Recrystallization from ether–petroleum ether gave white needles: mp 45–46°; pmr ($CDCl_3$) τ 3.64 (s, 0.9), 6.4 (m, 4.0), and 8.1 ppm (m, 4.1); ir (CCl_4) in order of decreasing intensity 1660, 1690, 1420, 2990, 2890, 2960, and 1225 cm^{-1}. *Anal.* Calcd for $C_6H_9ONCl_2$: C, 39.59; H, 4.98; N, 7.69; Cl, 38.95. Found: C, 39.61; H, 5.04; N, 7.61; Cl, 38.75. The method of synthesis, analysis, and other properties provide strong evidence that this white solid is 1-(dichloroacetyl)pyrrolidine. However, in the only pertinent literature reference we have found,[48] this compound, formed by the reaction of pyrrolidine with ethyl dichloroacetate, was reported to be a liquid, $n^{25}\text{D}$ 1.5182. We therefore treated pyrrolidine with dichloroacetyl chloride, obtained a solid product with the same melting point and the same ir and pmr spectra as the one obtained using 1,1-dichloro-2,2-difluoroethylene, and assumed that our structural assignment was correct.

At the concentration and in the solvent used for calorimetric measurements the pmr spectrum of 1-(2,2-dichloro-1,1-difluoroethyl)pyrrolidine was too weak and too obscured by the solvent spectrum to be useful. The pmr spectrum of samples prepared in a number of different ways showed that 1-(dichloroacetyl)pyrrolidine was also present. However, when pyrrolidine and excess 1,1-dichloro-2,2-difluoroethylene were mixed in a carefully dried nmr tube at −80° and the spectrum measured at 0° within an hour, a triplet (J = 7 Hz) and two multiplets with relative areas of 1:4:4 were observed at τ 4.1, 6.85, and 8.1 ppm, respectively. The only other absorption clearly present was a small doublet (J = 7 Hz) of unknown origin at 8.7 ppm. In a similar experiment, 0.40 ml of 1,1-dichloro-2,2-difluoroethylene, 0.400 ml of chloroform, and 0.200 ml of pyrrolidine were mixed at −80° and then kept at 0° for 15 min. The only absorption besides that of the adduct was the chloroform singlet. From comparison of the area of the chloroform peak with the peaks at τ 4.1, 6.85, and 8.1 ppm, yields of 96 ± 7, 97 ± 8, and 104 ± 6% were calculated for the adduct.

Enthalpy of Addition of Pyrrolidine to 1,1-Dichloro-2,2-difluoroethylene. An ampoule containing about 0.26 g (3.6 mmol) of pyrrolidine was broken under solution of 3 ml (34 mmol) of 1,1-dichloro-2,2-difluoroethylene in 26 ml of diethyl ether. Inasmuch as half of the total change in length of the mercury thread had taken place in less than 2 min, the half-time of the reaction is probably less than 1 min. Hence the reaction, which was followed for at least 40 min, must have been more than 99.9% complete in 10 min or less. To try to insure that the solution was completely mixed as quickly as possible in this particularly rapid reaction, it was stirred about 30 times during the first 2 min of reaction.

Attempts to determine the stoichiometry of the reaction by quantitative hydrolysis to 1-(dichloroacetyl)pyrrole and hydrofluoric acid yielded no more than about 90% of the theoretical amount of acid. Analysis by glpc showed that the reaction mixture was decomposing during analysis to give a number of products.

Acknowledgment. We should like to acknowledge the help of Dr. Albert C. Ruggles who made the attempts at addition of hydrogen fluoride to dichlorodifluoroethylene.

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[48] M. Joullié, *J. Am. Chem. Soc.*, 77, 6662 (1955).

The Crystal Structure of a Friedel–Crafts Intermediate. Methyloxocarbonium Hexafluoroantimonate

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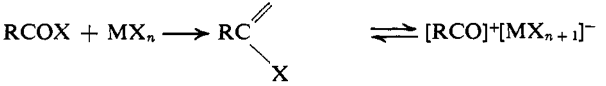
Contribution from The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778. *Received June 13, 1968*

Abstract: Oxocarbonium ions are postulated intermediates in Friedel–Crafts acylations. Crystals of methyloxocarbonium hexafluoroantimonate, $[CH_3CO]^+[SbF_6]^-$, are monoclinic, space group $P2_1/m$, with unit cell dimensions a = 5.758, b = 7.783, c = 7.879 Å, and β = 101°3′, Z = 2. Three-dimensional X-ray data were collected by the precession method (Mo Kα radiation) and estimated visually. The structure was refined by full-matrix least squares to a reliability index R_1 = 5.6% for 799 observed reflections. The crystal structure provides direct proof of an ionic structure in the solid state, and confirms the hypothesis that the oxocarbonium ion is linear. Some structural evidence that the positive charge in the cation is largely localized on the central carbon is discussed, and a molecular orbital calculation supporting this hypothesis is described.

Oxocarbonium ions, $[RCO]^+$, are believed to be intermediates in Friedel–Crafts acylation reactions,[1] in which acyl halides react with aromatic derivatives to yield aromatic ketones. These reactions are catalyzed

$$\text{RCOX} + \text{ArH} \xrightarrow{\text{MX}_n} \text{RCOAr} + \text{H}^+ + \text{X}^-$$

by acidic halides, MX_n, which combine variously[1] with acyl halides to form donor–acceptor complexes (I), or to generate oxocarbonium ions (II). The crystal structures of two such donor–acceptor complexes, benzoyl chloride–aluminum chloride[2] and benzoyl chloride–antimony pentachloride,[3] have been reported. Since a 1:1 addition compound of boron trifluoride and acetyl fluoride was first identified as $[CH_3CO]^+[BF_4]^-$ by Seel,[4] the existence of a number of stable oxocarbonium salts (II) has been demonstrated by infrared studies of the solids and by nmr methods in solution.[5-10] The present



$$\text{RCOX} + \text{MX}_n \longrightarrow \text{RC}(=\!{}^{\delta+}\text{OMX}_n{}^{\delta-})\text{X} \rightleftharpoons [\text{RCO}]^+[\text{MX}_{n+1}]^-$$

I II

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[1] For a review of this subject see G. Olah, "Friedel–Crafts and Related Reactions," Vol. 1, Interscience Publishers, New York, N. Y., 1963, pp 91–95, 665–680, 790–812. See also D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967, pp 283–294.

[2] S. E. Rasmussen and N. C. Broch, *Chem. Commun.*, 289 (1965).

[3] R. Weiss and B. Chevrier, *ibid.*, 145 (1967).

[4] F. Seel, *Z. Anorg. Allgem. Chem.*, 250, 331 (1943).

[5] B. P. Susz and J. Wuhrmann, *Helv. Chim. Acta*, 40, 722, 971 (1957).

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

[7] G. A. Olah, *Rev. Chim. Acad. Rep. Populaire Roumaine*, 7, 1139 (1962).

[8] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963).

[9] (a) D. Cook, *Can. J. Chem.*, 37, 48 (1959); (b) *ibid.*, 40, 480 (1962).

[10] G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 4442 (1966).

X-ray diffraction study[11] of $[CH_3CO]^+[SbF_6]^-$ [6-8] is the first direct structure determination of an oxocarbonium ion.[11a] The objectives of this investigation were (1) to define the nature of the crystal lattice and the degree of interionic association, (2) to establish the molecular geometry of the oxocarbonium ion, and (3) to determine what information on the distribution of charge in the cation could be obtained from the structural parameters.

Experimental Section

A. Data Collection. A white polycrystalline sample of $[CH_3CO]^+[SbF_6]^-$ was obtained from Dr. G. A. Olah. Needle-like single crystals (elongated along *b*) were grown by dissolving the sample in SO_2, then pumping off the solvent at −40°. Because this material is extremely sensitive to moisture, the crystals were transferred to thin-walled glass capillaries in a dry atmosphere.

A crystal of about 0.05 mm radius was aligned on a Buerger precession camera so that the *b* axis of the crystal was collinear with the spindle axis of the goniometer. The parameters of the monoclinic cell, $a = 5.758 \pm 0.006$, $b = 7.783 \pm 0.008$, and $c = 7.879 \pm 0.008$ Å, and $\beta = 101°3' \pm 6'$, give a calculated density of 2.671 g cm^{-3} for $Z = 2$. Because of the difficult experimental conditions, no direct determination of density was made. Absence of the $0k0$ reflections for *k* odd indicated the space group to be either $P2_1$ or $P2_1/m$.

The reciprocal lattice was recorded on a series of timed exposures of levels perpendicular to [100], [001], [101], and [10$\bar{1}$], using Zr-filtered Mo Kα radiation. In each of the four orientations, the zeroth, first, and second levels were obtained. The intensities were estimated visually with the use of a standard scale prepared from timed exposures of a representative reflection. Two independent readings of each reflection on each film were taken. Corrections for Lorentz and polarization factors, correlation of levels, averaging of reflections, and analyses of standard errors for each reflection were carried out with the aid of programs[12] written for the IBM 7094. A total of 978 unique reflections were photographed; of these 172 were below the observational limit, and 7 more (020, 040, 011, 002, 10$\bar{1}$, 11$\bar{1}$, 22$\bar{1}$) were eventually eliminated from the data set because they appeared to be significantly diminished by extinction. No absorption corrections were made but the linear absorption coefficient of $\mu = 42.7$ cm^{-1} for Mo Kα radiation suggests that absorption factors range between 1.4 and 1.5. The absolute scale factor and over-all temperature factor were estimated by Wilson's method.

B. Solution and Refinement of Structure. A three-dimensional sharpened Patterson function[13a] was computed, from which a preliminary structure consistent with space group $P2_1/m$ could be readily assigned. Of course the oxygen atom of the oxocarbonium ion could not be distinguished from the methyl carbon by Patterson analysis; in fact the vectors from these atoms to antimony are accidentally superimposed in the Patterson function. The structure was checked by computation of an electron density map[13a] calculated from phases based on the antimony atom alone.[13b] The methyl carbon and the oxygen atom could not be conclusively distinguished from this map either; the two peak heights were nearly equal, and although the atom eventually identified as oxygen was about 0.2 Å closer to the central carbon, we wished to refine the structure somewhat before making an assignment from calculated bond distances.

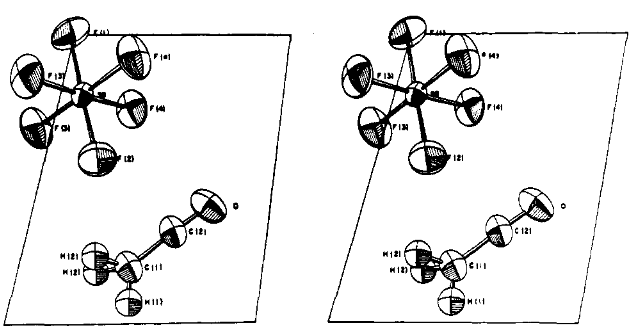

Figure 1. Three dimensional view of the structure of $[CH_3CO]^+$-$[SbF_6]^-$ showing the ions on the mirror plane at $y = {}^1/_4$. The *x* axis is horizontal while *z* is roughly vertical. Fifty per cent probability thermal ellipsoids are shown. Hydrogen atoms are drawn as 0.20-Å radius spheres.

Therefore, least-squares refinement[13b] of atomic positions and isotropic thermal parameters was initiated, assuming carbon-scattering factors[14a] for all three atoms of the oxocarbonium ion. Two cycles of refinement reduced

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

from 0.176 to 0.117. At this point the calculated position of one of the terminal atoms of the oxocarbonium ion was 0.25 Å closer to the central atom than the other, and oxygen-scattering factors[14a] were assigned to the atom with the shorter bond distance. Two cycles of refinement assuming anisotropic thermal motion reduced R_1 to 0.074. Some of the atomic parameters at this stage of the refinement have been reported in a preliminary communication.[11] Now anomalous scattering factors[14b] for antimony were introduced; seven reflections suspected of extinction were omitted from the data set, and card punching errors in five more reflections were discovered and corrected. Three more cycles of full-matrix anisotropic refinement reduced R_1 to 0.056 and

$$R_2 = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^{\,2}}\right\}^{1/2}$$

to 0.070. The mean parameter shift in the final cycle of refinement was 0.03σ, while the largest shift was 0.21σ. An electron density difference map calculated from the final structure factors (Table I) revealed peaks of height 0.4 e/Å^3 (H(1)) and 0.7 e/Å^3 (H(2)) in chemically reasonable positions for hydrogen atoms. By contrast, the highest peaks in this map, of amplitude 1.4 e/Å^3, appeared to arise from residual electron density within the hexafluoroantimonate ion. No attempt was made to refine these hydrogen positions in view of their very small contribution to the structure factors.

An effort was made to refine the structure in the noncentrosymmetric space group $P2_1$, but matrix singularities were encountered in the vicinity of the centrosymmetric structure. The normal values of the thermal displacements of atoms in the mirror plane in a direction perpendicular to this plane (Table II) suggest, however, that the space group is correctly assigned.

The observed and calculated structure factors have been deposited[15] with the ASIS National Auxiliary Publication Service, New York, N. Y., as Document No. NAPS-00085. Table I lists the final atomic parameters and their standard deviations. The root-mean-square components[13c] of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table II. The directions of thermal motion may be inferred from Figure 1, in which a three-dimensional view of the ions is given using ellipsoids to represent the anisotropic thermal motion.[13d] Bond distances, bond angles, and selected intramolecular contacts are presented in Table III, together with the standard errors calculated from the variance-covariance matrix obtained in the final least-squares cycle.[13c] It is noteworthy that little difference in

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(11) This research has been reported in preliminary form, F. P. Boer, *J. Am. Chem. Soc.*, **88**, 1572 (1966).

(11a) Note Added in Proof. More recently the structures of acetyl hexachloroantimonate [J. M. Le Carpentier and R. Weiss, *Compt. Rend.*, **265**, 797 (1967)] and of isobutyroyl hexachloroantimonate [J. M. LeCarpentier and R. Weiss, *Chem. Commun.*, 596 (1968)] have been reported. Values for the C–C and C–O bond lengths are very similar to those obtained in the present study.

(12) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

(13) (a) Fourier summations were performed using Shoemaker, Sly, and Van den Hende's program ERFR-2. (b) Structure factor and least-squares calculations were performed with Busing, Martin, and Levy's OR-FLS. (c) OR-FFE is a crystallographic function and error program by Busing, Martin, and Levy. (d) OR-TEP is a crystallographic thermal ellipsoid plotting program by C. K. Johnson.

(14) (a) Atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209. (b) The dispersion correction was taken from ref 14a, p 216.

(15) A copy of this table may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table I. Final Structure Parameters[a] and Standard Errors[b]

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Sb	0.0969(1)	0.25	0.2324(1)	202(3)	95(1)	146(1)		21(1)	
F(1)	−0.0233(24)	0.25	−0.0049(16)	530(49)	460(35)	167(18)		−131(23)	
F(2)	0.2250(25)	0.25	0.4654(16)	568(54)	483(38)	188(21)		32(28)	
F(3)	−0.1148(13)	0.0815(10)	0.2655(12)	514(35)	207(12)	437(31)	−155(14)	187(25)	−5(12)
F(4)	0.3122(14)	0.0847(7)	0.1929(13)	480(26)	162(9)	427(24)	119(14)	173(21)	24(12)
C(1)	0.4477(24)	0.25	0.8275(20)	299(41)	140(15)	192(24)		103(26)	
C(2)	0.6040(21)	0.25	0.7140(19)	294(46)	115(14)	223(28)		105(30)	
O	0.7362(23)	0.25	0.6288(17)	519(53)	255(21)	213(23)		172(30)	
H(1)[c]	0.477	0.25	0.937						
H(2)[c]	0.310	0.177	0.817						

[a] The anisotropic thermal parameters are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$. [b] Standard errors, given in parentheses, are multiplied by 10^4. [c] Not included in least-squares refinement. Positions determined from maxima in electron density map.

atomic or bond parameters could be discerned as a result of the dispersion correction and the changes in the reflection data introduced before the final three cycles of refinement (compare ref 11 to Tables I and III).

Table II. Root-Mean-Square Thermal Displacements along Principal Axes[a–c] (Å)

Atom	Axis 1	Axis 2	Axis 3
Sb	0.171(1)*	0.180(1)	0.214(1)
F(1)	0.172(13)	0.352(14)	0.376(14)*
F(2)	0.238(14)	0.308(15)	0.385(15)*
F(3)	0.181(7)	0.315(9)	0.372(12)
F(4)	0.180(7)	0.288(8)	0.367(10)
C(1)	0.192(15)	0.208(11)*	0.255(16)
C(2)	0.188(12)*	0.198(16)	0.267(17)
O	0.207(13)	0.280(12)*	0.310(16)

[a] Ordered on increasing magnitudes. [b] Standard errors multiplied by 10^3 are given in parentheses. [c] Thermal displacements perpendicular to the crystallographic mirror plane are indicated by asterisks.

Table III. Distances and Angles[a]

A. Bond Distances

Bond	Distance, Å	Bond	Distance, Å
Sb–F(1)	1.866(11)	C(1)–C(2)	1.385(16)
Sb–F(2)	1.843(12)	C(2)–O	1.108(15)
Sb–F(3)	1.843(6)	C(1)–H(1)	0.84 (est)
Sb–F(4)	1.854(6)	C(1)–H(2)	0.97 (est)

B. Bond Angles

Bond	Angle, deg	Bond	Angle, deg
C(1)–C(2)–O	177.2(1.6)	F(2)–Sb–F(3)	90.5(0.4)
F(1)–Sb–F(2)	178.2(0.4)	F(2)′–Sb–F(4)	90.8(0.5)
F(3)–Sb–F(4)′	178.1(0.3)	F(3)–Sb–F(3)′	90.7(0.5)
F(1)–Sb–F(3)	90.8(0.4)	F(3)–Sb–F(4)	90.7(0.4)
F(1)–Sb–F(4)	87.9(0.5)	F(4)–Sb–F(4)′	87.9(0.5)

C. Selected Intramolecular Contacts

Contact	Distance, Å	Symmetry transform of atom 2
C(2)···F(2)	2.638(21)	x, y, z
C(2)···F(4)	2.724(20)	$1 - x, -y, 1 - z;\ 1 - x, {}^1/_2 + y, 1 - z$
C(2)···F(1)	2.772(20)	$1 + x, y, 1 + z$
O···F(1)	2.952(19)	$1 + x, y, 1 + z$
O···F(2)	2.978(20)	x, y, z
H(1)···F(4)	2.71 (est)	$x, y, 1 + z;\ x, {}^1/_2 - y, 1 + z$
H(1)···F(1)	2.83 (est)	$1 + x, y, 1 + z$
H(2)···F(3)	2.33 (est)	$-x, -y, 1 - z$
H(2)···F(1)	2.65 (est)	$x, y, 1 + z$
H(2)···F(2)	2.78 (est)	x, y, z

[a] Standard errors calculated from the least-squares variance-covariance matrix are given in parentheses.

Description and Discussion of the Structures

A. Crystal Packing. The packing arrangement in a unit cell of $[CH_3CO]^+[SbF_6]^-$ is shown[13d] in Figure 2. An anion and a cation lie on the mirror plane at $y = {}^1/_4$, with the three principal atoms of the cation, the antimony, and two of the six fluorine atoms of the anion actually in the plane, while the other four fluorines are found as symmetry equivalent pairs above and below this plane (see also Figure 1). The inversion center at $^1/_2$, $^1/_2$, $^1/_2$ places a second pair of ions on the mirror plane at $y = {}^3/_4$.

No association of the oxocarbonium ions with $[SbF_6]^-$ ions other than ionic crystal packing is observed, in accord with the infrared spectrum.[6] The closest interionic contacts (Table IIIC) occur between the carbonyl carbon and four different fluorine atoms: F(2) and F(1) at distances of 2.638 and 2.772 Å, respectively, in the mirror plane, and two contacts of length 2.724 Å with F(4) from anions in the layers above and below that of the cation. Using a fluorine van der Waals radius of 1.35 Å, we calculate a contact radius of less than 1.35 Å for the carbonyl carbon, whereas a value of at least 1.57 Å might be expected for a neutral carbon atom.[16a] A reduced van der Waals radius would, however, be expected if the positive charge of the cation were localized on the carbonyl carbon (see below). The close coordination of four fluorines to carbon, as if to stabilize positive charge there, is certainly consistent with this hypothesis.[16b] On the other hand, the closest contacts of fluorine to oxygen are 2.952 and 2.978 Å, well above the sum of the van der Waals radii, 2.75 Å. Clearly the fluorines show no tendency to associate with oxygen. We note that partial bonding of fluorine to carbon is not indicated, since the Sb–F distances (Table IVA) are not affected.

B. The Hexafluoroantimonate Ion. Bond distances and angles in the $[SbF_6]^-$ ion (Table III) show only slight deviations from ideal octahedral symmetry; these may arise either from experimental error or crystal packing forces. The weighted average of the Sb–F bond distances is 1.851 Å. The hexafluoroantimonate

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(16) (a) van der Waals radii are obtained from L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. The van der Waals radius of carbon may be estimated indirectly in a number of ways. A value of 1.6 Å is obtained by extrapolating from the radii of the neighboring elements N and O; or we may obtain a value of 1.57 by using the heuristic equation (p 263): r (van der Waals) = 0.8 + r (single bond); or we may use the value 1.7 for the half-thickness of an aromatic molecule. (b) Similarly, close coordination of four chlorine atoms to the carbonyl carbon is found in crystals of acetyl hexachloroantimonate (ref 11a).

ion appears to be undergoing librational motion; the long axes of the thermal ellipsoids (Figure 1 and Table II) are roughly tangential to the Sb–F bonds. An approximate thermal correction to the Sb–F bond distances may be made by assuming the fluorine atoms ride on the antimony.[13c,17] These "corrected" distances are F(1), 1.917; F(2), 1.891; F(3), 1.887; and F(4), 1.892 Å; giving a weighted average of 1.894 Å. These values raise a question as to the accuracy of Sb–F bond distances of 1.95 Å[18] and later 1.77 Å[19] reported and tabulated[20] for $NaSbF_6$.

C. The Geometry of the Methyloxocarbonium Ion. The $[CH_3CO]^+$ ion is linear within experimental error. The C–C bond distance, 1.385 ± 0.016 Å, is unusually short, particularly when compared to the values of 1.458 and 1.460 Å in the respective isoelectronic species $CH_3C{\equiv}N$ and $CH_3C{\equiv}CH$, where C is also sp hybridized. The C–O distance of 1.108 ± 0.015 Å is about as short as the distances found in CO and in $[CO]^+$ in the $^2\Sigma^+$ state, and is significantly shorter than the carbonyl bond distances in formaldehyde or acetyl fluoride. A comparison of selected carbonyl bond distances and stretching frequences is given in Table IV; the short distance in the $[CH_3CO]^+$ ion appears to correlate well with its high infrared frequency.

Table IV. Comparison of C–O Bond Parameters

Molecule	Distance, Å	Frequency, cm^{-1}	Overlap population
CH_2O	1.230[a]	1743	0.86[e]
CH_3CFO	1.160[b]	1848[d]	
CO	1.128[c]	2170[c]	1.06[f]
$[CO]^+(^2\Sigma^+)$	1.115[c]	2214[c]	1.15[f]
$[CH_3CO]^+$	1.108	2294[d]	1.15

[a] D. W. Davidson, B. P. Stoicheff, and H. J. Bernstein, *J. Chem. Phys.*, **22**, 289 (1954). [b] P. W. Allen and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 236 (1951). [c] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1959, p 522. [d] Reference 6. [e] M. D. Newton and W. E. Palke, *J. Chem. Phys.*, **45**, 2329 (1966). [f] Reference 25.

D. Charge Distribution in the Methyloxocarbonium Ion. The valence structure for the methyloxocarbonium ion is frequently written as III, with the positive

$$\underset{\text{III}}{H_3{\equiv}C{-}C{\equiv}\overset{+}{O}:} \longleftrightarrow \underset{\text{IV}}{H_3{\equiv}C{-}\overset{+}{C}{=}\ddot{O}:} \longleftrightarrow \underset{\text{V}}{\overset{+}{H}_3{=}C{=}C{=}\ddot{O}:}$$

charge localized on oxygen. However, a valence structure with the positive charge localized on carbon can also be written (IV), and even structures of type V must be considered. (While hyperconjugated structures may not be of importance in alkyloxocarbonium ions, structures of type V can clearly play an important role in aroyl cations, where the analogous positive charge would be delocalized into the aryl rings.) Considerable evidence has now accumulated that in alkyloxocarbonium ions the positive charge is principally localized on the carbonyl carbon (structure IV), and we summarize this evidence below.

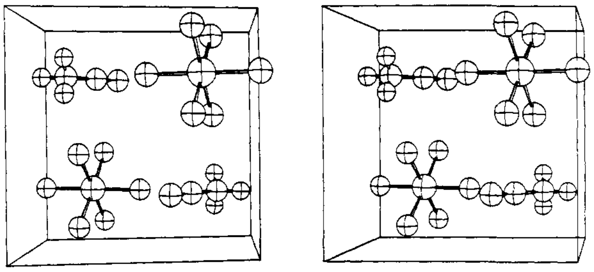

Figure 2. Three dimensional drawing of the unit cell of $[CH_3CO]^+$-$[SbF_6]^-$. The angle of view is perpendicular to the *xy* plane, with *y* vertical. A vertical twofold screw axis passes through the center of the cell ($x = {}^1/_2, z = {}^1/_2$).

(1) The chemical shifts of the methyl protons of $[CH_3CO]^+$, as well as the C^{13} chemical shift of the carbonyl carbon, are displaced considerably downfield from their values in acetyl fluoride.[6–8] Similarly, large deshielding effects have been observed for α-hydrogen atoms in cycloalkyloxocarbonium ions, and the β- and γ-hydrogens in these species also show substantial deshielding.

(2) The short bond distances observed in the methyloxocarbonium ion may be attributed to shortening of the normal single bond radius of the carbonyl carbon because this atom is present as a carbonium ion C^+ with one less electron than normal in its valence shell. The effect is most clearly seen in the $C–CH_3$ bond distance, which is about 0.08 Å shorter than the single bond distance for a neutral sp carbon atom. In fact, in structure reports of ions where carbon bears formal positive charge, such as the triphenylmethyl,[21] triphenylcyclopropenium,[22] and chlorotetraphenylcyclobutenium[23] cations, bond lengths to these carbon atoms have almost universally been shortened beyond the amounts required by hybridization alone. The carbon–oxygen bond length in $[CH_3CO]^+$ is also very short, but in this case part of the total change may result from changes in bond order, as well as from change in the carbon bond radius.

(3) Positive charge on the carbonyl carbon should give rise to a similar reduction of the van der Waals radius. We have already seen that such a contraction apparently occurs, and that the fluorine atoms of the anion pack in a way as to stabilize this charge.

(4) A molecular orbital calculation[24] on $[CH_3CO]^+$, parametrized by an exact LCAO-SCF wave function for carbon monoxide,[25] yields a net Mulliken charge[26] of +1.18 e on the carbonyl carbon atom. While this value is very probably overestimated because of the lack of an explicit self-consistent field procedure in our calculation,[24] it does indicate that there is little tendency for net positive charge to accumulate on the electronegative oxygen atom. Other calculated net charges are −0.35 for oxygen, −0.11 for the methyl

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(17) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

(18) N. Schrewelius, *Z. Anorg. Chem.*, **238**, 241 (1938).

(19) G. Teufer, *Acta Cryst.*, **9**, 539 (1956).

(20) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p M65; also Supplement, Special Publication No. 18, 1965, p M35s.

(21) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

(22) M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

(23) R. F. Bryan, *ibid.*, **86**, 733 (1964).

(24) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **52**, 890 (1964); M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *ibid.*, **53**, 1089 (1965); M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966); F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966); M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

(25) M. D. Newton, private communication.

(26) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

carbon, and +0.07 for each hydrogen atom. This last value is about the same as the calculated net charge for hydrogen in ethane, suggesting that the contributions of hyperconjugated valence structures, such as V, should not be substantial. The net orbital populations[26] indicate that electron density in the π system is concentrated in the O 2p atomic orbitals (1.48 e in each) at the expense of the C 2p orbitals (0.60 e each). This asymmetry in the electron distribution of the π bonds accounts for most of the net positive charge on C, and may tend to reduce the bond order somewhat from that of a "pure" triple bond. Mulliken overlap populations[26] are a thoretical measure of bond strength; the calculated C–O overlap population in $[CH_3CO]^+$, 1.15, is slightly greater than the value for carbon monoxide and about equal to that of $[CO]^+$. About 0.65 of this total is contributed by the π systems. Calculated overlap populations for C–O bonds are compared with bond lengths and infrared stretching frequencies in Table IV. Other calculated bond overlap populations for $[CH_3CO]^+$ are 0.72 for C–H and 1.03 for C–C.

The wave function was calculated by a nonempirical method[24] in which parameters for constructing the Hamiltonian matrix are derived from exact self-consistent field calculations on appropriate model compounds. The overlap and kinetic energy integrals between all atomic orbitals of the system are evaluated exactly, while the model compounds yield values for the diagonal Hamiltonian elements and the coefficients which are used in a modified Mulliken approximation to give the off-diagonal potential energy parts of the Hamiltonian. Exponents and diagonal matrix elements used in the present calculation were C(1s): 5.700, −11.284 au; C(2s): 1.625, −1.463; C(2p σ): 1.625, −0.756; C(2p π): 1.625, −0.114; O(1s): 7.700, −20.702; O(2s): 2.275, −2.573; O(2pσ): 2.275, −0.758; O(2p π): 2.275, −0.410; and H(1s): 1.200, −0.537.

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Relationship between the Absorption and Excitation Spectra and Relative Quantum Yields of Fluorescence of *all-trans*-Retinal

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Abstract: The relative quantum yields of fluorescence, ϕ_F, were calculated for different concentrations of *all-trans*-retinal. The ϕ_F were found to vary as a function of exciting wavelength. This effect was accounted for by photochemistry in competition with internal conversion in the vibrational levels of the first excited singlet state.

In a previous communication[2] we reported the fluorescence excitation spectrum of the biologically important *all-trans*-retinal. The uncorrected excitation spectrum maximized near the onset of the first absorption band of *all-trans*-retinal. The shape of the excitation spectrum was accounted for by a vibronic effect on photochemistry similar to other results obtained in this laboratory. This effect results from the fact that photochemistry is competitive with internal conversion in upper vibronic levels of the excited singlet states.[3]

Recently, other workers[4] revealed that in their investigation of *all-trans*-retinal in methylcyclohexane glasses at 77°K, the shape of the excitation spectrum varied with the concentration of *all-trans*-retinal, although at low absorbances (<0.3), they reproduced our absorption spectrum. At absorbances greater than 0.3, the maximum and short wavelength edge collapsed to yield, at absorbances greater than 2.0, an excitation spectrum similar to ours. They also concluded that the collapse of the short wavelength edge was a self-absorption effect which increased as the product of the cell path length and the concentration became large.

Experimental Section

We have repeated the fluorescence excitation spectrum of *all-trans*-retinal performing all experiments in 3-methylpentane glasses at 77°K and employing front-face emission geometry. The same kilowatt DC Zenon arc exciting source and suprasil dewar were used for all spectra. Three experiments were completed using three different fresh solutions of *all-trans*-retinal. The first experiment utilized a 2-mm suprasil cell and a solution whose absorbance was approximately 0.3; the second, a 1.0-cm suprasil cell and a solution whose absorbance was approximately 1.5; the third, a 2-mm suprasil cell and a solution whose absorbance equaled approximately 1.8. The uncorrected and corrected fluorescence excitation spectra from the first and third experiment are reproduced in Figures 1 and 2, respectively. The fluorescence excitation spectrum for the second experiment was similar to that of others.[4] Note that the excitation spectra vary depending upon concentration as would be expected. However, even at very low concentrations we could not duplicate our absorption spectrum without corrections for variation in quantum yields as a function of wavelength (see Discussion).

While we recognize that detector slit width can be a critical factor, we are confident that with small exciting slit widths (0.2 mm), a concentrated solution, a short path length cell (2 mm), large de-

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(1) Taken from a dissertation submitted in partial fulfillment of the Ph.D. degree.

(2) D. E. Balke and R. S. Becker, *J. Amer. Chem. Soc.*, **89**, 5061 (1967).

(3) R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, in press.

(4) G. L. Pool and A. U. Guzzo, private communication (1968). On the basis of more recent studies by these same authors, they have communicated that they are in agreement with the results as presently reported. We wish to acknowledge their stimulus for further investigation.