New Developments in Superacid Chemistry: Characterization of $H\overset{+}{C}{=}O$ and $F\overset{+}{C}{=}O$ Cations

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Mainly through the efforts of Nobel laureate George Olah and his co-workers over a period of 35 years, a sizeable inventory of small, weakly basic molecules have been protonated by superacids. Some exceedingly simple systems have nevertheless remained problematic, including the single-carbon bases CO and CO_2. However, the year 1997 saw some significant developments in this area, highlighted by a publication describing the NMR and IR spectra of the long-sought $H\overset{+}{C}{=}O$ cation and a paper by the Olah group on $F\overset{+}{C}{=}O$, a missing member in the series of haloformyl cations (and directly related to O-protonated carbon dioxide, $HO\overset{+}{C}{=}O$).

The detailed characterization of acylium ions, $R\overset{+}{C}O$, by Olah and co-workers in 1963[1] together with a copious literature[2] on Friedel–Crafts acylations long ago settled questions concerning the structure of these electrophiles. However, the direct observation of the simplest member of this family, $H\overset{+}{C}O$, has been elusive. A major difference between $R\overset{+}{C}O$ and $H\overset{+}{C}O$ concerns the acid–base equilibria in which they are involved; $H\overset{+}{C}O$ is in equilibrium with carbon monoxide [Eq. (a)], whereas a much more basic ketene is the neutral equilibrium partner of $R\overset{+}{C}O$ salts with an α-H atom in the R group.

$$CO + [H^+] \rightleftharpoons H\overset{+}{C}{=}O \qquad (a)$$

There is of course considerable indirect evidence for an $H\overset{+}{C}O$-like intermediate or transition state, since carbon monoxide in a solution of acid will formylate activated arenes (the well-known Gattermann–Koch reaction).[3] Furthermore, the reactivity of CO with arenes and adamantane in superacids such as SbF_5/HSO_3F (1/1) has been reported[4] along with the suggestion that the acylating species is an activated $H\overset{+}{C}{=}O$ molecule, either diprotonated or protosolvated.[5] With this background in mind, the recent report of the direct in situ observation of $H\overset{+}{C}O_{(s)}$ by de Rege et al.[6] is a most noteworthy event.

The key to success was the use of the strongest known member of the superacid family, HF/SbF_5 (1:1), together with the use of pressurized NMR and IR cells in which a gaseous pressure of carbon monoxide could be maintained in contact with the neat solution-phase acid during the measurements. These experimental conditions are not overly novel (Olah previously reported NMR experiments with pressurized CO), but some courage is involved given the corrosive nature of the superacid and the gaseous pressures. The NMR spectra of ^{13}C-enriched carbon monoxide show signals for three species in addition to those for the excess HF/SbF_5 (which serves as a "solvent"). These were identified as H_3O^+ (a common trace contaminant of HF/SbF_5 mixtures), complexed formyl fluoride ($H(F)C{=}O\cdots SbF_5$), and the elusive $H\overset{+}{C}{=}O$ cation. Formyl fluoride is the F^- adduct of $H\overset{+}{C}{=}O$, and there is an analogy here with protonated formaldehyde, which forms protonated fluoromethanol and other cations in HF/SbF_5.[7,8]

The ^{13}C NMR signal assigned to $H\overset{+}{C}{=}O$ is a singlet at $\delta = 139.5$ (85 atm), which is in very good agreement with a value of $\delta = 136$ calculated for $H\overset{+}{C}{=}O_{(g)}$ with ab initio methods. The worrysome absence of $^{13}C-{}^{1}H$ coupling was attributed to a rapid exchange of $H\overset{+}{C}{=}O$ with excess HF/SbF_5; indeed, only one ^1H signal is seen for these hydrogen atoms. However, the authors report an NOE for the ^{13}C signal when this ^1H signal is irradiated, an indication that appreciable amounts of $H\overset{+}{C}{=}O$ are present.

de Rege et al. also reported IR measurements of superacids under external ^{12}CO (and ^{13}CO) pressure. In addition to a relatively sharp signal for the $^{12}C{-}O$ and $^{13}C{-}O$ stretching mode in the complexed formyl fluoride, they observed a very broad absorption at 2110 (^{12}C) and 2060 cm^{-1} (^{13}C). Since no other carbonyl peak was observed, any signal from "free" $CO_{(s)}$ would have to be below the limits of detection. The extreme broadness of the $H\overset{+}{C}{=}O$ carbonyl stretch was attributed to a strong interaction of this cation with either SbF_5 or the counterion (or both).

There are two possibilities for the rapid exchange of hydrogen atoms observed in the NMR spectra: either an acid–base exchange involving a small equilibrium concentration of "free" CO or, as previously suggested by Olah,[5,9] an equilibrium involving a diprotonated $H\overset{+}{C}{=}\overset{+}{O}H$ cation. However, the results of de Rege et al. show that the basicity of carbon monoxide is near the limit of what the strongest superacid will protonate, since parallel experiments with pressurized CO in HSO_3F/SbF_5 (1/1) or HF/SbF_5 (1/1) in SO_2ClF (both slightly weaker superacid systems) did not produce the ^{13}C NMR signal at $\delta = 139.5$ attributed to $H\overset{+}{C}{=}O$. If the CO protonation by HF/SbF_5 (1/1) were truly "complete", there would have been no need for the NMR experiments under pressure. Given this, the rapid exchange of hydrogen atoms seems more likely to involve an equilibrium with "free" CO.

The combined evidence for the observation of $H\overset{+}{C}{=}O$ is strong but not totally conclusive. The ultimate proof for its existence may be provided by an X-ray structure, which is not an entirely unreasonable expectation given the recent work of Laube[10] and Minkwitz.[11]

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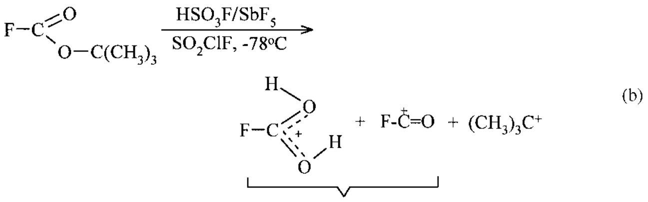
In another notable publication in the area of superacids, Olah et al.[12] reported the direct observation of the fluoroformyl acylium ion, $\mathrm{F\overset{+}{C}{=}O}$, together with direct NMR characterization of protonated fluoroformic acid $\mathrm{FC(OH)_2^+}$. The Olah group had previously reported[13] the analogous $\mathrm{Cl\overset{+}{C}{=}O}$, $\mathrm{Br\overset{+}{C}{=}O}$, and $\mathrm{I\overset{+}{C}{=}O}$ cations, but have only now managed to obtain $\mathrm{F\overset{+}{C}{=}O}$. The route to $\mathrm{F\overset{+}{C}{=}O}$ involved the protolytic cleavage of *tert*-butyl fluoroformate in a $\mathrm{SO_2ClF}$ solution of $\mathrm{HSO_3F/SbF_5}$ (1/1) at −78°C [Eq. (b)]. The $\mathrm{F\overset{+}{C}{=}O}$ species was observed as a doublet at $\delta = 117.5$ ($J_{\mathrm{CF}} = 322.4$ Hz) in the ^{13}C NMR spectrum, which is in reasonably good agreement with calculated values of $\delta = 131.1$ (IGLO) and 124.5 (GIAO-MP2).



(b)

Although $\mathrm{F\overset{+}{C}{=}O}$ is superficially related to $\mathrm{H\overset{+}{C}{=}O}$, the better analogy is to O-protonated carbon dioxide, $\mathrm{HO\overset{+}{C}{=}O}$. Like $\mathrm{H\overset{+}{C}{=}O}$, the $\mathrm{HO\overset{+}{C}{=}O}$ cation has been detected in outer space, and a number of gas-phase studies of this species have been reported. Olah and Shen[14] reported indirect evidence for superacid protonation of $\mathrm{CO_2}$ (and even diprotonated $\mathrm{CO_2}$ has been suggested as a reactive intermediate[5]), but in the gas phase the proton affinity of $\mathrm{CO_2}$ is 11.0 kcal mol^{-1} *less* than for CO.[15] It is somewhat superficial to compare gas-phase heats of protonation with possible solution-phase behavior, but since CO now appears to be among the weakest bases which can be protonated by the strongest superacid system, the evidence for $\mathrm{HO\overset{+}{C}{=}O_{(s)}}$ needs to be more direct (and the recent work with $\mathrm{H\overset{+}{C}{=}O}$ offers a good template). Unlike the case of CO, there is little evidence for the electrophilic carboxylation of arenes by $\mathrm{CO_2}$/acid in solution. In this regard the $\mathrm{(Hal)\overset{+}{C}{=}O}$ cations can serve as surrogates for aromatic carboxylation, although side reactions are usually a problem. The related $\mathrm{H_3CO\overset{+}{C}{=}O}$ cation has also been reported,[16] but methyl chloroformate in superacid appears to be an alkylating rather than acylating agent; nevertheless, the gas-phase acylation of arenes by $\mathrm{H_3CO\overset{+}{C}{=}O}$ has been shown.[17]

The protonated fluoroformic acid cogenerated along with $\mathrm{F\overset{+}{C}{=}O}$ is a very interesting species in its own right. As in the case of $\mathrm{F\overset{+}{C}{=}O}$, fluoroformic acid can be compared most closely with carbonic acid. Both free acids are extremely labile ($\mathrm{HFCO_2}$ has not yet been characterized) but form stable mono anions $\mathrm{FCO_2^-}$ and $\mathrm{HOCO_2^-}$. In earlier elegant work, Olah and White reported the preparation of monoprotonated carbonic acid,[18] and the present paper now extends this observation to protonated fluoroformic acid.

For the future, the development of techniques for generating higher gas pressures for the NMR and IR detection of labile carbocations would be rewarding. Furthermore, the continuing use of direct methods for analyzing structures—for example, single-crystal X-ray or powder methods—is to be encouraged.

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