product was composed of 25% *cis,cis,cis*-1,2,3-trimethylchlorocyclopropane and 75% *trans,cis,cis*-1,2,3-trimethylchlorocyclopropane as determined by integration of the nmr spectrum of the mixture and as inferred from the relative amounts of allylic cations produced. The nmr spectrum of *cis,cis,cis*-1,2,3-trimethylchlorocyclopropane had absorptions at δ 0.98 (m), from about 0.98 to 1.40 (m), and 1.57 (s). The nmr of *trans,cis,cis*-1,2,3-trimethylchlorocyclopropane had absorptions at δ 0.98 (m), from about 0.98 to 1.40 (m), and 1.40 (s).

1,1-Difluoro-2,2-dimethylcyclopropane was prepared by the method of Tarrant, *et al.*[35]

1,1-Difluorotetramethylcyclopropane[36] was prepared in an autoclave by the method of Knox, *et al.*[37] We experienced difficulty in separating the difluoride from unreacted tetramethylethylene. The desired product (of about 90% purity) was obtained by low-temperature bromination of the undiluted mixture of the two compounds followed by vacuum distillation. The yield of material was 24% from 0.3 mol of olefin and 0.3 mol of sodium chlorofluoroacetate.

Kinetic Studies. Plots of log of the ratios of the integrated intensities of the decreasing absorption over the sum of the decreasing absorption plus the increasing absorption [log $(I_d)/(I_d + I_i))$] against time were linear after temperature stability had been reached.

Rate constants were determined from the slopes of these lines. For ions **28a** and **b** only the vinyl resonances could be used and reproducibility was good only to about a factor of ten. For ion **32a** separate methyl resonances were observed and these could be used to determine the rate constants at different temperatures, from which the activation parameters could be determined. Temperatures were measured with a calibrated thermometer which fit into an nmr tube.

Acknowledgment. Support of the work by the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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[35] P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 77, 2783 (1955).

[36] D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, 32, 2980 (1967).

[37] L. H. Knox, E. Verlarde, S. Berger, S. Cuadriello, P. W. Landis, and A. D. Cross, *J. Amer. Chem. Soc.*, 85, 1851 (1963).

Electrostatic Catalysis by Ionic Aggregates. II. The Reversible Elimination of HCl from *t*-Butyl Chloride and the Rearrangement of 1-Phenylallyl Chloride in Lithium Perchlorate–Diethyl Ether Solutions[1,2]

Y. Pocker[3] and Richard F. Buchholz[4]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received August 7, 1969

Abstract: In lithium perchlorate–diethyl ether solutions (LPDE), the reaction of *t*-butyl chloride with either pyridine or lithium azide has the characteristics of a unimolecular elimination process, E1. Similarly, the dilution of radiochloride tracer during the reaction of *t*-butyl chloride with saline radiochloride is due, almost entirely, to an E1 process with little or no substitution accompanying it. The first-order rate constant, k_f, for the ionization of *t*-butyl chloride in LPDE solutions increases a millionfold on going from pure ether ($k_f^0 = 4.2 \times 10^{-11}$ sec^{-1}) to 5.5 *M* lithium perchlorate ($k_f = 4.8 \times 10^{-5}$ sec^{-1}). The rate of addition of HCl to isobutylene is proportional to $[HCl]^2$ in pure ether but is only first order in acid in LPDE solutions. The striking effect of LPDE solutions manifests itself in the addition reaction as well, thereby leaving the ratio $k_f/k_r = 5.3 \pm 0.2 \times 10^{-5}$ *M* essentially unaffected. Powerful electrostatic catalysis was also documented for the rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**): first-order rate constants were determined in pure ether ($k_i^0 = 2.5 \times 10^{-7}$ sec^{-1}) and in solutions containing up to 2.83 *M* lithium perchlorate ($k_i = 7.84 \times 10^{-3}$ sec^{-1}).

In part I[1] we showed that lithium perchlorate–diethyl ether solutions (LPDE) were media in which extremely powerful catalysis was operative with respect to the ionization of triphenylmethyl chloride and hydrogen chloride. This catalysis was essentially electrostatic in nature and was shown to arise from the capacity of $[Li^+(OEt_2)_m, ClO_4^-]_n$ ion pair aggregates to promote the ionization process.

In the present paper, the striking catalytic efficiency of LPDE solutions is further delineated, this time with respect to the elimination of HCl from *t*-butyl chloride in the presence of pyridine and lithium azide. We also report on the rates of radiochloride exchange between *t*-butyl chloride and lithium radiochloride as well as on the rates of olefin formation. Our data indicate that an electrostatically assisted E1 mechanism is under observation. We have further demonstrated that the addition of HCl to isobutylene is powerfully catalyzed by LPDE solutions but that the ratio, k_f/k_r, is independent of the lithium perchlorate concentration. The present paper also includes a report on the allylic rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) in LPDE solutions.[5] Our results, taken as a whole, clearly illustrate both the magnitude and the usefulness of the electrostatic catalysis associated with

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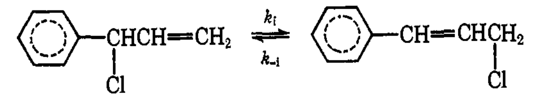
[1] Part I: *J. Am. Chem. Soc.*, 92, 2075 (1970).

[2] This work was supported in part by the National Science Foundation (GP-5103) and in part by the donors of the Petroleum Research Fund (PRF 2043-A4), administered by the American Chemical Society.

[3] To whom inquiries should be directed.

[4] Taken in part from the Ph.D. Thesis of Richard F. Buchholz, University of Washington, 1969.

[5] Only the rate of rearrangement of **1** is discussed here in view of the nature of this paper. A more complete investigation of **1** is under way in these laboratories.



1 2

LPDE solutions. Thus a number of ionization reactions can be catalyzed without the aid of ordinary proton donors and without the risk of obtaining solvolysis products. The present paper also attempts to define the wide range of catalytic efficiency of LPDE solutions in terms of the well characterized Y scale.[6,7]

Experimental Section

Materials. All methods of preparation and purification of materials used have been previously described, except for *t*-butyl chloride, pyridine, lithium azide, isobutylene, and 1-phenylallyl chloride (**1**). *t*-Butyl chloride (Eastman Organic Chemicals) was dried and fractionated over $CaCl_2$ (uncor bp 51.5°). Pyridine was dried and fractionated over $CaCl_2$ (uncor bp 114.5–115.0°). LiN_3 (K & K Laboratories) was dried at 100° under vacuum. Isobutylene was prepared by the dehydration of *t*-butyl alcohol with anhydrous oxalic acid.[8] It was purified by passage through an ice cold trap and a calcium chloride tower before dissolution in diethyl ether. **1** was prepared by following exactly the method of Caserio, *et al.*:[9] bp 57.0–57.5° (1.5 mm); uv max 253 mμ (ϵ 690–1000). These values are in accord with literature values.[9,10]

Kinetic Measurements. For the rate of acid production from *t*-butyl chloride, aliquots of the reaction mixture with pyridine present (5 ml) were introduced into cold neutral dry acetone (−80°) and the acid titrated to a Lacmoid end point with standard NaOH in methanol. In reaction mixtures having LiN_3, N_3^- behaves as a strong base and was quantitatively titrated with standard HCl in methanol to a Lacmoid end point. It should be noted that $C_5H_5N \cdot HCl$ present in the reaction mixtures behaves as a strong acid toward Lacmoid indicator. In cold dry acetone, HN_3, produced from the reaction N_3^- with acid, is neutral to Lacmoid indicator.

For the rate of alkene production, aliquots of the reaction mixture (5 ml) were quenched in an excess solution of Br_2 in acetic acid. Solid KI was then added along with water and starch solution. The liberated I_2, equal to excess Br_2, was then titrated with standard thiosulfate.

For measuring the dilution of radioactive tracer in the reaction between *t*-butyl chloride and LiCl [^{36}Cl], aliquots of the solutions (5 ml) were quenched in dry cold pentane (50 ml at −80°) containing Et_3N to precipitate the saline material (Et_3NHCl + LiCl). The coagulated precipitate was filtered off (no. 4 porosity sintered-glass filter), washed with dry pentane, and dissolved by drawing three portions of distilled water (5 ml each) through the filter. The counting solution (5 ml of scintillation liquid, 5 ml of 95% ethanol, and 0.5 ml of radioactive sample) was counted on a Packard Tri-Carb liquid scintillation spectrometer. After counting, aliquots (10 ml) were titrated potentiometrically against standard $AgNO_3$ to obtain specific activity. If a and b, respectively, are the concentrations of *t*-butyl chloride and LiCl and if c and $c - x$ are, respectively, the specific activities of the LiCl in the initial solution (counts extrapolated to zero time) and of a solution of LiCl and Et_3NHCl from the reaction, stopped after time t, then the first-order rate coefficient, k_f, was obtained by plotting $\log \{1 - (x/c)[(a + b)/a]\}$ against t and multiplying the slope by $-2.3[b/(a + b)]$.

The rate of acid loss and the rate of alkene loss for the study of HCl addition to alkene were determined by the above method for the elimination of HCl from *t*-butyl chloride.

All rates of rearrangement of **1** were obtained by following the increase of absorbance at 253 mμ on a Beckman DU-2 equipped with a D_2 lamp and a constant-temperature bath at 25.00 ± 0.05°. First-order rate plots were obtained following the appearance of **2** (ϵ 20,000)[9,10] and plotting $\log (A_\infty - A_t)$ against time. **1** quantitatively rearranges to **2**.[9,10]

Results and Discussion

Elimination of Hydrogen Chloride from *t*-Butyl Chloride. The elimination of HCl from *t*-butyl chloride in ether and in LPDE solutions can only be observed in the absence of free hydrogen chloride. Consequently the elimination was investigated by measuring the development of acidity in the presence of pyridine and lithium azide. Even though the eliminations become observable only in the presence of amine or azide ion, the rate is approximately independent of their concentration. This condition was shown to hold for all LPDE solutions (Tables I and II). These conclusions can only be reconciled on the assumption that the elimination is a unimolecular process and depends for its rate only on the ionization of *t*-butyl chloride, and that pyridine and azide ion act by retarding the retrograde

Table I. Initial Rates of Acid Production from *t*-Butyl Chloride in LPDE Solutions at 25°

[$LiClO_4$], M	[*t*-Butyl Cl], M	[Pyridine], M	k_f, sec^{-1}
0.00	1.8	2.5×10^{-3}	4.2×10^{-11} [a]
0.0577	1.8	2.5×10^{-3}	5.2×10^{-10}
0.108	0.90	2.5×10^{-3}	1.0×10^{-9}
0.266	0.90	2.5×10^{-2}	5.1×10^{-9}
0.529	0.90	2.5×10^{-2}	2.4×10^{-8}
0.974	0.18	2.5×10^{-1}	8.7×10^{-8}
1.05	0.90	2.5×10^{-2}	1.1×10^{-7}
1.59	0.18	2.5×10^{-1}	2.2×10^{-7}
2.42	0.90	1.2×10^{-2}	1.3×10^{-6}
2.42	0.90	2.5×10^{-1}	1.2×10^{-6}
2.80	0.18	2.5×10^{-2}	1.2×10^{-6}
2.86	0.90	1.2×10^{-2} [b]	2.0×10^{-6}
2.86	0.90	1.2×10^{-2} [c]	1.9×10^{-6}
3.56	0.18	2.5×10^{-2}	3.5×10^{-6}
4.45	0.18	2.5×10^{-1}	1.0×10^{-5}
5.46	0.18	2.5×10^{-1}	4.8×10^{-5}

[a] Our value is within an order of magnitude from a value predicted using the ionization of *p*-methoxyneophyl *p*-toluenesulfonate: S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961). Using their relationship, $Z = 104.2 + 8.11 \log k_1$, where $\log k_1$ for pure ether is −7.3, Z was calculated to be 45. An extrapolation of the Z value of Kosower[6] shows that for $Z = 45$, $\log k_1$ for *t*-butyl chloride is about −10.4. [b] [LiCl] = 1.0×10^{-2} M. [c] [LiCl] = 3.5×10^{-2} M.

Table II. Initial Rates of Acid Production from *t*-Butyl Chloride in 2.91 M $LiClO_4$ Solution[a]

Base	Concn, M	$10^6 k_f$, sec^{-1}	Method
LiN_3	3.3×10^{-3}	2.3	$d[H^+]/dt$
LiN_3	9.0×10^{-3}	2.4	$d[H^+]/dt$
LiN_3	2.4×10^{-2}	2.3	$d[H^+]/dt$
Pyridine	1.2×10^{-2}	2.3	$d[H^+]/dt$
LiN_3	2.5×10^{-2}	2.3	d[alkene]/dt
Pyridine[b]	2.5×10^{-1}	2.3	Isotopic dilution

[a] [*t*-Butyl chloride] = 0.90 M. [b] [$Li^{36}Cl$] = 2.8×10^{-2} M.

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(6) The solvent parameter Z using 1-ethyl-4-carbomethoxypyridinium iodide was unobtainable in pure ether (E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3267 (1958)) or in LPDE solutions due to the low solubility of this particular pyridinium iodide in these media. We have however utilized the charge-transfer bands observed with pyridine N-oxide and phenobetaine as measures of solvent polarity of LPDE solutions. Charge-transfer bands exhibit appreciable sensitivity to increases in lithium perchlorate concentration (Y. Pocker, R. F. Buchholz, and E. Green, unpublished observations).

(7) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957), and related papers.

(8) Y. Pocker, *J. Chem. Soc.*, 1292 (1960).

(9) (a) W. G. Young, F. Caserio, and D. Brandon, *Science*, **117**, 473 (1953); (b) F. F. Caserio, G. E. Dennis, R. de Wolfe, and W. G. Young, *J. Am. Chem. Soc.*, 77, 4182 (1955).

(10) (a) G. Valkanas and E. S. Waight, *J. Chem. Soc.*, 2720 (1959); (b) E. S. Waight and M. Weinstock, *Proc. Chem. Soc.*, 334 (1961); (c) G. Valkanas, E. S. Waight, and M. Weinstock, *J. Chem. Soc.*, 4248 (1963); (d) D. J. Rawlinson and R. M. Noyes, *ibid.*, 1793 (1963).

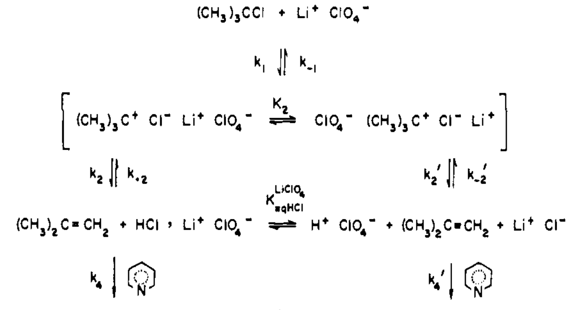
addition to the olefin. Both act by taking up the acid that is produced. These data are in agreement with the findings of Pocker[11] in nitromethane. He also observed that the elimination of HCl from *t*-butyl chloride became observable only in the presence of a base such as pyridine and the rate was independent of its concentration.

Using the fact that the amount of pyridine has little effect on the rate of acid production, the rate constants, k_f, for the elimination of hydrogen chloride from *t*-butyl chloride were determined in the presence of pyridine in ether and in LPDE solutions containing up to 5.46 *M* lithium perchlorate. The values obtained are listed in Table I. The tremendous catalytic ability of LPDE solutions can be judged from the fact that the rate constant increased 1 millionfold on going from pure ether to a 5.46 *M* lithium perchlorate solution. It is of interest to determine the dependence of the increase in k_f on the concentration of lithium perchlorate. Values of log ($k_f - k_f^0$), where k_f^0, the value in pure ether,[12] is 4.2×10^{-11} sec^{-1}, are plotted against log [$LiClO_4$]. In Figure 1, at lithium perchlorate concentrations lower than 0.1 *M*, an apparent limiting first-order dependence on $LiClO_4$ is found. As the concentration of lithium perchlorate increases, increased dependencies of two, three, and higher are observed.

The reaction between radiochloride ions and *t*-butyl chloride was studied by observing the dilution of tracer accompanying the reaction between chlorine of ordinary isotopic abundance in *t*-butyl chloride and chloride [^{36}Cl] ion supplied in the form of lithium chloride. The concurrent elimination produces hydrogen chloride which instantaneously exchanges its chloride with that of lithium radiochloride so that the dilution of tracer is not in itself an indication that chloride is being exchanged with *t*-butyl chloride. However as shown in Table II at 2.91 *M* $LiClO_4$, the rate coefficient for tracer dilution is the same as the rate coefficient for acid production in the presence of pyridine and azide ion and for the production of olefin. From this it can be deduced that there is little or no concurrent substitution by chloride ions.

The mechanism of the catalysis of the elimination of HCl from *t*-butyl chloride in LPDE solutions can be shown to follow that proposed for the ionization of trityl chloride and hydrogen chloride.[1] Scheme I

Scheme I



presents a set of simplified equilibria for acid production as measured in the presence of pyridine or azide ion. In the lower limit (*i.e.*, below 0.1 *M* salt), the apparent order in lithium perchlorate is one; consequently, for simplicity, one lithium perchlorate ion pair is used in the above scheme. The reverse reaction, the addition of acid to isobutylene, is retarded by pyridine which takes up acid (steps k_4 and k_{-4}') to form the relatively inactive pyridinium salts. Similarly when LiN_3 is used, it reacts with acid to form HN_3 and the corresponding lithium salts. Equilibrium K_5 is presented to show the regeneration of the catalyst when pyridine is used. Since we have shown (Table II) that the first-order rate coefficients of acid production in the presence of pyridine or azide ion are practically identical with those of olefin formation or isotopic dilution of the radiochloride salt, these experimental rate constants can only mean that they all measure one and the same rate limiting process.

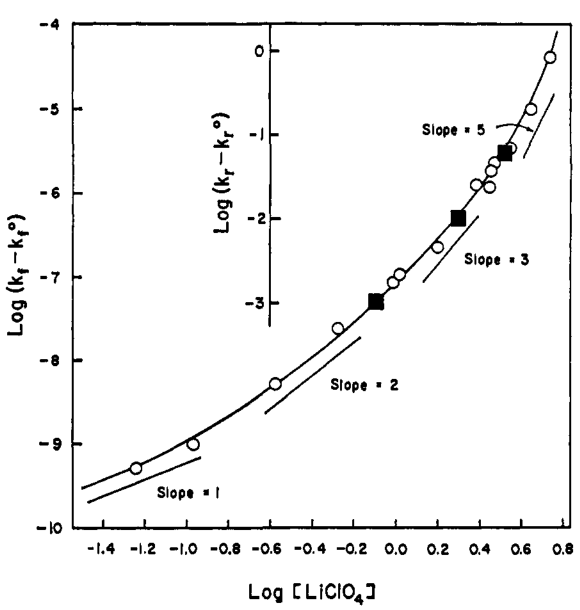


Figure 1. Plot of log ($k_f - k_f^0$) *vs.* log [$LiClO_4$] for *t*-butyl chloride (0.90 *M*) in the presence of pyridine at 25° (○); plot of log ($k_r - k_r^0$) *vs.* log [$LiClO_4$] for the addition of HCl to isobutylene (■).

In determining exactly the nature of the limiting process two observations must be taken into account: (a) the elimination rather than substitution is the predominant process and (b) the rates of acid production from *t*-butyl chloride are independent of the concentration and nature of the basic reagent. It is tempting to identify the rate-limiting process with the ionization of *t*-butyl chloride. This customary mechanistic deduction identifies the measured forward rate constant as k_1 from which it is then logically deduced that the bases pyridine, $^{36}Cl^-$, and N_3^- intervene only after *t*-butyl cation production. This deduction does not allow for the fact that the reaction is not subject to a mass law effect suggesting therefore that the rate-limiting elimination occurs from within an ion pair intermediate. Here a more general deduction would include the modification that the forward rate constant we are actually measuring in these media is k_1k_2/k_{-1}. According to this scheme the various bases only intervene after an internal proton transfer has occurred within the ion pair leading to HCl and olefin (k_4 and k_{-4} in Scheme I).

We were able to relate the ionizing capacity of LPDE solutions with formal *Y* values by using the respective first-order rate constants for the ionization of *t*-butyl

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[11] Y. Pocker, *J. Chem. Soc.* 1972 (1960).

[12] See Table I, footnote *a*.

Table III. The Addition of HCl to Isobutylene in Ether and LPDE Solutions at 25.0°

$[LiClO_4]$, M	10^2[Isobutylene], M	10[HCl],[a] M	Method	10^4k_r, M^{-1} sec^{-1}	$10^6k_r'$,[b] M^{-2} sec^{-1}	10^5K_{eq}, M
0.0	5.0	17	$-d(\text{alkene})/dt$	0.044	2.6	
	11.0	5.7	$-d(H^+)/dt$	0.014	2.5	
0.81	2.3	0.35	$-d(H^+)/dt$	8.5		5.6
	4.5	1.3	$-d(\text{alkene})/dt$	9.3		5.1
	4.6	0.27[c]	$-d(H^+)/dt$	8.8		5.2
2.0	3.3	0.30	$-d(H^+)/dt$	100		5.6
3.3	3.3	1.2	$-d(H^+)/dt$	630		5.1

[a] Total titrated HCl. [b] In pure ether the addition is a third-order process, $V = k_r'[\text{isobutylene}][\text{HCl}]^2$ where $k_r' = k_r/[\text{HCl}]$. In LPDE solutions, $V_{LiClO_4} = k_r[\text{isobutylene}][\text{HCl}]$. [c] $[\text{LiCl}] = 1.13 \times 10^{-2}\ M$.

chloride in these media. Apparent Y values calculated from $\log (k_f/k_f^0)$, where $k_f^0 = 9.24 \times 10^{-6}$ sec^{-1},[13] are plotted against lithium perchlorate concentration. An inspection of the plot indicates that pure ether has a Y value of -5.36 and that in a 6 M lithium perchlorate solution in ether corresponds to a Y value of 1.0 which in terms of ionizing capacity approximates a 60% ethanol–water solution. A 4.25 M LPDE solution is equivalent to an 80% ethanol–water solution. Pocker[11] found that the ionization rate constant k_f for t-butyl chloride in nitromethane is 2.4×10^{-6} sec^{-1}. This compares to our value of 2.3×10^{-6} sec^{-1} in 2.91 M LPDE solution. Both nitromethane and 2.91 M LPDE exhibit the same ionizing capacity even though the macroscopic dielectric constant of nitromethane is 39[14] and that of a 2.91 M LPDE solution is 7.7.[15,16]

Kinetics of Addition of Hydrogen Chloride to Isobutylene. The kinetics of this reaction were studied by following the disappearance of acid and by following the loss of isobutylene. The rates obtained by the two methods are practically identical (Table III). The stoichiometry of the addition in both pure ether and in LPDE is one whereby for each molecule of olefin only 1 mole of acid disappears to produce, at 25.0°, t-butyl chloride in practically quantitative yield. In pure diethyl ether, the kinetics show that the rates of addition $= k_r'[\text{olefin}][\text{HCl}]^2$. The third-order rate constant, k_r', as found in the concentration ranges of olefin and acid employed is 2.5×10^{-6} sec^{-1} M^{-2} obtained by dividing k_r by HCl concentration. The kinetic results do not define the form in which hydrogen chloride enters the rate expression, but they do define the activated complex as olefin,2HCl.

The very low electrical conductivity, infrared spectra, vapor pressure, and other properties[17] have shown that hydrogen chloride is monomeric and merely forms a hydrogen bonded complex with diethyl ether, $Et_2O \cdots HCl$, rather than diethyloxonium chloride, Et_2OH^+,Cl^-. The species Et_2OH^+ cannot be the dominant proton donating species, as this would lead to a first-order dependence on HCl, indicating, in our case, that the prevalent species $Et_2O \cdots HCl$ is the dominant proton donor.

The most attractive mechanism, as has been described for HCl addition to olefin in nitromethane,[8,18] involves a rate-determining proton transfer from molecular hydrogen chloride to olefin with a second molecule of acid acting to assist the proton transfer by hydrogen bonding to the developing chloride ion. While the kinetic description of the reaction path does not describe the structure of the transition state, two possibilities can be discussed. The first and simplest scheme might involve the carbonium ion hydrogen dichloride, $(CH_3)_3C^+,HCl_2^-$, which is not unlikely in view of the recent work by Harmon and coworkers[19] who prepared carbonium ion hydrogen dichlorides from ethereal solutions. The second scheme involves the addition of HCl to olefins through a synchronous route involving the simultaneous addition of the proton and the anion derived from two different molecules of acid.[20]

The addition of lithium perchlorate to ether changes the order of the addition of HCl to isobutylene to second order overall, first order in olefin and first order in HCl (Table III). The magnitude of this measured rate, k_r, was found to be dependent on $[LiClO_4]$ (Figure 1).

Any discussion of the measured addition rate constant, k_r, in terms of Scheme I must take into account the preservation of the equilibrium constant between elimination and addition, $K_{eq} = k_1k_2/k_{-1}k_{-2}$, in LPDE media and the implications from the previous discussion of the forward rate constant k_f. In a recent study in nitromethane, the addition of HCl to alkene was shown to proceed *via* a rate-determining proton transfer from HCl to alkene as assisted by a second HCl molecule followed by a rapid collapse of carbonium hydrogen dichloride ion pair.[18] Extending this to LPDE solutions, we visualize that $LiClO_4$ ion pairs assume the role of the second HCl molecule in facilitating the proton transfer. Consequently, we identify provisionally the measured reverse rate constant, k_r, with k_{-2} in Scheme I, implying that k_{-1} is significantly faster than k_2. We note that this interpretation predicts the observed constancy in the k_f/k_r ratios thus, $k_f/k_r = k_1/k_2$ $k_{-1}k_{-2}$. In LPDE solutions the addition of HCl to isobutylene can proceed by two limiting routes, eq 1.

$$\begin{aligned} V_{-2} &= k_{-2}[\text{olefin}][\text{HCl}][Li^+ClO_4^-] \\ V_{-2}' &= k_{-2}'[\text{olefin}][H^+ClO_4^-][Li^+Cl^-] \end{aligned} \qquad (1)$$

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(13) The value of t-butyl chloride in 80% ethanol–water. See ref 7.

(14) A. Schlundt, *J. Phys. Chem.*, **5**, 503 (1901).

(15) Assuming the continuing linear relationship, the value of 7.7 was found using the relationship found earlier: $\Delta D/\Delta C = 1.2$; $(D_x - 4.2)/2.91 = 1.2$.

(16) For a good study on the comparison of dielectric constant with Y values, see I. Koppel and V. Palm, *Reakts. Sposobnost Org. Soedin.*, **4** (4), 892 (1967).

(17) (a) W. Gerrard and E. D. Macklen, *Chem. Rev.*, **59**, 1105 (1959); (b) K. Wickert, *Naturwissenschaften*, **26**, 500 (1938).

(18) (a) Y. Pocker and K. D. Stevens, *J. Am. Chem. Soc.*, **91**, 4205 (1969); (b) Y. Pocker, K. D. Stevens, and J. J. Champoux, *ibid.*, **91**, 4199 (1969).

(19) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *ibid.*, 87, 1700 (1965).

(20) (a) R. C. Fahey and M. R. Monahan, *Chem. Commun.*, 936 (1967); (b) R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, 2781 (1967).

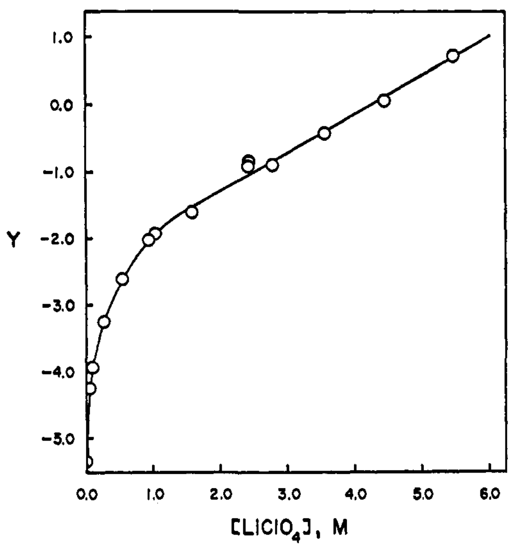

Figure 2. Plot of Y *vs.* the lithium perchlorate concentration.

These are interrelated by the equilibrium constant for the ionization of HCl in dilute LPDE solutions, $K_{\mathrm{eq\,HCl}}{}^{\mathrm{LiClO_4}} = [H^+ClO_4^-][Li^+Cl^-]/[HCl][Li^+ClO_4^-]$. In LPDE solutions of moderate concentration the order with respect to lithium perchlorate increases and the addition process can again be analyzed in terms of two routes, eq 2, which are interrelated by the

$$V_{-2} = k_{-2}[\text{olefin}][HCl][LiClO_4]^n$$

$$V_{-2}' = k_{-2}'[\text{olefin}][H^+ClO_4^-(Li^+ClO_4^-)_{n-m-1}] \times [Li^+Cl^-(Li^+ClO_4^-)_m] \qquad (2)$$

empirical expression

$$K_{\mathrm{eq\,HCl}}{}^{\mathrm{LiClO_4}} = \frac{[H^+ClO_4^-(LiClO_4)_{n-m-1}][Li^+Cl^-(Li^+ClO_4)_m]}{[HCl][LiClO_4]^n}$$

The addition of chloride ion as lithium chloride did not change the velocity of the addition (Table III) under conditions such that $[HCl]_{\mathrm{total}} = [HCl]_{\mathrm{free}}$ which is in complete agreement with the above scheme, eq 1.[21]

In pure ether the second HCl has the function of hydrogen bonding to the forming chloride ion, similar to its behavior in nitromethane. In LPDE solutions, $Li^+ClO_4^-$ ion pairs or higher aggregates can perform this function instead of the HCl[22] by stabilizing the Cl^- in the form of the triple ion, $Cl^-Li^+ClO_4^-$, the overall reaction being the formation of a quadruple ion intermediate, $(CH_3)_3C^+Cl^-Li^+ClO_4^-$. Perhaps the most exciting feature of this study is that the true catalytic nature of lithium perchlorate in diethyl ether was firmly documented. For the entire range of LPDE solutions used, we noted that the ratio k_f/k_r is constant ($k_f/k_r = 5.3 \pm 0.2 \times 10^{-5}$ M) and is independent of the lithium perchlorate concentration, confirming the true catalytic nature of LPDE solutions (Table III).

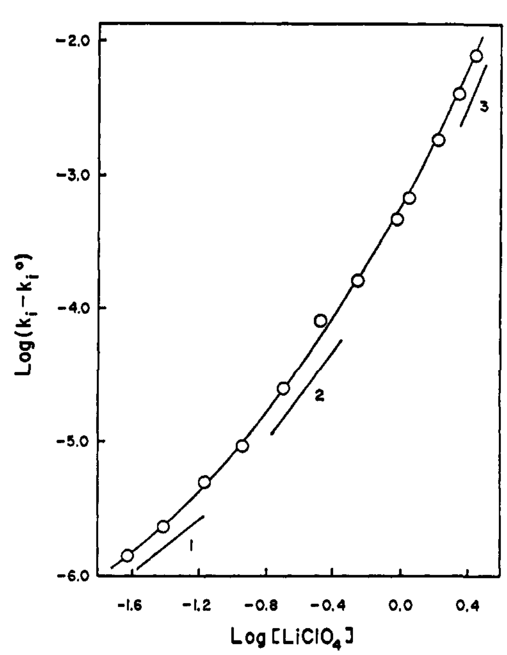

Figure 3. Plot of log (k_i − $k_i{}^\circ$) for **1** *vs.* log [LiClO$_4$].

Rearrangement of 1-Phenylallyl Chloride (1). The rearrangement of **1** to **2** was studied in the lithium perchlorate concentration range from 0.00 to 2.83 M and the values of the rate constant k_i are listed in Table IV. 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 $k_i{}^0 = 2.5 \times 10^{-7}$ sec^{-1} [23] are plotted against log [LiClO$_4$]. The order in [LiClO$_4$] is found to change from 1.0 to 3.0, Figure 3. The first-order rate constant for isomerization, k_i, was not affected by 160-fold excess of chloride ion over **1** as shown in Table V.

Table IV. Isomerization Rates of 1-Phenylallyl Chloride (**1**) in LPDE at 25.0° [a]

[LiClO$_4$], M	k_i, sec^{-1}	[LiClO$_4$], M	k_i, sec^{-1}
0.000	2.5×10^{-7} [b]	0.566	1.63×10^{-4}
0.0232	1.64×10^{-6}	0.967	4.64×10^{-4}
0.0387	2.60×10^{-6}	1.13	6.69×10^{-4}
0.0681	5.32×10^{-6}	1.70	1.86×10^{-3}
0.116	9.65×10^{-6}	2.27	4.04×10^{-3}
0.204	2.55×10^{-5}	2.83	7.84×10^{-3}
0.340	8.20×10^{-5}		

[a] [1-Phenylallyl chloride] = 9.50×10^{-5} M. [b] Extrapolated (ref 23).

Table V. Effect of Added LiCl on k_i[a]

10^3[LiCl], M	10^4k_r, sec^{-1}
0.00	4.61
1.48	4.69
4.46	4.63
14.8	4.64

[a] [1-Phenylallyl chloride] = 9.50×10^{-5} M, [LiClO$_4$] = 0.967 M at 25.0°.

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(21) In nitromethane (ref 8), Pocker found a decrease in the free HCl proportional to added NEt_4Cl and showed by ir measurements the formation of HCl_2^- ion. In LPDE solutions as in pure ether no ir frequencies associated with HCl_2^- ion were observed.

(22) Reference 18 shows that in nitromethane other hydrogen bonding substances such as phenol can take the place of the second HCl in hydrogen bonding to the forming chloride ion.

(23) Value extrapolated to pure ether ($Y = -5.36$) in Figure 4.

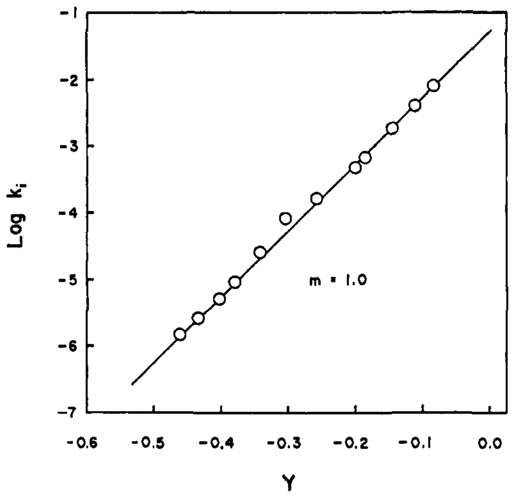

Figure 4. Plot of log k_i for **1** against Y, m = 1.0.

A plot of log k_i against Y deduced earlier for LPDE solutions is given in Figure 4. A linear plot of slope m = 1.0 is obtained. The intercept represents the value of k_i in pure ether. Valkanas and Waight[10a] have compared the rate constant for rearrangement of **1** at 25.0° in the dioxane–water range of 90–60% using the Y scale and also found a linear relationship of slope m = 1.0. The fact that LPDE solutions also gave a value of m = 1 shows LPDE solutions are consistent with the well-studied dioxane–water solutions.

We have previously reported[1] that the ionization rate constant of triphenylmethyl chloride (TCl) in LPDE solutions showed in the lower limit a second-order dependence on [$LiClO_4$]. Plotting log k_1 for the ionization of TCl against our Y scale for LPDE solutions gives a curved line. Here it should be noted that the limiting stoichiometric composition of the transition state associated with the ionization of TCl in LPDE solutions (<1 M) is TCl,2($Li^+ClO_4^-$). In general, when lithium perchlorate ion pairs or higher aggregates are participating in the ionization process of RX by multiple interaction mechanisms, a linear free energy relationship in terms of the Y values derived above would not be expected to hold. In this case, a more helpful approach is to delineate the catalytic efficiency of LPDE solutions in terms of extended parametric equations characterized by two or more interaction mechanisms. The applicability of such extended parametric equations to delineate electrostatic catalysis by ionic aggregates will be considered in future publications from this laboratory.

Electrolytic Oxidations of Organic Compounds.
II. N,N-Dimethylaminoalkenes[1]

John M. Fritsch,[2] Harold Weingarten, and James D. Wilson

Contribution from Monsanto Co., Central Research Department,
St. Louis, Missouri 63166. *Received August 18, 1969*

Abstract: Dimethylamino-substituted alkenes very readily undergo electrochemical oxidation, the multisubstituted examples being among the most easily oxidized neutral organic compounds known. Generally the initial oxidation products are the monocation radicals. Esr studies show that unpaired electrons polarize *away* from the dimethylamino groups in these species. Factors affecting the oxidation potentials of the aminoalkenes and the lifetimes and fates of the cation radicals produced are considered.

Many studies have been made of the electrooxidation of organic compounds,[3,4] but our understanding of this area is still far from perfect. The subject is complicated, largely because of the rapidity and complexity of reactions following the initial charge transfer. Recently several studies of general classes of compounds[3–7] have succeeded in establishing some of the basic features of electrooxidations, *e.g.*, that the initial step is a one-electron transfer, and what the effect of reactive-site blocking is on the lifetime of the radical cations. Developments in electroanalytical chemistry, both in theory and in technique, have greatly helped these studies.[3]

We have studied the chemical and electrochemical oxidations of a variety of dimethylamino-substituted alkenes (also called vinylamines or enamines) and report here in detail[1] the results of the electrochemical studies. The results of the chemical oxidations will be reported separately.[8]

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