

Remote Secondary Deuterium Isotope Effects. II.¹ Allylic Systems

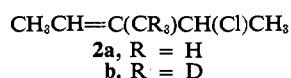
Sir:

The extent of 1,3 π interactions in allylic cations is a matter of considerable theoretical and experimental interest. The structural question at issue may be put in the following way. Is the electron deficiency (borne by carbon atoms) in the allyl cation, **1**, distributed equally between the terminal centers, as in **1a**, or is the central carbon atom also electron deficient due to 1,3 π interactions, as in **1b**? Quantum mechanical calculations of the valence bond (VB) type give a charge distribution similar to that in **1b**,² whereas *ab initio*



LCAO-MO SCF calculations give a charge distribution similar to that in **1a**.³ Available experimental evidence also yields conflicting predictions concerning the charge distribution in **1**. The nmr spectra of the allyl and 2-methylallyl cations reveal a substantial deshielding of the $>CH$ and the methyl protons.⁴ This has been interpreted to indicate a strong contribution of 1,3 π interactions as in **1b**. However, the relative solvolytic reactivities of allyl and β -arylallyl tosylates suggest that there is little charge delocalization into the aryl ring during the activation process, indicating a transition-state charge distribution similar to that in **1a**.⁵

Our approach to the determination of charge distribution in allylic cations has involved the investigation of the effect of remote isotopic substitution on the rates of solvolysis of secondary⁶ allylic chlorides. We here report the results of such a study of the solvolytic reactivity of 3-methyl- and 3-deuteriomethyl-4-chloro-2-pentene (**2**).



Chlorides **2a** and **b** were prepared by standard methods,⁷ and their rates of solvolysis were determined by a precise conductometric method.¹ The results are presented in Table I. Included for comparison are remote secondary isotope effects in the structurally related systems **3** and **4**. Limiting solvolysis of chlorides **2a** and **3a** should proceed *via* transition states resembling the symmetrical di- or trimethylallyl cation **5**.

(1) Part I: J. G. Jewett and R. P. Dunlap, *J. Am. Chem. Soc.*, **90**, 809 (1968).

(2) M. Simonetta and E. Heilbronner, *Theoret. Chim. Acta* (Berlin), **2**, 228 (1964).

(3) D. T. Clark and D. R. Armstrong, *ibid.*, **13**, 365 (1969).

(4) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 5682 (1964).

(5) A. Streitwieser, Jr., and J. B. Bush, quoted in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., p 361. The interpretation of this result is complicated by possible steric inhibition of conjugation in β -arylallyl cations. Furthermore, the small kinetic effect of the aryl group cannot be separated into conjugative and inductive components.

(6) Previous studies of the effect of 2-alkyl substitution on the solvolytic reactivity of allylic halides seem to have been confined to *primary* allylic systems (see R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); P. B. de la Mare in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 27). Solvolyses of such primary systems are probably largely bimolecular. Thus such studies have little bearing on the structures of strongly electron-deficient transition states in limiting reactions of allylic systems.

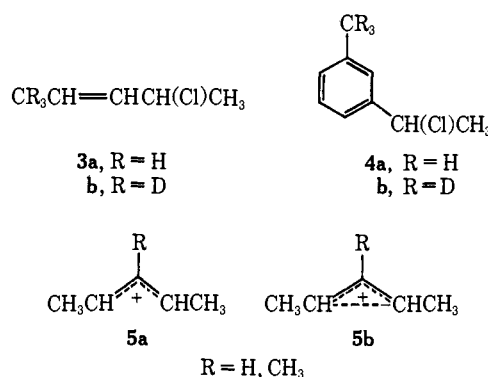
(7) H. O. House and R. S. Ro, *J. Amer. Chem. Soc.*, **80**, 2432 (1958).

Table I. Comparison of Remote Secondary Deuterium Isotope Effects for Limiting^a Solvolysis of Allyl and α -Phenethyl Systems at 25°

| Compd | Solvent | $k \times 10^4, \text{sec}^{-1}$ | k_H/k_D | Ref |
|------------------|----------|----------------------------------|-----------|-------------|
| 2 , R = H | 95% EtOH | 10.27 ± 0.01 | 0.965 | <i>b</i> |
| | | 10.64 ± 0.01 | | |
| 3 , R = H | 95% EtOH | 2.172 ± 0.001 | 1.132 | <i>c</i> |
| | | 1.919 ± 0.001 | | |
| 4 , R = H | 60% EtOH | 2.165 ± 0.001 | 0.974 | <i>b, d</i> |
| | | 2.222 ± 0.001 | | |

^a The question of "how limiting" are the solvolyses of secondary allylic chlorides in 95% ethanol is difficult to answer in a quantitative manner. That there is substantial electron deficiency in the solvolytic transition state seems clear from the following facts:⁸ (i) the *m* value for solvolysis of **3a** in aqueous ethanol is 0.97 whereas the corresponding *m* value for allyl chloride itself is 0.45; (ii) **3a** solvolyzes *ca.* 2.2×10^4 times faster than allyl chloride in *absolute* ethanol. ^b This work. ^c Reference 1. ^d See also ref 11.

Substitution of deuterium for hydrogen at a position adjacent (β) to centers which become electron deficient in solvolytic transition states generally results in a retardation of the solvolysis rate. Available evidence in-



dicates that the interaction mechanism responsible for these *normal* β -secondary deuterium isotope effects (in limiting solvolysis reactions) is best explained by a model involving hyperconjugation between the developing vacant p orbital and the β -C-H(D) orbital.^{4,8} The δ -CD₃ isotope effect⁹ on the solvolysis of **3** is normal and thus in accord with a charge distribution in the transition state involving substantial electron deficiency at the terminal carbon atoms of the allylic system (C-2 and C-4), as predicted by both **5a** and **5b**. On the other hand, the γ -CD₃ effect on the solvolysis of **2** is *inverse*. The latter effect is identical in electronic direction and essentially identical in magnitude with the effect observed for the ionization of CR₃CO₂H (R = H, D).¹⁰ Remote secondary isotope effects on carboxylic acid dissociation constants have been adequately explained in terms of a normal inductive interaction mechanism. Thus, it seems likely that the γ -CD₃ effect on the solvolysis of **2** is also inductive in origin. This conclusion is supported by the observation of a similar inverse kinetic effect of isotopic substitution at the *m*-methyl group on the solvolysis of **4**.¹¹ These results

(8) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963). These authors have shown that such β effects are slightly *inverse* in systems where hyperconjugation is stereoelectronically prohibited and *normal* when hyperconjugation is possible.

(9) The greek letter designates the position of the isotopic atom relative to the leaving group.

(10) A. Streitwieser and H. S. Klein, *J. Amer. Chem. Soc.*, **85**, 2759 (1963).

are accommodated most reasonably by a charge distribution in solvolytic transition states leading to symmetrical allylic cations that reflects little 1,3 π interaction, as in **1a** or **5a**.

Acknowledgment. The authors wish to thank the National Science Foundation (Grant GP 8703) for partial support of this work. Computations were performed at the Ohio University Computing Center.

(11) E. S. Lewis, R. R. Johnson, and G. M. Coppinger (*J. Amer. Chem. Soc.*, **81**, 3140 (1959)) report $(k_{\text{H}}/k_{\text{D}})_{\text{av}} = 0.988$ for solvolysis of **4** in aqueous acetone.

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Extended Hückel Calculations Related to the Chemistry of Titanocene

Sir:

Bis(π -cyclopentadienyl) complexes of nickel, cobalt, iron, chromium, and vanadium are fairly stable compounds and easily prepared by standard methods of organometallic synthesis. Contrastingly, all attempts to synthesize the corresponding titanium compound (π -C₅H₅)₂Ti^{II} have failed thus far. There is a compound of composition C₁₀H₁₀Ti, sometimes referred to in the literature as "titanocene" (see, e.g., ref 1, 2, and earlier references quoted there). This compound, however, is in fact a dimer;¹ in addition it exhibits ir and nmr spectra which are typical of σ - rather than of π -bound C₅H₅ ligands.² Whatever the structure of this compound, it is certainly not analogous to its neighbors in the 3d series. On the other hand, certain derivatives of (π -C₅H₅)Ti^{II} do exist: (π -C₅H₅)₂Ti(CO)₂ and (π -C₅H₅)₂Ti-bipyridine appear to be normal monomeric sandwich compounds with π -bound rings.³⁻⁵ Their parent compound (π -C₅H₅)₂Ti, while apparently not persisting as a stable compound, might occur, however, as a reactive intermediate in such reactions as catalytic alkyne hydrogenations⁶ or the reduction of gaseous nitrogen.⁷ In view of its elusive nature, it appears worthwhile to investigate the behavior of the hypothetical molecule (π -C₅H₅)₂Ti at least theoretically, in the hope of obtaining some guidance for further experimental investigations on the chemical properties of this species.

One aspect in which (π -C₅H₅)₂Ti would intrinsically differ from its neighbors in the 3d series can be derived from simple symmetry rules which have recently received attention in the literature: a molecule is a potential candidate for a spontaneous distortion whenever the symmetry coordinate of that distortion connects occupied and empty molecular orbitals of not too different energies (pseudo-Jahn-Teller effect).^{8,9} From recently

published MO calculations on metallocenes^{10,11} it is evident that (π -C₅H₅)₂Ti is unique among the 3d transition metal sandwiches in that the a_{1g} orbital (an essentially nonbonding metal d_{z²} orbital) remains unoccupied only in the titanium derivative.¹² Closely below the a_{1g} orbital there occur ligand π orbitals of e_{1g} and e_{1u} symmetry. We can therefore suspect that titanocene is set apart from other metallocenes by an increased tendency to undergo distortions of e_{1g} and e_{1u} symmetry. Of particular interest is the possibility of a spontaneous e_{1u} distortion, which involves a bending of the two metal-ring bonds away from axial symmetry. While such an analysis is feasible by second-order perturbation theory (see, e.g., ref 13), we shall apply here the simpler method of extended Hückel calculations as a function of the molecular geometry.

The evaluation of one-electron energies and wave functions follows closely the conventional Wolfsberg-Helmholz approach, with off-diagonal terms given as $H_{ij} = k \cdot S_{ij}(H_{ii} + H_{jj})/2$ ($k = 1.75$). The program used is described elsewhere.¹⁴ In order to keep computation times within justifiable limits, the following simplifications were used (single-parameter, Slater-type atomic orbitals were used throughout). Exponents were 1.35 (Ti-4s), 1.70 (Ti-3d), 0.75 (Ti-4p), 1.65 (C-2s), 1.44 (C-2p), and 1.20 (H-1s) were taken from ref 11 and 15. Diagonal elements H_{ii} are obtained as a function of atomic charges, from the tabulations given in ref 16 (metal) and 10 (carbon, hydrogen). Self-consistency is achieved, in the case of the linear geometry, with a charge of +0.69 on the metal atom, and -0.02 and -0.05 on C and H, respectively. In the bent conformations, the metal becomes less positive, mainly due to increased occupation of the d_{z²} orbital. Instead of recycling the calculations, however, we have kept the input parameters H_{ii} constant for all geometries. We estimate that a decrease of the metal charge by 0.04-0.08 unit would produce self-consistency for the bent conformations.¹⁷ The assumed geometry is essentially the same as in previous calculations on vanadocene, except that two sets of calculations were carried out, using metal-carbon distances of 2.26 and 2.47 Å, respectively.¹² Apart from reduced repulsions between the two rings at the larger distance of 2.47 Å, both Ti-C values yield almost identical potential surfaces. Single-electron energies thus obtained for a linear (π -C₅H₅)₂Ti molecule are in agreement with recently published results of extended Hückel calculations on vanadocene.^{10,11}

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(11) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91** 3432 (1969).

(12) Although our calculations are actually based on an eclipsed sandwich structure (symmetry D_{5h}), we have labeled the molecular orbitals for the linear conformation according to symmetry D_{5d} to facilitate comparison with previous calculations reported in the literature.

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(17) For the metal 4p_z orbital, a negative electron occupation appears in the population analysis. This is an artifact produced by the rules of the Mulliken population analysis: R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

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(2) J. J. Salzmänn and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967).

(3) J. G. Murray, *J. Amer. Chem. Soc.*, **83**, 1287 (1961).

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(5) E. O. Fischer and R. Amtmann, *J. Organometal. Chem.*, **9**, P 15 (1967).

(6) K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1178 (1966).

(7) E. E. Van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969).