to the apical F1, K–F1 = 3.042 (3) Å (and to the other equatorial fluorine, F4, K–F4 = 3.073 (3) Å), in contrast to most of the known fluorosilicates, where the K^+ ion interacts with *two* fluorine atoms, having a shorter distance to the apical than to the equatorial fluorine. It should be further noted that the shortest K–F2 distance seems to be longest among the shortest ones ever found in fluorosilicates,[12] demonstrating looser K–F interaction in the present case.

^{13}C, ^{19}F, and ^{29}Si NMR studies have shown remarkable behavior of **1** in solution. The data recorded at room temperature are given in Table I. Significantly, while the ^{19}F NMR shows a broad *singlet*, the ^{29}Si spectrum exhibits a *sextet* for two silicon atoms, and the ^{13}C NMR spectrum shows two *sextets* due to two kinds of ipso carbons, C1 (=C2) and C7 (=C13), and two narrower *sextets* due to two kinds of ortho carbons, C3 (=C6) and C8 (=C12, C14, C18). These data clearly demonstrate that all the five fluorine atoms are equivalent on the NMR time scale owing to rapid intramolecular exchange processes. Fast fluoride transfer between tetracoordinate and pentacoordinate silicon atoms is supported by comparison of the chemical shift and coupling constant data of **1** with those of typical tetracoordinate silanes such as Ph_2SiF_2 and pentacoordinate silicates such as $[Ph_2SiF_3]^-$. Firstly, the Si chemical shift (δ −90.03 ppm) of **1** is intermediate between those of Ph_2SiF_2 (δ −29.00 ppm) and $[Ph_2SiF_3]^-$ (δ −109.55 ppm). Secondly, the Si–F coupling constant (J_{SiF} = 134.74 Hz) is smallest in comparison with those of Ph_2SiF_2 ($^1J_{SiF}$ = 291.2 Hz) and $[Ph_2SiF_3]^-$ ($^1J_{SiF}$ = 238.06 Hz) and is comparable with the calculated average value (143 Hz) on the assumption that $^1J_{SiF}$ = 238 Hz (×3F) and $^4J_{SiF} \doteq 0$ Hz (×2F).

Variable-temperature ^{19}F NMR studies have shown two consecutive processes for the fluorine exchange. At −80 °C, three signals are observed due to the bridging F1 (δ −70.11 ppm), apical F3 and F5 (δ −115.69 ppm), and equatorial F2 and F4 (δ −142.15 ppm).[13] The first two signals coalesce at −33 °C, the last remaining as a broad singlet, and coalescence of all signals is observed at −16 °C. The first process should be attributable to a rapid exchange of the bridging fluorine atom between two silicon atoms, and the second, slower process is the intramolecular ligand exchange by the Berry pseudorotation,[3] the energy barriers being estimated to be 9.2 and 10.2 kcal/mol, respectively. Since the latter value is in the range of energy barriers reported for monosilicates $[Ar_2SiF_3]^-$,[3] the pseudorotation process appears to be little influenced by the *o*-silyl group in the present case.

In summary, **1** represents a novel case where solution and solid-state structures are not the same and serves as a good model (1) for nucleophilic attack on a tetrahedral silane by a fluoride ion—geometries of both silicon atoms are in the middle of the reaction coordinate for the tetrahedral to trigonal-bipyramidal transformation—and (2) for *intermolecular* fluorine exchange processes between pentacoordinate fluorosilicate and tetracoordinate silane,[4] which have frequently been spectroscopically detected. Furthermore, the high stability of **1** suggests utilization of the precursor **4** as a new chelating trapping agent for anions such as H^-, RO^-, and Cl^- as well as F^-.[14] We are currently engaged in study along this line and the synthesis of unsymmetrical *o*-disilyl analogues of **1**.

Supplementary Material Available: Synthesis, physical constants, and spectral and analytical data on compounds **1**, **3**, and **4**, ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra at room temperature and temperature-dependent ^{19}F NMR spectra of **1**, and tables of crystallographic data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (14 pages). Ordering information is given on any current masthead page.

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(13) At −80 °C, three small signals appeared near the major signals, possibly due to the trans isomer.

(14) Selective anion complexation has recently been studied by employing Lewis acidic metal compounds. 1,8-Diborylnaphthalenes and 1-boryl-8-silylnaphthalenes: (a) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (b) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640. (c) Katz, H. E. *Organometallics* **1987**, *6*, 1134. Si macrocycles: (d) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297. Sn macrocycles: (e) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. Hg macrocycles: (f) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1987**, *109*, 4714. Lehn's anion cryptates: (g) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (h) Dietrich, B.; Lehn, J.-M.; Guilhem, J.; Pascard, C. *Tetrahedron Lett.* **1989**, *30*, 4125.

Does the Hydroxycarbonyl Anion Convert to the Formate Anion in the Gas Phase? A Potential Surface Map of the H^-/CO_2 System

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Received October 30, 1989

Deprotonation of formic acid with HO^- in the gas phase yields mainly the formate ion (HCO_2^-) together with a lesser amount of the hydroxycarbonyl anion ($HOCO^-$).[1] Ab initio calculations suggest that HCO_2^- is the more stable of the two by some 160 kJ mol^{-1}.[2] It has been suggested[1] from a consideration of the charge reversal[3] spectra of these two ions[1,4] that slow interconversion of the two ions could occur on collisional activation.[5]

A potential energy surface map of the hydride ion–carbon dioxide system is shown in Figure 1; particular structures represented by the surface are shown in Scheme I. The map depicts the variation in energy as a function of two system coordinates, viz., (i) the distance of H^- from O_1 and (ii) the angle H^- makes to the O_1–C bonding direction. The coordinates are chosen to best represent the interconversion of the two adducts formed between H^- and carbon dioxide.[6,7] The map was constructed from 160 points. Each point was optimized at the RHF/6-31+G* level and energy refined by a single point calculation at RMP2-FC/6-311++G**//RHF/6-31+G* (GAUSSIAN 86).[8,9] Energies (with

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(1) Burgers, P. C.; Holmes, J. L.; Szulejko, J. E. *Int. J. Mass Spectrom. Ion Processes* **1984**, *57*, 159.

(2) MP2//4-31+G//4-31+G calculations: Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612. For a recent calculation on HCO_2^- (MP2/6-31G*), see: Masamura, M. *Theor. Chim. Acta* **1989**, *75*, 433.

(3) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Szulejko, J. E.; Bowie, J. H.; Howie, I.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *13*, 76.

(4) Bursey, M. M.; Harvan, D. J.; Parker, C. E.; Pedersen, L. G.; Hass, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 5489.

(5) Such a possibility has been considered in cognate systems: e.g., (a) $MeCO^-$ does not convert (experimentally) to $(CH_2CHO)^-$ because of a more favorable channel of $MeCO^-$ to yield Me^- + CO (Downard, K. M.; Sheldon, J. C.; Bowie, J. H. *Int. J. Mass Spectrom. Ion Processes* **1988**, *86*, 217), and (b) in contrast, the ions $MeCO_2^-$ and $(CH_2CO_2H)^-$ are interconvertible under conditions of collisional activation (O'Hair, R. A. J.; Gronert, S.; DePuy, C. H.; Bowie, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 3105).

(6) The two oxygen atoms are not equivalent, O_1 being of fixed origin and O_2 relaxing up and down about the O_1–C vector. Thus the map is not bilaterally symmetrical, although some parts are strictly stereochemically equivalent.

(7) The optimum geometry of H^-/CO_2 adducts are consistently coplanar at the RHF level. It is assumed that the system is coplanar throughout the variation of hydride coordinates. Of the remaining four molecular coordinates which the two-dimensional map cannot show, only three are significant, i.e., the O_1–C bonding distance, the C–O_2 distance, and the OCO angle.

(8) Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. *GAUSSIAN 86*, *Release C*; Carnegie Mellon University: Pittsburg, PA.

(9) A number of other optimizations were carried out at the RHF/6-311++G** level: these geometries and their subsequent MP2 energies are little different from those derived from RHF/6-31+G* optimizations. Optimized geometries are thus insensitive to the presence of diffuse and polarization functions on the hydride ion. However, gridding the MP2 energies against hydride coordinates effectively gives an MP2/6-311++G** variational location of adducts and saddlepoints.

(10) Geometry (RHF/6-31+G*): C_s (singlet state); O_1C (1.4225 Å), CO_2 (1.2192 Å), O_1H (0.9579 Å), O_1CO_2 (111.2793°), CO_1H (105.6417°). Energy (RMP2-FC/6-311++G**//RHF/6-31+G*), −188.74241 au.

(11) (a) The anti conformer of **1**:C_s (singlet state); O_1C(1.4541 Å), CO_2 (1.2036 Å), O_1H (0.9452 Å), O_1CO_2 (111.0766°), CO_1H (104.2624°). Energy, −188.740 21 au. (b) The syn conformer is the more stable of the two by 5 kJ mol^{-1}; presumably this is due to the attraction of H and O_2.

(12) Saddlepoint A: O_1C (1.27 Å), CO_2 (1.21 Å), CH (1.20 Å), O_1H (1.20 Å), O_1CO_2 (130°).

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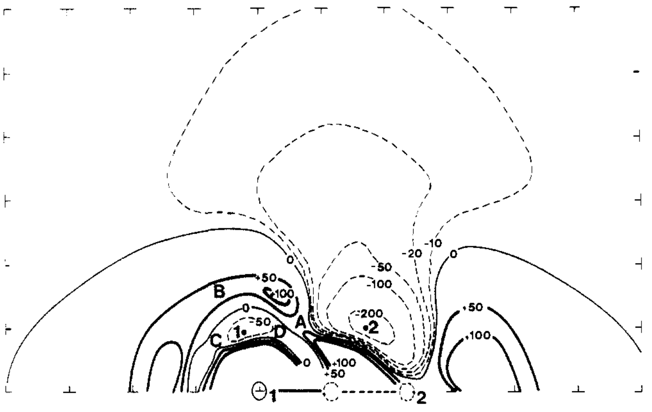
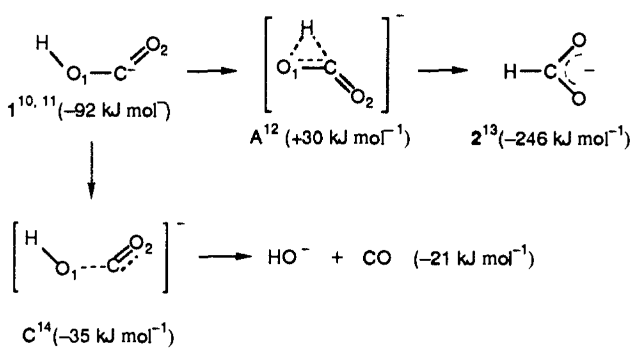


Figure 1. Potential surface map for the system H^-/CO_2 (RMP2-FC/6-311++G**//RHF/6-31+G*). **1** ≡ $HOCO^-$; **2** ≡ HCO_2^-; A is the saddlepoint for the reaction $HOCO^- \rightarrow HCO_2^-$; B is the saddlepoint for the reaction $HOCO^- \rightarrow H^- + CO_2$; C and D are saddlepoints for the reaction $HOCO^- \rightarrow HO^- + CO$.

Scheme I[a]



[a] All energies relative to $H^- + CO_2$ (0 kJ mol^{-1}).

respect to reactants H^- and CO_2) and geometries were computed for points on a rectangular 5 × 10 Å grid: at 1-Å intervals in flat potential regions and 0.125-Å intervals in regions where the energy varied in a complex manner.

The map shows that $HOCO^-$ (**1**) will not form directly from H^- and CO_2 in a thermal ion molecule reaction, since the saddlepoint (B) for this reaction is endothermic by some 65 kJ mol^{-1}. In contrast, there is no barrier to the formation of HCO_2^- (**2**) directly from H^- and CO_2. In principle, **1** is convertible **2** over saddlepoint A, but this barrier is endothermic by 122 kJ mol^{-1} even though the reaction is exothermic by 154 kJ mol^{-1} (see Figure 1 and Scheme I). In addition, there are two channels (through saddlepoints C and D) whereby $HOCO^-$ may decompose to HO^- and CO. This reaction is endothermic (Scheme I), but since the barrier to C is only 57 kJ mol^{-1}, it follows that $HOCO^-$ should dissociate to HO^- and CO rather than transform to the stable formate anion.[15]

$$HO_2CCO_2^- \xrightarrow{CID} HOCO^- + CO_2 \qquad (1)$$

$$MeO^- + Me_3SiOC(O)H \rightarrow HCO_2^- + Me_3SiOMe \qquad (2)$$

The hydroxycarbonyl and formate anions were synthesised in the mass spectrometer as shown in eqs 1 and 2. The hydroxycarbonyl ion was formed by collision-induced dissociation of carbon dioxide from deprotonated oxalic acid,[16] the formate ion by an S_N2 (Si) displacement.[17] The collisional activation mass spectra[18] of the two ions are as follows [*m/z* (loss) relative abundance]: $-HOCO^-$, 17 (CO) 100; HCO_2^-, 44 ($H^\bullet$) 100[19], 16 ($HCO^\bullet$) 1. Thus $HOCO^-$ specifically decomposes to HO^-, and since the spectra contain no common fragmentation, this indicates that conversion of $HOCO^-$ to HCO_2^- does not occur under the experimental conditions used in these experiments. Thus theory and experiment are in accord.

Acknowledgment. We thank R. N. Hayes (University of Nebraska–Lincoln) for the MS/MS/MS data on $HOCO^-$ and D. E. Lewis (South Dakota State University) for helpful discussion.

Registry No. Hydride ion, 12184-88-2; hydroxycarbonyl anion, 78944-70-4; formate anion, 71-47-6; carbon dioxide, 124-38-9.

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(13) C_{2v} (singlet state): CH (1.1172 Å), CO (1.2346 Å), HCO (114.750°). Energy, −188.80091 au.

(14) Saddlepoint C: O_1C (1.45 Å), CO_2 (1.20 Å), O_1H (0.96 Å), HO_1C (135°), O_2CO_1 (115°).

(15) A reviewer has asked that we compare our ab initio energies with experimentally determined standard enthalpies of formation. In order to do that, we must convert those experimental energies to be directly comparable to our standard system (i.e., H^- plus CO_2, 0 kJ mol^{-1}, see Figure 1 and Scheme I). ΔH°_f for H^-, HO^-, and HCO_2^- are 145, −137.4, and −464 ± 13 kJ mol^{-1}, respectively (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*(Suppl. 1)); for CO and CO_2, −110.5 and −393.5 kJ mol^{-1}, respectively (Benson, S. W. *Thermochemical Kinetics*; John Wiley and Sons, Inc.: New York, London, Sydney, 1968). From these values we obtain the following formation energies of products from the reactants H^- and CO_2 (taken as 0 kJ mol^{-1}): (a) HO^- + CO; 0 kJ mol^{-1} (cf. −21 kJ mol^{-1}, Scheme I); and (b) HCO_2^-; −216 kJ mol^{-1} (cf. −246 kJ mol^{-1}, Scheme I).

(16) O'Hair, R. A. J.; Bowie, J. H.; Hayes, R. N. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 275.

(17) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6443. Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

(18) (a) The spectrum of $HOCO^-$ was determined by a CA MS/MS/MS experiment measured with an MS 50 TA instrument; experimental details have been described previously (Burinsky, D. J.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 295. Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243). (b) The spectrum of HCO_2^- was measured under CA MS/MS conditions by using a VG ZAB 2HF instrument; for experimental details, see: Stringer, M. B.; Bowie, J. H.; Holmes, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3888.

(19) Since the electron affinity of CO_2 is negative (−0.60 ± 0.2 eV; Compton, R. N., Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1975**, *63*, 3821), the structure of *m/z* 44 may be $[O^{\bullet}(CO)]$.

Some Observations Concerning the Structure of Dilithiomethane

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Received October 26, 1989

As small-volume cationic charge centers and as a source of unoccupied valence orbitals, the early main group metals have a well-documented but remarkable organometallic chemistry. Unusual structural configurations are observed for organolithium,[1] -beryllium, and -aluminum compounds including semibridging σ–π coordination in organometallic acetylenes such as $(C_6H_5)_2AlC{\equiv}CC_6H_5$,[2] π back-donation which leads to planar three coordinate metal atom configurations as in $[BeN(CH_3)_2]_3$,[3] alkyl C–H coordination as in $LiB[CH_3]_4$[4] or $[LiC_6H_{11}]_2$,[5] and frontier

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(3) (a) Atwood, J. L.; Stucky, G. D. *Chem. Commun.* **1967**, 1169; (b) *J. Am. Chem. Soc.* **1969**, *91*, 4426.

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