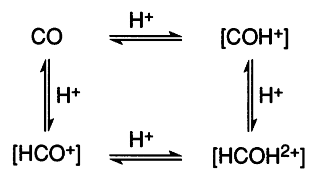
long-lived HCO^+ under such conditions in sufficiently high concentration. On the other hand, CO readily reacts with carbocations (*1*) and halogen cations (*8*) to give the corresponding stable acylium cations (RCO^+, R = alkyl, aryl, vinyl, halogen, and so on). In fact, the acetyl cation (CH_3CO^+) was isolated as the BF_4^- salt as early as 1940 by Seel (*1*).

In an elegant study, chemists from Exxon and the University of Utah (*4*) report the spectroscopic observation of the formyl cation in HF-SbF_5 medium [one of the most powerful Brönsted acids in the condensed phase, about 10^{18} times stronger than 100% sulfuric acid (*1*)] under CO pressure. This intriguing work became possible through a technique developed by the Exxon coauthor, Horváth, which permits the in situ examination of reaction mixtures by NMR and infrared spectroscopy at high pressures, up to 200 atm, with sample tubes constructed of single-crystal sapphire fitted with a titanium head and valve (*9*).

The reaction of ^{13}C-enriched CO with fluoroantimonic acid under varying carbon monoxide pressures up to 85 atm was investigated (*4*). At lower pressures, the O-complexed formyl fluoride–SbF_5 adduct was observed as a doublet of doublets centered at a ^{13}C NMR chemical shift of 179 parts per million (ppm) along with a single peak at 145 ppm in the proton-coupled spectrum at room temperature. Upon additional increase in CO pressure, the signal at 145 ppm moved to 139.5 ppm, with an increase in relative intensity compared with the formyl fluoride complex. At higher temperatures, the two sets of signals merged, indicating an exchange. The single peak at 139.5 ppm has been assigned to the formyl cation, which is consistent with the calculated value in idealized gas phase (136 ppm) by means of the GIAO-MP2 method (*10*). The authors (*4*) have tentatively assigned the 2110-cm^{-1} infrared absorption band to the formyl cation somewhat modified by the influence of the complex anions present in the superacid solution.

Another interesting observation reported is that no ^{13}C-^{1}H scalar coupling was observed in the ^{13}C NMR spectrum, indicating a fast proton exchange with the acid. This hypothesis was corroborated in the proton NMR spectrum, wherein no separate signal for the formyl cation was observed. Selective decoupling of the acid proton signals results in nuclear Overhauser enhancement of the formyl cation signal in the ^{13}C NMR spectrum. This enhancement is consistent with a rapid proton exchange on the NMR time scale. The authors were unable to freeze-out the exchange by lowering the temperature because of problems related to the viscosity. Furthermore, use of co-solvents of low nucleophilicity to alleviate the viscosity problems did not allow observation of the formyl cation. Interestingly, the acidity of Magic Acid (*1*) was not sufficient for the observation of HCO^+.

The authors' (*4*) interpretation of the fast proton exchange in the formyl cation involving the protoformyl dication and isoformyl cation is still speculative (see reaction scheme). Although protolytic activa-



tion of electrophiles to superelectrophiles (*11*) is a well-recognized concept, activation of the formyl cation to protosolvated formyl cation by the acid ($HCO^+\cdots H{\cdot}A$) can also explain the exchange results.

The invoked isoformyl cation (COH^+) has been characterized in the outer space as well as in the gas phase (*6*). However, the energy difference between formyl and isoformyl ions is too large (around 34 kcal/mol) for the latter (*6*) to be involved in the free state during the exchange process.

The report (*4*) does provide convincing evidence for the formation of long-lived formyl cation. The direct spectroscopic characterization of the formyl cation with the novel high-pressure technique may give further impetus for the quest to identify other elusive species such as CH_5^+ (an important intermediate in the superacid-catalyzed polymerization of methane to higher hydrocarbons) (*1*) in the condensed phase.

References

1. G. A. Olah and G. K. S. Prakash, in *Superacids*, J. Sommer, Ed. (Wiley-Interscience, New York, 1985), pp. 33–345; G. A. Olah's Nobel lecture, *Angew. Chem. Int. Ed. Engl.* **34**, 1393 (1995).
2. G. K. S. Prakash and P. v. R. Schleyer, Eds., *Stable Carbocation Chemistry* (Wiley-Interscience, New York, 1996).
3. G. A. Olah and S. J. Kuhn, in *Friedel-Crafts and Related Reactions*, G. A. Olah, Ed. (Wiley-Interscience, New York, 1964), vol. III, pp. 1153–1256.
4. P. J. F. de Rege, J. A. Gladyz, I. Horváth, *Science* **276**, 776 (1997).
5. D. Buhl and L. E. Snyder, *Nature* **228**, 267 (1970); W. Klemperer, *ibid.* **227**, 1230 (1970).
6. P. W. Harland, N. D. Kim, S. A. H. Petrie, *Aust. J. Chem.* **2**, 9 (1989); and references therein.
7. G. A. Olah, L. Ohannesian, M. Arvanaghi, *Chem. Rev.* **87**, 671 (1987).
8. G. K. S. Prakash, J. Bausch, G. A. Olah, *J. Am. Chem. Soc.* **113**, 3203 (1991).
9. I. T. Horváth and J. A. Millar, *Chem. Rev.* **91**, 1339 (1991).
10. G. A. Olah, G. Rasul, G. K. S. Prakash, unpublished results.
11. G. A. Olah, *Angew. Chem. Int. Ed. Engl.* **32**, 767 (1993).

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Arabidopsis central

genome-www.stanford.edu/Arabidopsis/

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Edited by David Voss

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