Electrostatic Catalysis by Ionic Aggregates. 4.[1] Rearrangement of 1-Phenylallyl Chloride in Lithium Perchlorate Solutions in Aprotic Solvents[2]

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Abstract: This investigation shows that the allylic rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) in aprotic solvents is subject to substantial rate enhancement by added lithium perchlorate. For example, at 25.0 °C the first-order rate constant of this isomerization reaction in pure ether is $k_i{}^0 = 2.5 \times 10^{-7}\ \mathrm{s}^{-1}$, while in solutions containing 3.39 M $LiClO_4$, it is $k_i = 2.14 \times 10^{-2}\ \mathrm{s}^{-1}$, showing an overall increase of 85 600-fold. Similarly, in the other solvents studied, the results show a varying magnitude of catalytic efficiency: tetrahydrofuran (0.0-1.53 M $LiClO_4$; 266-fold), propylene oxide (0.0-3.01 M $LiClO_4$; 7400-fold), diethyl carbonate (0.0-3.02 M $LiClO_4$; 9300-fold), and dimethylformamide (0.0-3.01 M $LiClO_4$; 40-fold). An analysis of the temperature dependence of the isomerization reaction shows that the energy of activation remains essentially constant in the individual salt-solvent systems, while the entropy of activation changes markedly. The pure solvents, diethyl ether, tetrahydrofuran, propylene oxide, diethyl carbonate, and dimethylformamide, give the Arrhenius activation energies: +17.0, +17.0, +17.1, +19.5, and +18.0 kcal/mol, respectively. Their corresponding entropies of activation are found to be: −33.6, −36.6, −32.9, −25.5, and −27.2 cal/(deg mol). Addition of $LiClO_4$ to these aprotic solvents produces a steady increase in the entropy of activation with no significant change in the energy of activation. The nature of the polar transition state and its stabilization by lithium perchlorate ion pairs and higher ionic aggregates in the various solvents studied are discussed.

Introduction

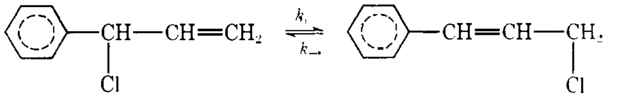
Increased interest in reactions carried out in fused salts[3-5] and the general lack of data on concentrated salt solutions in media of low dielectric led Pocker and Buchholz to study in detail the behavior of lithium perchlorate in diethyl ether.[1,6,7] Their selection of lithium perchlorate-diethyl ether solutions (LPDE) was supported by several observations reported in the literature. Lithium perchlorate had been found to be very soluble in diethyl ether and, at 30 °C, solutions of up to 6 M salt had been reported.[8,9] Earlier investigations[9-11] of the conductivity of LPDE solutions showed that the molar conductivity increased by a factor of several hundred with increasing salt concentration, despite a large increase in the viscosity, and it was suggested that the primary mechanism of conductance must be the transport of single ions within the complex aggregates, rather than the movement of the whole complexes. Sillén and Ekelin[9] had further noted that the vapor pressure data could not be explained in terms of lithium perchlorate aggregates, but the solutions must consist of clusters of $LiClO_4$-Et_2O complexes.

It had also been reported in the literature by Winstein and co-workers[12] that LPDE solutions accelerated the ionization reaction of *p*-methoxyneophyl *p*-toluenesulfonate and that of spirodienyl *p*-nitrobenzoate.[13] By comparison, the ionization of the sulfonate in acetic acid showed a very small rate enhancement.[12] In conclusion, Winstein et al.[13] stated that these reactions pointed up an interesting area of ionic organic reaction mechanisms and suggested such reactions might be useful practically and interesting theoretically.

Pocker and Buchholz[6] used trityl chloride as a sensitive probe of the ionic environment[14-16] in studying the LPDE solutions. They reported the fact that the apparent equilibrium constant increases from $K_{\mathrm{eqTCl}}{}^0 = 2.1 \times 10^{-12}$ M in pure ether to $K_{\mathrm{eqTCl}} = 1.4 \times 10^{-2}$ M at 5.05 M LPDE, which is a 7.0×10^9-fold increase. Likewise, they reported the equilibrium constant for the ionization of HCl in pure ether $K_{\mathrm{eqHCl}}{}^0$ was calculated as 9.0×10^{-8} M and at 5.05 M LPDE was found to be $K_{\mathrm{eqHCl}} = 2.4$ M, which is an increase of 2.5×10^6-fold. In order to be able to interpret these striking results, a study of the physical nature of the LPDE system was carried out by Pocker and Buchholz. They determined solubility-temperature curves, heats of solution, NMR spectra, and the molar dielectric increment.

The determination of the solubility-temperature curves, along with NMR and heat of solution data, supported the hypothesis that LPDE solutions exist as dietherate ions, $Li^+(OEt_2)_2ClO_4^-$, at concentrations below 4.25 M, and as the concentration increases to above 4.25 M, the solutions contain both the dietherate and monoetherate ions, $Li^+(OEt_2)ClO_4^-$. Thus, as the concentration of lithium perchlorate increases up to the solubility limit, the solution may be considered as changing gradually from fused $Li^+(OEt_2)_2ClO_4^-$ to fused $Li^+(OEt_2)ClO_4^-$. The ionization of the trityl chloride and hydrogen chloride were believed to be promoted by the electrostatic catalysis arising from the $[Li^+(OEt_2)_m, ClO_4^-]_n$ ion pair aggregates. The determination of the dielectric constants of LPDE solutions up to 0.5 M lithium perchlorate points out that the low dielectric constant of diethyl ether (4.34)[17] is increased in a linear fashion upon addition of the salt, but the increase is nowhere near dramatic enough to account for the enormous catalytic effects observed.

In order to obtain a better understanding of the factors which control the electrostatic catalysis in chemical processes, a study of the rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) in various organic solvents with added lithium perchlorate was undertaken. This reaction has been studied in detail by Waight and co-workers,[18a,b] and Rawlinson and Noyes.[18c] The reaction was first believed to proceed through a polar transition state which led to the formation of an intimate ion pair.[18a] Later, a polar transition state involving a cyclic type of structure (S_Ni' type) was proposed.[19] In either case, the development of partial charge was deemed important, and the reaction proved to be a good subject for the study of catalysis by ionic aggregates. The reaction was found to be first order in 1-phenylallyl chloride and proceeded in almost



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quantitative yield to the cinnamyl isomer, even at room temperature.[18,20]

Pocker and Buchholz studied this reaction in the LPDE system and achieved promising results which indicated both the magnitude and usefulness of the electrostatic catalysis associated with the LPDE solutions.[7] In the present work, the LPDE solutions were reinvestigated in greater detail, using the rearrangement reaction as a probe. In addition, other organic solvents were studied, using lithium perchlorate as the added salt. The selected solvents which produced meaningful results were tetrahydrofuran (THF), dimethylformamide (DMF), propylene oxide (PO), and diethyl carbonate (DC).

In our investigations of these various solutions, we have not only studied kinetically the magnitude of the catalysis and its relationship to lithium perchlorate, but we have also determined the important activation parameters, E_a, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$, in the hope that we might be able to delineate the energy requirements for the observed catalysis.

Experimental Section

Lithium Perchlorate. Reagent grade anhydrous $LiClO_4$ (G. Frederick Smith Chemical Co.) was recrystallized twice from distilled water in the form $LiClO_4{\cdot}3H_2O$ and then dried at 150 °C (0.5 mm) for at least 8 h.[6] The salt was stored in a sealed bottle in a desiccator until used, since it was necessary to keep the $LiClO_4$ completely anhydrous. The hydrate is not appreciably soluble in ether (0.139 g/100 cm^3 of solution at 25 °C).[8]

Diethyl Ether. Reagent grade anhydrous diethyl ether (Allied Chemical Co.) was distilled over $LiAlH_4$ (Metal Hydrides Inc.) just prior to use.[6]

Tetrahydrofuran. Reagent grade tetrahydrofuran (Aldrich Chemical Co.) was distilled over $LiAlH_4$ and then dried over NaH (Metal Hydrides Inc.) just prior to use.

Propylene Oxide. Reagent grade propylene oxide (Aldrich Chemical Co.) was distilled at 34.5 °C (760 mm) from a 3-ft fractionating column packed with metal staples and stored over fresh molecular sieves (Linde Division, Union Carbide Corp.) for 2 days prior to use.

Dimethylformamide. Reagent grade dimethylformamide (Aldrich Chemical Co.) was dried over BaO granules (Barium and Chemicals, Inc.) for 2 days and then distilled at 31 °C (2.5 mm) over fresh BaO granules. It was stored over molecular sieves 2 days prior to use.

Diethyl Carbonate. Reagent grade diethyl carbonate (Aldrich Chemical Co.) was distilled at 27–28 °C (5 mm) on a 3-ft spinning band column with a constant temperature jacket. It was stored over molecular sieves 2 days prior to use.

1-Phenylallyl Chloride. 1-Phenylallyl chloride (**1**) was prepared by the method of W. G. Young et al.:[20a] bp 49 °C (1.0 mm); UV max 253 nm (ϵ 1300 in ether) [lit.[18a] bp 50–60 °C (0.35 mm); UV max 253 nm (ϵ 1900)]. The samples contained about 5% of cinnamyl chloride which did not significantly alter the rate constants. The product chloride was stored in a dry ice-acetone bath to prevent spontaneous rearrangement to the cinnamyl chloride isomer, **2**.

Kinetic Measurements. All rates of rearrangement of 1-phenylallyl chloride were obtained by following the increase of absorbance at 253 nm (except for the solvent DMF where the wavelength 266 nm was used due to the interference of the amide carbonyl absorption at 253 nm). The absorbance increase was followed on a Beckman DU-2 equipped with a D_2 lamp and a constant temperature bath set at 25.0 ± 0.05 °C and controlled by a Sargent Thermonitor. In some cases when the rates of isomerization were appreciable, a Honeywell Electronic 19 recorder was used to monitor the absorbance. In the case of temperature dependence studies, temperatures above 20 °C were achieved using the Sargent Thermonitor, while those below 20 °C were achieved by use of a Formatemp Jr., Model 2095-2 in place of the Sargent Thermonitor. First-order rate plots were obtained following the appearance of **2** (ϵ 20 000)[18,20] and plotting log $(A_\infty - A_i)$ against time. In general, the first-order rate constants for isomerization were obtained with an accuracy of ±2%. The first-order plots were linear to at least 2 half-life times and in some cases where $\tau_{1/2} \leq 2$ h, the plots were linear up to 3 half-lives. Reactions in pure solvent or dilute salt solution with very long half-life times ($\tau_{1/2} > 24$ h) necessitated the calculation of "initial" rate constants associated with the first 10–25% of reaction. The 1-phenylallyl chloride rearranges quantitatively to cinnamyl chloride.[18,20]

Table I. Isomerization Rates of 1-Phenylallyl Chloride at 25.0 °C[a]

Solvent	[$LiClO_4$], M	k_i, s^{-1}	[$LiClO_4$], M	k_i, s^{-1}
Diethyl ether	0.00	2.5×10^{-7} [b]	2.02	2.56×10^{-3}
	0.0681	5.32×10^{-6} [b]	2.47	5.22×10^{-3}
	0.116	9.65×10^{-6} [b]	3.05	9.69×10^{-3}
	0.566	1.63×10^{-4} [b]	3.12	1.12×10^{-2}
	1.08	6.51×10^{-4}	3.26	1.26×10^{-2}
	1.50	1.26×10^{-3}	3.39	2.14×10^{-2}
Tetrahydrofuran	0.00	5.6×10^{-8} [c]	0.522	1.47×10^{-6}
	0.073	1.79×10^{-7}	1.06	6.33×10^{-6}
	0.216	5.27×10^{-7}	1.53	1.49×10^{-5}
Dimethylformamide	0.00	1.06×10^{-6}	1.12	3.01×10^{-6}
	0.054	1.25×10^{-6}	1.50	6.02×10^{-6}
	0.109	1.37×10^{-6}	2.14	9.95×10^{-6}
	0.453	1.65×10^{-6}	3.01	4.20×10^{-5}
Propylene oxide	0.00	2.2×10^{-7}	1.85	2.84×10^{-4}
	0.054	5.21×10^{-7}	2.11	3.77×10^{-4}
	0.196	2.77×10^{-6}	2.43	5.30×10^{-4}
	0.498	1.95×10^{-5}	2.82	1.27×10^{-3}
	0.976	4.44×10^{-5}	3.01	1.63×10^{-3}
	1.48	1.41×10^{-4}		
Diethyl carbonate	0.00	2.6×10^{-7}	1.28	8.72×10^{-5}
	0.016	3.62×10^{-7}	1.51	1.35×10^{-4}
	0.041	5.28×10^{-7}	1.76	3.75×10^{-4}
	0.073	7.06×10^{-7}	2.02	4.37×10^{-4}
	0.162	2.34×10^{-6}	2.29	5.75×10^{-4}
	0.324	5.78×10^{-6}	2.57	1.03×10^{-3}
	0.567	1.46×10^{-5}	2.79	1.51×10^{-3}
	0.729	2.26×10^{-5}	3.02	2.42×10^{-3}
	1.01	5.01×10^{-5}		

[a] [1-Phenylallyl chloride] = 4.1×10^{-5} M to 9.50×10^{-5} M. [b] Data from ref 7. [c] Estimated by extrapolation of Arrhenius plot.

Thermodynamic Activation Parameters. The effect of temperature on the rearrangement of 1-phenylallyl chloride was determined by obtaining the rate constant at various temperatures and different molar concentrations of lithium perchlorate for each solvent. For any given solvent and salt concentration, an Arrhenius plot was constructed from the data, and the energy of activation, E_a, was calculated from the slope. From the value of E_a, $\Delta H^{\ddagger}$ was obtained from the relationship: $\Delta H^{\ddagger} = E_a - RT$. The value of $\Delta G^{\ddagger}$ was obtained by means of the equation: $\ln k_{\text{rate}}h/kT = -\Delta G^{\ddagger}/RT$. The value of $\Delta S^{\ddagger}$ was obtained by means of the equation: $\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$.[21] The values for E_a and $\Delta H^{\ddagger}$ were obtained with an accuracy of ±0.5 kcal/mol. The corresponding values of $\Delta S^{\ddagger}$ were found to be accurate to within ±1.5 cal/(deg mol).

Results

Rearrangement of 1-Phenylallyl Chloride. The rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) was studied in the five solvents, diethyl ether, tetrahydrofuran, dimethylformamide, propylene oxide, and diethyl carbonate. In diethyl ether, the reaction was studied in the lithium perchlorate concentration range of 0.0 to 3.39 M, and the values of the rate constant k_i are listed in Table I. It should be noted that this is a more detailed investigation of the work previously reported by Pocker and Buchholz.[7]

The reaction in tetrahydrofuran was studied in the lithium perchlorate concentration range of 0.0 to 1.53 M. In a similar fashion, the reaction in dimethylformamide was studied in the lithium perchlorate range of 0.0 to 3.01 M, the reaction in propylene oxide in the lithium perchlorate concentration range of 0.0 to 3.01 M, and the reaction in diethyl carbonate in the lithium perchlorate concentration range of 0.0 to 3.02 M. The values of the rate constants k_i for all these systems are listed in Table I. It may be seen that an attempt was made to study

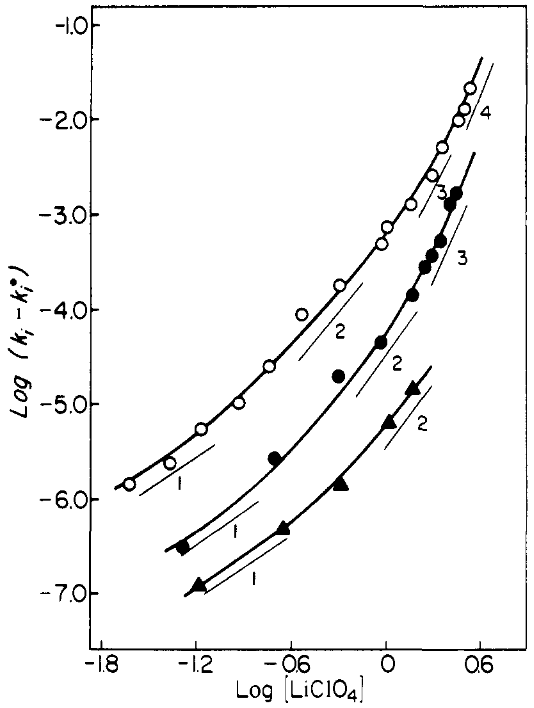


Figure 1. Plot of log ($k_i - k_i^0$) for 1-phenylallyl chloride vs. log [LiClO$_4$] at 25.0 °C: LPDE (○), LPPO (●), LP-THF (▲).

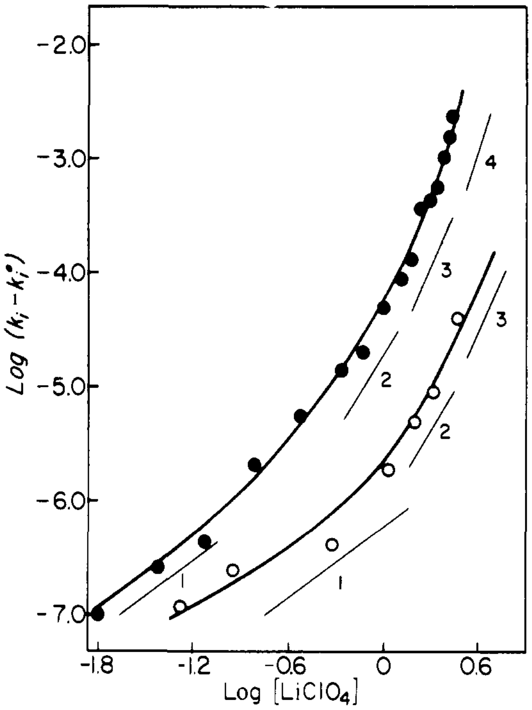


Figure 2. Plot of log ($k_i - k_i^0$) for 1-phenylallyl chloride vs. log [LiClO$_4$] at 25.0 °C: LP-DMF (○), LPDC (●).

Table II. Comparison of the Catalytic Effect in the Apparent Increase of k_i with added Lithium Perchlorate in Various Organic Solvents

Solvent	Range of [LiClO$_4$], M	Increase in k_i
Diethyl ether	0.0-0.566	6.52×10^2
	0.0-1.50	5.04×10^3
	0.0-3.05	3.88×10^4
	0.0-3.39	8.56×10^4
Tetrahydrofuran	0.0-0.522	2.63×10^1
	0.0-1.53	2.66×10^2
Dimethylformamide	0.0-0.453	1.56
	0.0-1.50	5.68
	0.0-3.01	3.96×10^1
Propylene oxide	0.0-0.498	8.86×10^1
	0.0-1.48	6.41×10^2
	0.0-3.01	7.41×10^3
Diethyl carbonate	0.0-0.567	5.62×10^1
	0.0-1.51	5.19×10^2
	0.0-3.02	9.31×10^3

the reaction in all the solvents over approximately the same range of lithium perchlorate concentration. However, the low solubility of lithium perchlorate in tetrahydrofuran precluded this.

It is of interest to examine the overall catalytic effect of each of these solvent systems on the reaction and to compare them. The results of the comparison of k_i at 0.0 M lithium perchlorate with k_i at higher concentrations of lithium perchlorate for the various salt-solvent systems are summarized in Table II. From this table, it is obvious that LPDE solutions exhibit the highest catalytic effect. It is interesting to note that LPDC solutions rank second, followed closely by LPPO, and then LP-THF, with LP-DMF being by far the least productive. Some other results that are of interest are: (1) the solvent with the highest dielectric constant, dimethylformamide, produces a salt-solvent system with very poor catalytic efficiency; (2) tetrahydrofuran, despite low solubility of lithium perchlorate, produces a salt-solvent system with a catalytic efficiency which is in reasonable agreement with the others; and (3) diethyl carbonate, a carbonate ester produces a salt-solvent system which exhibits a catalytic efficiency ranking second only to LPDE and is better than the other two ethers used, tetrahydrofuran and propylene oxide.

It is of interest to determine the dependence of the increase in k_i on the concentration of lithium perchlorate. Values of log ($k_i - k_i^0$) where $k_i^0 = 2.5 \times 10^{-7}$ s^{-1},[6] ([LiClO$_4$] = 0.0 M) were plotted against log [LiClO$_4$] for the LPDE solutions. The order in salt was found to change from 1.0 to 4.0, as shown in Figure 1. In a similar fashion, values of log ($k_i - k_i^0$), where k_i^0 is equal to the value of the rate constant at 0.0 M lithium perchlorate, were plotted against log [LiClO$_4$] for each of the other salt-solvent systems. We notice in Figure 1 that the order for LP-THF was found to change from 1.0 to 2.0. The lack of higher orders may simply be a result of the fact that the low solubility of lithium perchlorate in THF precludes one from obtaining comparable data at high salt concentration. For LP-DMF, the order was found to change from 1.0 to 3.0, as shown in Figure 2, and the results for LPPO shown in Figure 1 also exhibit a change in order from 1.0 to 3.0. On the other hand, LPDC shows an order change of 1.0 to 4.0, Figure 2. The LPDC system is the only system to show the same quantitative order change in [LiClO$_4$] as LPDE. In each case where a range of data is available, we can see that an increase in k_i is dependent upon a continuous increase in the lithium perchlorate concentration, as exhibited by the continuous change in order.

Activation Parameters of the Rearrangement of 1-Phenylallyl Chloride. The temperature dependence of the rate constant k_i, for the isomerization of 1-phenylallyl chloride, was determined for each of the various salt-solvent systems. The Arrhenius plots were used to determine the energy of activation, E_a, and then the other activation parameters were calculated from the standard equations.[21] The results for the various solvents we studied are shown in Table III. The corresponding Arrhenius plots are shown in Figure 3, LPDE; Figure 4, LP-THF; Figure 5, LP-DMF; Figure 6, LPPO; and Figure 7, LPDC. Some interesting observations can be made from these results. First, it is obvious in the case of each solvent

Table III. Activation Parameters for the Isomerization of 1-Phenylallyl Chloride at 25.0 °C

Solvent	$[LiClO_4]$, M	E_a, kcal/mol	$\Delta H^‡$, kcal/mol	$\Delta G^‡$, kcal/mol	$\Delta S^‡$, cal/deg-mol
Diethyl ether	0.00	+17.0	+16.4	+26.4	−33.6
	0.566	+17.2	+16.6	+22.6	−20.1
	1.08	+17.2	+16.6	+21.8	−17.4
	1.50	+17.2	+16.6	+21.4	−16.1
	2.02	+17.1	+16.5	+20.9	−14.8
	3.05	+17.0	+16.4	+20.2	−12.8
Tetrahydrofuran	0.00	+17.0	+16.4	+27.3	−36.6
	0.522	+17.3	+16.7	+25.4	−29.2
	1.06	+17.2	+16.6	+24.4	−26.2
	1.53	+17.0	+16.4	+24.0	−25.5
Dimethylformamide	0.00	+18.0	+17.4	+25.5	−27.2
	0.453	+18.4	+17.8	+25.3	−25.2
	1.12	+18.3	+17.7	+25.0	−24.5
	1.50	+18.2	+17.6	+24.5	−23.2
	2.14	+18.4	+17.8	+24.2	−21.5
	3.01	+18.4	+17.8	+23.4	−18.8
Propylene oxide	0.00	+17.1	+16.5	+26.3	−32.9
	0.498	+17.3	+16.7	+23.7	−23.5
	0.976	+17.3	+16.7	+23.3	−22.1
	1.48	+17.2	+16.6	+22.7	−20.5
	2.11	+17.2	+16.6	+22.1	−18.5
	3.01	+17.2	+16.6	+21.2	−15.4
Diethyl carbonate	0.00	+19.5	+18.9	+26.5	−25.5
	0.567	+18.9	+18.3	+24.0	−19.1
	1.01	+19.4	+18.8	+23.3	−15.1
	1.51	+19.6	+19.0	+22.7	−12.4
	2.02	+19.6	+19.0	+22.0	−10.1
	3.02	+19.5	+18.9	+21.0	−7.0

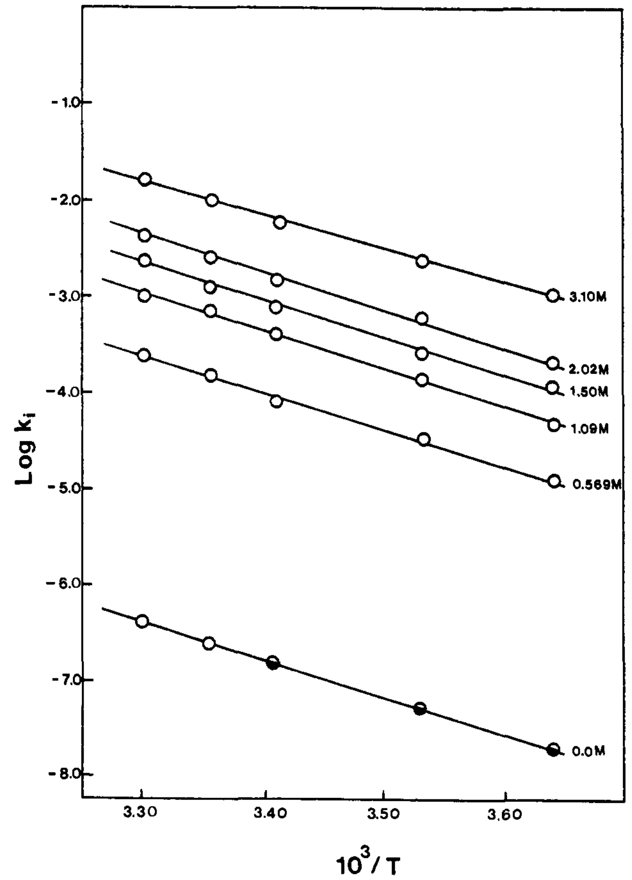


Figure 3. Determination of the temperature dependence of the rate constant for the isomerization of 1-phenylallyl chloride in $LiClO_4$-diethyl ether at 25.0 °C: (●) extrapolated value.

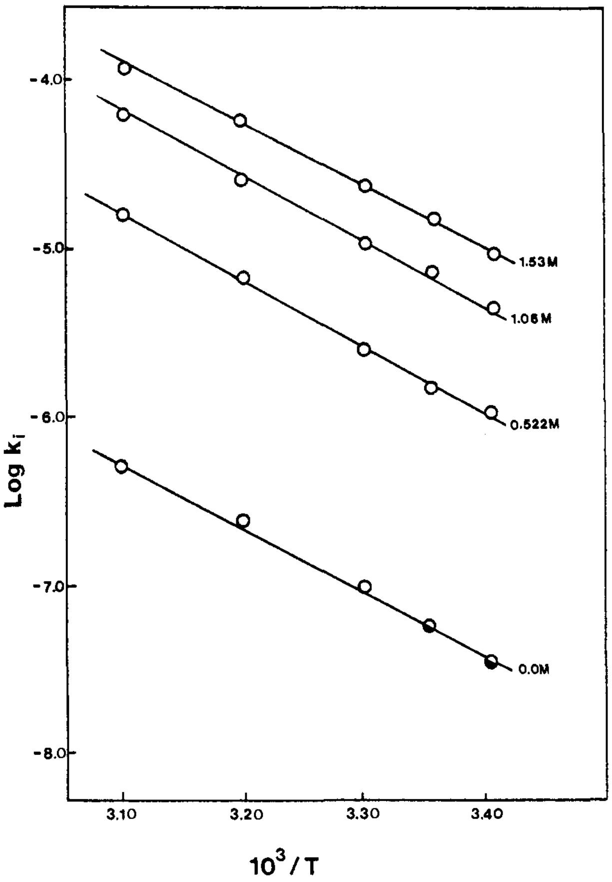


Figure 4. Determination of the temperature dependence of the rate constant for the isomerization of 1-phenylallyl chloride in $LiClO_4$-tetrahydrofuran at 25.0 °C: (●) extrapolated value.

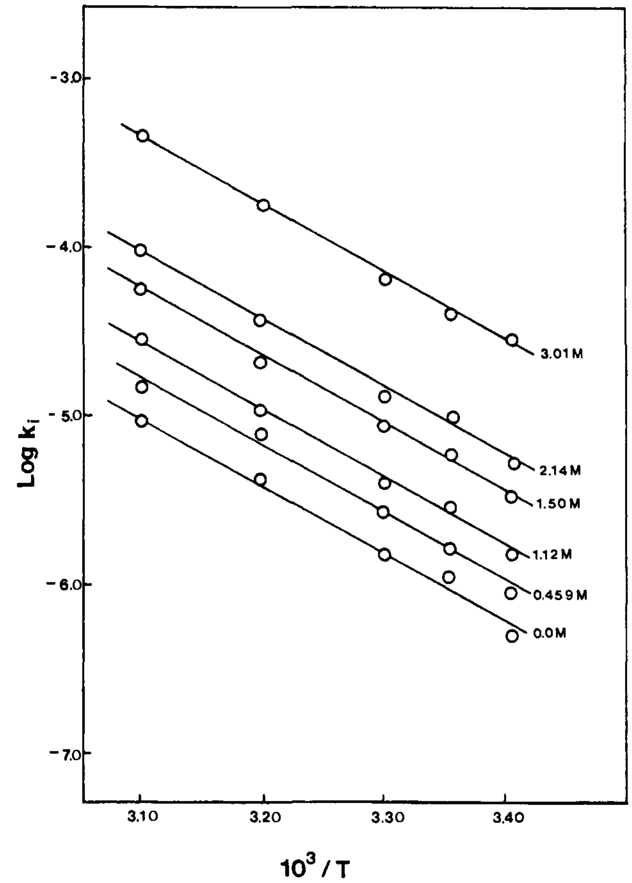


Figure 5. Determination of the temperature dependence of the rate constant for the isomerization of 1-phenylallyl chloride in $LiClO_4$-dimethylformamide at 25.0 °C: (●) extrapolated value.

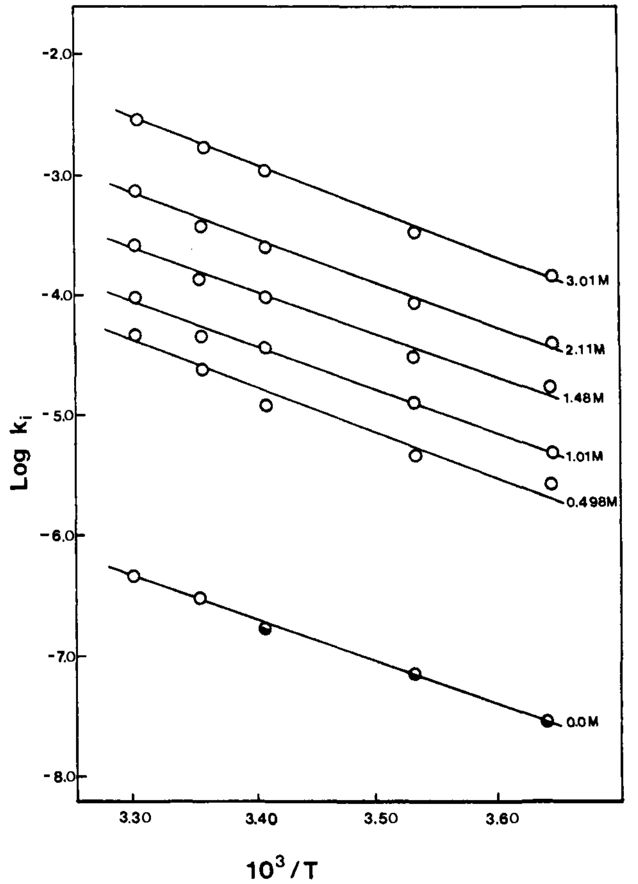


Figure 6. Determination of the temperature dependence of the rate constant for the isomerization of 1-phenylallyl chloride in $LiClO_4$-propylene oxide at 25.0 °C: (●) extrapolated value.

system that the decrease in the free energy of activation, $\Delta G^{\ddagger}$, with increasing lithium perchlorate concentration, is primarily dictated by an increase in the entropy of activation, $\Delta S^{\ddagger}$. In the case of each solvent system, it appears that, as the concentration of lithium perchlorate is increased, the enthalpy of activation, $\Delta H_{\ddagger}$, remains essentially constant, while the increase in the rate constant, k_i, is associated with a corresponding increase in $\Delta S^{\ddagger}$. Pocker and Buchholz, in their studies of the ionization and dissociation of trityl chloride in LPDE solutions, reported that the decrease in free energy of ionization of trityl chloride with increasing lithium perchlorate concentration appeared to be mainly dictated by an increase in the entropy of ionization.[6] The present study appears to correlate well with their results, as we see again that the entropy change seems to be the most significant.

It is also apparent from the data that the enthalpies of activation, $\Delta H^{\ddagger}$, for the three lithium perchlorate-ether systems, LPDE, LP-THF, and LPPO, are virtually identical within experimental error. In the case of LPDE and LPPO, the values of 0.0 M lithium perchlorate are almost all identical, and from Table I we see that the rate constants are nearly the same. In the case of LP-THF, the $\Delta G^{\ddagger}$ is somewhat higher and the $\Delta S^{\ddagger}$ is considerably lower, which is in agreement with the rate constant being several times slower. As the concentration of lithium perchlorate is increased in each of the ethers, the values of the parameters E_a and $\Delta H^{\ddagger}$ remain virtually constant and nearly identical for all three. This may be observed visually from the Arrhenius plots in Figures 3, 4, and 6, as the lines are obviously very near to being parallel, producing similar slopes, and similar values of E_a and then, subsequently, $\Delta H^{\ddagger}$. The values of $\Delta S^{\ddagger}$ increase with an increase in lithium perchlorate concentration, and this may be seen more clearly in Figure 8. It is interesting that the shape of the curves for the three ethers are very similar. From Table IV, it may be seen that each of the ethers shows a very large increase in $\Delta S^{\ddagger}$, as the first 0.5 mol of lithium perchlorate is added, and in each case, the effect becomes much less dramatic with each additional 0.5 mol quantity of the salt.

Table IV. Variation of $\Delta S^{\ddagger}$ with Increasing Molar Concentraton of Lithium Perchlorate in the Isomerization of 1-Phenylallyl Chloride[a]

	$\Delta(\Delta S^{\ddagger})$, cal/(deg mol), as [$LiClO_4$], M, increases				
Solvent system	0.0-0.5 M	0.5-1.0 M	1.0-1.5 M	1.5-2.0 M	2.0-3.0 M
LPDE	12.2	3.1	2.2	1.3	2.0
LP-THF	7.2	2.5	1.3		
LP-DMF	1.3	1.3	1.3	1.2	2.6
LPPO	8.7	2.4	1.6	1.5	3.0
LPDC	6.0	4.4	2.7	2.3	3.1

[a] These results are taken from Figure 8.

In the case of LP-DMF and LPDC, it is of interest to compare their results with those of the ethers. The E_a and $\Delta H^{\ddagger}$ for LP-DMF at 0.0 M lithium perchlorate shows a somewhat higher value than that of the ethers, but the value of $\Delta S^{\ddagger}$ is considerably higher, correlating with a larger value for k_i from Table I. The value of +18.0 kcal/mol for E_a is in reasonable agreement with that obtained in a more limited study by Valkanas and Waight, +19.0 kcal/mol,[18a] in the same solvent. In LPDC, it may be seen that at 0.0 M lithium perchlorate, the E_a and $\Delta H^{\ddagger}$ are higher than any of the values for the other solvents, but the value of $\Delta S^{\ddagger}$ is also the highest, although close

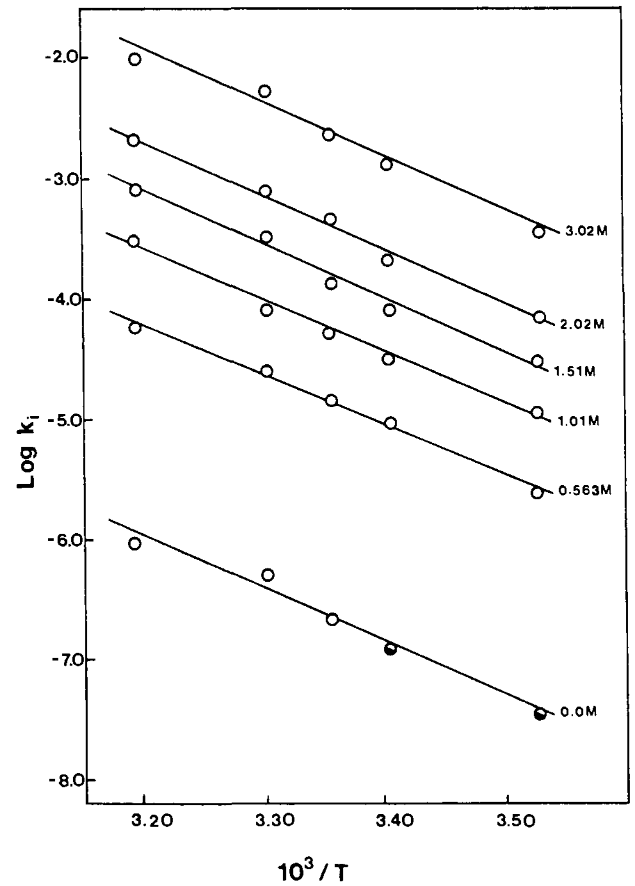


Figure 7. Determination of the temperature dependence of the rate constant for the isomerization of 1-phenylallyl chloride in $LiClO_4$-diethyl carbonate at 25.0 °C: (◒) extrapolated value.

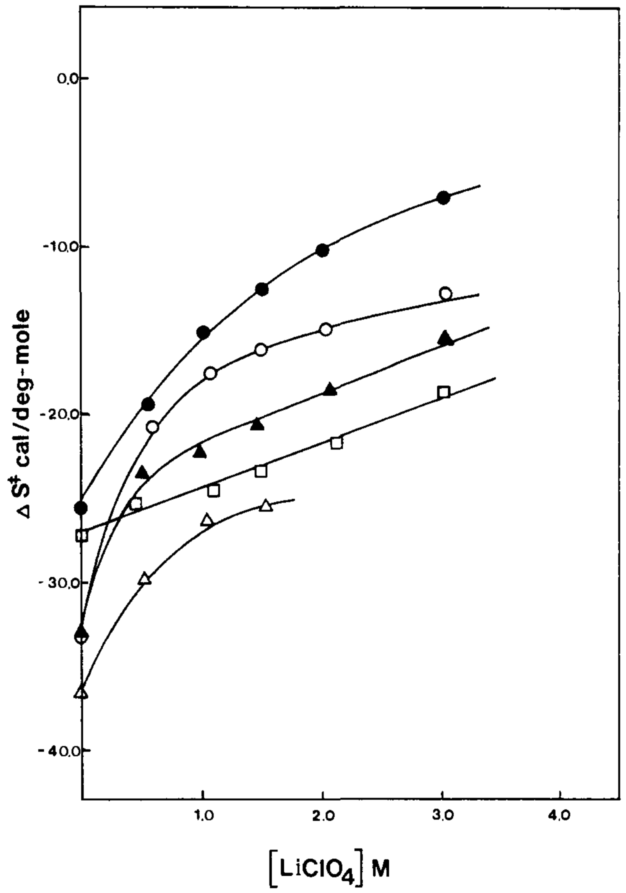


Figure 8. Plot of $\Delta S^{\ddagger}$ for the isomerization of 1-phenylallyl chloride vs. the molar concentration of lithium perchlorate: for LPDE (○), for LP-THF (△), for LP-DMF (□), for LPPO (▲), and for LPDC (●).

to that of LP-DMF. Thus, from Table I, we see the value for k_i is similar to that of LPDE and LPPO, the higher E_a being compensated for by a higher value of $\Delta S^{\ddagger}$. The values of E_a and $\Delta H^{\ddagger}$ remain fairly constant in LP-DMF and LPDC, with increasing molar concentration of lithium perchlorate, as seen in Table III. From the Arrhenius plots in Figures 5 and 7, it may be seen that the lines are nearly parallel, giving similar slopes and values. This is the same as was observed above for the ethers. With regard to the change in $\Delta S^{\ddagger}$ with molar concentration of lithium perchlorate in LP-DMF and LPDC, we notice some interesting results. LP-DMF exhibits a rather small steady change in $\Delta S^{\ddagger}$ and gives a plot which may best be represented by a straight line, Figure 8. On the other hand, LPDC gives a curve that is similar to the ethers but does not show as sharp a rise from 0.0 to 0.5 M lithium perchlorate, Figure 8.

In our studies of the lithium perchlorate solutions of several selected organic solvents, the relationship between the enthalpies and entropies of activation have been simplified by virtue of the fact that the energy of activation, and thus the enthalpy of activation, is virtually constant or exhibits a relatively small change, while the entropy of activation varies considerably over a large range of values. This is in contrast to the many different attempts in the literature using various methods reported by Leffler,[22] Hinshelwood and co-workers,[23-26] and Leffler and Grunwald[27] to find a meaningful linear relationship between enthalpies and entropies of activation. The various results produced by these investigators have been described as varying from approximately linear, to hook-shaped, to N-shaped, and it remains one of the most baffling problems in the field of enthalpy-entropy relationships.[27]

Discussion

We have shown that the isomerization reaction of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) may be effectively catalyzed by the addition of lithium perchlorate to various organic solvents. The solvents vary in their molecular structure, their dielectric constant, and their capacity to dissolve lithium perchlorate.[17] The question naturally arises as to which of the solvents with added lithium perchlorate offers the best salt-solvent system for electrostatic catalysis.

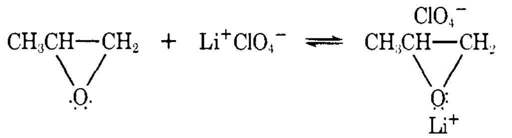
The well-studied LPDE system[1,6,7] seems to be the best of the group which was studied. LPDE offers a system that gives a high solubility of lithium perchlorate in an organic solvent of low dielectric constant[17] which allows solubility of most organic molecules one might desire to study. From Table II, it may be seen that LPDE produced the best overall catalytic effect by a factor of at least 4.2 and as high as 1000 when compared with the other solvents. Another advantage of LPDE is the fact that it produces the largest increase in the rate with addition of lithium perchlorate up to a 0.5 M solution and still produces the largest effect by comparison with the others, with addition of the salt up to a 1.5 M solution. This means that an experimenter can obtain useful catalytic results in a reaction where electrostatic catalysis could be utilized by adding relatively small amounts of lithium perchlorate to an ether solution of the reaction mixture. The only real difficulties presented by LPDE are: (1) the low boiling point of ether which makes storage of such salt solutions somewhat troublesome and causes minor difficulties in the study of reactions of long duration, and (2) the need for completely anhydrous conditions, as the hydrate of $LiClO_4$ is not appreciably soluble in ether.[8] All of these difficulties may be overcome without undue hardship by using good technique and using the solutions soon after their preparation.

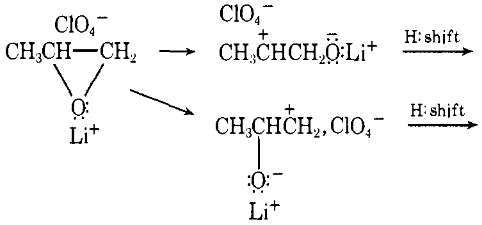
In considering the other solvents, it would seem that LPDC would be the second best salt-solvent system. It produced an overall catalytic effect which is better than all the others except LPDE, Table II. With the addition of smaller amounts of lithium perchlorate to give 0.5 M and up to 1.5 M solutions, its catalytic effect is comparable with that of LPPO and better than that of LP-THF. It does not have the two difficulties of LPDE solutions mentioned above, but it does have a lower limit of solubility of $LiClO_4$ (~4.5 M at 25 °C),[17] which might limit its utility. The LP-THF system might be considered quite useful in the lower concentration range of $LiClO_4$ as it produces catalytic effects in solutions of 0.5 and 1.5 M which compare reasonably well with all except LPDE, Table II. It has a higher boiling point than diethyl ether, but is difficult to keep free of water. Its major drawback, of course, is the minimal amount of $LiClO_4$ which may be dissolved in it.[17] The LP-DMF system is, by far, the worst of the group. From Table II it may be seen that even when large amounts of $LiClO_4$ are added the amount of apparent catalysis is quite small when compared with other solvents. DMF has some good features in that its boiling point as well as its solubility of $LiClO_4$ are high.[17]

The case of LPPO is rather an unusual one. This salt-solvent system gives results which are comparable to LPDC and better than LP-THF, and as far as physical properties and lithium perchlorate solubility, it closely resembles LPDE.[17] However, it has one unique feature which is a disadvantage and yet is very interesting in its own right at the same time. In the determination of the values of k_i, Table I, it was observed that the introduction of $LiClO_4$ into propylene oxide caused a change in absorbance in the reference and sample cells with time, in addition to the change in the sample cells caused by the isomerization reaction. This change appears to be caused by a rearrangement of the original epoxide molecule to a carbonyl compound, catalyzed by the $LiClO_4$. A product analysis was done, using VPC retention times and co-injection of known compounds. The results confirmed the products as acetone and propanal. At 3.43 M LPPO the approximate quantitative ratio of the two products appeared to be about 1:1. Since the extinction coefficient (ϵ) for acetone is 15.15,[28a] and that for propanal is 4.67,[28b] at 253 nm, the change in absorbance is not very large compared with that for 1-phenylallyl chloride even when one considers the fact that there is much more LPPO present than there is chloride. As a result, it is not very difficult to manually balance the DU-2 just prior to each reading to eliminate the change in absorbance caused by this side reaction. A test run at 2.45 M LPPO with a sample containing no chloride and one with chloride measured against a standard LPDE solution proved the validity of this method. It should be noted, however, that attempts to run reactions at concentrations of 3.50 M and higher become increasingly difficult because of this particular side reaction. At very high $LiClO_4$ concentrations, the side reaction increases to the point where it makes a strong bid to become the main reaction.

While for this particular study the side reaction discussed above is annoying, it is of considerable interest when considered by itself. Several papers have been published concerning the epoxide-carbonyl rearrangement and its catalysis by lithium salts.[29-32] In light of the published results, a possible scheme might be suggested for this reaction in the LPPO system, as shown in (1)-(3).

It would be of great interest to determine the actual product distribution into acetone and propanal, (3), at varying concentrations of $LiClO_4$ and the factors which are operative in (1) and (2) that would determine it. This is a subject for future study in these laboratories.


(1)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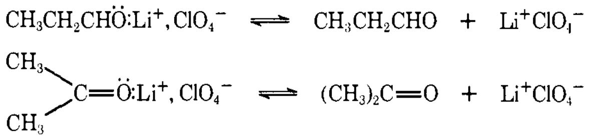

(3)

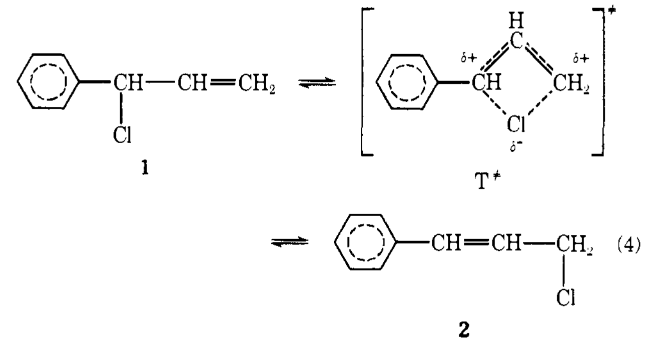
In summary, it might be said that the small ethers used in this study appear to be very useful as solvents for $LiClO_4$ in providing systems conducive to electrostatic catalysis. It has been suggested in the past that there is a strong affinity of diethyl ether for the lithium ion;[33] clearly, this affinity is associated with the ether oxygen. Therefore, by analogy, it is not difficult to see why tetrahydrofuran and propylene oxide would be good solvents for $LiClO_4$ and could thereby provide suitable systems for the study of electrostatic catalysis. It has not escaped our notice that, in the case of tetrahydrofuran and, to a lesser extent, in propylene oxide, the fact that the molecule is a ring and not as free to rotate as diethyl ether may have something to do with the lower rate enhancement observed in these two ether solvents. Other ethers, such as methyl propyl, ethyl propyl, or di-*n*-propyl ether are being investigated. The excellent results noted with diethyl carbonate might lead one to believe that dimethyl or propylene carbonates might be of utility, but our preliminary work found both of them to exhibit little or no catalysis in the presence of added $LiClO_4$. Diethyl carbonate has some ether-like oxygens in its carbonate ester function, but it also has a carbonyl which probably has a fairly strong affinity for the lithium ion but not so strong that it makes it inoperative for catalytic purposes. DMF, on the other hand, shows relatively low rate enhancements and one might suggest that the interaction of the lithium ion with the carbonyl is so strong that its effectiveness in stabilizing the transition state of the isomerization reaction is substantially reduced in comparison with other solvents. Evidence for the strong interaction of $LiClO_4$ with the carbonyl of an amide has been reported earlier for *N*-methylpropionamide[34] and dimethylacetamide.[35] One other point should be made and that is that Valkanas and Waight found there was no parallel between the rate constant for isomerization and the dielectric constant of the medium.[18a] We found the same fact to be in evidence in this study as shown in Table V. Thus, in the end one must conclude that the exact nature of the interaction between solvent and lithium perchlorate which produces the optimum conditions for effective electrostatic catalysis is not completely known. This subject would be an area of future study to be undertaken in these laboratories.

The rearrangement of 1-phenylallyl chloride to cinnamyl chloride was, at first, thought by Valkanas and Waight to proceed through a rate-determining step that probably involved an intimate ion pair,[18a] similar to that proposed by Winstein and co-workers.[36] Later work, however, led them to suggest the transition state for isomerization might better be represented by an S_Ni' type of structure, such as $T^{\ddagger}$ in eq 4.[19] Similar investigations of the rearrangement of 1-phenylallyl alcohol to 3-phenylallyl alcohol,[37] the rearrangement of 1-phenylallyl benzoate[38] and 1-phenylallyl *p*-nitrobenzoate[39] to the corresponding 3-phenylallyl esters, and the reaction of 1-phenylallyl [^{14}C]acetate in acetic acid[40] have been discussed

Table V. Solvent Effects on the Isomerization of 1-Phenylallyl Chloride at 25.0 °C[a]

Solvent	D^{20}	k_i, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
Dimethylformamide	36.7	1.06×10^{-6}	17.4	−27.2
Tetrahydrofuran	7.39	5.6×10^{-8}	16.4	−36.6
Diethyl ether	4.34	2.5×10^{-7}	16.4	−33.6
Diethyl carbonate	2.82	2.6×10^{-7}	19.5	−25.5
Propylene oxide	b	2.2×10^{-7}	16.5	−32.9

[a] $[LiClO_4]$ = 0.0 M. [b] Value not available, but is presumed to be somewhere between 2.0 and 6.0.



in terms of ionic mechanisms involving either free ions in water,[37,40] or ion pairs in solvents of low polarity.[38,39] Whichever type of mechanism is preferred in the present work, the results suggest in each case that the respective transition states have considerable ionic character. Thus, it would not be difficult to envisage the transition state in the rearrangement of 1-phenylallyl chloride to be influenced more strongly by the coulombic fields surrounding the lithium and perchlorate ions than either the initial or final states. This might lead one to propose that the free energy of activation for the rearrangement might be lowered as a result of a decrease in the enthalpy of activation as the molar concentration of lithium perchlorate is increased, thereby causing an apparent increase in k_i. We have observed that this is not the case, however. The enthalpy of activation remains essentially constant, and the entropy of activation shows the marked change which affects the lowering of the free energy of activation as the molar concentration of lithium perchlorate is increased. With these observations in mind, and using the results from Figures 1, 2, and 8, it may be possible to draw some conclusions about how the catalysis of the isomerization of 1-phenylallyl chloride to cinnamyl chloride occurs. Consider, first, the LPDE system. At moderate concentrations of lithium perchlorate in diethyl ether, further association may occur. Thus, $Li^+(OEt_2)_x$, ClO_4^- ion pairs may associate in diethyl ether to neutral pairs of ion pairs, $[Li^+(OEt_2)_x, ClO_4^-]_2$. Such associations, as well as still higher clusters, have been suggested to exist in moderately concentrated LPDE solutions.[9] In general, then, the formal kinetic orders depicted in Figures 1 and 2 represent the *minimum apparent molecularity* of such catalytic processes. Pocker and Buchholz showed that LPDE exists primarily as the dietherate, $Li^+(OEt_2)_2ClO_4^-$ at concentrations below 4.25 M.[6] Then, as the molar concentration of lithium perchlorate is increased going from 0.0 to about 0.04 M, the order in $LiClO_4$ goes from 0 to 1. Thus, the transition state of the isomerization becomes stabilized by an increase in entropy of activation of about 3.9 cal/(deg mol), lowering the free energy and increasing the rate constant k_i. Increasing the concentration of $LiClO_4$ to about 0.2 M brings an order change of 1 to 2. The transition state is stabilized by $2[Li^+(OEt_2)_2ClO_4^-]$ ionic aggregates, increasing the $\Delta S^{\ddagger}$ by about 4.6 cal/(deg mol), again lowering the $\Delta G^{\ddagger}$ and producing an increase in k_i. The next order change from 2 to 3 requires an increase in $LiClO_4$ concentration to about 1.50 M. This increase in $LiClO_4$ provides an increase in $\Delta S^{\ddagger}$ of about 9.0 cal/(deg mol) as the transition state is now affected by $3[Li^+(OEt_2)_2ClO_4^-]$ aggregates. The addition of this third aggregate produces the largest increase in entropy with change in order. The final order change which was observed in this work was from 3 to 4, producing an increase in $\Delta S^{\ddagger}$ of about 3.3 cal/(deg mol), surrounding the transition state with $4[Li^+(OEt_2)_2ClO_4^-]$ aggregates. It may be seen, then, that, as more and more $LiClO_4$ is added, it complexes with the solvent forming ionic aggregates, which then orient themselves around the ground state, and in increasing numbers around the highly polar transition state. These aggregates, whose number in turn depends on the concentration of $LiClO_4$, stabilize the partial charge development in the transition state, relative to the neutral ground state, decreasing the $\Delta G^{\ddagger}$ for the isomerization, thereby catalyzing the rate.[41] The aggregates of $Li^+(OEt_2)_2ClO_4^-$ may almost be envisioned as a "blanket" of electrostatic fields, as each change in order puts another piece of the blanket in place, until eventually one would assume that all the available orientations would be taken and perhaps the maximum value of k_i achieved.

In the case of the other solvents, a similar argument may be presented. For THF, by analogy with diethyl ether, we assume the presence of $Li^+(THF)_xClO_4^-$ ionic aggregates, where $x = 2$. Since the only order changes we could detect were 0 to 1 and 1 to 2, one might envision the orientation of $Li^+(THF)_xClO_4^-$ aggregates in the transition state as the $LiClO_4$ concentration was increased from 0.0 to 0.3 M in THF and the transition state being affected by $2[Li^+(THF)_xClO_4^-]$ aggregates as the $LiClO_4$ concentration increases from 0.3 to 1.50 M. In similar fashion, DMF gives a maximum molecular ratio of about 2.0, so we might expect at least an aggregate of $Li^+(DMF)_2ClO_4^-$.[17] Thus, with the increase of $LiClO_4$ concentration as the order changes from 0 to 1, then to 2 and then to 3, we might expect the transition state to be stabilized with $N[Li^+(DMF)_2ClO_4^-]$ where N may be 0, 1, 2, or 3. Likewise, with PO we calculate the maximum molecular ratio to be about 2.0[17] and expect at least an aggregate of $Li^+(PO)_2ClO_4^-$, and since the order changes from 0 all the way to 3, we might expect the transition state to be stabilized with $N[Li^+(PO)_2ClO_4^-]$, where $N = 0, 1, 2,$ or 3. In the last case, that of DC, we calculate the maximum molecular ratio to be about 1.7,[17] suggesting a mixture of $Li^+(DC)_xClO_4^-$ aggregates, where $x = 1$ or 2, with those having two molecules of DC predominating. Since the order change observed is 0 to 4, we might expect the transition state to be stabilized with $N[Li^+(DC)_xClO_4^-]$, where $N = 0, 1, 2, 3,$ or 4 and $x = 1$ or 2. This discussion then leads us to the possibility of writing the overall equation for the rearrangement of 1-phenylallyl chloride to cinnamyl chloride in $LiClO_4$ solutions of these various organic solvents as:

$$\begin{aligned} &\mathrm{Ph{-}CHCl{-}CH{=}CH_2} + N[\mathrm{Li^+(solvent)_xClO_4^-}] \\ &\rightleftharpoons [(\mathrm{Ph{-}CH{\dots}CH{\dots}CH_2})^+\mathrm{ClO_4^-}, \\ &\quad (N-1)[\mathrm{Li^+(solvent)_xClO_4^-}], \\ &\quad \mathrm{Li^+(solvent)_xCl^-}] \rightleftharpoons \mathrm{Ph{-}CH{=}CH{-}CH_2Cl} \\ &\qquad + N[\mathrm{Li^+(solvent)_xClO_4^-}] \qquad (5) \end{aligned}$$

where $N = 0, 1, 2, 3,$ or 4; solvent = DE, THF, DMF, PO, or DC; and $x = 0$ to 2.

This group of observations taken as a whole point out the surprising utility of lithium perchlorate solutions in various organic solvents as electrostatic catalysts and their many features which differ from those previously observed in the more familiar hydroxylic media.

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(41) The repeated finding that $\Delta\Delta H^{\ddagger} = 0$ for these powerful salt effects is fascinating and important. We wish to postpone a more detailed analysis of these data until our physico-chemical studies of these unusual electrolytic solutions are more complete. One line of reasoning would be that the negative enthalpy term for electrostatic stabilization is apparently offset by a positive enthalpy term for the release of ether molecules, but no such compensatory effect occurs with the respective terms in the entropy of activation. Clearly, the overall entropic effect is more complex and results in $\Delta\Delta S^{\ddagger}$ becoming more positive as the concentration of salt increases. It has not escaped our attention that, in some sense, this change in $\Delta\Delta S^{\ddagger}$ represents a partial "utilization" of electrostatic energy to drive the isomerization of **1** to **2**.

Electrostatic Catalysis by Ionic Aggregates. 5.[1] Aminolysis Reaction of *p*-Nitrophenyl Acetate with Imidazole and the Proton Transfer from *p*-Nitrophenol in Lithium Perchlorate–Diethyl Ether Solutions[2]

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Abstract: The equilibrium constant associated with the proton transfer from *p*-nitrophenol to imidazole in diethyl ether solutions is shown to be highly sensitive to the amount of added $LiClO_4$. For example, in pure ether $K_{\mathrm{eq}_{\mathrm{PNP}}}{}^0 = 1.87 \times 10^{-7}$, while in the presence of 4.58 M $LiClO_4$, it rises to a value of $K_{\mathrm{eq}_{\mathrm{PNP}}} = 1.21 \times 10^{-1}$, an apparent increase of 647 000-fold. The experimental results indicate that we are dealing with a dissociation into *p*-nitrophenolate and imidazolium ions rather than with an ionization into ion pairs. While the *p*-nitrophenolate and imidazolium ions act as if they are separated from one another, each probably exists as an ionic aggregate with $LiClO_4$ and solvent, consistent with the fact that K_{eq} shows a third-order dependence on the concentration of lithium perchlorate. The aminolysis reaction of *p*-nitrophenyl acetate by imidazole in lithium perchlorate–diethyl ether solution exhibits good second-order kinetics; in pure ether, $k_2 = 7.13 \times 10^{-7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and in solutions containing 4.96 M salt, $k_2 = 4.14 \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, an increase of 58 000-fold. Temperature dependence studies reveal that the energy of activation remains essentially constant throughout the increase in $LiClO_4$ concentration, while the entropy of activation increases steadily. A possible choice of mechanisms for the aminolysis reaction is discussed in terms of the available experimental evidence. Catalysis by ionic aggregates of $LiClO_4$ in diethyl ether is clearly documented and possible transition states are presented.

Introduction

In Part 4,[1] we showed that when anhydrous lithium perchlorate is dissolved in solvents of low ionizing capacity such as diethyl ether, tetrahydrofuran, propylene oxide, and diethyl carbonate, the resulting solutions exhibit a powerful catalysis with respect to the rearrangement of 1-phenylallyl chloride to cinnamyl chloride and that this catalysis appears to be essentially electrostatic in nature. In the case of dimethylformamide, a solvent of much higher dielectric constant and greater ionizing capacity, the catalysis was not so marked, but was exhibited nonetheless. A study of the activation parameters in each of these various lithium perchlorate–solvent systems revealed that the progressive decreases in the free energy of re-