SOLVENT EFFECTS ON SOLVOLYSIS OF 1,2,2-TRIS(p-METHOXYPHENYL)VINYL TOSYLATE

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Abstract: The solvolysis rates of tris(p-methoxyphenyl)vinyl tosylate were measured in various solvents. The trend of dispersed mY_{OTS} plots and low m values means that the reactive intermediate should be an sp-hybridized vinyl cation conjugated to the α -p-methoxyphenyl group.

A pure S_{N} 1 mechanism with an intermediate vinyl cation, uncomplicated by either anchimeric or nucleophilic assistance, has been concluded by Rappoport for the solvolysis of 1,2,2-triarylvinyl system.^{1,2)} Concerning the solvent effect on solvolysis of 1,2,2-tris(p-methoxyphenyl)vinyl tosylate, however, a linear mY correlation with a remarkably low m value of 0.41 has been reported at 75° C for the range of 90%-60% aqueous acetone.^{2a)} This extremely low m value should be incompatible with the k_c solvolysis process through a vinyl-cationic transition state, and suggested that this may be due to the presence of the α -p-methoxyphenyl group or to solvent participation.²⁾ These facts might imply a unique solvent dependence characteristic of vinyl sp-carbocationic solvolysis different from that of ordinary limiting sp²-carbocationic solvolyses. However, there are no solvolysis data available for any appropriate vinyl cation system for a complete set of solvents. In this paper, we have determined the solvolysis rates of 1,2,2-tris(p-methoxyphenyl)vinyl tosylate in the typical series of aqueous organic solvents, such as aq. acetone, aq. ethanol, aq. methanol, aq. trifluoroethanol, aq. hexafluoroisopropanol, and acid solvents, and the solvent effect on the solvolysis of this system was investigated in terms of the Winstein-Grunwald-Schleyer-Bentley equation (1), 3) aiming at the characterization of the mechanism or the transition state of the solvolysis of the vinyl tosylate

 $\log (k/k_{80E}) = mY_{OTS} + 1N_{OTS}$ (1) where the Y_{OTS} derived from 2-adamantyl tosylate at 45°C for tosylate reactivities.⁴)

1,2,2-Tris(p-methoxyphenyl)vinyl tosylate was prepared by the reaction

of tris(p-methoxyphenyl)vinyl bromide with silver OTs in MeCN; mp 143.5-144.5°C, lit.,^{2b)} mp 143°C. Solvolysis rates in aqueous binary solvents were followed conductometrically at 45° C using initial ester concentration of ca. 10^{-4} M and were summarized in Table 1.

In Fig. 1, logarithmic rates of tris(p-methoxyphenyl)vinyl tosylate at 45°C are plotted against the 2-adamantyl Y_{OTe} values at 45°C.⁴) The mYOTS correlation exhibits a widely split pattern and appears to give a general trend of m well below unity (m = 0.73, correlation coefficient (R) = 0.91). Application of Eq. (1) with m value of 0.62 and 1 value of -0.30 does not improve the linearity so much (R = 0.96). Simple linearity of mY Eq. was excellently held within each binary solvent series, $m_{AW} = 0.64$ for aq. acetones (R=0.999) and m_{FW} of 0.51 for aq. ethanols (R=0.999). While plots for aq. ethanol lie above those for aq. acetone, plots for less nucleophilic solvents such as acids, aq. TFE, and aq. HFIP also lie higher above the aq. acetone plots. Obviously, the pattern of deviations from the mY correlation is not consistent with what would be anticipated for a mechanistic involvement of the solvent nucleophilicity. A similar behavior was observed in the solvent effects on the aryl-assisted solvolysis of pmethoxyneophyl tosylates as shown in lower trace in Fig. 1, where no direct nucleophilic solvent assistance anticipated from is mechanistic viewpoint.⁵⁾ The dispersion behavior and reduced m value is compatible with the entire π -delocalization of cationic charge between assisting arylring and the reaction center in the transition state.⁵⁾

Solv. ^{b)}	10 ⁵ kt	Solv. ^{b)}	10 ⁵ kt	Solv.b)	10 ⁵ kt
100E	0.120	80M	2.16	97 T w	44.83
90E	0.420	60M	6.72	80T	34.87
80E	0.954	50M	11.4	50т	31.61
70E	1.48	80A	0.0786	30т	34.36
60E	2.58	70A	0.205	97HFIPw	1468
50E	3.87	60A	0.491	50HFIP	117.2
40E	7.1	50A	1.11	AcOH	0.360 ^{c)}
30E	15.7	40A	2.86	75AF	7.55
MeOH	0.654	30A	7.61	HCOOH	182

Table 1. Solvolysis Rates of 1,2,2-Tris(p-methoxyphenyl)vinyl Tosylate at 45°C^a)

a) Conductometrically determined. b) Volume percent of first named solvent while suffix of w means weight percent. E=EtOH, M=MeOH, A=acetone, T=trifluoroethanol, HFIP=hexafluoroisopropanol, and AF=acetic acid-formic acid. c) Extrapolated from data at other temperatures $(1.33 \times 10^{-5} s^{-1} at 55^{\circ}C)$ and $14.5 \times 10^{-5} s^{-1} at 75^{\circ}C$).

It is also highly likely that the identical correlation for the solvolysis of the vinyl tosylate must also be due to the effective charge delocalization with the α -p-methoxyphenyl group. The through-conjugation between the α -p-methoxyphenyl group and the reaction center should be much more effective in this system than in the aryl-assisted neophyl system.



Fig. 1. The mY plots for the solvolysis of 1,2,2-tris(p-methoxyphenyl) vinyl tosylate at 45° C (upper trace) and for the solvolysis of p-methoxyneophyl tosylate (lower trace); abscissa is Y_{OTs} derived from solvolysis rates of 2-adamantyl tosylate at 45° C.

Similar dispersions were observed generally for benzylic solvolyses giving stable, delocalized carbocations.⁶) While such data available are mostly for halide solvolyses, decrease in m value appears substantial and the split pattern of the my plot is generally significant. This characteristic feature is most likely to be caused by direct π -interaction of charged carbocation center with α -aryl group.

a conclusion, any nucleophilic solvent assistance mav be As unimportant in the transition state in the solvolysis of this vinyl tosylate, and there must be entire charge-delocalization of vinyl-cation into the α -aryl π -system. The vacant p orbital of vinyl sp-cation center must be conjugated with the p-methoxyphenyl group in essentially the same manner as in the benzylic carbenium ion. Substituent at the β -carbon of vinyl cation exerts little effect on the solvent effect behavior; the ß – aryls are orthogonal to the benzylic conjugation system. More important, the anchimeric assistance of β -p-methoxyphenyl group should not be the cause of characteristic deviation pattern. From laser flash photolysis observation, the 1-p-methoxyphenylvinyl cation generated by photoprotonation of p-methoxyphenylacetylene in TFE shows remarkably similar behavior to 1-p-methoxyphenylethyl cation.⁷) The substituent effect on the gas-phase stability of 1-phenylvinyl cation reveals that the sp-hybridized benzylic carbocations are dealt with as one of well-behaved cations which can be stabilized by an ample electron-donating conjugation, in the same category as the corresponding sp² benzylic carbocations.⁸⁾ All these facts are in line with the present results from the solvent effects of this vinyl cation solvolysis.

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