Structures and Isotopic Fractionation Factors of Complexes AHA$^-$ [1]

Sir:

Certain kinds of homoconjugate complexes, A_2L^-, have been found to give isotopic fractionation factors, $\phi_{A_2L^-}$, in the range of 0.25-0.35.[2] In the compounds that we have studied A^- is a nitrophenate anion, and our solvent has been acetonitrile (AN), but theory suggests that the phenomenon should not be limited to these specific circumstances. Equation 1 defines ϕ_{XL} for the general substance XL.[3,4]

$$\phi_{XL} = [XD]/[XH] \times (H/D)_{L_2O} \qquad (1)$$

The square brackets should, properly, indicate activities, but the measurements reported here were carried out in the common, nonexchanging solvent, AN, so that transfer activity coefficients[5] do not enter, and concentrations can be used in place of activities. Values of ϕ_{XL} below ~0.7 have usually been encountered in transition states, and have been taken to suggest that the reaction coordinate includes a transfer of L.[6] Other kinds of hydrogen have usually given large values of ϕ_{XL},[7-9] although thiols give values of 0.40-0.45,[10] and there have been scattered reports implying small ϕ_{XL} values for certain oxygen compounds.[11,12] Molecular hydrogen[13] and a few other special structures generate particularly low values of ϕ_{XL} for reasons that are usually apparent. In the present compounds A^- is chosen such that the potential function governing the motion of L^+ along the A-A axis has a double minimum with a weak central maximum.

The homoconjugate complexes were prepared by combining equimolar quantities of the appropriate acid and its tetramethylammonium salt. The nitrophenate complexes were isolated as solids and purified by recrystallization.[14] The OH absorption in the IR spectra of these complexes is typical of Hadži's type ii compounds.[15a,b] The NMR signal of the bridging proton occurs at very low field, as shown in Table I. These spectroscopic characteristics seem to be shared by all A_2L^- and B_2L^- with very low fractionation factors. They have been attributed by Zundel[15c] to the high polarizability of the hydrogen bonds which these compounds contain.

Unlike the complexes formed from pyridine 1-oxide and acids,[16] these complexes are in degenerate tautomeric equilibrium. Any given complex molecule contains one nitrophenol and one nitrophenate unit; each distorted by hydrogen bonding to the other, but both still giving identifiable bands in the electronic spectrum, as illustrated in Figure 1. Similar spectroscopic properties have previously been noted for the triethylamine complex with *p*-nitrophenol.[17] The degenerate interconversion is fast enough that no doubling of fingerprint bands is observable in the IR. This puts a lower limit of ~10^{11} s^{-1} on the rate constant for interconversion.[18] Presumably there is extensive proton tunnelling.

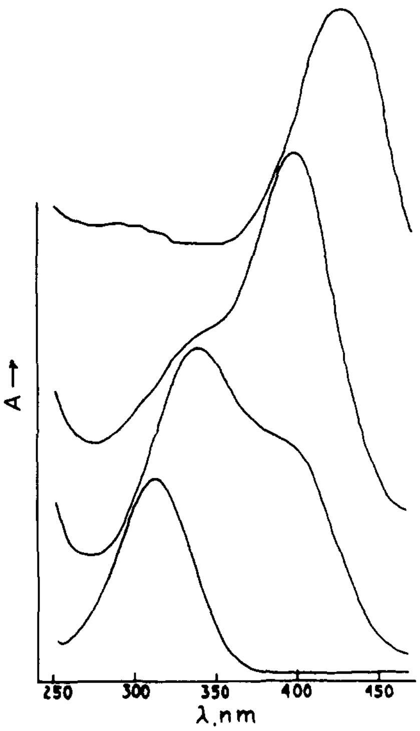


Figure 1. Electronic spectra of 4-nitrophenol derivatives in sulfolane. The top spectrum is 0.049 M tetraethylammonium 4-nitrophenate with a path length of 12.5 μm. The second is 0.079 M tetraethylammonium bi(4-nitrophenate), with a path length of 8.2 μm. The third is 0.073 M tetraethylammonium salt of the 4-nitrophenol-benzoate complex, with a path length of 11.7 μm. The bottom spectrum is 0.046 M 4-nitrophenol with a 10.4-μm path length.

Table I. Fractionation Factors and Chemical Shifts of A_2L^- and ALB

Substance	ϕ_{XL} [a]	τ_{XH} [b]
$(4\text{-}NO_2C_6H_4O)_2H^-$	0.27 ± 0.01	16.6
$[3,5\text{-}(NO_2C_6H_3O)_2]_2H^-$	0.33 ± 0.03	Blank
$(CF_3CO_2)_2H^-$	0.45 ± 0.02	19.75[d]
	0.61 ± 0.02[c]	
F_2H^-	0.60[e]	Blank
$[(CH_3)_2SO]_2H^+$	0.36[f]	Blank
$CF_3CO_2H{\cdot}OS(CH_3)_2$	0.51 ± 0.02[c]	16.20[d]
$CF_3CO_2H{\cdot}OP(C_4H_9)_3$	0.56 ± 0.02[c]	17.50[d]
CH_3CO_2H[g]	0.96 ± 0.02[h]	Blank

[a] Cited uncertainties are probable errors. Where no reference is given the value was measured in the present series of experiments. [b] In parts per million from tetramethylsilane. [c] K.-C. Chang, Ph.D. Thesis, University of Minnesota, 1975, p 61. [d] K.-C. Chang, *ibid.*, p 52. [e] Estimated from information given by A. J. Kresge and Y. Chiang, *J. Phys. Chem.*, **77**, 822 (1973). [f] Estimated from information given by J. M. Williams and M. M. Kreevoy, *J. Am. Chem. Soc.*, **89**, 5499 (1967). ϕ_{L_2O} was assumed to be unity when L_2O is a solute in Me_2SO. [g] Dissolved in water; other carboxylic acids and phenols seem to be similar. [h] V. Gold and B. M. Lowe, *J. Chem. Soc. A*, 1923 (1968).

Isotopic redistribution reactions were studied by equilibrating A_2H^- with $(C_6H_5)_3COD$ (ROD) in AN. In AN, ROH has a band at 3500 cm^{-1} which is free of interference, except for the weak absorbance due to the complex mentioned above. The absorbance due to ROH ~3500 cm^{-1} obeys the Beer-Lambert law, with extinction coefficient, ϵ, of 105. After correction for the weak absorption due to A_2H^-, the absorbance at 3500 cm^{-1} of solutions in AN originally containing 0.1-0.4 M of A_2H^- and ROD was used to determine the ROH concentration in the equilibrated solution. Since the initial concentrations were known all the final concentrations and the equilibrium constant, K_2, could be evaluated.

$$A_2H^- + ROD \underset{AN}{\overset{K_2}{\rightleftharpoons}} A_2D^- + ROH \qquad (2)$$

In each set of experiments the H_2O present in the solvent and the ROH present in the ROD were determined by making a series of parallel determinations on AN solutions to which no A_2H^- had been added. Assuming that K_3 is 1.00 in homogeneous AN solution, 1-6% ROH was found in the ROD and 2-6 $\times 10^{-3}$ M H_2O in the AN.

$$ROH + \tfrac{1}{2}D_2O \overset{K_3}{\rightleftharpoons} ROD + \tfrac{1}{2}H_2O \qquad (3)$$

These were appropriately taken into account in evaluating the final concentrations and K_2. In most experiments the corrections were small, and the final result is not sensitive to the exact value chosen for K_3.

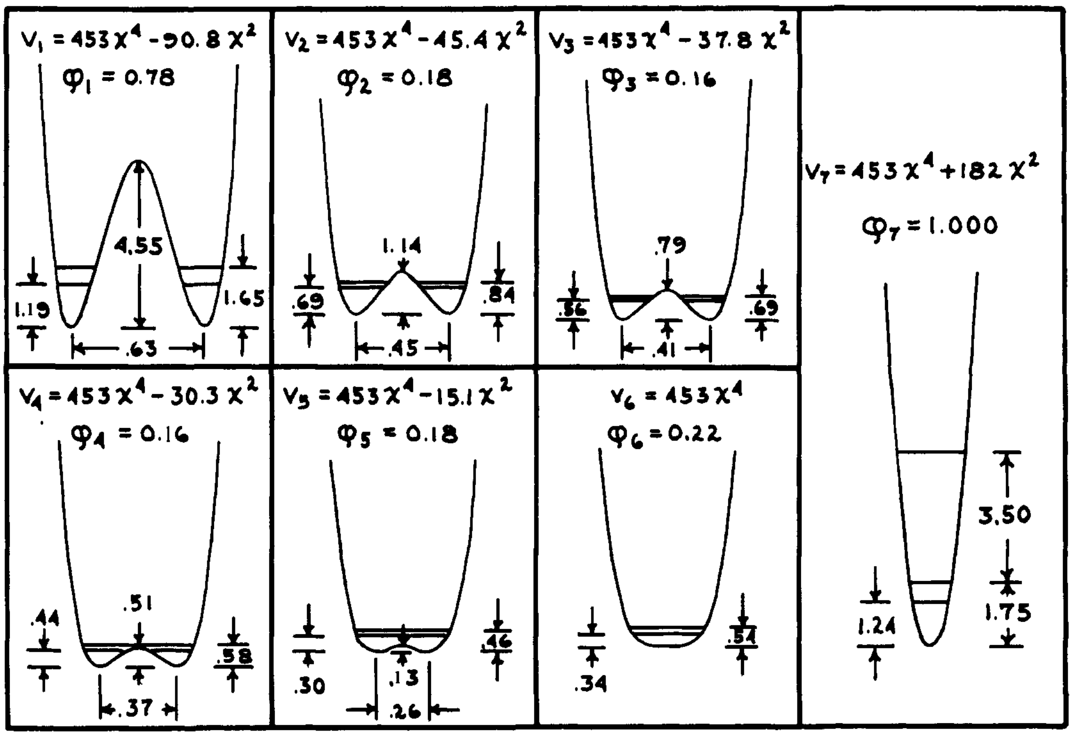


Figure 2. Calculated fractionation factors, ϕ_n, for various one-dimensional quartic-quadratic potential functions, V_n, for a hydrogen or deuterium between two identical bases of infinite mass. The lowest allowed energy level for hydrogen is shown to the right of each potential function, and that for deuterium, to the left. For V_7 the second allowed level for hydrogen is also shown, and the fundamental frequency. Where a central maximum occurs its height is shown, and its width in angstroms. The units of the potential functions and all the energy levels and energy level spacings are 10^3 cm^{-1}. The allowed energy levels were obtained by appropriately scaling dimensionless energy levels given by Laane.[22] Those for V_1 are actually slightly split by tunnelling. The average value is shown. The ϕ_n values were obtained from eq 4, using V_7 as the potential function for the standard substance. V_1 was chosen arbitrarily. V_7 was chosen so as to generate a fundamental vibration frequency of 3500 cm^{-1} and to have curvature at the minimum identical with that at the minima of V_1.

To get $\phi_{A_2L^-}$ from K_2, it should be multiplied by ϕ_{ROH}, where the latter, properly, applies to ROH in AN and the isotopic variants of water in L_2O of 50% deuterium content.[19] That value is not available but a fractionation factor of 1.04 has been determined for $(CH_3OC_6H_4)_3COL$ in homogeneous aqueous solution.[20] This has been used to calculate the $\phi_{A_2L^-}$ values shown in Table I, which also shows ϕ_{XL} values for a number of related substances, for comparison.

The ϕ_{XL} values in Table I can be systematized and understood by reference to the family of potential functions shown in Figure 2.[21,22] It represents the potential experienced by the proton or deuteron in a bridge bond between two identical bases of infinite mass. For a weak hydrogen bond there are two minima, separated by a central maximum. As the bond becomes stronger this maximum becomes smaller, the minima draw closer together. Finally the maximum disappears and the minima merge, as in HF_2^-. Allowed energy levels for these one-dimensional oscillators can be obtained by properly scaling the dimensionless values given by Laane.[22] If the reference substance, water, can be represented by one member of the family, fractionation factors, ϕ_n, can be approximated using eq 4.[23]

$$\phi_n = \exp\frac{hc}{kT}(ZPE_{H,n} - ZPE_{D,n} - ZPE_{H_2O} + ZPE_{D_2O}) \quad (4)$$

Zero-point energy (ZPE) is that taken from Figure 2, expressed in cm^{-1}. The other symbols have their usual significance. This simple model reproduces our observations with remarkable fidelity. A minimum value for ϕ_n, of about the right magnitude,[24] is predicted when the potential function just rises to the first allowed level for hydrogen. The spectroscopic evidence suggests that the central maximum in the bi(nitrophenate) ions approximates that in V_2.

The introduction of appreciable asymmetry into the hydrogen bond will tend to increase the energy level spacing[25] and raise ϕ_{XL}, as shown by the ϕ_{ALB} in Table I.

Although the number of well-established examples is still small, the conformance to the expectations of theory, described above, suggests that the phenomenon is general. Isotopic fractionation factors appear to provide a useful addition to the range of techniques for studying hydrogen bonds. Primary hydrogen isotope effects <4 should not be taken to necessarily require a rate-determining proton transfer.

References and Notes

(1) This work was supported by the National Science Foundation, through Grants GP-31360X and CHE 76-01181, to the University of Minnesota.
(2) The symbol L is used to denote a position which may be occupied by any one of the isotopes of hydrogen.
(3) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).
(4) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964).
(5) M. M. Kreevoy, "Isotopes in Organic Chemistry", Vol. 2, E. Burcel and C. C. Lee, Ed., Elsevier, Amsterdam, 1976, p 5.
(6) W. J. Albery, "Proton-Transfer Reactions", E. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 301.
(7) L. Melander, "Isotope Effects and Reaction Rates", Ronald Press, New York, N.Y., 1960, Chapter 5.
(8) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1973, Chapters 11, 12.
(9) R. L. Schowen, *Progr. Phys. Org. Chem.*, 281 (1972).
(10) F. W. Hobden, E. F. Johnston, H. P. Weldon, and C. L. Wilson, *J. Chem. Soc.*, 61 (1939).
(11) J. M. Williams and M. M. Kreevoy, *J. Am. Chem. Soc.*, **89**, 5499 (1967).
(12) J. A. K. Harmony, R. H. Himes, and R. L. Schowen, *Biochemistry*, **14**, 5379 (1975).
(13) Y. Bottinga, *J. Phys. Chem.*, **72**, 4338 (1967).
(14) An appropriate elemental analysis was obtained for each of the nitrophenate complexes.
(15) (a) D. Hadži, *Pure Appl. Chem.*, 11, 435 (1965); (b) D. Hadži and S. Bratas, "The Hydrogen Bond. Recent Developments in Theory and Experiments. II. Structure and Spectroscopy", P. Schuster, G. Zundel, and C. Sandarfy, Ed., North-Holland Publishing Co., Amsterdam, 1966, Chapter 12; (c) G. Zundel, ref 15b, Chapter 15.
(16) M. M. Kreevoy and K.-C. Chang, *J. Phys. Chem.*, **80**, 259 (1976).
(17) R. A. Hudson, R. M. Scott, and S. N. Vinogradov, *J. Phys. Chem.*, **76**, 1989 (1972).

(18) J. L. Wood. *J. Mol. Struct.*. **13,** 141 (1972).
(19) V. Gold. *Trans. Faraday Soc.*, **64,** 2770 (1968).
(20) V. Gold and C. Tomlinson. *J. Chem. Soc. B.* 1707 (1971).
(21) J. C. Speakman. *Struct. Bonding* (*Berlin*). **12,** 141 (1972).
(22) J. Laane. *Appl. Spectrosc.*. **24,** 73 (1970).
(23) Equation 4 is the usual zero point energy approximation for the equilibrium constant of an isotopic redistribution reaction (ref 5. p 16) except that the harmonic oscillator expression for zero-point energy has not been used. since the most significant V_n values are not well approximated by harmonic oscillators.
(24) The predicted minimum value is lower than the smallest value actually observed. but all the obvious approximations tend to produce too low a value. The breathing of the bases in the real molecules will tend to average ϕ_n up; the effective mass of the real bases is finite so that the effective mass of the oscillator is >1 for H or 2 for D: the stretching frequencies of water are <3500 cm^{-1}. The present treatment considers only the linear OHO force field. The formation of a strong hydrogen bond can be expected to strenghten the bending force fields[15b] and. thereby. to somewhat raise the fractionation factors.
(25) The linear hydrogenic vibration frequency of Cl_2H^- is raised from ~700 to ~1600 cm^{-1} by the introduction of crystal field dissymmetry into the solid: B. S. Ault and L. Andrews. *J. Chem. Phys.*. **63,** 2466 (1975): J. C. Evans and G. Y-S. Lo. *J. Phys. Chem.*. **70,** 11 (1966).
(26) M. M. Kreevoy was the guest of the Physical Chemistry Laboratory. Oxford. while this work was in progress. He wishes to thank Drs. W. J. Albery. and R. K. Thomas of that laboratory for stimulating discussions of this work. and many others for their encouragement and hospitality.

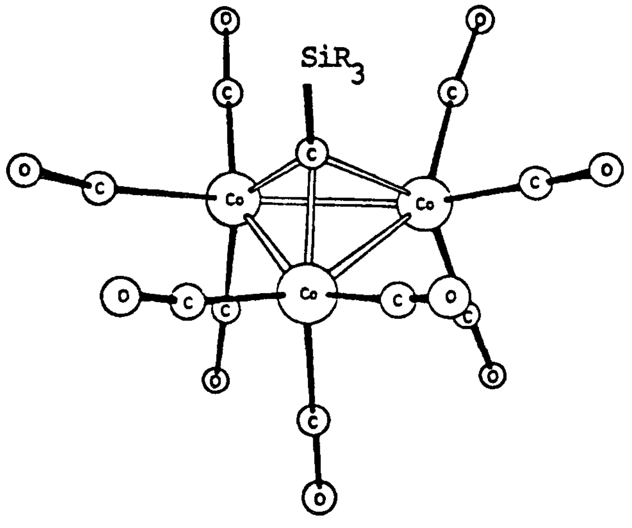
Maurice M. Kreevoy* [26]
Tai-ming Liang, Kwang-Chou Chang
Department of Chemistry
Laboratory for Chemical Dynamics
University of Minnesota. Minneapolis. Minnesota 55455

Received February 18. 1977

A General, High Yield Route to Novel Silicon-Functional Silylmethylidynetricobalt Nonacarbonyl Cluster Complexes[1]

Sir:

The generally applicable procedure for the preparation of alkylidynetricobalt nonacarbonyl complexes involves the reaction of an organic trihalide with dicobalt octacarbonyl.[2] We and others have used this reaction to prepare silyl-substituted methylidynetricobalt nonacarbonyls, I, including $Me_3SiCCo_3(CO)_9$,[3] $Me_2PhSiCCo_3(CO)_9$,[3] and other unspecified "$R_3SiCCo_3(CO)_9$" complexes.[4] This procedure has drawbacks in that it requires the preparation of the appropriate trihalomethyl silicon derivative. Furthermore, reactive functionality on silicon very likely would cause difficulties in this synthesis.



I

We have developed a new route to silylmethylidynetricobalt nonacarbonyl complexes, which uses readily available starting materials, is easily effected and generally proceeds in high yield. Its principal advantage, however, is that it is compatible with a wide diversity of reactive functionality on silicon. This new procedure uses the reaction of methylidynetricobalt nonacarbonyl with silicon hydrides (eq 1).

$$>\mathrm{SiH} + \mathrm{HCCo_3(CO)_9} \xrightarrow[\text{30 min}]{\text{toluene,reflux}} >\mathrm{SiCCo_3(CO)_9} + \mathrm{H_2} \tag{1}$$

These reactions were carried out under an atmosphere of carbon monoxide (to retard decomposition of the cluster complexes) using 1.0 g (2.26 mmol) of $HCCo_3(CO)_9$ and 5-12 mmol of the silane in 40 mL of dry toluene. The reaction mixture was stirred and heated at reflux (~105 °C) for 30 min. During this time, the originally purple color of the starting cluster changed to reddish purple. Upon completion of the reaction, the solvent was removed at reduced pressure and, in

Table I. $R_3SiCCo_3(CO)_9$ Compounds Prepared

Compd	R_3Si in $R_3SiCCo_3(CO)_9$[a]	Method of synthesis[b]	% yield	Mp, °C
1	Et_3Si	A	76	Softens above 70, dec
2	$Me_2(i\text{-}Pr)Si$	A	70	Softens above 110
3	$n\text{-}Pr_3Si$	A	81	85-86
4	Me_2PhSi	A	91	75[c]
5	$MePh_2Si$	A	60	84-85
6	Ph_3Si	A	39	139-140
7	$Me_2(EtO)Si$	A	48	120-122
8	Me_2ClSi	A	90	Apparent dec above 150
9	$Me_2(MeO)Si$	A/B	78	Dec at 140 without melting[d]
10	$Me_2(HO)Si$	A/B	76	Dec at 130 without melting[d]
11	$Me(MeO)_2Si$	A/B	73	Softens above 120
12	$Me(HO)_2Si$	A/B	81	Dec above 140 without melting
13	$(MeO)_3Si$	A/B	62	Softens above 120
14	$(HO)_3Si$	A/B	66	Dec above 150 without melting
15	Me_2FSi	C	93	205-206[d]
16	MeF_2Si	C	87	Softens above 170
17	F_3Si	C	85	Dec above 120
18	$Me_2(Me_3SiO)Si$	C	68	70-71
19	$Me(Me_3SiO)_2Si$	C	74	53-54
20	$(Me_3SiO)_3Si$	C	79	139-140

[a] All compounds listed have been characterized by combustion analysis and IR and NMR spectroscopy. [b] A: by reaction of $HCCo_3(CO)_9$ with the respective silicon hydride. A/B: by reaction of $HCCo_3(CO)_9$ with the respective chlorosilicon hydride followed by methanolysis or hydrolysis of the product. C: by further reaction of the respective hydroxysilane according to eq 2 or 3. [c] Reference 3. [d] M. O. Nestle, Ph.D. Thesis, Massachusetts Institute of Technology, 1977.