Trimethylperoxonium Ion, CH$_3$OO(CH$_3$)$_2^+$ [1]

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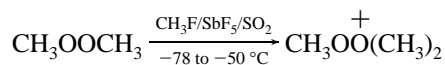Ross I. Wagner, and Karl O. Christe*,†

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Figure 1. ^{13}C NMR spectrum of CH$_3$OO(CH$_3$)$_2^+$ **2** in SbF$_5$/SO$_2$ at −50 °C.

Protonated hydrogen peroxide, hydroperoxonium ion H$_3$O$_2^+$, is an intermediate in the electrophilic hydroxylation of aromatics and in the oxygenation of alkanes with hydrogen peroxide and strong acids.[2,3] H$_3$O$_2^+$ has also been isolated as a crystalline salt under superacidic conditions and investigated by a variety of techniques, including NMR and IR/Raman spectroscopies.[4] However, no direct observation of the peroxonium ion H$_3$O$_2^+$ by ^{1}H NMR spectroscopy was so far possible due to fast proton exchange with the acid systems even at low temperature.[2–4] Previous ^{17}O NMR studies[5] of hydrogen peroxide in superacid media were also inconclusive.

Minkwitz et al.[6] were able to isolate protonated dimethyl peroxide, CH$_3$OO(H)CH$_3^+$, as a crystalline salt by protonation of dimethyl peroxide in HF/AsF$_5$. The structure of the peroxonium ion was characterized by vibrational and ^{1}H NMR spectroscopies. These authors also attempted to methylate CH$_3$OOCH$_3$ to obtain the trimethylperoxonium ion, CH$_3$OO-(CH$_3$)$_2^+$.[6] These attempts included the methylation of CH$_3$OOCH$_3$ by the strong methylating agents (CH$_3$)$_2$Cl$^+$MF$_6^-$, CH$_3$F/AsF$_5$, and CH$_3$F/SbF$_5$. However, no evidence for the formation of the CH$_3$OO(CH$_3$)$_2^+$ ion was obtained, and the sole product was the trimethyloxonium ion, (CH$_3$)$_3$O$^+$. It was suggested that the CH$_3$OO(CH$_3$)$_2^+$ ion, once formed, immediately decomposes to (CH$_3$)$_3$O$^+$.[6]

We report now the preparation and NMR spectroscopic characterization of CH$_3$OO(CH$_3$)$_2^+$ as a long-lived ion in superacid media and a study of its structure by theoretical methods. Addition of dimethyl peroxide[7] to a solution of CH$_3$F/SbF$_5$ in SO$_2$ at −78 °C, followed by gentle warming to about −50 °C, resulted in the formation of CH$_3$OO(CH$_3$)$_2^+$. The 300

$$\text{CH}_3\text{OOCH}_3 \xrightarrow[-78 \text{ to } -50\,^\circ\text{C}]{\text{CH}_3\text{F/SbF}_5/\text{SO}_2} \text{CH}_3\text{OO(CH}_3)_2^+$$

MHz ^{1}H spectrum showed two major absorptions at δ 5.26 (s, 6H) and δ 4.95 (s, 3H).[8] The 75 MHz ^{13}C NMR spectrum also exhibited two peaks at δ 85.6 (s) and δ 70.8 (s) (in the ratio 2:1). The ^{13}C NMR spectrum of the ion is shown in Figure 1. The ion is stable up to at least −20 °C without any decomposi-

tion to trimethyloxonium ion. The spectral data are consistent with the formation of CH$_3$OO(CH$_3$)$_2^+$ ion (*vide infra*).

Attempts to isolate the CH$_3$OO(CH$_3$)$_2^+$ SbF$_5^-$ salt as a neat crystalline solid were unsuccessful. Vacuum removal of the SO$_2$ solvent, first at −64 °C and then at −31 °C, resulted in a yellow tacky solid which, based on its low-temperature Raman spectrum, contained the SbF$_6^-$ anion and SO$_2$. Pumping on the sample at room temperature resulted in SO$_2$ evolution and a viscous brown liquid.

The ^{13}C NMR chemical shifts of the methyl groups in CH$_3$OO(CH$_3$)$_2^+$ were deshielded compared to that of CH$_3$OOCH$_3$. The carbon chemical shift at δ 85.6, assigned to the methyl group attached to the oxonium center, is 24.2 ppm deshielded compared to that of methyl group of CH$_3$OOCH$_3$. On the other hand, the carbon chemical shift at δ 70.8, assigned to the methyl group attached to the uncharged oxygen atom, is only 9.4 ppm deshielded compared to that of methyl group of CH$_3$OOCH$_3$. This indicates that the charge of the ion is mostly localized on the tricoordinated oxygen atom which has typical oxonium ion character. No NMR evidence was found for the (CH$_3$)$_2$OO-(CH$_3$)$_2^{2+}$ dioxonium ion under these conditions, although a limited equilibrium may not be necessarily detected.

To substantiate the observed experimental results, we have calculated the structures and ^{13}C NMR chemical shifts of CH$_3$OOCH$_3$, CH$_3$OO(CH$_3$)$_2^+$, and (CH$_3$)$_2$OO(CH$_3$)$_2^{2+}$. The structures were fully optimized at the ab initio correlated MP2/6-31G* level.[9] The minimum energy structure of CH$_3$OOCH$_3$ was found to be of C_2 symmetry (**1**), with a C−O−O−C dihedral angle of 124.4° (Figure 2) in fair agreement with the experimental value[10] of 119(10)° and the results from previous ab initio calculations.[11] The global minimum structure of CH$_3$OO(CH$_3$)$_2^+$ was found to be of C_s symmetry (**2**). The oxonium oxygen in **2** is pyramidal. The O−O bond distance of **2** (1.483 Å) is slightly longer than that of **1** (1.473 Å). The (CH$_3$)$_2$OO-(CH$_3$)$_2^{2+}$ dication **3** was also found to be a stable minimum. Its structure has D_2 symmetry with the two COC units in an almost

† Hughes *STX* and Rocket Propulsion Directorate.

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(7) Caution! Pure dimethyl peroxide is shock sensitive (Baker, G.; Pape, R.; Shaw, R. *Chem. Ind. (London)* **1964**, *48*, 1988) and should be handled only on a small scale and with appropriate safety precautions. For its synthesis and properties, see: Christe, K. O.; Pilipovich, D. *J. Am. Chem. Soc.* **1971**, *93*, 51. Christe, K. O. *Spectrochim. Acta*, **1971**, *27A*, 463.
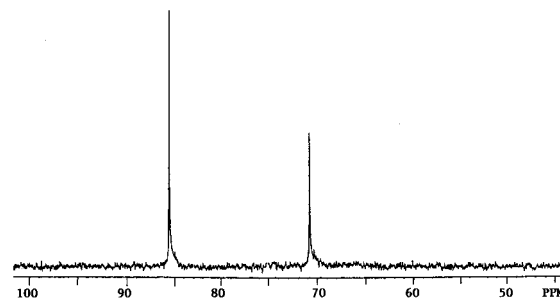
(8) Using glovebox and vacuum line techniques, approximately 1.5 mL of 50% v/v solution of SbF$_5$ in SO$_2$ was prepared in a 5 mm glass NMR tube, which was closed by a Teflon valve, and cooled to −78 °C in a dry ice/acetone bath. Dimethyl peroxide (50 mg) was added at −196 °C, and the mixture was warmed to −78 °C to effect solution. In the same manner, 30 mgs CH$_3$F was carefully added to the solution. Homogenity of the resulting solution was assured by vigorous stirring at −78 °C. ^{1}H and ^{13}C NMR spectra were recorded using internal lock provided by an acetone-d_6 capillary. ^{1}H and ^{13}C NMR resonances were referenced to external (capillary) tetramethylsilane.

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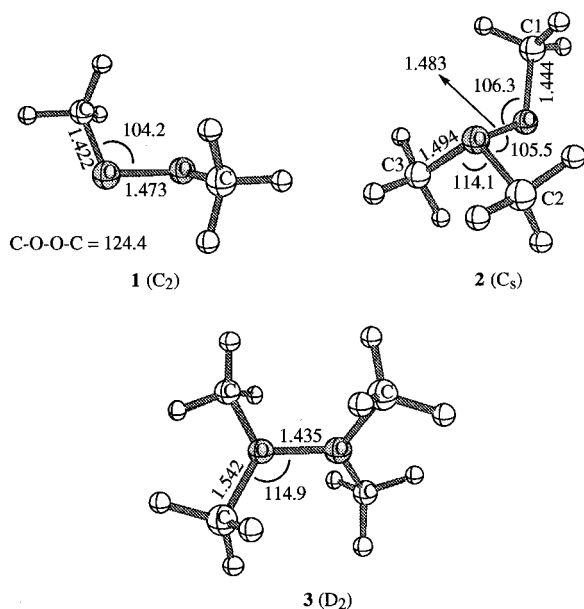(11) Christen, D.; Mack, H. G.; Oberhammer, H. *Tetrahedron* **1988**, *44*, 7363.

Figure 2. MP2/6-31G*-optimized structures of **1**−**3**.

perpendicular arrangement (dihedral angle between two COC units is 83.7°). The O−O bond distance of **3** (1.435 Å) is shorter than those in **1** or **2**.

The ^{13}C NMR chemical shifts of **1**−**3** were calculated by the IGLO (basis set II)[12,13] and GIAO-MP2 (basis set tzp/dz)[14,15] methods using the MP2/6-31G*-optimized geometries (Table 1). The GIAO-MP2 method includes correlation effects in the chemical shift calculations. The IGLO calculated δ ^{13}C NMR

Table 1. Calculated and Experimental ^{13}C NMR Chemical Shifts[a]

molecule	atoms	IGLO II[b]	GIAO-MP2/tzp/dz[b]	expt
CH$_3$OOCH$_3$ (**1**)		56.1	54.3	61.4
CH$_3$OO(CH$_3$)$_2$$^+$ (**2**)	O(CH$_3$)$_2$	76.8	88.6	85.6
	O(CH$_3$)	67.6	75.3	70.8
(CH$_3$)$_2$OO(CH$_3$)$_2$$^{2+}$ (**3**)		98.1	110.6	

[a] Calculated ^{13}C NMR chemical shifts were referenced to TMS (absolute shift, *i.e.*, σ(C) = 198.4 (IGLO II), 198.8 (GIAO-MP2)). [b] For MP2/6-31G* optimized geometries.

shift of **1** is 56.1, deviating by 5.3 ppm from the experimentally observed value. The GIAO-MP2-calculated δ ^{13}C NMR shift of **1** is 54.3, deviating by 7.1 ppm from the experimentally observed value of 61.4. The GIAO-MP2-calculated δ ^{13}C NMR shift values of **2** are 88.6 and 75.3 and agree very well with the experimental values of 85.6 and 70.8, respectively. The corresponding IGLO II values are 76.8 and 67.6. The difference between the experimental δ ^{13}C NMR shifts of the two methyl groups of **2** is 14.8, consistent with the corresponding differences of the IGLO and GIAO-MP2 values of 9.2 and 13.3, respectively. The GIAO-MP2-calculated δ ^{13}C NMR shift of the methyl group of the dioxonium ion **3** is 110.6, which is 56.3 ppm deshielded from the GIAO-MP2 value of **1**.

In conclusion, we have succeeded in the preparation and characterization of the until now elusive trimethylperoxonium ion, CH$_3$OO(CH$_3$)$_2$$^+$, and studied its structure by ^{1}H and ^{13}C NMR spectroscopies. Ab initio/IGLO/GIAO-MP2 theoretical ^{13}C NMR chemical shift calculations gave good correlation with the experimental data. The tetramethylperoxonium dication (CH$_3$)$_2$OO(CH$_3$)$_2$$^{2+}$ was not observed experimentally but was calculated to be a kinetically stable species at the MP2/6-31G* level.

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