Note

Kinetics of elimination reactions of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in acetonitrile

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1-Chloro-1-(4-methoxyphenyl)-2-phenylethane undergoes dehydrochlorination in acetonitrile to give *trans-p*-methoxy stilbene by E1 mechanism. The presence of electron donating *p*-methoxy group and the delocalisation of charge throughout the structure proposes a stable cation. The mass law effect and special salt effect are characteristic for a reaction involving the stable cation and these effects have been reported for the first time in a pure E1 reaction.

Solvolytic substitution reactions of cumyl chloride in aqueous organic solvents is characterised by its transition state stability by the formation of delocalized carbocation via resonance stabilization through π-bonds of benzene ring[1-4]. In our previous paper we reported the elimination of HCl from cumyl chloride by E1 mechanism in acetonitrile[5]. A properly oriented secondary system, 1-chloro-1-(4-methoxyphenyl)-2-phenylethane (1-*p*-anisyl-2-phenylethyl chloride-APEC), which can be stabilized by electron donation of the *p*-methoxy group and extended system of conjugation can behave similar to cumyl chloride in elimination reactions. It has been shown that the salts effect of cumyl chloride in solvolytic reaction is similar to secondary system, *p*-anisyl 2,2-dimethyl butyl chloride[6,7].
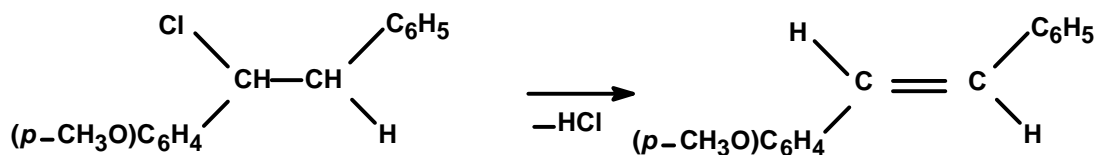
Results and Discussion

Rates of dehydrochlorination of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in pure acetonitrile were determined spectrophotometrically by studying the product peak. Unlike cumyl chloride[5] no backward reaction resulting an equilibrium state was observed. A cent percent elimination resulting the formation of *trans-p*-methoxy stilbene was noted (**Scheme I**). Like cumyl chloride there was no substitution reaction by acetonitrile[5,8]. The kinetic parameters at 25°C are given in **Table I**. These values are very similar to the corresponding values for cumyl chloride[5] and are characteristic for a unimolecular reaction.

The rate measurements were also carried out in the presence of added pyridine (a weak base). In the dehydrohalogenation studies of cumyl chloride pyridine is added to prevent the back addition of HCl to the nacent olefin. For the present substrate such back addition is not observed. If the elimination reaction has some bimolecular components in solvent acetonitrile, the better base pyridine can abstract the proton, then one would expect a change in the rate of reaction. Data in **Table II** show that added pyridine has practically no effect on the rate of elimination. Hence a unimolecular mechanism E1 ($D_N + A_N D_E$)[9] is suggested for the dehydrochlorination reaction of 1-chloro-1-(4-methoxyphenyl)-2-phenyle-thane. If unimolecular elimination operates an increase in elimination is expected in more polar solvent. Kinetic parameters in **Table I** showed that the rate of elimination reaction in dimethyl sulphoxide (DMSO) is more than 10 times than that in acetonitrile (dielectric constants of acetonitrile and DMSO are 35.94 and 46.45 respectively).

One of the strong evidence in favour of carbocation mechanism in nucleophilic substitution reaction (S_N1) is the observation of a mass law effect[10,11]. For E1 elimination reaction also a mass-law effect is possible, since a carbocation is involved in the rate-determining step; but it has not yet reported. An essential condition to show mass-law effect is the stability of the formed carbocation. The *p*-methoxy group and the extended conjugation throughout the two-phenyl rings can cause a good deal of stability to the carbocation intermediate for this substrate. The effect of added tetramethylammonium chloride (TMAC) on the rate of elimination of hydrogen chloride is presented in **Table II**. The reduction rate

Scheme I — Dehydrohalogenation of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane

Table I — Kinetic data for the elimination of hydrogen chloride from 1-chloro-1-(4-methoxyphenyl)-2-phenylethane

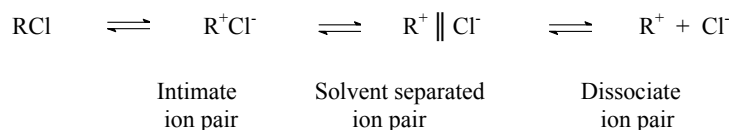| Solvent	Temp °C	$10^5 k_1 s^{-1}$	$10^5 k_1 s^{-1}$ at 298K	$\Delta H^{\neq} 298K$ kJ mol^{-1}	$-\Delta S^{\neq} 298K$ J mol^{-1} K^{-1}	$\Delta G^{\neq} 298K$ kJ mol^{-1}
CH$_3$CN	24.0	1.08				
	35.0	3.39				
	40.0	5.42	1.22	74	90	101
	50.0	13.1				
DMSO	19.0	8.10				
	23.2	11.5				
	35.0	34.8	14.0	59	137	99
	41.2	57.0				

Table II — Effect of added base (pyridine) and salts on the rate of dehydrochlorination of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane in acetonitrile at 40.0°C

[substrate] = 10^{-8} mol dm^{-3}

[Base/Salt] mol dm^{-3}	Pyridine 10^5 k$_1$ s^{-1}	LiClO$_4$		TMAC	
		10^5 k$_1$ s^{-1}	% variation	10^5 k$_1$ s^{-1}	% variation
Nil	5.42	5.42	—	5.42	—
0.005	—	7.80	44	5.12	-5
0.010	5.46	8.25	52	4.98	-8
0.020	5.39	8.87	64	4.52	-16
0.030	5.52	9.44	74	4.14	-23
0.050	5.44	10.9	101	3.44	-36
0.075	5.49	12.6	132	--	--

due to added TMAC is substantial. A concentration of 0.03 M gave a rate reduction of 23%. In acetonitrile if mass law effect is absent, an increase in rate of elimination is expected due to ionic strength effect. The complications due to salt induced medium effects[12] that are common in mixed solvents will be absent in acetonitrile. The mass law constant ($\alpha = k_{-1}/k_2$) computed by the method given by Zuman and Patel[13] give a value 11 which is substantial in comparison with the mass law constants reported for similar systems in solvolytic reactions[7].

E1 reactions can involve ion pairs, just as is true for S$_N$1 reactions[8,14]. Meng et. al.[8] suggested strong charge-dipole interactions between the carbocation and acetonitrile. For a stable carbocation in strongly interactive medium the solvent separated ion pair

formation is favoured (**Scheme II**). The effect of added LiClO$_4$ showed that the special salt effect is operative (**Table II**). With added LiClO$_4$, an initial steep rate acceleration that then decreased to the normal linear rate acceleration above 0.005 M salt concentration. Extrapolation of the linear portion of the curve to zero salt concentration gives a value of the rate constant (k^o_{ext}) which is more than the measured value (k^o_t) under identical conditions without added salt. The value for the rate ratio (k^o_{ext}/k^o_t) obtained was 1.39. This typical behaviour of initial rate acceleration followed by linear rate acceleration is called the special salt effect. This is due to the interaction of perchlorate ion with the solvent separated ion pair to give R$^+$ ‖ ClO$_4^-$ which being unstable under these conditions, goes to the products.

$$RCl \quad \rightleftharpoons \quad R^+Cl^- \quad \rightleftharpoons \quad R^+ \parallel Cl^- \quad \rightleftharpoons \quad R^+ + Cl^-$$

Intimate	Solvent separated	Dissociate
ion pair	ion pair	ion pair

Scheme II — Intermediates in the S_N1 solvolysis reaction

The stable carbocation formed during the elimination reaction is free to rotate, before going to product it take the required geometry for the formation of the most stable product. Thus no matter what the geometry of the original compound is, the more thermodynamically stable *trans* product predominates. Moreover in elimination reactions the solvent–separated ion pair prefers *trans* product[15]. The dehydrochlorination reaction of 1-chloro-1-(4-methoxyphenyl)-2-phenylethane forming *trans–p*-methoxy stilbene in acetonitrile follows E1 mechanism with the formation of ion pair intermediates.

Materials and Methods

1-(4-Methoxyphenyl)-2-phenyl ethanol was prepared by the grignard reaction of benzyl magnesium chloride with an etheral solution of *p*-anisaldehyde. The ether layer was separated, washed with sodium carbonate solution followed by water. It was dried over anhydrous sodium sulphate. The solvent was distilled off and the residual material is fractionally distilled under reduced pressure. The fraction boiling between 139-141°C at 38 mm. Hg pressure was collected. Repeated crystallization from *n*-hexane-benzene mixture gave the alcohol. The purity of the alcohol has been tested by TLC and m.p., 58°C (ref.16) and the structure was confirmed by NMR spectra. The alcohol is converted to 1-chloro-1-(4-methoxyphenyl)-2-phenylethane by treatment with thionyl chloride.

The rate of reaction is monitored by measuring the product peak due to the formation of *trans-p*-methoxy stilbene[17] spectrophotometrically (Hitachi 220A) at 325 nm. No peak due to *cis-p*-methoxy stilbene is observed in UV spectrum. The product analysis by NMR in CD_3CN confirmed that the only product in the reaction is *trans-p*-methoxy stilbene.

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