Notes

Azulene-to-Naphthalene Rearrangement. A Comment on the Kinetics[1]

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The thermal rearrangement of azulene to naphthalene (eq 1) was originally reported in 1947 by Heilbronner et

al.[2] As the first recognized thermal rearrangement of an aromatic compound,[3] this transformation has received considerable attention, especially in recent years.[3] A detailed study of the reaction in the gas phase revealed that isomerization of azulene obeys first-order kinetics[4] (data extrapolated to infinite pressure) and led Heilbronner to conclude[5] that "...the reaction is essentially homogeneous and monomolecular..."

Alder et al., on the other hand, have examined the thermal rearrangements of many substituted azulenes[6] and reached the conclusion that the reaction "...probably occurs by rearrangement of radical adducts".[6b] Equation 2 shows
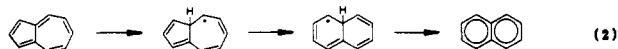
a greatly abbreviated version of the mechanism proposed. Several competing pathways were suggested for the actual interconversion of $C_{10}H_9$ radical intermediates, but the initial addition of a hydrogen atom represents the most controversial feature. Such a process obviously does not qualify as "homogeneous and monomolecular".

Independent support for this mechanism can be found in the observation by Wentrup et al.[7] that thermal rearrangement of azulene-*4-d* yields not only naphthalene-d_1 but also naphthalene-d_0 and naphthalene-d_2 (ca. 76:12:12, respectively). Clearly hydrogen atoms are lost and gained during this reaction. At least some portion of the rearrangement, therefore, must not be purely "monomolecular". Thus, Heilbronner's conclusion[5] about the molecularity of the azulene-to-naphthalene rearrangement cannot be entirely correct.

The fact remains, however, that first-order kinetics are obeyed.[4] Our recent studies on the rearrangement of az-

ulene-*1-*^{13}C, both with conventional heating[8] (hot quartz flow system) and with an infrared laser[9] ("cool" cell walls), have demonstrated the unimportance of wall effects in this reaction. The first step in eq 2, if it occurs, therefore, would have to involve hydrogen transfer from another gas-phase species, i.e., a bimolecular reaction. Thus, the labeling studies and the kinetics appear to be in conflict. It is the purpose of this paper to demonstrate that the radical mechanism (eq 2), even with bimolecular hydrogen atom transfer, *can* obey first-order kinetics.

Complete Radical Chain Mechanism. The mechanistic proposals of Alder et al.[6] (eq 2) focus primarily on the skeletal reorganization steps and leave the origin and ultimate fate of H· unspecified. A more complete mechanistic scheme, which involves no external hydrogen donor, is illustrated in eq 3-8. Thus, a diradical (B) formed by

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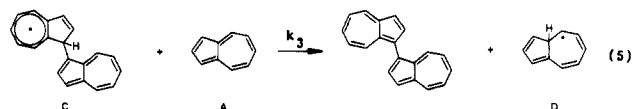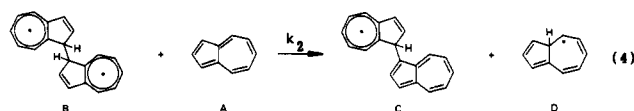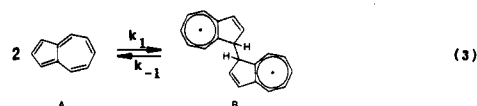
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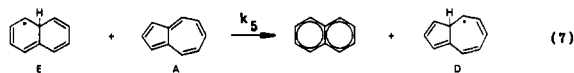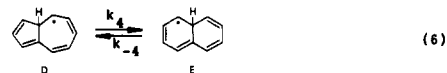
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bimolecular combination of two azulene molecules is suggested as the initial source of H· (eq 3). Such intermediates probably play a role in the high-temperature reactions of benzene and other aromatic hydrocarbons[10] (cf. formation of biphenyl from benzene).[10] The actual points of attachment on the two rings are unimportant in the present context. Rapid hydrogen shifts in the $C_{10}H_9$

(1) Thermal Rearrangements of Aromatic Compounds, Part 8. For Part 7, see ref 9. For Part 6, see: Scott, L. T.; Kirms, M. A. *Tetrahedron Lett.* **1982,** *23,* 1859-1862.

(2) (a) Heilbronner, E.; Plattner, P. A.; Wieland, K. *Experientia* **1947,** *3,* 70. (b) Heilbronner, E.; Wieland, K. *Helv. Chim. Acta* **1947,** *30,* 947-956.

(3) Scott, L. T. *Acc. Chem. Res.* **1982,** *15,* 52-58 and references cited therein.

(4) Kallen, H. J. Ph.D. Dissertation, Eidgenössische Technische Hochschule, Zürich, 1958; cited in ref 5, pp 263-8.

(5) Heilbronner, E. In "Nonbenzenoid Aromatic Compounds"; Ginsburg, D., Ed.; Interscience: New York, 1959.

(6) (a) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975,** 714-723. (b) Alder, R. W.; Wilshire, C. *Ibid.* **1975,** 1464-1468. (c) Alder, R. W.; Whiteside, R. W.; Whittaker, G.; Wilshire, C. *J. Am. Chem. Soc.* **1979,** *101,* 629-632.

(7) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. *J. Am. Chem. Soc.* **1980,** *102,* 5110-5112.

(8) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981,** *103,* 5875-5879.

(9) Scott, L. T.; Kirms, M. A.; Earl, B. L. *J. Chem. Soc., Chem. Commun.* **1983,** 1373-1374.

(10) Kinney, C. R.; DelBel, E. *Ind. Eng. Chem.* **1954,** *46,* 548-556.

radicals (e.g., D), as suggested by Alder et al.,[6] would make the initial point of hydrogen-atom transfer to azulene unimportant also.

Kinetic Analysis. If the skeletal isomerization step (eq 6) constitutes the rate-determining step in this mechanistic scheme, then the overall rate would be given by eq 9. The

$$\text{rate} = k_4[\text{D}] \qquad (9)$$

assumption is then made (vida infra) that all radical intermediates (B–E) transfer a hydrogen atom to azulene (eq 4, 5, and 7)[11] more rapidly than they react by any other bimolecular process. Under such circumstances, dimerization of D would be the only significant chain termination step (eq 8). Application of the steady-state approximation to radical intermediates B–E gives rise to eq 10–13, respectively.

$$k_1[\text{A}]^2 = k_{-1}[\text{B}] + k_2[\text{B}][\text{A}] \qquad (10)$$

$$k_2[\text{B}][\text{A}] = k_3[\text{C}][\text{A}] \qquad (11)$$

$$k_2[\text{B}][\text{A}] + k_3[\text{C}][\text{A}] + k_{-4}[\text{E}] + k_5[\text{E}][\text{A}] =$$
$$k_4[\text{D}] + k_6[\text{D}]^2 \qquad (12)$$

$$k_4[\text{D}] = k_{-4}[\text{E}] + k_5[\text{E}][\text{A}] \qquad (13)$$

Addition of eq 11–13 gives

$$2k_2[\text{B}][\text{A}] = k_6[\text{D}]^2$$

or

$$[\text{B}] = \frac{k_6[\text{D}]^2}{2k_2[\text{A}]} \qquad (14)$$

Substituting this expression for [B] into eq 10 gives

$$k_1[\text{A}]^2 = (k_{-1} + k_2[\text{A}])\left(\frac{k_6[\text{D}]^2}{2k_2[\text{A}]}\right)$$

or

$$\frac{2k_1k_2}{k_6}[\text{A}]^3 = (k_{-1} + k_2[\text{A}])[\text{D}]^2 \qquad (15)$$

At this point, it is important to recall the experimental results. Under the conditions employed (100–400 torr), the kinetic order measured for the rearrangement in eq 1 was actually 1.22, not 1.00. A kinetic order of 1.00 was obtained only by extrapolation of the data to infinite pressure. Such behavior is precisely what one finds for bona fide monomolecular thermal reactions in the gas phase, since energy transfer requires bimolecular collisions,[12] and Heilbronner's original conclusion[5] thus seemed quite reasonable. At infinite pressure, however, k_{-1} will be insignificant relative to $k_2[\text{A}]$, and eq 15 will reduce to

$$\frac{2k_1k_2}{k_6}[\text{A}]^3 = k_2[\text{A}][\text{D}]^2$$

or

$$[\text{D}] = \left(\frac{2k_1}{k_6}\right)^{1/2}[\text{A}] \qquad (16)$$

Substituting this expression for [D] into eq 9 results in

$$\text{rate} = k_4\left(\frac{2k_1}{k_6}\right)^{1/2}[\text{A}]$$

or

(11) Hydrogen-atom transfer from D to A would be degenerate: D + A $\rightleftharpoons$ A + D.

(12) Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973; Chapter 8.

$$\text{rate} = k[\text{A}] \qquad (17)$$

Thus, at high pressures of azulene, the radical chain mechanism depicted in eq 3–8 would actually obey first-order kinetics, assuming eq 6 is the rate-determining step. The assumption that radical intermediates B, C, and E react predominantly via hydrogen-atom transfer to azulene (eq 4, 5, and 7) is most reasonable at high pressures of azulene.

Conclusions. The first-order kinetics reported[4,5] for thermal rearrangement of azulene to naphthalene in the gas phase do not demand a monomolecular mechanism; they are equally compatible with a radical chain mechanism initiated by bimolecular coupling of two azulene molecules (eq 3–8). The mechanistic proposals of Alder et al.,[6] which deal with the details of eq 6, fall within this scheme and must therefore be considered *kinetically permissible*. It has previously been shown that azulene almost certainly rearranges by two or more separate pathways.[3] This paper eliminates the principal objection to the involvement of $C_{10}H_9$ radical species as intermediates on at least one of those pathways.[13]

(13) R. W. Alder,[6] after reviewing a preprint of this manuscript, has asked that I "...put in the point that wall reactions *for initiation* may be important under some conditions".

Electrochemical Obtention of *cis*- and *trans*-3,6-Dimethoxy-3,6-dimethyl-1,4-cyclohexadienes

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In the electrochemical oxidations of benzene compounds the formation of cation radical intermediates occurs by direct discharge of the aromatic ring at the anode.[1] Dimerization,[2-7] nuclear substitution,[8-10] and side-chain substitution[11-15] are the most usual processes that follow

(1) Weinberg, N. L. In "Technique of Electroorganic Synthesis", Part 1; *Wiley*: New York, 1974; Chapter IV.

(2) Erdtman, H. G. H. *Proc. R. Soc. London* 1934, *A143*, 191.

(3) Nyberg, K. *Acta. Chem. Scand.* 1970, *24*, 1609.

(4) Friend, W. E.; Ohnesorge, W. E. *J. Org. Chem.* 1963, *28*, 2435.

(5) Majeski, E. J.; Stuart, J. D.; Ohnesorge, W. E. *J. Am. Chem. Soc.* 1968, *90*, 633.

(6) Majeski, E. J.; Stuart, J. D.; Ohnesorge, W. E. *J. Chem. Soc. D* 1969, 1131.

(7) Eberson, L.; Olofsson, B. *Acta Chem. Scand.* 1969, *23*, 2355.

(8) Parker, V. D.; Burgert, B. E. *Tetrahedron Lett.* 1968, 3341.

(9) Parker, V. D.; Burgert, B. E. *Tetrahedron Lett.* 1965, 4065.

(10) Koyama, K.; Susuki, T.; Tsutsumi, S. *Tetrahedron Lett.* 1965, 627.

(11) Shono, T.; Matsumara, Y. *J. Org. Chem.* 1970, *35*, 4157.

(12) Sasaki, K.; Urata, H.; Uneyama, K.; Nagura, S. *Electrochim. Acta* 1967, *12*, 137.

(13) Inoue, T.; Koyama, K.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* 1964, *37*, 1597.

(14) Eberson, L.; Hlavaty, J.; Jonsson, L.; Nyberg, K.; Servin, R.; Sternerup, H.; Wistrand, L. G. *Acta. Chem. Scand. Ser. B* 1979, *B33*, 113.

(15) Nilsson, A.; Palmquist, U.; Peterson, T.; Ronlan, A. *J. Chem. Soc., Perkin Trans. 1* 1978, 708.