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Isotope Effect and Kinetic Studies of the Reaction of Tertiary Alcohols with Triphenylphosphine–Carbon Tetrachloride: Ion Pair or Concerted?

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Abstract—Kinetics of the reactions of 1,2,3-triphenyl-2-propanol (**1**), 1,2-diphenyl-2-propanol (**2**) and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**) with triphenylphosphine–carbon tetrachloride in the temperature range of 25–78°C in several solvents are investigated. In a non-polar solvent (CCl_4), the reaction of (**2**) proceeds via intermolecular anti E2 elimination and/or intermolecular S_N2 nucleophilic substitution (28% substitution, ratio of 2-alkene/1-alkene=1.06, $E/Z \geq 49$). In a polar solvent (CH_3CN) reaction proceeds via E1 and/or S_N1 (24% substitution, 2-alkene/1-alkene=1.9, $E/Z \geq 6$. At equilibrium, the ratio of 2-alkene/1-alkene is equal to 99 with $E/Z \geq 4.21$. The primary kinetic isotope effect (k_H/k_D) for the elimination pathway in the non-polar solvent is equal to 4.90 and 3.90 at temperatures of 25 and 60°C, respectively. A small secondary β-isotope effect of 1.10 was observed for substitution reaction at both temperatures. Direction of substitution (S_N2 vs. E2) depends on temperature and polarity of the solvent. The energetics ($\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$), the rate orders, and optimization of molecular geometry of intermediates by semiempirical methods (AM1 and CNDO) all agree with intermolecular E2 and S_N2 mechanisms. New rules for stereoselectivity and Hofmann–Saytzeff eliminations are considered.

Introduction

Recent interest in the stereoselective synthesis of olefins prompted a simultaneous investigation of the elimination reaction and the mechanism of the reactions of two model compounds 1,2,3-triphenyl-2-propanol (**1**) and 1,2-diphenyl-2-propanol (**2**) with heterogeneous aluminum oxide and thorium oxide,[1] semi-heterogeneous polystyryl diphenylphosphine in carbon tetrachloride,[2] and in this work with homogenous triphenylphosphine in carbon tetrachloride.

The dehydration of alcohols over metal oxides depends not only upon the steric interaction of the intermediate and/or transition state on the surface but is also strongly dependent on the preparation conditions of the catalyst and the reaction conditions (Table 1).[1]

The 2% cross-linked polystyryl diphenylphosphine in tetrachloromethane causes dehydration similar to that by aluminum oxide (i.e. anti-E2 elimination) (Table 1).[2]

Reaction of primary and secondary alcohols with triphenylphosphine–carbon tetrachloride constitutes a mild and efficient method for the conversion of alcohols into the corresponding alkyl halides.[3–6] The mechanism for the substitution reaction has been tested by several investigators.[4–6] They have demonstrated that in a polar solvent (acetonitrile), the reaction proceeds with racemization but in a non-polar solvent (carbon tetrachloride), inversion of configuration is observed. Optically active (*R*)-(+)-2-octanol in a polar-solvent (CH_3CN) produces 2-chlorooctane with 78% racemization but in a non-polar solvent (CCl_4) an inversion of configuration greater than 90% is observed.[5]

Table 1. Comparison of product distribution of dehydration reaction of **2** (reaction time 9 h, temperature 78°C (unless otherwise stated))

Reagent	Solvent	Con %	% (**6**)	% (**7**)	% (**8**)	**6/7**	**6+7/8**
$P{-}PPh_2$[a]	CCl_4	22.5[b]	100	Trace	Trace	V L[c]	–
$P{-}PPh_2$[a]	CH_3CN	29[b]	62	0	38	V L	1.630
$Al_2O_3{-}H$[d]	2-Hexanol	100[e]	25	11	64	2.30	0.560
$Al_2O_3{-}B$[d]	2-Hexanol	100[e]	19	16	56	1.2	0.630
Al_2O_3–Pure[d]	2-Hexanol	100[e]	17	26	57	0.650	0.750
ThO_2[d]	2-Hexanol	78[f]	49	21	30	2.30	2.30
$PhSO_3H$[g]	Benzene	100	81	19	1	4.3	99

[a] See Ref. 2.
[b] 36% Alkyl halide.
[c] Very large.
[d] See Ref. 1.
[e] 230°C.
[f] 350°C.
[g] Equilibrium conditions, 70°C, 2 h, (Refs. 7,8).

Keywords: stereoselective synthesis; semiempirical calculations; reaction mechanism; kinetic isotope effect.

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Dabbagh et al. reported that for the reaction of *erythro*-3-deuterio-2-butanol with triphenylphosphine–carbon tetrachloride the major pathway is substitution with elimination (100% anti E2, favoring the Saytzeff rule, and deuterium isotope effect equal to 2) as a minor pathway. Reaction with 1,1,1,3,3,3-hexadeuterio-2-methyl-2-propanol produced 85–90% isobutylene with k_H/k_D equal to 2.[6]

The question raised was whether reaction of tertiary alcohols with triphenylphosphine in carbon tetrachloride could be used in a stereoselective synthesis of hindered olefins. If so, what is then the mechanism of elimination for these reactions? What is the effect of temperature and polarity of solvent on the stereoselectivity and regioselectivity? How comparable are the dehydrations of **2** in homogenous triphenylphosphine in carbon tetrachloride with that of a heterogeneous system (aluminum oxide and thorium oxide), or with that of semi-heterogeneous cross-linked diphenylphosphine polystyrene in carbon tetrachloride? We believe we have found just the right system which can shed more light on the mechanism for the dehydration reactions of tertiary alcohols.

To answer these questions, we first studied the effects of varying temperature and the polarity of solvent on reactivity, stereoselectivity (i.e. the ratio of *syn*/*anti* elimination), and regioselectivity (i.e. the ratio of Saytzeff/Hofmann elimination). Second, we calculated the kinetics of elimination and substitution reactions [i.e. the energy of activation ($E_a^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$)]. Then, we studied the elimination reaction of 3,3,3-trideutero-1,2-diphenyl-2-propanol (**3**) and obtained a primary kinetic isotope effect. In order to gain more insight into these reaction mechanisms and their stereoselectivity, we have undertaken a semiempirical calculation (AM1 and CNDO) of the molecular geometry of the intermediate of the reactions of alcohol **2** with triphenylphosphine. It is the purpose of the present report to provide the evidence which serves to establish the fact that the mechanism of the reaction of tertiary alcohols with triphenylphosphine–carbon tetrachloride in a non-polar solvent (carbon tetrachloride) is concerted intermolecular anti E2 and intermolecular S$_N$2. In a polar solvent (acetonitrile), it proceeds via an ion pair mechanism (e.g. E1 and S$_N$1). One additional aim of the report is to show that these reactions are indeed stereoselective.

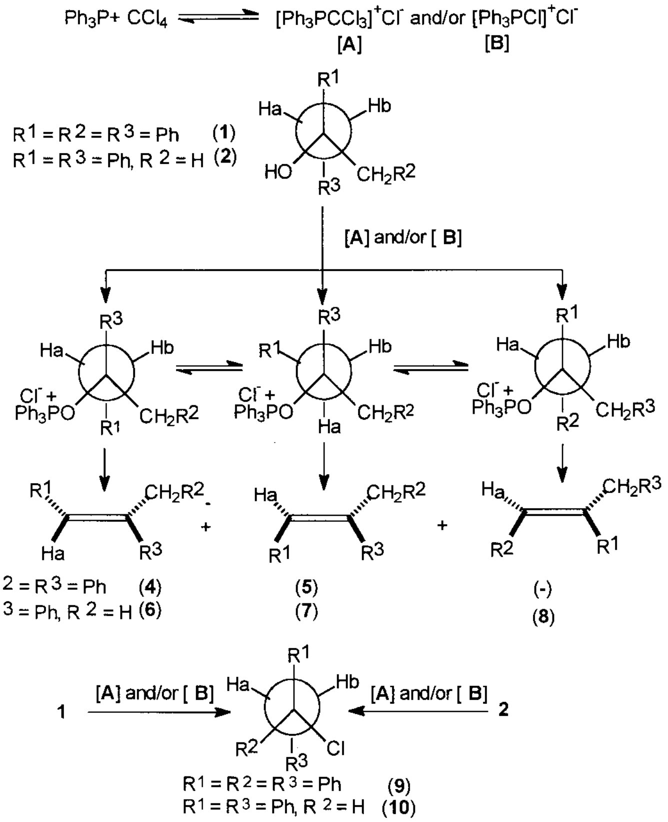
Initially the data for the reaction of tertiary alcohols with triphenylphosphine–carbon tetrachloride in a non-polar solvent (carbon tetrachloride) resembled that of acid-catalyzed dehydration of alcohols (e.g. E1 and S$_N$1 mechanism) (Table 2, Scheme 1). However, a closer examination of the data and comparison with other acid or base-catalyzed dehydration of alcohols encouraged us to re-examine this system.

The reaction of **2** with other acid or base reagents were less stereoselective and/or produced undesired side products (**UP**) in high yield (Table 2). The reaction of **2** with *p*-toluenesulfonic acid initially produced the kinetically controlled adducts (**6**/**8**=1.13) but quickly isomerized (within 2–3 h) to reach an equilibrium composition (**6**/**8**=30–40) indicating E1 mechanism, Tables 1 and 2. The reaction of **2** with phosphorus pentachloride showed unusual Saytzeff selectivity in which the formation of *E*-alkene **6** competed almost equally with **UP** and a minor amount of substitution. Thionyl chloride produced trace amounts of substitution and mostly **UP**. An

Table 2. Conversion, substitution, and elimination adducts for the reaction of **2** with hydrochloric acid, sulfuric acid, phosphorus pentachloride, thionyl chloride, and triphenyl-phosphine-tetrachloromethane

Reagents[a] (temp.)	Time (h)	% Conv.[b]	% **UP**[c]	Relative percent adducts				Ratio of (**6**/**8**)
				10	**6**	**7**	**8**	
A(78°C)[d]	8	66	0	28	37	Trace	35	1.10
A(78°C)	7	100	0	31.5	37	Trace	31.5	1.20
A(25°C)[e]	547	65	0	48	30	Trace	22	1.40
HCl(78°C)[f]	19	43	0	57	24.5	Trace	18.5	1.30
H_2SO_4[g]	48	77	0	–	56	Trace	44	1.30
PCl_5[h]	0.75	100	43.5	6.5	50	Trace	Trace	–
$POCl_3$ (45°C)[i]	24	–	–	–	5	2	46	1.13
$SOCl_2$[j]	1.25	100	100	Trace	0	0	0	–
B (70°C)[i,k]	<1	100	–	–	52	2	46	1.13
B (70°C)[k]	–	100	–	–	85	5	10	8.5
C(70°C)[k,l]	–	–	–	–	81	19	1	39.5
D(139°C)[k,m]	–	–	–	–	77	21	2	32
E(139°C)[k,n]	–	61	–	–	89	9	2	44.5

[a] A=Ph_3P–CCl_4.
[b] % conversion (by ^1H NMR).
[c] % **UP**=Undesired products.
[d] Reaction mixture kept at −15°C for three months, then at 78°C.
[e] Reaction mixture kept at −15°C for three months, then at 25°C.
[f] 36% HCl, $CDCl_3$–CCl_4.
[g] Conc., THF, reflux.
[h] THF, 30–45°C.
[i] Ref. 7.
[j] Reflux.
[k] B=TsOH-benzene.
[l] C=Equilibrium composition in TsOH-benzene.
[m] D=Equilibrium composition in *t*-BuOK-xylene.
[n] E=KNH_2–NH_3.



Scheme 1.

ion pair mechanism is consistent with these experimental observations.

Results

Reaction of 1,2,3-triphenyl-2-propanol (1)

Reaction of alcohol **1** with one or two molar ratios of triphenylphosphine in carbon tetrachloride was studied at 78°C over 200 h. The results are summarized in Table 3 (Scheme 1).

Polarity of solvents

The decomposition reactions of **2** were investigated in several solvents with various dielectric constants in order to compare the extent of bond-making and bond-breaking in polar and non-polar solvents (Tables 4 and 5).

Table 3. Conversion of **1** to alkenes at 78°C with triphenylphosphine–carbon tetrachloride (relative percentages were calculated by ^{1}H NMR; alkyl halides were not formed)

Time (h)	% Conv. (mol)		Ratio of **4/5** (mol)	
	1[a]	2	1[a]	2
2	<2	7	[b]	3.25
22	3	16	5.70	2.70
47	6	44	5.70	2.57
71	13	45.5	70	4.0
144	30	58	5.70	4.30
192	35	83	5.70	4.30

[a] Moles of triphenylphosphine.
[b] Trace amounts.

Table 4. Conversion of **2** to alkyl halides and alkenes in acetonitrile

Time (h)	Temp. (°C)	% Conv.	**10/6+7+8**	**6/7**	**6+7/8**
5	45	35	1.60	Large[a]	[b]
	78	86.5	0.113	14.5	1.60
13	45	51	4.60	Large[a]	[b]
	78	98	0.020	5.10	[b]
22	45	66.5	0.770	Large[a]	2.20
	78	100	[c]	6.25	[b]

[a] Trace of *Z*-alkene.
[b] No trace of 1-alkene.
[c] No alkyl halide.

Table 5. Comparison of dielectric constant of the solvents on the conversion of **2** to alkyl halides and alkenes in 9–10 h

Solvent	ϵ [D]	Temp. (°C)	%Conv.	**10/6+7+8**	**6/7**	**6+7/8**
CCl_4	2.2	78	61.5	0.550	Large[a]	1.20
$(CH_3)_2CO$[b]	21	45	48	0.430	Large[a]	1.10
CH_3CN	36	78	90	0.117	6.30	[c]
$(CH_3)_2SO$	49	70	37.5	[d]	Large[a]	1.75

[a] Trace of *Z*-alkene.
[b] Time 23 h and 30 min.
[c] No 1-alkene.
[d] No alkyl halide.

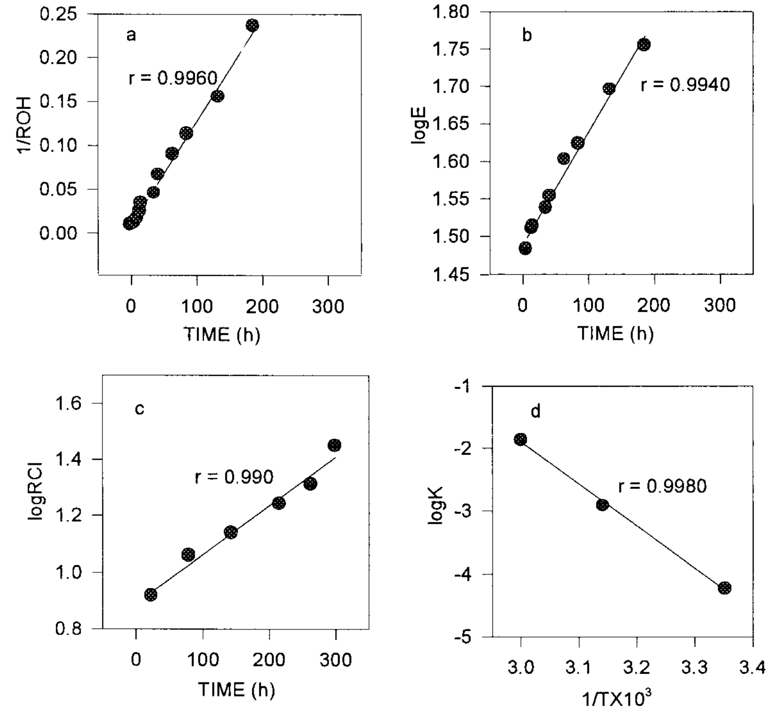


Figure 1. Typical plots of (a) second order rate for the disappearance of ROH **2**. (b) First order rate of appearance of *E*-alkene **6**. (c) First order rate of appearance of RCl **10**. (d) Arrhenius plot for the appearance of *E*-alkene **6**.

Table 6. Energetics for the rate of disapearance of alcohol **2** and for the rate of formation of alkenes and alkyl halides

Compd (#)	E_a (kcal/mol)	r[a]	$\Delta S^{\ddagger}$ (cal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)
ROH (**2**)[b]	16.70	0.9960	−16.62	19.25	16.11
RCl (**10**)[c]	14.90	0.990	−21.390	20.6840	14.3060
E-alkene (**6**)[c]	19.81	0.990	−8.59	21.78	19.21
1-alkene(**8**)[c]	16.10	0.990	−17.180	20.5740	15.4510

[a] Correlation coefficient.

[b] Second order rate equations are used to calculate the rate constants.

[c] First order rate equations are used to calculate the rate constants.

Kinetics

The rates of disappearance of alcohol **2** and the rate of formation of *E*-alkene **6**, 1-alkene **8**, and alkyl halide **10** were measured in pure carbon tetrachloride at various temperatures by ^{1}H Nuclear Magnetic Resonance Spectroscopy (NMR). The rate of intermediate decomposition was fast and non-measurable, Scheme 1. The rate constants for the reactions were calculated using the first ($\mathrm{Ln}\, a_0/a_0-x=\mathrm{k}t$) and second order rate equations [$(1/a)=\mathrm{k}t+(1/a_0)$]. The energy of activation, the entropies, Gibbs free energy, and the enthalpy were calculated using the first order rate constants as in the following expressions, $\log \mathrm{k}=-E_a/\mathrm{R}T+\log \mathrm{A}$, $A=(\kappa \mathrm{k}T/h)e^{\Delta S\ddagger/\mathrm{R}}$, $\Delta G^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger}$, $\Delta \mathrm{H}^{\ddagger}=E_a-\mathrm{R}T$, respectively (Fig. 1). The principal results are summarized in Table 6. The rate of decomposition of alcohol **2** was also fit by the second-order rate equation. The rate of formation of alkenes **6** and alkyl halide **10** showed good linearity with first order rate equation (Fig. 1).

Table 7. The corrected kinetic isotope effects for elimination and substitution reactions of 1,2-diphenyl-2-propanol (**2**) and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**) (average of two values (areas from ^{1}H NMR); for isotope effect corrections see equation 1 in Ref. 1)

Temp. (°C)	Time (h)	$(k_H/k_D)_{\mathrm{elim}}$	$(k_H/k_D)_{\mathrm{subst}}$
25	216	4.90	1.20
	312	3.60	1.20
	712	3.60	1.10
60	7	4.10	1.10
	23	3.80	1.10
	27	3.90	1.10

Isotope effects in the elimination and substitution reactions of 1,2-diphenyl-2-propanol in carbon tetrachloride

The kinetics were run simultaneously on the deuterated (**3**) and nondeuterated 1,2-diphenyl-2-propanol (**2**) so that even if they did not turn out to be absolute, the relative kinetic isotope effect would still be valid. The kinetic data are summarized in Table 7.

Calculation of kinetic isotope effect

The corrected kinetic isotope effects for the elimination and substitution steps were calculated using equation 1 in Ref. 1.

Discussion

Initially, we attempted to obtain high yields of olefins from some hindered tertiary alcohols **1** and **2**, Scheme 1. We were, however, surprised to find that under our experimental conditions, we were able to obtain only 5% olefins (E/Z=5.70) from **1** in 20 h and 54% olefin (E/Z=5.70) in 312 h, at 78°C. At higher temperatures (>100°C, most part of solvent was evaporated), 100% olefins (E/Z=0.60) were produced in 2 h without producing side products (at room temperature, no olefin was formed in 451 h). A twofold increase in the concentration of triphenylphosphine increased the rate by about three times, producing 83% olefin (E/Z=4.30) in 192 h (Table 2). We, therefore, decided to examine the less hindered alcohol **2**. It was known that under acidic conditions, kinetically controlled α-benzylstyrene (**8**) was produced in approximately equal amounts (1:1) with *trans*-α-methyl stilbene (**6**) in 0.40 h. The former alkene was rapidly converted to an equilibrium mixture of olefins (**6** and **7**) in 2 h (Table 1).[7,8] Much to our surprise, we found that under our experimental conditions (78°C) compound **2** converted 100% to a mixture of 32% 1,2-diphenyl-2-chloropropane (**10**), 36% *trans*-α-methyl stilbene (**6**), and 32% α-benzylstyrene (**8**). A trace amount of *cis*-α-methyl stilbene (**7**) was formed. The product ratio, however, remained unchanged in 50 h (2-methyl-2-propanol produced 90% elimination!).

In order to gain absolute certainty of the order of the decomposition reactions, the activation parameters of the decompositions, the kinetic isotope effect for the rate of decomposition of alcohol and the rate of formation of products, the reactions of **2** and **3** in various solvents and at different temperatures were investigated. These results are of utmost importance when evaluating any proposed decomposition mechanism. Any proposed mechanism must be consistent with stereochemistry of the reaction, the kinetics, the energetics, and the isotope effect.

The mechanism of elimination is consistent with stereochemistry of the reaction. The product distribution, although initially similar to the acid-catalyzed reaction, is far different in that, with triphenylphosphine–carbon tetrachloride and a non-polar solvent (CCl_4), it remained unchanged over 500 h whereas in the acid-catalyzed reaction the equilibrium was reached in less than 2 h (Tables 1–6).

We examined the system using a more polar solvent, acetonitrile, since it has been reported that halogenation occurs very rapidly in this particular solvent.[9]] In addition, Slagle et al. have demonstrated that the increased polarity of acetonitrile over carbon tetrachloride and chloroform is effective in disturbing the three-dimensional lattice such that the kinetic order changes from unimolecular to bimolecular. This allows for sufficient separation of the ion pair, promoting anion interchange. There is the possibility that the increased solvent polarity might affect intermediate decomposition such that carbon–oxygen cleavage might be considerably enhanced over carbon–chloride bond formation or elimination of a proton. This was tested by allowing (*R*)-(+)-2-octanol to react with triphenylphosphine-tetrachloromethane in acetonitrile and it was found that the 2-chlorooctane obtained was 78% racemic.[10] In this work, the product distribution in acetonitrile reached equilibrium composition in 22 h (Tables 5 and 6). Indeed, in the more polar solvent (acetonitrile), carbon–oxygen cleavage was sufficiently extensive to be responsible for the loss of stereoselectivity. This indicates the formation of a carbocation intermediate and that the reaction proceeds via S_N1 and E1 mechanism. In fact, in acetonitrile, carbon–chlorine cleavage was sufficiently extensive to be responsible for the conversion of alkyl halide **10** to alkenes! We have begun an investigation on the decomposition of **10** and hope to report the results in due course.

In the light of what has already been said, stereoselectivity seems to need redefinition! A reaction should be considered stereoselective if the product distribution is far from that of the thermodynamic equilibrium composition. Most acid-catalyzed reactions are not stereoselective because they form products near thermodynamic equilibrium composition. In other words, a high ratio of E/Z or Z/E does not necessarily mean high stereoselectivity unless this ratio is far from that of the equilibrium composition.

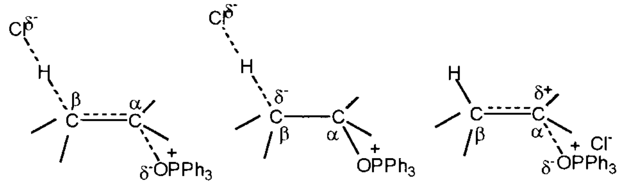
Another interesting observation is that the reaction of 2-butanol with triphenylphosphine-tetrachloromethane favored the Saytzeff elimination, but in the case of compound **2**, Hofmann elimination competed equally with Saytzeff elimination. This indicates that Hofmann–Saytzeff elimination does not depend on the reagent nor on the stability of products but it depends, instead, on steric interactions in the transition state and/or the intermediates (see also Refs. 1,2).

The mechanism is consistent with the energetics of the reaction. The relatively low $\Delta H^{\ddagger}$ is characteristic of concerted reactions, in which bond-making accompanies bond-breaking. In reactions in which the formation of ion pair cleavage of C–O bond is the rate-determining step, the $\Delta H^{\ddagger}$ is markedly higher with little new bond-making.

The rate of formation of products which is equal to the rate of decomposition of the intermediate is first order but the reaction proceeds via intermolecular S_N2 substitution or intermolecular anti E2 elimination. Of course, a true S_N2 or E2 reaction cannot be first order unless both substrate and nucleophile are one molecule.

The entropy of activation ($\Delta S^{\ddagger}$), on the other hand, decreases because of the loss of translational and rotational degree of freedom. The two reacting intermediates must attain a specific geometry to permit the bonding intermediates that occur as the transition state is approached. The entropy of activation for the 1-alkene formation step is much higher than that for the *E*-alkene or alkyl halide step. This substantiates that chloride ion and methyl group are molecularly constrained as close neighbors when compared to *E*-alkene or alkyl halide formation.

The magnitude of the kinetic isotope effect is a good representation of the position of the transition state along the reaction coordinate. The maximum isotope effect is expected from a linear symmetrical transition state with hydrogen positioned centrally between the two-acceptor centers. The kinetic isotope effect of 3.6–4.9 observed for



11 **12** **13**

Scheme 2.

elimination pathway indicates that the rate-determining step is the loss of proton. The transition-states **11** and **12** accord with this observation. Consequently, transition-state **13** may be rejected (Scheme 2).

The very small kinetic β-isotope effect of 1.15±0.05 observed for the substitution pathway (Table 7) indicates that this process has nearly balanced bond-making and bond-breaking in what is usually known as an S_N2 reaction.[6]

We would not consider the process to be kinetically controlled because of the lack of the formation of *Z*-alkene (**8**). How can a reaction be kinetically controlled when nearly equal amounts of the thermodynamically controlled isomer (*E*-alkene) and the least stable kinetically controlled isomer (1-alkene) are produced but the isomer with intermediate stability (*Z*-alkene) is formed in trace amounts?

Examination of molecular geometry of the intermediates (CNDO and AM1 semiempirical calculations)[11] clearly substantiates the back-side attack by the chloride ion from one intermediate to the vicinity of the methyl group ($-CH_3$), methylene group ($-CH_2$), and α-carbon (S_N2) of another intermediate. This model was tested for the elimination of **2** with aluminum oxide.[1] The most intriguing fact is that the semiempirical models of the intermediate and/or transition-state for aluminum oxide also exactly matched the experimental data as well. Formation of cluster(s) of ion pairs for such hindered molecules would have formidable energetics as also suggested by Ramos and Rosen.[12] Therefore, we believe that the semiempirical models provide a good representation of actual intermediate and/or transition-state. Attempts are under way to investigate these systems with more advanced semiempirical methods.

Conclusion

Kinetics (rate constant, energy of activation, enthalpy of activation, entropy of activation, free energy of activation), kinetic isotope effect, the stereochemistry, and semiempirical calculation of the optimized molecular geometry of the intermediates of the reaction of triphenylphosphine–carbon tetrachloride in a non-polar solvent (CCl_4) all suggest intermolecular anti E2 elimination and intermolecular S_N2 substitution. They also suggest that the reaction may not be kinetically controlled. The reaction is indeed stereoselective in non-polar solvents (high ratio of *E*/*Z*) but stereochemistry is lost in polar solvents in which the *E*/*Z* ratio is similar to that of equilibrium composition at higher temperatures. Elimination of the less hindered alcohol (2-butanol) favored the Saytzeff rule whereas elimination of the hindered alcohol **2** favored the Hofmann rule.

Experimental

General

^1H NMR spectra were measured on a Varian EM390 (90 MHz). IR spectra were obtained using a Shimadzu ZU-435. Melting points were taken using the Gallenkemp melting point apparatus and are uncorrected. Yields were calculated from ^1H NMR and/or isolated products are not optimized. Geometry optimization was performed by semiempirical calculations[11] (AM1 and CNDO) with the aid of the HyperChem computer program. All starting materials or solvents were obtained from Merck or Fluka Chemicals companies and were purified with proper purification techniques. All reaction temperatures were that of the oil bath ±0.2°C. 1,2,3-Triphenyl-2-propanol (1); 1,2-diphenyl-2-propanol (2) and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (3) were prepared as reported earlier.[1,2,7,8]

Typical procedure for the following the disappearance of alcohols and the appearance of alkyl halides and/or alkenes by ^1H NMR

In a 10 ml flask, 0.5 g (2.35 mmol) of **2**, 0.6 g (2.29 mmol) triphenylphosphine, and 6.3 ml (10.01 g, 65.04 mmol) of carbon tetrachloride were combined in a pressure vessel (equipped with Rotaflo stopcock), filled with 20 g of 3 mm glass beads topped with calcium chloride and kept in an oil bath at 78°C under dry nitrogen. The reaction progress was monitored by ^1H NMR, in which we removed and tested a small aliquot from each flask at suitable intervals (tetramethylsilane TMS was added as an internal standard). For alcohol **1**, the following chemical shifts (ppm) were used to calculate the relative percentage of adducts: two $-CH_2-$ groups $\delta=3.15$ (AB-quartet, **2**H, $J=15$ Hz), one –OH group $\delta=1.80$ (s, 1H), for *E*-alkene **4** a $-CH_2-$ group $\delta=4.10$ (s. 2H), and for *Z*-alkene **5** a $-CH_2-$ group $\delta=3.75$ (s, 2H). No peak for alkyl halide **9** was observed. For alcohol **2** the following chemical shifts were used to calculate the relative percentage of adducts: One $-CH_3$ group $\delta=1.50$ (s, 3H), one-OH group $\delta=1.55$ (s, 1H), or $-CH_2-$ groups $\delta=2.90$ (AB-quartet, 2H, $J=15$ Hz); for *E*-alkene **6** the CH_3 group $\delta=2.25$ (s, 3H); for 1-alkene **8** a $-CH_2-$ group $\delta=3.80$ (s, 2H), two –CH– groups $\delta=5.00$ and 5.45 (s, 1H); for alkyl halide **10** the CH_3 group $\delta=1.85$ (s, 3H), or $\delta=3.30$ $-CH_2-$ (s, 2H) groups. No peak for *Z*-alkene **7** was observed.

Typical competitive kinetic isotope effect as determined by ^1H NMR

To a high precision ^1H NMR tube, 0.106 g (0.50 mmol) 1,2-diphenyl-2-propanol (**2**), 0.262 g (1.00 mmol) of triphenylphosphine, 1 ml (10.32 mmol) carbon tetrachloride and tetramethylsilane were added. To another high precision ^1H NMR tube, 0.107 g (0.50 mmol) 3,3,3-trideuterio-2-propanol (**3**), 0.262 g (1.00 mmol) of triphenylphosphine, 1 ml (10.32 mmol) carbon tetrachloride and tetramethylsilane were added. After an initial run, the reactions were observed for 3 days at 60°C (a similar reaction was completed at 78°C in 10 h).

Reaction of 2 with triphenylphosphine–carbon tetrachloride in acetonitrile

The procedure was similar to carbon tetrachloride using 2.0 g (9.40 mmol) of **2**, 2.40 g (9.16 mmol) triphenylphosphine, and 3.50 ml (36.13 mmol) of carbon tetrachloride in 52 ml (989 mmol) of acetonitrile at 78°C (reaction was repeated at 45°C) under dry nitrogen (see Table 4).

Reaction of *2* with triphenylphosphine–carbon tetrachloride in dimethyl sulfoxide (DMSO)

The procedure was similar to carbon tetrachloride using 2.0 g (9.40 mmol) of **2**, 2.40 g (9.16 mmol) triphenylphosphine, and 2.0 ml (20.65 mmol) of carbon tetrachloride in 13.5 ml (19.00 mmol) of dimethyl sulfoxide at 78°C (see Table 5).

Reaction of 2 with triphenylphosphine–carbon tetrachloride in acetone

The procedure was similar to carbon tetrachloride using 2.0 g (9.40 mmol) of **2**, 2.40 g (9.16 mmol) triphenylphosphine, and 3.50 ml (36.13 mmol) of carbon tetrachloride in 20 ml (27.20 mmol) of acetone at 45°C under dry nitrogen (Table 5).

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References

1. Dabbagh, H. A.; Mohammed Salehi, J. *J. Org. Chem.* **1998**, *63*, 7619–7627.
2. Dabbagh, H. A.; Malekpoor, S. S.; Fagihi, K. H. *Iranian Polym. J.* **1998**, *7*, 149–156.
3. Downie, I. M.; Holmes, J. B.; Lee, J. B. *Chem. Ind. (London)* **1966**, *65*, 900–903.
4. Hooz, J.; Giliani, S. S. H. *J. Chem.* **1968**, *46*, 86–87.
5. Jones, L. A.; Sumner Jr, C.; Franzus, B.; Huang, T. T. S.; Snyder, E. I. *J. Org. Chem.* **1978**, *43*, 2821–2827.
6. Dabbagh, H. A.; Franzus, B.; Huang, T. T. S.; Davis, B. H. *Tetrahedron* **1991**, *47*, 949–960.
7. Ho, I.; Smith, J. G. *Tetrahedron* **1970**, *26*, 4277–4286.
8. Ho, I.; Smith, J. G. *Tetrahedron Lett.* **1970**, *41*, 3535–3538.
9. Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1970**, *35*, 1627.
10. Slagle, J. D.; Huang, T. T. S.; Franzus, B. *J. Org. Chem.* **1981**, *46*, 3526.
11. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
12. Ramos, S.; Rosen, W. *J. Org. Chem.* **1981**, *46*, 3530–3533.