

The proofs consist of enumeration of, say, bonding S-levels in reactants and products. If the number of bonding S-levels does not change, there will be no bonding  $\rightarrow$  antibonding correlations, and the process is thermally allowed. If the number of bonding S-levels is one less or one greater in the product, a crossing must occur. As an example, consider the  $2\pi \rightarrow 2\sigma$  case. In one component, containing, for example,  $m$   $\pi$ -orbitals in the reactant, there will be  $m/4$  bonding  $\pi$ -orbitals of S symmetry if  $m/2$  is even,  $(m + 2)/4$  if  $m/2$  is odd. In the same component of the product, now containing  $(m - 2)$   $\pi$ -orbitals, there will be  $m/4$  bonding S-levels if  $m/2$  is even,  $(m - 2)/4$  if  $m/2$  is odd. The product  $\sigma$ -levels will yield one bonding level of S symmetry; thus, the total number of bonding S-levels from the reactant  $\pi$ 's must exceed by one that from the product  $\pi$ 's for a thermally allowed reaction. There are three cases: (1)  $m = 4q_1$ ,  $n = 4q_2$ ; then there will be  $(q_1 + q_2)$   $\pi$ -bonding S-levels before,  $(q_1 + q_2)$  after. (2)  $m = 4q_1 + 2$ ,  $n = 4q_2$ ; this implies  $(q_1 + q_2 + 1)$  before,  $(q_1 + q_2)$  after. (3)  $m = 4q_1 + 2$ ,  $n = 4q_2 + 2$ ; this implies  $(q_1 + q_2 + 2)$  before,  $(q_1 + q_2)$  after. Case 2 satisfies the condition for the thermal process, and it is therefore required that  $m + n = 4q_1 + 4q_2 + 2 = 4q + 2$ ; cases 1 and 3 will lead to bonding  $\rightarrow$  antibonding correlations.

Certain special points concerning our selection rules deserve mention: (i) they apply to all concerted cycloaddition reactions, even though there may be considerable asymmetry in the rate at which the various different newly forming  $\sigma$ -bonds are established.<sup>3</sup> (ii) They need not apply to multistep cycloaddition reactions which proceed through discrete diradical or dipolar *intermediates*, containing a single newly formed  $\sigma$ -bond.

We may now tabulate the smaller ( $\Sigma\pi \leq 10$ ) allowed concerted cycloaddition reactions (Table I). In point of

Table I

| Type                              | Thermal         | Photochemical   |
|-----------------------------------|-----------------|-----------------|
| $2\pi \rightarrow 2\sigma$ (VII)  | $m$ $n$         | $m$ $n$         |
|                                   | 4 2             | 2 2             |
|                                   | 6 4             | 4 4             |
|                                   | 8 2             | 6 2             |
| $3\pi \rightarrow 3\sigma$ (VIII) | $m$ $p$ $p$     | $m$ $p$ $p$     |
|                                   | 2 2 2           | 4 2 2           |
|                                   | 2 4 4           |                 |
|                                   | 6 2 2           |                 |
| $4\pi \rightarrow 4\sigma$ (IX)   | $m$ $n$ $p$ $p$ | $m$ $n$ $p$ $p$ |
|                                   | 4 2 2 2         | 2 2 2 2         |

fact, the agreement with recorded experience is outstanding. Examples are well known which very probably follow the allowed thermal  $4 + 2$  (Diels–Alder reaction) and  $2 + 2 + 2^4$  processes, and the allowed photochemical  $2 + 2^5$  and  $4 + 4^6$  cases, though the

(3) As in the mechanism earlier proposed for the Diels–Alder reaction by one of us [R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959)].

(4) Norbornadiene + olefins, A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959); 1,3,5,7-tetramethylenecyclooctane + tetracyanoethylene, J. K. Williams and R. E. Benson, *ibid.*, **84**, 1257 (1962).

(5) Numerous cases cited in the review by R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p. 739.

relevant concerted reactions may well be substantially electronically unsymmetrical. But it must be emphasized that the nature of our relations as *selection rules* makes the allowed cases *permissive*, but not *obligatory*; consequently, the rules do not *per se* exclude multistep alternative mechanisms involving discrete intermediates. By the same token, it must be concluded that those cycloadditions which do occur in cases prohibited by our selection rules for concerted reactions must proceed through multistep mechanisms (e.g., formation of cyclobutane derivatives by dimerization of allenes and ketenes, and additions of perhalo- and percyanoethylenes to olefins, as well as dimerizations of *p*-xylenes and the rarely observed photochemical Diels–Alder reaction), a conclusion in good accord with emerging experience.<sup>7</sup>

In assessing the predictive power of our selection rules in discerning possible new reactions, the following special points should be kept in mind: (i) (*restrictive*) the activation energies for thermal reactions should increase with the total number of  $\pi$ -electrons, as the total of bond elongations and contractions increases in the transition state; (ii) (*restrictive*) unless special geometrical constraints are present, entropy factors can place severe barriers in the way of realization of more complicated cases; (iii) (*extensive*) the relationships apply to ionic components as well as to neutral molecules, e.g., allyl cation + cyclopentadiene  $\rightarrow$  bicyclo[1.2.3]octenyl cation is permitted, while allyl cation + ethylene  $\rightarrow$  cyclopentyl cation is prohibited.

The theoretical method used here has very wide applicability. We have already extended it to include the Cope and related rearrangements, and in studies of valence tautomers of  $(CH)_n$ ; these results will form the subject of future communications.

(6)  $\alpha$ -Pyridones: L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.*, **85**, 765 (1963);  $\alpha$ -pyrones: P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, **84** (1964); anthracenes: D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, **86**, 1389 (1964); naphthalenes: J. S. Bradshaw and G. S. Hammond, *ibid.*, **85**, 3953 (1963).

(7) Cf. P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964), and references there cited.

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## Salt-Like Behavior of the *t*-Butyl Chloride Solvolysis Transition State<sup>1,2</sup>

Sir:

One of the most intriguing results in physical organic chemistry is the plot of Winstein and Fainberg's<sup>3</sup> activation parameters for the solvolysis of *t*-butyl chloride in a series of aqueous ethanol solutions, a portion of which is reproduced in Figure 1. Although enthalpy–entropy plots are linear for many properties of many

(1) Solvent Effects in Organic Chemistry. VII. Contribution No. 1270 from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15213.

(2) This research was made possible through grants provided by the National Science Foundation (G-14583 and GP-2014) and the National Institutes of Health (GM-18072).

(3) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

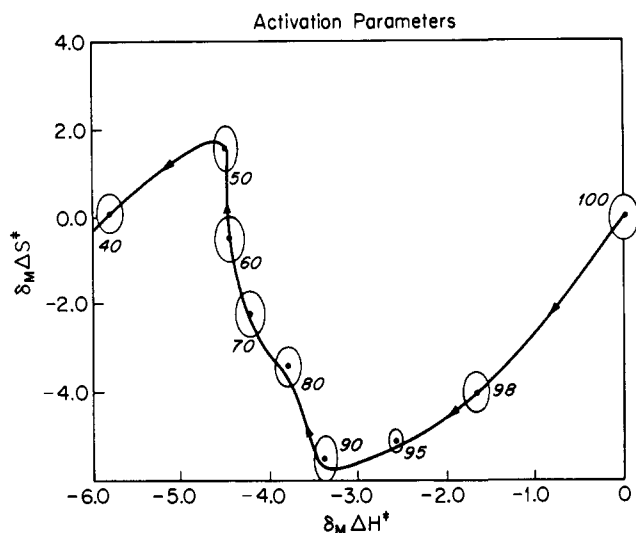


Figure 1. Isokinetic plot of Winstein and Fainberg's activation parameters for solvolysis of *t*-butyl chloride in aqueous ethanol solutions.<sup>3</sup>

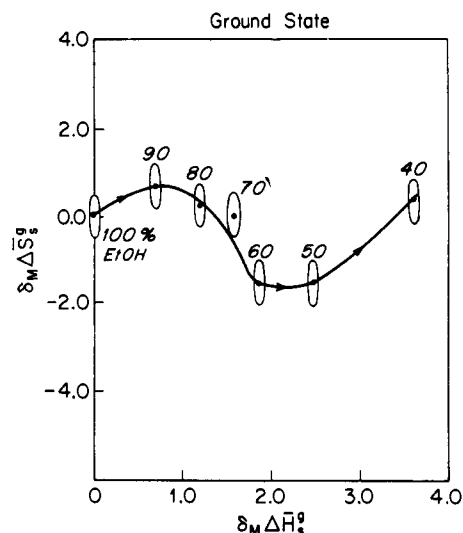


Figure 2. Relation between partial molal enthalpy and entropy of solution for *t*-butyl chloride in aqueous ethanol solutions.

systems,<sup>4,5</sup> the serpentine wanderings of the present example have been singled out for special comment<sup>5,6</sup> as being almost hopelessly complex. We wish to report a partial dissection of these results, which suggests that most of the complexity in Figure 1 is contributed by solvent effects on the *t*-butyl chloride ground state, while the transition state is following much simpler behavior like that exhibited by ordinary uni-univalent electrolytes.

We have already published an account<sup>7</sup> of such a dissection of the enthalpy of activation for *t*-butyl chloride solvolysis in highly aqueous ethanol, and more extensive data for this and several other cases are in press.<sup>8</sup> However, a complete dissection of the Winstein-Fainberg enthalpy-entropy plot over the whole range of aqueous ethanol solutions is not possible at present because entropy of solution data for the *t*-butyl chloride ground state in the high water region are not available. The reason for this is that the solvolysis of the substrate is so fast that it is very difficult to obtain the necessary Henry's law constants for calculation of the free energy of solution of the ground state in order to estimate the entropy of solution through the well-known equation  $T\Delta S = \Delta H - \Delta F$ , although Taft's recent work<sup>9</sup> suggests that this may not be out of the question. In aqueous ethanol solutions of lower water content, the rate of solvolysis is sufficiently slow so that Olson and Halford<sup>10-12</sup> succeeded in measuring Henry's law constants, and Winstein and Fainberg<sup>3</sup> have calculated free

energy of solution data ( $\Delta\bar{F}_s^0$ ) from pure ethanol to 40 vol. % ethanol-60% H<sub>2</sub>O. When combined with our measurements of  $\Delta\bar{H}_s^0$  (reported here for the first time) and their activation parameters,<sup>3</sup> a complete dissection of the solvent effect on all nine thermodynamic properties (the free energy, enthalpy, and entropy of activation and of solution for the ground and transition states) over this range of solvent variation results. To our knowledge, this is the first time such a detailed assignment of a solvent effect has been published.

Displayed in Table I are the appropriate properties, all referred to a standard state of 100% ethanol,

Table I. Solvent Composition, Volume % at 25°<sup>a</sup>

|                               | EtOH, % |       |       |       |       |       |       |
|-------------------------------|---------|-------|-------|-------|-------|-------|-------|
|                               | 100     | 90    | 80    | 70    | 60    | 50    | 40    |
| $\delta\Delta F^*(^a)$        | 0       | -1.75 | -2.77 | -3.58 | -4.30 | -5.03 | -5.87 |
| $\delta\Delta H^*$            | 0       | -3.38 | -3.79 | -4.23 | -4.46 | -4.50 | -5.81 |
| $\delta\Delta S^*$            | 0       | -5.5  | -3.4  | -2.2  | -0.5  | +1.8  | +0.1  |
| $\delta\Delta\bar{F}_s^{b,c}$ | 0       | +0.45 | +1.09 | +1.59 | +2.29 | +2.89 | +3.51 |
| $\delta\Delta\bar{H}_s^{b,d}$ | 0       | +0.67 | +1.18 | +1.57 | +1.84 | +2.44 | +3.61 |
| $\delta\Delta\bar{S}_s^{b,d}$ | 0       | +0.7  | +0.3  | -0.1  | -1.5  | -1.5  | +0.3  |
| $\delta\Delta\bar{F}_s^{b,e}$ | 0       | -1.30 | -1.64 | -1.99 | -2.01 | -2.14 | -2.36 |
| $\delta\Delta\bar{H}_s^{b,e}$ | 0       | -2.71 | -2.61 | -2.66 | -2.62 | -2.06 | -2.20 |
| $\delta\Delta\bar{S}_s^{b,e}$ | 0       | -4.8  | -3.1  | -2.3  | -2.0  | +0.3  | +0.4  |

<sup>a</sup> All processes at 25° for ground and transition state are for transfer from gas to solution.  $\Delta F$  and  $\Delta H$  are in kcal./mole units and  $\Delta S$  in entropy units. <sup>b</sup> From ref. 3. Recalculated to standard state in pure EtOH. <sup>c</sup> Olson and Halford values in ref. 3 used. Our signs are different because Winstein and Fainberg's calculations of  $\Delta\bar{F}_s^0$  are for transfer in opposite direction. <sup>d</sup>  $\Delta\bar{H}_s^0$  in 100% ethanol = 0.361 kcal./mole.

including the experimental partial molal heats of solution at infinite dilution ( $\Delta\bar{H}_s^0$ ) measured by us. The contributions of ground and transition states to the portion of the Winstein-Fainberg plot shown in Figure 1 are presented in Figures 2 and 3. Although one might reasonably suppose that the complex behavior portrayed in Figure 1 was due to the combined meanderings of both ground and transition state properties, it is immediately obvious that over this part of the solvent spectrum the transition state contribution approaches

(4) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1958).

(5) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.

(6) E. Grunwald, Ninth Conference on Reaction Mechanisms, Brookhaven National Laboratory, Sept. 1962.

(7) E. M. Arnett, P. McC. Duggleby, and J. J. Burke, *J. Am. Chem. Soc.*, **85**, 1350 (1963).

(8) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *ibid.*, **87**, 1541 (1965).

(9) G. A. Clarke, T. R. Williams, and R. W. Taft, *ibid.*, **84**, 2292 (1962).

(10) A. R. Olson and R. S. Halford, *ibid.*, **59**, 2644 (1937).

(11) A. R. Olson, W. D. Ruebsamen, and W. E. Clifford, *ibid.*, **76**, 5255 (1954).

(12) R. S. Halford, Thesis, University of California, Berkeley, Calif., 1938.

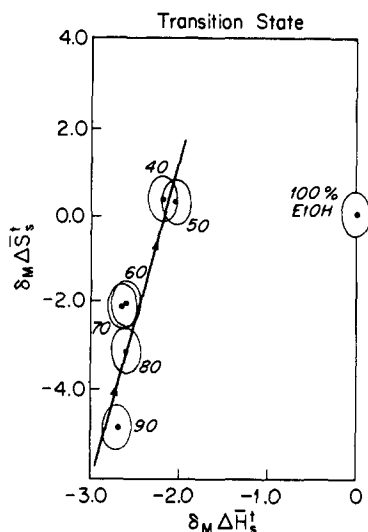


Figure 3. Isokinetic plot for solvation of *t*-butyl chloride transition state in aqueous ethanol solution.

simple linear behavior, the striking exception to which is the point for pure ethanol. Of particular importance is the fact that the points in Figure 3 follow a rational order<sup>6</sup> (indicating that their arrangement along the line is probably in response to a genuine physical effect and not just experimental errors) and that the  $\delta_M \Delta H / \delta_M \Delta S$  slope of this line (0.14) is nearly the same (0.15) as may be found for several simple salts in a similar series of aqueous methanol solutions as calculated from the data of Latimer and Slansky.<sup>13</sup>

The fact that the 100% ethanol point for the *t*-butyl chloride transition state is displaced from its  $\delta_M \Delta \bar{H}_s$  vs.  $\delta_M \Delta \bar{S}_s$  line, while the corresponding point for the simple salts is not, suggests strongly that the solvent is assuming a special role (presumably nucleophilic participation) in this medium.

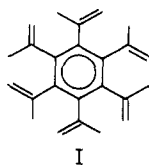
(13) W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940).

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### Hexaisopropenylbenzene, an Unreactive Polyolefin<sup>1,2</sup>

Sir:

Formally, hexaisopropenylbenzene (I) is a polyvinylbenzene and might at first glance be expected to exhibit high reactivity in addition and polymerization reactions.



Actually, it is nearly inert to even potent double-bond reagents.

(1) Crowded Benzenes. V. See *Tetrahedron Letters*, No. 50, 3803 (1964), for previous paper in this series.

(2) Supported by National Science Foundation Grant G-14583.

In classical terms, this might suggest some unusual kind of "aromaticity." However, this interpretation is theoretically unattractive and is not supported by n.m.r., infrared, or ultraviolet spectra. The surprising lack of reactivity is, however, quite consistent with the mutual shielding of adjacent isopropenyl groups since the transition state for addition would require creation of a system even more tightly congested than that of hexaisopropylbenzene, which we have described recently.<sup>3</sup>

**Preparation.** Diisopropenylacetylene<sup>4</sup> (0.16 mole) and dicobalt octacarbonyl<sup>3</sup> (0.053 mole) were heated at reflux in 125 ml. of Skellysolve C. Solvent was removed from the black solution and the viscous product was filtered. Extraction of the residue with Skellysolve B yielded finally a 4% yield of I melting at 260–263° after three recrystallizations from this solvent. The structure was assigned on the basis of the following data: (1) method of synthesis; (2) analysis (*Anal.* Calcd. for C<sub>24</sub>H<sub>30</sub>: C, 90.50; H, 9.50. Found: C, 90.74; H, 9.29); (3) molecular weight (the theoretical value of 318 was found by mass spectrometry and 294 by vapor pressure osmometer); (4) appearance of the n.m.r. spectrum (nearly identical with that of  $\alpha$ -methylstyrene, except for slight shifts and the complete absence of aromatic protons; in CS<sub>2</sub>, multiplets integrating in the ratio 1:1:3 were found at  $\tau$  4.96, 5.35, and 8.07 p.p.m. ( $\alpha$ -methylstyrene:  $\tau$  4.73, 5.00, and 7.90 p.p.m.)); (5) infrared spectrum<sup>5</sup> (in CS<sub>2</sub> also like that of methyl styrene with sharp bands at 3050, 2980, 2940, 1790 (overtone), 1635, 1360, 1220, and 885 cm<sup>-1</sup> (strongest in spectrum)); (6) ultraviolet spectrum (essentially that of an unconjugated polyolefin, indicating that the blocked vinyl groups are twisted out of the plane of the benzene ring). Strong absorption in the far-ultraviolet gradually dropped to a negligible value at about 310 m $\mu$ . At 290 m $\mu$ , a small shoulder ( $\epsilon$  284) may be compared with one ( $\epsilon$  100) for  $\alpha$ -methylstyrene at the same wave length. A gentle shoulder at 225 m $\mu$  ( $\epsilon$  2.55  $\times$  10<sup>4</sup>) may be compared with a peak at 243 m $\mu$  ( $\epsilon$  1.02  $\times$  10<sup>4</sup>) for  $\alpha$ -methylstyrene).

**Attempted Reactions.** Compound I resisted attempts to hydrogenate it at room temperature in cyclohexane in the presence of 5% palladium, rhodium, or platinum on carbon. It was recovered unchanged from standard hydroboration treatment<sup>6</sup> with sodium borohydride in diglyme followed by boron trifluoride etherate and aqueous acetic acid work-up.

Compound I was at first inert to 5% bromine in carbon tetrachloride, but on standing some substitution occurred as shown by HBr evolution. Treatment of I with 2% potassium permanganate in acetone for 40 hr. at room temperature produced no color change relative to an acetone control. There was no visible evidence of interaction with tetracyanoethylene or of compound formation with silver nitrate in ethanol.

(3) E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

(4) D. T. Mitchell and C. S. Marvel, *ibid.*, **55**, 4277 (1933).

(5) A large band was found in the far-infrared at 525 cm<sup>-1</sup>. This is far outside the range for hexasubstituted benzenes given by Jakobsen, which we used for structure proof in our previous paper.<sup>3</sup> Closer scrutiny indicates that Jakobsen's assignment was based on a single compound, and since we have found several hexasubstituted benzenes which give no band at all in this region, we consider his correlation to be of little value for this series.

(6) H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).