Vinylic Cations from Solvolvsis. XIX.¹ Low Tosylate-Bromide Reactivity Ratios in Vinylic 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 $(k_{\text{OTs}}/k_{\text{Br}})$ 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 SNI (and E1) reaction, the more ionic its transition state."2b

The possible contribution of nucleophilic participation to Hoffmann's ratios was emphasized, 48,b and it was suggested that the ratios "should be employed with caution as mechanistic criteria."4° 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 4nortricyclyl systems. Steric explanation was also offered for the low ratios observed for several cyclopropyl derivatives.⁵ The lowest ratio observed for SN1 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^{5b} where ring-opening is concerted with ionization.

The low $k_{\text{OTs}}/k_{\text{Br}}$ ratios in the vinylic 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 $k_{\text{OTs}}/k_{\text{Br}}$ ratios for solvolyses of compounds 1-5 which react exclusively via the k_c route.⁸ Most of the ratios are low in comparison

(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. Schöllokopf, 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. Heppolette, 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).

with those given by Hoffmann for solvolysis of saturated compounds to which reaction via the SN1 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 SN1 or for SN2 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 vinylic 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 substrates⁴ 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 $k_{\text{OTs}}/k_{\text{Br}}$ 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 $k_{\text{OTs}}/k_{\text{Br}}$ ratio is not necessarily higher for the faster reaction.¹⁴

(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).

(10) (a) P. E. Peterson and J. M. Indelicato, J. Amer. Chem. Soc., 6515 (1968); (b) W. M. Schubert and G. W. Barfknecht, ibid., 92, 207 (1970); (c) Z. Rappoport, T. Bässler, and M. Hanack, ibid., 92, 4985 (1970); (d) Z. Rappoport and A. Gal, J. Chem. Soc., Perkin Trans. 2, 301 (1973); (e) Z. Rappoport, Advan. Phys. Org. Chem., 7. 1 (1969); (f) Z. Rappoport and A. Gal, J. Org. Chem., 37, 1174 (1972). (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 vinylic systems, the comparison of the kots/kBr 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	$10^{4}k_{\rm Br}$. sec ⁻¹	$10^{4}k_{\text{OTs}}$, sec ⁻¹	kors/kB.
1	80% EtOH	105	2.86	200	71.5
	AcOH	120	$0.235^{c.d}$	180	765
	TFE	35	$0.415^{d.e}$	13.5°	32.5
	90% TFE	35	0.33 ^d , e	7.72°	23.4
	60% TFE	35	0.363 ^d .e	7.16°	19.7
2	70% acetone	120.3	0.75	18.81	25.1
3	80% EtOH	120.3	2.92	116°	40.0
	AcOH	120.3	0.4^{d}	113	283
4	70% acetone	120.3	2.14	68.01	31.8
	AcOH	120.3	$0.67^{c.d}$	58.21	86.8
	TFE	90.1	3.3	4300	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 Et_sN , 2,6-lutidine, or NaOAc. ^b Calculated from ref 10d. ^cA. 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 $[k_{\text{OTs}}/k_{\text{Br}}](6)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 6000 (AcOH, 120°)^{4c,15}; k_1(7\text{-Br})/k_1(5\text{-Br}) = 0.0066 (80\% EtOH, 105°)^{8,16} and 0.0033 (AcOH, 120°)^8 while <math>[k_{\text{OTs}}/k_{\text{Br}}](7)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 268 (80\% EtOH, 105°)^8 and 358 (AcOH, 120°);^{8,16} k_1(8\text{-Br})/k_1(5\text{-Br}) = 0.0047,^{4b} [k_{\text{OTs}}/k_{\text{Br}}](8)/[k_{\text{OTs}}/k_{\text{Br}}](5) = 2800 (80\% EtOH, 105°),^{4b,c} and k_1(8\text{-OTs})/k_1(5\text{-OTs}) = 5.3^{4c}$ 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

$$An\dot{C} = CR^{1}R^{2}$$

9

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 ethanolysis 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 $\pi(C==C)-n(X)$ conjugation is possible only for vinylic substrates. However, even for structurally similar vinylic systems $k_1(1-Br)/k_1(5-Br) = 0.8 (80\% \text{ EtOH}, 105^\circ)$ 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 $k_{\rm OTs}/k_{\rm Br}$ ratios are very poor guides for the polarity of the transition states. A more appropriate probe would be Hammett's ρ value for arenesulfonate

(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 triarylvinyl 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 ethanolysis of the arenesulfonates 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 $k_{\rm Br}^{23,24}$ and to a lower $k_{\rm OTs}$.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 arenesulfonate leaving groups are 1.76^{21} 1.86^{21} and 1.91^{7a} 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^{110,24} 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 and that of 5-Br.

(27) Combined steric-conjugation effects are highly important in the solvolysis of triarylvinyl derivatives. All four substituents are conjugated with the double bond, and c is 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 virityl cation, the c is 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_{OTe}/k_{Br} ratios in vinylic solvolysis is that a stabilizing $n-\pi$ ground-state conjugation as in Ar₂C-C-(Ar)=X⁺ is more important when X = OTs than when X = Br.¹ 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

⁽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).

are responsible for the relatively low k_{OTs} . Studies on this question and on other low and high $k_{\text{OTs}}/k_{\text{Br}}$ ratios in vinylic systems are continuing.

Acknowledgment. We are indebted to the Volkswagen Foundation for support of this work and to Professor P. v. R. Schleyer for discussions and comments.

vinyl is more favorable than to ethyl, while Br attachment to vinyl is *less* favorable than to ethyl: L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, J. Amer. Chem. Soc., 95, 6531 (1973). However, the small difference between the solvolysis rates of system 2 and the corresponding fluorenylidene derivatives⁷^a argues against high contribution of this effect.

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Synthesis and Structural Characterization of Platinum Carbonyl Cluster Dianions, $[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ (n = 2, 3, 4, 5). A New Series of Inorganic Oligomers¹

Sir:

We wish to report the preparation and structures of a new series of platinum carbonyl cluster dianions of general formula $[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ (n = 2, 3, 4, 5). These species are of particular interest in that they not only give rise to new kinds of metal cluster geometries formally derived by tinker-toy construction from a basic $M_3L_3(\mu_2-X)_3$ -type building block through direct metalmetal interactions but more importantly they also represent an approach to the synthesis of a unique type of unidimensional metal cluster polymer with desirable conductivity properties.

These anions can be prepared either from the reduction of $Pt(CO)_2Cl_2$ with alkali metals in the presence of carbon monoxide or more simply from the reduction of sodium hexacholoplatinate(IV) with carbon monoxide and methanolic sodium hydroxide at atmospheric pressure and room temperature. This latter method of synthesis is analogous to that used in the preparation² of polynuclear rhodium complexes, and the products isolated are similarly dependent upon the amount of added sodium hydroxide. The sequence below shows the dianions *isolated* with increasing concentration of reducing agent.

$$[\operatorname{PtCl}_{6}]^{2-} \xrightarrow{(1)} [\operatorname{Pt}(\operatorname{CO})\operatorname{Cl}_{3}]^{-} \xrightarrow{(2)} [\operatorname{Pt}_{15}(\operatorname{CO})_{30}]^{2-} \xrightarrow{(3)} \\ I \qquad II \\ [\operatorname{Pt}_{12}(\operatorname{CO})_{24}]^{2-} \xrightarrow{(4)} [\operatorname{Pt}_{6}(\operatorname{CO})_{18}]^{2-} \xrightarrow{(5)} [\operatorname{Pt}_{6}(\operatorname{CO})_{12}]^{2-} \\ III \qquad IV \qquad V$$

Step 2 of the overall reaction involves the formation of several intermediates including an insoluble platinum dicarbonyl polymer³ and $[Pt_3(CO)_6]_n^{2-}$ ($n \ge 6$) which are presently being investigated.⁴ Infrared solution

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

Chemical Society, Dallas, Texas, April 1973. (2) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, 102, 344 (1972), and references therein.

(3) (a) G. Booth and J. Chatt, J. Chem. Soc. A, 2131 (1969), and references therein; (b) G. Booth, J. Chatt, and P. Chini, Chem. Commun., 639 (1965).

(4) With Na-K alloy as a reducing agent one obtains a more reduced species which, because of its increased reactivity, has not yet been isolated in the solid state. Its infrared carbonyl frequencies of 1950 (vs) and 1745 (s) cm⁻¹ in THF solution correspond to that expected for the $[Pt_3(CO)_3(\mu_2-CO)_3]^{2-}$ monomer.

spectra (Table I) show an expected lowering of corresponding terminal and bridging carbonyl frequencies upon successive reduction of dianions II through V.

Table I. Infrared Absorptions in the Carbonyl Stretching Region of the $[Pt_{\delta}(CO)_{\delta}(\mu_2 - CO)_{\delta}]_n^2$ – Dianions

$[Pt_{3}(CO)_{3}(\mu_{2}-CO)_{3}]_{n}^{2-}$ anion	Color	$\nu_{\rm CO}$ (cm ⁻¹ , THF solution)	
II. $n = 5$	Yellow-green	2055 (vs), 1890 (w), 1870 (s), 1840 (w), 1825 (w)	
III, $n = 4$	Blue-green	2045 (vs), 2025 (sh), 1880 (w), 1860 (s), 1840 (sh), 1828 (w)	
IV, $n = 3$	Red-violet	2030 (vs). 1855 (sh), 1842 (s), 1835 (sh), 1810 (w)	
V, n = 2	Orange-red	1990 (vs), 1818 (m), 1795 (s)	

X-Ray structural investigations of these diamagnetic dianions⁵ have been carried out^{6,7} for II, IV, and V and are currently underway⁶ for III.⁸ The structures (Figure 1) of the $[Pt_3(CO)_3(\mu_2-CO)_3]_2^{2-}$ dianion (V), the $[Pt_3(CO)_3(\mu_2-CO)_3]_3^{2-}$ dianion (IV), and the $[Pt_3(CO)_3(\mu_2-CO)_3]_5^{2-}$ dianion (II) are all based upon the polymerization of a common triplatinum hexacarbonyl component by further direct Pt–Pt bonding.

The geometry of the hexaplatinum dianion (V), which has crystallographic C_2 -2 site symmetry, ideally conforms to D_{3h} - $\overline{6}2m$ hexagonal symmetry with the six platinum atoms arranged in a trigonal-prismatic array. Figure 1 shows a small but significant translational distortion of the two symmetry related $Pt_3(CO)_3(\mu_2$ -CO)_3 fragments from an eclipsed D_{3h} conformation by *ca*. 0.51 Å along one of the triangular Pt-Pt edges. Also observed is a detectable tilting in each triplatinum moiety of both the terminal and bridging carbonyls in an outward direction from their triplatinum plane. A comparison of its *trigonal-prismatic* metal framework which is in contradistinction with the *trigonal-antiprismatic* (or octahedral-like) metal array in the congener

(5) We are indebted to Mr. James Kleppinger at the University of Wisconsin (Madison) who carried out magnetic susceptibility measurements *via* the Faraday method.

(6) (a) $[P(C_{H5})_4]_2[P_{15}(CO)_3(\mu_2 \cdot CO)_5]_2$ (V): monoclinic, C2/c: a = 18.882 (4), b = 14.677 (3), c = 22.860 (7) Å, $\beta = 110.67$ (2)°, V = 5927 (2) Å³; $\rho_{obsd} = 2.47$ vs. $\rho_{calcd} = 2.45$ g cm⁻³ for Z = 4. Anisotropic least-squares refinement gave $R_1(F) = 5.6\%$ and $R_2(F) = 5.9\%$ for 1506 independent diffractometry data ($I > 2\sigma(I)$). (b) $[P(C_{cH5})_4]_2[P_{15}(CO)_3(\mu_2 \cdot CO)_3]_3$: monoclinic, C2/c: a = 20.123 (3), b = 14.311 (3), c = 26.433 (5) Å, $\beta = 115.22$ (6)°; V = 6886 (2) Å³; $\rho_{obsd} = 2.83$ vs. $\rho_{calcd} = 2.83$ g cm⁻³ for Z = 4. Anisotropic least-squares refinement gave $R_1(F) = 6.3\%$ and $R_2 = 6.8\%$ for 2436 independent diffractometry data ($I > 2\sigma(I)$). (c) $[As(C_{cH5})]_4]P t_3(CO)_3(\mu_2 \cdot CO)_3]_4$: triclinic, P1; a = 15.239 (5), b = 19.377 (14), c = 14.628 (5) Å, $\alpha = 106.66$ (4), $\beta = 101.10$ (3), $\gamma = 85.65$ (5)°; V = 4059 (3) Å³; the structural determination in progress involves the use of 5322 independent diffractometry data ($I > 2\sigma(I)$). (d) $[As(C_{cH5})]_4]P t_3(CO)_3(\mu_2 \cdot CO)_3]_4$ (II): triclinic, P1; a = 14.783 (8), b = 26.426 (13), c = 13.835 (4) Å, $\alpha = 102.73$ (3), $\beta = 118.16$ (3), $\gamma = 95.28$ (4)°; V = 4524 (3) Å³; $\rho_{obsd} = 3.33$ vs. $\rho_{calcd} = 3.33$ g cm⁻³ for Z = 2. Anisotropic least-squares refinement gave $R_1(F) = 5.9\%$ and $R_2(F) = 6.3\%$ for 3558 independent diffractometry data ($I > 2\sigma(I)$).

(7) For computation of distances and bond angles, see paragraph at end of paper regarding supplementary material.

(8) All crystallographic programs (except that for absorption corrections) utilized in the structural determinations and least-squares refinements were written by one of us (J. C. C.).