Tetrahedron Letters No.8, pp. 971-975, 1968. Pergamon Press. Printed in Great Britain.

APPLICATION OF THE LINNETT ELECTRONIC THEORY TO ORGANIC CHEMISTRY. 1

Raymond A. Firestone

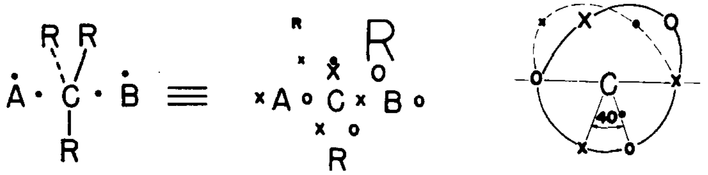
Process Research Department, MERCK & CO., Inc.
Rahway, New Jersey 07065

(Received in USA 22 September 1967)

The application of J. W. Linnett's double-quartet theory of chemical bonding (1) to organic chemistry has provided some new mechanistic interpretations, a selection of which are reported here in preliminary form.

A two-electron bond can be simply described by a doubly-occupied σ-orbital which has its maximum value along the internuclear axis so that the most probable position of both electrons is on this line. Sometimes a transformation elsewhere in the molecule causes a displacement of the two spin-sets about one of the atoms in the bond, forcing the bonding electrons somewhat apart and off the line. This will weaken the bond slightly and thus contribute to the activation energy of the reaction even though the bond in question is not itself being formed or broken. This constitutes, we believe, a new type of strain, which we propose to call L-strain.

The SN2 Reaction: The transition state for the SN2 reaction A: + $CR_3B \rightarrow ACR_3$ + :B can be formulated, in Linnett's terms, as $\dot{A}\cdot CR_3\cdot\dot{B}$. There is no need at any time for the central carbon atom to expand its valence shell (2). The two spin-sets about this atom, whose tetrahedral shapes must be maintained but whose disposition relative to each other is changing during reaction, are best arranged in the familiar shape:

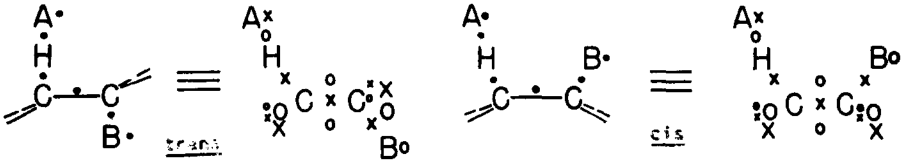


Even so, however, the three C-R bonds are subjected to an L-strain of about 40° each, as illustrated in the right-hand diagram (for a retention mechanism, in which the electrons must be arrayed as the corners of a cube, L-strain would be much higher, ca. 70°). This strain should constitute the major portion of the activation energy in the absence of external factors such as solvation. It can be semiquantitatively estimated from the angle strain in cyclopropane(3) (ca. 21 Kcal/mole), corrected for electron correlation, and comes to about 15 Kcal/mole. This is approximately correct for Finkelstein reactions in polar aprotic solvents (4).

When one of the R groups is multiply bonded, L-strain in the C-R bond at the transition state will be reduced because half of the electrons in the multiple bond will be forced into stronger bonding positions than they occupied in the ground state; thus allylic, benzylic and α-keto halides show enhanced SN2 reactivity (5). The observed geometric requirements for the α-haloketone effect are fulfilled (6). If A or B possesses other bonds, these too will suffer from L-strain in the transition state; it will be less, however, the more unshared electrons there are about the atom bonded to A or B, because this eases displacement of the two spin-sets from each other (α-effect) (7). Unshared electrons on A and B also facilitate reaction, and the more, the better; thus halide ions are especially good leaving groups, and methyloxonium cations are enormously more reactive than methylammonium. For the same reason, rates are increased when one R is divalent sulfur (8) or oxygen (9), a phenomenon not easily explained otherwise (9).

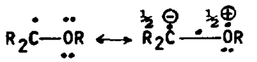
When the central carbon atom is replaced by others which bear no R groups, rates become very high, as for example, in displacements on Hal-Hal, O-O (10), O-Hal, S-Hal et al. Not only weak bonds fit this rule; proton transfers among hetero atoms are extremely fast despite the often high strength of the bonds being broken. Hydrogen bonds and trihalide ions are thus seen as minima along the SN2 reaction coordinate, resulting from their exceptionally favorable electronic configurations (1).

Elimination: For the E2 reaction, two planar transition states are possible.

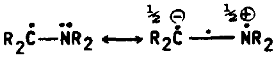


The first has better electron correlation than the second, while skew forms are highly strained because they require distortion of at least one tetrahedral spin-set. This picture is in accord with recent observations (11).

Radicals: The stability of radical next to S has been explained by valence-shell expansion (12). This explanation fails, however, for O,N and Hal, which also stabilize adjacent radicals (13). All these cases fit in with Linnett's three-electron bonds, e.g.:



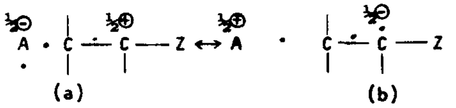
$R_2\dot{C}—\ddot{O}R \longleftrightarrow R_2\overset{\frac{1}{2}\ominus}{C}\overset{\cdot}{—}\overset{\frac{1}{2}\oplus}{\ddot{O}}R$



$R_2\dot{C}—\ddot{N}R_2 \longleftrightarrow R_2\overset{\frac{1}{2}\ominus}{C}\overset{\cdot}{—}\overset{\frac{1}{2}\oplus}{N}R_2$

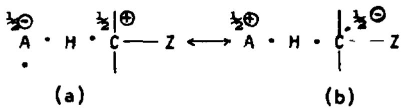
Recent evidence suggests that even adjacent carbon will stabilize a radical when it possesses unshared electrons, as a carbanion (14).

For radical additions and abstractions, we propose the following transition states:



(a) (b)

Addition



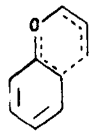
(a) (b)

Abstraction

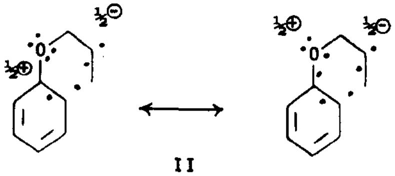
Many polar phenomena in radical reactions fit this picture well. Forms (a) will be favored by attacking radicals which are electronegative and which do not suffer from L-strain when the two spin-sets are greatly displaced. Forms (b) fit radicals with the oppositie properties. In (a), Z is preferably electron-releasing, and in (b), electron-attracting. Among radicals which tend to react at electron-releasing centers are RO• (15), (16), Cl• (15), Br• (15, 16), RS• (17) and CCl_3• (17). These adequately fulfill the requirements for (a), the latter by delocalization into Cl, a second-row element. Both CH_3• (15, 16, 18) and CF_3• (16) behave in the opposite sense because for them, L-strain in forms (a), 70°, is much greater than in (b), 30°. This factor overrides the high electronegativity of CF_3• since F cannot expand its valence shell.

Thermal Reactions: This class includes cycloadditions such as the Diels-Alder and 1,3-dipolar addition reactions, rearrangements such as the Claisen and Cope, and various types of pyrolytic eliminations. Only one representative of this group, the Claisen rearrangement, will be discussed here; similar transition states can be written for all the others, and will be presented in future publications.

In plase of the currently accepted multicentered transition state I, we prefer the less symmetrical II.



I



II

The three-electron bond to oxygen provides considerable extra stability, and makes it apparent why rearrangement is so difficult in the corresponding all-carbon system (19). N-allyl amines rearrange with intermediate difficulty (20, 21) because formation of the three-electron bond creates more L-strain on N than on O. That the π-bond energy of the product is not chiefly responsible for the order $O > N > C$ is indicated by the facility of rearrangement about S (22), and by the strongly accelerating effect of pressure (23).

The rather mysterious similarity between the effects of meta- and para-substituents on the Claisen rearrangement (24) is a natural consequence of interaction with the transient dipole created by the partial formal charges in II. Also in accord with this mechanism are the enormous accelerations observed in open-chain cases when the carbon atom corresponding to the electron-deficient C-1 in II bears a second oxygen atom (25) or a nitrogen atom (21).

The full paper, to be published elsewhere, will contain expanded discussions of these and other matters, including structure and reactivity of the common valence states of C, N, O and Hal in the light of the Linnett theory.

Discussions with Professor Linnett, and his encouragement, are gratefully acknowledged.

References

1) J. W. Linnett, *The Electronic Structure of Molecules*, Methuen & Co., London (1964). We use Linnett's symbols, although the number of drawings has been kept to a minimum.

2) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 350 (1965)

3) K. W. Egger, D. M. Golden and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964)

4) Farhet-Aziz and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, **1523**, (1961)

5) J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York (1962), p. 176

6) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958)

7) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962)

8) F. G. Bordwell and W. T. Brannan, *J. Am. Chem. Soc.*, **86**, 4645 (1964)

9) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, Rinehart and Winston, N. Y. (1959), p. 284

10) K. M. Ibne-Rasa and J. O. Edwards, *J. Am. Chem. Soc.*, **84**, 763 (1962)

11) C. H. DePuy, G. F. Morris, J. S. Smith and R. J. Smat, *J. Am. Chem. Soc.*, **87**, 2421 (1965)

12) C. C. Price and S. Oae, *Sulfur Bonding*, Ronald Press, N. Y. (1962), p. 27

13) Data on this point are too abundant for full quotation here. See, *inter alia*, M. L. Mihailovic and M. Miloradovic, *Tetrahedron*, **22**, 723 (1966); R. W. Martin, F. W. Lampe and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966); W. H. Urry, O. O. Juveland and F. W. Stacey, *ibid.* **74**, 6155 (1952); U. Schollkopf, U. Ludwig, M. Patsch and W. Franken, *Ann.*, **703**, 77 (1967)

14) P. T. Lansbury, V. A. Pattison, J. D. Sidler and J. B. Bieber, J. Am. Chem. Soc., **88**, 78 (1966)

15) R. S. Davidson, Quart. Rev., **21**, 249 (1967)

16) Compiled in A. J. Dijkstra, J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., (A), 105 (1967)

17) J. I. G. Cadogan and I. H. Sadler, J. Chem. Soc., (B), 1191 (1966)

18) L. Herk, A. Stefani and M. Szwarc, J. Am. Chem. Soc., **83**, 3008 (1961)

19) W. E. Doering and R. A. Bragole, Tetrahedron, **22**, 386 (1966). From the discussion above related to ref. 14, we would guess that rearrangement here is preceded by loss of a benzylic proton.

20) S. Marcinkiewicz, J. Green and P. Momalis, Tetrahedron, **14**, 208 (1961)

21) J. Ficini and C. Barbara, Tetrahedron Letters, 6425 (1966)

22) Y. Makisumi, Tetrahedron Letters, 6399 (1966)

23) K. R. Brower, J. Am. Chem. Soc., **83**, 4370 (1961); C. Walling and M. Naiman, ibid. **84**, 2628 (1962)

24) W. N. White and C. D. Slater, J. Org. Chem., **27**, 2908 (1962) and earlier papers; H. L. Goering and R. R. Jacobson, J. Am. Chem. Soc., **80**, 3277 (1958)

25) S. M. McElvain, H. I. Anthes and S. H. Shapiro, J. Am. Chem. Soc., **64**, 2525 (1942)