

Vinyl Cations from Solvolysis. XIX.¹ Low Tosylate-Bromide Reactivity Ratios in Vinyllic Solvolyses. Do k_{OTs}/k_{Br} Ratios Measure the Polarity of the Solvolytic Transition State?

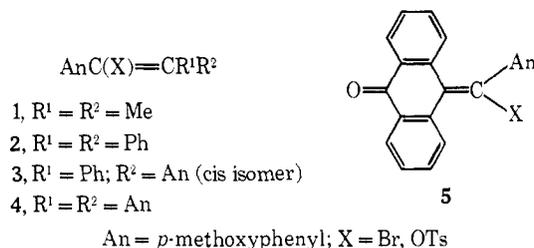
Sir:

A few years ago Hoffmann,² following DePuy and Bishop,³ suggested the ratio of the displacement rates of tosylate and bromide leaving groups (k_{OTs}/k_{Br}) as a mechanistic criterion for the extent of bond breaking in the solvolysis transition state. Ratios <1 were found mainly with primary substrates in reactions of nucleophiles which involve strong bond making. High ($>10^3$) ratios were found for easily ionized, mostly tertiary, substrates, and intermediate ratios characterize secondary substrates. Large ratios were suggested to indicate very ionic transition states and *vice versa*, and solvation and steric factors were assumed to be less important than the charge dispersal effects. It was generalized that "the faster an S_N1 (and $E1$) reaction, the more ionic its transition state."^{2b}

The possible contribution of nucleophilic participation to Hoffmann's ratios was emphasized,^{4a,b} and it was suggested that the ratios "should be employed with caution as mechanistic criteria."^{4c} Moreover, Bingham and Schleyer ascribed at least part of the trend in the high ratios observed for some bicyclic systems^{4c} to a relief of ground-state strain in the tosylates, which is absent in the bromides, and predicted ratios below unity for the solvolysis of the 1-bicyclo[2.2.1]heptyl and 4-nortricyclyl systems. Steric explanation was also offered for the low ratios observed for several cyclopropyl derivatives.⁵ The lowest ratio observed for S_N1 reaction of an acyclic system is four for the hydrolysis of the neopentyl system,^{2b,6} but a ratio of 0.71 was reported for the acetolysis of *cis,cis*-2,3-dimethylcyclopropyl derivatives^{2b} where ring-opening is concerted with ionization.

The low k_{OTs}/k_{Br} ratios in the vinyllic solvolysis of triarylvinyl systems^{7a} were suggested to be due to ground-state and steric effects.^{7a} Table I contains some of an extensive list of new data^{1,7b} on k_{OTs}/k_{Br} ratios for solvolyses of compounds 1-5 which react exclusively *via* the k_c route.⁵ Most of the ratios are low in comparison

with those given by Hoffmann for solvolysis of saturated compounds to which reaction *via* the S_N1 mechanism was assigned, but those in AcOH approach or even



exceed the value of 231 suggested as typical for the k_c route for secondary substrates.^{4c} The most unusual features are the ratios for compounds 5, where the bromide reacts faster than the tosylate in three solvents. *The ratios in 2,2,2-trifluoroethanol (TFE) and in 90% TFE are unprecedented and that in TFE is the lowest known either for S_N1 or for S_N2 reactions.*

These low ratios cannot be due to errors in extrapolation, since each pair of compounds was studied at the same temperature, to β -aryl participation which is excluded by the rate data and the presence of the α -anisyl group,⁹ nor to nucleophilic participation (k_s)⁸ in the transition state which is geometrically impossible in 5 due to the steric hindrance at the rear of the vinyllic system. Electrophilic^{10a-d} and nucleophilic^{10e,f} routes are excluded for reasons discussed elsewhere^{10d,f} and since k_1 for 5-OTs in AcOH is independent of the concentration of the NaOAc. Internal return, which by indirect evidence is unimportant in this respect for bridgehead substrates^{4c} was found (by using *cis-trans* isomerization as a mechanistic tool^{11a,b}) to be more pronounced for system 3 for the bromides than for the methanesulfonates in AcOH and in 80% EtOH.^{11b} Hence, the true k_{OTs}/k_{Br} ratios based on the ionization rate coefficients should be actually *lower* than those reported in Table I.

When the ratios are compared^{12,13} with those for the 1-adamantyl (6), 2-adamantyl (7), and 1-bicyclo[2.2.2]-octyl (8) systems, it is dramatically demonstrated that contrary to Hoffmann's generalization the k_{OTs}/k_{Br} ratio is not necessarily higher for the faster reaction.¹⁴

(1) Part XVIII: Z. Rappoport and J. Kaspi, *J. Amer. Chem. Soc.*, in press.

(2) (a) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753 (1965); (b) *ibid.*, 6762 (1965).

(3) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, 82, 2532 (1960).

(4) (a) Y. Inomoto, R. E. Robertson, and G. Sarkis, *Can. J. Chem.*, 47, 4599 (1969); (b) C. A. Grob, K. Kostka, and F. Kuhnen, *Helv. Chim. Acta*, 53, 608 (1970); (c) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 93, 3189 (1971).

(5) (a) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, 94, 125 (1972); (b) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, 94, 133 (1972).

(6) R. E. Robertson, R. L. Heppollette, and J. M. W. Scott, *Can. J. Chem.*, 37, 803 (1959); R. E. Robertson, *Suom. Kemistilehti A*, 33, 63 (1960).

(7) (a) Z. Rappoport and J. Kaspi, *J. Chem. Soc., Perkin Trans. 2*, 1102 (1972); (b) unpublished results.

(8) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, 92, 2542 (1970).

(9) P. G. Gassman, J. Zeller, and J. T. Lamb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. Fentiman, Jr., *J. Amer. Chem. Soc.*, 91, 1545 (1969).

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(11) (a) Z. Rappoport and Y. Apeloig, *Tetrahedron Lett.*, 1845 (1970); (b) submitted for publication; (c) *Tetrahedron Lett.*, 1817 (1970).

(12) Values from the literature were extrapolated to the reaction temperature of 5 using activation energies from the literature. For k_{OTs}/k_{Br} ratios at 25° for systems 6-8 see ref 13.

(13) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2538 (1970).

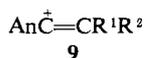
(14) Since the k_{OTs}/k_{Br} ratios are high for bicyclic systems and low for vinyllic systems, the comparison of the k_{OTs}/k_{Br} ratios with the reactivities is highly dependent whether k_{Br} or k_{OTs} is taken as a model for the reactivity.

Table I. Tosylate-Bromide Reactivity Ratios for Some Vinylic Solvolyses

Compound	Solvent ^a	T, °C	10 ⁴ k _{Br} , sec ⁻¹	10 ⁴ k _{OTs} , sec ⁻¹	k _{OTs} /k _{Br}
1	80% EtOH	105	2.8 ^b	200	71.5
	AcOH	120	0.235 ^{c,d}	180	765
	TFE	35	0.415 ^{d,e}	13.5 ^e	32.5
	90% TFE	35	0.33 ^{d,e}	7.72 ^e	23.4
	60% TFE	35	0.363 ^{d,e}	7.16 ^e	19.7
2	70% acetone	120.3	0.75 ^f	18.8 ^f	25.1
	80% EtOH	120.3	2.92	116 ^g	40.0
3	AcOH	120.3	0.4 ^d	113	283
	70% acetone	120.3	2.14 ^f	68.0 ^f	31.8
4	AcOH	120.3	0.67 ^{c,d}	58.2 ^f	86.8
	TFE	90.1	3.3	430 ^g	130
5	80% EtOH	105	3.5 ^d	2.63	0.75
	AcOH	120	1.2 ^d	6.2	5.15
	TFE	35	0.108 ^d	0.017	0.157
	90% TFE	35	0.068 ^d	0.0158	0.231

^a The solvent was buffered with Et₃N, 2,6-lutidine, or NaOAc. ^b Calculated from ref 10d. ^c A. Gal, Ph.D. Thesis, The Hebrew University, 1972. ^d The rate constant decreases during the run due to common ion rate depression. The value given is the extrapolated initial value. ^e From ref 1. ^f From ref 7a. ^g Extrapolated from data at lower temperatures.

Thus, $k_1(6\text{-Br})/k_1(5\text{-Br}) = 2.1^{15}$ and $[k_{\text{OTs}}/k_{\text{Br}}](6)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 6000$ (AcOH, 120°)^{4c,15}; $k_1(7\text{-Br})/k_1(5\text{-Br}) = 0.0066$ (80% EtOH, 105°)^{8,16} and 0.0033 (AcOH, 120°)⁸ while $[k_{\text{OTs}}/k_{\text{Br}}](7)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 268$ (80% EtOH, 105°)⁸ and 358 (AcOH, 120°)^{8,16}; $k_1(8\text{-Br})/k_1(5\text{-Br}) = 0.0047$,^{4b} $[k_{\text{OTs}}/k_{\text{Br}}](8)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 2800$ (80% EtOH, 105°),^{4b,c} and $k_1(8\text{-OTs})/k_1(5\text{-OTs}) = 5.3^{4c}$ while $[k_{\text{OTs}}/k_{\text{Br}}](8)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 15,750$ (AcOH, 120°).^{4c} Moreover, compounds 1–5 show an extensive common ion rate depression in AcOH, TFE, and 90% TFE and >90–95% of the products are formed from “dissociated” cations.^{1,11b} The ions, **9**, are therefore



more stable than the *tert*-butyl cation, since common ion rate depression in the solvolysis of *t*-BuBr is low,¹⁷ while $k_{\text{OTs}}/k_{\text{Br}}$ of >4000 was estimated for the ethanolytic of the *tert*-butyl system at 50°.^{2b}

Such comparisons may be unjustified since Hoffmann's generalization is based on substitution at a saturated carbon which differs in other respects from the vinylic solvolysis¹⁸ and a stabilizing $\pi(\text{C}=\text{C})-\text{n}(\text{X})$ conjugation is possible only for vinylic substrates. However, even for structurally similar vinylic systems $k_1(1\text{-Br})/k_1(5\text{-Br}) = 0.8$ (80% EtOH, 105°) and 0.2 (AcOH, 120°) while the corresponding ratios of $k_{\text{OTs}}/k_{\text{Br}}$ ratios are 95 and 149, respectively. Furthermore, the ion derived from system 5 is more selective (and therefore stable) than those derived from systems 2–4,¹⁹ in spite of the lower $k_{\text{OTs}}/k_{\text{Br}}$ ratios for system 5. Clearly, if the stability of the ions is related to the structure and the polarity of the transition states leading to them,²⁰ the $k_{\text{OTs}}/k_{\text{Br}}$ ratios are very poor guides for the polarity of the transition states. A more appropriate probe would be Hammett's ρ value for arenosulfonate

(15) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 5977 (1970).

(16) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

(17) L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 960 (1940).

(18) For example, the Winstein-Grunwald *m* values are low for solvolysis of triarylvinylic systems (Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, **91**, 5246 (1969), and ref 7a) and high for systems 6–8.¹³

(19) The extent of common ion rate depression in AcOH is higher for 5-Br than for 2-Br, 3-Br, and 4-Br.

(20) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

leaving groups, where the steric and conjugation effects are nearly constant. Kevill, *et al.*, suggested that the similar ρ values for the ethanolytic of the arenosulfonates of **6** and **7** are consistent with the steric explanation for the $k_{\text{OTs}}/k_{\text{Br}}$ ratios and not with a different extent of bond breaking.^{21,22}

The importance of solvation⁵ is demonstrated in the relatively high ratios in the acetolysis.

The low ratios for system 5 are due both to enhanced k_{Br} ^{23,24} and to a lower k_{OTs} .²⁵ While the former effect is predicted, since the ground state of 5-Br is much more crowded than those of compounds 1–4 or of 5-OTs,²⁶ it is not yet clear if steric²⁷ or electronic²⁸ effects or both

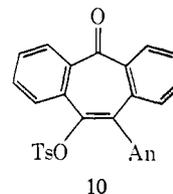
(21) D. N. Kevill, K. C. Kolwyck, D. M. Shold, and C.-B. Kim, *J. Amer. Chem. Soc.*, **95**, 6022 (1973).

(22) The ρ values for arenosulfonate leaving groups are 1.76,²¹ 1.86,²¹ and 1.91^{2a} for systems 6, 7, and 4, respectively, suggesting a similar charge development in the transition states of the bicyclic and the vinylic systems.

(23) Based on indirect comparison of the data of Table I and on the additivity of the effects of β -aryl substituents^{11c,24} and taking into account the retarding effect of the carbonyl group, 5-Br is at least 10 times faster than 2-Br.

(24) Z. Rappoport and Y. Houminer, *J. Chem. Soc., Perkin Trans.*, **2**, 1506 (1973).

(25) That 5-OTs (which was prepared from 5-Br and AgOTs in MeCN) is not the rearranged isomer **10** is shown by the formation of



>95% of 5-Br from 5-OTs and Br⁻, and by the mass spectrum where the base peak is at *m/e* 135 (AnCO⁺).

(26) Space filling models of **1-4** and of 5-OTs could be built but not that of 5-Br.

(27) Combined steric-conjugation effects are highly important in the solvolysis of triarylvinylic derivatives. All four substituents are conjugated with the double bond, and cis interactions result in twisting of both the α - and β -aryl groups from the plane of the double bond. On approaching the transition state, which may resemble the linear vinyl cation, the cis interaction at the back of the leaving group is relieved but that between the leaving group and the cis β -substituent increases due to the increased proximity and decreases with the elongation of the C-X bond.

(28) A possible explanation to the low $k_{\text{OTs}}/k_{\text{Br}}$ ratios in vinylic solvolysis is that a stabilizing $\text{n}-\pi$ ground-state conjugation as in Ar₂C=C(Ar)=X⁺ is more important when X = OTs than when X = Br.^{7a} This effect would be more pronounced with 5 due to its carbonyl group. A differential ground-state effect in the same direction is suggested by thermodynamic data that OEt (a possible model for OTs) attachment to

