyl cations. These spectral investigations have been made with the fluoroborate salts prepared by Meerwein's method *and* with the ions which we have found can be generated in H_2SO_4, 30% SO_3–H_2SO_4, and CF_3CO_2H solutions from corresponding ortho esters or ketals.



a, $R_1 = OCH_3$; $R_2 = CH_3$
b, $R_1 = OC_2H_5$; $R_2 = C_2H_5$
c, $R_1 = CH_3$; $R_2 = CH_3$
d, $R_1 =$ *o*- and *p*-FC_6H_4; $R_2 = CH_3$
e, $R_1 = H$; $R_2 = CH_3$
f, $R_1 = H$; $R_2 = C_2H_5$

In the case of c, the nmr spectra provide an approximate value for the activation energy for rotation about the CH_3O–C bond.

Experimental Section

Preparation of Starting Materials. Methyl Orthocarbonate. Methyl orthocarbonate was prepared by the addition of 1 mole of chloropicrin in methanol to 3.5 moles of sodium methoxide in sufficient methanol to effect solution. It is important that the

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(3) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965).

(4) R. H. Martin, F. W. Lampe, and R. W. Taft, *ibid.*, **88**, 1353 (1966).

(5) F. W. Lampe, private communication.

(6) (a) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960); (b) H. Meerwein, V. Hederick, H. Morschel, and K. Wunderlich, *ibid.*, **635**, 1 (1960).

(7) E. H. Cordes, *Progr. Phys. Org. Chem.*, in press.

methanol used be rigorously dry. It is recommended that the methanol be distilled from magnesium–magnesium methoxide just prior to use. The chloropicrin in methanol is added to the reaction mixture slowly with stirring. It is also important that the reaction temperature be maintained at about 50° by a water bath. If the temperature becomes too high, poor yields result; if the temperature is too low, excess chloropicrin will collect, which after a short time will lead to a violent and dangerous exothermic reaction. Two to three hours after addition of the chloropicrin is complete, the reaction is cooled in an ice bath and hexane is added (150–200 ml of hexane in a reaction designed to yield 20 g of product). The hexane–methanol slurry is transferred to separatory funnel and washed quickly, first several times with dilute sodium hydroxide solution, and finally with water. The hexane solution is dried as quickly as possible with barium oxide. The hexane is removed by distillation and the product is distilled slowly under dry nitrogen on a spinning-band column, bp 113–114°. If appreciable amounts of chloropicrin are found by vpc in the distillate, a second distillation from sodium methoxide may be necessary. The yield is 20–30%.

_p_-Fluorobenzophenone Dimethyl Ketal. The dimethyl ketal of *p*-fluorobenzophenone was prepared in two ways, first, by reaction for 3 days at room temperature of *p*-fluorobenzophenone with methyl orthoformate in anhydrous methanol containing a trace of *p*-toluenesulfonic acid as a catalyst. The product was isolated by extraction with hexane from a strongly basic solution of methanol and water, followed by vacuum distillation. The yield was poor.

A better synthesis was found in the reaction of *p*-fluorobenzophenone dichloride, $(p\text{-FC}_6H_4)_2CCl_2$, with 2 moles of sodium methoxide in methanol. After filtering off the sodium chloride and concentration of the methanol solution, the product crystallizes on cooling from the methanol liquor, mp 52°. The *p*-fluorobenzophenone dichloride is easily available from reaction of the ketone in benzene and carbon tetrachloride with phosphorus pentachloride.

Methyl _p_-Fluoroorthobenzoate. The methyl orthobenzoate ester of *p*-fluorobenzoic acid was prepared by the addition of the *p*-fluorobenzotrichloride to a refluxing solution of 3.2 moles of sodium methoxide in methanol. The product was isolated by filtering off the sodium chloride and vacuum distillation on the spinning-band column at 20 mm, bp 106–107° (20 mm).

_p_-Fluorobenzotrichloride. Chlorine was passed into 70 g of refluxing *p*-fluorotoluene and irradiated with a sun lamp until a reflux temperature of 210° had been reached. The product was then distilled on the spinning-band column, bp 97–98° (19 mm), yielding 50 g. If the reaction is interrupted at a reflux temperature of 190°, the product isolated is *p*-fluorobenzal chloride, bp 91–92° (19 mm).

Ethyl Carbonate–Boron Trifluoride Complex. Since diethyl ether is apparently a stronger base than ethyl carbonate, the BF_3 complex of ethyl carbonate cannot be prepared in ether or with boron trifluoride etherate. Passage of BF_3 into a pentane solution of ethyl carbonate however, yields a copious, white, crystalline precipitate, $(EtO)_2C{=}O\ BF_3$, mp 91.5–92°. The boron trifluoride is removed from the complex under vacuum at 0.01 mm.

Alkoxymethyl Fluoroborates. The alkoxycarbonium ion fluoroborates were prepared from the corresponding ortho esters according to the procedure reported by Meerwein,[6] with the following precautions. The ortho esters were purified by distillation (under vacuum in the case of ethyl orthocarbonate) in dry nitrogen through a spinning-band column. A center cut was used in the preparation of the salt. Eastman purified, boron trifluoride etherate was redistilled under nitrogen immediately prior to use and the fraction boiling at 126° was used. The diethyl ether used was distilled prior to use under dry nitrogen from lithium aluminum hydride. The reaction was carried out in an all-glass, greaseless apparatus under a positive static pressure of dry nitrogen. At the end of the reaction the ether was removed through a filter stick with a positive pressure of nitrogen. The product was washed several times with copious quantities of ether, dried with a stream of warm dry nitrogen, and transferred to the vacuum lock of a nitrogen glove box, where it was vacuum dried for 24 hr. The product was then taken into the drybox.

The fluoroborate salts, except for trimethoxycarbonium fluoroborate, were recrystallized from methylene chloride. The following melting points were taken in sealed capillaries under nitrogen. Analysis gave the following results: $(CH_3O)_3C^+BF_4^-$, mp 184–185° (lit.[6] mp 138°) (*Anal.* Calcd: C, 25.02; H, 4.69. Found: C, 25.09; H, 4.56); $(EtO)_3C^+BF_4^-$, mp 126.5–127° (lit.[6] mp 118°) (*Anal.* Calcd: C, 35.9; H, 6.41; B, 4.62; F, 32.5. Found: C, 36.2; H, 6.67; B, 4.82; F, 31.7); $CH_3C(OCH_3)_2^+BF_4^-$, mp 115–115.5°; $p\text{-FC}_6H_4C(OMe)_2^+BF_4^-$, mp 99–100°.

Two attempts to prepare the salt of $(C_6H_5)(p\text{-FC}_6H_4)^+COCH_3$ by the addition of boron trifluoride etherate to the dimethyl ketal of *p*-fluorobenzophenone in ether were without success. No crystalline product separated from the reaction mixture even after cooling in an ice–water bath.

Sulfuric Acid Solutions of Alkoxymethyl Cations Generated from Ortho Ester or Ketal. The cations reported in Tables II–VIII were generated as stable ions in H_2SO_4 or 30% $SO_3 \cdot H_2SO_4$[8] by addition through a capillary of the appropriate ortho ester or ketal either neat or in carbon tetrachloride to partially frozen acid. During the addition, the solution is cooled by judicious immersion in a Dry Ice–acetone bath. Triethoxy-, trimethoxy-, and *p*-fluorophenyldimethoxymethyl cations could be generated in sulfuric acid in this manner. For methoxydimethyl-, dimethoxymethyl-, dimethoxy-, and diethoxymethyl cations it was necessary to use 30% $SO_3 \cdot H_2SO_4$ with the appropriate ketal or ortho ester. Although the dimethoxymethyl cation fluoroborate is stable in 96% sulfuric acid, attempts to generate the dialkoxymethyl cations in 96% sulfuric acid from ortho esters gave mostly the normal ester and the usual alkyl sulfate. Alkyl orthoformates in sulfuric acid decompose rapidly with CO evolution. In general, methoxymethyl cations were more cleanly generated in sulfuric or fuming sulfuric acid solutions than the corresponding ethoxymethyl cations, perhaps because of the side hydride transfer reactions in the latter.

Trifluoroacetic Acid Solutions of Alkoxymethyl Cations Generated from Ortho Esters. The trimethoxy- and triethoxymethyl cations are generated from the ortho ester upon addition to trifluoroacetic acid. The triethoxymethyl cation generated in this manner is stable for over 1 week at room temperature. The trimethoxymethyl cation, however, disappears slowly with the concurrent appearance of a new peak at −4.0 ppm, identified by the addition of methanol to trifluoroacetic acid as methyl trifluoroacetate, and a second peak identical in chemical shift with dimethyl carbonate. The decomposition is indicated to be due to trifluoroacetate ion. The trimethoxymethyl cation fluoroborate salt is quite stable (for over 1 week) in trifluoroacetic acid, in concentrations as great as 10%. On addition of sodium trifluoroacetate to solutions of $(CH_3O)_3C^+BF_4^-$ in trifluoroacetic acid, the carbonium ion decomposes to methyl trifluoroacetate and methyl carbonate.

Alkoxymethyl Cation Fluoroborate Solutions. Solutions of approximately 6% (volume) of these salts in various solvents (used for nmr measurements) were in general stable with the exception of $(CH_3O)_3C^+BF_4^-$ in acetonitrile. A reaction occurs over a period of several hours producing dimethyl carbonate and a species whose nmr spectrum is consistent with the formation of $CH_3C{\equiv}NCH_3^+$.

Procedures. Cryoscopic Measurements. Sulfuric acid (96 wt %) was adjusted to an approximate freezing point of 10.10°. Two hundred milliliters (387 g) of this sulfuric acid were pipetted into a jacketed freezing-point cell using a calibrated, 100-ml pipet. The cell consisted of a closed vessel with entry sleeves for thermometer, a coiled "up–down" stirrer, and dry N_2 and sample ports. After 0.5 day with stirring, the freezing point of the acid was determined by a cooling curve, a typical value being 10.17°.

To partially frozen sulfuric acid was then added 4.55 g of ethyl orthocarbonate of 99% purity by means of a calibrated pipet. A freezing-point depression constant of 6.25, as suggested by Wyatt,[9] from freezing-point depressions of $(NH_4)_2SO_4$ and K_2SO_4 (mp 10°), was used. Calculated "*i*" factors of 5.2 and 5.1 were obtained from the cooling curves (ΔT_f = 1.99–2.03°).

Nuclear Magnetic Resonance Measurements. Approximately 6% fluoroborate salt solutions for nmr were prepared under dry nitrogen and run in sealed tubes. Hydrogen nmr spectra were obtained with Varian A-60. The reference for sulfuric acid solutions was external pure tetramethylsilane (TMS). The spectrometer was calibrated between TMS and chloroform. In solvents other than sulfuric acids, internal TMS was used as a reference.

F nmr spectra were measured by the side-band technique relative to tetrafluorotetrachlorocyclobutane (TFTCCB) either as an internal standard or, where sulfuric acid was the solvent, as an external standard in carbon tetrachloride.[10]

Low-temperature measurements were made using the standard Varian variable-temperature probe for the A-60. In the instance where rate measurements were being made on $CH_3C^+(OCH_3)_2$, the

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[8] N. C. Deno, *Progr. Phys. Org. Chem.*, **4**, 161 (1964).

[9] P. Wyatt, *J. Chem. Soc.*, 1175 (1953).

[10] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).

temperature inside the probe was checked before and after each measurement with a small thermometer of the type commonly found on a Nester and Faust spinning-band column. The variation in the nitrogen flow temperature was 0.2° or less.

Infrared Spectra. Infrared spectra of trimethoxymethyl fluoroborate were taken in Nujol mull, hexachlorobutadiene mull, as a film on KBr, and in methylene chloride solution. No gross differences were observed in the carbonium ion spectrum between these methods. A film deposited from methylene chloride (on potassium bromide salt plates) gave the best results for the trimethoxymethyl fluoroborate. Excellent spectra for the triethoxymethyl fluoroborate were obtained in methylene choride and in acetonitrile using a 0.1-mm path potassium bromide cell. Spectra of triethoxymethyl fluoroborate films in KBr were somewhat less satisfying due to a tendency to crystallize; however, these were used to cover regions obscured by the methylene chloride and acetonitrile. The spectrum of ethyl orthocarbonate was also obtained in sulfuric and in trifluoroacetic acid films between salt plates protected by polyethylene film. The latter spectra agreed with those of the carbonium ion fluoroborate and ethanol in the same solvents. The spectral results are summarized in Table I.

Table I. Infrared Frequencies for Trimethoxymethyl and Triethoxymethyl Cation Fluoroborates[a]

$(CH_3O)_3C^+BF_4^-$/film		$(EtO)_3C^+ BF_4^-$/ CH_2Cl_2 and CH_3CN	
Frequency, cm^{-1}	Assignment for C_{3h} sym	Frequency, cm^{-1}	Assignment (no sym)
1710 (w)		1550 (s)	CH_2 deform.
1675 (w)	BF_4^- $\nu_3 + \nu_4$ Td sym	1450 (s)	CH_3 asym bend (deform.)
1575 (s)	CH_3 asym bend (deform.)	1435 (s)	
1560 (sh)		1380 (s)	CH_3 sym bend
1525 (sh)		1340 (s)	Asym stretch
1380 (s)	ν_{20} asym stretch	1030 (s)	BF_4^-
1030 (s)	ν_3 BF_4^- Td sym	990 (ms)	Et–O stretch
960 (s)	ν_{21} CH_3–O stretch	890	CH_3CH_2
755 (ms)	ν_{12} out-of-plane bend	755 (ms)	Out-of-plane bend
600 (s)	ν_{22} in-plane bend	602 (s)	In-plane bend
525 + 537	ν_4 BF_4^-Td sym	575 (s)	In-plane bend
		525 (s)	BF_4^-

[a] sh = shoulder, s = strong, ms = medium strong, w = weak.

Spectra of the carbonium ion fluoroborates, $CH_3C^+(OCH_3)_2$ and p-$FC_6H_4C^+(OCH_3)_2$, were taken in dry methylene chloride and as films on potassium bromide. The following absorptions were observed: ($CH_3C^+(OCH_3)_2$ as a film) 3000 (s, br), 1600 (s), 1525 (s), 1430 (m), 1420 (m), 1400 (s), 1370 (sh), 1000–1100 (br, s), 990 (sh, s), 930 (s), 850 (s), 800 (m), 780 (m), 610 (s), 595 (s), 537 (m), 525 (m), and 475 (m) cm^{-1}; (p-$FC_6H_4C^+(OCH_3)_2$ in CH_2Cl_2) 1580 (s), 1540 (s), 1460 (s), 1390 (s), 1540 (s), 1460 (s), 1390 (s), 1380 (m, sh), 1155 (m), 1000–1100 (br, s), 980 (msh), 842 (m), 612 (m), 600 (s), and 525 (m) cm^{-1}.

Potassium bromide pellets of $(CH_3O)_3C^+BF_4^-$ invariably resulted in the appearance of the spectrum of methyl carbonate in spite of the most rigorous attempts to dry the potassium bromide used, and to protect the sample from water. Harshaw analytical grade potassium bromide freshly opened was given additional drying. The sample was ground and loaded into the pellet press in the drybox. The pellet was prepared in such a way that the faces of the pellet contained only pure potassium bromide. In view of these precautions to exclude water, it is felt that the formation of methyl carbonate is due to methylation of the bromide ion by the cation, probably at the time the potassium bromide sinters and flows. Such reactions are known in the exchange of ligands or inorganic ions[11] in pressing potassium bromide pellets.

A difference was observed in the spectrum of the fluoroborate ion depending on the phase. In films and potassium bromide, the fluoroborate ion shows a doublet in the region of 525 cm^{-1} which has been attributed to isotope doubling.[12] In methylene chloride solution, however, this doublet is replaced by a single sharp peak at 525 cm^{-1}.

Solutions, films, and mulls were prepared in a nitrogen-filled glove box. The methylene chloride was dried in the drybox with molecular sieve or transferred from phosphorus pentoxide into a sealed ampoule on a vacuum line. Spectra to 625 cm^{-1} were recorded on a Beckman IR-8; the potassium bromide region was recorded by a Perkin-Elmer Infracord Model 137, with potassium bromide optics.

The criterion used for an acceptable spectrum was the absence of the carbonyl band of the normal ester (for example, $CH_3OC(O)OCH_3$ in the case of $(CH_3O)_3C^+$).

Ultraviolet Spectra. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer after flushing the spectrophotometer with dry nitrogen. Samples were run in both 1.0- and 0.1-cm path-length cells.

Ultraviolet spectra of the triethoxymethyl fluoroborate were taken in acetonitrile distilled from phosphorous pentoxide followed by distillation on a vacuum line from trityl fluoroborate. Spectra of the triethoxycarbonium ion, from the ortho ester, were also taken using water-white sulfuric acid. No spectral transition in the ultraviolet of molar extinction coefficient greater than 10 was found at wavelengths longer than 1900 A. If special care is *not* taken to cool the sulfuric acid and to add the ortho ester slowly, decomposition takes place with the formation of products which absorb in the 2100–2200-A region of the ultraviolet.

Ultraviolet spectra of the $CH_3C^+(OCH_3)_2BF_4^-$ in methylene chloride and water-white, 96% sulfuric acid were also notable only for the lack of any absorption of extinction coefficient >10 above 1900 A.

The p-$FC_6H_4C^+(OCH_3)_2BF_4^-$ ion in methylene chloride exhibits a transition at 2640 A (ϵ 4.2 × 10^3). This is sufficiently close to that of p-$C_6H_4CO_2H$ however to make the carbonium ion spectrum suspect. The experimental difficulty lies in the fact that in the dilute solution solution (10^{-3} M) required to obtain the spectrum, it is difficult to reduce contamination by water to this level.

Raman Spectra. Preliminary Raman spectra of the trialkoxymethyl fluoroborates were run in methylene chloride and trifluoroacetic acid without the desired success. The major problem aside from the usual ones of light scattering, etc., is that the fluoroborate ion itself obscures a good deal of the region of interest. It was also found, that unless recrystallized salts were used, solutions turned yellow and a gas was evolved when the sample was placed in the spectrophotometer. An attempt to add $(EtO)_4C$ to trifluoroacetic acid in sufficient concentration to make the $(C_2H_5O)_3C^+$ observable failed due to formation of $(EtO)_2C{=}O$ and CF_3CO_2Et. Raman lines, however, were observed at 340, 990, 1100, and 1464 cm^{-1} for $(EtO)_3C^+$ BF_4^- salt. Literature values[12] for the fluoroborate ion Raman lines are 353 (w) 769 (s), and 984–1016 cm^{-1}.

Results and Discussion

Nmr Spectra. In sulfuric acid at room temperatures trialkoxycarbonium ions $(RO)_3C^+$ exist as stable ions. Solutions may be prepared by addition of the fluoroborate salts or by generation from the ortho ester according to the reaction

$$(RO)_4C + 2H_2SO_4 \longrightarrow (RO)_3C^+ + ROSO_3H + H_3O^+ + 2HSO_4^- \quad (1)$$

Reaction 1 is indicated by the following freezing-point depression experiment. Ethyl orthocarbonate (0.07 m) in H_2SO_4 (mp 10.1°) gives an "i" factor of 5.1 ± 0.1. The room temperature proton nmr spectra of solutions of $(RO)_4C$ (prepared by slow addition to cold sulfuric acid) confirm reaction 1. The integrated absorption intensities (of C–H resonances) agree with the ratio predicted by eq 1. Further, the positions of the signals for these solutions correspond to a composite of the spectra of solutions of the Meerwein salt, $(RO)_3C^+BF_4^-$, and of ROH in sulfuric acid. The spectrum of $(CH_3O)_3C^+$, as expected, consists of a single, sharp peak and that for $(C_2H_5O)_3C^+$ of a simple triplet–quartet. The positions of resonance for all of the ions Ia–d are recorded in Tables II–VIII.

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(11) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

(12) N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

Table II. F Nmr Shielding in *p*-Fluoro-Substituted Phenylmethoxymethyl Cations in H_2SO_4

Ion	δ, ppm[a]
$p\text{-}FC_6H_4C(C_6H_5)_2^{+\,b}$	−30.0
$p\text{-}FC_6H_4C(C_6H_5)(OCH_3)^{+\,c}$	−27.2
$p\text{-}FC_6H_4C(OCH_3)_2^{+\,d}$	−20.2

[a] Relative to external tetrachlorotetrafluorocyclobutane, 40% (wt) in CCl_4. [b] Generated from $(p\text{-}FC_6H_4)(C_6H_5)_2COH$. [c] Generated from $(p\text{-}FC_6H_4)(C_6H_5)C(OCH_3)_2$. [d] Generated from BF_4^- salt in H_2SO_4.

Table III. H Nmr Shielding of Methoxy Group in Methoxymethyl and Related Cations

Ion	δ, ppm[a]	Solvent
$(CH_3O)_2C(o\text{-}FC_6H_4)^+$	4.83	H_2SO_4
$(CH_3O)_2C(OH)^+$	4.9	H_2SO_4
$(CH_3O)_2C(CH_3)^+$	4.95	30% $SO_3\cdot H_2SO_4$
$(CH_3O)_3C^+$	5.0–5.1	H_2SO_4
$(CH_3O)_2CH^+$	5.20	30% $SO_3\cdot H_2SO_4$
$(CH_3O)C(CH_3)_2^+$	5.3	30% $SO_3\cdot H_2SO_4$
$(CH_3O)C(p\text{-}FC_6H_4)\text{-}(C_6H_5)^+$	5.3	H_2SO_4

[a] External TMS reference.

Table IV. H Nmr Shielding of Ethoxy Group in Ethoxymethyl and Related Cations[a]

Ion	δ(CH_2), ppm[b]	δ(CH_3), ppm[b]	Solvent
$(C_2H_5)_2OH^+$	5.2	2.3	H_2SO_4
$(C_2H_5O)_3C^+$	5.4–5.5	2.1–2.3	H_2SO_4
$(C_2H_5O)_2C(OH)^+$	5.5	2.23	H_2SO_4
$(C_2H_5O)_2CH^+$	5.6	2.09	30% $SO_3\cdot H_2SO_4$

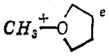
[a] $J_{HH} = 7 \pm$ cps. [b] External TMS reference.

Table V. H Nmr Shielding of Triethoxymethyl and Related Compounds in $DCCl_3$[a]

Substance	δ(CH_2), ppm[b]	δ(CH_3), ppm[b]
$(C_2H_5)_2OBF_3$	4.17	1.34
$(C_2H_5O)_2COBF_3$	4.52	1.43
$(C_2H_5)_3O^+BF_4^-$	4.77	1.42
$(C_2H_5O)_3C^+BF_4^-$	4.79	1.50

[a] $J_{HH} = 7 \pm 1$ cps. [b] Internal TMS reference.

Table VI. H Nmr Shielding of Methyl and Formyl Protons in Methoxymethyl and Related Cations

Ion	δ, ppm	Solvent
$CH_3C(OCH_3)_2^+$	3.2[a]	30% $SO_3\cdot H_2SO_4$
$(CH_3)_2C(OCH_3)^+$	3.4[a]	30% $SO_3\cdot H_2SO_4$
$CH_3C^+{=}O^c$	4.2[b]	SO_2
$(CH_3)_3C^{+\,d}$	4.35[a]	SbF_5
 [e]	4.43[b]	TFAA
$HC(OCH_3)_2^+$	9.3[a]	30% $SO_3\cdot H_2SO_4$
$HC(OC_2H_5)_2^+$	9.4[a]	30% $SO_3\cdot H_2SO_4$
$HC(CH_3)_2^{+\,d}$	13.5	SbF_5

[a] External TMS reference. [b] Internal TMS reference. [c] G. Olah, *et al., J. Am. Chem. Soc.*, **84**, 2736 (1962); *ibid.*, **86**, 1361 (1964). [d] See ref 16. [e] P. Peterson, private communication.

Table VII. H Nmr Shielding of Trimethoxymethyl and Triethoxymethyl Cations in Organic Solvents[a]

Solvent	$(CH_3O)_3C^+$ δ, ppm[b]	$(C_2H_5O)_3C^+$ δ(CH_3), ppm[b]	δ(CH_3), ppm[b]
$C_6H_5NO_2$	...	5.1	-1.65
TFAA	4.50	4.90	1.62
CH_2Cl_2	4.47	...	...
$DCCl_3$	...	4.79	1.50
CH_3CN	4.26	4.70	1.50

[a] $J_{H-H} = 7 \pm 1$ cps. [b] Internal TMS reference.

Table VIII. Temperature Dependence of Nmr Spectral Shifts for $CH_3C(OCH_3)_2{}^+BF_4^-$ in Trifluoroacetic Acid

T, °K	$\delta^{CH_3O}_{\text{separation}}$, cps at 60 Mc	k, sec^{-1}
287	0	38
285	9.4	32
281	13.1	24
<259	17.1	..

The successive replacement of C_6H_5 groups in the $p\text{-}FC_6H_4C(C_6H_5)_2^+$ ion by OCH_3 groups leads to increased (aromatic) F nmr shielding (Table II). The increase corresponds to increased π electron charge density at the fluorine (and its bonded carbon) atom.[13] The increase also gives the order of increasing cation stabilization energy suggested by the relationship of Taft and McKeever[14] and by the results of Martin, *et al.*[3,4] This order of stabilization energies accords with the results of Meerwein,[6] namely, that the following reaction occurs to essential completion.

$$(C_6H_5)_3C^+ + C(OCH_3)_4 \longrightarrow {}^+C(OCH_3)_3 + (C_6H_5)_3COCH_3 \quad (2)$$

Since the conditions of Meerwein's reaction were heterogeneous, we have confirmed the observation under homogeneous conditions. One equivalent of methyl orthocarbonate was added to a solution of trityl fluoroborate in carefully dried acetonitrile. Reaction 2 occurs very rapidly and goes to essential completion without formation of a precipitate. Both products were identified by their nmr spectra.

The alkoxymethyl cations are also generated in trifluoroacetic acid solutions from the ortho ester. The results in this solvent are given in Tables VI and VII. Although the alkoxymethyl cations have large stabilization energies, they are readily discharged by the following two general modes of reaction (eq 3 and 4).

$$(RO)_3C^+ + H_2O = (RO)_2C{=}O + H^+ + ROH \quad (3)$$

$$(RO)_3C^+ + N^\nu = (RO)_2C{=}O + RN^{\nu+1} \text{ (N is a nucleophile of charge } \nu) \quad (4)$$

The lifetime of alkoxymethyl cations generated in trifluoroacetic acid from the ortho ester is limited by reaction 4 involving the trifluoroacetate ion which is also generated. Reaction 4 has also apparently been observed ($N^\nu = Br^-$) in pressing KBr pellets of the Meerwein salts, since the spectrum obtained corresponds to the products of reaction 4. Reaction 4, as expected of a nucleophilic displacement, occurs at a substantially faster rate for R = CH_3 than R = C_2H_5. Thus room temperature solutions of $(CH_3O)_3C^+BF_4^-$ in acetonitrile decompose quite readily whereas $(C_2H_5O)_3C^+BF_4^-$ is stable for moderate periods in acetonitrile at room temperatures (*cf.* the Experimental Section for additional details).

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(13) *Cf.* R. W. Taft, *et al., J. Am. Chem. Soc.*, **85**, 3146 (1963).
(14) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965).

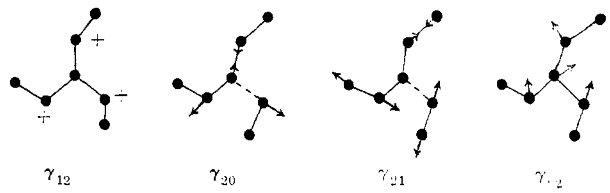


Figure 1.

The shielding of the OCH_3 and OC_2H_5 hydrogens in the alkoxymethyl cations, $CH_3OCR_1R_2^+$ and $C_2H_5OCR_1R_2^+$, generally reflect the result expected on a charge density basis.[15] With decreasing electron release from R_1 and R_2 the resonance occurs at lower field strength (*cf.* Tables III and IV). It is also to be noted that the shielding in the alkoxymethyl cations corresponds very closely to that in similar cations. For example, compare $(CH_3O)_3C^+$ and $(CH_3O)_2COH^+$ (Table III); $(C_2H_5O)_3C^+$, $(C_2H_5O)_2COH^+$, $(C_2H_5)_3O^+$, and $(C_2H_5)_2OH^+$ (Tables IV and V). The shielding of methyl and formyl protons in alkoxymethyl and related cations show similar trends (Table V). Table VII illustrates that the shieldings are solvent sensitive. The shifts to higher field in CH_3CN solution suggest that a weak Lewis acid–base interaction occurs between the cation and this solvent.

The greater downfield shift, 5.0 ppm in sulfuric acid, of the trimethoxymethyl cation as compared to 4.35 ppm for the *t*-butyl cation may seem somewhat surprising.[16] However, comparison with methyl orthocarbonate, reveals that $(\mathit{CH}_3O)_3C^+$ is about 1.8 ppm additionally downfield. Similar comparison finds the $(CH_3)_3C^+$ of the order of 2.3 ppm downfield from the usual methyl attached to an sp^2 carbon in a double bond.

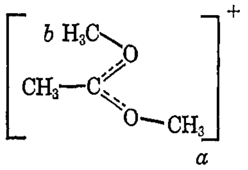
The proton nmr spectra of the alkoxymethyl cations is temperature dependent. Compared to room-temperature spectra, $(C_2H_5O)_3C^+BF_4^-$ in $DCCl_3$ at −60° gives a line broadening of the ethyl quartet and triplet by a factor of approximately 2. Resolution into more than one ethyl signal was not achieved. However, the CH_3O and $\mathit{CH}_3\mathit{CH}_2O$ signals of $(CH_3O)_2CH^+$ and $(C_2H_5O)_2CH^+$ are very broad at room temperatures, but may be "sharpened up" by slightly warming the sample. The signal for the former is very nearly resolved into two peaks at room temperature. With $(CH_3O)_2CCH_3^+$ in trifluoroacetic acid solution resolution into two CH_3O peaks of equal intensity was observed below 14° and the temperature dependence was evaluated from 259 to 287°K (Table VIII). The values of the rate constants for restricted C–OCH_3 rotation were obtained from the equations[17]

$$k = \frac{1}{\tau} = \pi\left(\frac{(17.1)^2 - \delta^2}{2}\right)^{1/2}$$

and at coalesence (287°)

$$k = \frac{(17.1)\pi}{\sqrt{2}}$$

The activation energy for restricted rotation obtained from the data of Table VIII is 11 ± 4 kcal/mole (ΔF^* = 15 kcal/mole). The source of uncertainty in the figure arises from the uncertainty in temperature, for it is to be noted that the shift separation is very favorable for precise work. Since the two CH_3O peaks are of equal intensity we believe the following structure is the only important rotational isomer present. The



low-field CH_3O may be ascribed to *b* and the high field to *a* by analogy with the results of Hammond and Neuman for the $CH_3C(NHCH_3)_2^+$ ion. The activation energy for restricted rotation (11 ± 4 kcal) compares favorably with similar rotational activation energies of 9–25 kcal/mole[18] for $CH_3C(NHCH_3)_2^+$ and 12–24 kcal/mole[19] for $CH_3C(O)N(CH_3)_2$. The observations with $HC(OCH_3)_2^+$ noted above suggest a larger activation energy for restricted rotation in this cation than in $CH_3C(OCH_3)_2^+$.

Infrared Spectra. It is expected that the infrared spectrum of trimethoxymethyl fluoroborate will bear a strong resemblance to that of methyl borate,[20] and to a lesser extent to that of the carbonate ion. The fundamental vibrations (based on an assumed C_{3h} symmetry) which should be found in the infrared spectrum are depicted in Figure 1, excluding carbon–hydrogen fundamentals.

The absorptions found in the spectrum of trimethoxycarbonium fluoroborate at 525, 537, 1030, and 1675 cm^{-1} may be unambiguously assigned to the fluoroborate anion.[12]

In Table IX below are assignments which have been made for some fundamentals of isoelectronic ions and molecules of similar symmetry.[21]

Table IX[a]

	Asym stretch	Out-of-plane bend	In-plane bend
CO_3^-	1450–1440	880–860	700
NO_3^-	1380–1350	840–815	720
$(CH_3O)_3B$	1355	662	525
$(CH_3O)_3C^+$	1380	755	600
$CH_3CO_2^-$	1560		
CH_3NO_2	1580		

[a] Values in cm^{-1}.

The assignment of the trimethoxymethyl cation absorptions (Tables I and IX) at 600 cm^{-1} to the ν_{22} and ν_{12} out-of-plane and in-plane bending modes, respectively, is based upon the analogies given in Table IX. The strong band at 960 cm^{-1} is assigned (Table I) to ν_{21}, the methyl carbon–oxygen stretch. The carbon–

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(15) G. Fraenkel, *et al.*, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(16) G. Olah, *et al.*, *ibid.*, **85**, 1328 (1963).

(17) 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, pp 222–224.

(18) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655 (1963).

(19) (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965).

(20) R. Servoss and H. Clark, *J. Chem. Phys.*, **26**, 1179 (1957).

(21) (a) G. Hertzberg, "Infrared and Raman Spectra," P. Van Nostrand Co., New York, N. Y., 1945; (b) L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963.

oxygen stretch is found also at 960 cm^{-1} in methyl carbonate.

The assignment (Tables I and IX) of the asymmetric stretching mode ν_{20} to the 1380-cm^{-1} absorption is based upon the following argument. The C–O bond of CO_3^{2-} is expected to have greater double-bond character than that of $C\text{–}(OCH_3)_3^+$, for example, because of the greater $-\sigma_R$ value of the O^- than the OCH_3 group.[22] Consequently, the ν_{20} mode is expected (as assigned) at a lower frequency for the latter than the former ion. The assignment is supported by the fact (Table I) that $CH_3C(OCH_3)_2^+$ and p-$FC_6H_4C(OCH_3)_2^+$ ions, which are expected to have a C–O bond with somewhat more double-bond character than that of $C\text{–}(OCH_3)_3^+$, give absorptions at slightly higher frequencies (1400 and 1390 cm^{-1}, respectively), whereas the corresponding absorptions in the 1575-cm^{-1} region are shifted to lower frequencies (1525 and 1540 cm^{-1}, respectively). Using $CH_3CO_2^-$ as a model for $\mathrm{C}\overset{\cdots}{\text{---}}\mathrm{O}$ with $\sim$0.5 π bond order and CO_3^{2-} as a model for $\mathrm{C}\overset{\cdots}{\text{---}}\mathrm{O}$ with -0.33 π bond order,[23] our assignment indicates that the above alkoxymethyl cations have $\mathrm{C}\overset{\cdots}{\text{---}}\mathrm{O}$ π bond order in the range of 0.2–0.3.

The absorption at 1575 cm^{-1} is assigned (Table I) to the asymmetric methyl bending mode by analogy with the very strong absorption found for this mode in methyl borate.[24] The absorptions at 1525, 1560, and 1710 cm^{-1} (Table I) are unassigned but are probably combination and/or overtone absorptions. We may speculate on the basis of the methyl borate analogy regarding the Raman-active totally symmetric stretching vibration, ν_6. The ν_6 mode occurs at 726 cm^{-1} in $(CH_3O)_3B$ and 1050 cm^{-1} in CO_2^{2-}. Methyl borate exhibits a medium intensity combination band between ν_6 and ν_{22}. Assuming that the most intense combination band of the $(CH_3O)_3C^+$ ion would be of the same symmetry leads to the apparently reasonable estimate of $\nu_6 = 925\text{–}960$ cm^{-1} for this ion.

The arguments presented above for the $(CH_3O)_3C^+$ have been extended, with reservations about C_{3h} symmetry, to make the partial assignments listed in Table I for $(C_2H_5O)_3C^+$. Colthop[25] reports a trend to higher frequency in the carbon–oxygen stretch in going from methyl to higher homologs. Such a trend is observed in the alkyl borates.[26] Therefore the strong band at 990 cm^{-1} is attributed to the ethyl carbon–oxygen stretch. The 890-cm^{-1} band corresponds to the appearance of a similar band found in going from the methyl to ethyl in ethers, carbonates, and formates.

The observation that in films of trimethoxymethyl fluoroborate the carbon–hydrogen stretch expected in the region of 2900 cm^{-1} is extremely weak is worthy of note. Klingensmith and Arnett have made the same observation in the spectra of films of the trianisylcarbonium ion, although in solutions of deuteriochloroform the carbon–hydrogen stretch did appear as weak bands.[27] Francis[28] has noted that the intensity of carbon–hydrogen stretch *decreases* in going from paraffins to esters whereas the intensity of carbon–hydrogen deformations *increases*.

Ultraviolet Spectra. The ultraviolet spectra of the alkoxymethyl cations either as fluoroborate salts or as generated in sulfuric acid from ortho esters exhibited no allowed transitions above 2000 A. Although methyl borate has no allowed ultraviolet transition above 2000 A, esters of alkylboric and alkylboronic acids evidently do have intense ultraviolet absorptions in the 2400–2600-A region of the spectrum. These highly allowed transitions in the near-ultraviolet spectrum of RB–OR or $RB(OR)_2$ may be represented as a charge transfer from oxygen to boron or a $\pi \rightarrow \pi^*$ transition.[29] The carbonate ion exhibits a low intensity absorption near 2100 A, probably $n \rightarrow \pi^*$. Edward[30] has reported the ultraviolet spectra of R_2C^+OH and of $CH_3CH_2C^+(OH)_2$, $\lambda_{max} < 190$ mμ, an observation which is in obvious accord with those given above.

The present results offer no conflict with the notion that configuration interaction of the states $^+C\text{—}O$ and $C{=}O^+$ is expected to shift the transition energy to the blue in the methoxymethyl cation compared to methyl borate.

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[22] R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

[23] L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1944, Chapter VI.

[24] Although the assignment of 1575 cm^{-1} to CH_3 deformation places the band some 90–100 cm^{-1} out of the region usually assigned (see Table VI, footnote *c*), the assignment is in keeping with observed increases in C–H deformation frequencies with increasing electronegativity of X in CH_3X: *cf.* W. L. Jolly, *J. Am. Chem. Soc.*, **85**, 3083 (1963).

[25] W. Colthop, *J. Opt. Soc. Am.*, **40**, 397 (1950).

[26] R. L. Werner and K. O'Brien, *Australian J. Chem.*, **8**, 355 (1955).

[27] G. B. Klingensmith and E. M. Arnett, private communication.

[28] S. Francis, *J. Chem. Phys.*, **19**, 942 (1961).

[29] B. G. Ramsey and J. E. Leffler, *J. Phys. Chem.*, **67**, 2242 (1963).

[30] J. T. Edward and I. C. Wang, *Can. J. Chem.*, **40**, 966 (1962); H. J. Campbell and J. T. Edward, *ibid.*, **38**, 2109 (1960).