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Kinetics of Terminal Alkyne sp Carbon–Hydrogen Bond Activation Catalyzed by Silver(I)†

Glenn S. Lewandos,* James W. Maki, and Jill P. Ginnebaugh

Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859

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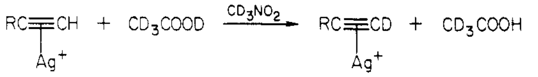
Activation of the sp carbon–hydrogen bond in a series of terminal alkynes is promoted by prior π coordination of silver(I) trifluoromethanesulfonate to the triple bond. The activation, monitored by exchange of protium for deuterium by using proton NMR spectroscopy, is catalytic in silver salt. For the exchange the rate expression is rate = k_1 [RC≡CH·AgOTf] + k_2[RC≡CH·AgOTf][CD_3COOD]. The deuterated alkyne reacts faster than the protiated alkyne ((rate/[RC≡CH] ÷ rate/[RC≡CD]) = 0.46 ± 0.07), consistent with increase in p character of the alkyne terminal carbon in the rate-determining step. The rate of deuterium exchange is linearly correlated with the decrease in terminal sp carbon–hydrogen bond stretching frequency upon silver(I) π coordination but nonlinearly with the change in proton NMR chemical shift of the hydrogen bound to the terminal sp carbon upon silver(I) π coordination.

Introduction

With declining petroleum feedstocks, the last decade has seen growing interest in the selective activation of hydrocarbon C–H bonds in order to make better use of available supplies.[1] The majority of papers have reported sp^3 C–H bond activation (intramolecular[2] and intermolecular[3]), sp^2 C–H bond activation,[4] the alkyl–alkylidene equilibrium,[5] and the alkylidene–alkylidyne equilibrium,[6] but little work has been done on the mechanism of sp C–H bond activation. Most interest has centered upon synthetic use of the already activated sp C–H bond in metal acetylides.[7]

In earlier work we observed that upon silver(I) π coordination to terminal alkynes the terminal sp C–H bond is weakened and polarized.[8] The silver π coordination makes the terminal hydrogen *only* active toward exchange with deuterium (eq 1).[9] In one example, 1,7-octadiyne π coordinated to silver(I) trifluoromethanesulfonate (triflate, OTf) undergoes deuterium exchange a minimum of 10^5 times faster than without silver.



$$\underset{Ag^+}{RC\equiv CH} + CD_3COOD \xrightarrow{CD_3NO_2} \underset{Ag^+}{RC\equiv CD} + CD_3COOH \qquad (1)$$

A logical mechanism for the exchange in eq 1 involves formation of an intermediate silver acetylide, followed by deuterium incorporation. However, our studies showed that while silver acetylide formation does occur to a significant extent in the absence of deuterium source, its formation is kinetically slow (days) compared to the rate of deuterium exchange (minutes). Thus, silver acetylide formation cannot occur prior to or during the rate-determining step.

Because (a) the site of initial silver ion coordination to a terminal alkyne is well-defined, (b) alkyne terminal C–H bond activation occurs in homogeneous solution at rates that are convenient to monitor, (c) the activation is selective toward one type of hydrogen, and (d) the activation is catalytic in silver ion, the terminal (alkyne)silver(I) π complexes are promising model compounds for study of some basic principles of C–H bond activation. In this paper we report the effect of deuterium donor concentration upon rate of exchange and the presence of an inverse kinetic deuterium isotope effect. The mechanistic implications of these observations will be discussed.

Experimental Section

Materials and Equipment. Silver triflate (Aldrich) was recrystallized from pentane/ethyl ether mixtures and dried under vacuum. It was stored in the dark, and all transfers of the hygroscopic salt were performed in a glovebag under a flow of dry nitrogen. The alkynes (Farchan) were stirred over calcium hydride prior to distillation and were stored over activated molecular sieves. All liquids were stored in vials fitted with Mininert valves, and sampling was done with gas-tight, predried microsyringes. Before use, solvents and solutions were degassed with dry nitrogen.

Proton NMR spectra and IR spectra were obtained as described previously.[9]

Syntheses of Terminal Alkynes-*1*-d_1. The alkynes 1-hexyne-*1*-d_1, 3-methyl-1-pentyne-*1*-d_1, and 3,3-dimethyl-1-butyne-*1*-d_1 were prepared by the following procedure: In a flame-dried, nitrogen-flushed flask a small amount of sodium hydroxide (53 mg, 1.33 mmol) was added with stirring to 99% D_2O (77 g, 3.85 mol). The alkyne (0.041 mol) was added, and the two-phase mixture was stirred for a minimum of 7 h. The layers were separated under nitrogen atmosphere. The organic layer was dried with molecular sieves, filtered, and distilled. The percent deuterium incorporation at the terminal carbon of the alkyne was estimated by repeated integration of the proton NMR spectrum.[10] No incorporation of deuterium at other than the terminal carbon could be detected. The percent deuterium incorporation (±3%)

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† Dedicated to the memory of the late Rowland Pettit.

[1] (a) Masters, C. "Homogeneous Transition-metal Catalysis"; Chapman and Hall: London, 1981; Chapter 3. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapters 7 and 12.

[2] Examples: (a) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (b) Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713.

[3] Examples: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Crabtree, R. H.; Millea, M. F.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147.

[4] Examples: (a) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Chem. Commun.* **1981**, 186. (b) Parshall, G.; Klabunde, U. *J. Am. Chem. Soc.* **1972**, *94*, 9081.

[5] Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

[6] (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 7667. (b) Holmes, S. J.; Schrock, R. R. *Ibid.* **1981**, *103*, 4599.

[7] (a) Hurdlik, P. F.; Hurdlik, A. M. In "The Chemistry of the Carbon-carbon Triple Bond", Part I; Patai, S., Ed.; Wiley: Chichester, 1978; p 256 and references therein. (b) Sladkov, A. M.; Ukhin, L. Y. *Russ. Chem. Rev.* (*Engl. Trans.*) **1968**, *37*, 748.

[8] Lewandos, G. S. *Tetrahedron Lett.* **1978**, 2279.

[9] Ginnebaugh, J. P.; Maki, J. W.; Lewandos, G. S. *J. Organomet. Chem.* **1980**, *190*, 403.

[10] In the presence of silver(I) the terminal proton resonance appears downfield and distinct from the resonances of protons on the α- and β-carbons.[9] Thus, even small amounts of residual terminal protium can be detected in the presence of terminal deuterium.

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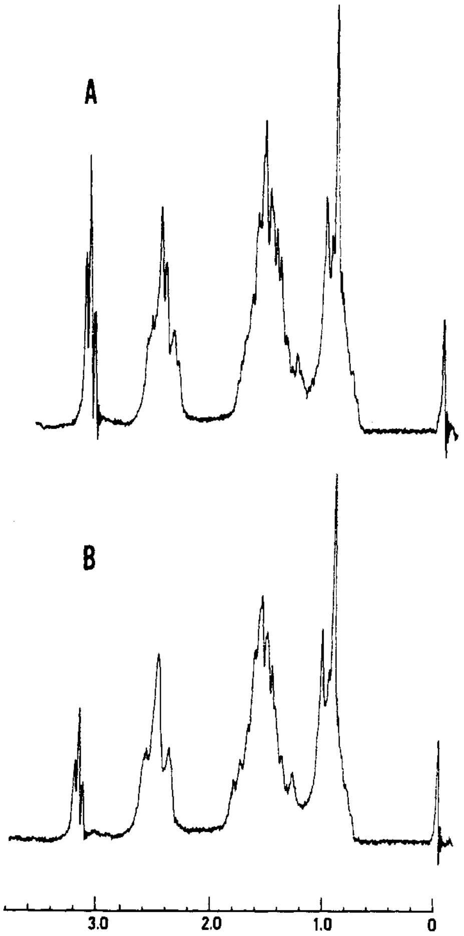


Figure 1. The proton NMR spectra of (1-hexyne)silver triflate (0.4 M) in CD_3NO_2 at 35 °C: A, prior to addition of CD_3COOD; B, after addition of CD_3COOD.

was as follows: 1-hexyne, 79%; 3-methyl-1-pentyne, 75%; 3,3-dimethyl-1-butyne, 80%.

Kinetics. Kinetic measurements were made with a Varian T-60 NMR spectrometer with a constant probe temperature of 35 °C. All samples contained Me_4Si as internal standard. The resolution was maintained between 0.8 and 1.0 Hz. Phase adjustment of the signal and integral drift control were optimized for each sample so that a flat base line was observed before and after each integral trace.

In each kinetic run, silver triflate was added to an NMR tube. Nitromethane-d_3 with Me_4Si and alkyne were added. The area of terminal proton resonance was determined relative to the resonance due to hydrogen on sp^3 carbon(s). During this period no change in relative area was observed. Enough acetic acid-d_4 was added to bring the concentrations of alkyne and AgOTf to ~0.4 M and to provide the desired ratio of alkyne to acetic acid-d_4. The spectrum was continually integrated to determine decrease in concentration of sp-carbon-bound proton as a function of time. Commonly, 25–40 separate integrals were taken during a run. Figure 1 illustrates the proton NMR spectra of a representative alkyne (1-hexyne) prior to acetic acid-d_4 addition and after addition. The clearly separated terminal proton resonance is seen to decrease in area after the addition. When the system reached equilibrium, a final spectrum was obtained to measure accurately chemical shift. Finally, the solution volume, and hence molar concentration, was determined by measurement of solution height in the volume precalibrated NMR tube.

The exchange was quantitative, with no loss of alkyne due to competing side reactions. The loss of terminal proton resonance was accompanied by appearance of a resonance at approximately δ 10.1 (varies with concentration) from CD_3COOH. The sum of these two areas was always equal to that of the initial terminal proton. Also, the sum of the two areas was always constant with respect to resonances of proton on sp^3 carbon. No absorbances were seen in the olefinic region from alkyne polymerization.

Initial rates of reaction (to 15% conversion) were calculated. Rates reported are averages of three independent determinations unless noted otherwise.

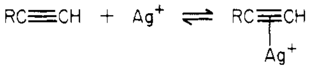
The kinetics measurements to measure H/D isotope effects were made in the same way except (a) deuterated alkynes and CH_3COOH were used and (b) the increase in peak area of the proton bound to sp carbon was monitored as a function of time. Rates for alkynes with less than 100% deuterium at the terminal carbon are corrected to 100% deuterium content for data to be comparable to that of protiated alkynes. Exchange was quantitative with no alkyne loss.

Role of Solvent in H/D Exchange. Silver triflate (40 mg, 0.156 mmol) was transferred to an NMR tube under an atmosphere of dry nitrogen. Acetic acid-d_4 (200 μL, 3.48 mmol) with Me_4Si was added to give a suspension. No nitromethane-d_3 was present. The terminal alkyne (0.156 mmol) was added to yield a homogeneous solution, and the resulting proton NMR spectrum was integrated periodically over 9 h.

Results and Discussion

To elucidate the mechanism of the reaction in eq 1, we determined the dependence of reaction upon [RC≡CH·AgOTf], [CD_3COOD], and solvent.

Effect of Solvent. While the D exchange reaction can be carried out in other solvents (acetone, acetic acid),[11] this kinetic work was done in nitromethane-d_3. This is because there exists a dynamic equilibrium between free and complexed alkyne in solution (eq 2). Earlier work has shown that more stable π complexes to silver are formed in this solvent.[9,12] With nitromethane-d_3 the reactions of π-coordinated alkynes can be facilitated rather than there existing a significant amount of uncoordinated and unreactive alkyne in solution.



$$\mathrm{RC{\equiv}CH} + \mathrm{Ag^+} \rightleftharpoons \underset{\mathrm{Ag^+}}{\mathrm{RC{\equiv}CH}} \qquad (2)$$

An initial reaction was carried out on the alkynes (1-hexyne, 3-methyl-1-pentyne, 3,3-dimethyl-1-butyne, 1,5-hexadiyne) with equimolar amount of AgOTf and excess CD_3COOD. Without solvent the reactions were so rapid (equilibrium reached in <5 min) that accurate rate measurements could not be made. Qualitatively, complete D exchange was observed at a rate equal to or faster than that observed in 0.4 M nitromethane-d_3. Without AgOTf no exchange occurred under these conditions. Thus, the deuterium exchange (eq 1) does not require solvent, and specific solvation need not be invoked in any general mechanistic scheme.

Effect of CD_3COOD Concentration. Terminal alkynes π coordinated to silver(I) undergo D exchange a minimum of 10^5 times faster than uncoordinated alkynes.[9] If the rate-determining step of D exchange (eq 1) involves the deuterium donor acid, CD_3COOD, the rate of exchange should show a dependence upon changing acid concentration.

In Table I, data for the D exchange of alkynes with varying concentration of CD_3COOD are shown. The rates of exchange were measured at varying initial concentration of (alkyne)silver triflate π complex. This is because the alkynes differ in the stability of π complexes formed. The actual concentration of π complex ready for D exchange at any time is a function of the equilibrium constant for the equilibrium in eq 2. Since these complexes are of 1:1 stoichiometry between alkyne and AgOTf[9] and the degree of π complexation is a linear function of observed proton NMR chemical shift vs. maximum possible chemical

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[11] Gregston, D. K.; Lewandos, G. S., unpublished observations.

[12] Solodar, J.; Petrovich, J. P. *Inorg. Chem.* 1971, *10*, 395.

Table I. Rate Constants for Deuterium Exchange with Protium on the sp Carbon of Terminal Alkynes (Eq 1)[a]

alkyne	[complex], M	$[D^+]$,[b] M	10^3(rate/[complex])-(exptl),[c] s^{-1}	10^3k_1, s^{-1}	10^3k_2, s^{-1}	10^3(rate/[complex])-(calcd), s^{-1}
1-hexyne	0.40	0.40	3.7 (2)	3.5	0.5	3.7
	0.36	2.0	4.5 (2)			4.5
	0.40	4.0	5.7 (1)			5.5
3-methyl-1-pentyne	0.39	0.40	1.6 (3)	1.3	0.7	1.6
	0.39	2.0	2.7 (0.8)			2.7
	0.39	4.0	4.3 (0.2)			4.1
3,3-dimethyl-1-butyne	0.38	0.40	2.2 (5)	1.4	2.0	2.2
	0.38	2.0	4.7 (4)			5.4
	0.38	4.0	9.6 (0.3)			9.4
1,5-hexadiyne	0.40	0.40	1.0 (0.9)	0.8	0.5	1.0
	0.39	0.80	1.1 (2)			1.2
	0.38	4.0	2.7 (2)			2.8
	0.39	8.0	4.8 (2)			4.8

[a] All measurements were with [alkyne] = [AgOTf] = 0.4 M in CD_3NO_2, and [complex] is the actual concentration of (alkyne)AgOTf as measured by proton NMR spectroscopy. [b] $[D^+]$ = concentration of CD_3COOD. [c] Number in parentheses indicates standard deviation; e.g., 3.7 (2) is 3.7 ± 0.2; 2.7 (0.8) is 2.7 ± 0.08.

shift,[9,12] the actual concentration of (alkyne)silver triflate π complex in solution can be estimated. This is done by measuring the chemical shift of the proton bound to sp carbon in the D exchange solution and the maximum possible chemical shift with a large excess of silver triflate. With [alkyne] = [AgOTf] = 0.4 M, percent of alkyne π coordinated is as follows: 1-hexyne = 96–100%, 3-methyl-1-pentyne = 90–96%, 3,3-dimethyl-1-butyne = 90–94%, 1,5-hexadiyne = 95–97%. The percent depends upon [CD_3COOD], with decreasing percent complexation associated with greater [CD_3COOD]. Thus, the [complex] value in Table I was experimentally determined for each kinetic run.

Experimental rates were measured during the first 15% conversion. Initial rates were used in order to (a) minimize effect of the reverse of reaction 1 upon the observed rate and (b) minimize importance of slow side reactions that may assume kinetic importance at higher conversion.

If the reaction were first order in π complex and zero order in CD_3COOD, the quotient of rate/[complex] should be a constant, k_1. The data in Table I show that this quotient is not a constant, and the rate exhibits a partial dependence upon [CD_3COOD]. The kinetics data are consistent with a rate expression for D exchange occurring by two competing mechanisms. If both mechanisms have first-order dependence upon [complex] and if one has first-order dependence upon [CD_3COOD], the rate expression in eq 3 is valid. This rate expression can be

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][CD_3COOD] \quad (3)$$

rearranged to give eq 4. With the measured rates and

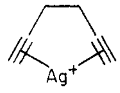
$$\text{rate}/[\text{complex}] = k_1 + k_2[CD_3COOD] \quad (4)$$

known values of[complex] and [CD_3COOD], unique values of rate constants k_1 and k_2 should exist if eq 3 and 4 are valid. Best fit experimental values for k_1 and k_2 are found in Table I.

For an illustration of how experimental values of k_1 and k_2 fit eq 4, substitution of k_1, k_2, and [CD_3COOD] values into it should yield calculated values of rate/[complex] similar to experimental values. There is reasonably close agreement (considering the limitations of rate measurements by NMR spectroscopy) between measured and calculated values.

For the monoynes, k_1 values decrease in the order R = *n*-butyl > *sec*-butyl ≃ *tert*-butyl. The k_2 values decrease in the approximate inverse order R = *tert*-butyl > *sec*-butyl > *n*-butyl. It appears that steric, electronic, and/or field effects that facilitate one of the competing mechanisms either are not operative or have the opposite effect in the other mechanism.

For the diyne, 1,5-hexadiyne, the k_1 and k_2 rate constants are small compared to those of the monoynes. This may be due to the chelating ability of 1,5-hexadiyne (1) or the ability to form extended chains (2) in which the activating effect of each Ag ion is divided between two simultaneously coordinated triple bonds. Earlier studies showed that, in solution, stoichiometries of the predominant (alkyne)silver π complexes are 1:1 (for both monoynes and diynes) and that diynes have both triple bonds coordinated to silver.[9] Thus, there is experimental support for Ag(I) increasing its coordination number in the presence of diynes.[13,14]



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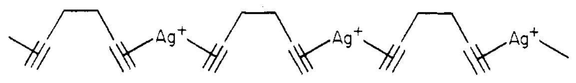

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Equilibrium in Deuterium Exchange. When the deuterium exchange (eq 1) is done with equimolar C≡CH and CD_3COOD, the reaction should go to statistical equilibrium (50% C≡CH and 50% C≡CD) in the absence of thermodynamic isotope effects. However, since the zero-point energy term will account for almost all of an equilibrium isotope effect, the equilibrium will move such that the heavier isotope will preferentially be in the bond with the highest frequency.[15] For the reaction in eq 1, equilibrium should be reached with less than 50% formation of C≡CD because deuterium favors the high-frequency O–D bond in the reactants.

Table II lists the percent C≡CH and C≡CD at equilibrium in the silver-promoted exchange. Values are for

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(13) The solid-state structure of (1,7-octadiyne)AgOTf as determined by X-ray diffraction is analogous to that of 2. Davis, R. E.; Lewandos, G. S. unpublished observation.

(14) For a report of the variable coordination ability of AgOTf with alkenes see: Lewandos, G. S.; Gregston, D. K.; Nelson, F. R. *J. Organomet. Chem.* **1976**, *118*, 363. For a report of the variable coordination ability of CuOTf with alkenes, see: Salmon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889 and references therein.

(15) Ritchie, C. D. "Physical Organic Chemistry"; Marcel Dekker: New York, 1975; p 221.

Table II. Position of Equilibrium in Reaction of Alkyne with CD_3COOD (Eq 1)[a]

alkyne	ratio of alkyne: CD_3COOD	% $C\equiv CH$	% $C\equiv CD$
1-hexyne	1:1	63	37
3-methyl-1-pentyne	1:1	59	41
3,3-dimethyl-1-butyne	1:1	61	39
1,5-hexadiyne	1:2	62	38

[a] Initial concentrations were [alkyne] = [AgOTf] = 0.4 M in CD_3NO_2. All percentages were determined by comparison of proton NMR integration areas of resonances for proton bound to sp carbon with proton on carbon α to the carbon-carbon triple bond. The results for each alkyne are an average from a minimum of three separate reactions.

Table III. Rates of Protium Exchange with the Deuterium of Terminal Alkynes ($RC\equiv CD$) (Reverse of Eq 1)[a]

	10^3(rate/[complex]), s^{-1}		rel reactivity of
alkyne	$RC\equiv CH$[b] reactn	$RC\equiv CD$[c] reactn	$C\equiv CH$/$C\equiv CD$
1-hexyne	3.7	8.7	0.42
3-methyl-1-pentyne	1.6	3.0	0.53
3,3-dimethyl-1-butyne	2.2	5.6	0.40

[a] All measurements were with [$RC\equiv CD$] = [AgOTf] = [CH_3COOH] = 0.4 M in CD_3NO_2. [b] Data taken from Table I. [c] Rates are corrected for the actual amount of deuterated alkyne present in the mixture of deuterated and undeuterated alkynes.

1:1 starting ratios of $C\equiv CH$ and CD_3COOD. Position of equilibrium shows no clear dependence upon alkyne, for values are the same within experimental error.

Catalysis of Deuterium Exchange. The deuterium exchange reaction is catalytic in silver triflate. Equimolar 3,3-dimethyl-1-butyne and CD_3COOD (each 0.4 M in CD_3NO_2) react to give the usual thermodynamic mixture (61% *t*-$C_4H_9C\equiv CH$, 39% *t*-$C_4H_9C\equiv CD$) when AgOTf concentration is 0.1 M. Each silver ion must activate an average of 1.56 sp C–H bonds for exchange with deuterium. This is a minimum number of turnovers.[16] While reaction 1 is reaching equilibrium, silver ion is initiating also the reverse of reaction 1 and the unproductive reactions shown in eq 5 and 6.

$$\underset{Ag^+}{RC\equiv CH} + H^+ \longrightarrow \underset{Ag^+}{RC\equiv CH} + H^+ \qquad (5)$$

$$\underset{Ag^+}{RC\equiv CD} + D^+ \longrightarrow \underset{Ag^+}{RC\equiv CD} + D^+ \qquad (6)$$

Reaction rates with greater than 1:1 alkyne to AgOTf ratio have not been measured because these reaction mixtures may contain a variety of complex stoichiometries. At higher ratios, complexes with 2:1 or greater stoichiometries are probable. Contributions of these species to reaction rates of 1:1 complexes would make mechanistic analysis more difficult.

Kinetic Deuterium Isotope Effect. Should cleavage of the sp carbon-hydrogen bond occur before or during the rate-determining step in deuterium exchange, a kinetic primary isotope effect would be expected. To test this hypothesis, we synthesized 1-hexyne-*1*-d_1, 3-methyl-1-pentyne-*1*-d_1, and 3,3-dimethyl-1-butyne-*1*-d_1 by using a variation of the method of Dessy et al. for selective incorporation of deuterium at sp carbon.[17]

With monodeuterated alkynes, rates of protium exchange for deuterium at the sp carbon can be measured. The reaction is the reverse of that shown in eq 1. The protium source was CH_3COOH. The appearance of an NMR resonance for protium bound to sp carbon was monitored as a function of time by repeated integration. The reactions had equimolar amounts of alkyne, silver triflate, and CH_3COOH, in order for rates to be comparable to those of the forward reaction. The results are in Table III.

Because of the complexity of the kinetics of the forward reaction, we have not evaluated k_1 and k_2 for the reverse reaction. Instead the data in Table III are presented in terms of rate/[complex] for direct comparison of forward and reverse reactions.

The deuterium isotope effect seen in silver-catalyzed activation of the alkyne C–H bond is inverse and is sizeable ($(\text{rate}/[\text{complex}])_H/(\text{rate}/[\text{complex}])_D = 0.46 \pm 0.07$). Inverse isotope effects have been associated with a secondary effect in which the bond to hydrogen is not broken in the rate-determining step, but vibrational patterns change in going from reactant to activated complex.[18,19] The zero-point energy differences between C–H and C–D bonds in their lowest vibrational levels are reflected in the force constants and vibrational frequencies of the bonds. Larger force constants and greater zero-point energy differences in the activated complexes than in the reactants lead to an inverse isotope effect.

If the terminal sp carbon of the alkyne were undergoing a change in hybridization to sp^2 along the reaction coordinate, the magnitude of the secondary isotope effect could be estimated from the relationship

$$k_H/k_D = \exp(0.187/T)\,\{\textstyle\sum \nu_H - \nu_H^{\ddagger}\}$$

where sums are taken over fundamental stretching and bending vibrations for ground state and activated complex terminal C–H bonds.[19] With use of the approximate frequencies of 3025 ($C{=}CH$ stretch),[20] 1255 ($C{=}CH$ in-plane bend), 998 ($C{=}CH$ out-of-plane bend), 3215 ($C\equiv CH$ stretch),[9] and 630 ($C\equiv CH$ bend) cm^{-1},[20] k_H/k_D is calculated to be 0.61. Thus, our isotope effects are in the direction expected for increased p character at the terminal carbon in going from reactants to activated complex. The magnitude of our effects are greater than expected on the basis of simple integer hybridization change. Of course, in the actual silver complexes stretching and bending frequencies may be different from those used in the model calculations. A further source of disagreement could be that energy differences between deuterated and undeuterated complexes may not be adequately described by vibrational energy differences alone. In addition, in organometallic systems hybridization of carbon bound to

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(16) Work is underway to determine the maximum number of catalytic turnovers and to optimize catalyst efficiency.

(17) Dessey, R. E.; Okuzumi, Y.; Chen, A. *J. Am. Chem. Soc.* **1962**, *84*, 2899.

(18) Saunders, W. H., Jr. In "Survey of Progress in Chemistry", Scott, A. F., Ed.; Academic Press: New York, 1966; Vol. 3, p 117.

(19) (a) Drenth, W.; Kwart, H. "Kinetics Applied to Organic Reactions"; Marcel Dekker: New York, 1980; pp 128–130. (b) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

(20) Socrates, G. "Infrared Characteristic Group Frequencies"; Wiley: Chichester, 1980; p 35, wherein $H_2C{=}CHM$ (M = metal) is used as a model for a vinylidenemetal complex.

metals may be other than the integer values sp and sp^2. In any case, the one or more mechanisms operative in deuterium exchange appear to involve change in hybridization of the terminal sp carbon to $sp^{\approx 2}$.

Some transition metals can convert alkynes to the corresponding vinylidenemetal (vinyl cation–metal) complexes (eq 7).[21] The reaction is known for M = Pt,[22] Rh,[23] Fe,[24] Ru,[25] Mn,[26] and Re.[27] There is no experimental evidence of similar chemistry for the group 1B metals, although Heasley et al.[28] have suggested without proof the step in eq 8 as the mechanism for conversion of RC≡CH/MeOH/I_2/$AgNO_3$ to $RCOCHI_2$.

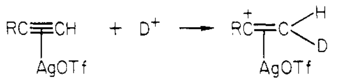
$$RC{\equiv}CH + M^+ \xrightarrow{\text{step 1}} R\underset{+}{C}{=}C(H)M \xrightarrow{\text{step 2}} R(H)C{=}C{=}\underset{+}{M} \leftrightarrow R(H)C{=}\underset{+}{C}M \quad (7)$$

$$RC{\equiv}CH + Ag^+ \rightarrow R\underset{+}{C}{=}C(H)Ag \quad (8)$$

If the reaction in eq 8 occurred before or during the rate-determining step in the mechanism of deuterium exchange, the hybridization change would be consistent with observed inverse isotope effect.[29]

Halevi has posited that there are differences in inductive effect between C–H and C–D bonds, with deuterium being more electropositive than protium.[30] Thus, interaction between a positive charge and the carbon end of a C–D bond would be more favorable than the same interaction with a C–H bond.[31] Silver ion π coordinated to the triple bond represents a positive charge that would more readily σ coordinate to the terminal carbon bearing deuterium. The inductive effects of the terminal ≡CH(D) bonds in eq 8 would lead to a secondary kinetic isotope effect in the observed direction.

As an alternative to mechanisms proceeding through a vinylidenesilver species, a mechanism for the path dependent upon acid concentration might involve direct electrophilic attack of D^+ upon the terminal (alkyne)-AgOTf π complex (eq 9). Although attack of D^+ upon a cationic complex may not appear facile, there is ample precedent for exchange of H^+ and D^+ with protium on a cyclopropenyl cation[32] and the trityl cation.[33] Again, the hybridization change would be in the direction supported by our results.



$$\underset{AgOTf}{RC{\equiv}CH} + D^+ \longrightarrow \underset{AgOTf}{R\overset{+}{C}{=}C}\!<^{H}_{D} \quad (9)$$

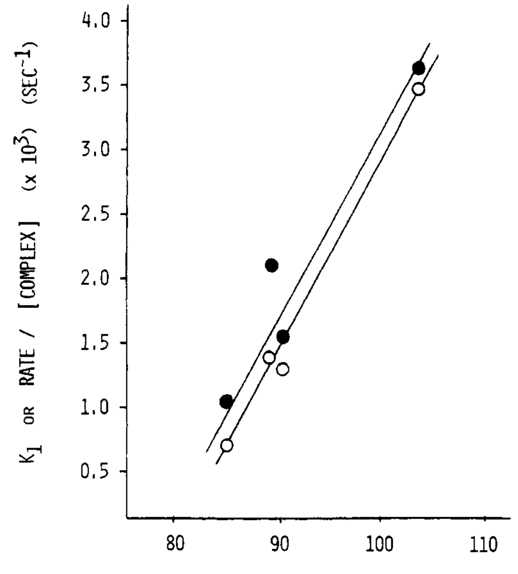


Figure 2. Dependence of k_1 and rate/[complex] on the change in IR stretching frequency of the alkyne terminal sp C–H bond caused by Ag(I) π coordination ([alkyne]) = [AgOTf] = 0.4 M; ○, k_1; ●, rate/[complex]).

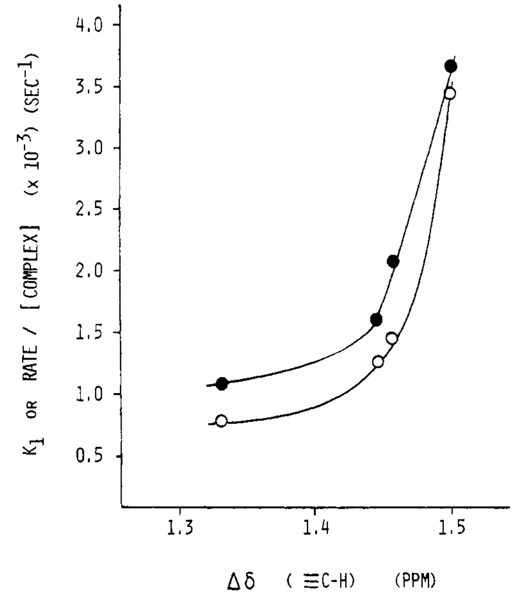


Figure 3. Dependence of k_1 and rate/[complex] on the change in proton NMR chemical shift of the hydrogen on sp carbon of a terminal alkyne caused by Ag(I) π coordination ([alkyne] = [AgOTf] = 0.4 M; ○, k_1; ●, rate/[complex]).

Correlation of Deuterium Exchange Rate with Spectroscopic Properties. The proton NMR chemical shifts and IR stretching frequencies for the free alkynes and 1:1 π complexes have been reported.[9] When the deuterium exchange kinetic data for the four alkynes (rate/[complex], k_1, and k_2) are plotted against changes in spectroscopic parameters upon silver ion π coordination (change in IR stretching frequency for the sp C–H bond and change in NMR chemical shift of the proton on the

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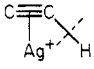
sp carbon), a positive correlation is seen in four cases. Figure 2 shows a linear relationship between change in IR stretching frequency and both k_1 and rate/[complex]. There is no linear relationship between change in proton NMR chemical shift and both k_1 and rate/[complex] (Figure 3). However, as k_1 and rate/[complex] increase, there is an increase (nonlinear) in change in chemical shift. The nonlinearity is caused by the diyne, 1,5-hexadiyne. Monoynes exhibit a nearly linear dependence.

The dependence of deuterium exchange upon change in terminal sp C–H stretching frequency caused by π coordination implies that initial π coordination can dispose the resulting complex to C–H bond activation. Chrisment and Delpuech have found that acidity of noncoordinated terminal alkynes correlates well with $\equiv$CH stretching vibration changes.[34] In our case, cause of the linear relationship may be as simple as electron withdrawal by the π-coordinated electronegative silver ion weakening the C–H bond and raising the ground-state energy of the reactant complex. At the other extreme is direct interaction between silver ion and the terminal C–H bond. Formation of a nonlinear 2-electron, 3-center bond between silver ion and terminal C–H bond (**3**) would remove electron density from the C–H bond and weaken it. The formation of nonlinear 2-electron, 3-center bonds has been observed in the ground state by neutron diffraction analysis[35] and supported by solution studies.[36] Consistent with our observation of alkyne C–H bond activation, the 3-center interaction in cyclohexenylmanganese tricarbonyl renders the bridging hydrogen acidic, thereby permitting deprotonation and electrophilic substitution.[37]



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The increasing downfield chemical shift upon silver ion π coordination that correlated with increasing k_1 and rate/[complex] can be explained by the same principles as for the IR changes. π coordination of silver ion could deshield the terminal proton by inductive electron withdrawal and thereby activate the terminal C–H bond. A 2-electron, 3-center interaction with silver ion would deform the C$\equiv$C—H bond angle to <180°; the resulting anisotropic effect would deshield the terminal proton. Greater deshielding due to greater strength of 2-electron, 3-center interaction would be reflected in more facile terminal C–H bond activation.

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Registry No. RC$\equiv$CH·AgOTf (R = 1-hexyne), 74910-01-3; RC$\equiv$CH·AgOTf (R = 3-methyl-1-pentyne), 74915-00-7; RC$\equiv$CH·AgOTf (R = 3,3-dimethyl-1-butyne), 74915-01-8; RC$\equiv$CH·AgOTf (R = 1,5-hexadiyne), 83573-31-3; Ag^{1+}, 14701-21-4; 1-hexyne, 693-02-7; 3-methyl-1-pentyne, 922-59-8; 3,3-dimethyl-1-butyne, 917-92-0; 1,5-hexadiyne, 628-16-0; 1-hexyne-*1*-d_1, 7299-48-1; 3-methyl-1-pentyne-*1*-d_1, 83573-30-2; 3,3-dimethyl-1-butyne-*1*-d_1, 6833-44-9; deuterium, 7782-39-0; silver triflate, 2923-28-6.

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Why Life Exists[†]

Michael J. S. Dewar* and Eamonn Healy

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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The chemical inertness of tetracoordinated carbon, on which life depends, is commonly attributed to the fact that carbon has no d AOs, or empty or doubly occupied AOs, in its valence shell. Silicon is much more reactive than carbon because it can use 3d AOs to form additional bonds. The same argument is used to explain the inability of the second period elements to form hypervalent compounds. This interpretation is now shown to be probably incorrect. The special features of second period elements are probably due solely to the smaller size of their atoms.

Life is made possible by the stability of carbon compounds of very varied types, even when they are thermodynamically unstable, as a result of the slowness of reactions involving them, and this in turn is due primarily to the unreactivity of quadrivalent carbon. This inertness is commonly attributed to the fact that carbon has only four AOs in its valence shell so it can form at most four electron-pair bonds. Quadrivalent carbon can therefore form a bond to some other atom or group only if one of the preexisting bonds is broken, either before or in concert with formation of the new bond. The energy required to weaken or break the preexisting bond represents a barrier to the reaction in question, even if the net effect is exothermic. While the other typical group 4 elements resemble carbon in being quadrivalent, their valence shells include d AOs as well as s and p AOs. Consequently they can form electron-pair bonds to more than four other atoms, so they can react by direct addition, to form pentacoordinated adducts, without the need to break preexisting bonds. The consequent lack of an activation barrier naturally makes such reactions much faster than in the case of carbon. For example, whereas carbon tetrachloride reacts only very slowly with cold water, silicon tetrachloride

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[†] Dedicated to Rowland Pettit, a founding member of our research group.

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