Electrostatic Catalysis by Ionic Aggregates. III. The Isomerization of (−)-Menthone by Hydrogen Chloride and Perchloric Acid in Lithium Perchlorate–Diethyl Ether Solutions[1]

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Abstract: The acid-catalyzed isomerization of (−)-menthone (**1**) to (+)-isomenthone (**2**) was studied in ether and in lithium perchlorate–diethyl ether solutions (LPDE) at 25.0°. $Li^+ClO_4^-$ forms a complex with menthone ($K_1^{LiClO_4}$ = 7.3 ± 0.3 M^{-1}) which is stable with respect to the isomerization process indicating that the Li^+ is relatively ineffective as an electrophilic catalyst. In pure ether, HCl catalysis is first order in menthone but second order in acid, $k_3 = 1.63 \pm 0.02\ M^{-2}\ sec^{-1}$. In LPDE solutions, dissolved HCl is partially converted into Et_2OH^+, ClO_4^-, and Li^+Cl^- and the overall catalysis is the sum of two third-order kinetic terms, one first order in free menthone and second order in free HCl and the other first order in free menthone, Et_2OH^+, ClO_4^-, and Li^+Cl^-. The capacity of LPDE solutions to increase dramatically the ionization of hydrogen chloride is correlated here with the catalytic efficiency of both HCl and $HClO_4$ in the (−)-menthone (**1**) ⇄ (+)-isomenthone (**2**) equilibration.

In part I[4] of this series, we have shown that lithium perchlorate in diethyl ether (LPDE) has a striking capacity to assist the ionization of both triphenylmethyl chloride and hydrogen chloride. The enhanced ionization of HCl in LPDE solutions was characterized by an empirical mass-action expression represented by eq 1a, which, under limiting conditions

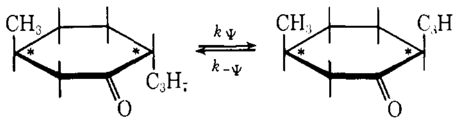
$$K_{HCl}^{LiClO_4} = \frac{[H^+ClO_4^-(Li^+ClO_4^-)_{n-m-1}][Li^+Cl^-(Li^+ClO_4^-)_m]}{[HCl][Li^+ClO_4^-]^n} \qquad (1a)$$

($[Li^+ClO_4^-]$ = 0.01–1.08 M), was identified with the equilibrium constant represented by eq 1b. In a

$$HCl + Li^+ClO_4^- \rightleftharpoons H^+ClO_4^- + Li^+Cl^-$$

$$K_{eq\,HCl}^{LiClO_4} = \frac{[H^+ClO_4^-][Li^+Cl^-]}{[HCl][Li^+ClO_4^-]} \qquad (1b)$$

subsequent paper, part II,[5] we have shown that the powerful catalytic efficiency of LPDE solutions manifests itself also in the addition of HCl to isobutene, a process involving a slow proton transfer in the rate-determining step. One of the many interesting properties of LPDE solutions which we have noted is the extraordinarily wide range of acidity which can be obtained in this system using dilute solutions of a relatively weak acid. Thus the striking catalytic effect of $Li^+ClO_4^-$ on the addition of various HX acids to olefins can be accommodated by the fact that LPDE solutions are capable of transforming relatively weak Brønsted acids into the strongly acidic $H^+(OEt_2)_n$, ClO_4^- ion pairs. The kinetics of (−)-menthone (**1**) ⇄ (+)-isomenthone (**2**) equilibration (eq 2) have been widely used to characterize general acid–base catalysis in nonaqueous solvents.[6–15] It appeared to us that this well-characterized isomerization would provide a good system for delineating the kinetic behavior of HCl in LPDE solutions. The present paper reports on such a kinetic study and enables us to characterize the catalytic species present in these media and to compare their effectiveness.



1 **2** (2)

Experimental Section

All materials and solutions were prepared and purified as previously reported[4] except (−)-menthone (**1**). **1** was prepared by the sodium dichromate oxidation of (−)-menthol,[16] bp 91–92° (11 mm), $[\alpha]^{25}{}_{5461\text{Å}}$ −22.8° (0.0893 g in 10 ml of ether).

Reaction solutions were prepared at the temperature of the thermostated bath, 25.00 ± 0.05°. A portion of the reaction mixture was placed in the jacketed cell of a Bendix automatic digital polarimeter, Model 965 with mercury lamp (5461 Å). Rotations were recorded as a function of time and the pseudo-first-order coefficients were determined in the usual way from final rotations after ten or more half-lives.

Anhydrous $HClO_4$ in Ether. $AgClO_4$ which had been dried for 24 hr at 160° (0.05 mm) was titrated using a very slight excess of dry HCl in ether. The AgCl precipitate was filtered and the trace amounts of HCl were removed by aspiration using a stream of *dry* nitrogen until the silver nitrate test proved negative. The anhydrous $HClO_4$ was determined by titration.

Results and Discussion

The isomerization of menthone is an equilibration (eq 2) and the polarimetric first-order specific rate

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

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[5] Part II: Y. Pocker and R. F. Buchholz, *ibid.*, **92**, 4033 (1970).

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[15] J. F. Bunnet and L. A. Retallick, *J. Amer. Chem. Soc.*, **89**, 423 (1967).

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Table I. Observed Isomerization Rate Constants, k_α, in LPDE Solutions[a]

$[Li^+ClO_4^-]$, M	[Menthone], M	$[HCl]_t$,[b] M	$[HCl]_f$,[c] M	$[H^+ClO_4^-]$,[d] M	$[Li^+Cl^-]$,[e] M	k_α,[f] 10^3 sec^{-1}
0.00	0.0573	0.465				3.45
	0.0573	0.424				2.89
	0.0458	0.424				2.92
	0.0344	0.424				2.93
	0.0229	0.424				2.94
	0.0573	0.253				1.07
	0.0573	0.0735				0.0876
0.0720	0.0573	0.640	0.638	1.60×10^{-3}		6.75
		0.362	0.361	1.21×10^{-3}		2.18
		0.230	0.229	9.55×10^{-4}		1.20
		0.135	0.134	7.35×10^{-4}		0.372
0.192	0.0573	0.384	0.382	2.26×10^{-3}		2.23
		0.186	0.184	1.58×10^{-3}		0.805
		0.0714	0.0705	9.70×10^{-4}		0.250
0.436	0.0573	0.416	0.413	4.31×10^{-3}		2.20
		0.339	0.335	3.86×10^{-3}		1.67
		0.222	0.219	3.13×10^{-3}		1.05
		0.0824	0.0806	1.88×10^{-3}		0.353
1.00	0.0573	0.428	0.418	9.60×10^{-3}		1.88
		0.211	0.203	6.70×10^{-3}		0.860
		0.0829	0.0787	4.16×10^{-3}		0.320
1.18	0.0573	0.394				1.69
	0.0286	0.396				1.70
	0.0191	0.393				1.69
	0.00573	0.400				1.67
1.30	0.0573	0.403	0.395	7.50×10^{-3}	2.15×10^{-2}	1.52
		0.250	0.245	5.10×10^{-3}	1.91×10^{-2}	0.885
		0.154	0.151	3.50×10^{-3}	1.75×10^{-2}	0.558
		0.0748	0.0730	1.80×10^{-3}	1.58×10^{-2}	0.253
1.52	0.0573	0.449	0.433	1.56×10^{-2}		1.79
		0.265	0.253	1.19×10^{-2}		0.985
		0.124	0.116	8.05×10^{-3}		0.437
2.08	0.573	0.412	0.386	2.64×10^{-2}		1.60
		0.205	0.186	1.84×10^{-2}		0.725
		0.0803	0.0691	1.12×10^{-2}		0.260
2.64	0.0573	0.0103	0.0103	3.8×10^{-3}	1.51×10^{-2}	0.0403
3.48	0.0573	0.495	0.385	1.12×10^{-1}		2.12
		0.324	0.237	8.71×10^{-2}		1.31
		0.164	0.100	5.70×10^{-2}		0.526

[a] At 25.0°. [b] Total dissolved HCl. [c] Free HCl concentration calculated using the equilibrium constant for the lithium perchlorate assisted ionization of HCl (see ref 4). [d] The perchloric acid concentration, $[HClO_4]$, was calculated from data reported for eq 1a and 1b in ref 4. [e] The Li^+Cl^- concentration is the same as the $H^+ClO_4^-$ concentration unless otherwise stated. In some cases additional Li^+Cl^- was introduced. [f] $k_\alpha = (2.3/t) \log [(\alpha_e - \alpha_o)/(\alpha_e - \alpha_t)$.

coefficient, k_α, is actually the sum of the forward and reverse specific rate coefficients, $k_\alpha = k_\psi + k_{-\psi}$. The equilibrium mixture in ether consists of about 70% **1** and 30% **2** which makes the equilibrium constant, $K_{eq} = k_\psi/k_{-\psi} = 2.3$.[17] This enables one to separate k_α into the forward, $k_\psi = k_\alpha/[1 + (1/K_{eq})]$, and the reverse specific rate coefficient, $k_{-\psi} = k_\alpha/(1 + K_{eq})$. In accord with general custom we have treated our data in terms of k_α, always keeping in mind the more complex nature of this constant.[15] Fundamental to this simplifying treatment is the fact that in ether the ratio $k_\psi/k_{-\psi}$ is independent of salt or acid concentration indicating that the association constant between menthone and salt or acid is practically the same as that between isomenthone and the respective salt or acid.[14]

There is a strong indication from the kinetic data presented in this paper that the HCl-catalyzed menthone equilibration follows third-order kinetics in ether, $V = k_3[HCl]^2[M]_f$, with $k_3 = 1.62 \pm 0.02 \times 10^{-2}\ M^{-2}$ sec^{-1} at 25.0° (Table I). This value is in close agreement with the value of $1.3 \times 10^{-2}\ M^{-2}$ sec^{-1} reported by Weissberger[11] for a 0.5 M menthone and 0.05 M HCl solution in ether at 20°. It appears from earlier studies that molecular HCl forms a complex with menthone (eq 3) in a preequilibrium step. This must be followed by a rate-determining attack on the complex by a second HCl molecule which acts on the one hand

$$M + HCl \overset{K_1^{HCl}}{\rightleftharpoons} M \cdot HCl \tag{3}$$

as a proton abstractor from carbon and on the other as a chloride ion abstractor from the M·HCl complex. This mechanistic interpretation accords with the kinetic behavior reported by earlier workers.[6-14] The specific rotation of the menthone–acid complex is different from that of pure menthone and the equilibrium constants for the formation of the complex in a given solvent are generally deduced from a comparison of polarimetric readings at time zero of menthone solutions in the presence of HCl and in its absence. Weissberger[12] reported a value for the equilibrium constant of about 15 M^{-1} at 20° in benzene while Stevens[14]

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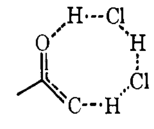
(17) For discussion of the conformations of **1** and **2** and the effect on the stability of the equilibrium between the two epimers, see C. Djerassi, P. A. Hurt, and C. Beard, *J. Amer. Chem. Soc.*, **86**, 85 (1964). They show K_{eq} ($1 \rightleftharpoons 2$) is approximately independent of solvent with the equilibrium mixture containing 70% **1** and 30% **2**. See also J. Osiecki, Ph.D. Thesis, Stanford University, 1960. B. Rickborn [*J. Amer. Chem. Soc.*, **84**, 2414 (1962)] reports K_{eq} ($1 \rightleftharpoons 2$) = 2.44 ± 0.04 (25°) which gives 70.9 ± 0.3% **1** at equilibrium. Reference 14 reports 65% **1** and 35% **2** at 25° and 70% **1** and 30% **2** at 0° in nitromethane.

found a value of 9.2 ± 0.5 M^{-1} at 25° in nitromethane. In ether, the value of K_1^{HCl} (eq 3) is not known, but it must be small (<0.1 M^{-1}) because solutions containing both menthone and HCl had at time zero the same rotation as the control solutions containing pure menthone in ether. In fact, at constant menthone concentration, both the initial and final rotations were found to be approximately independent of acid concentration indicating that the equilibrium constant for the formation of the isomenthone·HCl complex, K_2^{HCl}, is also small (<0.1 M^{-1}). The low value for K_1^{HCl} in ether is due to the much higher concentration of ether molecules coupled with the fact that ether is also a slightly better base than menthone with regard to HCl.[18] Weissberger[10a] found earlier that ether added to a CCl_3COOH solution in benzene reduced the rate of isomerization of menthone which he likewise attributed to the higher basicity of ether. The kinetic results do not define the form in which HCl enters the rate expression but they do define the stoichiometry of the activated complex as M·2HCl. The fact that the rate constant, k_3, is relatively unaffected by the activity of the ether or by salt concentration as will be shown later in Table V suggests to us a transition state which can be represented by **3**.



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Menthone (**1**) did not isomerize when placed in LPDE solutions containing up to 3 M lithium perchlorate. Also, a 1.85 M $LiClO_4$ solution, containing 0.06 M menthone and 7.1 × 10^{-3} M LiCl, remained unchanged after 20 hr. However, the observed rotations of **1** in LPDE, α_{obsd}, became more positive as the concentration of lithium perchlorate was increased (Table II), allowing us to calculate an equilibrium constant, $K_1^{LiClO_4} = 7.3 \pm 0.3$ M^{-1}, for the reaction represented by eq 4.

Table II. The Equilibrium Constant for the Formation of the Menthone–$LiClO_4$ Complex at 25.0° [a]

$[LiClO_4]$, M^b	α_{obsd},[c] deg	$K_1^{LiClO_4}$, M^{-1}
0.00	−0.0204	
0.083	−0.0172	6.5
0.19	−0.0148	6.9
0.192	−0.0146	7.4
0.40	−0.0126	7.5
0.436	−0.0123	7.2
0.69	−0.0115	7.6
0.84	−0.0112	7.6
1.68	−0.0104	7.5
2.26	−0.0103	7.4

[a] Total menthone concentration was kept at 0.0573 M. [b] Total $LiClO_4$ added. [c] α_{obsd} for 0.0573 M M·$LiClO_4$ complex is −0.0097°. $[\alpha]^{25}{}_{5461\text{Å}}$ −6.5° for M·$LiClO_4$.

$$M + LiClO_4 \underset{}{\overset{K_1^{LiClO_4}}{\rightleftharpoons}} M\cdot LiClO_4 \qquad (4)$$

In ether, the velocity of the $HClO_4$ catalyzed menthone isomerization was found to be first order in both menthone and $HClO_4$, *i.e.*, $V = k_2[M]_f[HClO_4]_t$ with $k_2 = 0.26$ M^{-1} sec^{-1} at 25.0° (Table III). Also, at constant menthone concentration, the initial and final rotations of the reaction mixture were, within experimental error, independent of $HClO_4$ concentration indicating that the equilibrium constant characterizing the M·$HClO_4$ complex formation, eq 5, must have a small

$$K_1^{LiClO_4} = [M\cdot LiClO_4]/[M][LiClO_4] \qquad (5)$$

value in ether. Since the catalytic constant for $HClO_4$ is defined as $k_2 = V_\alpha/[HClO_4]_f[M]_f$ and under our conditions $[HClO_4]_t = [HClO_4]_f$ and the ratio $[M]_t/[M]_f$ is very near unity, it is not surprising that $k_2 \simeq k_\alpha/[HClO_4]_t = 0.26$ M^{-1} sec^{-1} at 25.0°.

Table III. $HClO_4$ Catalysis of the Menthone Isomerization[a]

$[LiClO_4]$, M	$[HClO_4]$ × 10^2, M	[Menthone] × 10^2, M	$k_\alpha{}^b$ × 10^3, sec^{-1}	$k_\alpha/[HClO_4]_t$ × 10, M^{-1} sec^{-1}
0.00	1.45	5.73	3.70	2.6[c]
0.00	1.47	2.87	3.80	2.6[c]
0.00	1.44	11.5	3.45	2.4[c]
0.00	4.27	5.73	11.0	2.6[c]
0.204	1.41	5.73	1.90	1.3
0.202	4.35	5.73	5.55	1.3
0.200	1.44	5.73	1.90	1.3
0.204	1.43	1.15	1.85	1.3
0.556	1.41	5.73	0.755	0.53
0.940	1.46	5.73	0.330	0.23
2.62	1.41	5.73	0.0187	0.013

[a] At 25.0°. [b] $k_\alpha = k_\psi + k_{-\psi} = (2.3/t)\log[(\alpha_e - \alpha_o)/(\alpha_e - \alpha_t)]$. [c] $k_\alpha/[HClO_4]_t = k_2$ since $[M]_t \cong [M]_f$ and $[HClO_4]_t \cong [HClO_4]_f$.

In LPDE solutions k_α is still first order in total $HClO_4$ concentration but the ratio $k_\alpha/[HClO_4]_t$ decreases with increasing lithium perchlorate concentration from its value in ether (0.26 M^{-1} sec^{-1}) down to a value 200 times lower (0.0013 M^{-1} sec^{-1}) in the presence of 2.6 M $LiClO_4$. The decrease in the value of this ratio with increasing lithium perchlorate concentration requires an explanation. While k_α is experimentally deduced in terms of the total menthone concentration,[19] the correct rate expression in terms of primary steps involves the free menthone concentration.[20] In the presence of $HClO_4$ alone, we have noted above that $[M]_t \cong [M]_f$; however, this is not so in the presence of $LiClO_4$. Here account must be taken of the fact that the menthone·$LiClO_4$ complex is inactive with regard to the isomerization process. Equation 6 gives the relationship between total and free menthone and allows the evaluation of the catalytic rate constant of $HClO_4$ in LPDE solutions (Table IV).

$$k_2 = (k_\alpha/[HClO_4]_t)(1 + 7.3[LiClO_4]_f)$$

$$[M]_t = [M]_f + [M\cdot LiClO_4] = [M]_f(1 + 7.3[LiClO_4]_f) \qquad (6)$$

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[18] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223 (1963).

[19] The change in the total observed rotation, α, allows calculation of the pseudo-first-order rate constant

$$k_\alpha = \frac{2.3}{t}\log\frac{\alpha_e - \alpha_o}{\alpha_e - \alpha_t}$$

where α_e is the observed equilibrium rotation, α_o is the observed initial rotation, and α_t is the rotation at time t.

[20] For a more extensive mathematical treatment of the kinetics, see ref 9. Weissberger shows that the rate which is observed and the rate from primary steps can be written as

$$k_\alpha[M]_t = k[M]_f[A][B]$$

where [A] and [B] are the concentrations of the acid and base, respectively.

Table IV. Evaluation of k_2[a]

[LiClO$_4$], M	k_2, M^{-1} sec^{-1}
0.00[b]	0.26
0.20[b]	0.26
0.56	0.25
0.94	0.17
2.6	0.026

[a] $k_2 = k_\alpha(1 + 7.3[LiClO_4]_f)/[HClO_4]_f$ where $[LiClO_4]_f$ stands for the concentration of free salt calculated from eq 4. [b] Average value of $k_\alpha/[HClO_4]_f$ is used in these calculations (Table III).

At low concentrations of $Li^+ClO_4^-$ (<0.56 M), k_2 is approximately constant and has the same value as that found in pure ether (0.26 M^{-1} sec^{-1}). However, this value is seen to decrease at higher salt concentrations so that in the presence of 2.6 M $Li^+ClO_4^-$, k_2 has one-tenth of its value in pure ether.

A prime factor, which may account for this reduction, is the fact that the rate-determining step for the enolization involves the abstraction of a carbon bound proton by a general base. In LPDE solutions, the most prevalent base is the ether molecule itself. We know, however, from our earlier studies,[1a] that the concentration of free ether molecules is significantly reduced as the concentration of $Li^+ClO_4^-$ increases. This arises from the fact that each lithium ion binds at least two ether molecules. In a 0.2 M lithium perchlorate solution, there are about 48 ether molecules available to solvate each lithium ion. If two ether molecules are removed in this solvation process we are left with 46 free ether molecules; *i.e.*, *ca.* 98% of the original ether molecules are still free to act as proton abstractors. In contrast, at 2.6 M lithium perchlorate, there are only, on the average, 3.5 ethers available to solvate each lithium ion; removing two for solvation leaves, on the average, 1.5 ether molecules to act as base. We also know from our earlier studies[1a] that strong electrostatic fields are operative in such media which further reduce the freedom or activity of the remaining unbound 3.6 M ether. These factors appear to accommodate the tenfold decrease in k_2 noted in Table IV.[21]

The isomerization of (−)-menthone (**1**) in LPDE solutions with added HCl at 25.0° is first order in menthone but no longer second order in HCl concentration as found in pure ether. The order in free HCl, found by plotting log k_α against log $[HCl]_f$, decreased from a value of 2 in pure ether down to a threshold value close to 1 in 1 M lithium perchlorate.[22] *A priori*, one would anticipate that the catalytic behavior of HCl in LPDE would be the sum of two terms, one representing a concerted catalysis by two HCl molecules and the other representing catalysis by $H^+ClO_4^-$ with ether acting as general base. We note, however, that the LPDE-catalyzed ionization of HCl produces equal amounts of both $H^+ClO_4^-$ and Li^+Cl^-. In view of the need for a general base in the enol-forming step, we would expect Li^+Cl^- also to function in this capacity. The fact that hydrogen chloride is present in ethereal solutions largely in its molecular form, HCl, rather than as Et_2OH^+, Cl^-, implies that Cl^- is a much stronger base than ether. Indeed, we find that the specific rate coefficient, k_α, for HCl catalysis in LPDE solutions is well represented by eq 7. This equation takes into

$$k_\alpha = \frac{k_3^*[H^+ClO_4^-][Li^+Cl^-] + k_3[HCl]_f^2}{1 + 7.3[Li^+ClO_4^-]} \qquad (7)$$

account catalysis by two terms and also includes a correction for the free menthone concentration.[23]

Equation 7 can be expressed in terms of $[Li^+ClO_4^-]$ and [HCl] using the reactions given in eq 1a and 1b. With these substitutions, k_α can be treated as the sum of two components, one first order in HCl and the other second order in HCl, leading to eq 8a which, under limiting conditions, $[Li^+ClO_4^-] \leqslant 1$ M, becomes eq 8b.[24] For any given concentration of lithium

$$k_\alpha = \frac{k_3^* K_{HCl}{}^{LiClO_4}[Li^+ClO_4^-]^n[HCl]_f + k_3[HCl]_f{}^2}{1 + 7.3[Li^+ClO_4^-]} = \frac{k_2^*[HCl]_f + k_3[HCl]_f{}^2}{1 + 7.3[Li^+ClO_4^-]} \qquad (8a)$$

$$k_\alpha = \frac{k_3^* K_{eq\,HCl}{}^{LiClO_4}[LiClO_4][HCl]_f + k_3[HCl]_f{}^2}{(1 + 7.3[LiClO_4])} \qquad (8b)$$

perchlorate and varying HCl, the plot of the ratio

$$k_\alpha(1 + 7.3[LiClO_4])/[HCl]_f$$

against $[HCl]_f$ was found to be linear with an intercept, k_2^*, and a slope, k_3. More than 40 kinetic runs were analyzed by this method[24] and the values deduced for k_2^*, k_3^*, and k_3 are reported in Table V. It will be noted that over the entire range of lithium perchlorate concentrations studied, k_3 is a constant, and has a value identical with that reported above for HCl in pure ether. On the other hand the catalytic coefficient, k_3^*, decreases *ca.* 120-fold as we change from dilute to 3.48 M $Li^+ClO_4^-$.

Table V. Calculated Values of k_2^*, k_3^*, and k_3[a]

[LiClO$_4$], M	k_2^*, M^{-1} sec^{-1}	k_3^*,[b] M^{-2} sec^{-1}	k_3,[c] M^{-2} sec^{-1}
0.000			0.0162[d]
0.072	2.0×10^{-3}	500	0.016
0.192	6.5×10^{-3}	490	0.016
0.436	1.5×10^{-2}	330	0.015
1.00	3.1×10^{-2}	140	0.014
1.30	3.4×10^{-2}	84[e]	0.016
1.52	3.9×10^{-2}	70[e]	0.016
2.08	5.8×10^{-2}	32[e]	0.016
3.48	1.4×10^{-1}	4.4[e]	0.016

[a] At 25.0°. [b] $k_3^* = k_2^*/K_{eq\,HCl}{}^{LiClO_4}[LiClO_4]$ where values of $K_{eq\,HCl}{}^{LiClO_4}[LiClO_4]$ can be found in part I[4] of this series. [c] Slope from the plot of $k_\alpha(1 + 7.3[LiClO_4])/[HCl]_f$ against $[HCl]_f$. [d] Value found in pure ether (Table I). [e] When $[LiClO_4] > 1$ M, $k_3^* = k_2^*/K_{HCl}{}^{LiClO_4}[LiClO_4]^n$ where values for $K_{HCl}{}^{LiClO_4}[LiClO_4]^n$ can be found in part I[4] of this series.

Accepting the minimum stoichiometric composition of the activated complex associated with k_3^* as (Li^+Cl^-, M, $H^+ClO_4^-$)‡, we note that the rate-determining step

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(21) Accepting the stoichiometric composition of the activated complex as (Et_2O, M, $HClO_4$), a more quantitative treatment would be to replace γ_{Et_2O} by the ratio of the activity coefficients between the ground state and the transition state, $\gamma_{Et_2Of}\gamma_{Mf}\gamma_{HClO_4f}/\gamma_{\ddagger}$.

(22) Above this concentration of lithium perchlorate, the order in $[HCl]_f$ rises slightly with increasing $[Li^+ClO_4^-]$.

(23) If $K_1{}^{HClO_4}$ or $[HClO_4]$ were large enough, eq 6 would have required the added term, $K_1{}^{LiClO_4}[HClO_4]$.

(24) Values of $K_{eq\,HCl}{}^{LiClO_4}[LiClO_4]$ are found in part I of this series.[4] When $[LiClO_4] > 1$ M, this term is replaced by an empirical mass-action expression $K_{HCl}{}^{LiClO_4}[LiClO_4]^n$ (see eq 1a) values of which are also reported in part I of this series.

in the enolization process is accompanied by a formal charge neutralization similar to that reported in part I[4] for the recombination of the trityl ion with chloride ion in LPDE solutions. Our earlier data[4] show that the

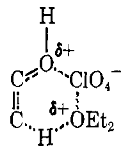
$$\mathrm{Li^+, Cl^- + MH^+, ClO_4^- \xrightarrow{R.D.} HCl + Li^+, ClO_4^- + enol} \quad \text{(i)}$$

$$\mathrm{Li^+, Cl^- + (C_6H_5)_3C^+, ClO_4^- \xrightarrow{R.D.} (C_6H_5)_3CCl + Li^+, ClO_4^-} \quad \text{(ii)}$$

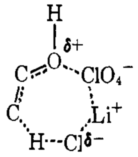
rate coefficient for step ii decreases *ca.* 100-fold on going from dilute to 3 M $\mathrm{LiClO_4}$ and it is consequently not surprising that a similar reduction in rate was noted for reaction i. Account being taken of the equilibrium given by eq 1, one might expect the contribution of the kinetic term, $k_3^*[\mathrm{HClO_4}][\mathrm{LiCl}]$, to increase with $[\mathrm{LiClO_4}]$ whereas that of the term $k_8[\mathrm{HCl}]^2$ to decrease. This prediction is amply confirmed by the observation that in ether containing HCl, d log k_α/d log [HCl] = 2, whereas a limiting threshold order of 1 in HCl is found for ethereal solutions containing around 1 M $\mathrm{LiClO_4}$.

The kinetic base strength of a lithium chloride ion pair relative to an ether molecule was deduced from the ratio, at low salt concentrations, of k_3^* to $k_2/[\mathrm{Et_2O}]$. It appears that with respect to the enolization step, $\mathrm{Li^+Cl^-}$ ion pairs are 2×10^4 more effective as bases than ether molecules.

We visualize the activated complex in the $\mathrm{H^+ClO_4^-}$-catalyzed menthone isomerizations in terms of an enolization of $\mathrm{MH^+ClO_4^-}$ ion pairs assisted by general base **B** as represented in **4a** and **4b**. The respective complexes with **B** = $\mathrm{Et_2O}$ (**4a**) and with **B** = $\mathrm{Li^+Cl^-}$ (**4b**) involve a much higher degree of charge separation than the concerted enolization process represented by **3**. This difference in the behavior of the two acids is not surprising inasmuch as the dominant form of HCl in ether is $\mathrm{Et_2O \cdots HCl}$ whereas that of $\mathrm{HClO_4}$ is $\mathrm{Et_2OH^+\text{-}ClO_4^-}$.



4a



4b

In the present work we have shown that lithium perchlorate alone is not an effective catalyst for the isomerization of menthone in ether. Nevertheless, its presence in LPDE solutions is of considerable importance in interpreting acid catalysis in these media. For a fuller understanding of its behavior a number of effects have been considered. (a) $\mathrm{Li^+ClO_4^-}$ powerfully promotes the ionization of HCl by partially converting it to $\mathrm{H^+ClO_4^-}$ and $\mathrm{Li^+Cl^-}$ (eq 1). The term $k_2[\mathrm{H^+ClO_4^-}][\mathrm{Li^+Cl^-}][\mathrm{M}]_f$ was found to be the dominant contributor to the overall rate of acid catalysis when HCl is dissolved in LPDE solutions (Table V). (b) $\mathrm{Li^+ClO_4^-}$ forms a complex with menthone, $K_1^{\mathrm{LiClO_4}} = 7.3 \pm 0.3\ M^{-1}$ (Table II), thereby reducing the concentration of free menthone (eq 6). (c) The salt also decreases the concentration and activity coefficient of free ether molecules in solution. The overall factor is as high as 10 in the presence of 2.6 M $\mathrm{LiClO_4}$ (Table IV and related discussion). (d) Electrostatic charges imbedded in a hydrophobic environment are conducive to complex formation (as shown here with $>\mathrm{C{=}O \cdots M^+, X^-}$) and are also capable of producing large rate accelerations (as shown in part I[4] and part II[5] in this series) and can therefore be of value as models of certain enzymatic processes in which stabilization by ion pairs plays an important role.[25]

(25) D. E. Koshland, Jr., and K. E. Neet, "Annual Review of Biochemistry," Vol. 37, P. D. Boyer, Ed., Annual Reviews, Inc., Palo Alto, Calif., 1968, p 369.