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Secondary Deuterium Isotope Effects on the Stability of the Silver Ion-Olefin Complexes¹

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The pronounced secondary deuterium isotope effects on the stability of the electron donor-acceptor complexes between olefins and silver ions, reported previously from this laboratory, have been studied in greater detail. Experiments with specifically deuterated propylenes show that the isotope effect is much larger when deuterium is directly bound to the unsaturated carbon atoms ("α-effect") than when it is in β-position to the double bond ("β-effect"). Both effects are "inverse": deuteration leads to an increase in complex stability. The isotope effect is logarithmically additive and approximately independent of the degree of alkyl substitution in the olefin. Enthalpies and entropies of formation have been determined for several silver ion-olefin complexes in ethylene glycol solutions in the temperature interval 0-40°.

Introduction

In a previous publication from this laboratory³ it was reported that the stability of the silver ion-olefin complexes becomes *greater* when hydrogen atoms in the olefin are replaced by deuterium. This effect is of potential interest from the point of view of the nature of the silver ion-olefin interactions and also of the secondary equilibrium isotope effects of this kind. In view of this, it has now been studied in greater detail and the results obtained are summarized and discussed in the present paper. The enthalpies and entropies of formation of several silver ion-olefin complexes in

ethylene glycol solutions have been determined and are also reported.

The equilibrium constants of complexing between olefins and Ag⁺ ions have been determined at 0, 25, and 40° by the gas chromatographic technique with the use of ethylene glycol solutions of silver nitrate on firebrick support as the stationary phase. Muhs and Weiss⁴ have recently discussed the relation between the experimentally determined partition coefficients (*H*) and the concentration of silver nitrate dissolved in ethylene glycol ([AgNO₃]). In the low concentration region where the "salting-out" effect is negligible, the following linear dependence holds

$$H = H_0(1 + K[\text{AgNO}_3]) \quad (1)$$

where *H*₀ and *K* are equilibrium constants, *H*₀ for the process of solution of olefin in the ethylene glycol solvent and *K* for the formation of 1:1 complexes between the dissolved olefins and silver ions.

As a result of "salting out," the solubility of olefin is decreased at higher silver concentrations; *H* values become therefore smaller than predicted by eq. 1, and plots of *H* against [AgNO₃] show curvatures. The equilibrium constant *K* can nevertheless be obtained by dividing the limiting slope at zero [AgNO₃] by the intercept. Alternatively, *K* can be calculated from the rearranged eq. 1

$$K = \left(\frac{H}{H_0} - 1 \right) / [\text{AgNO}_3] \quad (2)$$

provided [AgNO₃] is low enough so that the salting-out effect can be neglected.

(1) Issued as N.R.C. No. 8433.

(2) National Research Council Postdoctoral Fellow, 1961-1963.

(3) R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).

(4) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

Experimental

Columns containing 0, 1, 2, 3, and 4 *M* solutions of silver nitrate (Baker and Adamson, reagent grade) in ethylene glycol (Fisher Certified reagent) as the stationary phase were constructed. The required amount of AgNO₃ was dissolved in ethylene glycol at 40° and the density of the solutions was determined at 0, 25, and 40°. The solutions were exposed to light as little as possible. Twenty grams of each of the solutions was added to 80 g. of Johns-Manville Chromosorb P, 30–60 mesh, in flasks which were then rotated slowly overnight. The columns were made of stainless steel tubing, 0.25-in. o.d., 24 ft. long. Before filling they were washed with acetone and ethyl acetate and during use were kept immersed in a water (or ice-water) thermostat. The amount of packing added to each column (about 75 g.) was determined.

Most olefins were Phillips Petroleum Co. pure grade or A.P.I. research samples. The purity of any other samples used was checked gas chromatographically. The source of the deuterated olefins has been given in the earlier publication³; deuteriopropylenes have been obtained from Merck Sharp and Dohme, Montreal, Canada.

Mixtures of olefins containing 10⁻³ to 10⁻² μmole of each component were flushed onto the columns from a U-shaped bypass injector.³ The effective injection time was a few tenths of a second. Helium was used as the carrier gas. The inlet and the outlet pressure of the carrier gas and its flow rate were measured, the latter by means of a soap bubble flowmeter. The flow rates were generally between about 50 and 60 cc./min. A hydrogen flame ionization detector was used, with the recorder chart speed set at 1 in./min. The adjusted retention times (*t*_r') were obtained by subtracting the retention time of CH₄ from the retention times of the olefins. The partition coefficients (*H*) were calculated from the equation

$$H = \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right] F t_r' / V_L \quad (3)$$

where *p*_i and *p*_o are the inlet and outlet pressure of the carrier gas, *F* is the carrier gas flow rate at column temperature, and *V*_L is the volume of the liquid phase at column temperature.

Results

Equilibrium Constants, Enthalpies, and Entropies of Complex Formation. Plots of eq. 1 were constructed for all the olefins studied and they were similar to those reported by Muhs and Weiss.⁴ Below about 1 *M* [AgNO₃] the curvature due to salting out was negligible but increased at higher silver nitrate concentrations. The ratios of the limiting slopes at zero [AgNO₃] to the intercepts gave the values of *K*. Very much the same values of *K* were also obtained by using the data obtained only from the 1 and 0 *M* (pure ethylene glycol) columns and eq. 2, in agreement with the observation of negligible curvatures due to the salting-out effect at 1 *M* and lower silver nitrate concentrations. The values of *K* for a number of olefins at 0, 25, and 40° are listed in Table I. The corresponding values obtained by Muhs and Weiss at 40° are also given for comparison. The two sets of values

at 40° do differ somewhat but probably not by more than the stated experimental uncertainty.⁴

For determination of the enthalpies and entropies of complex formation, considerable mutual consistency of the data is required if meaningful results are to be obtained. One of the experimental difficulties arises from the need to have an accurate knowledge of the silver ion concentration in the glycol solutions. Columns of this kind are likely to deteriorate with use. Analyses, kindly performed by M. Bednas of the analytical section of this division, have shown at the end of the experimental work about 15 to 20% smaller concentrations of dissolved AgNO₃ in the columns used than the nominal concentrations (as originally prepared). The amount of "reduced" silver was determined by analyzing for Ag⁺ before and after digestion with boiling HNO₃. For example, the unused 1 *M* (nominal) column packing showed 12% reduction and the used packing 16% reduction. Aliquots of the original solutions, on the other hand, analyzed after several months standing in stoppered bottles in the dark, showed Ag⁺ concentrations agreeing with the nominal concentrations to within 1 to 2%. In view of these results, the absolute *K* values, calculated using the nominal concentrations, may be uniformly 15 to 20% higher than given in Table I. However, the change in concentration is slow and the *relative* retention times for a number of olefins, usually run simultaneously or in close succession, were found to be very well reproducible at widely different stages of this study. Thus, although the absolute values of *K* may be in doubt to the extent that they may be up to about 15 to 20% higher, the relative values, and therefore also the enthalpies of complex formation, are not appreciably affected by this uncertainty. The uncertainty in the entropies of complex formation due to this cause is not large; all the values would be uniformly 0.3 to 0.4 e.u. less negative if the lower (analytical) AgNO₃ concentrations were employed instead of the corresponding nominal values. The values of the enthalpies of complex formation in Table I, calculated for the temperature ranges 0–25 and 0–40° are indeed in close agreement, the latter values being regarded as more accurate in view of the larger temperature interval. To assess these data, it should be pointed out that, for example, an error of only 4% in the ratio of the *K* values at the extremes of the temperature interval introduces an error of close to 0.5 kcal./mole for the interval 25–40°. (The $-\Delta H$ values for this interval are therefore not listed in Table I, except for cyclopentene, for which measurements at 0° were not made.) The corresponding errors in the 0–40° interval are only one-third as large. The same considerations rule also against any attempt to establish from the *K* values at the three temperatures whether the enthalpies and entropies of complex formation vary appreciably with the temperature.

The mean $-\Delta H$ and ΔS values for the temperature interval 0–40° show that the variation in the equilibrium constants *K* in the olefin series is primarily determined by a variation in the enthalpies.

Secondary Deuterium Isotope Effects. The effect of deuteration on the retention times of ethylene, propylene, *trans*-2-butene, *cis*-2-butene, and 1,3-butadiene has been determined at 0, 25, and 40°. The

Table I. Equilibrium Constants, Enthalpies, and Entropies of Olefin-Silver Ion Complex Formation in Glycol Solutions

Olefin	K , l./mole				$-\Delta H$, kcal./mole		ΔS , e.u. 0-40°
	0°	25°	40°	40° ^a	0-25°	0-40°	
C ₂ H ₄	30.6	17.5	13.5	22.3	3.6	3.5	-6.0
RCH=CH ₂							
CH ₃ CH=CH ₂	13.3	7.5	5.9	9.1	3.7	3.5	-7.5
C ₂ H ₅ CH=CH ₂	16.1	8.8	6.8	7.7	3.9	3.7	-8.0
<i>n</i> -C ₃ H ₇ CH=CH ₂	12.1	6.7	5.2	4.9	3.8	3.6	-8.1
<i>i</i> -C ₃ H ₇ CH=CH ₂	15.2	8.0	6.1	5.1	4.2	3.9	-8.8
<i>cis</i> -RCH=CHR							
CH ₃ CH=CHCH ₃	8.7	4.9	3.9	5.4	3.7	3.4	-8.2
C ₂ H ₅ CH=CHCH ₃	10.1	5.6	4.4	4.3	3.9	3.6	-8.5
<i>trans</i> -RCH=CHR							
CH ₃ CH=CHCH ₃	2.6	1.6	1.4	1.4	3.0	2.6	-7.7
C ₂ H ₅ CH=CHCH ₃	2.8	1.8	1.4	1.1	2.9	2.9	-8.7
R ₂ C=CH ₂							
C ₂ H ₅ (CH ₃)C=CH ₂	8.0	4.4	3.5	3.0	3.8	3.5	-8.6
RCH=CR ₂							
(CH ₃) ₂ C=CHCH ₃	1.52	1.01	0.87	0.8	2.7	2.4	-7.8
R ₂ C=CR ₂							
(CH ₃) ₂ C=C(CH ₃) ₂	0.45	0.34	0.29	0.1	1.8	1.9	-8.5
Cycloolefins							
C ₆ H ₈	<i>b</i>	10.2	7.2	7.3	<i>b</i>	4.3 ^c	-9.9 ^c
Di-olefins							
CH ₂ =CHCH=CH ₂	7.6	4.5	3.6	4.2	3.4	3.2	-7.7

^a The data of Muhs and Weiss. ^b Not determined at 0° because of the excessively long retention time on the column used. ^c $-\Delta H$ and ΔS evaluated from K values at 25 and 40°.

most convenient and accurate way of expressing the results for the deuterio isomers (d) of an olefin is relative to the corresponding protio isomer (h). In this manner some of the errors in the experimental measurements are eliminated or greatly reduced. In view of eq. 2 and 3, and taking the data from the columns with 0 and, for example, 1 *M* glycol solutions of AgNO₃ (indicated by subscripts 0 and 1, respectively)

$$\frac{K_d}{K_h} = \left[\frac{(t_r'(d))}{(t_r'(h))}_1 \frac{(t_r'(h))}{(t_r'(d))}_0 - \left(\frac{H_0}{H_1} \right)_h \right] / \left[1 - \left(\frac{H_0}{H_1} \right)_h \right] \quad (4)$$

Since the ratio $(H_0/H_1)_h$ of the partition coefficients for the protio isomers on the pure ethylene glycol (H_0) and 1 *M* AgNO₃ column (H_1) is considerably smaller than unity, K_d/K_h is primarily determined by the relative retention times $[t_r'(d)/t_r'(h)]$ on the two columns. The values on the 1 *M* AgNO₃ column have been measured accurately. The corresponding values on the pure ethylene glycol column, $[t_r'(h)/t_r'(d)]_0$, are more difficult to determine experimentally for the studied olefins because the isotope effect here is quite small. The effect is primarily due to the differences in volatilities (boiling points) of the deuterio and protio isomers and is in opposite direction to the effect due to complexing. It has been studied in some detail before⁵ in our laboratory, and we have combined this earlier information with some additional measurements to assess the values of $[t_r'(h)/t_r'(d)]_0$. A 48-ft. long pure ethylene glycol on firebrick column was constructed and the relative retention times were determined at 0° for *cis*-C₄H₈-2/*cis*-C₄D₈-2 and for *trans*-C₄H₈-2/*trans*-C₄D₈-2. The two determinations gave identical $[t_r'(h)/t_r'(d)]$ values, which amounted to 1.0049 per deuterium atom. It was assumed, as found earlier,⁵ that this isotope effect is directly proportional to the number of deuterium atoms in the olefin. A decline with tem-

perature of the same magnitude as observed previously⁵ would reduce the isotope effect per deuterium atom from 1.0049 at 0° to 1.0039 at 25° and 1.0031 at 40°. These three values were adopted to calculate $[t_r'(h)/t_r'(d)]_0$ at the three temperatures for the deuterio isomers containing various numbers of deuterium atoms. It should be stressed that since the isotope effect on the pure ethylene glycol column is considerably smaller than the isotope effect due to complexing, it introduces only a relatively small correction into the latter and the procedure adopted for its evaluation appears to be quite adequate.

Equation 4 can of course be also used for AgNO₃ concentrations other than 1 *M*. This particular column (1 *M*) was selected because it contains enough AgNO₃ to make the complexing effect sufficiently large for accurate determination while at the same time the salting-out effect is still negligible. The salting-out effect would generally tend to cancel between the protio and deuterio isomers of an olefin. Thus, although with the 2 *M* AgNO₃ columns the salting-out effect can no longer be considered negligible, when eq. 4 is applied to the data obtained with the 0 and 2 *M* columns, the K_d/K_h values are in practically all cases within about 1% the same as obtained with the data from the 0 and 1 *M* columns and do not show any systematic trends. In the case of 1,3-butadiene, however, the K_d/K_h values from the 2 *M* column are uniformly larger by about 2%. This is most likely due to the fact that, unlike the other olefins studied and in agreement with earlier observations,⁴ 1,3-butadiene shows that at higher AgNO₃ concentrations a 1:2 complex begins to be formed as well and this is already noticeable at a 2 *M* concentration.

Table II gives the K_d/K_h values at the three temperatures for the deuterio olefins studied. Most of the values are based on the data from the 0 and 1 *M* columns. As indicated in the table, several of the values were calculated from the data obtained with the 0 and 2 *M* columns, either because measurements were

(5) W. E. Falconer and R. J. Cvetanović, *Anal. Chem.*, **34**, 1064 (1962).

Table II. Deuterium Isotope Effects in the Olefin-Silver Ion Complex Formation in Glycol Solutions^a

Olefin	K_d/K_h			$-\Delta H_d - \Delta H_h$, ^b kcal./mole	$\Delta S_d - \Delta S_h$, cal./mole deg.
	0°	25°	40°		
Ethylenes					
<i>trans</i> -CHD=CHD	1.085	1.065	1.073	0.05	-0.01
C ₂ D ₄	1.161 ^c	1.129 ^c	1.126 ^c	0.13	-0.2
Propylenes					
CH ₃ CD=CH ₂	1.041	1.038	<i>d</i>	<i>d</i>	<i>d</i>
CH ₃ CH=CD ₂	1.076	1.064	1.048	0.11	-0.3
CH ₃ CD=CD ₂	1.111	1.100	1.072 ^c	0.15	-0.3
CD ₃ CH=CH ₂	1.027	1.024	1.010 ^c	0.07	-0.2
CD ₃ CD=CD ₂	1.144	1.129	1.096 ^c	0.18	-0.4
Butene-2					
<i>trans</i> -C ₄ D ₈ -2	1.157	1.127	1.116 ^c	0.15	-0.3
<i>cis</i> -C ₄ D ₈ -2	1.133	1.108	1.090	0.16	-0.3
1,3-Butadiene					
1,3-C ₄ D ₆	1.173	1.136	1.113	0.22	-0.5

^a The values given in the table are for the deuterium-containing isomers, d, relative to the corresponding protio isomer, h. ^b Determined from the K_d/K_h values at 0 and 40°. ^c Calculated from the relative retention times on the 2 M AgNO₃ column. All the other values are based on the relative retention times on 1 M AgNO₃; the two sets of data differ in most cases by less than 1% (butadiene values from the 2 M column are uniformly larger by about 2%, as discussed in the text). ^d Not determined.

not done on the 1 M column (C₂D₄) or because they were of doubtful accuracy. The differences in the mean enthalpies and entropies of complex formation for the interval 0-40° are given in the last two columns of Table II.

The only one of the C₂H₂D₂ isomers listed in Table II is the *trans*-1,2-dideuterioethylene. Both the *cis*-1,2- and the 1,1-dideuterioethylene were found to have identical retention times with the *trans* isomer, even in special experiments at a temperature as low as -20°.

Discussion

The factors responsible for the variation in the stability of the silver ion-olefin complexes with olefin structure have been extensively investigated and discussed in the past. In general, electronic, steric, and structural strain effects are involved, but unfortunately, the relative importance of these factors is not known with certainty.

The stability of the complexes is almost always discussed in terms of the variations in the values of the equilibrium constants since most of the measurements have been made at a single temperature. The two very conspicuous trends, established quite early,⁶⁻⁸ are (1) a general decrease in stability with increasing double bond substitution, and (2) a considerably greater stability of the *cis* than of the corresponding *trans* isomers of internal olefins.

If, as may be assumed intuitively,⁶ the olefins act mainly as electron donors and silver ion as electron acceptor, the stability of the complexes should increase with increasing alkyl substitution of the olefin as a result of the greater inductive electron release to the double bond. The opposite trend is observed and this suggests steric hindrance to complex formation by the bulky substituents.^{6,9} However, the more recent view,^{10,11} now generally believed to be more reasonable, is

that the stability of the silver ion-olefin coordination bond depends also on a back donation of electrons to the olefin from the silver ion. The two contributions have been formalized¹² as resulting from overlap of the filled π -orbital of the olefin with the vacant s-orbital of silver (σ -bond) and from overlap of a filled d-orbital of silver with the vacant antibonding π -orbital of the olefin (π -bond). The relative importance of the two contributions is not known, although they are likely to be of the same order of magnitude.¹³ In view of this uncertainty, it is not possible to predict whether an inductive electron release to the double bond would increase or decrease complex stability. In the latter case, it would be entirely unnecessary to postulate important steric effects. On the basis of a recent qualitative estimate,¹⁴ the contribution from the σ -bond should predominate, at least in some cases. Under such conditions adverse steric effects of the bulky alkyl groups would have to be invoked. Additional evidence in support of the likely importance of steric effects has been quoted by Muhs and Weiss.⁴ Nevertheless, an unambiguous separation of the two effects, the electronic and the steric, is very difficult, and it still remains to some extent unsettled.

The greater stability of the complexes of *cis* isomers of internal olefins has been ascribed either to (1) a more adverse steric effect of the two alkyl groups when they are *trans* to each other,⁸ or (2) a contribution from the relief of strain of the crowded alkyl groups in the *cis*-olefin when the complex is formed and the unsaturated carbon atoms assume some sp³ character.^{4,16}

Information on the changes in the enthalpies and entropies of complex formation should, in principle, provide additional insight into the nature of the interactions involved. The data in Table I show that the variation in the values of K , and thus in complex stability, is primarily determined by variations in the enthalpies of complex formation. The entropies of

(6) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).
 (7) H. J. Lucas, R. S. Moore, and D. Pressman, *ibid.*, **65**, 227 (1943).
 (8) F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *ibid.*, **74**, 333 (1952).
 (9) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).
 (10) J. Chatt and L. A. Duncanson, *ibid.*, 2939 (1953).
 (11) J. Chatt in "Cationic Polymerization," P. H. Plesch, Ed., J. Heffner and Sons, Cambridge, 1953, p. 40.

(12) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).
 (13) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).
 (14) S. P. McGlynn, quoted in ref. 15.
 (15) J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).
 (16) R. B. Turner, D. B. Nettleton, and M. Perelman, *ibid.*, **80**, 1430 (1958).

complexing on the whole vary relatively little. They are all negative, as would be expected for an association process, and are comparable in magnitude, for example, to the entropy changes in the polyalkylbenzene-iodine monochloride complexes.¹⁷ In the present case, however, a linear enthalpy-entropy relation is not followed. Traynham and Olechowski¹⁵ have also found approximately constant ΔS values for complexes of several cyclic olefins with silver ion in aqueous solutions. At the same time, the absolute values of both the enthalpy and entropy of complexing of cyclopentene, the only olefin in common in the two studies, are greater for the process in aqueous solution than the corresponding values in ethylene glycol solution obtained in the present work. The existence of appreciable differences between the processes in the two media has already been noted and discussed.⁴

Although ΔS values in Table I are approximately the same, there appears nevertheless to be some variation. On the whole the loss of entropy on complex formation tends to increase somewhat with increasing size of the alkyl substituents. This could be interpreted to signify a somewhat greater physical restraint in the complexes of the olefins containing bulkier substituent groups. Such a trend would be in agreement with the postulated importance of steric effects for the decrease in $-\Delta H$ values with increasing substitution. Some "irregularities" in this trend could then be rationalized in terms of an opposing effect due to the inductive electron release to the double bonds tending to increase complex stability. However, because of the relatively small differences involved and still appreciable experimental uncertainties in the ΔH and ΔS values, these views must be regarded as only tentative.

The data on the secondary deuterium isotope effects summarized in Table II show in all cases slightly larger K and $-\Delta H$ values for the deuterio isomers of the studied olefins. An inverse secondary equilibrium isotope effect is therefore exhibited in all cases. The loss of entropy may also be slightly larger in the case of the deuterio isomers, although the differences are here very small.

Of particular interest in Table II are (a) the relative magnitudes of the inverse isotope effect (K_d/K_h) for molecules of varying degree of alkyl substitution and (b) the effect of partial deuteration of propylene at various positions in the molecule. The following generalizations can be made.

(1) The isotope effect per deuterium atom is considerably larger for deuterium atoms directly attached to the unsaturated carbon atoms (for brevity in the following referred to as " α -effect") than when they are in β -position to the double bond (" β -effect").

(2) The α - and β -isotope effects are of the same sign, both are "inverse" ($K_d > K_h$).

(3) The isotope effects are to a good approximation logarithmically additive. Thus, for all the olefins in Table II the total isotope effect, for example at 0°, is approximately given by the expression

$$K_d/K_h = (1.040)^{n_\alpha} + (1.010)^{n_\beta} \quad (5)$$

(17) N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 4202 (1955).

where n_α and n_β are, respectively, the total numbers of deuterium atoms in the α - and β -positions.

(4) The α - and β -effects per deuterium atom for all the olefins in Table II appear to remain very nearly the same regardless of the number of alkyl substituents in the molecule. The largest difference between the observed values of K_d/K_h at 0° listed in Table II and the values calculated from eq. 5 is only 1.3% and in most cases it is less than 1%. (For 1,3-butadiene- d_6 it is taken that $n_\alpha = n_\beta = 3$.)

(5) The isotope effect for *cis*-2-butene- d_8 is about 2% smaller than for the corresponding *trans* isomer.

Interpretation of the secondary deuterium isotope effects still presents great difficulties.¹⁸ Without an adequate knowledge of the structural parameters and the vibrational characteristics, it is not possible to establish the structural factors responsible for the observed inverse isotope effects. The present work is therefore restricted primarily to reporting the experimental findings. Nevertheless, it is necessary to discuss briefly the experimental results in terms of the rationalizations proposed in the literature for related cases.

It is necessary first to consider whether the observed deuterium isotope effects may be due to the smaller nonbonded repulsions of deuterium atoms rather than to those of hydrogen atoms, as outlined by Bartell.¹⁹ It is convenient to discuss separately the nonbonded interactions with the silver ion (for brevity called the "direct steric effect") and the nonbonded interactions of H and D atoms between themselves and with the skeletal carbon atoms (the "indirect steric effect").

It appears that a steric isotope effect is likely to be appreciable only in the cases of severe overcrowding.²⁰ A direct steric isotope effect could still be important in the silver ion-olefin complexes since it is possible that the stability of these complexes is strongly influenced by the adverse steric effects of the bulky substituents, as already discussed. The observed isotope effects indeed qualitatively agree with the intuitive predictions which could be made on this basis: the stability of the deuterio complexes is greater and the β -effect is considerably smaller than the α -effect. Nevertheless, some of the observations seem to indicate that the direct steric effect is probably unimportant. Thus, if the direct steric isotope effect is indeed important, then the pronounced decrease in complex stability in going, for example, from ethylene to propylene and to *trans*-2-butene must also be primarily due to the adverse steric effect of the methyl groups tending to keep the silver ion away from the double bond. Under such conditions, it would be expected that the α -isotope effect should be most pronounced in ethylene and smaller in propylene and 2-butene, because of the weaker nonbonded interactions of the silver ion with the α -CH bonds in the last two olefins as a result of the presence of the methyl substituents. Contrary to these predictions, the α -effect per deuterium atom appears to be closely the same for the three olefins, indicating that the direct steric isotope effect is probably unimportant. Some caution should

(18) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(19) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).

(20) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **86**, 1733 (1964).

be exercised in accepting this conclusion in view of the purely qualitative nature of the argument.

The indirect steric effect would result in the present case from greater H---H (and H---C) repulsions in the tetrahedral than in the plane trigonal configuration.¹⁹ On complexing, it is likely that the unsaturated carbon atoms assume a partial tetrahedral configuration and the increased nonbonded repulsions have to be overcome. Such interactions will be smaller in the complexes of deuterio olefins and their stability will therefore be greater. In this interpretation, the basic cause of both the α - and β -effects is the same, although the α -effect is expected to be greater,¹⁹ as observed. The approximate constancy of the α -effect would suggest approximately equal configurational changes for various olefins; it is difficult to say whether such a constancy is feasible.

The small difference between the isotope effects of *cis*- and *trans*-2-butene (shown in Table II) is probably due to an indirect steric effect. As mentioned earlier, the exceptionally large K of *cis*-2-butene is probably due to an appreciable relief of strain from the two crowded methyl groups when the complex is formed. In the *cis*-2-butene- d_8 the overcrowding is slightly reduced and the decreased contribution from strain relief results in a slightly smaller K_d/K_h value than for the *trans* isomer. There is no similar effect in the *cis*-1,2-dideuterioethylene, and its isotope effect is the same as for the *trans* isomer.

The approximate treatment of Streitwieser, *et al.*,²¹ which is based on anticipated changes in characteristic frequencies of CH bond vibrations, can be readily applied to the α -isotope effect observed in the present work. As pointed out by Bartell,¹⁹ the changes in frequencies in going from a plane trigonal to a tetrahedral configuration may be largely determined by the same factors as the indirect steric effect just discussed, and there may therefore be an extensive analogy between the two approaches. The magnitude of the α -isotope effect is given by the expression

$$\ln \frac{K_d}{K_h} = \frac{0.187}{T} \sum_i [W_i(\text{complex}) - W_i(\text{olefin})] \quad (6)$$

where the sum includes the characteristic frequencies associated with the vibrations of all the α -CH bonds which become replaced by CD bonds in the deuterio isomer. The observed inverse isotope effects ($K_d > K_h$) can be accounted for by an expected increase in the frequency of the out-of-plane CH bending vibrations when the olefinic sp^2 configuration assumes a partial sp^3 character in the complex. Equation 6 can explain the observed logarithmic additivity of the isotope effects and perhaps also their approximate independence of the degree of alkyl substitution of the olefin.

The β -effect observed in the present work, unlike the β -effects observed in solvolysis (which are generally ascribed to a less effective hyperconjugative stabilization by CD_3 than by CH_3), could perhaps be treated in a

manner analogous to the Streitwieser's treatment of the α -effect. However, such a treatment of the β -effect would be much more difficult and would be of very dubious validity.

In the empirical approach of Halevi^{18,22} it is assumed that there is a greater effective inductive electron release from CD bonds than from the corresponding CH bonds. If applied to the present results, it could readily explain the difference in the magnitudes of the α - and the β -effects, their logarithmic additivity, and independence of the degree of substitution of the olefins. The fact that K_d is greater than the corresponding K_h in all cases would imply (and thus provide evidence for the postulate) that an increasing inductive release of electrons to the double bond does *increase* the stability of the complexes.¹⁸ This would then be in agreement with the early assumptions⁶ that the decrease in complex stability with alkyl substitution is caused by steric hindrance (and not by adverse inductive effects). The secondary deuterium isotope effects observed in the present work can thus be fully reconciled with the predictions based on Halevi's approach. An extensive discussion of the formal character of this approach and of several criticisms of it has been given recently by Halevi and his co-workers,^{18,22,23} including specifically its bearing on the effect of deuteration on the stability of the metal ion-olefin complexes.¹⁸

The above brief discussion illustrates the difficulties associated with any attempt to rationalize in a simple manner the secondary deuterium isotope effects. The various simplified treatments are based on the assumption that, at least in some cases, it is possible to isolate a single major contributing factor. In the general case it would be difficult to disentangle different contributions and assess quantitatively their relative importance. All the contributions must ultimately reflect themselves in changes of vibrational characteristics and thus in a difference of the free energies, or in the present case, to a good approximation, in the enthalpies of complex formation.

A secondary deuterium isotope effect on the stability of the molecular complex of chloranil with toluene (and similarly with *m*-xylene) has been observed by Halevi and Nussim.²³ Deuteration of the methyl group in toluene resulted in a 7% decrease in the equilibrium constant, and this decrease was ascribed to a less effective hyperconjugative stabilization by CD_3 than by CH_3 . There is a formal analogy between this effect and the β -effect observed in the present work. However, the two are in opposite direction, one *decreasing* and the other *increasing* complex stability. On the other hand, the more recent study by Halevi and Ravid²⁴ of the HCl-alkylbenzene complexes shows close analogy with the present findings: both nuclear deuteration of benzene and toluene and methyl deuteration of the latter *increase* complex stability, in agreement with the postulated greater inductive electron release from CD bonds.

(22) E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

(23) E. A. Halevi and M. Nussim, *ibid.*, 876 (1963).

(24) E. A. Halevi and B. Ravid, *Pure Appl. Chem.*, 8, 339 (1964).

(21) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, 80, 2326 (1958).