

# Reactions of Primary Alkyl Fluorides with Sodium Naphthalene and Related Compounds<sup>1,2</sup>

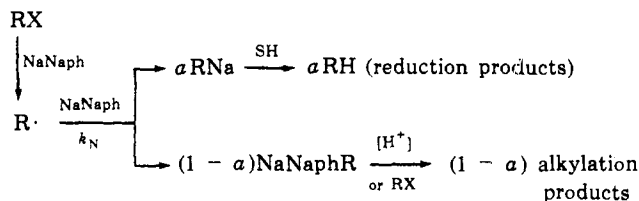
John F. Garst\* and Franklin E. Barton, II

Contribution from the Department of Chemistry, The University of Georgia, Athens, Georgia 30602. Received June 7, 1973

**Abstract:** Primary alkyl fluorides react with sodium naphthalene in DME at conveniently slow rates. The reaction of 5-hexenyl fluoride gives both 1-hexene and methylcyclopentane in ratios which correlate with the concentration of sodium naphthalene. This is strong evidence for a mechanism in which 5-hexenyl radicals are initially formed. These cyclize in competition with their reduction by sodium naphthalene. If the rate constant for cyclization of 5-hexenyl radicals is taken as  $\sim 10^5 \text{ sec}^{-1}$ , then the data require that the rate constant for reaction of 5-hexenyl radicals with sodium naphthalene be  $\sim 1.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . Sodium biphenyl reacts in parallel fashion. The rate constants for reactions of lithium, sodium, and potassium naphthalenes with 5-hexenyl fluoride are 0.03, 0.0003, and  $0.000003 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively. No reaction of cesium naphthalene with 5-hexenyl fluoride was observed. The implications of these and related data are discussed. It is suggested that there is substantial negative charge localization in the activated complexes for the reactions.

Several recent studies support Scheme I as the mechanism of reactions of sodium naphthalene<sup>3</sup> (Na-

## Scheme I



Naph,  $\text{NaC}_{10}\text{H}_8$ ) with alkyl chlorides. A similar mechanism applies to alkyl bromides and iodides, but their reactions are complicated by the formation of alkyl dimers, which are obtained in only trace quantities from alkyl chlorides.<sup>2,5-14</sup>

Part of the evidence for alkyl radical intermediates is that 5-hexenyl halides lead to methylcyclopentane as well as 1-hexene.<sup>5</sup> Cyclization is attributed to intermediate 5-hexenyl radicals,<sup>15,16</sup> which cyclize with a

(1) Based on the Ph.D. Dissertation of Franklin E. Barton, II, The University of Georgia, Athens, 1969.

(2) Part of this work has been reported in preliminary form: J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

(3) The 1965 revision of the IUPAC rules of nomenclature<sup>4</sup> requires that the substance ( $\text{NaC}_{10}\text{H}_8$ ) called "sodium naphthalene" here be named "sodium dihydronaphthylide." Another name, "sodium naphthalenide," had been in common use for many years. Unfortunately, the IUPAC preempted "sodium naphthalenide" as their name for the substance commonly called "naphthylsodium." In our opinion, the IUPAC sanctioned name for  $\text{NaC}_{10}\text{H}_8$  is inordinately cumbersome. We adopt "sodium naphthalene," abandoning "sodium naphthalenide" to avoid confusion with naphthylsodium.

(4) IUPAC, "Nomenclature of Organic Chemistry," Butterworths, London, 1965, pp 66-67.

(5) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).

(6) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **88**, 4262 (1966).

(7) G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 5363 (1966).

(8) J. F. Garst, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D65 (1968).

(9) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968).

(10) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968).

(11) J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969).

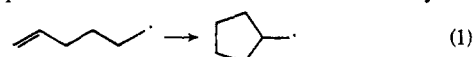
(12) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).

(13) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, **92**, 5761 (1970).

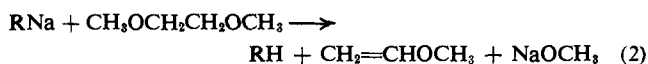
(14) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

(15) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3482 (1963).

rate constant of about  $10^5 \text{ sec}^{-1}$ .<sup>17</sup> Control experiments showed that the cyclization of 5-hexenylsodium, which could provide an alternative route to cyclic

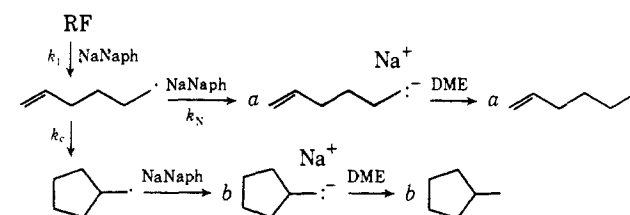


products, does not compete effectively with its reaction with the solvent.<sup>2,5,8</sup>



An additional test of Scheme I could be provided by determining the effect of the concentration of sodium naphthalene on the extent of cyclization. According to Scheme I, which is specialized to a 5-hexenyl halide in Scheme II, the molar ratio of products 1-hexene/

## Scheme II



methylcyclopentane should increase with increasing concentration of sodium naphthalene. This trend was confirmed in crude experiments with 5-hexenyl chloride,<sup>8</sup> but such reactions are not subject to convenient control of concentration homogeneity, since they appear to occur as rapidly as the reagents are mixed. Accordingly, we examined the possible reactions of sodium naphthalene with simple alkyl fluorides, in hopes that they would proceed more slowly than those of alkyl chlorides, but in parallel fashion. Concentration homogeneity would not be a problem then, and the systems might be amenable to quantitative study.

## Experimental Section

**General.** Visible and uv spectra and optical density data were obtained with a Cary Model 14 spectrophotometer with a sample

(16) M. Julia, *Accounts Chem. Res.*, **4**, 386 (1971), and references cited therein.

(17) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

compartment cover which would contain an entire reaction vessel. Except for experiments 137–145, which were at ambient temperatures, the reactions were conducted in a thermostated bath regulated to  $\pm 0.05^\circ$  at 25, 35, and  $45^\circ$ . Infrared spectra were determined using Perkin-Elmer spectrophotometers Models 257, 421, and 621. Nmr spectra were obtained on Varian A-60 and HA-100 instruments. Mass spectra were determined using Hitachi RMU-6 and RMU-7 instruments with vpc inlet techniques.

Varian Aerograph Models 600 and 1200-1 vapor phase chromatographs with flame ionization detectors were used for all vpc analyses. The following columns were employed: (1) 10 ft  $\times$  0.25 in. 20% poly(phenyl ether) (5-ring); (2) similar to column 1, 20 ft long; (3) 10 ft  $\times$  0.25 in. 10% QF-1; (4) similar to column e, 20% QF-1; (5) 12 ft  $\times$  0.25 in. 10% 8N8 Flexol Plasticizer; (6) similar to column 5, 10 ft long; (7) 7 ft  $\times$  0.25 in. saturated AgNO<sub>3</sub> in propylene glycol, 20%; (8) 7 ft  $\times$  0.25 in. 10% Carbowax 20M. Except for column 7, which used 60–80 Diatoport-P, acid washed, the supports were 60–80 Chromosorb W, DMCS treated.

**Solvents.** Ether solvents were refluxed over sodium, fractionally distilled, stored off the vacuum manifold over Fisher 4A molecular sieves, and stored on the vacuum manifold as degassed solutions containing the disodium adduct of benzophenone. Solvents were distilled through the vacuum manifold into reaction vessels as needed.

**Reactions.** Reactions of sodium naphthalene with alkyl fluorides were carried out in evacuated vessels. These were fitted with three side arms, one containing a fritted disk, one attached to an optical cell, and one with a breakseal leading to a chamber in which the alkyl fluoride was placed. Sodium was distilled through several constrictions to form a mirror with the fritted disk between the mirror and the main body of the reaction vessel. Solvent was distilled from storage into the main body of the vessel, into which had been placed the desired amount of naphthalene. The solution of naphthalene was allowed to pass through the fritted disk to contact the sodium mirror, then it was filtered back through the disk into the main chamber of the reaction vessel. When a solution of sodium naphthalene of the desired optical density had been obtained, the fritted disk and sodium mirror were cut away with a hand torch. The alkyl fluoride was added through a breakseal. The vessel was immersed in the constant-temperature bath, from which it was occasionally withdrawn for optical density measurements. In some early runs, the alkyl fluoride was introduced through rubber serum caps with a syringe. The observations for such experiments were identical with those for which the breakseal technique was employed (the syringe technique was used only for more concentrated sodium naphthalene solutions).

After a reaction was complete, a side arm was cut off and fitted with a serum cap through which samples were withdrawn for analyses. Reaction mixtures were generally colored at the end, due to colored organic anions (RC<sub>6</sub>H<sub>5</sub><sup>-</sup>) and colloidal sodium fluoride.

**Analyses.** Vpc analyses were performed directly on the reaction mixtures, with no prior treatment except exposure to air. Peaks were assigned by coinjection of authentic materials on several of the columns described above. Confirmation of assignments and assurance of complete separations resulted from comparisons of mass spectra of authentic materials and reaction products, each led into the mass spectrometer from a vapor phase chromatograph. For each assigned peak, the mass spectra of authentic materials and reaction products were identical.

Column 2 was used for quantitative analyses. It cleanly separated 1-hexene, 1,5-hexadiene, methylcyclopentane, methylenecyclopentane, cyclohexene, cyclohexane, methanol, methyl vinyl ether, 5-hexenyl fluoride, DME, naphthalene, and alkylation products when used at  $60^\circ$ . Alkylation products were not examined in detail, but they were detected by vpc as materials with longer retention times than naphthalene. Vpc traces of product mixtures from reactions of 5-hexenyl chloride and 5-hexenyl fluoride were found to be similar in form in the region of alkylation products.<sup>18</sup>

The C<sub>6</sub> products (1-hexene and methylcyclopentane) were deter-

mined quantitatively by disk or digital integration of peaks and comparison with internal standard cyclohexane, which is not a reaction product. When sodium naphthalene was in excess, yields could be accurately and reproducibly determined, based on the complete consumption of the 5-hexenyl fluoride. The C<sub>6</sub> hydrocarbons were formed in  $56 \pm 2\%$  yield.<sup>20</sup> In kinetic runs, it was convenient to have 5-hexenyl fluoride present in considerable excess. Yields could be determined for such experiments, based on sodium naphthalene consumed, but such determinations were much less reproducible, running around 40%.

In the experiments with the most dilute sodium naphthalene solutions (ca.  $3 \times 10^{-4} M$ ), introduction of 5-hexenyl fluoride was sometimes accompanied by immediate destruction of some of the sodium naphthalene. The concentration of 5-hexenyl fluoride used in these runs was about  $7 \times 10^{-2} M$ . Destruction of 30% of  $3 \times 10^{-4} M$  sodium naphthalene corresponds to  $\sim 0.14$  mol % impurity in the alkyl fluoride. In view of the problems in the quantitative handling of the volatile and highly toxic alkyl fluoride (LD<sub>50</sub> for intraperitoneal injection in mice = 2.8 mg/kg),<sup>21</sup> no attempt was made to purify those samples further. "Killing" was insignificant at higher concentrations of sodium naphthalene, and it did not seem to have an effect on the kinetics of the reactions.

**Extinction Coefficients.** The extinction coefficients of the alkali arenes are not necessary for the determination of rate constants, since their concentration variations followed (pseudo) first-order kinetics. They are necessary to establish the initial conditions, for the determination of reaction stoichiometry, and for the analysis of the quantitative significance of the extent of cyclization. For sodium naphthalene in DME, we found  $\epsilon$  2500 at 8200 Å. For sodium biphenyl in DME,  $\epsilon$  12,500 at 6450 Å. These are the analytical wavelengths used in following the kinetics of the reactions.

**Alkyl Halides.** 5-Hexenyl fluoride<sup>22</sup> was first prepared by the procedure of Pattison and Norman.<sup>21</sup> In the final distillation, the fraction boiling at  $91^\circ$  was taken (lit. bp  $91.5^\circ$  (740 Torr));<sup>21</sup> yield, 70%. *Anal.* Calcd: C, 70.548, H, 10.854, F, 18.598. Found: C, 70.57; H, 10.88; F, 18.41.<sup>23</sup> Nmr and ir consistent with structure. A second procedure was preferred. To a stirred solution of *N,N*-diethyl-*N*-1,1,2-trifluoro-2-chloroethylamine<sup>24,25</sup> (0.20 mol) in anhydrous diethyl ether (100 ml) at reflux, 5-hexen-1-ol (0.20 mol) was added dropwise over 3–4 hr. After complete addition, the mixture stood 48 hr. It was then passed through columns of neutral alumina and sodium carbonate, which were washed through with additional diethyl ether. Fractional distillation, with retention of material boiling at  $91^\circ$ , gave 0.16 mol (82% yield) of a substance identical (nmr, ir, and vpc retention time) with that prepared by the first method.

Tetrahydrofuryl fluoride was prepared by the second method from tetrahydrofurfural. The fraction boiling at  $115^\circ$  was taken; yield, 75%. *Anal.* Calcd: C, 57.678; H, 8.714; F, 18.250. Found: C, 57.54; H, 8.75; F, 18.13. Nmr and ir consistent with structure.

Several attempts to prepare cyclopentylmethyl fluoride by both methods failed; methylenecyclopentane was the only product detected.

Hexyl and octyl fluorides were obtained commercially and purified by fractional distillation on an annular Teflon still.

## Results

Near room temperature, sodium naphthalene and some other alkali arenes (MAr) react relatively slowly with primary alkyl fluorides in DME. Since alkali fluorides precipitate as the reactions proceed, initial rates should be most significant. Nonetheless, for the disappearance of alkali arenes good pseudo-first-order plots (RF in large excess) are obtained for 1.5–5 half-lives. Second-order rate constants derived from these data show scatter, but no dependence on the initial

(18) Alkylation products of reactions of several alkyl halides with sodium naphthalene have been characterized.<sup>19</sup> In our laboratories, a brief examination of the alkylation products of the reaction of 5-hexenyl chloride was carried out by Dr. Yo Miyagi. The nmr and ir spectra of materials isolated by preparative vpc indicate that they are of the types previously reported,<sup>19</sup> primarily alkylated dihydronaphthalenes. In other studies with  $\alpha,\omega$ -dihaloalkanes, we have shown that the product balance for reactions with sodium naphthalene is near 100%.<sup>14</sup>

(19) D. Lipkin, G. J. Davis, and R. W. Jordan, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D60 (1968).

(20) This yield is in good agreement with reduction product yields for other primary alkyl halides.<sup>9,14</sup>

(21) F. L. M. Pattison and J. J. Norman, *J. Amer. Chem. Soc.*, **79**, 2311 (1957).

(22) F. W. Hoffmann, *J. Org. Chem.*, **14**, 105 (1940).

(23) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

(24) D. E. Ayer, *Tetrahedron Lett.*, 1065 (1962).

(25) L. H. Knox, E. Verlarde, S. Burger, D. Cuadrillo, and A. D. Cross, *Tetrahedron Lett.*, 1249 (1962).

**Table I.** Kinetics of Reactions of Sodium Naphthalene with Alkyl Fluorides in DME at 25°

Expt	RF	[RF] <sub>0</sub> , M	[NaNaph] <sub>0</sub> , M	k, M <sup>-1</sup> sec <sup>-1</sup>
137 <sup>a</sup>	5-Hexenyl fluoride	0.0774	0.028	2.3 × 10 <sup>-4</sup>
138 <sup>a</sup>		0.0400	0.0046	3.7 × 10 <sup>-4</sup>
142 <sup>a</sup>		0.066	0.032	2.8 × 10 <sup>-4</sup>
143 <sup>a</sup>		0.0187	0.062	3.1 × 10 <sup>-4</sup>
144 <sup>a</sup>		0.0383	0.0041	3.4 × 10 <sup>-4</sup>
145 <sup>a</sup>		0.0390	0.0023	2.5 × 10 <sup>-4</sup>
146		0.158	0.022	2.3 × 10 <sup>-4</sup>
147		0.154	0.030	3.1 × 10 <sup>-4</sup>
148		0.0777	0.0026	2.8 × 10 <sup>-4</sup>
159		0.0670	0.00049	3.2 × 10 <sup>-4</sup>
160		0.0694	0.00028	2.1 × 10 <sup>-4</sup>
			Av for 11 expt	2.8 ± 0.5 <sup>b</sup> × 10 <sup>-4</sup>
153	n-Hexyl	0.0785	0.031	1.7 × 10 <sup>-4</sup>
155		0.0864	0.0032	2.7 × 10 <sup>-4</sup>
			Av	2.2 ± 0.5 <sup>c</sup> × 10 <sup>-4</sup>
154	n-Octyl	0.0584	0.036	1.9 × 10 <sup>-4</sup>
156		0.0557	0.0048	2.6 × 10 <sup>-4</sup>
			Av	2.2 ± 0.4 <sup>c</sup> × 10 <sup>-4</sup>
	Tetrahydrofurfuryl fluoride	0.0329	0.11	4.0 × 10 <sup>-4</sup>

<sup>a</sup> Ambient temperature (23–25° in controlled temperature instrument room). The results of experiments 137–145 are indistinguishable from those of experiments 146–160. They are therefore included. <sup>b</sup> Standard deviation. <sup>c</sup> Limit of variation for two experiments.

concentration of alkali arene (varied by a factor of 100 for the reaction of sodium naphthalene with 5-hexenyl fluoride in DME) or alkyl fluoride (varied by a factor of 10 for the same reaction).

In Table I are the kinetic data for reactions of 5-hexenyl, hexyl, octyl, and tetrahydrofurfuryl fluorides with sodium naphthalene in DME at 25°. Temperature effects on the same reaction are detailed in Table II. Table III gives ratios of 1-hexene and methylcyclo-

pentane formed in reactions of 5-hexenyl fluoride with sodium naphthalene and sodium biphenyl. Table IV gives metal ion effects on rates of reactions of alkali naphthalenes with 5-hexenyl fluoride in DME, while Table V summarizes the results of some other reactions of alkali arenes with alkyl fluorides.

**Table II.** Effect of Temperature on Rate of Reaction of Sodium Naphthalene with 5-Hexenyl Fluoride in DME

Expt	Temp, °C	10 <sup>4</sup> k <sup>a</sup>
See Table I	25	2.8 ± 0.5 <sup>b</sup>
207, 208, 210, 211	35	9 ± 3 <sup>c</sup>
213, 214, 215	45	19 ± 1 <sup>c</sup>

ΔH<sup>‡</sup> = 17.6 ± 1.3<sup>d</sup> kcal/mol

ΔS<sup>‡</sup> = -16 ± 4<sup>d</sup> cal mol<sup>-1</sup> °K<sup>-1</sup> (1 M ref state)

<sup>a</sup> In M<sup>-1</sup> sec<sup>-1</sup>. <sup>b</sup> Standard deviation for 11 runs. <sup>c</sup> Limits of observed variations for experiments indicated. <sup>d</sup> Standard deviation from linear least-squares analysis of data for 18 runs, 11 at 25°, 4 at 35°, and 3 at 45°.

**Table III.** Ratios of 1-Hexene/Methylcyclopentane Formed in Reactions of Sodium Naphthalene and Sodium Biphenyl with 5-Hexenyl Fluoride in DME at 25°

Expt	[NaAr] <sub>0</sub> , <sup>a</sup> M	1-Hexene/ Methylcyclo- pentane	k <sub>N</sub> /k <sub>o</sub> , <sup>b</sup> M <sup>-1</sup>
For Sodium Naphthalene			
138	4.6 × 10 <sup>-3</sup>	15.2	1.5 × 10 <sup>4</sup>
144	4.1 × 10 <sup>-3</sup>	16.5	1.9 × 10 <sup>4</sup>
148	3.8 × 10 <sup>-3</sup>	12.8	1.5 × 10 <sup>4</sup>
145	2.3 × 10 <sup>-3</sup>	7.6	1.6 × 10 <sup>4</sup>
159	0.49 × 10 <sup>-3</sup>	2.1	1.2 × 10 <sup>4</sup>
160	0.28 × 10 <sup>-3</sup>	2.0	2.1 × 10 <sup>4</sup>
			Av 1.6 × 10 <sup>4</sup>
For Sodium Biphenyl			
194	6.3 × 10 <sup>-3</sup>	16.8	1.2 × 10 <sup>4</sup>
191	6.2 × 10 <sup>-3</sup>	11.9	0.8 × 10 <sup>4</sup>
192	0.51 × 10 <sup>-3</sup>	1.4	0.8 × 10 <sup>4</sup>
195	0.41 × 10 <sup>-3</sup>	1.6	1.1 × 10 <sup>4</sup>
			Av 1.0 × 10 <sup>4</sup>

<sup>a</sup> Initial concentration of sodium arene. <sup>b</sup> Calculated from eq 4.

**Table IV.** Metal Ion Effects on Rates of Reactions of Alkali Naphthalenes with 5-Hexenyl Fluoride in DME at 25°

Expt	Alkali naphthalene	10 <sup>4</sup> k <sup>a</sup>
165–166	LiNaph	270 ± 20 <sup>b</sup>
See Table I	NaNaph	2.8 ± 0.5 <sup>c</sup>
202	KNaph	0.02 <sub>5</sub> <sup>d</sup>
200–201	CsNaph	<0.005 <sup>e</sup>
		No reaction observed
216 (5-hexenyl chloride)	CsNaph	~20,000 <sup>f</sup>

<sup>a</sup> In l. mol<sup>-1</sup> sec<sup>-1</sup>. <sup>b</sup> Limits of variation in two experiments. <sup>c</sup> Standard deviation for 11 experiments. <sup>d</sup> When [RF]<sub>0</sub> = 0.0682 M, half the optical density due to NaNaph disappeared in 6 days. <sup>e</sup> No detectable decrease in CsNaph optical density in 5 days. Limit is based on the assumption that a 4% decrease could have been detected with certainty. A smaller limit is likely. <sup>f</sup> Estimated from time (75 sec) for decrease of CsNaph optical density to half its original value when [CsNaPh]<sub>0</sub> = 7.5 × 10<sup>-3</sup> M and [RF] = 3.14 × 10<sup>-3</sup> M. If second-order kinetics apply, the value obtained is probably accurate to within a factor of 2.

**Table V.** Rates of Some Other Reactions of Alkali Arenes with Alkyl Fluorides

Expt	Alkali arene	Fluoride	Sol- vent	Temp, °C	10 <sup>4</sup> k <sup>a</sup>
175	NaNaph	5-Hexenyl	THF	25	2.1
161–162	LiNaph	n-Hexyl	DME	25	75 ± 10 <sup>b</sup>
163–164	LiNaph	n-Octyl	DME	25	122 ± 8 <sup>b</sup>
177, 180	LiBiph <sup>c</sup>	5-Hexenyl	DME	25	124 ± 2 <sup>b</sup>
196, 198	CsBiph	5-Hexenyl	DME	25	NR <sup>d</sup>
171	NaBiph	5-Hexenyl	DME	25	1.4
167	LiAnth <sup>e</sup>	5-Hexenyl	DME	25	NR <sup>f</sup>
185	CsAnth	n-Hexyl	DME	25	NR <sup>f</sup>

<sup>a</sup> In l. mol<sup>-1</sup> sec<sup>-1</sup>. <sup>b</sup> Limits of variations in two experiments. <sup>c</sup> Lithium biphenyl. <sup>d</sup> Reaction was noted but its rate was the same whether or not the alkyl fluoride was present. Thus, CsBiph reacts at an appreciable rate with DME. <sup>e</sup> Lithium anthracene. <sup>f</sup> No observable decrease in optical density in 5 days.

The rate constants reported here are defined to differ by a factor of 2 from those reported previously.<sup>2</sup> The present rate constants correspond to the following rate law, where the factor of two accommodates the stoichiometry of the reactions ( $2\text{MAr} + \text{RF} \rightarrow \text{products}$ ).<sup>26, 27</sup>

$$-d[\text{MAr}]/dt = 2k[\text{MAr}][\text{RF}] \quad (3)$$

Reactions of sodium naphthalene with 5-hexenyl fluoride in DME gave 1-hexene and methylcyclopentane in combined yields of 54–58%, based on alkyl fluoride consumed in experiments in which sodium naphthalene was in excess. Cyclohexane, cyclohexene, methylenecyclopentane, 1,5-hexadiene, and  $\text{C}_{12}$  hydrocarbons were not detected as products by vpc.

The ratio of yields (1-hexene/methylcyclopentane) varied considerably, following a consistent trend with initial sodium naphthalene concentration when the latter was below  $10^{-2} M$  (Table III). At higher concentrations of sodium naphthalene, the product ratio was large (as high as 37 in expt 137) and more erratic.

Reactions of lithium naphthalene and lithium biphenyl with 5-hexenyl fluoride gave ratios 1-hexene/methylcyclopentane which were much smaller, ranging from  $\sim 0.05$  to  $\sim 4$ . The observed ratios were erratic, and we could not establish a trend with initial concentration of lithium naphthalene. If anything, it seemed that higher lithium naphthalene concentrations gave lower product ratios, in contrast to the reactions of sodium naphthalene. We have no explanation and we will not consider this aspect of lithium naphthalene reactions further.

## Discussion

**Possible Double Bond Participation.** It is conceivable that the olefinic group of 5-hexenyl fluoride could participate in some way in the transition states for reactions with alkali naphthalenes. Reactions of sodium naphthalene with 5-hexenyl, hexyl and octyl fluorides in DME all proceed with the same rate constant, within experimental error (Table I). Therefore the possibility of participation seems remote. This view is supported by the correlation of the extent of cyclization with the initial concentration of sodium naphthalene (Table III), which would not have been expected if cyclization accompanied double bond participation in the initial reaction step.

The reaction of lithium naphthalene with 5-hexenyl fluoride appears to occur at 2–4 times the rates with hexyl and octyl fluorides. These small effects cannot be regarded as significant at this time, but coupled with other peculiarities (see Results) they suggest that there are significant differences between the sodium and lithium systems. Since lithium naphthalene gives the same ratio of reduction and alkylation products as sodium naphthalene in DME, it is unlikely that these differences lie in the fundamental mechanisms of the reactions.<sup>28</sup>

(26) Previously reported rate constants were for the following rate law:  $-d[\text{NaNaph}]/dt = k[\text{NaNaph}][\text{RF}]$ .<sup>2</sup> This rate is twice the rate of passage of systems through the transition state, since a second NaNaph is consumed in a fast step following the initial rate-determining step of the reaction mechanism. Although the error so introduced is small ( $1.4 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1}$ ), it would be a mistake to use this rate constant in an analysis for  $\Delta S^\ddagger$ ;  $\Delta H^\ddagger$ , however, would not be affected.

(27) Measurements of the molar ratio sodium naphthalene/5-hexenyl fluoride consumed in DME gave  $2.0 \pm 0.1$ .

**Extent of Cyclization in Reactions of 5-Hexenyl Fluoride.** If Schemes I and II describe reactions of sodium naphthalene with 5-hexenyl fluoride, then eq 4 should give the variation of the extent of cyclization with the initial concentration of sodium naphthalene (see Appendix for derivation of eq 4). Here  $x_0 =$

$$rx_0 + 1 = e^{rx_0/(1+s)} \quad (4)$$

$[\text{NaNaph}]_0$ ,  $r = k_N/k_c$ , and  $s = 1\text{-hexene/methylcyclopentane}$ . It is seen from Table III that the variations in the product ratios are well described by eq 4 with  $r = 1.6 \times 10^4 M^{-1}$ . This lends strong support to Scheme II as the mechanism of the reaction.

By combining absolute rate data with the relative rate data of Walling, *et al.*,<sup>29</sup> Carlsson and Ingold have estimated  $k_c$  as  $\sim 10^5 \text{ sec}^{-1}$ .<sup>17</sup> Therefore  $k_N$  is  $\sim 1.6 \times 10^9 M^{-1} \text{ sec}^{-1}$  and the reaction of sodium naphthalene with 5-hexenyl radical is nearly diffusion controlled.<sup>30</sup>

Sodium biphenyl in DME has about the same reactivity as sodium naphthalene toward 5-hexenyl radicals (Table III). The data imply a rate constant  $\sim 1.0 \times 10^9 M^{-1} \text{ sec}^{-1}$ .

It is not surprising that these radical-radical reaction rate constants are quite large. Many stable free radicals (*e.g.*, galvinoxyl) are efficient scavengers for reactive alkyl radicals. Sodium naphthalene and sodium biphenyl must be ranked with the best of these.

**Metal ion effects** on reactions of alkali naphthalenes with 5-hexenyl fluoride in DME are dramatic (Table IV). When the concentration of 5-hexenyl fluoride is about  $0.08 M$ , the half-life of the pseudo-first-order reaction with lithium naphthalene is about 2.6 min. Under similar conditions, there was no reaction with cesium naphthalene after 5 days. This represents a spread of at least a factor of  $5 \times 10^4$  in the rates. Separated by factors of about 100, the rate constants for sodium and potassium naphthalenes lie between those for lithium and cesium.

To chemists conditioned to think of organocesium compounds as being much more reactive than organolithium compounds, these results may appear startling. They certainly stand in contrast to the relative reactivities of alkylolithiums and alkylcesiums. In fact, the traditional order has been reported even for reactions which are supposed to be electron transfer reactions of organic radical anions with alkyl halides, the reactions of alkali benzophenone ketyls with propyl halides in dioxane, for which the cesium compound has been assigned a reactivity about  $10^3$  times that of the lithium compound, with sodium between.<sup>31</sup> Previous discussions of this general topic have emphasized that a constant order of metal ion effects on reactivities of organoalkali compounds is not to be expected from theoretical considerations, nor is it found in practice.<sup>32</sup>

(28) Data for reactions of lithium, sodium, and cesium naphthalenes with 1,4-dihalobutanes and 1,5-dihalopentanes are given by J. F. Garst in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, Chapter 9, p 525.

(29) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).

(30) Considering that only 1/4 of the initial collisions of pairs of radicals are electronic singlets, the maximum rate constant might be  $\sim 2.5 \times 10^9 M^{-1} \text{ sec}^{-1}$  instead of the  $\sim 10^{10} M^{-1} \text{ sec}^{-1}$  expected for solvents of the viscosity of DME.

(31) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 343 (1960).

(32) See discussion of J. F. Garst in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, N. Y., 1969, Chapter 8.

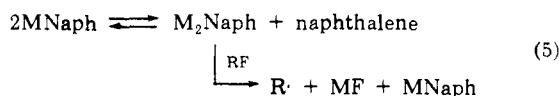
The direction of metal ion effects is determined by such factors as the relative concentration of negative charge in reactant and transition states and the solvating power of the medium.

It is noteworthy that the same direction of metal ion effects found for alkyl fluoride reactions extends, at least in part, to alkyl chlorides. The reaction of cesium naphthalene with 5-hexenyl chloride is slow enough to observe on a laboratory time scale (Table IV). Other alkali naphthalenes react too rapidly.

The metal ion effects could have practical value. Sodium biphenyl is widely used as a reagent effecting the quantitative release of organically bound halogens.<sup>33,34</sup> For simple alkyl fluorides, the reaction with sodium biphenyl would be impractically slow (Table V). However, lithium biphenyl or lithium naphthalene in DME would react at an acceptable rate.

**Nature of the Reactants and Activated Complexes.** The present data do not afford a basis for definitive characterizations of the reactants and activated complexes, but limited discussion seems warranted. The observed metal ion effects are consistent with the fact that other studies require aggregation at least to ion pairs for alkali arenes in DME.<sup>35</sup> For sodium naphthalene, the ion pair dissociation constant at 25° can be estimated as  $\sim 5 \times 10^{-6} M$ ,<sup>36</sup> so that at our high concentrations virtually complete ion pair formation is assured. Aggregation could well be more extensive, but little information is available regarding that possibility. Changes in aggregate composition over the concentration range we investigated ( $3 \times 10^{-4}$ – $6 \times 10^{-2} M$ ) might have been reflected in the observed rate constants, but no trend with initial sodium naphthalene concentration was found. Tentatively, we assume ion pairs as the prevalent aggregates in our solutions.

On this basis, the first-order dependences on alkali naphthalenes imply that the activated complexes must be constructed from one alkali naphthalene ion pair (and one alkyl fluoride molecule). This rules out reactions 5 as possible rate-determining sequences, leav-



ing the initial step of Schemes I and II as the most reasonable possibility.

The major feature of the present data is the metal ion effect. Its direction can be made consistent with activated complex anions with either larger or smaller cation affinities than the naphthalene radical anion by proposing that interionic Coulombic factors are not outweighed, or are outweighed, respectively, by cation solvation.<sup>32</sup> Activated complex anions with larger cation affinities than naphthalene radical anion correspond to greater reactivities of contact than solvent separated ion pairs. For activated complex anions of smaller cation affinities than naphthalene radical anion, solvent separated ion pairs would be more reactive than contact ion pairs.

(33) F. L. Benton and W. B. Hamill, *Ind. Eng. Chem., Anal. Ed.*, **14**, 449 (1942).

(34) L. M. Liggett, *Anal. Chem.*, **26**, 748 (1956).

(35) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966).

(36) Estimated from the fact that  $4.6 \times 10^{-6}$ ,  $5.6 \times 10^{-6}$ , and  $6.0 \times 10^{-6} M$  were found for sodium biphenyl, sodium triphenylene, and sodium perylene, respectively, in DME at 25°.<sup>35</sup>

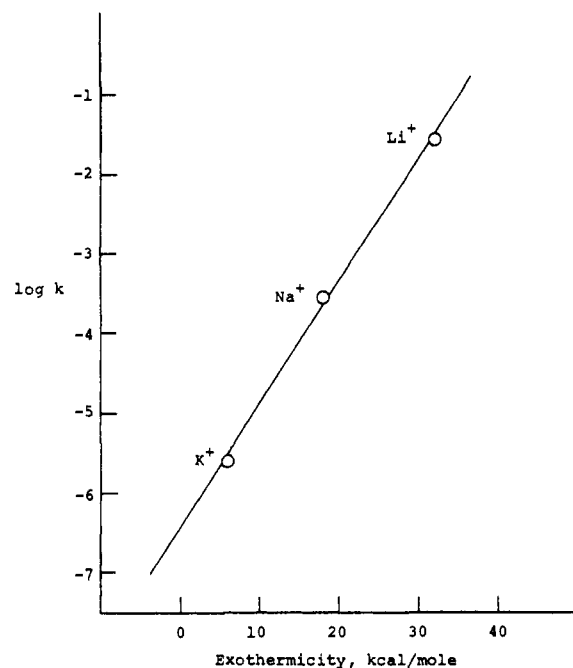
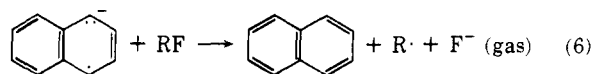


Figure 1. Correlation of free energies of activation in DME (proportional to  $\log k$ ) with computed gas phase exothermicities of reactions of alkali naphthalenes with 5-hexenyl fluoride.

The gas phase Coulombic factors involved can be assessed semiquantitatively for the overall reaction (eq 6). For free anions in the gas phase, reaction 6 is



endothermic by about 30 kcal/mol (bond dissociation energy for a primary alkyl fluoride =  $\sim 106$  kcal/mol;<sup>37</sup> electron affinities of naphthalene and fluorine atoms = 3.5 and 80 kcal/mol, respectively).<sup>38,39</sup> Ion pairing in the gas phase converts the reaction to an exothermic one for all cations except cesium. The exothermicities are:  $\text{Li}^+$ ,  $\sim 32$  kcal/mol;  $\text{Na}^+$ ,  $\sim 18$  kcal/mol;  $\text{K}^+$ ,  $\sim 6$  kcal/mol;  $\text{Cs}^+$ ,  $\sim 0$  kcal/mol. These figures result from the application of Coulomb's law assuming 2.5 Å as the effective radius of the naphthalene radical anion<sup>35</sup> and Pauling's radii for alkali metal and fluoride ions. The quantitative aspects of this analysis depend on the choice of ionic radii, which are by no means well established.<sup>39</sup>

It is seen that the observed rates in solution run parallel with the exothermicities calculated for the gas phase reaction of ion pairs. This is illustrated in Figure 1, where  $\log k$  is plotted against the calculated gas phase exothermicity. This plot resembles the "cationic" plots of Warhurst, in which  $\log k$  is plotted against  $1/(r_c + 2)$ ,  $r_c$  being the cation radius in Å.<sup>40</sup> We have little faith in the significance of the linearity of such plots. However, if linear, they constitute a kind of linear free

(37) From a tabulation of S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 215. For ethyl and propyl fluorides, the dissociation energy of RF is 106 kcal/mol.

(38) W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966); R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966); W. E. Wentworth and E. Chen, *J. Phys. Chem.*, **71**, 1929 (1967).

(39) F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1972. Electron affinities, p 57; ionic radii, p 52.

(40) A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, **58**, 948 (1962).

energy relationship. In the case of Figure 1, the reader should note that the value for potassium is not well established statistically, since it was determined from only one kinetic experiment.

To us, these considerations suggest that it is likely that the activated complex anions have larger cation affinities (more concentrated and localized negative charge) than naphthalene radical anion. In turn, this suggests that the reactions should proceed more slowly in solvents of better cation solvating abilities. In the present work, the only solvent variation attempted was between DME and THF. In DME the reactant ion pairs are believed to be principally of the "loose" or "solvent separated" variety, although the balance of the equilibrium with "tight" or "contact" ion pairs may be close at room temperature (higher temperatures favor contact ion pairs).<sup>41,42</sup> In THF at room temperature, contact ion pairs are favored. We were greatly surprised to find essentially the same rate constant for the reaction of sodium naphthalene with 5-hexenyl fluoride in THF as in DME. We defer further discussion of the significance of this finding until further studies have been performed.

It was anticipated that  $\Delta S^\ddagger$  might provide a clue to the nature of the activated complexes. Desolvation of activation would accompany conversion of primarily solvent separated reactant ion pairs into primarily contact activated complex ion pairs, leading to anomalously positive values of  $\Delta S^\ddagger$ . Unfortunately, scatter (up to a factor of 2 in the rate constant for a given system and temperature) resulted in an Arrhenius plot that is not very definitive of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ . Due to this scatter, a referee's suggestion that the plot may be curved cannot be confirmed or refuted. The  $\Delta S^\ddagger$  derived by least-squares analysis ( $\sim -16$  kcal/mol) does not seem informative.

#### Relationship to Alkali Ketyl-Alkyl Halide Reactions.

It is assumed that reactions of alkali benzophenone ketyls with alkyl halides follow a mechanism parallel to Scheme 1.<sup>43,44</sup> However, the reaction of lithium benzophenone ketyl with propyl chloride in dioxane is slower than the reaction of cesium benzophenone, with other alkali metal intermediates. It is also found that more polar ether solvents lead to faster rates, although really the reactions are curiously insensitive to solvent variation: the spread in reactivity of potassium benzophenone ketyl toward propyl chloride is only a factor of 5 from dioxane to DME.<sup>45</sup>

In the gas phase, inverse metal ion effects on ion pair reaction rates would be expected for two reactions in which the relative cation affinities of reactant and activated complex anions were opposite. If the ketyl-alkyl halide reaction involved negative charge delocalization in going from reactant to activated complex, while

the naphthalene radical anion-alkyl halide reaction involved corresponding charge localization, the observed directions of metal ion effects (in solution) would be predicted (for the gas phase). This model also predicts correctly the direction of the solvent effect on the ketyl-alkyl halide reaction. Provided that the orders of metal ion effects are the same in solution as in the gas phase, it accounts for all the presently available data, and it is consistent with the fact that ketyls are much more charge localized than hydrocarbon radical anions.

A detailed accounting would have to involve other factors. In dioxane the prevalent species of alkali ketyls are probably higher aggregates than ion pairs,<sup>47</sup> and even in the most polar solvents (DME and DMF) they exist as contact, not solvent separated, ion pairs.<sup>48a</sup>

Recently Wong and Hirota have contrasted the behaviors of ketyls and hydrocarbon radical anions in electron transfer reactions with their parent ketones and hydrocarbons.<sup>48b</sup> In the ketyl case, the reactions are slowed by more polar solvents, just the opposite of the results of Warhurst and Whittaker for reactions of ketyls with alkyl halides.<sup>46</sup> In the hydrocarbon case, the reactions are promoted by more polar solvents, which is the opposite of the direction predicted by our tentative model for the reactions of aromatic hydrocarbon radical anions with alkyl fluorides.

For the reactions of ketyls with ketones, Wong and Hirota proposed a rate-determining association of an ion pair with a ketone with accompanying loss of a solvent molecule from the coordination sphere of the alkali ion. It seems clear that a corresponding model cannot apply to the ketyl-alkyl halide reactions studied by Warhurst, since the solvent effects are in opposite directions. Similarly, we doubt that the reactions of hydrocarbon radical anions with hydrocarbons are reasonable models for hydrocarbon radical anion-alkyl halide reactions. In one case, the reactions are thermoneutral and produce no net change in molecular structures. In the other, they are not thermoneutral and the products contain anions of very different cation affinities from the reactants.

**Biphenyl and Anthracene Radical Anions.** In view of the fact that anthracene is much more readily reduced than naphthalene, the lack of reactivity of the alkali anthracenes toward alkyl fluorides is not surprising. For anthracene, the analog of reaction 6 (free ions, gas phase) is endothermic by  $\sim 40$  kcal/mol, rather than the  $\sim 30$  kcal/mol for naphthalene.

Nor are the similar reactivities of alkali biphenyls and alkali naphthalenes surprising. According to radical anion titration studies, corrected for ion pairing differences, the reduction potentials of biphenyl and naphthalene differ by only 0.04 V, about 1 kcal/mol in standard free energy.<sup>49</sup> Thus, very similar behavior in processes which oxidize the corresponding radical anions is to be anticipated. If the rates followed reduction potentials precisely, the reactions of biphenyl radical anions would have been slightly faster than those of naphthalene radical anions. However, the predicted

(41) N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968).

(42) Y. Karasawa, G. Levin, and M. Szwarc, *J. Amer. Chem. Soc.*, **93**, 4614 (1971).

(43) D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955).

(44) For the particular case of lithium benzophenone ketyl reacting with alkyl iodides in THF, substantial evidence supporting this mechanistic assumption has been obtained.<sup>45</sup>

(45) J. F. Garst and C. D. Smith, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, Apr 1973, No. ORGN-97.

(46) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966).

(47) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

(48) (a) K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971); (b) B. F. Wong and N. Hirota, *ibid.*, **94**, 4419 (1972).

(49) J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71**, 3063 (1967).

differences would be small, and they could be obscured by scatter or modified by ion aggregation and solvation factors.

**Relationship to Electrochemical Reductions.** It is noteworthy that simple alkyl fluorides have not been reduced electrochemically. Solvents or supporting electrolytes are invariably reduced at lower potentials than that which would be required for an alkyl fluoride. Indeed, this is usually the case even for simple alkyl chlorides, which are more reactive than fluorides.<sup>50</sup>

Naphthalene, however, is readily reduced electrochemically. Its reduction is a reversible, one-electron process leading to the naphthalene radical anion.<sup>51</sup>

If naphthalene is reduced at much lower potentials than alkyl chlorides and fluorides, how can it be that its reduction product, the naphthalene radical anion, will reduce alkyl chlorides and fluorides? The answers deal with the faulty logic implicit in this question. The electrochemical potential for the reversible reduction of naphthalene reflects the standard free energy change for the process. For a highly irreversible process such as the reduction of an alkyl halide,<sup>52</sup> an observed potential would relate to the free energy of *activation*, *i.e.*, to the *rate* of the process. The thermodynamics of alkyl chloride or fluoride reduction could be as favorable as or more favorable than for naphthalene reduction, even though the former are more difficult to reduce at an electrode than naphthalene. Thus, the electrochemical data do not speak to the question, "Should the naphthalene radical anion react by electron transfer to an alkyl chloride or fluoride?" Fry discussed this point in his recent monograph,<sup>50</sup> where he cited the fact that alkyl chlorides *can* be reduced electrochemically in the presence of naphthalene.<sup>53</sup> This is a kind of "catalytic" reduction in which the naphthalene is reduced, then the naphthalene radical anion so generated reacts with the alkyl chloride, regenerating (at least partly) the naphthalene.

Of course, another major difference between the chemical and electrochemical reductions of alkyl halides is in the differing environments of the reactants. The electrochemical reductions are heterogeneous, and the solvent and electrolyte conditions are not easily made the same for the two types of experiments.

Electrochemical alkyl halide reductions were recently reviewed by Fry.<sup>50</sup> The original mechanism of von Stackelberg and Stracke is precisely parallel to Scheme I, the electrode playing the role of sodium naphthalene and the alkyl anion forming branch (not the alkylation branch) being followed.<sup>54</sup> Although there has been considerable discussion and confusion over possible

SN1 and SN2 descriptions of these electrode processes, the von Stackelberg-Stracke mechanism seems correct in the light of subsequent experiments. Thus, the heterogeneous and homogeneous reductions follow parallel mechanisms.

**Acknowledgment.** We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for grants supporting this work.

## Appendix

**Derivation of Eq 4.** Equation 4 follows from Scheme II provided that RF is in excess and that  $a = b$ , where  $a$  and  $b$  are stoichiometric coefficients defined in Scheme II. Let  $h = [1\text{-hexene}]$  formed,  $g = [\text{methylcyclopentane}]$  formed,  $x = [\text{NaNaph}]$ ,  $x_0 = [\text{NaNaph}]_0$  (initial concentration of NaNaph),  $y = [\text{RF}]$ , and  $y_0 = [\text{RF}]_0$ . Then

$$dh/dg = ak_Nx/bk_c \quad (1A)$$

Since experiments show that  $b \simeq 0.9a$ , and since the error introduced by ignoring this slight inequality is small compared to observed variations,  $b = a$  is assumed hereafter. Let

$$r = k_N/k_c \quad (2A)$$

Then

$$dh/dg = rx \quad (3A)$$

But

$$x = x_0 - 2(h + g)/a \quad (4A)$$

Thus

$$dh/dg = rx_0 - 2r(h + g)/a \quad (5A)$$

Integration gives

$$h + g = [a(rx_0 + 1)/2r] + Ce^{-2rg/a} \quad (6A)$$

$C$  is evaluated from the fact that  $h = 0$ , when  $g = 0$ .

$$C = a(rx_0 + 1)/2r \quad (7A)$$

Thus

$$h + g = [a(rx_0 + 1)/2r](1 - e^{-2rg/a}) \quad (8A)$$

Let

$$s = h/g \quad (9A)$$

If  $2y_0 \geq x_0$  (a condition met in all our experiments), then

$$h + g = g(1 + s) = ax_0/2 \quad (10A)$$

$$g = ax_0/2(1 + s) \quad (11A)$$

Substituting for  $g$  and  $h$  in the integrated equation (eq 8A)

$$rx_0 = (rx_0 + 1)(1 - e^{-rx_0/(1+s)}) \quad (12A)$$

which rearranges to

$$rx_0 + 1 = e^{rx_0/(1+s)} \quad (4)$$

(50) A. J. Fry, "Synthetic Organic Electrochemistry," Harper and Row, New York, N. Y., 1972. Alkyl halide reactions, p 170 ff; catalytic processes involving naphthalene, pp 67-68, 112, 134, and 198-199.

(51) H. A. Laitinen and S. Wawzonek, *J. Amer. Chem. Soc.*, **64**, 1765 (1942).

(52) See, for example, the Experimental Section of F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).

(53) Unpublished results of J. W. Sease and R. C. Reed and of A. J. Fry and W. E. Britton cited in D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 67 (1955).

(54) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).