Table III. Conductivity Adjusted for Density

Material	Density, d (g cm^{-3})	Conductivity (vol), σ (Ω^{-1} cm^{-1}) (25 °C)	Conductivity (wt), σ/d (cm^2 Ω^{-1})- (g^{-1})) (25 °C)
Cu	8.92	5.8×10^5	6.5×10^4
Au	19.3	4.1×10^5	2.1×10^4
$(SNBr_{0.4})_x$	2.67	3.8×10^4	1.4×10^4
Fe	7.86	1.0×10^5	1.3×10^4
$(SN)_x$	2.30	3.7×10^3	1.6×10^3
Hg	13.6	1.0×10^4	7.4×10^2
$cis\text{-}[(CH)(AsF_5)_{0.14}]_x$	0.8	5.6×10^2	7.0×10^2

are observed in certain cases—ca. 10^{11} increase when cis-$(CH)_x$ is converted to cis-$[(CH)(AsF_5)_{0.14}]_x$. Furthermore, *surprisingly large room temperature conductivities are obtained with several dopants.* Some of the $(CH)_x$ derivatives, even in the form of polycrystalline, *uncompressed, nonaligned* films, have an electrical conductivity much greater than polycrystalline *compressed* pellets of $(SN)_x$,[11] (TTF)-(TCNQ),[12] etc. (Table II). Indeed, the conductivity of cis-$[(CH)(AsF_5)_{0.14}]_x$ is identical with that commonly found for *single* crystals of (TTF)(TCNQ) (Table II). This strongly suggests that aligned films of $(CH)_x$ derivatives should have still higher conductivities.

The highly conducting polymers formed from $(CH)_x$ and electron-withdrawing species may be charge-transfer π complexes of the type believed to be formed during the halogenation of olefins. Stable colored compounds which may be charge-transfer and/or carbonium ion complexes of this type have been obtained by the action of bromine on certain substituted ethylenes.[13] These latter observations suggest that the substances formed from $(CH)_x$ and electron-attracting species may consist of a positively charged $(CH)_x$ chain acting as a polycation with appropriate halogen, etc., anions situated at intervals adjacent to the chain.

Although the resistivity (ρ) of a material is usually defined on a volume basis, it can also be defined on a mass basis (ρd) where d is the density. Since the bulk density of the $(CH)_x$ derivatives obtained from the dimensions and weight of a film is considerably smaller ($\sim$0.5-1 g cm^{-3}) than that of most metals, the conductivity adjusted for density of a material such as cis-$[(CH)(AsF_5)_{0.14}]_x$ is comparable with that of many metals (Table III).

Films of cis-$(CH)_x$ doped with AsF$_5$ have been used as ubstitute "wires" in simple electrical circuits. For example, such films with contacts $\sim$1 cm apart having a weight of $\sim$10 mg will carry sufficient current to cause a flashlight bulb to glow brightly when connected to two 1.5-V flashlight batteries.

Considering possible polyacetylene derivatives, replacement of some or all of the hydrogen atoms in $(CH)_x$ with organic or inorganic groups, copolymerization of acetylene with other acetylenes or olefins, and the use of different dopants should lead to the development of a large new class of conducting organic polymers with electrical properties that can be controlled over the full range from insulator to semiconductor to metal.

References and Notes

(1) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
(2) C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
(3) M. Akhtar, C. K. Chiang, M. J. Cohen, J. Kleppinger, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, J. Milliken, M. J. Moran, D. L. Peebles, and H. Shirakawa, *Ann. N.Y. Acad. Sci.*, in press.
(4) H. Shirakawa and S. Ikeda, *Polym. J.*, **2**, 231 (1971). H. Shirakawa, T. Ito and S. Ikeda, *ibid.*, **4**, 460 (1973). T. Ito, H. Shirakawa, and S. Ikeda, *J.*

Polym. Sci., Polym. Chem., **12**, 11 (1974); **13**, 1943 (1975). See also M. Hatano, S. Kambara, and S. Okamoto, *J. Polym. Sci.*, **51**, S-26 (1961).
(5) D. J. Berets and D. S. Smith, *Trans. Faraday Soc.*, **64**, 823 (1968).
(6) G. M. Holob and P. Ehrlich, *J. Polym. Sci., Polym. Phys.*, **15**, 627 (1977).
(7) S. B. Mainthia, P. L. Kronick, H. U. E. F. Chapman, and M. M. Labes, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **4**, No. 1 (1963); H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **29**, 213 (1956); H. Akamatu, Y. Matsunaga, and H. Kuroda, *ibid.*, **30**, 618 (1957); T. Uchida and H. Akamatu, *ibid.*, **34**, 1015 (1961); J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).
(8) H. Endres, H. J. Keller, and R. Lehmann, *Inorg. Nucl. Chem. Lett.*, **11**, 769 (1975); J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.*, **99**, 749 (1977); A. S. Foust and R. H. Soderberg, *ibid.*, **89**, 5507 (1967); A. E. Underhill, D. M. Watkins, and R. Pethig, *Inorg. Nucl. Chem. Lett.*, **9**, 1269 (1973); T. J. Marks, D. F. Webster, S. L. Ruby, and S. Schultz, *J. Chem. Soc., Chem. Commun.*, 444 (1976); A. Gleizes, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 3545 (1975).
(9) J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, *J. Am. Chem. Soc.*, **99**, 286 (1977); T. J. Marks, *Ann. N.Y. Acad. Sci.*, in press.
(10) C. K. Chiang, M. J. Cohen, D. L. Peebles, A. J. Heeger, M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, and M. J. Moran, *Solid State Commun.*, **23**, 607 (1977); W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1977).
(11) M. M. Labes, *Pure Appl. Chem.*, **12**, 275 (1966).
(12) L. B. Coleman, Ph.D. Thesis, University of Pennsylvania, 1975.
(13) R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1171 (1952); R. E. Buckles and W. D. Womer, *ibid.*, **80**, 5058 (1958).
(14) Department of Physics, University of Pennsylvania.
(15) Department of Chemistry, University of Pennsylvania.
(16) Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokahama, Japan.

C. K. Chiang,[14] M. A. Druy,[15] S. C. Gau[15]
A. J. Heeger,[14] E. J. Louis,[15] A. G. MacDiarmid*[15]
Y. W. Park,[14] H. Shirakawa[15,16]

Department of Chemistry, Department of Physics and
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104
*Received September 6, 1977*

Protonation and Ionization of 4-Chlorocyclohexene in Superacid. A Fast 1,2-Hydride Shift in the 4-Cyclohexenyl Cation

Sir:

Recently we reported the ring contraction of the 3-cyclohexenyl cation (1), generated from 3-chlorocyclohexene (2), to the 1-methylcyclopentenyl cation (3) and measured the rate of this transformation in FSO$_3$H-SbF$_5$ (4:1)-SO$_2$FCl solution.[1] It is conceivable that the first step of this reaction is the formation of the 4-cyclohexenyl cation (4) from 1, by a 1,2-hydride shift. This same transformation is involved in the isotope scrambling observed in a sample of 1 labeled with deuterium.[2] The scrambling occurred at a temperature (-65 °C) much lower than that at which the rate of ring contraction (1 → 3) becomes reasonably fast (-20 °C); by extrapolation it was estimated that $k_{-1} \approx 10^4 k_2$ (Scheme I). At the same time, since none of the homoallylic ion 4 was ever evidenced[1-3] in equilibrium with 1, it follows that, in Scheme I, $k_{-1} \gg k_1$.

Generation of the 4-cyclohexenyl cation (4) from various precursors (5) in superacid solutions has been attempted before.[3] In each case, the ring-contracted isomer 3 was the only

Scheme I

$$k_1 \ll k_{-1}; \ k_2 \ll k_{-1}$$
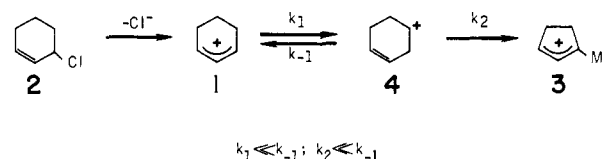
Scheme II
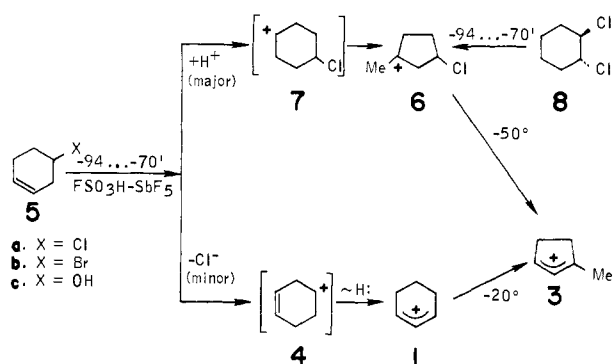
monomeric product observed.[3a,4] It was therefore concluded that ring contraction of **4** is much faster than the intramolecular hydride shift (i.e., $k_2 \gg k_{-1}$).[3a] This conclusion was later re-emphasized as a characteristic property of cyclic homoallylic cations.[5]

We report here results which resolve the apparent contradiction between the papers cited above[1-5] and elucidate the reaction mechanism of 4-cyclohexenyl substrates (**5**) in superacid.

4-Chlorocyclohexene (**5a**) was synthesized from 4-cyclohexenol[6] and triphenylphosphine in carbon tetrachloride.[7] Column chromatography (silica gel, Woelm, pentane as eluent) followed by distillation gave **5a** free of its isomer **2**.[8] The reaction of **5a** in superacid[9] under carefully controlled conditions,[1] at −94 to −70 °C, led to the 3-chloro(methyl)cyclopentyl cation (**6**) (identified by ^{1}H NMR), obviously formed by the protonation of the double bond of **5**, followed by ring contraction in the chlorocyclohexyl cation (**7**)[10] (Scheme II). The same ion **6** was obtained by the ionization of *trans*-1,2-dichlorocyclohexane (**8**) under the same conditions and identified by trapping with CO at −78 °C, then methanol at −100 °C.[11] No methylcyclopentenyl cation (**3**) was seen by NMR in the original solution (from the reaction of **5**) at −70 °C.[12] Some low intensity absorptions were seen, however, at δ 2.4–2.6 and 3.9–4.0. The origin of these absorptions was revealed in the better resolved spectra obtained at −48 °C, when the 3-chloro(methyl)cyclopentyl cation (**6**) eliminates HCl to form **3**. These spectra indicated the presence in the mixture of the 3-cyclohexenyl cation (**1**) by its signals[1,3a] at δ 2.50 (quintuplet, $J = 6.5$ Hz, β-CH₂) and 3.92 (triplet, $J = 6.5$ Hz, α-CH₂). Since ion **1** was not similarly observed when the chloro cation **6** was generated from dichlorocyclohexane (**8**) and converted to the methylcyclopentenyl cation (**3**), it appears that **1** is formed from **5** by ionization of chloride followed by a fast 1,2-hydride shift (Scheme II). This is in agreement with the previous studies on the hydrogen scrambling[2] and ring contraction[1] of **1** (Scheme I).

The integration of NMR spectra, both at −70 °C and during the transformation of **6** → **3** (at −48 °C)[13] indicated that under our conditions, the protonation of the double bond of **5** is favored over the heterolysis of the C–Cl bond by more than a 4:1 margin.[14] The failure of previous workers[3a] to observe any of the minor product **1** from various precursors (**5**) in several superacid systems might be due to the polymeric side

products reported,[3a,9b] which probably masked the NMR signals of **1**. Since the ring contraction of **1** is very slow at −50 °C,[1,13] the methylcyclopentenyl cation observed in their study[3a] should be also formed by the protonation path (**5** → **7** → **6** → **3**). The failure to see the intermediate **6** or compounds of similar structures[3a] was probably due to overheating. Actually **6**, first identified by us in the reaction of *trans*-dichlorocyclohexane (**8**), was not observed by the previous workers from that precursor either, but **3** was reported as the only observable product.[3a]

It is interesting to compare the reactivity of the two isomeric cyclohexenyl chlorides in superacid. The allylic isomer **2** reacts by ionization of chloride, exclusively. No double-bond protonation was observed,[1,3a] although the double bond of allylic chlorides is not appreciably deactivated toward electrophilic attack, which is in fact observed in nonionizing media.[15] The activation of the chlorine by the allylic double bond of **2** is, however, so important that the protonation of the double bond in superacid simply cannot compete. On the other hand, the homoallylic double bond of **5** does not comparably activate the chlorine atom toward ionization, so that protonation is the major reaction of **5** in superacid, with the chloride ionization being the minor process.

References and Notes

(1) D. Fărcaşiu and L. Craine, *J. Chem. Soc., Chem. Commun.*, 687 (1976).
(2) G. Seybold, P. Vogel, M. Saunders, and K. B. Wiberg, *J. Am. Chem. Soc.*, **95**, 2045 (1973).
(3) (a) G. A. Olah, G. Liang, and Y. K. Mo, *J. Am. Chem. Soc.*, **94**, 3544 (1972). Variable amounts of polymer were usually formed. (b) See also P. A. Buttrick, C. M. Y. Holden, and D. Whittaker, *J. Chem. Soc., Chem. Commun.*, 534 (1975).
(4) T. S. Sorensen, *J. Chem. Soc., Chem. Commun.*, 45 (1976).
(5) G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, **39**, 2394 (1974).
(6) G. J. Gogek, R. Y. Moir, and C. B. Purves, *Can. J. Chem.*, **29**, 946 (1951).
(7) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966); J. B. Lee and I. M. Downie, *Tetrahedron*, **23**, 359 (1967); J. B. Lee and T. J. Nolan, *ibid.*, **23**, 2789 (1967).
(8) Bp 70–71 °C (85 Torr) (lit. bp 69 °C (74 Torr)): F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **91**, 5774 (1969). No **2** was seen on GLC analysis, while other impurities amounted to <0.2%.
(9) (a) Molar ratios of FSO₃H to SbF₅ to **5a** = 4:1:0.26; the acid was diluted with SO₂FCl (0.7 vol). (b) No polymeric material was formed in our experiments.
(10) In ion **7** the positive charge was written at C-4, as being the farthest position from the electronegative chlorine substituent.
(11) D. Fărcaşiu, *J. Chem. Soc., Chem. Commun.*, 394 (1977).
(12) The signal for the CH₃ group of **3** (δ 3.62[1,3a]) is well separated from the spectrum of **6** (δ 5.43, CHCl; 4.80, α-CH₂s; 4.27, CH₃; and 3.19, β-CH₂[11]).
(13) The concurrent isomerization of **1** to **3** has a half-life of 94 days at −45 °C.[1]
(14) For another case of competition between ionization and protonation, see S. Masamune, M. Sakai, A. V. Kemp-Jones, and T. Nakashima, *Can. J. Chem.*, **52**, 855 (1974).
(15) Cf., for instance, the acylation of allyl chloride: P. Rosenmund and K. Grubel, *Angew. Chem.*, **80**, 702 (1968).

Dan Fărcaşiu
Corporate Research Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036
Received September 20, 1977