Reactions of Aromatic Radical Anions. 12. Kinetic Studies of the Reaction of Radical Anions of Varying Reduction Potential with *n*-Hexyl Bromides, Iodides, and Chlorides

Shelton Bank* and Donald A. Juckett

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. *Received March 15, 1976*

Abstract: The second-order rate constants for the reduction of *n*-hexyl iodides, bromides, and chlorides by aromatic radical anions of an expanded reduction potential series have been determined. The series includes biphenyl ($-E_{1/2}$, 2.80 V), naphthalene ($-E_{1/2}$, 2.60 V), pyrene ($-E_{1/2}$, 2.10 V), anthracene ($-E_{1/2}$, 1.98 V), fluoranthene ($-E_{1/2}$, 1.77 V), and perylene ($-E_{1/2}$, 1.67 V). The relationship between the log of the rates and the reduction potentials of the radical anions at constant halide is not linear. Similarly, the relationship between the log of the rates and the carbon–halogen bond strength plus electron affinity of the halogen at constant aromatic radical anion is not linear. The effects of structural variations and of ion pairing on the reaction rates are considered. These patterns indicate changes in the position of the transition state in going from a highly exothermic to a less exothermic reaction. The possibility of an organic halide radical anion intermediate is considered. The relationship between this work and electrochemical reduction and Grignard formation is discussed.

It has been known for some time that aromatic radical anions, such as sodium naphthalene, provide a low-energy pathway for the reduction of alkyl halides.[1] This reaction has elicited considerable interest from a mechanistic point of view,[2] and more recently, kinetic studies have contributed to our understanding.[3-5] Our previous kinetic study of the reactions of sodium naphthalene and anthracene with *n*-hexyl bromide and chloride supported the generally accepted mechanism.[5] The hexyldihydronaphthyl anion, formed by radical–radical anion coupling, is a discrete intermediate and reacts more slowly with alkyl halide than does the radical anion. For a given radical anion, halide variation exhibits an unusual range of reactivity, covering 11 powers of 10. In reactions with *n*-hexyl bromide, variation of the aromatic species gave rise to a linear relationship between the half-wave potential and the rate constants.

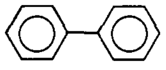
In this work, the reaction of *n*-hexyl bromide with aromatic radical anions has been extended to cover a wider range of reduction potential. In addition, comparable kinetic data for iodides and chlorides are considered. This markedly expanded scale of reactivity serves to provide answers to two questions about the relationship between structure and reactivity: can the relative reactivities be accounted for similarly, on the basis of linear relationships with reduction potential, and to what extent are there mechanistic changes in going from "highly favored" reductions to apparently "unfavored" reductions.

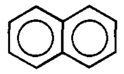
The first question derives in part from the desire to test rigorously the scope of the linear relationship observed in the limited initial range of reduction potentials. Additionally, it provides necessary data for the formulation and testing of useful models, relating reduction potentials and rates of electron-transfer reactions. In this regard, electron-transfer reactions of aromatic radical anions can be productive since the well-known reduction potentials can be varied by over a volt, and reaction rates lie in conveniently measured ranges.

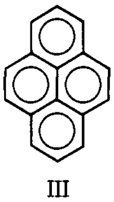
The second question derives from the fact that while we can account for many facile reductions in terms of favorable reduction potential differences (e.g., biphenyl $-E_{1/2}$, 2.80[6] V; and iodides $-E_{1/2}$, ~1.70[6] V), electron transfers, when the reduction potential differences are unfavorable, are more perplexing (e.g., anthracene $-E_{1/2}$, 1.46 V; and cnlorides $-E_{1/2}$, ~2.2 V). Even organic fluorides are reduced, albeit slowly, by sodium naphthalene.[4] The important question as to how the "unfavorable" electron transfers occur is a large one. We seek in this work to see how and in what way they are mechanistically related to "favorable" electron transfers.

Results and Discussion

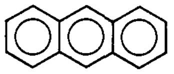
The series of hydrocarbons included in the study are biphenyl (I), naphthalene (II), pyrene (III), anthracene (IV), fluoranthrene (V), and perylene (VI). The structures and the half-wave reduction potentials[6] for the first, and where applicable, the second reduction are noted below. All values for reduction potentials are vs. SCE. The second reduction leads to an aromatic dianion, and although there is no evidence that the dianions of aromatic compounds react more readily with alkyl halides than anion radicals, there is sufficient evidence that they are more reactive toward proton sources and ether solvents.[7] In this light, it is important to insure the absence of dianion contributions to the study of the reactions of radical anions with the alkyl halides. Perylene dianion is the most readily formed of the series and will be considered as the limiting example:

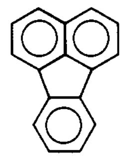

I

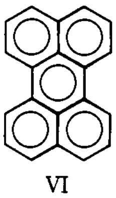

II


III

	I	II	III
$-E_{1/2}$ (1)	2.80	2.60	2.10
$-E_{1/2}$ (2)			2.57


IV


V


VI

	IV	V	VI
$-E_{1/2}$ (1)	1.98	1.77	1.67
$-E_{1/2}$ (2)	2.44	2.18	2.06

$$2\mathrm{Pe}\cdot^{-} \overset{k}{\rightleftarrows} \mathrm{Pe}^{2-} + \mathrm{Pe} \qquad (1)$$

The equilibrium constant in tetrahydrofuran is 1.6×10^{-5}.[8] Accordingly, when the known concentration of neutral pery-

Table I. Second-Order Rate Constants for Reaction of Aromatic Radical Anions and Halides

Radical anion	Halide	Concn, M	k_1, $M^{-1}\,s^{-1}$	No. of determinations
Biphenyl	n-$C_6H_{13}Cl$	8.5×10^{-3}	3.2 ± 0.2	5
Pyrene	n-$C_6H_{13}Cl$	0.5	7.0 ± 1.0	5
	n-$C_6H_{13}Cl$	0.1	7.0 ± 0.8	4
	n-$C_6H_{13}Br$	0.01	$5.8 \pm 0.4 \times 10^3$	6
	n-$C_6H_{13}Br$	0.05	$6.4 \pm 0.4 \times 10^3$	6
Fluoranthene	n-$C_6H_{13}Br$	0.05	1.56 ± 0.4	3
	n-$C_6H_{13}Br$	0.1	1.58 ± 0.8	4
	n-$C_6H_{13}Br$	0.5	$1.56 \pm .6 \times 10^{-1}$	4
	n-$C_6H_{13}I$	0.2	$3.6 \pm 0.2 \times 10^2$	7
Perylene	n-$C_6H_{13}Br$	0.1	$5.8 \pm 0.2 \times 10^{-1}$	4

lene is 5×10^{-2} M, and of perylene radical anion at the onset of reaction is 2×10^{-5} M, the concentration of perylene dianion is $\sim 10^{-13}$ M. The ratio of perylene dianion to perylene radical anion, therefore, is $\sim 5 \times 10^{-9}$. The overall rate law can be expressed as the sum of reaction of the radical anion and the dianion

$$\frac{-d[Pe\cdot^-]}{dt} = [RX][Pe\cdot^-](2k_1 + 5 \times 10^{-9}k_2) \qquad (2)$$

where k_1 and k_2 are the rate constants for the radical anion and dianion respectively. Since the average measured value of k_1 is $\sim 3 \times 10^{-1}\ M^{-1}\ s^{-1}$, contributions from the dianion of greater than 10% are expected only if $k_2 \geq 1.2 \times 10^7\ M^{-1}\ s^{-1}$. Such a large bimolecular rate constant for the reaction of the dianion with alkyl halide is unlikely, because the more facile protonations of the perylene dianion by water and alcohols have bimolecular rate constants of only $\sim 1 \times 10^6\ M^{-1}\ s^{-1}$.[7a] Additionally, extensive participation of dianion requires deviation from first-order dependence on radical anion and inverse dependency on the neutral aromatic. The least-squares treatment for the first-order behavior of these reactions has correlation coefficients of 0.99 or greater, and moreover, the rate constant was independent of the concentration of the neutral aromatic.

Table I records the second-order rate constants for the reactions of these several radical anions with n-hexyl halides. The rate law for the disappearance of radical anion was determined from the first-order decay of radical anion under pseudo-first-order conditions. In all cases strict first-order dependency on radical anion was observed. First-order dependency for the halide was determined by varying the halide concentration. Table II is a composite of all the known bimolecular rate constants for the reactions of aromatic radical anions and n-alkyl halides.

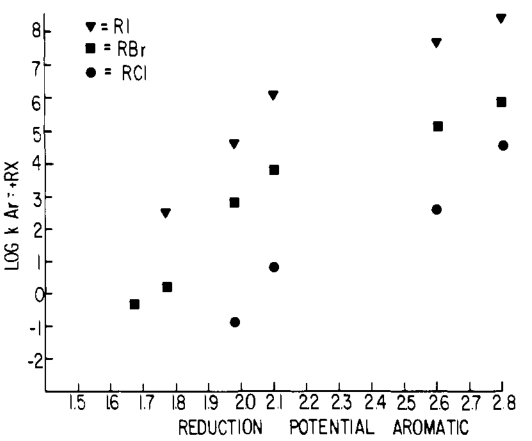


Figure 1. Relationship between the log of the rates of reduction of n-alkyl iodides, bromides, and chlorides by aromatic radical anions and the reduction potentials of the radical anions.

Extrathermodynamic Relationships. For the reaction of various aromatic radical anions with a given halide, the reversible polarographic half-wave reduction potentials are used as a measure of the thermodynamic driving force. Entirely analogous results are obtained if Hückel molecular orbital calculated energies are used. The comparisons of rate data and thermodynamic data are so called "extrathermodynamic" relationships[9] and relate to the question of the nature of the transition state. As shown in Figure 1, for the reaction of bromides, there is a monotonic decline in second-order rate constants as the reduction potential of the aromatic diminishes. Parallel effects are found for the other alkyl halides. Most significantly, however, as the span of reduction potential increases, the relationship between the bimolecular rate constants and reduction potentials is not a linear function. The observed curve shows an increase in reaction rate sensitivity as the reduction potential of the reducing agent is diminished. This nonlinearity requires differing transition states, since a linear relationship is evidence for similar transition states. The quantitative relationship between the free energy and the activation energy is

$$\delta\Delta G^{\ddagger} = \alpha\delta\Delta G^{\circ} \qquad (3)$$

where α reflects the extent to which the transition state resembles product. Viewed in this way, the value of α changes throughout the aromatic variation and becomes larger, indi-

Table II. Composite of Bimolecular Rate Constants of Various Aromatic Anion Radicals and Various Alkyl Halides[a]

	Alkyl halide			
Aromatic, $E_{1/2}$	RI	RBr	RCl	RF
Biphenyl, 2.80	$2.2 \pm 0.1 \times 10^8$ [b]	$6.5 \pm 0.5 \times 10^5$ [b]	$3.2 \pm 0.2 \times 10^4$	1.4×10^{-4} [d]
Naphthalene, 2.60	$4.7 \pm 0.3 \times 10^7$ [b]	$1.5 \pm 0.2 \times 10^5$ [e]	$4.0 \pm 0.2 \times 10^2$ [e]	$2.2 \pm 0.5 \times 10^{-4}$ [d]
Pyrene, 2.10	1.2×10^6 [c]	$6.4 \pm 0.4 \times 10^3$	7.0 ± 0.8	
Anthracene, 1.98	$4.4 \pm 0.4 \times 10^4$ [e]	$6.6 \pm 0.4 \times 10^2$ [e]	$1.3 \pm 0.2 \times 10^{-1}$ [e]	NR[d]
Fluoranthene, 1.77	$3.6 \pm 0.2 \times 10^2$	1.6 ± 0.6		
Perylene, 1.67		$5.8 \pm 0.2 \times 10^{-1}$		

[a] At 20.0 °C in THF with the exception of Anth + $C_6H_{13}Cl$ which was run at 20.0 °C in DME. [b] From ref 3 using butyl halides. [c] Private communication from B. Bockrath using butyl iodide. [d] From ref 4. [e] From ref 5.

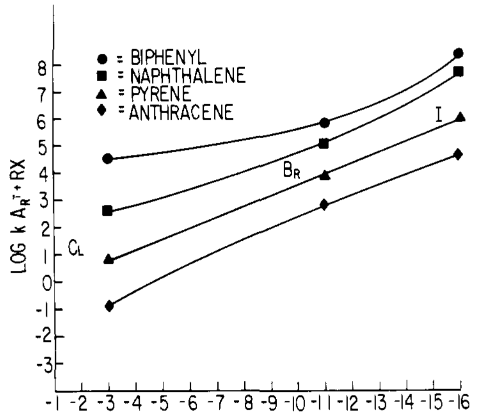


Figure 2. Relationship between the log of the rates of radical anion reduction of *n*-alkyl halides and the carbon–halogen bond strength plus electron affinity of the halogen.

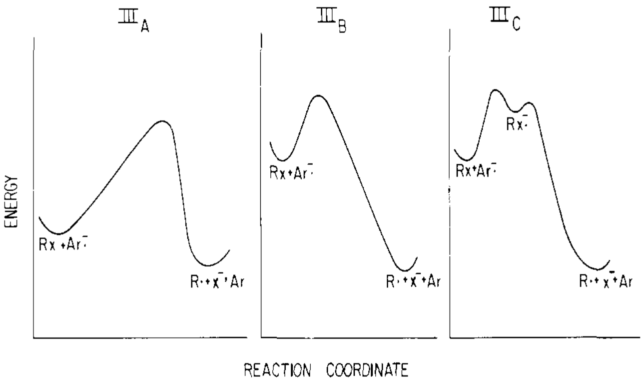


Figure 3. Energy diagrams representing possible reaction paths. IIIA depicts one-step reaction with late transition state. IIIB depicts one-step reaction with early transition state. IIIC depicts intermediacy of organic halide radical anion.

cating a later transition state. This is in accord with the Hammond postulate of an early transition state for highly exothermic reactions, and a later transition state for less favorable reactions. An estimation of the magnitude of the change can be obtained by using the extensive bromide data and assuming that the limiting portions of the curve can be treated as linear. In this way a value of $\alpha = 0.22$ is obtained for the highly reactive radical anions and 0.63 for the less reactive radical anions. While these numbers are only approximations, they indicate the type of change in the timing of the transition state.

For the reaction of various halides with a given aromatic, where initial reaction cleaves the carbon–halogen bond to produce an organic radical and a halide ion, a reasonable thermodynamic relationship is the sum of the carbon–halogen bond strength and the electron affinity of the halogen atom.[10] In Figure 2, for the highly reactive biphenyl radical anion, the curve is concave upwards; for the little reactive pyrene and anthracene, the curves are convex upwards; while for naphthalene, the curve is approximately linear. Loss of linearity does not necessarily make the treatment valueless, for the thermodynamic relationship in Figure 2 is both reasonable and has physical meaning in the observed pattern. This pattern indicates that the position of the transition states changes in going from the highly exothermic reactions to the less exothermic. The less exothermic reactions involve late transition states (Figure 3A), which should have radical-like character with considerable carbon–halogen bond cleavage and some charge concentration on the halide.

The more exothermic reactions could involve an early transition state (Figure 3B) in the one-step production of radical and halide, with the concomitant expectation of little carbon–halogen bond breaking:

$$\mathrm{Ar\cdot^-} + \mathrm{RX} \xrightarrow{k_1} \mathrm{R\cdot} + \mathrm{X^-} + \mathrm{Ar} \tag{4}$$

Alternatively, they could involve an organic halide radical anion intermediate (Figure 3C). In these species the antibonding electron level is concentrated largely in the carbon–halogen bond, and subsequent bond cleavage to radical and halide is fast. Further characteristics of this reaction path involve charge dispersal and little carbon–halogen bond breaking in the rate-determining step, k_1.

$$\mathrm{Ar\cdot^-} + \mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RX\cdot^-} + \mathrm{Ar} \tag{5}$$

$$\mathrm{RX\cdot^-} \xrightarrow{k_2} \mathrm{R\cdot} + \mathrm{X^-} \tag{6}$$

The reduction potential of the aromatic affects the rate of the initial electron transfer, and though formally the reverse step must be considered, it is unlikely that the rate competes with the decomposition rate, k_2.[3] Although these two possibilities for the more exothermic reactions are indeed distinct, they are difficult to distinguish. The structures for the early transition state and for the intermediate radical anion are probably very similar and would, therefore, respond similarly to structural and solvent variations. They differ in the classical sense, in which transition states and intermediates differ, but only trapping probes can distinguish between them. Accordingly, we shall examine first the extensive data in which either or both of these two possibilities are distinguished from the late transition state and then consider their possible differentiation.

Ion Pairing Effects. The state of ion pairing of the aromatic radical anion and counterion is expected to affect differently the two kinds of reactions. For the later transition state with greater bond cleavage, more charge is concentrated on the halide, and the rate of reaction for tight ion pairs would be greater.[3,5] In contrast, the early transition state involves charge dispersal, and in this case reaction will be favored for the freer species.[3,5] The relative reactivities of loose to tight ion pairs for the sodium naphthalene reduction of butyl iodide, hexyl chloride, and hexyl fluoride are, respectively, 36,[3] 6,[5] and 1.3.[4a] The greatest rate difference between types of ion pairs is observed for the highly exothermic iodide reduction, where loose ion pairs react much faster. The reactivity difference between the types of ion pairs decreases in going to the chloride and the fluoride and is in accord with a later transition state with increasing bond cleavage.

Structural Effects. For the energetically less favorable reductions, the transition state involves extensive bond cleavage and considerable radical character. As such, substituent changes in the organic structure should reflect radical stability, with comparable rate changes. For the energetically favorable reductions, radical stability is not expected to be important and organic structure variation should have minor effects upon reaction rate. This is supported by the relative yields of dimeric products from competition experiments with the naphthalene radical anion, Table III. For the propyl iodides[2e] and benzyl and benzhydryl chlorides,[11] the distribution of dimeric hydrocarbons is statistical. The production of radicals, therefore, does not reflect the energy difference between the primary and secondary on the one hand, or benzyl or benzhydryl on the other hand. For the far less energetically favored reduction with fluorides, significant deviations from a statistical distribution are observed and are easily explained by a preferential formation of the benzhydryl radical relative to the benzyl radical.

Table III. Dimer Yields From Competition Experiments with Naphthalene Radical Anion and Halides

RX	R^1X	R-R	$R-R^1$	R^1-R^1	Ref
n-PrI[a]	i-PrI	24	50	26	2c
$PhCH_2Cl$[b]	Ph_2CHCl	23	49	24	11
$PhCH_2F$[b]	Ph_2CHF	8	68	24	11

[a] Using sodium naphthalene in dimethoxyethane. [b] Using lithium naphthalene in tetrahydrofuran.

Table IV. Rates and Relative Rates of Reduction of Phenyl Halides with Sodium Naphthalene and Sodium Anthracene in THF at 20 °C

	Anth·⁻		Naph·⁻	
Halide	k[a]	k_{rel}[b]	k[a]	k_{rel}[b]
Iodobenzene	4.0×10^4	0.91		
Bromobenzene	1.54	2.3×10^{-3}	6.4×10^3	4.5×10^{-2}
Chlorobenzene			6.0×10^2	1.5
Fluorobenzene			19.4	10^5

[a] In l. mol^{-1} s^{-1}. [b] Relative to hexyl X with the same radical anion.

Table IV records the rates and rates relative to the n-alkyl halides for the phenyl halides with sodium anthracene and naphthalene. For the exothermic iodide reaction with anthracene, the phenyl and n-hexyl react at essentially the same rate. Thus the substantial difference in stability between the phenyl and n-hexyl radical does not appear to contribute to this reaction. On the other hand, for the less exothermic bromide reaction, the phenyl halide is much slower, and moreover the rate difference increases as the reduction potential of the aromatic decreases in going from naphthalene to anthracene. This is precisely what is expected for a reaction in which the transition state involves increasing radical-like character. The surprisingly high relative reactivity of chlorobenzene and the enormous relative reactivity of fluorobenzene are discussed below.

Organic Halide Radical Anion. Rigorous discrimination between an early transition state and the organic halide radical anion intermediate can be afforded by trapping experiments, which involve either rearrangement or loss of stereochemical integrity before reduction to the anion. For the one-step process, this competing reaction occurs after loss of halide and therefore the efficiency of trapping is halide independent. For the organic halide radical anion intermediate, halide dependence on trapping efficiency is possible by direct reaction of the intermediate with a second molecule of reducing agent:

$$\begin{tikzcd}
RX \arrow[r, "k_1", "Ar\cdot^-"'] & RX\cdot^- \arrow[r, "k_2"] \arrow[d, "k_3"', "Ar\cdot^-"] & R\cdot + X^- \arrow[d, "k_4"', "Ar\cdot^-"] \\
 & R^- + X^- & R^-
\end{tikzcd}$$

To the extent that k_3 contributes, then some anion is formed in a route that does not involve radical, and the ratio of k_2/k_3 would depend on the specific halide. Although a great variety of radical rearrangements or stereochemical integrity trapping experiments have been investigated,[12] they have unfortunately, in all cases but one, utilized a single halide and a single reducing agent, and therefore efficiency as a function of halide or reducing agent is unknown. The sole exception involves the reduction and cyclization of all the 5-hexenyl halides.[2a] While there are differences, the variations are not considered significant due to difficulty in controlling solution homogeneity. The truly definitive distinction must await further data; however, there are some qualitative data that suggest an organic halide radical anion intermediate. Of particular note in this regard is the enhanced reactivity of fluorobenzene relative to hexyl fluoride and chlorobenzene relative to hexyl chloride. The alkyl halide reactions are clearly exothermic and radical-like transition states are expected. The fact that phenyl is as fast for chlorides and faster for fluorides signals a mechanism change. The reduction potential of chlorobenzene is substantially lower than that for n-hexyl chloride,[13] and the antibonding orbital for chlorobenzene is of lower energy.[14] The reduction potentials of the alkyl and aryl fluorides are unknown, but it is reasonable that fluorobenzene is easier to reduce.[15] The rate accelerations can be accounted for if the phenyl halides are reacting with sodium naphthalene via an organic halide radical anion, but the alkyl halides via a radical path. While this requires assumptions about the relative reduction potentials, it is difficult to envision a single step process with an early transition state to account for the marked rate increase for the phenyl substituent.

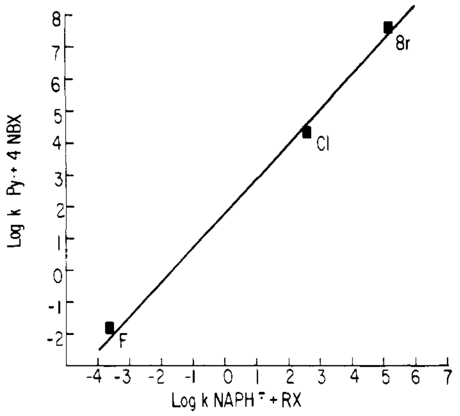


Figure 4. Relationship between the log of the rates of reduction of 4-nitrobenzyl halides with 1-ethyl-4-carbomethoxypyridinyl radical and the log of the rates of reduction of n-alkyl halides by sodium naphthalene.

Comparison of the phenyl halide reduction with the reaction of the stable 1-ethyl-4-carbomethoxypyridinyl radical and 4-nitrobenzyl halides,[16] Figure 4, records a linear relationship between the logs of the rates of the two reactions as a function of halide. This linearity is important for two reasons. First, the pyridinyl radical reactions have been established as electron-transfer processes by solvent and substituent effects. Second, the pyridinyl radical reactions are characterized by rate-limiting steps that differ for each halide, i.e., for the bromides, organic halide radical anion formation, whereas for the fluorides, radical formation. To the extent that the linear relationship between the two reductions indicates similar mechanisms, the organic halide radical intermediate rather than an early transition state is indicated.

Relationship to Other Reductions. These considerations could have relevance to the observed electrochemical reduction of alkyl chlorides in the presence of catalytic quantities of naphthalene, when in fact the alkyl chlorides cannot be reduced at that electrode surface in the absence of naphthalene.[17] Electron transfer with considerable bond cleavage probably involves far greater geometrical orientation of the halide and the electron source than for an early electron transfer, which could occur at longer distances. The electrode surface, restricted by immobility and the double layer, cannot adopt the required geometry as well as a soluble reducing agent. Another example is the structural effect for reduction of alkyl bromides and chlorides. The half-wave potentials for n-butyl and *tert*-

butyl bromide are −2.23 and −2.19 V,[18] but for *n*-pentyl and *tert*-pentyl chloride are −2.79 and −2.64 V.[19] The chloride reduction shows a large effect of structure which is consonant with the view that the transition state occurs later.

Finally this work bears in part on the recent work that has been done on the mechanism of the Grignard reagent. Whitesides concludes, from the structural effect on the rate of formation of Grignard reagents, that reaction involves rate-determining formation of organic halide radical anion.[20] His work used bromides, and our results are supportive of his conclusions. Additionally, the observation of significant structural effects when the thermodynamics of reaction are less favorable, raises the possibility of a radical-like mechanism for Grignard formation from less easily reducible halides.[21]

Experimental Section

Materials. Naphthalene was obtained from Eastman Organic Chemical (No. 168) or Matheson Coleman and Bell (No. NX5). Anthracene (No. AX 1590) and fluoroanthrene (No. 1214) were obtained from Matheson Coleman and Bell. Biphenyl (No. 721) was obtained from Eastman Organic Chemicals. Samples of pyrene and perylene were donated by Professor W. D. Closson. Alkyl and aryl halides were obtained either from Eastman Organic Chemicals or Matheson Coleman and Bell. The halides were distilled from calcium hydride and stored over calcium hydride. Purity of halides was determined by vapor phase chromatography. Tetrahydrofuran, chromoquality from Matheson Coleman and Bell, was distilled from benzophenone sodium ketyl prior to use.

Solutions of sodium biphenyl and sodium naphthalene were prepared from sodium metal, and the aromatics are described previously.[5] The other radical anions were prepared by electron transfer from sodium naphthalene to THF solutions of the corresponding aromatic in large excess.

Kinetic Procedures. Kinetic measurements were made on a rapid-mixing stopped-flow spectrophotometer as described previously.[5] The wavelengths that were used to monitor reaction for the various aromatic radical anions were in nm; biphenyl, 630; naphthalene, 775; pyrene, 730; anthracene, 720; fluoranthane, 510; and perylene, 577. All kinetic data reported are the averages of a minimum of their determinations at each concentration.

References and Notes

(1) W. Schlenk, J. Apprenrodt, A. Michael, and A. Thal, *Chem. Ber.*, **47**, 473 (1914).
(2) (a) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971); (b) J. F. Garst, F. E. Barton, II, and J. I. Morris, *J. Am. Chem. Soc.*, **93**, 4310 (1971); J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969); *J. Am. Chem. Soc.*, **91**, 3385 (1969); J. F. Garst, J. T. Barbas, and F. E. Barton, II, *ibid.*, **90**, 7159 (1968); J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966); (c) G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966); (d) G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968); (e) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 5433 (1969).
(3) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 2618 (1973).
(4) J. F. Garst, R. D. Roberts, and B. N. Abels, *J. Am. Chem. Soc.*, **97**, 4926 (1975); J. F. Garst and F. E. Barton, II, *ibid.*, **96**, 523 (1974); *Tetrahedron Lett.*, 587 (1969).
(5) S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97**, 567 (1975).
(6) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955); G. J. Hoijtink and J. Van Schooten, *ibid.*, **73**, 355 (1954).
(7) (a) G. Levin, C. Sotphen, and M. Szwarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972); (b) J. C. Carnahan and W. D. Closson, *J. Org. Chem.*, **37**, 4469 (1972).
(8) A. Rainis and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 3008 (1974).
(9) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 156 ff.
(10) (a) T. L. Cottrell, "The Strength of Chemical Bond", Butterworths, London, 1954; D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969; (b) P. Kebarle in "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed., Wiley, New York, N.Y., 1972, p 48.
(11) H. E. Zieger, I. Angres, and D. Mathisen, *J. Am. Chem. Soc.*, **98**, 2580, (1976).
(12) (a) S. J. Cristol and R. V. Barbour, *J. Am. Chem. Soc.*, **88**, 4261 (1966); *ibid.*, **90**, 2832 (1968); (b) J. F. Carst, W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966); (c) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967); (d) J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969); (e) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **94**, 8475 (1972)) (f) P. K. Freeman, L. L. Hutchenson, and J. N. Blazevjich, *J. Org. Chem.*, **39**, 3605 (1974).
(13) The reduction potentials vs. SCE are: chlorobenzene, −2.57 V; hexyl chloride, −2.80 V; F. L. Lambert and G. B. Ingall, *Tetrahedron Lett.*, 3231 (1974).
(14) K. Fukui, K. Morokuma, H. Kata, and T. Vonezawa, *Bull. Chem. Soc. Jpn.*, **36**, 217 (1963), and references cited therein.
(15) The 4,4′-difluoro- and 4-fluorobiphenylide radical anions are known; A. A. Allred and L. W. Bush, *Tetrahedron*, **24**, 6883 (1968).
(16) M. Mohammad and E. M. Kosower, *J. Am. Chem. Soc.*, **93**, 2713 (1971).
(17) J. W. Sease and R. C. Reed, *Tetrahedron Lett.*, 393 (1975).
(18) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5322 (1960).
(19) F. L. Lambert and G. B. Ingall, *Tetrahedron Lett.*, 3229 (1974).
(20) R. J. Rogers, H. L. Mitchell, V. Fujiward, and G. M. Whitesides, *J. Org. Chem.*, **39**, 857 (1974).
(21) H. Bodewitz, Doctoral Thesis, Free University of Amsterdam, 1975.

An Alternative Mechanism for the Formation of 1,4-Disilacyclohexa-2,5-dienes from Acetylenes and Silylenes[1]

Thomas J. Barton* and John A. Kilgour

Contribution from the Department of Chemistry, Iowa State University,
Ames, Iowa 50011. Received March 29, 1976

Abstract: To account for the formation of 1,4-disilacyclohexa-2,5-dienes (disilins) from the reaction of silylenes and acetylenes, a mechanism involving a Diels-Alder addition of an acetylene to a 1,4-disila-1,3-butadiene is proposed. This novel diene could arise from opening of a 3,4-disilacyclobutene, and, indeed, the permethyldisilacyclobutene is found to react with acetylenes to afford the predicted disilacyclohexadienes. Experiments are described which indicate that under static pyrolysis conditions the disilacyclobutenes arise from silylene and not disilene reactions with the acetylenes. While tetramethyldisilene does react with 2-butyne to produce the permethyldisilin, attempted crossover experiments rule out dissociation of the disilene to two molecules of silylene. Thus it is concluded that the two mechanisms, silylene and disilene, merge at a disilacyclobutene intermediate. The combined experiments do not rule out a σ-dimerization of an initially formed silacyclopropene but do provide an alternate mechanism which is consistent with all known facts.

One of the best known and certainly most perplexing problems in organosilicon chemistry is the nature of the reaction between silylenes (R_2Si:) and acetylenes. In 1961 Vol'pin and co-workers initiated a series of experiments designed to synthesize a silacyclopropene.[2-4] It was predicted that this system would be stabilized by π-delocalization through an empty 3d