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VINYLIC CATIONS FROM SOLVOLYSIS. V. COMMON ION RATE DEPRESSION AND STABILITY OF SOME VINYL CATIONS IN ACETOLYSIS

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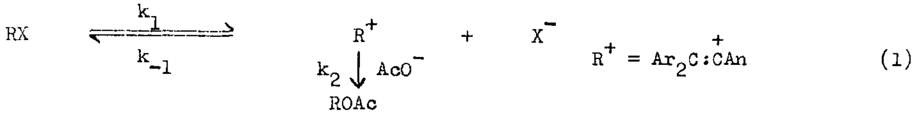
Vinyl cations are now accepted members of the carbonium ion family[1] but little is known regarding their stability. This can be inferred from the nature of the solvolysis products,[2] and from the ability of the cations to discriminate between the solvent and the leaving group or added anions.[3] The present communication describes the selectivity of some vinyl cations towards the leaving group and acetate ion in acetic acid.

Solvolysis of trianisylvinyl bromide (TAVBr) and chloride and of 2,2-diphenyl-1-anisylvinyl bromide in unbuffered AcOH shows irregular kinetics and blackening of the reaction mixtures, probably due to reactions involving the acid formed. In the presence of excess sodium or potassium acetate (MOAc) the major product is a triarylvinyl acetate together with some 1,2,2-triarylethanone. The first order rate coefficient decreases strongly during a run, as shown by its ratio to the initial value at one and two half-lives, i.e., by $k_1^{50\%}/k_1^{o}$ and $k_1^{75\%}/k_1^{o}$, respectively (Table). In the presence of 0.04M Bu_4NBr the rate coefficient is 10-times smaller than k_1^{o}.

Acetolysis via <u>dissociated</u> carbonium ions which can be captured competitively by the leaving group and the lyate ion (eqn. 1) is described by eqn. 2, where $\alpha = k_{-1}/k_2$. Eqn. 1



$$\mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c} \mathrm{R}^+ \\ k_2 \big\downarrow \mathrm{AcO}^- \\ \mathrm{ROAc} \end{array} + \mathrm{X}^- \qquad \mathrm{R}^+ = \mathrm{Ar_2C{:}\overset{+}{C}An} \qquad (1)$$

$$1/k_{obs} = 1/k_1 + \alpha/k_1 \left([X^-] / [AcO^-] \right) \qquad (2)$$

neglects reaction with AcOH and the complex equilibria of free halide and acetate ions with their ion pairs, triplet ions and quadruplets.[4] Neither the concentrations nor the reactivities of the various species are known, but plots of $1/k_{obs}$ vs. $[X^-]_t/[AcO^-]_t$, where $[X^-]_t$ and $[AcO^-]_t$ are the total concentrations, are linear (correlation coefficient 0.99) when $[MOAc] / [RX] > 2$. The Table lists the k_1^o values (from the intercept) and the α' values (defined by slope $= \alpha'/k_1^o$). The α' values which are composed from a product of α and several dissociation constants for the various species are higher for NaOAc than for KOAc, and their increase with the NaOAc concentrations in different runs can be rationalized if the reaction is carried mainly by free ions.

Surprisingly, in the acetolysis of 0.035M α-bromo-p-methoxystyrene ("monoanisylvinyl bromide" - MAVBr) with 0.084M NaOAc, k_1 remains constant within a run ($10^5k_1 = 1.67 \pm 0.04$ at 120° and 7.57 ± 0.10 sec^{-1} at 141°). A higher but constant k_1 value ($10^5k_1 = 2.62 \pm 0.15$ sec^{-1} at 120°) is obtained on addition of excess bromide ion (0.04M Bu_4NBr with 0.035M MAVBr and 0.04M NaOAc). In the absence of NaOAc the reaction is autocatalytic, much faster, and the product is p-methoxyacetophenone. This is probably due to solvolysis via electrophilic addition-elimination. No common-ion rate depression is observed at 45.4° in the acetolysis of 0.04M p-methoxybenzyl bromide in the presence of 0.08M and 0.16M NaOAc ($10^5k_1 = 5.39 \pm 0.21$ and 8.16 ± 0.27 sec^{-1}, respectively) but k_1 increases with the ionic strength.

The addition-elimination mechanism for MAVBr is rejected since the k_{MAVBr} / k_{TAVBr} values are not much different in 80% EtOH and in AcOH,[3b] since no products such as diacetates were observed, and since $k_{CH_3CO_2H} / k_{CH_3CO_2D}$ is ca. 1.1 for the solvolysis of the related 1,2-dianisyl-2-phenylvinyl bromide.[5]

The above data call attention to four important mechanistic points. a)Over 90% of the acetolysis products are formed from "dissociated" vinyl cations. b)The relative difficulty in the formation of vinyl cations is not due to their instability. Once the leaving group is lost, stabilization of the sp-hybridized vinyl cation,[3c] is not lower than that of the p-methoxybenzyl cation. c)The triarylvinyl cation is much more selective and therefore has a longer life than the monoarylvinyl cation. This is not due to β-aryl participation, as shown by the stereochemistry and the kinetics.[5] Stabilization by structures with charge on the β-carbon is contradicted by the similar selectivity of the β,β-diphenyl- and the β,β-dianisyl compounds. A model shows that the empty p-orbital in the triarylvinyl ion is shielded sterically by the α and β-aryl groups. The shielding is further increased by

Table. Acetolysis of triarylvinyl halides.

Compound [a]	Conc., M	Added salt	Conc., M	T, °C	$10^5 k_1^o$ sec^{-1} [b]	α'	$k_1^{50\%}/k_1^o$	$k_1^{75\%}/k_1^o$
$An_2C{:}CAnBr$	0.035	KOAc	0.084	120.3	9.3	9.6	0.268	0.186
	0.035	NaOAc	0.084	120.3	6.7	11.3	0.245	0.155
	0.035	NaOAc	0.23	120.3	10.5	20.8	0.390	0.268
	0.018	NaOAc	0.48	120.3	13.3	26.0	0.665	0.570
	0.035	NaOAc	0.084	141.5	31.2	5.9	0.402	0.268
$An_2C{:}CAnCl$	0.035	NaOAc	0.084	141.5	2.9	4.3	0.467	0.328
$Ph_2C{:}CAnBr$	0.035	NaOAc	0.084	120.3	2.0	9.3	0.282	0.181
	0.035	NaOAc	0.084	141.5	12.8	7.8	0.316	0.230

[a] An = p-anisyl. [b] $1/k_{obs}$ vs. $[X^-]_t / [AcO^-]_t$ plot is linear up to at least 75% reaction.

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electrostatic repulsion between the electron-rich diarylvinyl group and negatively charged nucleophiles. The life-time of the triarylvinyl ion increases compared to that of the monoarylvinyl ion, and the more polarizable and reactive bromide is captured rather than acetate. d)Grunwald-Winstein m values[6] for the solvent pair AcOH- 80% EtOH are 0.71 for MAVBr and 0.36-0.48 for TAVBr at 120°. This, we believe, reflects the fact that the steric and electronic hindrance to the approach of solvent (or nucleophile) is more severe in the transition states where the incipient p-orbital is in the plane of the substituents than in the sp-hybridized ions. In the triarylvinyl ion both lobes of the orbital are in the plane of the bulky groups and such hindrance is very effective, while most of the hindrance is absent in the monovinyl ion.

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