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VINYLIC CATIONS FROM SOLVOLYSIS. VI. CIS-TRANS ISOMERIZATION AS A TOOL FOR STUDYING VINYL CATION FORMATION

Zvi Rappoport and Yitzhak Apeloig

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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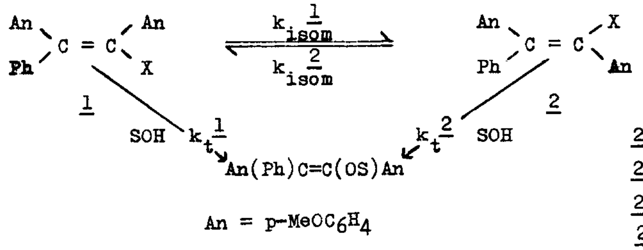
An important tool for investigating the nature and distribution of the cationic intermediates in solvolysis is the comparison of various rate coefficients connected with that for the ionization process.[1] Of these only titrimetric (k_t)[2] and exchange (k_{ex})[3] rates were used in vinylic systems. Racemization (k_{rac}) and polarimetric (k_{α}) rate coefficients cannot usually[4] be determined for planar vinylic systems. We suggest therefore the use of the analogous rate coefficient for the cis-trans isomerization (k_{isom}) of vinylic substrates for studying ion-pair phenomena in vinylic systems and the formation of vinyl cations under non-solvolytic conditions.

In vinyl halide derivatives having vinylic or allylic hydrogens cis-trans isomerization can occur by a variety of mechanisms, e.g., via prototropy, α,β - or β,γ - "elimination-addition", consecutive S_N2' reactions or via "addition-elimination" routes.[5] This communication describes the solvolysis and the accompanying cis-trans isomerization (eqn. 1) of cis- (1) and trans-(2) 1,2-dianisyl-2-phenylvinyl halides,[6] in which most of the above routes are blocked, and suggests the use of some criteria which help to establish the connection between the isomerization and the ionization processes.



(1)

1-Br , X=Br
1-Cl , X=Cl
1-OAc, X=OAc
1-H , X=H

2-Br , X=Br
2-Cl , X=Cl
2-OAc, X=OAc
2-H , X=H

Solvolysis of 1-Cl, 1-Br and 2-Br was followed titrimetrically or potentiometrically and the isomerization was followed by infra-red method.

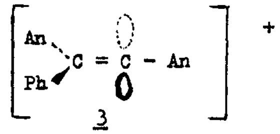
In 80% EtOH (containing NaOH) the solvolysis of 1-Br and 2-Br gives constant k_t and is accompanied by a slower cis-trans isomerization. Since the 1-Br $\rightleftharpoons$ 2-Br equilibrium was not established during the solvolysis, the value of the equilibrium constant in AcOH was used and from it the observed k_{isom} ($=k^{1}_{isom} + k^{2}_{isom}$) was found to be approximately equal to k_t. Earlier work[6,7] on this system and the data of the Table are in line with the S_N1 mechanism and since solvolysis via a dissociated cation should show common-ion rate depression[8] it followes that a substantial fraction of the formed ions return with isomerization from the ion-pair stage.

In acetolysis (in the presence of NaOAc) k_t decreases during a run, e.g., with 0.044M of 1-Br and 0.087M of NaOAc, the rate coefficient after two half-lives ($k_t^{75\%}$) is only 14% of the extrapolated initial value(k_t^{o}). This is ascribed to a common ion rate depression by the formed bromide ion and a plot of $1/k_t$ vs. the $[Br^-]/[OAc^-]$ ratio is linear as required by eqn. 3 which is derived from eqn. 2 where 3 is the dissociated vinyl cation. The

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^- + R^+ \xrightarrow{k_2\ ,\ OAc^-} ROAc \qquad (2)$$

$$1/k_t = 1/k_1 + (k_{-1}/k_1k_2)\,[X^-]/[OAc^-] \qquad (3)$$

accompanying cis-trans isomerization is faster than the solvolysis and an equilibrium of 54% 1-Br to 46% 2-Br is established during the reaction. Since it was shown that the cation 3 is linear and captures acetate, chloride and thiolate anions equally from both sides of the cationic orbital, a similar capture by Br^- necessarily gives isomerization. The amount



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of isomerization by this mechanism can be evaluated from the isomerization under conditions when no solvolysis takes place since then k^{1}_{isom} should equal k_t^{o} 1. With excess bromide ion the solvolysis is practically stopped and under these conditions the observed k_{isom} = $k^{1\text{-}Br}_{isom} + k^{2\text{-}Br}_{isom} = 8.3\ 10^{-5}\ sec^{-1}$, a value almost equal to k_t^{o} 1-Br + k_t^{o} 2-Br at the same ionic strength (Table). Since k_t^{o} values are for solvolysis via dissociated ions most of the isomerization is carried by dissociated ions.[9] In line with this, in the solvolysis of 1-Br

Table. Solvolysis and Isomerization of 1-Br and 2-Br.[a]

Compound	Solvent	T, °C	$10^5 k_t^o$	$10^5 k_{isom}$	K_{eq}[b]	$\frac{k_t^o\ 1\text{-Br}}{k_t^o\ 1\text{-Cl}}$	$\frac{k_{isom}\ 1\text{-Br}}{k_{isom}\ 1\text{-Cl}}$	$\frac{k_{isom}\ 1\text{-Br}}{k_{isom}\ 1\text{-H}}$
1	80% EtOH[c]	120.3	25.2	ca. 25[d]	< 2.3[e]	82.5	ca. 80[d]	> 100
2			29.2	ca. 29[d]				
1	AcOH[f]	120.3	4.0	6.6	1.17	42	28	ca. 4
2			4.2	6.7				
1	AcOH[g]	120.3		8.3	1.17			
2				8.4				
1	50%AcOH-50% HCO_2H	99.7	29.3	30.0	1.13	12.3	ca. 12[h]	0.70[i]
2			32.0					

[a] [1-Br] and [2-Br] =0.044 M. [b] K_{eq} = [1-Br]/[2-Br] at equilibrium. [c] [NaOH] =0.39 M. [d] Based on an assumed K_{eq} of 1.17. [e] Equilibrium is not achieved during the reaction and the value quoted is based on the 70% 1-Br observed after 2 half-lives. [f] [NaOAc] = 0.087M. [g] [NaOAc] =0.011M ; [Bu_4NBr] =0.076M ; $k_t^{40\%}/k_t^o$ =0.08. [h] Approximate value due to difficulties in estimating $k_{isom}^{1\text{-Cl}}$. [i] Based on one point experiment for 1-H .

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and 2-Br in the presence of 0.076 M LiCl most of the product is a 1:1 mixture of 1-Cl and 2-Cl and k_{isom} is 25% of its value in the absence of added chloride ions.[10]

The following arguments for the connection between k_{isom} and the ionization eliminate the most probable competing route, that of isomerization via electrophilic addition-elimination[11] and may be used for other systems. (a)Isomerization (but not solvolysis) with a rate coefficient of the same order of magnitude as in AcOH takes places in the aprotic solvent acetonitrile. (b)The electrophilic isomerization, e.g., by H^+, should be faster in the more acidic AcOH than in 80% EtOH, contrary to the data of the Table. (c) The ethylenes 1-H and 2-H cannot isomerize via ionization but should isomerize faster than 1-Br and 2-Br via the electrophilic route if the(Markovnikov) formation of $AnCHX-\overset{+}{C}An_2$ is much faster than the (anti-Markovnikov) formation of $An_2CH-\overset{+}{C}(An)X$.[12] Considering the values of $k_{isom}^{1\text{-Br}}/k_{isom}^{1\text{-H}}$ in 80% EtOH and AcOH (Table) and the differences in the inductive effects of H and Br the bromides cannot isomerize mainly via the electrophilic route. The observed ratio $k_{isom}^{1\text{-Br}}/k_{isom}^{1\text{-OAc}} > 100$ supports this conclusion. (d) In electrophilic addition

$k_t^{o\,\underline{\text{1-Br}}}/k_t^{o\,\underline{\text{1-Cl}}}$ should be near unity since σ_I and σ_R for Cl and Br are similar. However, if a C-X bond cleavage is involved in the rate determining step, both $k_t^{o\,\underline{\text{1-Br}}}/k_t^{o\,\underline{\text{1-Cl}}}$ and $k_{isom}^{\underline{\text{1-Br}}}/k_{isom}^{\underline{\text{1-Cl}}}$ should have close values. This is indeed found and the values are similar to the titrimetric ratios found for saturated substrates.[13] (e)The solvent isotope effect k_{AcOH}/k_{AcOD} is ca. 1.1 for both the solvolysis and the isomerization. A different value is expected for electrophilic isomerization.[14]

In 50% AcOH-50% HCO_2H $k_t^{75\%}/k_t^{o} = 0.57$ and judging from this and the $k_t^{o\,\underline{\text{1-Br}}}/k_t^{o\,\underline{\text{1-Cl}}}$ value the isomerization is probably mainly via <u>3</u>. However, the $k_{isom}^{\underline{\text{1-Br}}}/k_{isom}^{\underline{\text{1-H}}}$ value points to a possible intervention of the elctrophilic isomerization although the value can be also explained by electrophilic assistance to the S_N1 process. This and related systems are currently being investigated.

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