tively flat in going from 135 to 180° may make a rigorous experimental determination of the geometry rather difficult. Our most stable calculated linear geometry (r = 1.083 Å) lies only 6.7 kcal/mol above the calculated equilibrium geometry. Nevertheless, on the basis of the present and previous[4,5] *ab initio* calculations and the stated[3] experimental uncertainties, we conclude that the CH_2 ground state is nonlinear with a geometry close to r = 1.096 Å, θ = 135.1°.

Since there is a great deal of current interest[11] in rapidly convergent CI expansions for molecules, Table III includes the seven most important spatial configurations in our natural orbital expansion near the minimum. We note that (1) all of these configurations involve only valence orbitals, (2) the SCF configuration dominates, (3) the second most important orbital occupancy involves six electrons outside closed shells, and (4) the single excitation $2a_1 \rightarrow 4a_1$ is very important.

Table III. The Seven Most Important Spatial Configurations in the Natural Orbital Expansion of $^3B_1$ CH_2 at θ = 135°, r = 2.1 bohr[a]

	Excitation	Spatial configuration	Coefficient
1.		$1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1$	0.97914
2.	$2a_1\ 1b_2 \rightarrow 4a_1\ 2b_2$	$1a_1^2\ 2a_1\ 1b_2\ 3a_1\ 1b_1\ 4a_1\ 2b_2$	0.07269
3.	$2a_1 \rightarrow 4a_1$	$1a_1^2\ 2a_1\ 1b_2^2\ 3a_1\ 1b_1\ 4a_1$	0.06393
4.	$1b_2^2 \rightarrow 2b_2^2$	$1a_1^2\ 2a_1^2\ 3a_1\ 1b_1\ 2b_2^2$	0.05686
5.	$1b_2^2 \rightarrow 4a_1^2$	$1a_1^2\ 2a_1^2\ 3a_1\ 1b_1\ 4a_1^2$	0.05246
6.	$2a_1^2 \rightarrow 4a_1^2$	$1a_1^2\ 1b_2^2\ 3a_1\ 1b_1\ 4a_1^2$	0.05027
7.	$1b_2\ 1b_1 \rightarrow 2b_2\ 2b_1$	$1a_1^2\ 2a_1^2\ 1b_2\ 3a_1\ 2b_2\ 2b_1$	0.04725

[a] The coefficients incorporate the effects of all triplet spin eigenfunctions corresponding to the given orbital occupancy.

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(11) G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 87 (1966).

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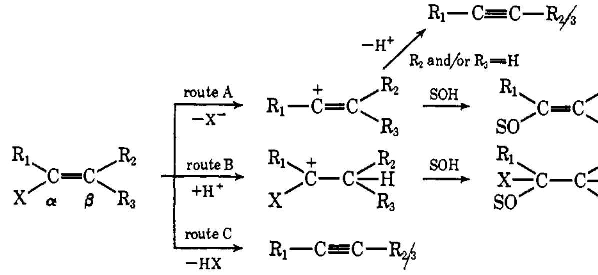
Vinyl Cations from Solvolysis

Sir:

In a recent communication Schubert and Barfknecht commented[1] regarding the solvolyses of vinyl halides which are proposed to occur by the SN1 mechanism (eq 1, route A) that "plausible under some, but not all, of the conditions used is hydrolysis *via* protonation of the alkene" (eq 1, route B). From studies on the hydrolysis of α-bromo-p-aminostyrene (**1a**) in aqueous buffers and perchloric acid they concluded that for **1a** "the vinyl carbonium ion mechanism for this compound is definitely incorrect and that hydrolysis most probably occurs *via* acid catalyzed hydration."[1] For compounds having a *trans*-hydrogen atom at the double bond in respect to the leaving group X a third mechanism must be considered. In this mechanism, especially under neutral or alkaline conditions, the corresponding acetylene beside route A can also be formed by a concerted elimination of HX (route C). In contrast an acetylene formation is not possible *via* route B. Table I shows predictions for reaction *via* the electrophilic addition–elimination route (for both Markovnikov and anti-Markovnikov additions) or *via* the vinyl cation intermediate, for 20 different phenomena. The experimental data for the systems **1–12** so far investigated are given in the last two columns. It is clear that the data are compatible only with the SN1 route, except for reactions of **5** in HCOOH,[2] of **1a** in acidic media,[1] and of **1b** in unbuffered AcOH.[3] In the latter three cases the addition–elimination route was already suggested and it is significant that the same substrates in nonacid media (*i.e.*, **5** in MeOH–H_2O,[4] **1a** in 80% EtOH,[5] and **1b** in buffered AcOH[3]) react (according to Table I) only *via* route A. As an example of a concerted elimination (route C) in nonacidic solvent compound **8** shall be given. Besides route C, route A can be made responsible for the acetylene formation; examples are **1c**, **4**, **5**, **7**; in the case of **9** the acetylene formation can only be explained through route A.



(1)

1, R_1 = YC_6H_4; R_2 = R_3 = H
1a, Y = p-NH_2; X = Br
1b, Y = p-MeO; X = Br
1c, Y = H; X = OSO_2Ar
2, R_1 = Ar_1; R_2 = Ar_2; R_3 = Ar_3; X = Cl, Br, I, OSO_2Ar, OSO_2F, OSO_2CF_3
3, R_1 = Ar_1; R_2 = Ar_2; R_3 = ArS; X = OSO_2Ar
4, R_1 = CH:CMe_2; R_2 = R_3 = H or Me; X = Br
5, R_1 = R_2 = Me; R_3 = H; X = OSO_2Ar, OSO_2CF_3
6, R_1 = R_2 = Ph; R_3 = morpholyl; X = Cl, Br
7, R_1 = cyclopropyl; R_2 = R_3 = H; X = Cl, I
8, R_1 = R_3 = Me; R_2 = H; X = OSO_2Ar, OSO_2CF_3
9, R_1 = cyclopropyl; X = I
9a, R_2 = Me; R_3 = H
9b, R_2 = H; R_3 = Me
10, Ar–CX:C:CPh_2; X = Cl
11, R_1 = Me; R_2 = R_3 = Ph; X = OSO_2CF_3
12, R_1 = t-Bu; R_2 = R_3 = H; X = OSO_2CF_3

While **1a** solvolyzes in acidic media *via* addition–elimination,[1] extrapolation to pH of Schubert's k_{obsd} data[1] in water gives $k^{50°}$ = 1.4 10^{-7} sec^{-1} (and lower values at higher pH), by using Grob's data[5] $k_1^{50°}$ = 0.035 sec^{-1} in basic 80% ethanol. The difference of at least five orders of magnitude in rate is a real discrepancy, which at present is difficult to explain.[6]

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(1) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970).

(2) See Table I, footnote *oo*.

(3) See Table I, footnote *aa*.

(4) See Table I, footnote *u*.

(5) See Table I, footnote *p*.

(6) This difference is even higher if account is taken of the difference in the two solvents. It was suggested by Professor W. M. Schubert (private communication) that this is due to formation of sufficient amount of unneutralized protons, so that Grob's data really reflect addition mechanism by these protons. On the other hand, Schubert and Barfknecht[1] did not consider the possibility of electrophilic acceleration of the solvolysis by protons, *via* protonation on the bromine, which should contribute to SN1 solvolysis even under acidic conditions.

Table I. Predicted and Observed Behavior in Vinylic Solvolysis

Phenomena	Predicted for: Electrophilic addition–elimination[a]	Predicted for: Solvolysis *via* vinyl cations	Obsd	For
1. Reactivity in aprotic, ROH, or aqueous organic solvent				
a. With added base	No (or very slow) reaction	Reaction	Reaction in EtOH–H_2O,[p–t] MeOH–H_2O,[u–w] DMF–H_2O,[x] Me_2CO–H_2O,[y] AcOH[t,y,z,aa,bb]	**1**,[p,u] **2**,[q,t,x–z,aa,ff] **4**,[r] **5**,[u] **7**,[v,w] **9**[bb]
b. No added base	No[b] or autocatalytic reaction	Reaction	Reaction in EtOH–H_2O,[s] DMF–H_2O,[x] CH_2Cl_2,[cc] $CHCl_3$,[cc] CH_3NO_2,[cc] dioxane,[cc] MeOH,[cc] Me_2CO,[cc] DMF,[t] Me_2CO–H_2O,[dd] AcOH[bb,ee]	**2**,[t,x] **3**,[cc,ee] **5**,[s] **9**,[bb] **10**[dd]
2. Reactivity in RCOOH				
a. Containing $RCOO^-$	Reaction[c]	Reaction[c]	Reaction in AcOH,[t,z,aa,ff–hh] HCOOH[t,ff]	**2**[t,z,aa,ff–hh]
b. Not containing $RCOO^-$	Autocatalytic reaction[c]	Reaction[c]	Reaction in AcOH[aa]	**2**[aa]
3. Solvent isotope effect				
a. Alkyl-substituted alkenes	Small	Small or none	No or small effect	**2**,[z] **5**[s]
b. Aryl-substituted alkenes	Appreciable	Small or none	Small effect	**2**[hh,jj]
4. Effect of increasing acidity	Rate enhancement	No effect on the rate or rate enhancement[d,e]	rate enhancement	**1a**[ii]
5. Effect of added base[f]				
a. In nonacidic solvent	Rate retardation	No effect on the rate[e]	No effect on the rate	**1**,[p] **2**,[q,t,x,y,ff] **5**,[u] **7**,[v,w]
b. In RCOOH	Rate retardation followed by base-independent reaction[g]	No effect on the rate[e]	No effect on the rate	**2**,[t,z,aa,ff] **4**,[r] **5**,[s]
6. Effect of Ag^+ ions	No catalysis[a]	Rate enhancement	Rate enhancement	**2**,[t,y] **6**,[kk] **7**,[v,w] **10**[dd]
7. Effect of increasing solvent polarity	Small rate retardation	Rate enhancement	Rate enhancement	**1**,[p] **2**,[q,y,ff] **3**,[ll,mm] **4**,[r] **5**,[s] **6**,[kk] **10**[dd]
8. Order of reaction in substrate	First[a]	First[a]	First	**1–5**, **7**,[p–z,aa,ee,ff,ii,jj,ll,nn,oo] **10**[dd]
9. Autocatalysis in neutral media	Expected[h]	Not expected	Not found	**3**[mm]
10. Effect of electron-donating R_1	Large rate enhancement	Large rate enhancement	Large rate enhancement	**2**,[x,y] **3**,[ll] **4**,[r] **5**,[u] **10**[dd]
11. Effect of electron-donating R_2 and/or R_3	Large rate enhancement[h]	Small rate changes[i]	Small rate changes	**2**,[q,x,y,aa,ff] **3**,[ll] **4**[r]
12. Effect of more electron attracting or better leaving group X	Rate retardation	Rate enhancement	Rate enhancement	**2**,[q,x–z,gg] **3**[ee,nn]
			Rate retardation	**5**[oo]
13. Common ion effect	Not expected	Expected[j]	Obsd	**2**,[x,aa,ff] **3**[ll]
14. Capture of the intermediate by added anions	Possible	Possible[k]	Found	**2**[q,t,y]
15. Concurrent *cis–trans* isomerization of the substrate	Possible[k]	Possible[k]	Found	**2**,[gg] **9**[bb]
16. Stereochemistry of the solvolysis	Dependent on steric effects in the transition states[l]	Dependent on steric effects in the transition states[l]	1:1 *cis*:*trans* mixture	**2**,[t] **9b**[bb]
			Retention	**3**[nn]
17. Scrambling of the α and β carbons	Usually not expected	Expected for bridged ion	Found	**3**[nn]
18. 1,2 Shift when R_2 and/or R_3 are better electron donors than R_1	Not expected	Possible	Found	**3**,[nn] **2**,[jj] **11**[pp]
19. Products	$R_1C(OS){=}CR_2R_3$	$R_1C(OS){=}CR_2R_3$	Found	**2**,[t,aa,ff] **3**,[ll,mm] **7**,[v,w] **9**[bb]
	$R_1COCHR_2R_3$[m]	$R_1COCHR_2R_3$[m]	Found	**2**,[q,t,x,y,aa,ff] **4**,[r] **5**,[s,u] **9**[bb]
		$R_1C{\equiv}CR_2$[n]	Found	**1c**,[o,u] **4**,[r] **5**,[s,u] **7**,[o,v,w] **9**[bb]
	$R_1C(OS)_2CHR_2R_3$		Not found	
	$R_1CH(OS)C(OS)R_2R_3$		Not found	
20. Solvolysis in AcOD	Deuterium incorporation into the products	No D incorporation	No D incorporation	**7**,[qq] **12**[pp]

[a] Only cases of rate-determining addition are considered since in other situations differentiations between the two mechanisms are easily achieved by kinetics alone. [b] Dependent on the concentrations and the nature of the alkene. [c] Becomes faster on increasing the acidity of the solvent. [d] Rate enhancement is expected in the case of electrophilic assistance by the formed proton *via* protonation of the leaving group. [e] Except for solvation or special interactions with the leaving group. [f] Except for salt effects. [g] Addition by the solvent. [h] Especially for protonation on the α carbon provided that the $^+CR_2R_3$ ion is more stable than the $^+CR_1X$ ion. [i] In the absence of neighboring group participation. The actual direction of the change depends on the balance of the inductive and the conjugative effects. [j] Although not necessarily observable. [k] Depending on the relative rates of protonation, ionization, internal rotation, and product formation. [l] The steric effects determining the *cis–trans* ratios of the products are expected to be similar in the transition states of both routes. [m] For S = H. [n] For R_3 = H. [o] A concerted elimination cannot be excluded. [p] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47,** 194 (1964). [q] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, **91,** 5246 (1969). [r] C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969). [s] P. J. Stang and R. H. Summerville, *J. Amer. Chem. Soc.*, **91,** 4600 (1969). [t] Z. Rappoport and Y. Apeloig, *ibid.*, **91,** 6734 (1969). [u] P. E. Peterson and J. M. Indelicato, *ibid.*, **91,** 6194 (1969). [v] S. A. Sherrod and R. G. Bergman, *ibid.*, **91,** 2115 (1969). [w] M. Hanack and T. Bässler, *ibid.*, **91,** 2117 (1969). [x] L. L. Miller and D. A. Kaufman, *ibid.*, **90,** 7282 (1968). [y] Z. Rappoport and Y. Kaspi, *ibid.*, **92,** 3220 (1970). [z] W. M. Jones and D. D. Maness, *ibid.*, **91,** 4314 (1969). [aa] Z. Rappoport and A. Gal, submitted for publication. [bb] D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92,** 228 (1970). [cc] G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968). [dd] M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, **92,** 1082 (1970). [ee] G. Modena and U. Tonellato, *Chem. Commun.*, in press. [ff] Z. Rappoport and Y. Apeloig, submitted for publication. [gg] Z. Rappoport and Y. Apeloig, *Israel J. Chem.*, **7,** 34p (1969). [hh] Z. Rappoport, Y. Kaspi, and Y. Apeloig, unpublished results. [ii] Reference 1. [jj] Z. Rappoport and A. Gal, unpublished results. [kk] S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90,** 2432 (1968). [ll] G. Modena, U. Tonellato, and F. Naso, *Chem. Commun.*, 1363 (1968). [mm] G. Modena and U. Tonellato, *ibid.* 1676 (1968). [nn] G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *ibid.*, 1520 (1969). [oo] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90,** 6515 (1968). [pp] M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *ibid.*, **92,** 3802 (1970). [qq] R. G. Berman, unpublished results.

An additional argument for route A is the rearrangement of vinyl derivatives in solvolysis reactions. It is difficult to explain the products without suggesting vinyl cation intermediates. Examples are the solvolysis of *t*-butylvinyl triflate,[7] and 1-adamantylvinyl triflate,[8] leading predominantly to rearranged products, and the solvolysis of **9**[9] and **11**.[8] Additional examples for rearrangement reactions involving vinyl cations will be published in the near future.[10]

In general for the solvolysis of vinyl derivatives it can be suggested that the relationship between routes A, B, and C is as follows.

Route B. The rate is strongly dependent upon the H^+ concentration of the reaction media.

Route A. The rate should be almost independent of the solvent pH.

Route C should exhibit increasing rates with increasing concentration on base, but is limited to certain structural features of reactant as mentioned above.

From the available data it is difficult to predict the relative values of the corresponding *k*'s, but it can be concluded that several mechanisms may operate, and the addition–elimination route may be important for some compounds in acidic media, but the S_N1 route operates under nonacidic conditions. The dependence of the solvolysis rate upon H^+ concentration may be in future work an easy way to distinguish between the possible mechanisms.

Acknowledgments. We are indebted to Drs. W. M. Schubert, University of Washington, G. Modena, University of Padova, and R. G. Bergman, California Institute of Technology, Pasadena, Calif., for communicating their unpublished results.

(7) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem.*, **82,** 323 (1970).

(8) See Table I, footnote *pp*.

(9) See Table I, footnote *bb*.

(10) A. Ghenciulescu, N. Youssif, and M. Hanack, unpublished results.

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Molecular Dynamics of π–π Complex Formation by Deuterium Quadrupolar Relaxation[1]

Sir:

π–π complexes between an electron donor molecule (D) and an acceptor molecule (A) (EDA complexes)[2] have been extensively studied in recent years.[3–6] How-

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(1) Nuclear Relaxation and Molecular Properties. IV; part III: Ch. Brevard, J. P. Kintzinger, and J. M. Lehn, *Chem. Commun.*, 1193 (1969).

(2) No assumption about the electronic structure of these complexes is made here. See R. S. Mulliken and W. B. Person, *J. Amer. Chem. Soc.*, **91,** 3409 (1969); M. J. S. Dewar and C. C. Thomson, Jr., *Tetrahedron, Suppl.*, 7, 97 (1966).

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