COMMUNICATIONS

LETTERS

Inverse Secondary Equilibrium Isotope Effects on Silver-Ethylene and Silver-Ethylene-d_1 Complexes*

Kwang Bum Hong, Kyung-Hoon Jung† and Sung Hoon Kang

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

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The principal objective of this study is to investigate the origin of the inverse secondary equilibrium isotope effects on silver–ethylene and silver–ethylene–d_1 complexes in the condensed phase at 273 °K.

Almost all results reported to date on the study of the equilibrium isotope effects for Ag–C_2H_4 and Ag–CH_2CHD complexes formation have entrained a serious deficiency in the interpretation of the observations,[1-3] namely, the lack of the adequate knowledge of the physical insight for the system adds some vagueness to the correlation between the equilibrium phenomena and the structural properties. In this communication we report the successful attainment of the correlation between the isotope effect and the structural properties of the complexes as well as the interaction properties of the complex–solvent medium.

In the present study, the geometrical parameters were adopted from the work of SCF study[4] since the measured values were not available in the literatures. The geometrical parameters of $Ag^+(C_2H_3D)$ were assumed to be the same as those of $Ag^+(C_2H_4)$ without any alterations. The assigned internal valence coordinates for silver–ethylene complex are shown in Figure 1. The normal coordinate analysis[5] was carried out to generate the observed frequencies[6] using the iteration technique. For this calculation, some transfer force constants adopted were those of transition metal–ethylene π complexes[7] and were used as the first approximation. The calculated frequencies are given in Table 1 together with observed ones and shown very good agreement within 1.3% of the average deviations. In order to obtain K_D/K_H value, a two-stage gas chromatograph with FID was used. The resolving was preformed by 100 ft × 1/8[11] S.S. silver nitrate/ethylene glycol column at 273 °K. The typical chromatogram is displayed in Figure 2.

TABLE 1: Frequency Assignments for Silver–Ethylene and Silver–Ethylene–d_1 Complexes[a]

	Observed[b]	Calculated[c]	
		$Ag^+(C_2H_4)$; C_{2v}	$Ag^+(C_2H_3D)$[d]; C_1
A_1			
CH–s–stretch.		2934	2921
C=C stretch.	1579	1606(1.7 %)	1579
CH_2 sciss.	1320	1275(3.4 %)	1176
CH_2 wag.	971	954(1.8 %)	980
Ag–C stretch.		219	215
A_2			
CH–a–stretch.	3009	3026(0.6 %)	3021
CH_2 rock.		1229	822
CH_2 twist.	873	873(0.0 %)	1193
B_1			
CH–s–stretch.		2910	2212(CD–s–stretch)
CH_2 sciss.		1388	1346(CHD–sciss)
CH_2 wag.	990	1000(1.0 %)	907(CHD wag.)
Ag–C stretch.	275	274(0.4 %)	268
B_2			
CH–a–stretch.		3014	2975
CH_2 rock.		806	615(CHD rock.)
CH_2 twist.		1068	1024(CHD twist.)

[a] All units in cm^{-1}; [b] Observed frequencies for $Ag^+(C_2H_4)$ from *ref.* (6); [c] This work; [d] Since $Ag^+(C_2H_3D)$ belongs to c_1 point group, the tabulation according to the class of $Ag^+(C_2H_4)$ is for the comparison.

The inverse equilibrium isotope effects, K_D/K_H, for $Ag^+(C_2H_4)$ and $Ag^+(C_2H_3D)$ in condensed phase can be expressed in terms of total average molecular partition functions. Translation and rotational motions of the complexes become hindered because of the intermolecular interaction between $AgNO_3$ and ethylene glycol. Hence, the intermolecular potential in the system can be expressed in terms of the mean

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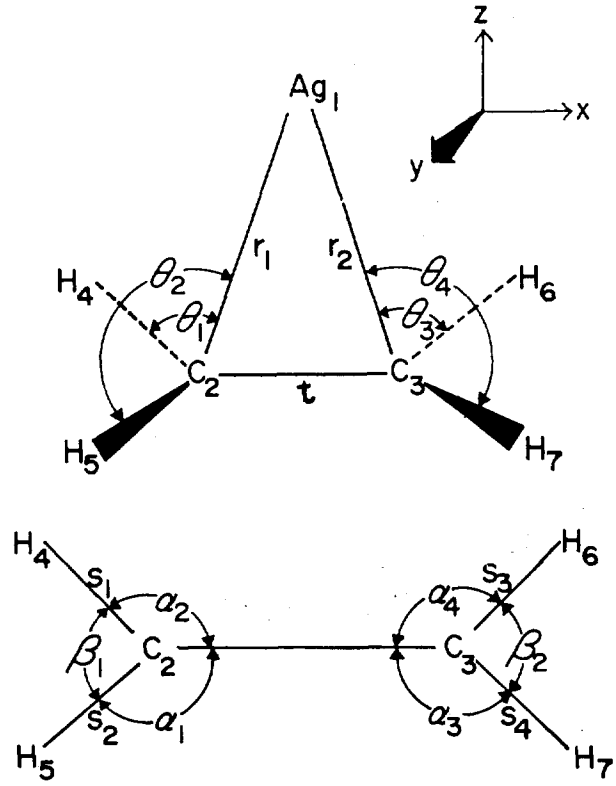

Figure 1. Internal valence coorpinates for silver-ethylene complex.

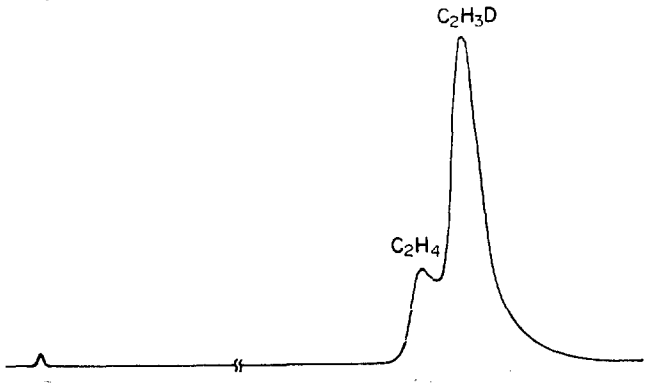

Figure 2. Gas chromatograms of ethylene and ethylene-d_1 on a $AgNO_3$/ethylene glycol column at 273°K. Retention times: C_2H_4(123 min); C_2H_3D(128 min).

TABLE 2: Deuterium Isotope Effects of Silver-Ethylene Complex Formation in Ethylene Glycol Solution

	K_D/K_H		
	273K	298K	313K
C_2H_3D/C_2H_4	1.047[a](1.056)[b]	(1.04[illegible])[b]	(1.041)[b]
trans-$C_2H_2D_2/C_2H_4$	1.085[d](1.086)[c]	1.065[d]	1.073[d]
C_2D_4/C_2H_4	1.161[d](1.168)[c]	1.129[d]	1.126[d]

[a] Observed value; [b] Calculated values; [c] *ref.* (11); [d] *ref.* (2).

square forces exerted on the translational and the mean square torques on the rotational motions. In the present system, however, the reduced partition function[8], f, depends only upon the internal vibrations of the complexes because of the frozen nature at 273°K and can be expressed in the form of,

$$\frac{K_D}{K_H} = \frac{(S_1/S_1')\prod_i^{3N-6}(U_{1i}'/U_{1i})\exp[(U_{1i}-U_{1i}')/2]\left[\frac{1-\exp(-U_{1i})}{1-\exp(-U_{1i}')}\right]}{(S_2/S_1')\prod_i^{3N-6}(U_{2i}'/U_{2i})\exp[(U_{2i}-U_{2i}')/2]\left[\frac{1-\exp(-U_{2i}')}{1-\exp(-U_{2i}')}\right]} \quad (1)$$

where subscripts 1 and 2 represent the complex and the free ethylene, respectively. The primed quantities are for the deuterated molecules. U_i has its usual meaning, *i. e.*, $h\nu_i/kT$. The symmetry numbers, S, for C_2H_4, C_2H_3D, $Ag^+(C_2H_4)$, and $Ag^+(C_2H_3D)$, are 4, 2, 2, and 1, respectively. Eq.(1) can be resolved into three terms by simple manipulation and is given by Eq. (2),

$$\frac{K_D}{K_H} = (VP)\times(ZPE)\times(EXC) \quad (2)$$

where the term VP represents the vibrational product which arises from the calssical vibrational partition functions. ZPE is the zero-point energy. And EXC is the vibrational excitation term. The calculated values of K_D/K_H at three different temperatures, *i. e.*, 273, 298, and 313 °K, are given in Table 2 and compared with the observed one at 273°K. Some thermodynamic quantities[9] calculated using Eq. (2) at 273°K., *i. e.*, $\Delta\Delta G$, $\Delta\Delta H$, and $\Delta\Delta S$, are found to be −29.5 cal/mol, −64.0 cal/mol, and −0.13 *e.u.*, respectively.

Examination of the data in Table 2 reveals several interesting points. The positive contributions are due to ZPE and EXC terms whereas the negative contribution comes from VP. And the nature of VP shows the similar trend as Redlich-Teller product rule[10] for the isotopically substituted compounds. The temperature dependence of each term also shows some interesting phenomena. Since VP term is temperature independent and the slight positive effect of EXC cancels negative dependency of ZPE, the overall effect shows very small temperature dependency.

In order to obtain the contribution of the external modes for the isotope effects, the stability constants for $Ag^+(C_2H_4)$ and $Ag^+(C_2H_3D)$ are calculated both in water and ethylene glycol solutions at 273 °K, *i.e.*, K_D/K_H=212.4/205.4 in water and K_D/K_H=31.4/30.4 in ethylene glycol solutions. Since the stability constant at any solvent medium can be resolved into its external and internal contributions, its external part can be deduced from Eq. (2) by considering the known value of VP. The calculated values show very good agreement with the experimental results.[2,11] And the large variations of the stability constants at different solvent media seem to be mainly due to solvent properties rather than the internal properties of the complexes. The deduced values of the stability constants were analyzed with respect to two sources of contributions, *i.e.*, the internal and the external modes, and shown the inverse isotope effects. The negative contribution from the external mode showed more or less the same magnitude as the case of VP. Considering the actual magnitude of each term in Eq. (2) and a modified equation which includes the external and the internal modes, it was found that the major contribution is due to ZPE term although the

stability constants are largely affected by the solvent medium in the course of the complex formation process. It is thus concluded that the only sources of the inverse secondary equilibrium isotope effects for the complexes are mainly molecular vibrations. From the foregoing discussion, we may therefore characterize the relative importance of the contribution from each vibrational mode and found several modes as the major contributors. These are two positive effects from CH_2 rocking and CH_2 twisting modes, and three negative effects from CH_2 wagging, CH_2-*s*-stretching, and CH_2 scissoring modes.

The results demonstrate that theoretical calculations based on the reduced partition function quantitatively support the experimental observations. This preliminary study provides a better understanding on the physical insight of the secondary isotope effects and clarify some vagueness of the molecular properties of metal–olefin complex formation process.

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Lithium *n*-Butylborohydride. An Excellent 1, 2-Selective Reducing Agent of Conjugated Enones

Sunggak Kim† and Young Choon Moon

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

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Lithium *n*-butylborohydride generated from *n*-butyllithium and borane–dimethyl sulfide complex in equimolar ratio in toluene–*n*-hexane is exceedingly effective for selective 1, 2 reductions of enones.

Selective 1, 2 reduction of conjugated ketones with hydride reducing agents is often difficult to achieve in oragnic synthesis due to the competitive occurrence of 1, 2 and 1, 4 reduction[1]. In general, 1, 4 reduction takes place favorably when the double bond is further conjugated with an aromatic ring or contained in a five- or a six-membered ring.

Although lithimum n-butylborohydride, a representative monoalkylborohydride reducing agent[2], was recently utilized for the stereoselective reduction of conjugated enones successfully during the total sythesis of Erythronolide B[3] and (–)-N-methylmaysenine[4] by Corey, the characteristic features of this reducing agent have not fully been explored. On the other hand, it has been demonstrated that the mode of the reduction of lithium, potassium tri-secbutylborohydride (L, K-Selectride) with conjugated cyclohexenones depends critically on the presence or the absence of β-substituent[5].

In view of these facts, we were encouraged to undertake the reaction of lithium *n*-butylborohydride with acyclic and cyclic enones. The potentially useful results obtained prompt us to report this communication.

We have observed that treatment of conjugated enones with lithium *n*-butylborohydride, generated from *n*-butyllithium and borane-dimethyl sulfide complex in equimolar ratio[6], in toluene–*n*-hexane at –78 °C produced high yields of the corresponding allylic alcohols, in most cases uncontaminated with 1, 4 reduction products.

Table 1 summarizes the results for selected model compounds, which demonstrated the synthetic usefulness of this reagent. Reduction was carried out in toluene–n–hexane (approximately 15:1) using equimolar amounts of conjugated enones and the reducing agent.

The reduction of acyclic enones (entries 1, 2 and 3) afforded exclusively the corresponding allylic alcohols *via* 1, 2 reduction. It is of interest to note that chalcone (entry 2) was reduced by lithium n–butylborohydride in 100 % 1, 2–selectivity in contast with predominant 1, 4 reduction by diisobutylaluminum hydride (1, 2/1, 4:35/65)[7].

β-Substituted cyclohexenones (entries 4 and 5) underwent