concentration occurring for almost complete removal of the DMF. If k_{DMF}* is not in error then the value of $k_{DMF}/k_{TME} > 10$ may be the result of the adduct from TME and $O_2(^1\Delta_g)$ transferring oxygen to DMF, to give the ozonide, **4**, and regenerating TME. If this is the case, it will greatly complicate the determination of competitive rate constants in the gas phase. Such a study is now underway.

In conclusion we should note that the determination of the absolute rate constant for the reaction between TME and $O_2(^1\Delta_g)$ is particularly relevant to processes dealing with air pollution. TME is widely employed as a "typical" highly reactive internally double bonded olefin in smog chamber studies. For example, it was employed recently by Bufalini and Altshuller in their studies of the photooxidation of nitric oxide–olefin mixtures.[30] Our value of the rate constant for the reaction of $O_2(^1\Delta_g)$ with TME to form the allylic hydroperoxide can be compared to the rate of the reaction between ozone and TME, determined by Vrbaski and Cvetanovic,[31] 1.0×10^5 l. mole^{-1} sec^{-1} *vs.* 1.8×10^4 l. mole^{-1} sec^{-1}.[32]

Acknowledgment. The authors wish to acknowledge helpful discussions with Drs. C. S. Foote, P. R. Story, and R. P. Wayne. One of us, W. S. G., acknowledges an Air Pollution Special Postdoctoral Fellowship from the Consumer Protection and Environmental Health Service, National Air Pollution Control Administration. This research was supported by Grants AP 00109 and AP 00771 from the Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U. S. Public Health Service.

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Electrostatic Catalysis by Ionic Aggregates. I. The Ionization and Dissociation of Trityl Chloride and Hydrogen Chloride in Lithium Perchlorate–Diethyl Ether Solutions[1]

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Abstract: Lithium perchlorate is shown to form with diethyl ether two crystalline etherates, a monoetherate, $LiClO_4 \cdot Et_2O$, and a dietherate, $LiClO_4 \cdot 2Et_2O$. The nmr spectra of $LiClO_4$-Et_2O solutions show a rapidly exchanging ether solvation sphere around the lithium ion down to −100°. The shift downfield of the methylene and methyl protons of diethyl ether in lithium perchlorate–diethyl ether mixtures (hereafter LPDE) relative to pure ether can be accounted for by an average ether to lithium perchlorate ratio of 2:1 below 4.25 *M* and both 2:1 and 1:1 ratio above 4.25 *M* $LiClO_4$. The molar dielectric increment, $\Delta D/\Delta C$, as determined in dilute LPDE solutions is 1.2. The ionization of triphenylmethyl chloride (hereafter TCl) was used as a sensitive probe in the study of LPDE solutions with respect to their capacity to assist ionization and sustain dissociation. Rates of exchange were monitored between TCl and $^{36}Cl^-$ under a variety of conditions and a complete kinetic analysis was carried out in terms of triphenylmethyl chloride ionization and ion recombination. The dissociation constant of TCl increases 7×10^9-fold on going from pure ether to a 5.05 *M* $LiClO_4$ solution. The tremendous catalytic effect of LPDE solutions was also documented with respect to HCl solutions in ether.

Increased interest in reactions carried out in fused salts[4-6] and the general lack of data on concentrated salt solutions in media of low dielectric prompted us to study the behavior of lithium perchlorate in diethyl ether. Lithium perchlorate is very soluble in ether and at 30° solutions containing up to 6 *M* salt can be obtained.[7,8] In the latter concentration region there are, on the average, 1.2 ether molecules available to solvate each lithium perchlorate. Such highly concentrated salt solutions in solvents of low dielectric have been considered by Kraus[9] to be like fused salts with small amounts of solvent added. Our studies start with dilute

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solutions and end with those approaching a fused monoetherate salt. Lithium perchlorate–diethyl ether solutions, hereafter LPDE, have been shown to promote the ionization reaction of *p*-methoxyneophyl *p*-toluenesulfonate. Winstein and coworkers[10] found that the rate of ionization is increased by a factor of 10^5 on going from pure ether to a 0.1 *M* lithium perchlorate solution in ether. Earlier, Sillén and coworkers[11–13] had employed LPDE to keep the ionic strength constant in electrochemical studies of silver halide complexes.

The present investigation was initiated to get a better understanding of the factors which promote ionization and sustain dissociation. Trityl chloride was selected as a sensitive probe of the ionic environment in studying these lithium perchlorate–diethyl ether mixtures.[14–16] When facing the problem of interpreting the ionization of trityl chloride and of hydrogen chloride in LPDE, it was important to determine first the nature of the cationic and anionic species present. Earlier investigations of the conductivity[8,17,18] of LPDE showed that the molar conductivity increased by a factor of several hundred with increasing salt concentration, in spite of the fact that the viscosity also increased by several powers of ten. The suggestion was made[8,17,18] that the main mechanism of conductance must be the transport of single ions within these complex aggregates rather than the movement of the whole complexes. Certain similarities were noted between the above suggestion and the theory of proton conductance in water as proposed by Bernal and Fowler.[19] Ekelin and Sillén have additionally noted that the vapor pressure data could not be explained in terms of lithium perchlorate aggregates and that these solutions must consist of clusters of $LiClO_4$–Et_2O complexes. In our investigations of LPDE solutions we have determined, *inter alia*, solubility–temperature curves, heats of solution, nuclear magnetic resonance spectra, and the molar dielectric increment.

Experimental Section

Lithium Perchlorate. Reagent grade anhydrous $LiClO_4$ (G. Frederick Smith Chemical Co.) was found unsuitable for our use. Consequently it was recrystallized twice from distilled water in the form $LiClO_4 \cdot 3H_2O$ and finally dried at 160° (0.5 mm) for at least 8 hr. $LiClO_4$ was also prepared from LiOH and $HClO_4$, purified, and dried as above. Care was taken to obtain completely anhydrous $LiClO_4$ since the hydrate is not appreciable soluble in ether (0.139 g/100 cc of solution at 25°).[7]

Diethyl Ether. Reagent grade anhydrous diethyl ether (Baker and Adamson) was distilled over $LiAlH_4$ (Metal Hydrides Inc.) just prior to use.

Solubility. Copper constantan thermocouples were used with one end in ice water and the other end in the $LiClO_4$–Et_2O solution. The millivolts were recorded on a Honeywell Electronic 19 recorder and were converted to temperature with the use of standard tables.[20] The sample cell was made of two concentric tubes with the sample in the inner tube and an outer tube which was placed in the cooling solution. The inner tube was sealed with a rubber stopper through which were placed the thermocouple and the stirrer. Ice water, Dry Ice–acetone, and liquid nitrogen were used as coolants. All the solutions were cooled slowly and stirred vigorously to prevent supersaturation. The temperature was taken from the graph at the point where there was a break in the cooling curve, a leveling out, showing that crystallization was taking place.

Etherate Composition. $LiClO_4$ solutions in ether were cooled slowly with vigorous stirring until no more crystals appeared. The solution was filtered through a cooled funnel, and the total weight of the $LiClO_4$–ethereate was determined. The ratio of Et_2O–$LiClO_4$ was determined after driving off the ether at 80°. In some cases the ratios were up to 5% too high since ether is easily occluded during crystallization from these viscous media. One sample kept at 40° for 2 days with a trap, allowing only the exit of ether, analyzed as anhydrous $LiClO_4$.

Nmr Study. $LiClO_4$ solutions in ether were run on a Varian Associates A-60 at the temperature of the instrument (~37°). The methylene and methyl peaks of LPDE solutions were shifted downfield from those of pure ether. Each peak of the methyl triplet and the methylene quadruplet showed the same shift even in the most concentrated solution. The temperature study was run on an HR-60.

Heat of Solution. The calorimeter has a dewar equipped with a Beckman thermometer and a magnetic stirrer. The heat capacity was found to be 43.4 cal/deg using the standard heats of solution of NH_4Cl and KI in water. The heat capacity of calorimeter with 400 ml of ether was 197 cal/deg. Samples of 2.051 and 0.992 g of $LiClO_4$ were dissolved in 400 ml of ether and changes in temperature of 0.487 and 0.235°, respectively, were recorded.

Dielectric Constant. A WTW dipolemeter, using a fixed frequency of 2 MHz, was equipped with a DFL-2 cell and maintained at 25.0 ± 0.1°. A standard linear relationship was obtained by plotting meter readings against the dielectric constants of known solvents. All solvents, except ether, were dried ($MgClO_4$) and fractionally distilled for the best results. The dielectric constant was measured in solutions containing up to 0.5 *M* $LiClO_4$. These measurements were limited by the range of the instrument and by the increasing conductivity of the above solutions.

Lithium Chloride. Reagent grade LiCl (Baker and Adamson) was purified by the same method as $LiClO_4$. To enhance the rate of solution of LiCl in LPDE, anhydrous LiCl was dissolved in dried purified acetone, precipitated with dry ether as a voluminous fluffy precipitate, filtered, and dried as above.

Triphenylmethyl Chloride. Reagent grade triphenylmethylcarbinol (Eastman Organic Chemicals) was recrystallized from Baker and Adamson reagent grade CCl_4 (4 cc/g) until the recrystallizing solution was colorless and the crystals were white. The carbinol was then converted to the chloride and purified by the standard method.[21] The melting point[22] and ir[23] were in close agreement with those reported.

Equilibrium Constant for Trityl Chloride. All spectral measurements were made on a Beckman DU-2 equipped with a constant-temperature bath set at 25.0 ± 0.05° controlled with a Sargent Thermonitor. In some cases where the rate of hydride abstraction was appreciable, a Honeywell Electronic 19 recorder was used to monitor the transmittance.

Stock solutions of TCl and $LiClO_4$ in ether, with and without LiCl or HCl, were mixed at 25.0° and the absorbance of the trityl ion was monitored at 406 or 430 mμ. Solution aliquots, 5 ml, were put into 20 ml of cold neutral, dry acetone (−80°) and titrated with Et_3N in dry toluene to a Lacmoid end point. Under these conditions TCl is inert and one titrates only free HCl. The TCl was in turn determined by converting it into HCl with warm ethanol and titrating. Absorbance divided by 3.6×10^4 gave the concentration of trityl ions.[24] $K_{\mathrm{eq}_{\mathrm{TCl}}}$ was obtained from the ratio $[T^+] \times [Cl^-]/[TCl]$ for several $LiClO_4$ concentrations at 10, 15, 20, and 25°. Plots of log $K_{\mathrm{eq}_{\mathrm{TCl}}}$ against $1/T$ were used in the determination of the corresponding thermodynamic parameters.

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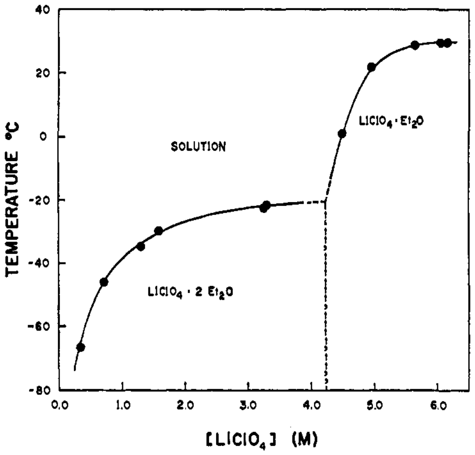

Figure 1. Solubility-temperature curves of lithium perchlorate in diethyl ether presented as a phase diagram showing the regions of lithium perchlorate dietherate and monoetherate stability.

Lithium Radiochloride. Reagent grade LiOH (Fisher Scientific Co.) was titrated to slight excess with [^{36}Cl]hydrochloric acid obtained from Oak Ridge National Laboratories as a 4.0 *M* solution and diluted with hydrochloric acid of normal isotopic abundance. The solution was evaporated to dryness and purified by the method described above for LiCl.

Radiochloride Exchange. Stock solutions of TCl in ether and $H^{36}Cl$ or $Li^{36}Cl$ in LPDE solution were stored at 25°. Aliquots of each were quickly mixed and then quenched in cold dry pentane (−80°) containing Et_3N to precipitate the saline material ($Et_3NHCl + LiCl$). The coagulated precipitate was filtered off using no. 4 porosity sintered glass filter and the pentane solution containing TCl was counted in a Geiger-Müller liquid sample tube of about 12-ml capacity, an Ekco Electronics Ltd. N529 scaler being used. All counts were corrected for background and specific activity of TCl.

The values of log $\{1 - (x/c)[(a + b)/a]\}^{-1}$ were plotted against time where x is the counts at time t, c is the total counts, a is [TCl], and b is total [Cl$^-$]. The slope of the line is then multiplied by $-2.3b/(a + b)$ to give the exchange rate constant, k_{ex}. The various values of k_{ex} for any particular [LiClO$_4$] were plotted against total [Cl$^-$]. The intercept was then taken as k_1, the forward ionization rate constant.

The Equilibrium Constant for Hydrogen Chloride. The equilibrium constant, $K_{eq_{TCl}}$, was determined as described above using excess LiCl to ensure that the contribution of HCl to the total [Cl$^-$] was negligible. We were able to do this for solutions where [LiClO$_4$] $\geqslant$ 0.4 *M*. Values of [T$^+$]/[TCl] were experimentally determined for a series of HCl concentrations. These values were then used to obtain the concentration of chloride ions $[Cl^-] = K_{eq_{TCl}} \times [TCl]/[T^+]$. [H$^+$] was derived from the relationship $[T^+] + [H^+] = [Cl^-]$ and was used to evaluate the concentration of undissociated HCl from the total concentration of acid present. $K_{eq_{HCl}}$ was then calculated from the expression, $K_{eq_{HCl}} = [H^+][Cl^-]/[HCl]$.

Anhydrous HClO$_4$ in Ether. AgClO$_4$ which had been dried for 24 hr at 160° (0.05 mm) was titrated using a slight excess of HCl in ether. The AgCl precipitate was filtered, the total amount of acid in solution was determined by titration, and the trace amounts of HCl present in solution were independently analyzed by a potentiometric titration with silver nitrate.

Dependence of [T$^+$][HCl]/[TCl] on [HClO$_4$]. Stock solutions of TCl and HClO$_4$-HCl in ether were mixed at 25.0°. Absorbance measurements were carried out at 406 or 430 mμ to determine [T$^+$]. Aliquots were titrated for total acid in cold acetone (−80°) to a Lacmoid end point with Et_3N in toluene, while the amount of TCl was determined by converting it to HCl with warm methanol. A similar procedure was used for determining the dependence of [T$^+$][HCl]/[TCl][HClO$_4$] on [LiClO$_4$].

Results

Solubility of Lithium Perchlorate in Diethyl Ether. The only previous solubility data reported were those of Willard and Smith,[7] who showed that at 25° ether dissolves a maximum of 53.2% by weight of lithium perchlorate, an amount corresponding to a mole fraction of 0.44 or a concentration of 6.06 *M*. In the present work, the solubility of lithium perchlorate in ether was determined as a function of temperature and the results are given in the form of a phase diagram in Figure 1. On cooling LPDE solutions containing up to 4.2 *M* salt, the crystals obtained analyzed as $LiClO_4 \cdot 2Et_2O$ and were stable below −20° in a dry atmosphere. On cooling more concentrated LPDE solutions, the crystals obtained analyzed as $LiClO_4 \cdot Et_2O$, and were stable at room temperature in a dry atmosphere. We found no evidence for either higher or lower etherates.

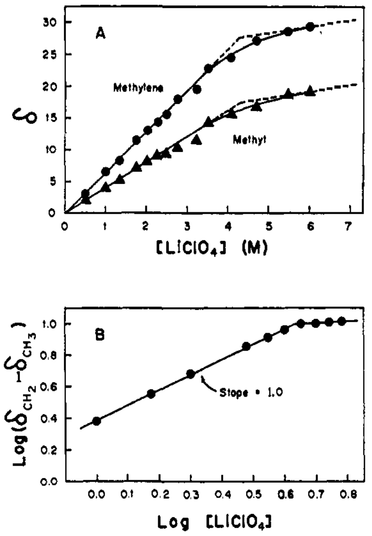

Figure 2. (A) Chemical shift, δ, for the methylene (●) and methyl (▲) protons of diethyl ether *vs.* the molar concentration of lithium perchlorate. The dotted lines represent calculated chemical shifts for the pure dietherate and monoetherate-dietherate mixture calculated by eq 2. (B) Plot of the log ($\delta_{CH_2} - \delta_{CH_3}$) *vs.* the log [LiClO$_4$] (*M*) showing first-order dependence for concentrations up to [LiClO$_4$] = 4.25 *M*.

Heat of Solution. Dissolving lithium perchlorate in ether liberates heat. Our measurements show that the integral heat of solution, ΔH_s, is −4.98 kcal/mole for 1/200 (0.046 *M*) and a 1/400 (0.023 *M*) mole ratio at 25°. An enthalpy of etheration, ΔH_{eth} = −167.2 kcal/mole, was calculated from the lattice energy,[25] U = −162.2 kcal/mole, and the heat of solution, ΔH_s, $\Delta H_{eth} = \Delta H_s + U$.

It is interesting to compare our values for the heats of solution and etheration in ether with those in water where ΔH_s is −6.24 kcal/mole and ΔH_{H_2O} is −168.5 kcal/mole.[26]

The van't Hoff equation (1) was applied to the solubility data given in Figure 1. For the region below −20°, the heat of solution of the dietherate was calculated to be −2.5 kcal/mole, whereas above −20°, in the

$$\log \frac{s_2}{s_1} = \frac{-\Delta H}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

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(25) The lattice energy, U, was calculated from the heats of formation $U = \Delta H^f_{cation} + \Delta H^f_{anion} - \Delta H^f_{salt}$. The data were obtained from (a) A. F. Kapustinskii and K. B. Yatsimirskii, *Zh. Obshch. Khim.*, **19**, 2191 (1949); (b) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950; (c) JANAF Thermodynamic Data.

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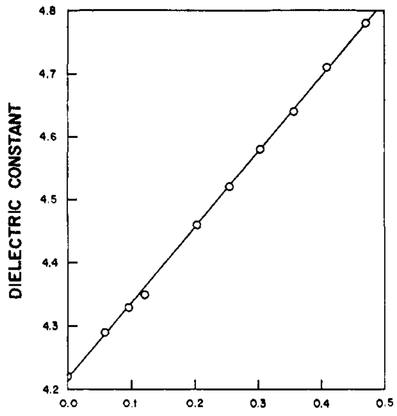

Figure 3. Plot of the dielectric constant of LPDE solutions *vs.* the molar concentration of lithium perchlorate at 25°.

region of the monoetherate, the heat of solution was calculated to be −1.2 kcal/mole. This 1:2 ratio is consistent with the formation of the mono- and dietherate.

Nuclear Magnetic Resonance Study. Preliminary nmr studies have shown that on adding lithium perchlorate to ether both the methylene and the methyl proton peaks are shifted downfield. This deshielding of the proton environment is due to the association of the lithium ion with the oxygen of the ether.[27] All solutions studied show a time-averaged set of peaks. In Figure 2A, the observed proton shifts, δ (cycles per second), relative to pure ether are plotted against the lithium perchlorate concentration. The methylene peaks are shifted more than the methyl due to their closer proximity to the oxygen. The plot of log ($\delta_{CH_2} - \delta_{CH_3}$) against the log of lithium perchlorate concentration in Figure 2B shows the first-order dependence on lithium perchlorate up to 4.25 *M*. The dependence on lithium perchlorate concentration above 4.25 *M* is close to zero and indicates that the maximum effect of the lithium ion on the ether solvent has occurred at 4.25 *M*. At this concentration only two ethers are available to solvate each lithium perchlorate.

Assuming all the lithium perchlorate below 4.25 *M* is present as the dietherate (solubility study), the chemical shift for the methylene protons, δ_{CH_2}, is the sum of the weighted shifts of the dietherate, δ-dietherate, and pure ether, δ-ether, as expressed by $\delta_{CH_2} = P_1(\delta_{dietherate}) + P_2(\delta_{ether})$. The mole fraction of the dietherate is P_1 and the mole fraction of ether is P_2. Since δ_{obsd} was measured from pure ether, then δ-ether can be set equal to zero. The observed chemical shift is then $\delta_{obsd} = P_1\delta_{dietherate}$, where the mole fraction, P_1, of the dietherate is $2[LiClO_4]/[Et_2O]$.

From Figure 2A, $\delta_{dietherate}$ was determined to be 27.6 cps. The mole fraction, P_1, calculated from these nmr data, $\delta_{obsd}/\delta_{dietherate}$, is approximately equal to the mole fraction, x_1, calculated from the mole fraction data of Sillén[8] and Chu.[17] The values are given in Table I.

Table I. Comparison of the Mole Fraction Calculated and the Mole Fraction Data of Sillén[a] and Chu[b]

$[LiClO_4]$, *M*	P_1[c]	x_1	δ_{obsd},[d] cps
0.5	0.11	0.10	3.0
1.0	0.23	0.22	6.3
1.5	0.34	0.33	9.4
2.0	0.46	0.44	12.7
2.5	0.57	0.56	15.7
3.0	0.69	0.68	18.9
3.5	0.80	0.80	22.1
4.0	0.89	0.93	24.6

[a] See ref 8. [b] See ref 17. [c] Calculated from $\delta_{obsd}/\delta_{dietherate} = \delta_{obsd}/27.6$. [d] Values taken from Figure 2a.

The slight decrease in δ_{obsd} from the straight line relationship above 3.5 *M* lithium perchlorate is apparently due to the breakdown of the dietherate and the formation of some monoetherate complexes and perhaps some lithium perchlorate complexes. For solutions above 4.25 *M* lithium perchlorate, the amount of monoetherate starts to become predominant. The maximum shift for the monoetherate, $\delta_{monoetherate}$, is found to be about 30.4 cps. The data extrapolated to 7.15 *M* lithium perchlorate at which concentration the ratio of ether to lithium perchlorate is one to one. For solutions above 4.25 *M*, δ_{obsd} is governed by eq 2, and the relative con-

$$\delta_{obsd} = \frac{2[LiClO_4] - [Et_2O]}{[Et_2O]}(30.4) + \frac{2([Et_2O] - [LiClO_4])}{[Et_2O]}(27.6) \qquad (2)$$

tributions of the mono- and dietherates to the total shift are listed in Table II.

Table II. The Relative Contributions to the Total Chemical Shift by the Mono- and Dietherates[a]

$[LiClO_4]$, *M*	δ_{mono}	δ_{di}	δ_{total}	$\delta_{total\ obsd}$
4.5	2.5	25.3	27.8	26.4
5.0	6.8	21.4	28.2	27.8
5.5	12.7	16.0	28.7	28.8
6.0	17.4	11.8	29.2	29.3

[a] Calculated values using eq 2.

Cooling a 0.135 *M* lithium perchlorate solution down to −100° showed no separation of peaks nor appearance of any peaks except those of the methyl and methylene protons. The one-half peak heights became broadened by only 1 cps compared to the room-temperature peaks, a phenomenon generally ascribed to the increased viscosity of the medium. The exchange rate of the ether in the solvation shell must be greater than 10^4 sec^{-1} even at the low temperature. Meiboom and coworkers[28] have found that lithium perchlorate in absolute methanol showed no separation of peaks even down to −110°, an observation which they similarly attributed to a very fast exchange.

Dielectric Constant of LPDE. The dielectric constants of LPDE solutions containing up to 0.5 *M* lithium perchlorate are plotted in Figure 3. Using the observed linear relationship given in eq 3, the dielectric constant of the substance D_{comp} was calculated as 16.

$$D_{obsd} = D_{ether} + X_2(D_{comp} - D_{ether}) \qquad (3)$$

D_{comp} can be attributed either to lithium perchlorate or to a lithium perchlorate–ether complex, both of which should cause an increase in the dielectric constant,

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Table III. The Equilibrium Constant for Trityl Chloride in LPDE at 25°

[LiClO$_4$], *M*	[T$^+$]/[TCl]	[T$^+$], *M*	[HCl], *M*[a]	[LiCl], *M*[b]	[Cl], *M*[c]	$K_{\mathrm{eq}_{\mathrm{TCl}}}$, *M*
0.0116	1.3×10^{-7}	5.5×10^{-8}	4.22×10^{-2}		1.8×10^{-4}	2.3×10^{-11}
0.0232	3.69×10^{-7}	1.30×10^{-7}	2.90×10^{-2}		2.0×10^{-4}	7.4×10^{-11}
0.0580	1.31×10^{-6}	3.75×10^{-7}	2.00×10^{-2}		3.3×10^{-4}	3.5×10^{-10}
0.116	4.64×10^{-6}	7.78×10^{-7}	1.54×10^{-2}		3.7×10^{-4}	1.5×10^{-9}
0.166	9.14×10^{-6}	1.29×10^{-6}	1.35×10^{-2}		2.7×10^{-3}	3.4×10^{-9}
0.205	1.80×10^{-5}	5.55×10^{-7}	7.33×10^{-3}		4.0×10^{-4}	5.6×10^{-9}
0.266	3.17×10^{-5}	1.37×10^{-6}	9.14×10^{-3}		3.1×10^{-4}	1.3×10^{-8}
0.336	8.94×10^{-5}	2.00×10^{-6}	4.95×10^{-4}		1.80×10^{-4}	1.61×10^{-8}
0.438	1.53×10^{-5}	6.67×10^{-7}	3.86×10^{-3}	2.00×10^{-3}	2.30×10^{-3}	3.58×10^{-8}
0.476	2.52×10^{-4}	2.33×10^{-6}	4.29×10^{-4}		1.33×10^{-4}	3.36×10^{-8}
0.478	1.22×10^{-5}	7.22×10^{-7}	8.25×10^{-4}	3.06×10^{-3}	3.30×10^{-3}	4.03×10^{-8}
0.478	1.19×10^{-5}	1.69×10^{-6}	1.19×10^{-3}	3.06×10^{-3}	3.34×10^{-3}	3.97×10^{-8}
0.625	5.20×10^{-4}	4.81×10^{-6}	4.29×10^{-4}		1.48×10^{-4}	7.70×10^{-8}
0.828	1.48×10^{-3}	1.37×10^{-5}	4.29×10^{-4}		2.00×10^{-4}	2.96×10^{-7}
0.872	7.59×10^{-5}	3.03×10^{-6}	4.44×10^{-4}	3.92×10^{-3}	4.12×10^{-3}	3.13×10^{-7}
0.872	1.23×10^{-4}	4.92×10^{-6}	4.92×10^{-4}	2.35×10^{-3}	2.57×10^{-3}	3.06×10^{-7}
0.872	3.02×10^{-4}	1.22×10^{-5}	5.56×10^{-4}	7.83×10^{-4}	1.02×10^{-3}	3.08×10^{-7}
1.08	3.79×10^{-5}	1.44×10^{-6}	4.92×10^{-4}	1.89×10^{-2}	1.91×10^{-2}	7.24×10^{-7}
1.33	5.25×10^{-3}	1.48×10^{-5}	4.29×10^{-4}		2.69×10^{-4}	1.42×10^{-6}
1.35	1.09×10^{-2}	2.76×10^{-5}	2.69×10^{-4}		1.88×10^{-4}	1.98×10^{-6}
1.35	1.00×10^{-2}	2.72×10^{-5}	2.69×10^{-4}		1.88×10^{-4}	1.89×10^{-6}
1.54	1.51×10^{-4}	5.86×10^{-6}	4.71×10^{-4}	2.27×10^{-2}	2.30×10^{-2}	3.47×10^{-6}
1.54	1.95×10^{-4}	2.33×10^{-6}	4.45×10^{-4}	1.98×10^{-2}	2.02×10^{-2}	3.94×10^{-6}
1.54	6.93×10^{-4}	8.28×10^{-6}	4.29×10^{-4}	4.95×10^{-3}	5.38×10^{-3}	3.73×10^{-6}
1.54	3.20×10^{-4}	3.83×10^{-6}	4.29×10^{-4}	1.19×10^{-2}	1.23×10^{-2}	3.94×10^{-6}
1.80	2.61×10^{-4}	1.04×10^{-5}	5.82×10^{-4}	2.72×10^{-2}	2.75×10^{-2}	7.22×10^{-6}
1.80	2.60×10^{-2}	6.81×10^{-5}	3.36×10^{-4}		2.74×10^{-4}	7.12×10^{-6}
1.83	3.12×10^{-4}	7.12×10^{-6}	1.21×10^{-3}	2.41×10^{-2}	2.53×10^{-2}	7.90×10^{-6}
1.83	1.43×10^{-3}	3.37×10^{-5}	6.76×10^{-4}	4.82×10^{-3}	5.50×10^{-3}	7.86×10^{-6}
1.83	7.91×10^{-4}	1.85×10^{-5}	8.42×10^{-4}	9.65×10^{-3}	1.05×10^{-2}	8.30×10^{-6}
1.83	2.54×10^{-3}	5.97×10^{-5}	7.25×10^{-3}	2.41×10^{-3}	3.14×10^{-3}	7.97×10^{-6}
2.40	3.08×10^{-1}	1.51×10^{-5}	8.64×10^{-5}		8.64×10^{-5}	2.66×10^{-5}
2.41	7.51×10^{-4}	1.72×10^{-5}	3.67×10^{-4}	4.12×10^{-2}	4.15×10^{-2}	3.12×10^{-5}
2.94	3.13×10^{-3}	1.15×10^{-5}	4.83×10^{-4}	3.13×10^{-2}	3.36×10^{-2}	1.05×10^{-4}
2.94	1.87	2.28×10^{-5}	5.78×10^{-5}		5.78×10^{-5}	1.07×10^{-4}
3.56	8.85×10^{-3}	2.55×10^{-5}	*d*	3.40×10^{-2}	3.40×10^{-2}	3.02×10^{-4}
3.58	1.08×10^{-2}	2.00×10^{-5}	4.43×10^{-4}	3.27×10^{-2}	3.31×10^{-2}	3.58×10^{-4}
3.72	1.32×10^{-5}	1.20×10^{-5}	1.12×10^{-4}	2.98×10^{-2}	2.99×10^{-2}	3.95×10^{-4}
3.72	1.31×10^{-5}	1.82×10^{-5}	1.35×10^{-4}	2.98×10^{-2}	2.99×10^{-2}	3.92×10^{-4}
3.96	1.72×10^{-2}	1.81×10^{-5}	4.50×10^{-5}	4.15×10^{-2}	4.15×10^{-2}	7.14×10^{-4}
3.96	1.71×10^{-2}	2.20×10^{-5}	8.79×10^{-5}	4.15×10^{-2}	4.15×10^{-2}	7.10×10^{-4}
3.96	1.68×10^{-2}	9.35×10^{-6}	6.54×10^{-4}	4.15×10^{-2}	4.22×10^{-2}	7.10×10^{-4}
4.48	1.52×10^{-1}	1.75×10^{-5}	6.00×10^{-5}	1.98×10^{-2}	1.98×10^{-2}	3.01×10^{-3}
4.48	1.52×10^{-1}	2.56×10^{-5}	3.21×10^{-5}	1.98×10^{-2}	1.98×10^{-2}	3.01×10^{-3}
4.96	9.71×10^{-2}	7.14×10^{-6}	9.55×10^{-2}		9.00×10^{-2}	8.75×10^{-3}
5.05	2.44×10^{-1}	9.44×10^{-6}	*d*	4.36×10^{-2}	4.36×10^{-2}	1.07×10^{-2}
5.05	7.28×10^{-1}	4.73×10^{-5}	2.09×10^{-4}	2.35×10^{-2}	2.37×10^{-2}	1.73×10^{-2}

[a] Total titrated hydrogen chloride in equilibrium mixture. [b] Blank spaces indicate that no LiCl was added. [c] [Cl$^-$] is the sum of [LiCl] (*M*) plus [Cl$^-$] from ionization of HCl. [d] No detectable concentration of HCl.

D_{obsd}, with increasing the mole fraction, X_2, of the lithium perchlorate.

The Equilibrium Constant for Trityl Chloride. When TCl is dissolved in dry ether, no T$^+$ can be detected. When lithium perchlorate is added, the characteristic yellow color of T$^+$ is observed as a pair of equal intensity peaks at 406 and 430 mμ. As more lithium perchlorate is added, the color becomes progressively more intense. When the concentrations of lithium perchlorate and total TCl are kept constant, the ratio of the amount of color formed to the amount of colorless material is inversely proportional to added lithium chloride (eq 4). This dependence is exemplified in

$$\frac{[\mathrm{color}]}{[\mathrm{colorless}]} = \frac{[\mathrm{T^+}]}{[\mathrm{TCl}]} = \frac{K}{[\mathrm{Cl^-}]} \tag{4}$$

Figure 4. The addition of chloride ions in sufficient amount suppresses *entirely* the color associated with these solutions, indicating that in the presence of lithium perchlorate, ionized TCl behaves like free T$^+$ but is actually present as $\mathrm{T^+ClO_4^-(Li^+ClO_4^-)_x}$. Our observations appear to rule out the existence of detectable concentrations of T$^+$Cl$^-$ ion pairs as found in other solvents.[15] At any lithium perchlorate concentration and with the chloride ion concentration held constant, the amount of trityl ion is directly proportional to the trityl chloride concentration. These and related examples can be found in Table III.

At any lithium perchlorate concentration then, an apparent equilibrium constant, K_{eq}, can be deduced for the dissociation of trityl chloride (eq 5), and the values

$$\mathrm{TCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{T^+} + \mathrm{Cl^-}$$

$$K_{\mathrm{eq}_{\mathrm{TCl}}} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{T^+}][\mathrm{Cl^-}]}{[\mathrm{TCl}]} \tag{5}$$

obtained with [LiClO$_4$] = 0.01 − 5.0 *M* are listed in Table III. Experimentally it was hard to determine the values of the equilibrium constant below 0.01 *M*

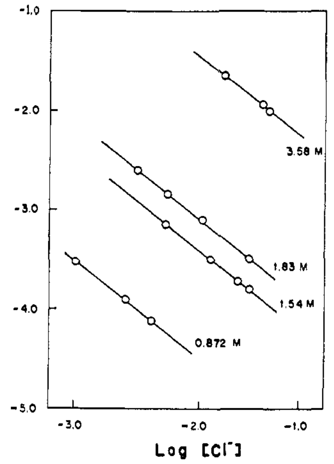

Figure 4. Plot of the log ([T+]/[TCl]) *vs.* the log of the molar chloride ion concentrations at 25° showing inverse first-order dependence of [T+]/[TCl] on [Cl-].

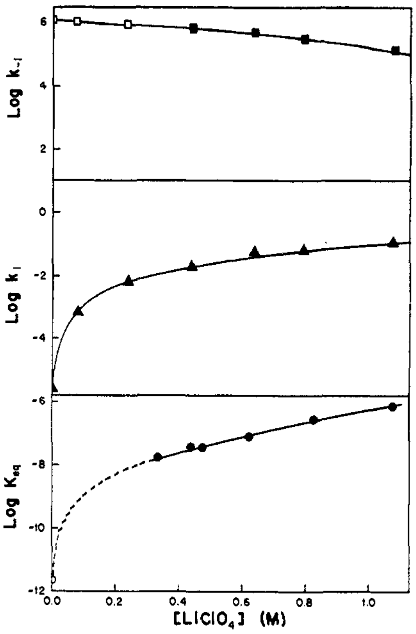

Figure 5. Plot of the rate constant for ion recombination, k_{-1}, *vs.* the molar lithium perchlorate concentration: calculated by dividing k_1 by K_{eq} for TCl (■), using the dotted portion of the K_{eq} curve (□). Plot of the ionization rate constant, k_1, *vs.* the molar lithium perchlorate concentration (▲). Plot of experimentally determined values of K_{eq} *vs.* the molar lithium perchlorate concentration (●). The dotted portion of the curve is a smooth curve drawn from the data used to obtain K_{eq} for TCl in Figure 6.

lithium perchlorate since the amount of trityl ion present was too small to be accurately determined spectrophotometrically. Also, when lithium chloride was used, the equilibrium constant could not be obtained below 0.4 *M* lithium perchlorate since lithium chloride is not very soluble in dilute LPDE solutions. At high salt concentration above 5 *M*, the equilibrium constant could not be accurately determined due to the high viscosity of these solutions coupled with the fast rate of hydride abstraction from ether by trityl ion. Once the equilibrium constant for the ionization of HCl in LPDE was determined, $K_{eq_{TCl}}$ (eq 5) could be independently determined using HCl instead of LiCl.

Ionization Rate Constant, k_1. In order to determine the ability of LPDE to promote ionization, the radiochloride exchange rates between TCl and $Li^{36}Cl$ or $H^{36}Cl$ were studied in detail. The exchange rate was found to be the sum of a first-order component, k_1(TCl), and a small second-order component, k_2[TCl][Cl-], eq 6. As the concentration of lithium perchlorate increases the former component became dominant and the latter negligibly small.

$$(\text{rate})_{ex} = k_{ex}[\text{TCl}] = k_1[\text{TCl}] + k_2[\text{TCl}][\text{Cl}^-] \quad (6)$$

The values of the ionization rate constant, k_1, were determined in the lithium perchlorate range 0–1.08 *M* (see Experimental Section) and are given in Table IV. Exchange rates in solutions containing [$LiClO_4$] > 1.08 *M* are too fast to be studied by the above method and require special instrumentation.

Table IV. The Ionization Rate Constant, k_1, and Ion Recombination Rate Constant, k_{-1}, for Various Lithium Perchlorate Concentrations at 25°

[$LiClO_4$], *M*	k_1, sec^{-1}	$10^{-6}k_{-1}$, M^{-1} sec^{-1}	$K_{eq_{TCl}}$, M[a]
0.000	2.5×10^{-6}	1.2[b]	2.1×10^{-12}[c]
0.076	7.0×10^{-4}	1.1	6.3×10^{-10}
0.237	6.0×10^{-3}	0.8	6.9×10^{-9}
0.438	1.9×10^{-2}	0.6	3.1×10^{-8}
0.445	1.9×10^{-2}	0.6	3.2×10^{-8}
0.636	5.6×10^{-2}	0.51	1.1×10^{-7}
0.793	7.2×10^{-2}	0.33	2.1×10^{-7}
1.08	1.1×10^{-1}	0.15	7.2×10^{-7}

[a] All values taken from smooth curve of $K_{eq_{TCl}}$ (Figure 5) unless otherwise noted. [b] Extrapolated value. [c] Calculated from k_1 and k_{-1}.

The Ionization of HCl. While studying the ionization and dissociation of trityl chloride, we also found it necessary to delineate the behavior of hydrogen chloride both in pure ether and in LPDE. A small amount of hydrogen chloride, generally around 10^{-4} *M*, is present in ether solutions containing trityl chloride. When lithium perchlorate is added, color is produced; however hydrogen chloride alone does not produce any color. Actually, when hydrogen chloride is dissolved in LPDE, small amounts of perchloric acid and lithium chloride are produced. Since we had previously determined the dependence of [T+]/[TCl] on lithium chloride,

Table V. The Second-Order Dependence of [T+][HCl]/[TCl] on Perchloric Acid[a]

10^2[$HClO_4$], *M*	[T+]/[TCl]	10^3[HCl], *M*	$\frac{10^4[T^+]}{[TCl]} \times \frac{[HCl]}{[HClO_4]^2}$, M^{-1}
0.855	5.5×10^{-6}	3.6	2.7
0.855	6.3×10^{-6}	4.0	3.4
2.02	2.1×10^{-5}	5.1	2.6
2.02	2.5×10^{-5}	5.1	3.1
2.48	6.9×10^{-6}	28	3.1
2.51	2.2×10^{-5}	28	2.9
2.51	6.4×10^{-5}	10	3.5
4.25	1.3×10^{-4}	6.5	4.6
4.68	3.0×10^{-4}	2.3	3.2
6.15	3.5×10^{-5}	29	2.7
6.28	2.7×10^{-5}	5.9	4.0
6.28	1.5×10^{-4}	10	3.8
6.28	4.6×10^{-4}	2.7	3.2
			Av 3.3

[a] In ether at 25°, [$LiClO_4$] = 0.0 *M*.

Table VI. The Increase in [T$^+$]/[TCl] at Constant [HCl]/[HClO$_4$] with Increase in LiClO$_4$ Concentration at 25°

[LiClO$_4$], M	$10^5R^{a,b}$	$10^3(R - R_0)^c$/[LiClO$_4$], M^{-1}
0.0000	2.2	
0.0080	3.6	1.8
0.0124	4.5	1.8
0.0125	4.5	1.8
0.0245	6.8	1.9
0.0350	8.1	1.7
0.0503	11	1.8
0.0624	13	1.9
0.0820	17	1.8

[a] R represents the ratio [T$^+$][HCl]/[TCl][HClO$_4$]. [b] [HCl]/[HClO$_4$] = 0.46. [c] R_0 represents the value of R at [LiClO$_4$] = 0.

Table VII. The Equilibrium Constant for Hydrogen Chloride in LPDE at 25°

[LiClO$_4$], M	[T$^+$]/[TCl]	[HCl], M^a	[H$^+$], M^b	[Cl$^-$], M^c	$K_{eq_{HCl}}$, M
0.478	2.54×10^{-4}	4.43×10^{-4}	1.51×10^{-4}	1.57×10^{-4}	5.35×10^{-5}
0.478	2.01×10^{-4}	5.65×10^{-4}	1.92×10^{-4}	1.99×10^{-4}	6.76×10^{-5}
0.478	1.48×10^{-4}	11.2×10^{-4}	2.65×10^{-4}	2.70×10^{-4}	6.38×10^{-5}
0.478	1.03×10^{-4}	25.0×10^{-4}	3.85×10^{-4}	3.88×10^{-4}	5.98×10^{-5}
0.478	0.803×10^{-4}·	43.9×10^{-4}	4.96×10^{-4}	4.98×10^{-4}	5.63×10^{-5}
0.872	1.66×10^{-3}	1.74×10^{-4}	1.63×10^{-4}	1.89×10^{-4}	1.77×10^{-4}
0.872	1.50×10^{-3}	2.08×10^{-4}	1.88×10^{-4}	2.07×10^{-4}	1.89×10^{-4}
0.872	1.37×10^{-3}	2.72×10^{-4}	2.10×10^{-4}	2.29×10^{-4}	1.77×10^{-4}
0.872	1.14×10^{-3}	3.70×10^{-4}	2.56×10^{-4}	2.75×10^{-4}	1.90×10^{-4}
0.872	1.03×10^{-3}	5.27×10^{-4}	2.91×10^{-4}	3.05×10^{-4}	1.68×10^{-4}
0.872	0.769×10^{-3}	9.54×10^{-4}	3.96×10^{-4}	4.08×10^{-4}	1.69×10^{-4}
0.872	0.632×10^{-3}	14.6×10^{-4}	4.88×10^{-4}	4.97×10^{-4}	1.66×10^{-4}
0.872	0.628×10^{-3}	15.3×10^{-4}	4.90×10^{-4}	5.00×10^{-4}	1.60×10^{-4}
0.872	0.331×10^{-3}	55.8×10^{-4}	9.43×10^{-4}	9.49×10^{-4}	1.60×10^{-4}
1.08	2.64×10^{-3}	2.50×10^{-4}	2.26×10^{-4}	2.74×10^{-4}	2.48×10^{-4}
1.08	0.952×10^{-3}	22.6×10^{-4}	7.43×10^{-4}	7.61×10^{-4}	2.50×10^{-4}
1.54	2.61×10^{-3}	3.03×10^{-3}	1.33×10^{-3}	1.34×10^{-3}	5.89×10^{-4}
1.54	5.49×10^{-3}	6.50×10^{-3}	6.13×10^{-3}	6.34×10^{-3}	5.98×10^{-4}
1.80	6.19×10^{-3}	1.12×10^{-3}	1.14×10^{-3}	1.16×10^{-3}	1.18×10^{-3}
1.80	3.00×10^{-3}	5.15×10^{-3}	2.40×10^{-3}	2.41×10^{-3}	1.12×10^{-3}
2.41	2.19×10^{-2}	5.80×10^{-4}	1.43×10^{-3}	1.43×10^{-3}	3.53×10^{-3}
2.41	0.74×10^{-2}	50.1×10^{-4}	4.16×10^{-3}	4.19×10^{-3}	3.48×10^{-3}
2.94	4.75×10^{-2}	3.7×10^{-4}	2.20×10^{-3}	2.21×10^{-3}	1.3×10^{-2}
2.94	1.54×10^{-2}	33.0×10^{-4}	6.79×10^{-3}	6.82×10^{-3}	1.4×10^{-2}
2.94	1.04×10^{-2}	77.0×10^{-4}	10.4×10^{-3}	10.4×10^{-3}	1.4×10^{-2}
3.58	2.25×10^{-2}	6.80×10^{-3}	1.59×10^{-2}	1.59×10^{-3}	3.72×10^{-2}
3.58	1.00×10^{-2}	35.1×10^{-3}	3.58×10^{-2}	3.58×10^{-3}	3.65×10^{-2}
3.58	1.14×10^{-2}	27.6×10^{-3}	3.14×10^{-2}	3.14×10^{-3}	3.57×10^{-2}
5.05	1.22×10^{-1}	3.40×10^{-3}	9.06×10^{-2}	9.06×10^{-2}	2.41

[a] Total titrated hydrogen chloride concentration minus hydrogen ion concentration. [b] Calculated by use of the equation: [T$^+$] + [H$^+$] = [Cl$^-$]. [c] Calculated from $K_{eq_{TCl}}$ (Figure 6) and ratios of [T$^+$]/[TCl].

we found it necessary to determine also the dependence of this ratio on perchloric acid and on hydrogen chloride. In the absence of lithium perchlorate, perchloric acid added to trityl chloride in ether produces the colored trityl ion and hydrogen chloride. With a constant concentration of perchloric acid, the ratio [T$^+$]/[TCl] was shown to be inversely proportional to the hydrogen chloride concentration. Our study shows that over a perchloric acid concentration range of 8.55×10^{-3} to 6.28×10^{-2} M, the ratio [T$^+$][HCl]/[TCl]·[HClO$_4$]^2 has a constant value of $3.3 \pm 0.4 \times 10^{-4}$ M^{-1} as exemplified in Table V. When lithium perchlorate is added to trityl chloride in ether containing a constant concentration of perchloric acid and hydrogen chloride, the amount of color produced increased linearly with the lithium perchlorate concentration. In fact, a constant value of 1.8×10^{-3} M^{-1} was found for the ratio [T$^+$][HCl]/[TCl][HClO$_4$][LiClO$_4$], as shown in Table VI.

The above observations allowed us to evaluate the equilibrium constant for the dissociation of hydrogen chloride, $K_{eq_{HCl}}$, at lithium perchlorate concentrations higher than 0.4 M, by the method described in the Experimental Section. The values so obtained are listed in Table VII.

Discussion

We have shown that lithium perchlorate forms two types of crystalline etherates, a monoetherate, $LiClO_4 \cdot Et_2O$, and a dietherate, $LiClO_4 \cdot (Et_2O)_2$.[29] Recently lithium perchlorate was shown to form a 1:2 complex with DMSO.[30] Other lithium salts such as $LiAlH_4$[31] and $LiBH_4$[32] are known to form crystalline mono- and dietherates with diethyl ether and other ethers. It is generally considered that solid lithium salt etherates consist of an ionic lattice in which the ether molecules are coordinated to the lithium ions. The very high solubility of lithium perchlorate in ether was also ascribed to the strong affinity of the solvent molecules to the lithium ion.[33] Our nmr and heat of solution data, taken in conjunction with the solubility study presented in Figure 1, tend to favor the hypothesis that the less concentrated solutions of lithium per-

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(29) No higher etherates of LiClO$_4$ could be isolated in crystalline form.

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(31) E. Wiberg and W. Gosele, *Z. Naturforsch.*, **11B**, 487 (1956).

(32) E. Wiberg, H. Noth, and R. U. Lacal, *ibid.*, **11B**, 490 (1956).

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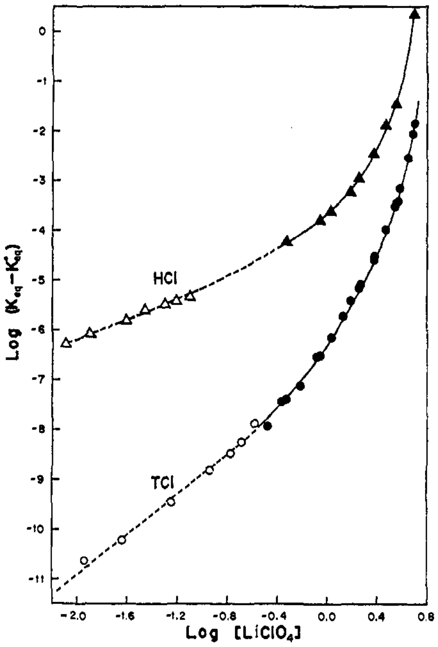

Figure 6. Plot of log ($K_{eq} - K_{eq}{}^0$) for HCl *vs.* the log of the molar concentration of lithium perchlorate: from direct measurement (▲), calculated from Table VII and values of K_{eq} for TCl (△). Plot of the log ($K_{eq} - K_{eq}{}^0$) for TCl *vs.* the log of the molar lithium perchlorate: from direct measurement (●), using the calculated portion of the K_{eq} curve of HCl (○).

chlorate (<4.25 *M*) contain primarily dietherate ions, $Li^+(OEt_2)_2$, while the more concentrated solutions, [LiClO$_4$] > 4.25, contain both dietherate, $Li^+(OEt_2)_2$, and monoetherate, $Li^+(OEt_2)$, ions. A 4.25 *M* solution of lithium perchlorate appears to be identical in every respect with fused $Li^+(OEt_2)_2ClO_4^-$. Furthermore, as the concentration of lithium perchlorate increases up to its solubility limit, the solution may be considered as changing gradually from fused $Li^+(OEt_2)_2ClO_4^-$ to fused $Li^+(OEt_2)ClO_4^-$.

According to the Bjerrum model[34] the minimum radius for ion pair formation, eq 7, in diethyl ether, a

$$r_{\min} = \frac{Z_A Z_B e^2}{2DkT} \qquad (7)$$

medium of dielectric constant 4.2 at 25°, is 67 Å. Assuming all ions to be randomly distributed in ether, then the average distance between a pair of oppositely charged ions is 67 Å at a lithium perchlorate concentration of 2.8 × 10^{-3} *M*. The theory would further predict that for all concentrations above 2.8 × 10^{-3} *M* lithium perchlorate, most ions would exist as ion pairs or higher aggregates. Actually, at 0.05 and 0.1 *M* the calculated average distance between ions is 12 and 9.4 Å, respectively. When trityl chloride is dissolved in LPDE solutions it is under the influence of the coulombic fields surrounding the lithium ions and the perchlorate ions. The transition state for ionization in ether must resemble the fully formed T^+Cl^- ion pair much more closely than it resembles the initial molecule. Therefore the lithium and perchlorate ions must strongly catalyze the ionization by virtue of the much stronger interaction of their coulombic fields with the highly polar transition state than with the weakly polar initial state. Consequently such fields could be regarded as pulling apart the trityl chloride molecule. Interestingly Pickert and associates[35] have proposed that cations in low coordination with structural oxygen ions present in AlO$_4$ and SiO$_4$ tetrahedra are the catalytically active sites in zeolites. They, like us, also note that electrostatic fields larger than 1 V/Å could cause substantial electronic shifts of the bonding electrons in the reactant molecules. Likewise, it has not escaped our notice that recently Koshland and Neet[36] have reviewed the hypothesis that the electrostatic stabilization of a developing carbonium ion in the hydrophobic cleft may be important in understanding the catalytic efficiency of the enzymes β-amylase[37] and lysozyme.[38]

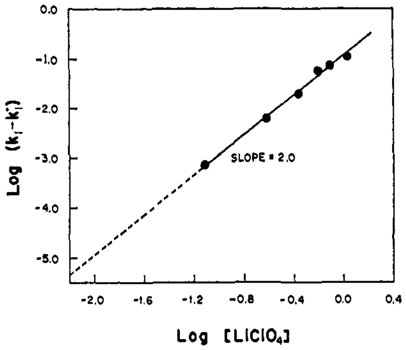

Figure 7. Plot of the log ($k_1 - k_1{}^0$) *vs.* log [LiClO$_4$]. Second-order dependence for the increase in ionization rate constant, k_1, on lithium perchlorate concentration is shown for the range [LiClO$_4$] = 0.01–1.08 *M*.

The tremendous catalytic effect of lithium perchlorate on the ionization of trityl chloride can be seen from the fact that the apparent equilibrium constant increases from $K_{eq_{TCl}}{}^0$ = 2.1 × 10^{-12} *M* in pure ether to $K_{eq_{TCl}}$ = 1.4 × 10^{-2} *M* at 5.05 *M* lithium perchlorate, which is a 7 billion fold increase. The effect of lithium perchlorate is best indicated by plotting log ($K_{eq_{TCl}} - K_{eq_{TCl}}{}^0$) against log [LiClO$_4$] as shown in Figure 6. The curve as drawn shows every slope from 2 to 12 and it would appear that lithium perchlorate ion pairs and higher aggregates participate in the ionization process as electrostatic catalysts. They act in various numbers, from various positions in a manner that cannot be accurately described, otherwise than statistically. However, at the lowest lithium perchlorate concentrations studied the slope appears to reach a limiting gradient of 2. Our data on the dependence of the ionization constant k_1 on lithium perchlorate concentration in the region 0.01–1.08 *M* also show a limiting gradient of 2, as can be seen from plot of log ($k_1 - k_1{}^0$) against log [LiClO$_4$] given in Figure 7. In the concentration region up to 0.1 *M* lithium perchlorate, the increase in $K_{eq_{TCl}}$ parallels that of k_1; we conclude therefore that the ion recombination constant k_1 decreases little on

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Table VIII. Thermodynamic Parameters for the Ionization of TCl[a]

[LiClO$_4$], M	pK_I[b]	$\Delta F°$, kcal/mole	$\Delta H°$, kcal/mole	$\Delta S°$, cal/deg
0.707	−6.82	9.37	10.2	2.8
0.823	−6.65	9.06	10.3	4.2
1.14	−6.06	8.25	10.7	8.2
1.46	−5.65	7.65	11.5	12.9

[a] All data for 25.0°. [b] $pK_I = -\log K_{eq_{TCl}}$.

going from pure ether to 0.1 M lithium perchlorate (Figure 5). However, the higher than second-order dependence of $K_{eq_{TCl}}$ of [LiClO$_4$] in the region 0.1–1.08 M appears to be accounted for by a significant decrease in k_{-1} in this region. As the concentration of lithium perchlorate increases, the dielectric constant, the ionic environment, and the viscosity all increase. We note from our own measurements that the dielectric constant increases linearly with [LiClO$_4$] and, furthermore, that a plot of log (k_{-1}/k_{-1}^0) has a straight line dependence on $1/D$ (Figure 8). While no adequate theory exists for treating ion recombinations in solvents of low dielectric, the trend is in accord with the theory that the larger the concentration of electrolyte the slower is the rate of recombination of two oppositely charged ions.[39]

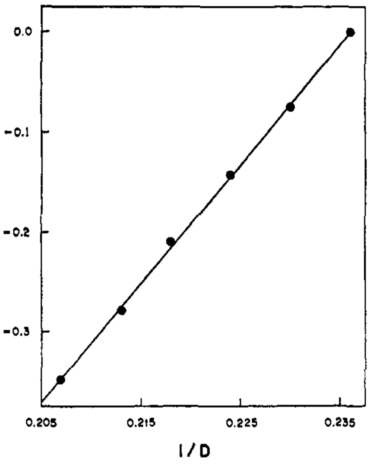

Figure 8. Plot of the linear relationship between log (k_{-1}/k_{-1}^0) and $1/D$.

The energy requirements of $K_{eq_{TCl}}$ in the concentration region, [LiClO$_4$] = 0.7–1.5 M, are presented in Table VIII. The decrease in the free energy of ionization of TCl with increasing concentration of LiClO$_4$ appears to be mainly dictated by an increase in the entropy of ionization.

The picture we shall build of the SN1 type ionization in LPDE solutions, from the above observations, is inevitably more involved than the conventional picture applying to SN1 reactions in ionophilic solvents. At the lower concentrations used we have apparently a real reaction order of two in [LiClO$_4$] and can formulate a catalytic path consistent with this limiting second-order dependence, as shown in eq 8.[40] Likewise the

$$\mathrm{TCl} + 2\mathrm{Li^+ClO_4^-} \rightleftharpoons \mathrm{T^+ClO_4^-Li^+ClO_4^-} + \mathrm{Li^+Cl^-}$$

$$K_{eq_{TCl}}^{\mathrm{LiClO_4}} = \frac{[\mathrm{T^+ClO_4^-Li^+ClO_4^-}][\mathrm{Li^+Cl^-}]}{[\mathrm{TCl}][\mathrm{Li^+ClO_4^-}]^2} = 1.25 \times 10^{-7}\, M^{-1} \quad (8)$$

catalysis by perchloric acid the region [HClO$_4$] can be formulated as in eq 9.[41] Furthermore, we find that

$$\mathrm{TCl} + 2\mathrm{H^+ClO_4^-} \rightleftharpoons \mathrm{T^+ClO_4^-H^+ClO_4^-} + \mathrm{HCl}$$

$$K_{eq_{TCl}}^{\mathrm{HClO_4}} = \frac{[\mathrm{T^+ClO_4^-H^+ClO_4^-}][\mathrm{HCl}]}{[\mathrm{TCl}][\mathrm{H^+ClO_4^-}]^2} = 3.3 \times 10^{-4} M^{-1} \quad (9)$$

in the concentration range [LiClO$_4$] = 0.01–1.08 M, the enhanced ionization of hydrogen chloride shows a first-order dependence on [LiClO$_4$], which we formulate as in eq 10.

$$\mathrm{HCl} + \mathrm{Li^+ClO_4^-} \rightleftharpoons \mathrm{H^+ClO_4^-} + \mathrm{Li^+Cl^-}$$

$$K_{eq_{HCl}}^{\mathrm{LiClO_4}} = \frac{[\mathrm{H^+ClO_4^-}][\mathrm{Li^+ClO_4^-}]}{[\mathrm{HCl}][\mathrm{Li^+ClO_4^-}]} = 7.0 \times 10^{-5} \quad (10)$$

Consequently, in LPDE solutions containing both TCl and HCl the ionization constant, $K_{eq_{TCl}}$, at low lithium perchlorate concentrations, is the sum of three terms as expressed in eq 11. The ratio of colored to colorless

$$K_{eq_{TCl}} = K_{eq_{TCl}}^0 + K_{eq_{TCl}}^{\mathrm{LiClO_4}}[\mathrm{LiClO_4}]^2 + K_{eq_{TCl}}^{\mathrm{HClO_4}}[\mathrm{HClO_4}]^2 \quad (11)$$

material under these conditions can be expressed as the sum of three terms as in eq 12. The first term in eq

$$\frac{[\text{color}]}{[\text{colorless}]} = \frac{K_{eq_{TCl}}^0}{[\mathrm{Cl^-}]} + \frac{K_{eq_{TCl}}^{\mathrm{LiClO_4}}}{K_{eq_{HCl}}^{\mathrm{LiClO_4}}}\frac{[\mathrm{LiClO_4}][\mathrm{HClO_4}]}{[\mathrm{HCl}]} + K_{eq_{TCl}}^{\mathrm{HClO_4}}\frac{[\mathrm{HClO_4}]^2}{[\mathrm{HCl}]} \quad (12)$$

12 corresponds to the color produced in pure ether and a negligible contributor to the total amount of color. The second term pertains to the data given in Table VI where the ratio $K_{eq_{TCl}}^{\mathrm{LiClO_4}}/K_{eq_{HCl}}^{\mathrm{LiClO_4}}$ has a value of $1.8 \times 10^{-3}\ M^{-1}$, while the last term pertains to data presented in Table V.

The equilibrium constant for the ionization of HCl in pure ether, $K_{eq_{HCl}}^0$, was calculated from the ratio $K_{eq_{TCl}}^0/[([\mathrm{T^+}]/[\mathrm{TCl}])([\mathrm{HCl}]/[\mathrm{HClO_4}])]_0$ as $9.0 \times 10^{-8}\ M$. The tremendous catalytic efficiency of LPDE solutions can be seen from the fact that at 5.05 M lithium perchlorate, $K_{eq} = 2.4\ M$, an increase of 2.5×10^6-fold. The dependence of $K_{eq_{HCl}}$ on [LiClO$_4$] is best indicated by a log–log plot as shown in Figure 6. The curve as drawn shows every slope from 1 to 12. Thus ion pairs and

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(39) E. S. Amis, "Solvent Effects on Reaticon Rates and Mechanisms," Academic Press, New York, N. Y., 1966.

(40) Because of the complex nature of LiClO$_4$ in ether, the equilibria will be discussed, mainly for simplicity, in terms of the stoichiometric concentration of ion pairs. It should be noted, however, that data from vapor pressure measurements (ref 8) indicate increasing amounts of dimeric ion pairs in solutions above 0.1 M lithium perchlorate. Furthermore, it has been shown in our laboratories that $\mathrm{T^+ClO_4^-}$ is insoluble in pure ether but that its solubility increases with [LiClO$_4$], which leads us to infer the presence of $\mathrm{T^+ClO_4^-Li^+ClO_4^-}$ aggregates.

(41) The degree of aggregation of HClO$_4$ in ether is not known. In our discussion, we have assumed that in the very dilute region it is largely present as $\mathrm{H(Et_2O)_n{}^+ClO_4^-}$ ion pairs which for simplicity we have written as $\mathrm{H^+ClO_4^-}$. There are no vapor pressure data on the HClO$_4$–Et$_2$O system for obvious reasons.

higher aggregates apparently dispose themselves about the HCl molecule in such a way as to reduce its free energy of ionization. The group of observations as a whole presents many features which have little precedent in hydroxylic media, and it is our hope that they may provide an understanding of the great penetration of electrostatic forces in hydrophobic media as well as in fused salts.

The Solvolysis of 1-Chloroaziridines[1]

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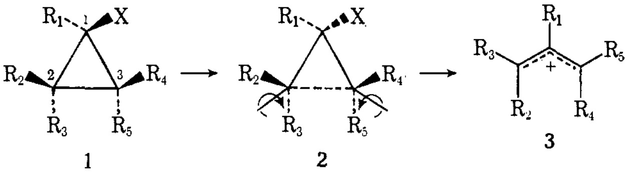
Abstract: The solvolytic behavior of N-chloroaziridine and five methyl-substituted N-chloroaziridines has been investigated. The fate of the N-chloroaziridines under solvolytic conditions was found to be very similar to that observed for the acetolysis of cyclopropyl tosylates. For all of the N-chloroaziridines investigated the ionization of the N–Cl bond was accompanied by cleavage of the aziridine ring. The relative rates of solvolysis correlated quite well with the anticipated results based on the theory that N-chloroaziridines would solvolyze with an electrocyclic disrotatory ring opening as predicted by the Woodward–Hoffmann molecular orbital symmetry considerations. Rate accelerations as large as 1.5×10^5 resulted from the substitution of two methyl groups on the aziridine ring. A detailed comparison of the solvolysis of N-chloroaziridines with the solvolysis of cyclopropyl tosylates has been made. In general, methyl substitution in the aziridine system results in a larger rate acceleration than analogous methyl substitution in the cyclopropyl system.

Although the ring opening of cyclopropyl derivatives to give allylic cations has been known for some time,[3] it was only with the advent of the Woodward–Hoffman molecular orbital symmetry considerations[4] that a theoretical basis was provided for the apparent anomalous behavior of the incipient cyclopropyl cation.[5–7] As shown by a variety of labeling experiments, including isotopic studies,[8] the bond of the three-membered ring which is cleaved in the formation of the allylic cation is not attached directly to the carbon bearing the leaving group. In accord with molecular orbital symmetry considerations for the electrocyclic opening of cyclopropanes it should be the C_2–C_3 bond of **1** which is broken as the X group leaves with its pair of bonding electrons. The elegant studies of DePuy,[5] Schleyer,[6,7] and Schöllkopf[6,7] have established that, as the X group of **1** starts to leave as shown in **2**, concerted cleavage of the C_2–C_3 bond occurs with a disrotatory motion about the C_1–C_2 and C_1–C_3 bonds. As indicated in structure **2** this rotation is stereospecific with the groups *cis* to the leaving group both rotating inward and the groups *trans* to the leaving group rotating outward to eventually produce the allyl cation **3**.



Our recent studies of the nitrogen analog of the carbonium ion[1,9] suggested to us that the nitrenium analog of the cyclopropyl cation should show the same properties of ring cleavage and stereospecific disrotatory movement of substituents. For an aziridine such as **4** the concerted cleavage would be expected to proceed as shown in **5** with the group *cis* to the leaving group (R_1 and R_4) rotating inward and the groups *trans* to X rotating outward. If the aziridine system behaved exactly like the cyclopropyl system the cleavage of **4** should lead initially to **6** either as a discrete intermediate or as a point along the reaction pathway. As shown, **6** would be a planar molecule. However, a 90° rotation of either the C_1–N bond or the C_2–N bond of **6** would give **7**, the isoelectronic nitrogen analog of an allene. Both **6** and **7** might be expected to be short-lived under the reaction conditions and both would be expected to yield the product mixture **8**. The direct conversion of **5** into **7** also requires

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(1) Paper X in a series on The Chemistry of Nitrenium Ions. For the previous paper in this series see P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969). See also P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

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(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965). See also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); M. J. S. Dewar, *Tetrahedron, Suppl.*, No. 8, 75 (1966); W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).

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(9) P. G. Gassman and B. L. Fox, *J. Amer. Chem. Soc.*, **89**, 338 (1967); P. G. Gassman, F. Hoyda, and J. Dygos, *ibid.*, **90**, 2716 (1968); P. G. Gassman, G. Campbell, and R. Frederick, *ibid.*, **90**, 7377 (1968); P. G. Gassman and R. L. Cryberg, *ibid.*, **91**, 2047 (1969); and P. G. Gassman and A. Carrasquillo, *Chem. Commun.*, 495 (1969).