with their molecular environments, and further work on these effects is needed to interpret the variety of situations shown in this paper.

It is to be noted that the numerous structures surveyed here belong primarily to carbohydrate chemistry, although many others outside the field have shown the same anomeric-type effect. In other words, the anomeric effect is becoming an important conceptual tool in conformational chemistry. The method used here to evaluate and refine it, so as to then achieve a more precise prediction ability, combines crystallographic data and dynamic fragment information derived from their energy hypersurfaces. Their correlation as suggested by the Mislow-Dunitz-Bürgi proposals is very promising for static and dynamic assessment of the geometry, the stability, and reactivity of the "anomeric fragments".

Acknowledgment. We express our sincere appreciation to Dr. David G. Watson of the Cambridge Crystallographic Center and to the referees for their helpful, constructive advice.

Registry No. 2,2-Dimethoxypropane, 77-76-9.

Supplementary Material Available: Bibliographic information and reference codes of the data base used, 3D structure of four unusual conformers with one ϕ_i near 0° and the other near 90° (10 pages). Ordering information is given on any current masthead page.

Reductive Fragmentation of 9,9-Diarylfluorenes. Concurrent Radical Anion and Dianion Cleavage. Electron Apportionment in Radical Ion Fragmentations[1]

Thomas D. Walsh

Contribution from the Department of Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina 28223. *Received April 22, 1986*

Abstract: Both radical anions and dianions of 9,9-diarylfluorenes cleave an aryl ring after reduction by alkali metals or naphthalenide radical anions in ether solvents. The relative amount of cleavage through each intermediate depends on the alkali metal cation, the solvent, and the presence or absence of 18-crown-6 ether. The tendency for dianion cleavage parallels that for disproportionation of radical anions to dianions and neutral hydrocarbons. Radical anion fragmentation is proposed to proceed via heterolytic cleavage in which electron flow is in the direction which offsets the charge distribution in the radical ion. In the present case, this initially affords 9-arylfluorenyl radical and aryl anion, which subsequently undergo electron exchange to form the more stable 9-arylfluorenyl anion and aryl radical.

Many types of compounds are known to undergo reduction to radical anions or dianions, followed by cleavage of one or more bonds. This reaction is not limited to the cleavage of C-H or C-C bonds but can be observed in the cleavage of bonds involving a large variety of other elements.[2] Despite the large number of examples known, in relatively few cases has the mechanism of the reductive cleavage been determined.

The first feature which needs to be addressed is the determination of the species which is responsible for the fragmentation: radical anion or dianion. Some workers have invoked both, under different reaction conditions[3] or upon observing different products.[4] In cases in which the initially reduced radical anion is sufficiently stable to allow observation of the rate of its disappearance, a first-order kinetic rate law establishes its dissociation. However, in many cases a second-order rate law has been observed, and several other radical anion mechanisms proposed, with the rate law interpreted as involving dimerization[5] or steady-state concentrations of a reversibly formed intermediate[6] or explained by using ion-pair association arguments.[7] Several authors have advanced arguments in favor of radical anion[8] or dianion[8c,9a,10] dissociation without determining the rate law.

Dianion intermediacy has been invoked in cases in which the radical anion is observed to be stable, but further reduction produces cleaved products.[9] It has also been required in studies in which a second-order rate law is accompanied by an inverse dependence of the rate on the concentration of unreduced starting material, as required by the mechanism shown in Scheme I (counter ions omitted for simplicity), in which dianion is produced

---

[1] Preliminary reports: 186th National Meeting of the American Chemical Society, Washington, DC, August 1983, *Abstracts of Papers*, ORGN-26. 35th Southeastern Regional Meeting of the American Chemical Society, Charlotte, NC, November 1983, *Abstracts of Papers*, p 120.

[2] (a) Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 287-306, 362-373. (b) Perrin, C. L. In *Progress in Physical, Organic Chemistry*; Cohen, S. G., Streitwieser, A., Jr., Taft, R. W., Eds.; Interscience: New York, 1965; Vol. 3, pp 165-316. (c) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400-406. (d) Staley, S. W. In *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; John Wiley & Sons: New York, 1972; Vol. 2, pp 309-348. (e) Petrov, E. S.; Terekhova, M. I.; Shatenshtein, A. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1973**, *42*, 713-724. (f) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243-277. (g) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; American Chemical Society, Washington, 1983. (h) Todres, Z. V. *Tetrahedron* **1985**, *41*, 2771-2823. Also, most of the references cited in this paper describe reductive bond cleavages.

[3] Remers, W. A.; Gibs, G. J.; Pidacks, C.; Weiss, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 5513-5514.

[4] Kiesele, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 254; *Angew. Chem. Suppl.* **1983**, 210-221.

[5] Kopping, M. D.; Woolsey, N. F.; Bartak, D. E. *J. Am. Chem. Soc.* **1984**, *106*, 2799-2805.

[6] Ito, O.; Aruga, T.; Matsuda, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1113-1115.

[7] Tabner, B. J.; Walker, T. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1295-1297, and previous papers in the series.

[8] (a) Walsh, T. D.; Ross, R. T. *Tetrahedron Lett.* **1968**, 3123-3126. (b) Walborsky, H. M.; Aronoff, M. S.; Schulman, M. F. *J. Org. Chem.* **1971**, *36*, 1036-1040. (c) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Tetrahedron* **1982**, *38*, 3687-3692. (d) Patel, K. M.; Baltisberger, R. J.; Stenberg, V. I.; Woolsey, N. F. *J. Org. Chem.* **1982**, *47*, 4250-4254.

[9] (a) Eargle, D. H., Jr. *J. Org. Chem.* **1963**, *28*, 1703-1705. (b) Elschenbroich, C.; Gerson, F.; Reiss, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 60-64.

[10] Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290-6299.

0002-7863/87/1509-1511$01.50/0

by disproportionation of two radical anions.[11,12] In these cases, the dianion may be the cleaving species even if its concentration is too low to allow detection.

Scheme I

$$\mathrm{Ar{-}R} + e^- \rightarrow \mathrm{Ar{-}R}^{\bullet -}$$

$$\mathrm{Ar{-}R}^{\bullet -} \xrightarrow{k_1} \mathrm{Ar}^- + \mathrm{R}^\bullet$$

$$\mathrm{Ar{-}R}^{\bullet -} \xrightarrow{k_1} \mathrm{Ar}^\bullet + \mathrm{R}^-$$

$$2\mathrm{Ar{-}R}^{\bullet -} \overset{K_d}{\rightleftharpoons} \mathrm{Ar{-}R}^{2-} + \mathrm{Ar{-}R}$$

$$\mathrm{Ar{-}R}^{2-} \xrightarrow{k_2} \mathrm{Ar}^- + \mathrm{R}^-$$

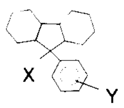
$$\mathrm{Ar}^\bullet, \mathrm{R}^\bullet + \mathrm{Ar{-}R}^{\bullet -} \xrightarrow{\text{fast}} \mathrm{Ar}^-, \mathrm{R}^- + \mathrm{Ar{-}R} \text{ and/or combination products}$$

When the radical anion is shown to be the cleaving species, the question arises as to which fragment becomes the radical and which accepts the extra electron to be the anion. This is a difficult question to answer, since it is possible that the initially formed anion–radical pair may not correspond to the most stable electron distribution; subsequent equilibration may reverse the roles of the fragments. This question has been considered in detail,[1,13] and a principle has recently been published by Maslak and Guthrie which states that there is "an inherent preference for radical anion scission reactions which occur with regioconservation of spin density."[13b]

We report here an investigation of the reductive cleavage of 9,9-diarylfluorenes in 1,2-dimethoxyethane (DME), initiated by alkali metals. Potassium-induced cleavage has been reported,[12] and the effects of lithium and sodium serve to show that this system provides information concerning each of the features mentioned above.

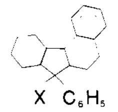
Results

The ArR compounds employed (**1a–f**) are shown below. All except **1f** readily cleave an aryl ring after reduction by alkali metal in DME, to form an arylfluorenyl anion. At room temperature, half-lives are of the order of many minutes. Compound **1f** is relatively unreactive.



1: X = C_6H_5
2: X = H

a: Y = H
b: Y = p-O CH_3
c: Y = p - CH_3
d: Y = m-O CH_3
e: Y = p - C_6H_5



1f: X = C_6H_5
2f: X = H

The progress of the reaction can easily be followed by observing the disappearance of the blue-green radical anions $1^{\bullet -}$,[14] simultaneous with the appearance of the yellow-orange arylfluorenyl anion 2^-.[15]

Initial reduction of solutions of **1a–e** resulted in immediate formation of minute amounts of **2**. Apparently, protonation by the small amounts of residual water allows facile C–C bond cleavage. Lagu, Mark, and Jezorek observed formation of tetraphenylmethane upon electrochemical reduction of **1a** in dimethylformamide with added hydroquinone but no cleavage without it.[16]

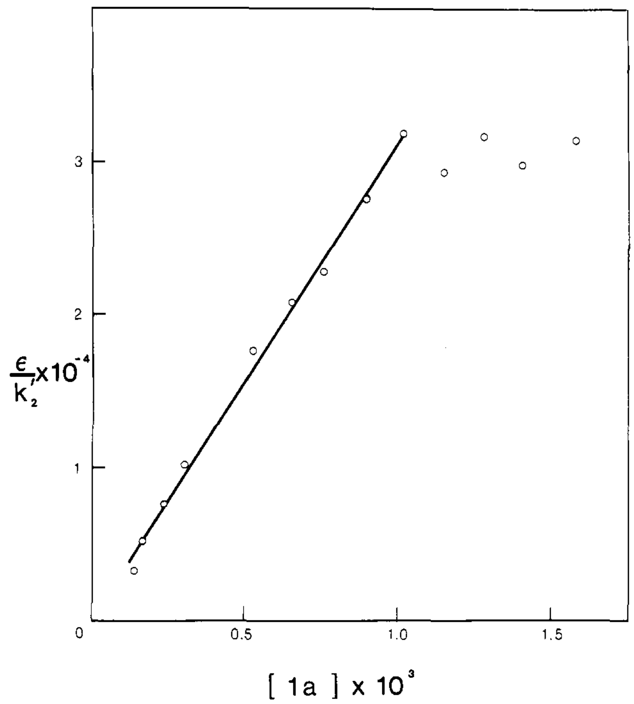


Figure 1. Dependence of observed second-order rate constant on the concentration of unreduced 9,9-diphenylfluorene, **1a** (Na, 25.0 °C).

Stoichiometry. Half of the radical anions cleave; the other half regenerate neutral **1**, either by reducing the free-radical product fragment from radical anion cleavage to an anion or by being produced in the disproportionation equilibrium of Scheme I. This stoichiometry was established in two ways: 1. In one experiment, attempted complete reduction of all **1a** by metallic lithium allowed estimation of the molar absorptivity of $\mathbf{1a}^{\bullet -}$ as being ≥7200 M^{-1} cm^{-1} (compare with 8040 ± 2710 as the best estimate of three other experiments). The radical anion was allowed to react completely, and then the process was repeated. In three successive runs, after complete reaction of the radical anion, 38, 39, and 54% of the **1a** was available for the next attempt. 2. Lithium naphthalenide was used in some runs as the reducing agent for **1a**. By using values of $\epsilon_{820} = 3030$ for $C_{10}H_8^{\bullet -}$ [17] and $\epsilon_{524} = 1800$ for $\mathbf{2a}^-$,[15] the amount of $\mathbf{2a}^-$ formed relative to the lithium naphthalenide used was 0.48 ± 0.11 and 0.50 ± 0.13 in two runs. Assuming a 1:1 ratio of $C_{10}H_8Li$ to $\mathbf{1a}^{\bullet -}$, this agrees with the above.

Kinetics. The mechanism shown in Scheme I affords a rate law of the form

$$-\mathrm{d}[\mathrm{ArR}^{\bullet -}]/\mathrm{d}t = 2k_1[\mathrm{ArR}^{\bullet -}] + 2k_2'[\mathrm{ArR}^{\bullet -}]^2 \qquad (1)$$

where

$$k_2' = k_2K_d/[\mathrm{ArR}]\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \qquad (2)$$

The integrated form of the rate law is

$$\frac{[\mathrm{ArR}^{\bullet -}]}{[\mathrm{ArR}^{\bullet -}]_0} = [(1+\alpha)e^{2k_1t} - \alpha]^{-1} \qquad (3)$$

where

$$\alpha = k_2'[\mathrm{ArR}^{\bullet -}]_0/k_1 \qquad (4)$$

Equation 3 is more sensitive to the value of k_1 than to that of $k_2'[\mathrm{ArR}^{\bullet -}]_0$, so that more confidence can be placed in the cal-

---

[11] Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359–5363.

[12] Walsh, T. D.; Megremis, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3897–3898.

[13] (a) Guthrie, R. D.; Maslak, P. *Bull. Soc. Chim. Belg.* **1982**, *91*, 454. (b) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628–2640.

[14] Janzen, E. G.; Harrison, W. B.; Pickett, J. B. *J. Organomet. Chem.* **1969**, *16*, P48–P50.

[15] Solov'yanov, A. A.; Beletskaya, I. P.; Reutov, O. A. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *19*, 1592–1603.

[16] Lagu, A.; Mark, H. G., Jr.; Jezorek, J. R. *J. Org. Chem.* **1977**, *42*, 1063–1067.

[17] Karasawa, Y.; Levin, G.; Szwarc, M. *Proc. R. Soc. London, A* **1971**, *326*, 53–71.

Table I. Effect of Dilution on Rate Constants (Na, 25.0 °C)

cell path length, cm	$k_1 \times 10^5$ (s^{-1})	$k_2K_d/\epsilon \times 10^8$ (M cm s^{-1})	N^a
0.10	2.42 ± 0.13	5.70 ± 1.02	2
1.0	2.92 ± 0.22	5.26 ± 0.83	3
10.0	2.24 ± 0.77	5.5 ± 7.3	3
all	2.29 ± 0.67	5.45 ± 3.21	8

[a] Number of determinations.

culated values of the former. This shows up in the relative errors involved in their determination, and in the degree of constancy from experiment to experiment, even from run to run within the same experiment. In particular, when the second-order path is essentially unimportant relative to the first-order path (e.g., lithium experiments), very little confidence can be placed in the quantitative values of the second-order rate constant.

The difficulty in measuring the molar absorptivity, ϵ, of $\mathbf{1a}^{\bullet-}$ introduces considerable uncertainty into the value of k_2' calculated from $k_2'[\mathrm{ArR}^{\bullet-}]_0$. Consequently, we prefer to present the effective second-order constant k_2'/ϵ

$$k_2'/\epsilon = k_2'[\mathrm{ArR}^{\bullet-}]_0 B/(A_0 - A_\infty)\ \mathrm{cm\ s^{-1}} \qquad (5)$$

where B is the optical cell path length in cm and $(A_0 - A_\infty)$, the difference in initial and final absorbance values, is assumed to be affected only by $\mathbf{1}^{\bullet-}$ and to be a valid measure of its concentration. This leads to $k_2K_d/\epsilon[\mathrm{ArR}]$, by using eq 2.

Scheme I requires that k_2'/ϵ be inversely proportional to the concentration of unreduced **1**. In all runs, **1** was kept in large excess over $\mathbf{1}^{\bullet-}$, so that [**1**] changed little throughout the reaction: 10% in the worst case, typically about 1%. Figure 1 shows the required linear relationship between ϵ/k_2' and [**1a**], from one experiment with sodium metal, in which successive runs at 25.0 °C involved decreasing [**1a**]. The slope of the line corresponds to $k_2K_d/\epsilon = (3.01 \pm 0.14) \times 10^{-8}$ M cm s^{-1}. This compares well with the average value for 21 runs of $(3.97 \pm 0.89) \times 10^{-8}$. However, the initial flat portion in Figure 1 does not fit this picture. We have no explanation for this change except that, since these points correspond to the least reliable estimates of k_2'/ϵ, the constant values observed may be fortuitous.

Thus, the mechanistically significant kinetic parameters to be used in this discussion are k_1 and k_2K_d/ϵ, the latter equal to $k_2'[\mathrm{ArR}]/\epsilon$.

Further evidence to support the above rate law was obtained by varying the initial concentration of $\mathbf{1a}^{\bullet-}$ over 50-fold (accomplished by changing the cell path length and keeping the initial absorbance reasonably constant). Table I shows that this has no effect on either rate constant, with sodium metal at 25.0 °C. Note that the second-order constant in the 10-cm cell has so much uncertainty as to have little quantitative value. Table I also establishes that $\mathbf{1a}^{\bullet-}$ obeys Beer's Law over this concentration range.

It is desirable to discuss the total reactivity of $\mathbf{1}^{\bullet-}$ and the fraction of the total reaction occurring through the first-order path under any set of conditions.

From eq 3 and 4, we can define the reactivity, R, as the reciprocal of the first half-life

$$R = \frac{1}{t_{1/2}} = \frac{2k_1}{\ln\{(2+\alpha)/(1+\alpha)\}}\ s \qquad (6)$$

Also, if the instantaneous fraction of the reaction occurring through the first-order path is f_1

$$f_1 = \frac{k_1}{k_1 + k_2'[\mathbf{1}^{\bullet-}]} \qquad (7)$$

then, the average fraction, F_1, from $[\mathbf{1}^{\bullet-}]_0$ to $[\mathbf{1}^{\bullet-}]_t$ is

$$F_1 = \frac{\ln\{(1+\alpha)/(1+\alpha[\mathbf{1}^{\bullet-}]/[\mathbf{1}^{\bullet-}]_0)\}}{\alpha\{1 - [\mathbf{1}^{\bullet-}]/[\mathbf{1}^{\bullet-}]_0\}} \qquad (8)$$

The experimental rate constants obtained from any one kinetic run are k_1 and $k_2'[\mathbf{1}^{\bullet-}]_0$, from which α follows directly, and thus R. To obtain F_1, one need only specify the extent of reaction.

It is convenient to define a standard set of conditions so that comparisons between different sets of experiments can be made; R^0 and $F_1{}^0$ are the reactivity and first-order fraction under these standard conditions, respectively. These standard conditions are

$$\epsilon[\mathbf{1}^{\bullet-}]_0/[\mathbf{1}] = 1 \times 10^3\ \mathrm{L\ mol^{-1}\ cm^{-1}} \qquad (9)$$

and

$$[\mathbf{1}^{\bullet-}]_0/[\mathbf{1}^{\bullet-}] = 16 \qquad \text{(i.e., 4 half-lives)} \qquad (10)$$

Equation 9 represents conditions close to most of those actually encountered. If $\epsilon = 8000$ M^{-1} cm^{-1} and $[\mathbf{1}] = 1 \times 10^{-3}$ M, then $[\mathbf{1}^{\bullet-}] = 1.25 \times 10^{-4}$ M, corresponding to an absorbance of 1.0 in a 1-cm cell.

Each kinetic run provides a value of α from which the mechanistically significant $k_2K_d/\epsilon k_1 = k_2'[\mathbf{1}]/\epsilon k_1$ is obtained, by using eq 4 and 5. Multiplication of this latter value by eq 9 yields the value of α needed for $F_1{}^0$.

The effect of the alkali metal used is shown in Table II. All three metals have similar k_1 values at 25 °C, with identical activation parameters for lithium and sodium. It is difficult to assess the reliability of the k_1 activation parameters for potassium: that path represents a very minor proportion of the total process.[12] Since eq 3 is more sensitive to k_1 than to $k_2'[\mathrm{ArR}^{\bullet-}]_0$, and since the linear correlation coefficient is so near unity, they appear to be reasonably valid. The reliability of the second-order activation parameters for lithium suffers as discussed above. In any event, there is considerably more variation among metals for the second-order path than for the first-order one.

In some experiments, new materials were added between runs, and their effect on the rate was measured. Table III shows that adding $\mathrm{KBPh_4}$ to solutions involving other metals effectively changes the reaction to resemble that with potassium metal. Saturation of a potassium cation solution with KI has little effect on the reaction; there might be a slight increase in the second-order proportion of the reaction. Finally, addition of 18-crown-6 polycyclic ether to a potassium solution greatly increases $F_1{}^0$.

One test of the effect of reducing the polarity of the solvent was made. Reduction of **1a** with lithium metal in tetrahydropyran (THP) shows the same reaction characteristics as reduction in DME. However, at 30 °C, $F_1{}^0 = 0.03$; k_1 is only 4% of k_1 in DME whereas k_2K_d/ϵ is 100 times as large.

In three experiments designed to measure the molar absorptivity of $\mathbf{1}^{\bullet-}$, naphthalene radical anion, $\mathrm{N}^{\bullet-}$, was used as the reducing agent. In two of those runs, with lithium metal, the rate of decrease of absorbance at 44.5 °C was measured at two wavelengths: 640 nm (near $\lambda_{\max}$ of $\mathbf{1}^{\bullet-}$) and 800–820 nm (near $\lambda_{\max}$ of $\mathrm{N}^{\bullet-}$). In both cases, $[\mathrm{C_{10}H_8}]$ and [**1a**] were kept sufficiently large so that they did not change more than 3% throughout any run. The value of the first-order rate constant, k_{obsd}, obtained from following the decrease of absorbance is the same, regardless of which wavelength is monitored. By using the mechanism in Scheme I and allowing $\mathrm{N}^{\bullet-}$ as well as $\mathbf{1}^{\bullet-}$ to reduce intermediate

Table II. Effect of Alkali Metal on the Reductive Fragmentation of **1a**[a]

	k_1				k_2K_d/ϵ					
metal	$\Delta H^\ddagger$	$\Delta S^\ddagger$	r^2	$(k_{\mathrm{rel}})_{298}$	$E_a{}^b$	$\log_{10} A^b$	r^2	$(k_{\mathrm{rel}})_{298}$	$(F_1{}^0)_{298}$	$(R^0{}_{\mathrm{rel}})_{298}$
Li	24.7 ± 1.5	3.8 ± 4.9	0.981	(1.0)	(43 ± 13)	(23 ± 7)	0.573	(1.0)	0.99	(1.0)
Na	25.1 ± 1.0	4.8 ± 3.4	0.985	0.84	30.3 ± 1.0	15.0 ± 1.4	0.991	75	0.52	2.0
K	18.8 ± 0.8	−17.1 ± 2.7	0.988	0.57	33.1 ± 0.9	18.1 ± 0.6	0.994	804	0.08	12.9

[a] $\Delta H^\ddagger$, E_a in Kcal mol^{-1}; $\Delta S^\ddagger$ in cal K^{-1} mol^{-1}; r = linear regression correlation coefficient. [b] Arrhenius parameters.

Table III. Effect of Added Materials on the Reductive Fragmentation of **1a**

run	T (°C)	metal	mol added	k_1[a] × 10^5	k_2K_d/ϵ[b] × 10^8	$F_1{}^0$
179–1	44.5	Li		50.7	1.26	0.987
–3	25.0		8.3 $KBPh_4$	1.30	37.0	0.088
–4	25.0		2.2 **1a**	1.98	33.8	0.135
135–3	25.0	Na		2.53	10.2	0.368
–4	25.0		0.2 $KBPh_4$	0.494	34.4	0.040
173–1	25.0	K		2.12	58.8	0.090
–2	25.0		satd KI	1.65	84.0	0.053
337–1	30.0	K		2.35	174	0.037
–2	30.1		1.7 18-crown-6	8.18	13.4	0.568
343–1	30.1	Li	solvent THP	0.26	27	0.027
–2	48.7		solvent THP	0.79	110	0.021

[a] s^{-1}. [b] M cm s^{-1}.

Table IV. Reduction of **1a** in the Presence of Naphthalene (DME, 44.5 °C)

run	$[C_{10}H_8]/[\mathbf{1a}]$	N[a]	$k_1 \times 10^4$ (s^{-1})	K[b]
153, 179	0.000	13	5.073 ± 0.469	
187	0.854 ± 0.015	6	0.849 ± 0.158	0.078 ± 0.018
195	0.661 ± 0.019	10	0.949 ± 0.134	0.068 ± 0.013

[a] Number of determinations. [b] Equation 12.

Table V. Effect of Substituents on the Rate of Fragmentation (Lithium, 35 °C)

compd	substituent	$(k_1)_{rel}$	$(k_2K_d/e)_{rel}$	$(R^0)_{rel}$	$F_1{}^0$	$(k_2K_d/\epsilon)_{rel}$[a]
1a	H	(1.00)	(1.00)	(1.00)	0.97	(1.00)
1b	p-OCH_3	1.3	186	8.7	0.23	1.5
1a	p-CH_3	0.66	4.4	0.81	0.83	1.4
1d	m-OCH_3	1.9	581	25	0.13	6.6
1e	p-C_6H_5	0.092	138	5.6	0.03	

[a] Potassium metal, 25 °C; ref 12.

Table VI. Products of Substituted Diaryl Fluorenes, **1b–e**

compd	substituent	$(PF/ArF)_{Li}$[a]	conversion (%)	F_1[b]	$(PF/ArF)_K$[c]
1b	p-OCH_3[d]	3.6 (0.53[e])	34	0.44	0.12
	p-OCH_3[f]	0.44 (0.37[e])	39		
1c	p-CH_3	0.45	63	0.88	0.40
1d	m-OCH_3[g]	4.7 (1.8[h])	71	0.42	2.8
	m-OCH_3[i]	2.9 (2.3[h])	65		
1e	p-C_6H_5	ca 25	20	0.04	[j]

[a] PF = 9-phenylfluorene, **2a**; ArF = 9-arylfluorene, **2b–e**. [b] Average fraction of products formed through first-order path. [c] Reference 12: potassium metal, DME, room temperature. [d] Seven reductions over an 11-day period, varying temperatures: 31% of the product is 4-(9*H*-fluoren-9-yl)phenol; 45% is 4-(9-phenylfluoren-9-yl)phenol. [e] **2a**/(**2b** + 4-(9*H*-fluoren-9-yl)phenol). [f] Three reductions over a 2-h period, 40 °C: 3% of the product is 4-(9*H*-fluoren-9-yl)phenol; 74% is 4-(9-phenylfluoren-9-yl)phenol. [g] Twenty-two reductions over a 25-day period, varying temperatures: 37% of the product is 3-(9*H*-fluoren-9-yl)phenol; 14% is 3-(9-phenylfluoren-9-yl)phenol. [h] **2a**/(**2d** + 3-(9*H*-fluoren-9-yl)phenol). [i] Four reductions over a 1-h period, 40 °C: 3% of the product is 3-(9*H*-fluoren-9-yl)phenol; 46% is 3-(9-phenylfluoren-9-yl)phenol. [j] **2e** not detected.

free radicals to anions, k_{obsd} can be related to the apparent K for the electron-exchange equilibrium, eq 11, (in which ion-association effects are neglected: at 20 °C in DME, $Na^+N^{\bullet-}$ have been shown to be loose ion pairs[17]).

$$N^{\bullet-} + \mathbf{1a} = N + \mathbf{1}^{\bullet-} \tag{11}$$

It can be shown that

$$K = \frac{[N]/[\mathbf{1a}]}{(2k_1/k_{obsd} - 1)} \tag{12}$$

where k_1 is the first-order constant observed in the absence of naphthalene. Table IV shows the results obtained. The mean value of K at 44.5 °C from these data, 0.073 ± 0.011, is comparable to 0.102 reported by Szwarc for electron transfer from sodium naphthalenide to biphenyl at 20 °C in DME.[17] This procedure may be useful for measurement of other electron-exchange equilibria.

Product studies using substituted 9-aryl-9-phenylfluorenes, **1b–e**, with lithium are described below. Their rate behavior is shown in Table V. As expected, **1c** behaves very much like the parent, **1a**. The others show decreased $F_1{}^0$ values and increased reactivity relative to **1a**. Especially noteworthy is the fact that **1e** follows essentially exclusive second-order kinetics; a pure second-order rate law is as satisfactory as the concurrent first- and second-order expression of eq 1.

A solution of 7,7-diphenylbenzo[*c*]fluorene, **1f**, in DME was reduced by using potassium. No change in the visible spectrum of $\mathbf{1f}^{\bullet-}$ was noted over a four-month period at room temperature; after two more months, features of the anion corresponding to loss of a phenyl group became apparent.

Product Studies. Reduction of **1a** yields only 9-phenylfluorene (and, presumably, benzene), after addition of oxygen-free methanol. No other products are detected by either GLC or HPLC.

When lithium naphthalenide was used as the reducing agent for **1a**, a 3% yield of phenylated naphthalenes was observed, in which the ratio of 1-phenylnaphthalene/2-phenylnaphthalene is 1.3. The total conversion of **1a** to products was 4%. Cheng, Headley, and Halasa observed 2–3% phenylated naphthalenes in the reduction of halobenzenes by sodium naphthalenide in tetrahydrofuran (THF); their ratio of isomers was 1.7 ± 0.8. These have been shown to arise from substitution of sodium naphthalenide by phenyl radicals.[18,19]

Substitution of one of the phenyl rings, in compounds **1b–e**, allows determination of factors affecting the ease of ring cleavage. Product data from reactions using lithium metal are shown in Table VI; potassium results[12] are included for comparison. Where reported, the F_1 values are somewhat higher than the $F_1{}^0$ values in Table V, because they refer to the actual conditions of these experiments, in which the concentrations of $\mathbf{1}^{\bullet-}$ were kept low to increase the first-order contribution to product formation. The short-time reductions of **1b** and **1d** involved higher concentrations and, presumably, lower F_1 values. The products from **1c** and **1e** are comparable to those observed with potassium. However, the ether substituents also cleave the oxygen–methyl bond to yield phenolic products; this was not observed to any appreciable extent with the potassium salts.[12] Presumably, the C–C bond cleavage is much more facile with the latter, so that the O-methyl fragmentation cannot effectively compete. At 25 °C, the potassium salt of $\mathbf{1d}^{\bullet-}$ is seven times more reactive than the lithium salt. The contribution of the O-methyl cleavage to the overall reaction of the lithium salts is reflected in higher rates relative to those of $\mathbf{1a}^{\bullet-}$, compared to those of the potassium salts. For the methoxy-substituted starting materials **1b** and **1d**, the product ratios of interest are the ones in parentheses in Table VI.[20]

Omitting the ratio for **1e**, a Hammett $\rho = 1.8$ is obtained for the five runs shown plus hydrogen. This is in the same direction but somewhat smaller than that obtained with potassium.[12] That is, electron-withdrawing groups enhance that ring's tendency to cleave, relative to H. The kinetic data (Table V) indicate that these effects operate through a facilitation of cleavage by electron-withdrawing groups, rather than a retarding effect of electron-donating groups.

Discussion

The kinetic results described above show that 9,9-diarylfluorenes react by two paths: one involving the radical anion and the other

---

(18) Cheng, T. C.; Headley, L.; Halasa, A. F. *J. Am. Chem. Soc.* **1971**, *93*, 1502–1503.

(19) Sargent, G. D. *Tetrahedron Lett.* **1971**, 3279–3282.

(20) This can be seen by the resemblance of these values for the long-time experiments to both of the corresponding values for the short-time ones, in which the effect of 9*H*-fluoren-9-ylphenol formation is minimal. Since the amount of 9-phenylfluoren-9-ylphenol produced in the short-time experiments is larger than in the long-time ones, this argues against appreciable reductive cleavage of this compound; rather, it appears that the 9*H*-fluoren-9-ylphenols arise mainly from subsequent reduction and cleavage of **2b** or **2d**.

the dianion, formed by disproportionation of the radical anion. Other mechanisms have been invoked to explain a second-order rate law,[5-7] but none of them is consistent with the inverse dependency of the rate constant on the concentration of unreduced starting material.

Two concurrent paths have been invoked by Remers et al. to explain different products in the Birch reduction of indoles and quinolines.[3] Product studies of reductive cleavages and sigmatropic rearrangements[4,21] have concluded that radical anion reactions are favored by conditions favoring loose ion pairs, whereas tight ion pairs react via dianions formed by disproportionation of radical ions. However, no kinetic data were obtained to support these conclusions.

In the current study, kinetic data show that the amount of reaction through the dianion is indeed determined by those factors known to affect disproportionation. In general, conditions favoring loose ion pairs discourage disproportionation: solvents of high polarity (DME vs. THP), small cations (Li^+ vs. K^+), and addition of cation-complexing agents (18-crown-6 ether).[22] These conditions all have been shown to increase $F_1{}^0$ in this study. They are known to have very large effects: disproportionation of 1,1,3-triphenylindene has been observed to decrease by ten orders of magnitude by complexing the sodium ion with 15-crown-5 ether and lowering the temperature by 75 °C (the latter known to favor loose ion pairs[23]).[4] Also, Rainis and Szwarc found that K_d in DME for anthracene and perylene is lowered by one or two orders of magnitude as the cation is varied from lithium to potassium.[24]

This is not to say that tight ion pairs disproportionate more than loose ones for, as Garst has cogently pointed out,[25] when tight ion pairs are the dominant ion-pair subspecies, then loose ion pairs must disproportionate even more than tight ones. Nor do we want to say that loose ion pairs only react via radical ions and tight ones only via dianions. Examination of the k_1 activation parameters (Table II) shows that they are different for potassium (tight ion pairs) than for either lithium or sodium (loose ones), the latter pair having indistinguishable values. Thus, tight ion pairs also react via radical anions. The fact that all k_1 values are similar for the three cations (within an order of magnitude within ±50 °C of room temperature) shows that the main effect of changing reaction conditions is to affect the disproportionation equilibrium, thereby altering $F_1{}^0$.

It is likely that the dianions are intrinsically more reactive than the radical anions. Assuming equal reactivity, i.e., $k_1 = k_2$, results in estimates of K_d of 0.2 (lithium) and 300 (potassium), much larger than reported values of 10^{-7}–10^{-10} for K_d of anthracene and perylene in DME.[24] Thus, it is likely that $K_d << 0.2$, requiring $k_2 > k_1$.

The behavior of substituted diarylfluorenes, **1b–e**, raises some interesting points. The methoxy-substituted fluorenes, **1b** and **1d**, have low $F_1{}^0$ values with lithium (Table V), reflecting the more tightly bound state of the ion pair, in which the lithium ion is attracted to the oxygen of the ether.

The *p*-phenyl-substituted derivative, **1e**$^{\bullet-}$, reacts essentially exclusively via the second-order path but has no structural feature requiring enhancement of its ion pair tightness. Instead, the two essentially comparable π systems must greatly increase its tendecy to disproportionate to dianion. (This assumes the same mechanism for its cleavage—a reasonable assumption, although the required inverse relationship between [**1e**] and the second-order rate constant was not examined.) No change in the rate law is required by the added complication in this instance of biphenyl ring reduction or of biphenyl formation and subsequent equilibration with **1e**$^{\bullet-}$, although the former could easily be responsible for a reversal of the charge movement upon cleavage (see below).

Table VII. Electron Affinities (eV) of Substituted Toluenes, $XC_6H_4CH_3$

X	EA (gas)[a]	E_{LUMO}[b]	adiabatic EA[c]	$XC_6H_4{}^{\bullet}/C_6H_5{}^{\bullet}$[d]
H	−1.11	+0.246	+0.13	(1.0)
p-CH_3	−1.07	+0.130	+0.30	1.4
m-CH_3	−1.06	+0.196	+0.21	1.2
p-OCH_3		+0.011	+0.43	3.1
m-OCH_3		+0.074	+0.35	1.8

[a] Reference 34. The more positive the value, the higher the EA. [b] Energy of lowest unoccupied MO of neutral compound (MNDO), ref 32. The more positive the value, the lower the EA. [c] Difference in ΔH_f for radical anion and neutral compound (MNDO). The more positive the value, the higher the EA. [d] Product ratio of cleavage of $XC_6H_4SC_6H_5{}^{\bullet-}$, ref 35.

Electron Apportionment in Radical Anion Fragmentation. The similarity in product distributions for lithium and potassium salts of **1b–e** and the positive ρ value point to loss of the aryl substituent as an anion, leaving the arylfluorenyl free radical behind in the former, the anion in the latter. Specifically, the large values of the two Hammett ρ values (3.4 for K, 1.8 for Li, excluding **1e**) indicate a substantial degree of charge separation in both cases. These ρ values closely parallel the trends in the rates of benzene ring hydrogen exchanges with KNH_2 in ammonia reported by Shatenshtein,[26] including the pronounced accelerating effect of a *p*-phenyl group on the rate of exchange (three times the effect of *m*-OCH_3), despite its small values of σ and σ_I.[27] In addition, the order of cleavage is inconsistent with that expected for aryl free radical leaving groups.[28]

The stability of the incipient substituted phenyl anion is the dominant factor in determining the course of the reaction. If the arylfluorenyl free radical **2**$^{\bullet}$ were a factor, we would expect little difference among the various substituents.[29] In fact, they have a pronounced rate and product effect. Also, the *p*-phenyl-substituted **1e**$^{\bullet-}$ should yield **2e**$^-$ instead of **2a**$^-$ if arylfluorenyl radical stability were a factor; the opposite is observed. If an arylfluorenide anion were formed, rates and products should be related to the pK_A's of the conjugate acids of compounds **2**;[30] however, the effect may be small.[31] In fact, an inverse relationship exists between product ratios and acid strength. No relationship is observed for rates, except that the most acidic hydrocarbon corresponds to **2f**; **1f**$^{\bullet-}$ is essentially unreactive.

Control by phenyl anion stability rather than arylfluorenyl stability is reasonable. Development of charge in the former does not require any atom rehybridization or reorganization (other than breaking of the bond). The carbon of the fluorenyl ring, in contrast, is initially saturated and must reorganize to allow delocalization; the aryl substituent acts to hinder this and is likely to be twisted in the radical, as it has been shown to be in the anion.[31]

The above evidence for formation of phenyl anion appears to be inconsistent with the observation of phenyl-substituted naphthalenes when lithium naphthalene is used as the reducing agent for **1a**. The yield and isomer distribution are consistent with those reported for attack of phenyl radicals on naphthalenide radical anion.[18,19]

These apparently contradictory observations can be reconciled in either of two ways: either the effect of substituents on bond

---

(21) Itoh, M.; Yoshida, S.; Ando, T.; Miyaura, N. *Chem. Lett.* **1976**, 271–274.

(22) Szwarc, M.; Jagur-Grodzinski, J. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 2, pp 90–108.

(23) Hogen-Esch, T. E. In *Adv. Phy. Org. Chem.* Gold, V.; Bethell, D., Eds.; Academic Press: New York, 1977; Vol. 15, pp 164–167.

(24) Rainis, A.; Szwarc, M. *J. Am. Chem. Soc.* **1974**, *96*, 3008–3010.

(25) Garst, J. F. In *Solute–Solvent Interactions*, Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969; p 588.

(26) Shatenshtein, A. I. In *Adv. Phy. Org. Chem.* Gold, V., Ed.; Academic Press: New York, 1963; Vol. 1, pp 187–188.

(27) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; pp 244, 247.

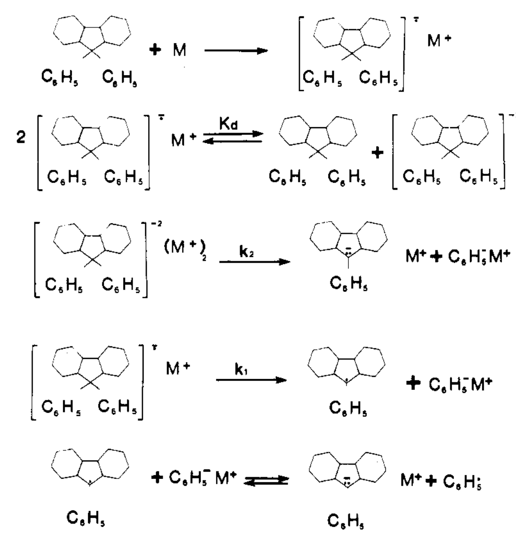
(28) (a) Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5504–5507. (b) Solomon, S.; Wang, C. H.; Cohen, S. G. *J. Am. Chem. Soc.* **1957**, *79*, 4104–4107.

(29) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. 1, pp 293–298.

(30) (a) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173–179. (b) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503–507.

(31) Browne, S. E.; Asher, S. E.; Cornwall, E. H.; Frisoli, J. K.; Harris, L. J.; Salot, E. A.; Sauter, E. A.; Trecoske, M. A.; Veale, P. S., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1432–1440.

Scheme II



cleavage is manifested prior to the cleavage, or a phenyl radical is formed from the anion at a point after cleavage occurs.

If the former were true, the only process which could be affected by substituents in the phenyl ring would be the ease of reduction itself—specifically, the abstraction of an extra electron into the phenyl ring from the fluorene system, generating an excited state of the radical anion, a substituted phenyl radical ion. Subsequent heterolytic cleavage would afford a neutral phenyl radical and arylfluorene anion directly. For this to occur, the electron affinity of these rings must reflect the trends observed. It is difficult to see why *m*- and *p*-OCH_3 groups would differ greatly in this regard. Indeed, both vertical and adiabatic electron affinities of the corresponding toluenes have been calculated, by using MNDO;[32,33] results are shown in Table VII. It is clear that no such parallel exists; as expected, the two OCH_3 positions have comparable influence, and all substituents increase the ring electron affinity relative to hydrogen as has been observed.[34]

There is an example of such a parallel in solution. Bunnett and Creary[35] have shown that $XC_6H_4SC_6H_5$ radical anions cleave to XC_6H_4 and C_6H_5 radicals, with preference for the former in all cases involving *m*- and *p*-methyl and -methoxyl groups. Note that the product ratios, listed in Table VII, parallel the gas-phase electron affinities.[36] Thus, this effect would be expected to be observable in our study if it were significant.

The second possibility, however, is entirely reasonable. Once delocalization of the arylfluorenyl radical occurs, the two fragments in the solvent cage find themselves in an unstable arrangement relative to electron exchange from phenyl anion to **2**$^\bullet$, generating phenyl radical and **2**$^-$.

Thus, the proposed course of the reaction is shown in Scheme II for the parent compound, 9,9-diphenylfluorene, **1a**, in which the tightness of the ion pair is not indicated. Fragmentation proceeds by heterolytic cleavage of the C–C bond, producing $C_6H_5^-$ and **2a**$^\bullet$. Since the excess electron density in **1a**$^{\bullet -}$ undoubtedly lies in the biphenyltype π system, this corresponds to electron movement away from the electron-rich region of **1a**$^{\bullet -}$. Subsequent electron transfer, probably within the solvent cage, generates the more stable pair, $C_6H_5^\bullet$ and **2a**$^-$.

Since this reaction initially apportions the electrons in a contrathermodynamic direction, so that a subsequent electron transfer is needed to establish equilibrium, there must be some overriding factor determining the electron flow in the fragmentation.

As proposed several years ago[1,13a] and recently published by Maslak and Guthrie,[13b] there is a theoretical basis for predicting the observed direction of fragmentation; namely, that *radical ion bond cleavage proceeds heterolytically to produce electron flow in the direction which offsets the charge distribution in that radical ion, with regioconservation of spin density.* This is illustrated for radical anions, in which the excess electron density in $X–Y^{\bullet -}$ is considered to reside largely in Y

$$X\!-\!Y^{\bullet -} \longrightarrow X\!:^- + [+Y^{\bullet -}] \longrightarrow X\!:^- + \cdot Y$$

Actual formation of $[+Y^{\bullet -}]$, an excited state of $Y^\bullet$, may be averted by an avoided crossing of the diabatic surface leading to it with one describing fragmentation of the σ^*-occupied configuration into the final products.

Whether or not this is a general rule, applying in all cases, remains to be seen. Guthrie has emphasized[13] that regioconservation of spin density offers a kinetic advantage over transfer of spin density; the latter is not necessarily forbidden. In particular, in situations in which large electronegativity differences exist in the two fragments, these may dominate the fragmentation.

There are indications that the rule may hold in other situations. For example, aliphatic nitro radical anions are believed to cleave to form alkyl radicals.[38] Interestingly, however, rates of cleavage of simple nitroalkyl radical anions follow the order 1° > 2° > 3°, suggesting anionic charge development in the alkyl group.[39] Unfortunately, these authors did not prove a one-electron process; however, they did obtain semiquantitative evidence for it.[40]

Several potential limitations to this rule come to mind. If the extra odd electron in an anion radical is located in a σ^* orbital, as has been suggested for several molecules,[28,41] then neither side of the radical anion has a charge excess. However, even here there may be some effect: ab initio calculations of solvated $CH_3Cl^{\bullet -}$,[42] which would be expected to fit this picture, show more than half the charge in diffuse orbitals in the CH_3 portion, which charge is wholly transferred to chlorine in the products.[42a]

A symmetrical radical ion would also not provide information about this aspect of the cleavage, although it may react in the same manner.

In one case, arguments have been advanced in opposition to this principle of electron apportionment, in studies of the cathodic fragmentation of diphenylmethyl *p*-nitrophenyl sulfide,[43] but were based on the behavior of intermediates which could have been the result of subsequent electron exchange between other primary products, as we have observed.

What is clearly needed are more cases which provide unequivocal evidence with regard to this rule. Such evidence must have two features. First, radical anion cleavage must be proven, since dianion cleavage can produce two anions, whether homolytically of heterolytically. Second, a clear statement about trends affected by radical or anion stabilities of the products must be able to be made and shown to be relevant leading up to the transition state of the fragmentation. Such statements, then, must involve relative rates of cleavage and not chemical behavior of the fragments later in the reaction. In our case, for instance, phenyl radicals are produced eventually, but the initial process generates negative charge at the cleaving carbon of the phenyl ring.

Some examples do exist which might be investigated to speak to this issue. The nitroalkane cleavage[38,39] and the possible exception[43] mentioned above are prime candidates. Also, conjugated

---

(32) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784–790.

(33) MNDO program: Thiel, W. *QCPE* **1978**, *11*, 353.

(34) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295–1296.

(35) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740–3743.

(36) Substitution of sulfur for carbon certainly affects absolute values but probably not trends. However, since solution electron affinities show a different trend,[37] the mechanistic significance of this correlation is doubtful.

(37) Lawler, R. G.; Tabit, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 5671–5672.

(38) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647–657.

(39) Gibson, R. H.; Crosthwaite, J. C. *J. Am. Chem. Soc.* **1968**, *90*, 7373–7375.

(40) Gibson, R. H., personal communication.

(41) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121–4125.

(42) (a) Canadell, E.; Karafiloglou, P.; Salem, L. *J. Am. Chem. Soc.* **1980**, *102*, 855–857. (b) Clark, T. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 203–212. (c) Clark, T.; Illing, G. *J. Chem. Soc., Chem. Commun.* **1985**, 529–530.

(43) Farnia, G.; Severin, M. G.; Capobianco, G.; Vianello, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1–8.

cyclopropanes are known to undergo reductive cleavage of the cyclopropane ring, generating negative charge at the eventually remote carbon.[44] Radical anion cleavage, although indicated, has not been proven.[2d] The manifold of reactions labeled $S_{RN}1$ involves production of negative ions and aryl radicals from initial radical anions in which negative charge lies predominantly in the aryl ring.[2g] Examples of cleavages slow enough to allow determination of the actual cleavage rates are needed. However, the presumed electron apportionment here is in agreement with the relative fragment stabilities, thus limiting the significance of these systems in this context.

Finally, the relationship between this study and the extensive work of Tabner and co-workers[7] on the reductive cleavage of hydrogen from the fluorene system should be mentioned. In almost every facet, our work and theirs show contrasting behavior. For example, they see a second-order rate law with lithium but first order with potassium.[45] For one case in which a second-order rate law was observed, no dependence of the rate on the concentration of unreduced starting material was seen.[46] Also, cleavage rates of several fluorenes parallel the pK_A's of the hydrocarbon.[46]

These differences must be due to some factor related to the different C_9 substituents (hydrogen in Tabner's cases, aryl in ours). One factor may be that hydrogen, being smaller and lighter than phenyl, is much more effective in allowing C_9 to rehybridize upon fragmentation, allowing delocalization to occur earlier in the reaction and thereby resulting in a greater influence of the fluorene ring system on the transition state. Also, because of the smaller size of hydrogen, metal-ion interaction in Tabner's systems is expected to be more intimate than in our case, as Tabner has noted.[45,46]

Experimental Section

Materials. The preparation of substituted fluorenes has been described.[12] Preparation[47] of 7-phenyl-7*H*-benzo[*c*]fluorene, **2f**, followed literature methods, mp 135–138 °C (lit. 138 °C[48]). 7,7-Diphenylbenzo[*c*]fluorene, **1f**, was obtained[47] by the Grignard reaction of 2-bromo-1-phenylnaphthalene[49] with benzophenone, followed by ring closure of the alcohol by using HCl/acetic acid: mp 203–5.5 °C; *m/e* 369 (31), 368.1555 (100, calcd for $C_{29}H_{20}$ 368.1566), 367 (14), 292 (12), 291.1149 (45), 289 (18);[50] UV nm (OD) 244 (1.75), 306 (0.41), 317 (0.54), 325 (0.45), 332 (0.35, sh), 341 (.53).

Preparation of 4-(9*H*-fluoren-9-yl)phenol followed literature methods, mp 177–180 °C (lit 176 °C[51]). Other hydroxy-substituted fluorenes were prepared as usual[12] by using the tetrahydropyranyl ethers as hydroxyl protecting groups, followed by $LiAlH_4$ reduction of the acetates produced by ring closure in acetic acid. For 3-(9*H*-fluoren-9-yl)phenol: mp 146–149 °C; UV (95% EtOH) nm (OD) 267 (0.81), 275 (sh, 0.65), 292 (0.25), 304 (0.36); ^1H NMR ($CDCl_3$) δ 4.62 (s, 1 H), 4.97 (s, 1 H), 6.41 (d, $J = 2$, 1 H), 6.65 (dd, $J = 2, 8.0$, 1 H), 6.75 (d, $J = 7.5$, 1 H), 7.13–7.38 (m), 7.77 (d, $J = 7.5$, 2 H); ^{13}C NMR ($CDCl_3$, APT) δ 53.5 (CH), 113.2–129.2 (8 CH), 140.3–155.0 (4 quaternary C). For 4-(9-phenylfluoren-9-yl)phenol: mp 192–194 °C; UV (95% EtOH) nm (OD) 273 (1.72), 297 (0.49), 309 (0.81); ^1H NMR ($CDCl_3$) δ 4.63 (s, 1 H), 6.65 (d, $J = 8.7$, 2 H), 7.05 (d, $J = 8.7$, 2 H), 7.19 (s, large), 7.22–7.39 (m), 7.75 (d, $J = 7.4$, 2 H); ^{13}C NMR ($CDCl_3$, APT) δ 114.9–129.3 (9 CH), 138.1–154.1 (5 quaternary C). For 3-(9-phenylfluoren-9-yl)phenol: mp 237–238 °C; UV (95% EtOH) nm (OD) 272 (0.95), 296 (0.29), 308 (0.45); ^1H NMR ($CDCl_3$) δ 4.66 (s), 6.60 (t, $J = 1$), 6.65 (dd, $J = 1, 8.0$), 6.9 (d, $J = 7.7$), 7.08 (t, $J = 7.9$), 7.19 (s, large), 7.21–7.41 (m), 7.74 (d, $J = 7.4$); ^{13}C NMR ($CDCl_3$, APT) δ 113.7–129.5 (11 CH), 140.3–155.4 (5 quaternary C).

All metals were of 99.95% purity (Alfa). Lithium was dissolved in liquid ammonia in the evacuated reaction apparatus and filtered into a side-arm tube which was separated from the main compartment by a coarse glass frit, and then the ammonia was removed. Sodium and potassium were triply vacuum distilled into a similar tube. In two experiments, sodium was obtained by pyrolysis of NaN_3 and then triply distilled.

Solvents were purified by distillation from $LiAlH_4$ followed by vacuum distillation into a preliminary storage flask containing Na–K alloy. After remaining in the preliminary flask for about a week, the solvent was redistilled into the permanent storage flask over alloy. This procedure prevented discoloration and residue formation in the DME flask. Before each run, vigorous stirring of the deep blue solution for about an hour preceded vacuum-line distillation into the reaction apparatus.

Kinetic Studies. All reactions were conducted by using vacuum-line techniques in a sealed apparatus which was all glass except that a greaseless vacuum stopcock (Ace 8193-04) separated the optical cell from the rest of the apparatus, in order to prevent solvent distillation between compartments during the run. Temperature studies used a vacuum-jacketed absorption cell equipped with a thermistor well; others used a standard cell in a calibrated, thermostatted cell holder.

The rate of disappearance of radical anion was analyzed by following the decrease in absorbance at 620–640 nm, by using a Cary 14 spectrophotometer. The wavelength of maximum absorption varied little with metal: 636 ± 1 nm (Li), 635 ± 3 nm (Na), 630 ± 3 nm (K). Several successive kinetic determinations were made with the same solution; a large excess of hydrocarbon ensured an essentially constant concentration throughout the run, since the accumulated amount of conversion was kept low. The concentration of unreduced starting material for each run was calculated by using the initial absorbance (extrapolated to the time of contact with the mirror, by using the rate constants determined for the run), a molar absorptivity of 8000 L mol^{-1} cm^{-1}, and a stoichiometry which regenerates half the starting material. All concentrations were corrected for density changes of DME.[52]

Values of k_1 and $k_2'C_0$ were obtained by using a weighted nonlinear least-squares program[53] which also calculates the best initial (and, if desired, infinity) absorbance value(s), by using the integrated rate expression for concurrent first- and second-order reactions (eq 3). The weights for each observation were calculated as being inversely proportional to the variance, by using the analytical expression,[53] and included the variance in A_∞. This produces the greatest weights near unit absorbance. Typically, the standard error of estimate is less than 0.003 absorbance units over 80–90+% reaction. For the calculation of mean values, observations were weighted as inversely proportional to their variances.

Product Studies. After the final kinetic study, degassed methanol was added to the reaction solution through a breakseal. Air was admitted, and then solid NH_4Cl was added to neutralize the basic solution, which was decanted from the solid after a short time.

Products were analyzed either by GLC[12] or by HPLC (H_2O/CH_3CN, Whatman ODS-3, 240–270 nm UV detector). The phenolic products from $\mathbf{1b}^{\bullet-}$ and $\mathbf{1d}^{\bullet-}$ were also identified by comparison of their UV spectra, observed in the HPLC detector, with those of authentic samples; also, reaction with dimethyl sulfate converted them to the corresponding methoxy compounds, whose HPLC relative areas adjusted accordingly. Product ratios were calibrated by using standard mixtures, but internal standards were not added, so that absolute yields were not determined.

Homogeneous Reductions. Purified[17] naphthalene in DME was reduced with metal in the usual vacuum apparatus. Before addition of **1a** to the solution of naphthalene radical anion, $N^{\bullet-}$, the stopcock was left in contact with the solution to age the Teflon. This was not completely successful and resulted in large uncertainty in the subsequent determination of $\epsilon_{\mathbf{1a}^{\bullet-}}$. Addition of **1a** to the solution resulted in decrease of absorption at 820 nm and an increase at 630–640 nm. By using $\epsilon_{N^{\bullet-}}$ (820 nm) = 3030[17] and experimentally determined values for the relative absorbance of each species at the wavelength of the other species' maximum, $\epsilon_{\mathbf{1a}^{\bullet-}}$ (630–640 nm) was calculated to be 9800 ± 830 L mol^{-1} cm^{-1} (Li, run 195, 636 nm), 14 200 ± 5700 (Li, run 207, 636 nm), and 5520 ± 960 (K, 630 nm). The last value is of doubtful significance, since $K^+N^{\bullet-}$ in DME shows two absorption maxima, at 774 and 820 nm, indicating a substantial fraction of contact ion pairs.

Subsequently, kinetic runs were made with the lithium experiments by the usual technique, following the loss of absorption at both 640 and 820 nm. The first-order rate constants obtained were the same at both wavelengths, within experimental error.

For run 195, air was admitted at the conclusion of five kinetic runs, and the solution was allowed to stand over solid NH_4Cl and then decanted. Both 1-phenylnaphthalene and 2-phenylnaphthalene were detected by comparison of retention times with those of authentic samples

---

(44) Staley, S. W.; Fox, M. A.; Hirzel, T. K. *J. Am. Chem. Soc.* **1976**, *98*, 3910–3916.

(45) Casson, D.; Tabner, B. J. *J. Chem. Soc. B.* **1969**, 887–892.

(46) Casson, D.; Tabner, B. J. *J. Chem. Soc. B* **1970**, 1560–1564.

(47) Prepared by Theresa K. Lanning.

(48) Dufour, M.; Perin, F.; Jacquinon, P. *Bull. Soc. Chim. Fr.* **1973**, 3166.

(49) Wittig, G.; Hellwinkel, D. *Chem. Ber.* **1964**, *97*, 769–788.

(50) Mass spectral analysis was obtained from the Pennsylvania State University Mass Spectrometry Facility, University Park, PA.

(51) Mathieu, A. *Bull. Soc. Chim. Fr.* **1971**, 1526–1533.

(52) Carvajal, C.; Tölle, K. J.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5548–5553.

(53) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103, 162–167.

on two GLC columns (SP2100 Silicone and Carbowax 20M). Also, HPLC (silica A column, hexane) confirmed their presence by comparison of both retention times and UV spectra with those of authentic samples.

Acknowledgment. I acknowledge helpful comments of Prof. J. F. Garst and discussions with Prof. J. R. Kuppers. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research, which was also supported in part by funds from the Foundation of the University of North Carolina at Charlotte and from the State of North Carolina.

Registry No. 1a, 20302-14-1; **1b**, 78229-08-0; **1c**, 78229-09-1; **1d**, 78229-10-4; **1e**, 78229-11-5.

Electron Transfer Catalyzed Reactions. Electrochemical Induction of the Hydrogen Atom Transfer Oxidation of Alcohols and Other Substrates by Aromatic Halides

Claude P. Andrieux,[1a] Jeanine Badoz-Lambling,[1b] Catherine Combellas,[1b] Daniel Lacombe,[1b] Jean-Michel Savéant,*[1a] André Thiébault,[1b] and Dominique Zann[1a]

Contribution from the Laboratoire d'Electrochimie de l'Université Paris 7, Unité de Recherche Associée au CNRS N° 438 "Electrochimie Moléculaire", 75 251 Paris Cedex 05, France, and the Laboratoire de Chimie et Electrochimie des Matériaux Moléculaires, E.S.P.C.I., Unité de Recherche Associée au CNRS N° 429, 75005 Paris, France. *Received July 31, 1986*

Abstract: The reduction of aryl halides in the presence of primary or secondary alcohols in liquid ammonia or in pure alcohol leads to the formation of the corresponding carbonyl compounds along an electrocatalytic process consuming a vanishingly small amount of electricity. The aryl radical generated upon electrochemical reductive cleavage of the aryl halide first abstracts a H atom from the alcohol leading to an hydroxyalkyl radical which deprotonates into the ketyl anion radical, which is itself oxidized into the carbonyl compound. Side reactions are the reduction of the aryl radical and of the hydroxyalkyl radical. A detailed study of the feasibility and the mechanism of the reaction has been carried out by cyclic voltammetry and preparative scale electrolysis. The results underscore the fact that besides its acid–base properties, the H-atom donation ability of the solvent can play an important role in the course of electrochemical reactions. The electron stoichiometry, varying between 0 and 2, and the product distribution are functions of the redox and acid–base properties of the radical resulting from H-atom abstraction and of the redox and cleavage characteristic of the aryl halide anion radical. The reaction allows the oxidation of a large variety of substrates under electrochemically reducing conditions, those which lead to the formation of the aryl radical from the starting aryl halide.

The electrochemical reduction of aryl halides (ArX) has been the object of a large number of previous investigations (for recent reviews see ref 2). It has been shown that the anion radical $\mathrm{ArX}^{\bullet-}$ resulting from the uptake of a first electron is unstable in most cases

$$\mathrm{ArX} + e^- \rightleftarrows \mathrm{ArX}^{\bullet-} \tag{0}$$

$$\mathrm{ArX}^{\bullet-} \xrightarrow{k_1} \mathrm{Ar}^{\bullet} + \mathrm{X}^- \tag{1}$$

and undergoes a cleavage reaction yielding the aryl radical, $\mathrm{Ar}^{\bullet}$, and the halide ion. The rate constant of the cleavage reaction, k_1, has been determined in a number of cases either by direct electrochemical methods when it is not too large ($k_1 \lesssim 10^4\ \mathrm{s}^{-1}$) or by redox catalysis methods when it is larger.[3a] It was shown that the lifetime of the anion radical, $\mathrm{ArX}^{\bullet-}$, varies considerably, from almost complete stability to nanoseconds, as a function of the nature of the aryl residue and of the halogen atom.[3]

The fate of the resulting aryl radical has also been the object of several investigations. Aryl radicals appear to be easily reducible species, much more than the usual aryl halides from which they derive.[4] In solvents which are poor hydrogen atom donors, such as liquid ammonia, they thus undergo an immediate further electron transfer, at the potential where they are formed, yielding the corresponding aryl carbanion and eventually the hydrocarbon, ArH, upon proton transfer from acidic impurities or from the solvent itself:[5]

$$\mathrm{Ar}^{\bullet} + e^- \rightleftarrows \mathrm{Ar}^- \tag{3}$$

$$\mathrm{Ar}^{\bullet} + \mathrm{ArX}^{\bullet-} \rightarrow \mathrm{Ar}^- \tag{3'}$$

$$\mathrm{Ar}^- + \mathrm{H}^+ \rightarrow \mathrm{ArH}$$

The second electron transfer reaction can occur concurrently at the electrode surface and in the solution from the $\mathrm{ArX}^{\bullet-}$ anion radical, giving rise to a competition between an "ECE" (reactions 0 + 1 + 3) and a "DISP" (reactions 0 + 1 + 3′) process.[6] The

---

(1) (a) Université de Paris 7. (b) ESPCI.

(2) (a) Hawley, M. D. In *Encyclopedia of Electrochemistry of the Elements, Organic Section*; Bard, A. J.; Lund, H., Eds.; Dekker: New York, 1980; Vol. XIV. (b) Becker, J. Y. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 6, pp 203–285.

(3) (a) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107 and references cited therein. (b) The cleavage rate constant varies as a function of the halogen atom in the order I > Br > Cl. The variation with the nature of Ar makes a roughly linear correlation appear between the activation free energy of cleavage and the standard potential of the $\mathrm{ArX}/\mathrm{ArX}^{\bullet-}$ couple: the more negative the potential the faster the cleavage.[3a,c] (c) Andrieux, C. P.; Savéant, J. M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815. (d) From the evidence gained so far, reactions 0 and 1 appear as sequential even for the fastest cleavage reactions.[3a] It is, however, not excluded that with the fastest cleaving systems and with the low value of the electron transfer driving force, the two reactions could become concerted[3c,f] as they have been shown to be in the case of aliphatic halides.[3c,e] (e) Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (f) Andrieux, C. P.; Savéant, J. M. *J. Electroanal. Chem.* **1986**, *205*, 43.

(4) (a) Although not determined with accuracy, the potential region where $\mathrm{Ar}^{\bullet}$ are reduced can be estimated to be around −0.3 V vs. SCE in organic solvents, at room temperature,[4b] i.e., aryl radicals are more than 1 V easier to reduce than usual aryl halides. (b) Jaun, B.; Breslow, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(5) Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1978**, *89*, 335.