Organic and Biological Chemistry

Stable Carbonium Ions. LXXIX.[1] ^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopic Investigation of Hydroxy- and Alkoxycarbonium Ions. Determination of the Magnitude and Sign of the Geminal Coupling Constants

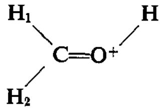
Anthony M. White[2] and George A. Olah

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 30, 1968*

Abstract: An nmr study of ^{13}C-enriched hydroxycarbonium ions (protonated formaldehyde) is reported. Homonuclear and heteronuclear double-resonance techniques were used to determine the relative signs of the geminal and vicinal coupling constants. A geminal coupling constant of +21.7 Hz was found and both vicinal coupling constants were found to be positive. Similar values of the geminal coupling constants were found in the methoxycarbonium ion and the chloromethoxycarbonium ion. The allylic coupling constants in the alkoxycarbonium ions were also determined, the *trans*-allylic coupling being greater than the *cis*. The results are discussed in terms of comparisons with related uncharged compounds. The question of the assignment of the isomers of protonated methyl formate is also discussed.

Considerable interest centers on the protonation of carbonyl groups under strong acid conditions, in which exchange of the added proton is slowed sufficiently to permit its observation by nmr spectroscopy.[3] In the majority of protonated carbonyl compounds studied, hindered rotation about the C–O bond has been observed on the nmr time scale at low temperature.[3]

The simplest system that has been studied which exhibits this behavior is hydroxycarbonium ion (protonated formaldehyde) itself (**1**). This ion has been generated from methylene chloride in fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution and its nmr spectrum, at −60°, shows a chemical-shift difference between the protons in the methylene group.[4] The hydroxycarbonium ion (**1**) is isoelectronic with ethylene and this analogy was used to assign the protons H_1 and H_2. The two vicinal coupling constants of 21.1 and 8.7 Hz were taken to indicate a *trans* and *cis* relationship of H_1 and H_2 to H_3. This analogy with isoelectronic uncharged systems has been used in assignment of a number of other protonated carbonyl compounds including protonated aldehydes[4–6] and protonated carboxylic acids.[6–8]



1

A second feature of protonated formaldehyde is the magnitude of the geminal coupling constant (22.2 Hz).[4] No determination of the sign of this coupling constant or of the signs of coupling constants in any related carbonium ions has been reported.

In connection with a study of ^{13}C chemical shifts in carbonium ions,[9,10] the nmr spectrum of protonated formaldehyde with a 50% ^{13}C-enrichment was studied. In view of the fundamental nature of this carbonium ion we have made a detailed study of its nmr spectrum and now report the results of this analysis together with the results of homonuclear and heteronuclear double irradiation experiments which give the signs of the vicinal and geminal coupling constants relative to that of the direct ^{13}C–H coupling constant. A reinvestigation of the closely related methoxycarbonium and chloromethoxycarbonium ions at 100 MHz is also reported, the nmr spectra of which, at 60 MHz, did not allow determination of the geminal or allylic coupling constants due to an insufficient chemical-shift difference between the geminal protons.[11]

Results

Hydroxycarbonium Ion (Protonated Formaldehyde). The nmr spectrum of ion **1**, 50% enriched in ^{13}C, consists, at −60°, of an ABX spectrum due to the ^{12}C species and an ABMX spectrum[12] due to the ^{13}C species (Figures 1 and 2). The proton spectrum of the ^{13}C species is a superimposition of two ABM spectra, one for each value of the ^{13}C (X) spin number.[13] Since

---

[1] Part LXXVIII: L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968).

[2] National Institutes of Health Postdoctoral Research Investigator, 1966–1968.

[3] See earlier papers in this series and G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

[4] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967).

[5] M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967).

[6] H. Hogeveen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 696 (1967).

[7] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 3591 (1967).

[8] H. Hogeveen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 809 (1967).

[9] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967).

[10] G. A. Olah and A. M. White, *ibid.*, **90**, 1884 (1968).

[11] G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 2993 (1967).

[12] H_1 is designated as A, H_2 as B, H_3 as M, and the ^{13}C as X (see **1**).

[13] J. A. Pople and T. Schaefer, *Mol. Phys.*, **3**, 547 (1960).

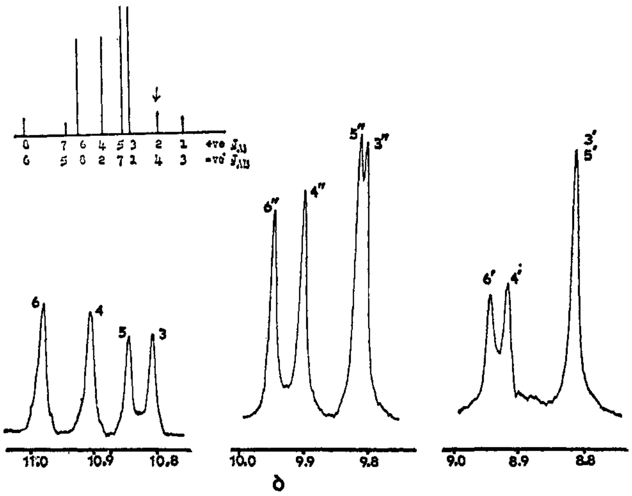


Figure 1. The AB part of the 100-MHz spectrum of hydroxycarbonium ion (**1**). Peaks due to the acid solvent system have been omitted as have the small outer transitions in each of the three AB subspectra. Lines 3'', 4'', 5'', 6'' are due to the ^{12}C species and 3, 4, 5, 6 and 3', 4', 5', 6' to the ^{13}C species. The assignment of transitions is based on positive values for J_{12}, J_{13}, and J_{23} and the numbering of transitions is that used in ref 16. The M part of the spectrum is shown in Figure 2A. The inset shows diagrammatically the low-field AB subspectrum together with the two assignments of transitions for J_{12} positive and J_{12} negative. The position of the irradiating frequency which gave the M spectrum shown in Figure 2C is indicated by the arrow.

J_{CH_1} and J_{CH_2} differ by 11.4 Hz, the two AB subspectra are not identical. J_{COH_3} is of sufficient magnitude to enable identification of the separate M spectra corresponding to the two ^{13}C spin states. Analysis of these ABM subspectra gave directly the coupling constants J_{13}, J_{23}, and J_{12} and the values of ν_1, ν_2, and ν_3 from each of the subspectra gave J_{CH_1}, J_{CH_2}, and J_{COH_3}.

It was found that the low-field M subspectrum was associated with the high field AB subspectrum and thus J_{COH_3} is of opposite sign to the direct couplings J_{CH_1} and J_{CH_2}, the latter being both assumed to be positive.[14] In addition, analysis of the ABM spectrum showed that J_{13} and J_{12} have the same sign. To find the signs of J_{13} and J_{23} relative to the direct ^{13}C–H coupling constants, heteronuclear double irradiation of the ^{13}C nucleus was used.[15] Irradiation of the highest field doublet in the ^{13}C (X) spectrum (see Figure 3) collapsed lines 9 and 9' in the M part of the spectrum (Figure 2) showing that J_{13} and J_{23} have the same sign as J_{CH_1} and J_{CH_2} and are therefore positive. Similarly irradiation of the lowest field doublet collapsed line 12 and 12'. The sign of the remaining coupling constant J_{12}, was related to J_{13} and J_{23} by the spin-tickling method.[15] The two possible assignments of transitions corresponding to J_{12} positive and J_{12} negative are shown in Figure 1.[16] The assignment corresponding to J_{12} positive was found to be correct by selectively irradiating transitions in the AB part of the spectrum and observing the effect on transitions in the M part. Thus irradiation of line 2 causes splitting of the connected transitions **9** (progressive) and **11** (regressive) as shown in Figure 2.

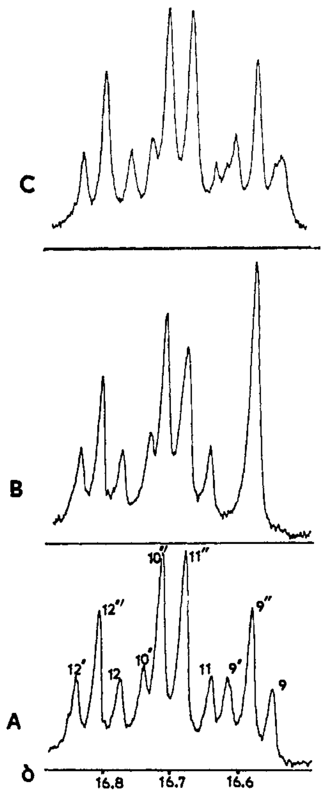
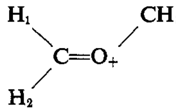


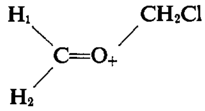
Figure 2. (A) The M part of the 100-MHz spectrum of hydroxycarbonium ion (**1**). The ^{12}C species gives the lines 9'', 10'', 11'', and 12'' and the two X subspectra due to the ^{13}C species give lines 9, 10, 11, 12, and 9', 10', 11', 12', respectively. The numbering of transitions (based on positive values for J_{AX} and J_{BX}) is that used in ref 16. (B) The M part of the spectrum with irradiation of the high-field doublet in the ^{13}C spectrum (see Figure 3). Lines 9 and 9' collapse to a singlet which falls underneath line 9'', showing that J_{13} and J_{23} have the same sign as the direct couplings J_{CH1} and J_{CH2}. (C) The M part of the spectrum with irradiation (spin tickling) of line 2 (Figure 1) in the AB part of the spectrum. Line 9 is connected progressively giving a broad doublet and line 11 is connected regressively giving a sharp doublet showing that J_{12} has the same sign as J_{13} and J_{23}.

The ^{13}C chemical shift was found by obtaining indor spectra[15,17] from the M transitions in the proton spectrum and thus locating connected ^{13}C transitions. Combination of the indor spectra from four of the transitions in the proton spectrum gave the complete ^{13}C spectrum of the ion, which is shown in Figure 3. The ^{13}C spectrum consists of the X part of two superimposed ABX subspectra corresponding to the two possible spin states of the M proton. The location of the connected transitions determined in this manner confirmed the relative sign determination of J_{13} (J_{23}) and J_{CH_1} (J_{CH_2}) described above.

Methoxycarbonium and Chloromethoxycarbonium Ions. The structural similarity of **2** and **3** to the hydroxycarbonium ion (**1**) suggests that similar values for the geminal coupling constants should be found. An investigation of these ions at 60 MHz showed that



2



3

---

(14) M. Karplus, *J. Amer. Chem. Soc.*, **84**, 2458 (1962).

(15) For a review of double resonance methods see: R. A. Hoffman and S. Forsen, *Progr. Nmr Spectrosc.*, **1**, 15 (1966).

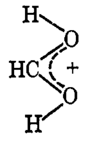
(16) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1967, p 357.

(17) E. B. Baker, *J. Chem. Phys.*, 37, 911 (1962).

the chemical-shift difference between H_1 and H_2 was insufficient for this coupling constant to be determined.[11] At 100 MHz, the shift difference is, in both cases, large enough to allow observation of the outer transitions in the AB part of the spectrum. The spectra were analyzed as ABX_3 and ABX_2 cases and, after obtaining trial parameters, the LAOCN3 iterative computer program[18] was used to compute a best fit with the experimental spectra. The parameters obtained in this manner are given in Table I. In both cases the four-bond allylic coupling constants $J_{1,4}$ and $J_{2,4}$ have the same sign. The assignment of H_1 and H_2 indicated in the structures shown (**2** and **3**) is discussed below. The direct ^{13}C–H coupling constants were determined from the ^{13}C satellite spectra of the ions, obtained in natural abundance.

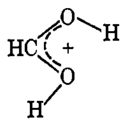
Discussion

One remarkable feature in the comparison of hydroxycarbonium ion and ethylene (see Table I) is the similarity in the values for the vicinal coupling constants (with respect to both sign and magnitude). As noted previously, this similarity has been noted in a number of other systems and appears to generally hold in protonated carbonyl compounds in spite of large differences in the geminal H–H and directly bonded ^{13}C–H coupling constants. The assignment of H_1 and H_2 in hydroxycarbonium ion is based on the magnitude of these vicinal coupling constants H_1 being at highest field. More difficulty is encountered in assigning the geminal protons in the two alkoxycarbonium ions studied. One feature of hydroxycarbonium ion is the magnitude of the direct ^{13}C–H coupling constants, J_{CH_2} being larger than J_{CH_1} by 11.4 Hz. A similar difference has been found in protonated formic acid,[9] J_{CH} in the isomer in which the two hydroxyl protons are *cis* to the formyl proton (**4**) being smaller, by 9.0 Hz, than that in the isomer (**5**) having one *cis*- and one *trans*-hydroxyl proton.



4

J_{CH} = 235.8 Hz



5

J_{CH} = 244.8 Hz

The trends in direct ^{13}C–H coupling constants in vinyl derivatives have been interpreted in terms of interaction with the lone pairs on the substituent.[19,20] In compounds of type **6**, J_{CH_1} is found to be larger than J_{CH_2}, when X is Cl, Br, I, all of which have available lone pairs.[20] A further example of this type is found in the oxime of formaldehyde **7** in which J_{CH_1} (177 Hz) is found to be larger than J_{CH_2} (163 Hz).[21] Our observations that the larger C–H coupling in protonated formaldehyde and protonated formic acid is associated with the geminal proton which is *cis* to the lone pair on oxygen seems consistent with these results.

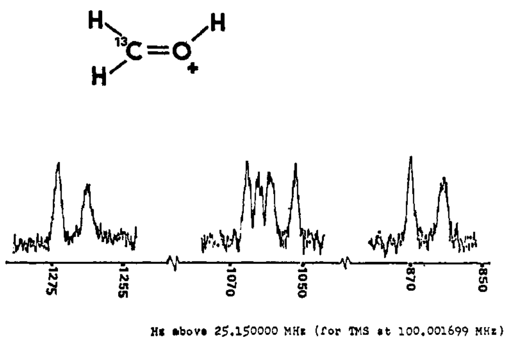
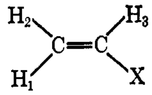
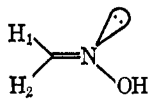


Figure 3. The ^{13}C indor spectrum of hydroxycarbonium ion (**1**). The spectrum consists of the X part of two ABX subspectra, one for each spin state of the hydroxyl proton. The spectrum was obtained from lines 12′, 10′, 11′, and 9′ in the proton spectrum of the ion (see Figure 2) and is a superposition of the pairs of ^{13}C transitions obtained in this manner (the spectrum has been redrawn and extraneous base line removed for simplicity of presentation). The direct spectrum would consist of equal intensity lines; that this is not completely true for the indor spectrum is due to the fact that it was obtained from transitions in the proton spectrum, some of which are connected progressively and some of which are connected regressively, to transitions in the ^{13}C spectrum.

Using this criterion for methoxycarbonium ion (**2**) leads to the assignment of H_1 to the highest field resonance and H_2 to the lowest field resonance. The effect, on the chemical shifts of the geminal protons, of replacing the hydroxyl proton in protonated formaldehyde by a methyl group is thus almost identical (0.16 ppm) for the *cis*- and *trans*-geminal protons. This effect on chemical shifts is smaller than in the analogous olefin compounds,[22,23] but in both series the direction of the charge is the same (*i.e.*, to higher field, see Table I).



6



7

A similar difference in the C–H coupling constants was found in chloromethoxycarbonium ion (**3**) and this difference was used to assign the methylene protons, H_1 being the highest field resonance. The effect of substituting chlorine for a proton in the methyl group of methoxycarbonium ion is thus to result in a greater deshielding of H_1 as compared to H_2. The analogous olefin compounds show an almost identical trend.[23,24]

Geminal Coupling Constants. The geminal coupling constant in formaldehyde has been shown to be large and positive (+ 40–42 depending on solvent).[25,26] The magnitude and sign of this coupling constant have been discussed in terms of the molecular orbital approach to the calculation of coupling constants,[27–29] the large increase, compared to ethylene, being ascribed to two effects. First, the electronegativity of the oxygen will

---

[18] A more recent version of the program described by S. M. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **47**, 5443 (1967).

[19] H. S. Gutowsky and C. Juan, *Discussions Faraday Soc.*, **34**, 52 (1962).

[20] G. Hruska, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **43**, 2827 (1965).

[21] T. Yonezawa and I. Morishima, *J. Mol. Spectrosc.*, **27**, 210 (1968).

[22] See Table I, footnote *d*.

[23] See Table I, footnote *e*.

[24] See Table I, footnote *f*.

[25] B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963).

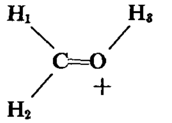
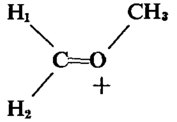
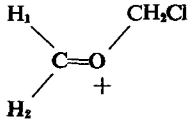
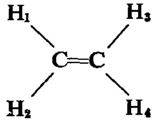
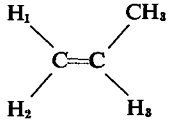
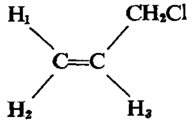
[26] B. L. Shapiro and F. A. L. Anet, private communication, see ref 27.

[27] A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965).

[28] A. A. Bothner-By and J. A. Pople, *J. Chem. Phys.*, **42**, 1339 (1965).

[29] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966).

Table I. Nmr Data for Hydroxy- and Alkoxycarbonium Ions

			Chemical shifts[a]					Coupling constants[b]								
Compound	Solvent	Temp, C°	H_1	H_2	H_3	CH_3–CH_2Cl	^{13}C	J_{12}	J_{13}	J_{23}	J_{14}	J_{24}	$J_{1^{13}C}$	$J_{2^{13}C}$	$J_{3^{13}C}$	Ref
	FSO_3H-SbF_5-SO_2	−60	9.820	9.940	16.70		−29.2[c]	+21.7	+9.0	+19.0			+198.4	+209.8	−8.7	
	FSO_3H-SbF_6-SO_2	−60	9.661	9.775		5.585										
	SbF_5-SO_2	−60	9.704	9.818		5.632		20.79 (+)			0.88 (−)	0.97 (−)	+197	+212		
	SbF_6-SO_2	−60	10.059	9.989		7.023		18.43 (+)			1.09 (−)	1.54	+198	+215		
	CCl_4		5.350	5.350				+2.3	+11.4	+19.1			+156.2	+156.2	−2.4	*d*
	CCl_4		4.951	4.874		1.662		+2.08	+10.02	+16.81	−1.75	−1.33				*e*
	CCl_4		5.313	5.169		3.985		+1.27	+10.11	+16.92	−1.38	−0.93				*f*

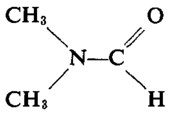
[a] In parts per million (ppm) from external (capillary) TMS for the ions, ppm from internal TMS for unchanged compounds. [b] In hertz, signs given in parentheses are inferred from those determined in related systems. [c] Parts per million from $^{13}CS_2$. [d] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41,** 2114 (1963). [e] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83,** 231 (1961). [f] A. A. Bothner-By and H. Gunther, *Discussions Faraday Soc.*, **34,** 127 (1962).

withdraw σ electrons from the methylene group causing a positive change in the coupling constant and second, donation of the electrons from a lone-pair orbital on oxygen into the antisymmetric methylene bonding orbital will also cause a numerical increase. Qualitatively, the effect of protonation on formaldehyde is to increase the electronegativity of the oxygen and to remove an oxygen lone pair from interaction with the methylene group. The former effect would lead to an increase in the coupling constant and the latter to a decrease. Removal of lone pair interaction would be expected to be the dominant of these two effects and this is in agreement with the observed decrease of 20 Hz in the geminal coupling constant of formaldehyde on protonation. Some remaining interaction from the rehybridized lone pair orbital is probably still present as evidenced by the differences in the two direct C–H coupling constants discussed previously.

The replacement of the proton on oxygen by a methyl group, as in methoxycarbonium ion, would not be expected to change significantly the populations of the symmetric or antisymmetric bonding orbitals of the methylene group and, as is found, the geminal coupling constants differ only slightly.

The smaller coupling constant in chloromethoxycarbonium ion, again using the molecular orbital approach, can be attributed to electron withdrawal from the antisymmetric methylene orbital. The observed decrease, when compared to methoxycarbonium ion, is greater (2.36 Hz) than for the corresponding olefins (0.81 Hz) (see Table I).

Allylic Coupling Constants. The allylic coupling constants observed in methoxy and chloromethoxycarbonium ions show a reversal in trend to the analogous olefin compounds. In these, and in other olefin compounds, the *cis*-allylic coupling constant is found to be larger in absolute magnitude than the *trans*.[30] The same relative magnitudes are also found in other carbonium ions, such as protonated acetaldehyde and protonated acetone, in which the methyl group is attached to carbon rather than to a heteroatom. Our observation, that when the methyl group is attached to oxygen, as in the two alkoxycarbonium ions studied, the *trans*-allylic coupling constant is greater than the *cis*, has an analogy with an uncharged compound in that the same trend is observed in dimethylformamide.[31,32]

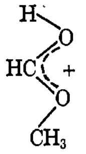


$J_c^4 = 0.4$ Hz

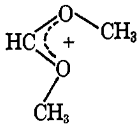
$J_t^4 = 0.8$ Hz

8

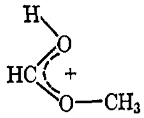
The question of the relative magnitude of the *cis*- and *trans*-allylic coupling constants is of importance in the assignment of isomers in protonated esters,[33] and, in particular, protonated methyl formate. Our original, tentative assignment of the major isomer to the *cis–cis* structure (**9**) has recently been disputed[34] on the grounds that this structure is inconsistent with the observation that the isomer observed for the dimethoxycarbonium ions has the *cis–trans* structure (**10**) and by analogy protonated methyl formate should be assigned the structure **11**. This structure has also been proposed by Hogeveen using a similar method of assignment.[35]



9



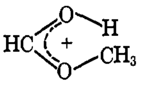
10



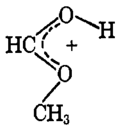
11

The dimethoxycarbonium ion can be generated from trimethyl orthoformate in 1:1 *M* fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution. The only isomer observed under these conditions has two nonequivalent methyl resonances as found by Borsch; however, in contrast to his observation, the high-field resonance is coupled by 0.9 Hz to the methine proton; the low-field methyl resonance shows an unresolved coupling of *ca.* 0.3 Hz. We could find no evidence for a second isomer of the dimethoxycarbonium ion.

Protonated methyl formate is present in two isomeric forms.[33] In the major isomer (90%), the vicinal HCOH coupling constant is 3.5 Hz showing a *cis* relationship of the hydroxyl and methine proton. In this isomer the methoxy protons are coupled to the methine proton by 0.9 Hz. The other isomer observed (10%) has the hydroxyl proton *trans* to the methine proton (J = 14.0 Hz) and an unresolved coupling (*ca.* 0.3 Hz) of the methine proton to the methyl protons. Discounting the possibility that this second isomer is the *trans–trans* isomer **12**, the only assignment consistent with the nmr spectra is **13**. This assignment requires that the *cis*-allylic coupling constant be small (*ca.* 0.3 Hz) and provided that the assumption can be made that this coupling constant will be unchanged in the dimethoxycarbonium ion, the lowest field methyl resonance in **10** must be that due to the methyl which is *cis* to the methine proton. This leads to the conclusion that the *trans*-allylic coupling constant in this ion is larger (0.9 Hz) than the *cis*-allylic coupling constant (0.3 Hz), as found in the methoxy- and chloromethoxycarbonium ions. This observation also leads to the conclusion that the major isomer of protonated methyl formate is **11**.



12



13

Methyl formate itself has been shown[36] to exist in the planar *cis* form (the methyl group *cis* to the carbonyl oxygen, **14**) thus minimizing direct interaction of the oxygen lone pairs.[37] The corresponding *trans* form has not been detected[38] and the *trans*/*cis* ratio has been shown to be less than 1% (ΔG = >2.7 kcal/mol). The

---

(30) S. Sternhall, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(31) E. W. Randall and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **8**, 365 (1962).

(32) D. G. de Kowalewski and V. J. Kowaleski, *Ark. Kemi*, **16**, 373 (1961).

(33) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).

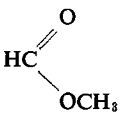
(34) R. F. Borsch, *ibid.*, **90**, 5303 (1968).

(35) H. Hogeveen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 816 (1967).

(36) R. F. Curl, *J. Chem. Phys.*, **30**, 1529 (1959).

(37) N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 263 (1963).

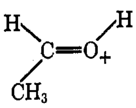
(38) T. Miyazawa, *Bull. Chem. Soc. Jap.*, **34**, 691 (1961).



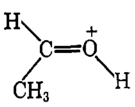
14

coupling constant between the methyl group and the methine proton in methyl formate has also been found[39] to be 0.85 Hz, a value which lends additional support for the assignment of **11** to the major isomer of protonated methyl formate.

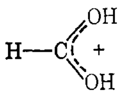
The results of molecular orbital calculations on protonated formaldehyde, protonated acetaldehyde, and protonated formic acid, have been recently published.[40] In the case of protonated acetaldehyde **15** was calculated to be more stable than **16** by 1.5 kcal. In the case of protonated formic acid, **5** was calculated to be the most stable isomer, the *trans–trans* isomer **17** being less stable by 1.5 kcal and isomer **4** by 6.0 kcal. These results are in disagreement with those found experimentally if the assignments of the isomers were correct. It was suggested that use of the *cis*- and *trans*-vicinal coupling constants in making the experimental assignments might be incorrect. If indeed the basis of the assignments were changed and the *cis*-vicinal coupling constant was taken to be greater than the *trans*, the calculations and the experimental observations would be in good agreement. We feel however, that our present results provide additional evidence for the validity of the original assignments. In particular the differing $J_{^{13}CH}$ coupling constants in protonated formaldehyde and protonated formic acid and their analogy with those observed in formaldoxime are completely consistent with the *trans*-vicinal coupling constants being larger than the *cis*. In the two isomers of protonated acetaldehyde, we have found a corresponding difference in the two $J_{^{13}CH}$ coupling constants. Again the coupling for the proton *cis* to the lone pair on oxygen (isomer **16**) is larger (203 Hz) than that in the isomer in which this proton is *trans* to the oxygen lone pair (193 Hz) (**15**). In addition the effect on the chemical shifts of the geminal protons in protonated formaldehyde upon substitution of the hydroxyl proton by methyl and chloromethyl groups parallels so closely the changes observed in the corresponding olefins as to indicate that olefins are good model compounds for assigning the nmr spectra of protonated carbonyl compounds.



15



16



17

Experimental Section

Nmr Spectra. Proton spectra were obtained at 100 MHz using a Varian Associates Model HA100 nmr spectrometer. Line positions were determined using the associated frequency counter and were referenced against external (capillary) TMS. The 60-MHz spectra were obtained using a Varian A56-60A spectrometer. All spectra were recorded at −60°.

The sweep 25.1-MHz frequency required for ^{13}C irradiation was generated using either the equipment described previously[10] or by using a specially constructed crystal-controlled oscillator, the frequency of which was swept using a voltage ramp to vary capacitance in series with the crystal. The irradiating frequency was fed to the probe *via* a radiofrequency amplifier, attenuator, and double-probe adapter and was monitored with a Hewlett-Packard 5245L electronic counter. The observing frequency (100 MHz) was determined using the same counter equipped with a plug-in unit.

For obtaining indor spectra,[17] the HA100 spectrometer was operated in the internal lock, frequency sweep mode, the first upper side band of capillary TMS being used for the lock signal. It is necessary, for indor operation, to "sit" on a peak associated with the ^{13}C species in the proton spectrum and monitor changes in the absorption at this sweep frequency as the irradiating frequency is swept through the ^{13}C region. This was achieved either by maintaining the recorder arm of the spectrometer at the desired frequency and monitoring the output using a Sanborn recorder or by using an external audio oscillator to generate the sweep frequency and using the HA100 recorder to observe the indor spectra. For simplicity of operation the former method was found to be the more satisfactory and, in addition, the internal sweep frequency was found to be less susceptible to drift than the HP 200CD audio oscillator used to generate the sweep frequency externally.

The ^{13}C chemical shifts were calculated with respect to TMS as reference using the relation[41]

$$\delta_{^{13}C}{}^{TMS} = \frac{\Gamma_i - 3.9769331}{3.9769331} \times 10^6 + \delta_H$$

where $\Gamma_i = \nu_0/f_i, f_i$ is the measured ^{13}C frequency, ν_0 is the observing frequency of any peak in the proton spectrum, and δ_H is the chemical shift, in parts per million (ppm), of this peak from TMS. For upper side band operation using a TMS lock, ν_0 can be conveniently taken as the sum of the observing frequency (derived from the V4311 unit) and the lock modulation frequency, in which case δ_H is equal to zero. The ratio ν_0/f_i for external TMS was found experimentally to be the same as that previously determined for internal TMS (3.9769331).[41]

The ^{13}C chemical shifts obtained in this manner were converted to $^{13}CS_2$ as reference using the relationship[41]

$$\delta_{^{13}C}{}^{CS_2} = \delta_{^{13}C}{}^{TMS} - 194.6$$

Preparation of the Ions. Protonated formaldehyde was generated by the reaction[4] of the methylene chloride (50% ^{13}C enriched, from Merck Sharp and Dohme of Canada Ltd.) with freshly distilled fluorosulfuric acid and antimony pentafluoride (1:1 *M*) diluted with sulfur dioxide (50% by volume) at −10°. All operations were carried out on a vacuum line. Methoxycarbonium ion was generated, either from dimethoxymethane in FSO_3H–SbF_5–SO_2 solution at −60° or from chloro methyl ether in SbF_5–SO_2 solution.[11] Chloromethoxycarbonium ion was generated from *sym*-dichloro methyl ether in SbF_5–SO_2 solution.[11] Dimethoxycarbonium ion was generated from trimethyl orthoformate in FSO_3H–SbF_5–SO_2 solution at −60°.

Analysis of the Spectra. The nmr spectra of the methoxycarbonium ion and chloromethoxycarbonium ion were analyzed using a slightly modified version of Bothner-By and Castellano's LAOCN3 program,[18] using a Univac 1108 computer. The calculated spectrum was plotted using a CalComp plotter, a line width of 0.30 Hz being found to give the best fit with the experimental spectra. Analysis of the ^{13}C–H coupling constants was aided by time averaging the spectra (*ca.* 100 scans) using a Varian C-1024 computer of average transients. These coupling constants are considered accurate to within ±3 Hz. Other coupling constants determined are considered to be accurate to within ±0.1 Hz in the case of hydroxycarbonium ion and ±0.05 Hz in the case of the two alkoxycarbonium ions. Chemical shifts were determined to the nearest 0.1 Hz (± 0.001 ppm).

Acknowledgment. Support of the work through a grant of the National Institutes of Health is gratefully acknowledged.

---

[39] (a) D. G. de Kowalewski, and V. J. Kowalewski, *Mol. Phys.*, **8**, 93 (1964); (b) N. V. Riggs and S. M. Verma, *Tetrahedron Lett.*, **34**, 3767 (1968).

[40] Data communicated by E. L. Mackor at the Conference on Carbonium Ions, Cleveland, Ohio, October 1968; P. Ros, *J. Chem. Phys.*, **49**, 4902 (1968).

[41] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).