b.p. 135–136° (3.5 mm.), lit.[15] b.p. 135–140° (1.5 mm.). The v.p.c. (silicone gum rubber at 100°) of both the crude and the distilled product showed one peak whose retention time was identical with that of an authentic sample.

In a blank experiment, a solution of 0.05 mole of nitrile III (R = n-C_4H_9) and 0.1 mole of n-butyl bromide in 25 ml. of ether was added to 0.1 mole of sodamide[11] in 150 ml. of liquid ammonia. After 3 hr., excess ammonium chloride was added, and the reaction mixture was worked up as described above. Distillation of the crude product afforded 9.99 g. (87%) of recovered starting nitrile, b.p. 135–136° (3.8 mm.),[15] which was indicated to be pure by v.p.c.

The blank experiment was repeated omitting the n-butyl bromide. After the ammonia was evaporated, water and ether were added. The solid was collected, dried, and recrystallized successively from 95% ethanol, methanol, and water to afford 5.21 g. of product, m.p. 226–230°, which appeared to be a mixture of α,α-di-n-butylphenylacetamidine and α,α-di-n-butylphenylacetamide. None of the original nitrile III was recovered. The infrared spectrum of the solid showed, besides aromatic and aliphatic absorptions, bands at 3500–3000 (NH) and 1725–1550 cm.$^{-1}$ (C=N and C=O); nitrile absorption was absent. An analysis of the solid for nitrogen (9.23%) suggested a mixture of 56% amidine and 44% amide; however, neither compound was isolated.

B. By Sodium Hydride.—To a stirred slurry of 17.48 g. (0.4 mole) of sodium hydride reagent[13] in 200 ml. of refluxing monoglyme, under dry nitrogen, was added a solution of 11.7 g. (0.1 mole) of phenylacetonitrile and 54.8 g. (0.4 mole) of n-butyl bromide in 100 ml. of monoglyme over a period of 30 min. Refluxing was continued for 3 hr., and the reaction mixture was then worked up as described above for monoalkylations of phenylacetonitrile by means of sodium hydride. Distillation of the crude product yielded 21.8 g. (95%) of α,α-di-n-butylphenylacetonitrile (III, R = n-C_4H_9), b.p. 134–136° (3.5 mm.).[15] Both the crude and the distilled product were indicated to be pure by v.p.c. as in the corresponding experiment with sodamide.

The corresponding reaction with benzyl chloride was effected similarly. Fractionation of the resulting crude product afforded 8.48 g. (41%) of 2,3-diphenylpropionitrile, b.p. 160–163° (3.5 mm.),[3] and 17.22 g. (58%) of 1,2,3-triphenyl-2-cyanopropane, b.p. 215–218° (3.5 mm.), lit.[3] b.p. 185–186° (0.6 mm.). Each product exhibited one v.p.c. peak whose retention time was identical with that of an authentic sample.

Alkylation of 2-Phenylhexanenitrile with Benzyl Chloride.—To a stirred suspension of 0.05 mole of sodamide[11] in 250 ml. of anhydrous liquid ammonia was added a solution of 9.68 g. (0.05 mole) of 2-phenylhexanenitrile (II, R = n-C_4H_9)[16] in 15 ml. of anhydrous ether. After the reaction mixture had been stirred for 2 hr., it was worked up essentially as described above for monoalkylations of phenylacetonitrile by means of sodamide. The resulting residue was fractionated to afford 10.77 g. (82%) of crude 1,2-diphenyl-2-cyanohexane (IV), which was identified by v.p.c. using a 2-ft. silicone gum rubber column and indicated to consist of 91% of IV and 9% of II (R = n-C_4H_9). Redistillation afforded IV, b.p. 120–121° (0.07 mm.), which was indicated to be pure by v.p.c.

Anal. Calcd. for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.69; H, 7.97; N, 5.45.

Alkylation of Diphenylacetonitrile with β-Phenylethyl Bromide. A. With Sodamide.—This reaction was performed essentially as described for phenylacetonitrile employing 0.05 mole of sodamide[11] in 250 ml. of liquid ammonia, 9.66 g. (0.05 mole) of diphenylacetonitrile, and 9.26 g. (0.05 mole) of β-phenylethyl bromide(reaction period, 4 hr.). After work-up, the crude residue was crystallized from methanol to afford 9.43 g. (64%) of 2,2,4-triphenylbutyronitrile (V), m.p. 100–101°.

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.74; H, 6.44; N, 4.74.

B. With Sodium Hydride.—This reaction was accomplished essentially as described for phenylacetonitrile employing 9.66 g. (0.05 mole) of diphenylacetonitrile, 9.26 g. (0.05 mole) of β-phenylethyl bromide, and 2.19 g. (0.05 mole) of sodium hydride reagent.[13] Crystallization of the resulting oil from methanol afforded 8.95 g. (60%) of 2,2,4-triphenylbutyronitrile (V), m.p. 97.5–99.5°; 1.56 g. (16%) of starting nitrile was recovered.

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[15] N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70**, 3091 (1948).

[16] The starting compound, which was prepared by n-butylation of sodiophenylacetonitrile in toluene and distilled, was indicated by v.p.c. to be 90% pure, being contaminated with 6% of I and 4% of III (R = n-C_4H_9). The 9.68 g. used contained 0.05 mole of II (R = n-C_4H_9).

Organometallic Chemistry. XII.[1] The Thermal Decomposition of n-Butyllithium, a Kinetic Study[2,3]

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Received June 28, 1965

The thermal decomposition of decane solutions of n-butyllithium to butene-1 and lithium hydride was observed to follow the first-order rate law for one to two half-lives. A linear correlation was evident between the first-order rate constant and the percentage of carbon-bound lithium, with k_1 doubling as the percentage of carbon-bound lithium was dropped from approximately 96 to 76% by the addition of increments of lithium butoxide. Extrapolation to 100% carbon-bound lithium at 130, 140, and 150° gave values for 10^3k of 2.2, 6.0, and 14.0 min.$^{-1}$. The ΔH^* and ΔS^* were calculated to be 31 kcal. mole^{-1} and -1 e.u., respectively, the rate increase brought about by the added alkoxide apparently being reflected in a more favorable entropy term. A kinetic isotope effect (k_H/k_D) in the range 3 to 4 was determined by measuring the decomposition rate for β,β-dideuteriobutyllithium. A transition state of the concerted, four-center type is proposed in which charge distribution and product stability play an important role.

While an enormous body of both theoretical and practical knowledge concerning numerous types of elimination reactions has been accumulated,[5] very little is known about the thermal elimination of alkali metal hydride from an organometallic substrate. Since this is, perhaps, the simplest reaction that these

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[1] Paper XI: R. A. Finnegan, *Trans. N. Y. Acad. Sci.*, **27**, 730 (1965).

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this work.

[3] (a) Preliminary announcement of this work has been made at the 149th National Meeting of the American Chemical Society, April 1965; Abstracts, p. 38P. See also footnotes 17–19 in ref. 3b. (b) R. A. Finnegan, *Chem. Ind.* (London), 895 (1962).

[4] Petroleum Research Fund Graduate Research Fellow, 1962–1964. This paper is based on a thesis submitted by H. W. Kutta to the Department of Chemistry, The Ohio State University, in partial fulfillment of the requirements for the degree of Master of Science, June 1964.

[5] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII; (b) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 6; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, Chapter 12; (d) J. S. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; Chapter 8; (e) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., London, 1963.

substances can undergo, it seems ideally suited for quantitative study. The reaction proceeds, in the simplest cases, with the formation of an olefin and the corresponding metal hydride. Ethylsodium,[6] for

$$\mathrm{RM} \xrightarrow{\Delta} \mathrm{R_{-H}}\ (\text{olefin}) + \mathrm{MH}$$

example, gives rise on heating to ethylene and sodium hydride. Morton[7-10] has collected considerable data concerning the pyrolysis of amylsodium and pentenylsodium. The significance of the volatile products (pentane and mixed pentenes) formed in the pyrolysis of amylsodium is somewhat obscrured by the concurrence of at least four different reactions. There is the initial elimination of sodium hydride with the formation of pentene-1, the metalation of the product olefin by amylsodium yielding pentenylsodium and pentane, the isomerization of pentene-1 to pentene-2 in a surprisingly fast catalytic reaction, and, finally, the decomposition of pentenylsodium itself. Morton[8] has emphasized the view that the decomposition as well as most other reactions of alkali metal compounds proceed by the homolytic dissociation of the carbon–metal bond. While there are several indications that certain organoalkali metal systems may engage in free-radical processes, we are not convinced of the necessity for adopting a free-radical interpretation as being so generally applicable.

Potassium alkyls, as might be expected, undergo the hydride elimination reaction with relative ease even at room temperature.[1] Carbon–carbon cleavage is also significant with these compounds, whereas with sodium compounds such cleavages (fragmentation or alkide elimination) are important only when the metal alkyl is devoid of β hydrogens.[11] The products observed upon pyrolysis of neopentylsodium, for instance, have been interpreted in terms of a β elimination of methylsodium.[3b] A geminal metal hydride elimination was ruled out and no evidence was obtained which required interpretation in terms of a homolytic dissociation or a disproportionation mechanism. A similar reaction has been observed in the case of neopentylpotassium[12]; however, in view of the complexity of the reaction mixture, no mechanistic conclusions could be drawn. The simplest metal alkyls, the methyl derivatives of lithium,[13] sodium,[14] and potassium,[14] decompose in a stepwise fashion whose details have not yet been elucidated. A disproportionation scheme has been proposed[13,14] for these decompositions and, at least in the case of methyllithium, seems reasonable in view of the independent characterization of the presumed intermediate, methylenedilithium.[15,16] Such derivatives of the heavier metals (tri- and even tetrametallomethane intermediates have been suggested[14]) would appear to have questionable stability because of the high charge density accumulated on the carbon atom. A plausible alternate path for the decomposition of methylpotassium has been suggested[12] which supposes an α elimination of potassium hydride and the formation of methylene. A free-radical route may also be envisioned[8,17] for these decompositions, and while this may well obtain in the gas phase, the occurrence of homolytic dissociation in the highly polar solid phase is considered unlikely.

Finally, there are several examples of aromatization which apparently proceed by the elimination of metal hydride (or alkide) from a cyclic unsaturated organometallic substrate.[18] In this connection there should also be mentioned the alkylation and arylation of pyridine[19,20] by organolithium compounds which involve the alimination of lithium hydride from an initially formed adduct, although in these cases the metal is situated on nitrogen rather than on carbon.

Knowledge of the mechanism of the thermal decomposition of alkali metal alkyls would have implications regarding the mechanisms of other transformations which these substances undergo. Accordingly, we desired to carry out kinetic measurements on this reaction and chose to begin this work with a study of lithium alkyls. This choice was dictated by the experimental convenience stemming from the solubility of the lithium reagents, and by the theoretical simplicity anticipated for the kinetic behavior of these solutions in contrast to that expected for the heterogeneous sodium and potassium systems.

Ethyl- and butyllithium have been studied previously by Ziegler and Gellert.[21] In particular, butyllithium was found to decompose slowly at 100° and rapidly at 150° to give a mixture of butene-1 (92%) and butane (8%) along with lithium hydride and polymeric materials. The butane presumably arises from the metalation of the product olefin by the starting material. When the reaction was carried out in a vacuum line, the extent of this side reaction could be reduced to the point where butane constituted less than 1% of the gaseous product. The polymers are thought to result from butadiene formation as illustrated in the over-all scheme, eq. 1–4.

$$\mathrm{CH_3CH_2CH_2CH_2Li} \longrightarrow \mathrm{CH_3CH_2CH{=}CH_2} + \mathrm{LiH} \qquad (1)$$

$$\mathrm{CH_3CH_2CH_2CH_2Li} + \mathrm{CH_3CH_2CH{=}CH_2} \longrightarrow \mathrm{CH_3CHLiCH{=}CH_2} + \mathrm{C_4H_{10}} \qquad (2)$$

$$\mathrm{CH_3CHLiCH{=}CH_2} \longrightarrow \mathrm{CH_2{=}CHCH{=}CH_2} + \mathrm{LiH} \qquad (3)$$

$$\mathrm{CH_3CH_2CH_2CH_2Li} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \text{polymer} \qquad (4)$$

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[6] W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **61**, 588 (1929).

[7] A. A. Morton and E. J. Lampher, *J. Org. Chem.*, **20**, 839 (1955).

[8] A. A. Morton and E. J. Lampher, *ibid.*, **21**, 93 (1956).

[9] A. A. Morton and H. E. Newey, *J. Am. Chem. Soc.*, **64**, 2247 (1942).

[10] A. A. Morton and E. F. Cluff, *ibid.*, **74**, 4056 (1952).

[11] Exceptions to this are cases where fragmentation is accompanied by relief of strain or provides more highly resonance stabilized products: P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **29**, 1682 (1964); **28**, 3234 (1963); H. G. Richey, Jr., and E. A. Hill, *ibid.*, **29**, 421 (1964); E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *ibid.*, **28**, 2161 (1963); R. A. Finnegan and R. S. McNees, *ibid.*, **29**, 3234 (1964).

[12] R. A. Finnegan, *Tetrahedron Letters*, 1303 (1962).

[13] K. Ziegler, *Nature*, **176**, 59 (1955).

[14] W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **52**, 1254 (1930).

[15] K. Ziegler, British Patent 778,619 (July 10, 1957); *Chem. Abstr.*, **52**, 1203 (1958).

[16] E. W. Duck, British Patent 852,933 (Nov. 2, 1960); *Chem. Abstr.*, **55**, 10314 (1961).

[17] E. L. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

[18] (a) H. Gilman and C. W. Bradley, *J. Am. Chem. Soc.*, **60**, 2333 (1938); (b) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, **15**, 108 (1948); *Compt. rend.*, **239**, 1222 (1954); (c) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, **78**, 5950 (1956); H. Pines and M. Kolobieski, *ibid.*, **79**, 1698 (1957); (d) A. A. Morton and R. A. Finnegan, *J. Polymer Sci.*, **38**, 19 (1959); (e) J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 613 (1964).

[19] K. Ziegler and H. Zieser, *Ann. Chem.*, **485**, 174 (1931), *Ber. deut. chem. Ges.*, **63**, 1847 (1930).

[20] For a recent mechanistic study, see R. A. Abramovitch and C.-S. Giam, *Can. J. Chem.*, **41**, 3127 (1963).

[21] K. Ziegler and H.-G. Gellert, *Ann. Chem.*, **567**, 179 (1950).

Calculations based on half-times reported by Ziegler and Gellert[21] for this decomposition at various temperatures lead to a value of 20 ± 5 kcal. mole^{-1} for ΔH^*. A value of 21 kcal. mole^{-1} as "apparent activation energy" has been mentioned[22] without experimental detail for the decomposition of butyllithium over the temperature range 60–100°. A corresponding value of 36 kcal. mole^{-1} was given[22] for the decomposition of ethyllithium.

When butyllithium was decomposed at 135° in cumene solution, the gaseous product consisted of a 60:40 mixture of butene-1 and butane.[23] The high proportion of butane (40%) implied a considerable amount of metalation; however, carbonation of the reaction mixture after gas evolution was complete yielded no C_5 acids and only traces of cuminic acids. The absence of bicumyl among the products[24,25] was taken by Bryce-Smith[23] to indicate the nonintermediacy of butyl free radicals, although Morton[8] has interpreted these results as being in accord with the homolytic view of the decomposition.

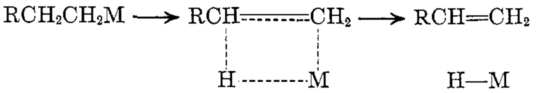
t-Butyllithium has been pyrolyzed in refluxing heptane to provide a 94:6 mixture of isobutylene and isobutane.[26] These products are presumed to arise by steps analogous to eq. 1 and 2. More recently, the interesting case of *sec*-butyllithium, in which the three butenes are obtained, has been examined.[27,28] The catalog of lithium alkyl elimination reactions may be completed by mentioning the facile ring-opening (alkide elimination) reaction undergone by cyclopropylcarbinyllithium.[29,30]

The mechanism of the hydride elimination reaction has been discussed[8,23] only in terms of the mode of carbon–metal bond cleavage. On the one hand, a rate-determining homolysis has been proposed which is followed by a disproportionation to yield the product olefin and metal hydride as illustrated in eq. 5. This view has been disputed by Bryce-Smith on the basis of his cumene experiment described above, and, although he did not advance an alternate proposal, we considered that a heterolytic analog of eq. 5 was a formal possibility (eq. 6). Other alternatives which seem not to have been previously discussed include a geminal elimination (concerted or stepwise) with the production of a carbene which may then rearrange to an olefin as shown in eq. 7. A final possibility, illustrated in eq. 8, involves a concerted, four-center[31] type transition state similar to that operating during the thermal elimination of hydrogen halide from certain alkyl halides. We considered this latter to be a most likely mode of decomposition and, in fact, adopted this mechanism as a working hypothesis at the outset of this work. In view of the aggregate nature of the lithium alkyls in solution,[26,32] it must be borne in mind that the mechanisms illustrated may be *gross oversimplifications* as several (analogous) pathways may be envisioned which involve more than one molecule of the substrate.[33]

$$\mathrm{RCH_2CH_2M \longrightarrow RCH_2CH_2\cdot + \cdot M \longrightarrow RCH{=}CH_2 + MH} \quad (5)$$

$$\mathrm{RCH_2CH_2M \longrightarrow RCH_2CH_2^- + {}^+M \longrightarrow RCH{=}CH_2 + MH} \quad (6)$$

$$\mathrm{RCH_2CH_2M \longrightarrow MH + RCH_2\dot{C}\dot{H} \longrightarrow RCH{=}CH_2} \quad (7)$$



$$\mathrm{RCH_2CH_2M \longrightarrow \underset{H\,\cdots\cdots\,M}{RCH\cdots\cdots CH_2} \longrightarrow \underset{H-M}{RCH{=}CH_2}} \quad (8)$$

In an effort to provide additional evidence which might be used to distinguish between various mechanistic proposals, a kinetic study of lithium alkyl pyrolysis was initiated and the present paper describes the results obtained with *n*-butyllithium and *β,β*-dideuteriobutyllithium.

Experimental Procedures

Solvents and Reagents.—Decane (Phillips Petroleum Co.) was washed with concentrated sulfuric acid until the acid remained colorless. It was then washed with water, dried over Drierite, and distilled from a mixture of calcium hydride and lithium aluminum hydride, b.p. 172–174°. The decane was stored over lithium aluminum hydride and dry, prepurified grade nitrogen was bubbled through the solvent to remove any traces of dissolved oxygen and to provide an inert blanket during storage. The ether used was anhydrous grade. Sodium wire was pressed into a freshly opened can of ether, the can was then closed with a serum cap, and the air over the ether was removed by flushing with dry, prepurified grade nitrogen. Freshly distilled reagent grade benzyl chloride was used in the analyses.

Preparation of *n*-Butyllithium Solution for Pyrolysis.—All equipment brought into contact with butyllithium solutions during the preparation, transfer, storage, analysis, and pyrolysis work was dried at 110° for at least 24 hr. and cooled in an inert atmosphere. To a 500-ml. round-bottomed flask equipped with a magnetic stirring bar and a nitrogen inlet, was added through an adapter attached to the center neck of the flask 300 ml. of *n*-butyllithium solution in hexane (15% by weight, Foote Mineral Co.). During the addition the flask was continuously flushed with nitrogen. A vacuum of 0.5–2.0 mm. was then applied, the stirrer was started, and the flask was maintained at a temperature of approximately 40°. After a portion of the solvent was removed, the vacuum pump was shut off and 50 ml. of purified decane was added. A constant pressure of nitrogen was maintained in the flask to prevent any contamination by the atmosphere. The vacuum was applied again and after 2 hr. an additional 25 ml. of decane was added in the same fashion. Pumping was then continued for as long as 4 hr. to ensure complete removal of the low-boiling solvent. The solution was then filtered through a fine porosity sintered-glass frit with the aid of the vacuum pump and nitrogen pressure. This procedure was carried out several times during the course of this work in order to prepare stock solutions of butyllithium in decane. These solutions, analyzed by the method described in a subsequent section,

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[22] J. B. Taylor and E. Warhurst, personal communication, reported in G. E. Coates, "Organo-Metallic Compounds," Methuen and Co. Ltd., London, 1960, p. 20.

[23] D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

[24] The suggested[23] presence of small amounts of "higher alkylbenzenes" may be of interest in view of recent reports that aromatic hydrocarbons may be alkylated by lithium alkyls.[18] The possibility that α-methylstyrene was involved must also be considered.

[25] Similarly, bicumyl was not detected when *sec*-butyllithium was pyrolyzed in cumene solution: R. A. Finnegan and H. W. Kutta, to be published.

[26] M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

[27] W. H. Glaze, J. Lin, and E. G. Felton, *J. Org. Chem.*, **30**, 1258 (1965). We are indebted to Professor Glaze for a copy of this paper prior to publication.

[28] Our own experience with *sec*-butyllithium, as well as with isobutyl- and *t*-butyllithium, will be described in a subsequent publication.[8,25]

[29] P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *J. Am. Chem. Soc.*, **86**, 2247 (1964).

[30] Ring opening was also noted when benzylcyclopropane was treated with sodium alkyls: R. A. Finnegan and R. S. McNees, unpublished observations.

[31] Reference 5d, p. 517.

[32] D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

[33] In eq. 8, for example, a concerted but polycentric transition state can be written which does not imply a *cis* elimination.

ranged from about 3 to over 4.5 *N* butyllithium and containing, with one exception, between 91 and 96% carbon-bound lithium.

In order to adjust the percentage of carbon-bound lithium, an arbitrary amount of lithium butoxide (0.5 to 1.0 g.) was added to the solution which was then shaken frequently over periods of 1 to 4 days. The added salt seemed to dissolve rather slowly. At the end of the shaking period, the mixture was filtered, using the technique described above. After reanalysis and the carrying out of the desired kinetic runs, the process was repeated to lower even further the percentage of carbon-bound lithium.

The solutions of butyllithium when freshly prepared were very nearly colorless. On aging for some time at room temperature (in the light) a slight straw yellow color developed. No precipitate was observed and reanalysis even after several weeks gave the same or nearly the same results as when the solutions were fresh.

Analysis of the Butyllithium Solutions.—The problems attending the analysis of lithium alkyl solutions have been known for some time and arise from the presence of alkaline substances other than the lithium alkyls. These contaminants are assumed to be mainly lithium alkoxide and hydroxide formed by reaction of the lithium alkyl with adventitious air and moisture. A number of procedures have been devised for the determination of the carbon-bound lithium content and these have very recently been summarized by Gilman and Cartledge.[34] We first employed the now classical "double titration" method of Gilman and Haubein[35-37] but obtained somewhat erratic results apparently in common with other workers.[36,38] Next was briefly evaluated the iodine method of Clifford and Olsen[38] which was also found wanting, in part at least, because of the difficulty of maintaining a standard solution of iodine in ether. Substitution of heptane for ether was unsatisfactory because of the lesser solubility of iodine in this solvent.

At this stage we investigated the use of a method which seemed in principle to be the most convenient of any which had at that time been described in the literature, and, as we are unaware of its having been applied in this connection, a brief account is given here. The method is a variant of the Zerewitinoff determination and consists simply of hydrolyzing an aliquot of the butyllithium solution, measuring the volume of gas evolved, and titrating the hydrolysis mixture with standard acid. In this way, the amount of carbon-bound lithium (butane volume) and the total alkali (titration) can be ascertained by the use of a single aliquot, rather than two as required by other methods. Although results with excellent precision could be obtained, a difficulty resides in the fact that the gas evolved is somewhat soluble in the solvent in which the butyllithium is introduced. Since this solubility is proportional to the partial pressure of the butane, it can be reduced by increasing the total volume of the system; however, this soon leads to the situation where one is required to measure a small difference between two large numbers. In view of its simplicity, this method appears to be worthy of further study, provided that an accurate calibration to account for the dissolved gas can be applied.

Finally, we reverted to the double-titration method and found that by following closely the procedure outlined by the Foote Mineral Co.[39] excellent reproducibility was realized. All of the analytical data reported here were obtained by this procedure and the details of the method, as well as representative titration values, have been set forth by Kutta.[40]

The accuracy of this method of analysis when carefully executed is considered to be quite high,[34,36,37,39] at least for solutions with a high carbon-bound lithium (low alkoxide) content. The accuracy decreases, however (underestimation of lithium alkyl content), as the amount of alkoxide present increases.[41,42] For example, for solutions with carbon-bound lithium contents in the range 70–80%, this error may be as high as 8–9%.[41] In the present work, solutions containing from 76 to 96% carbon-bound lithium were employed and we estimate an average error in the concentration figures of 2–5%.

Preparation of β,β-Dideuteriobutyllithium.—Diethyl ethylmalonate, after reaction with sodium hydride and deuterium oxide, was hydrolyzed by heating in 40% aqueous sodium deuterioxide solution followed by acidification with phosphoric acid-d_3. Decarboxylation of the malonic acid provided butyric acid which was reduced with lithium aluminum hydride to obtain β,β-dideuteriobutyl alcohol. Reaction of the alcohol with dry hydrogen chloride according to the procedure of Gerrard and Hudson[43] produced the corresponding alkyl chloride which, after distillation, was shown by gas chromatography to contain only 0.2% *sec*-butyl chloride. The deuterium content was determined by n.m.r. analysis. Comparison of the relative intensities of the methyl (τ 9.08) and methylene (τ 8.6 and 6.54) signals was made from the average of several integrations of the spectrum. It was found that 76% of the β hydrogens were substituted by deuterium. The chloride thus obtained was converted to the lithium reagent as follows.

Lithium wire (3.08 g., 0.44 g.-atom, Lithium Corp. of America) cut into very small pieces was rinsed with hexane and added to a four-necked, 500-ml., round-bottomed flask containing 100 ml. of hexane. The hexane had been purified as described above for the purification of decane. The flask was fitted with a stirrer, condenser, thermometer, and a dropping funnel. The equipment had been baked at 110° for 24 hr. and, after assembly, was flamed out with a bunsen burner while being flushed with helium. The contents of the flask were then maintained under a blanket of helium throughout the operation. To initiate the reaction, 2–3 ml. of the deuterated butyl chloride was added and the reaction mixture was heated to 60°. The mixture turned dark indicating that reaction had commenced, and heating was discontinued. The remainder of the halide was added over a period of 70 min. as the well-stirred reaction mixture was allowed to cool slowly down to room temperature. A total of 19 g. (0.21 mole) of the halide was thus added over a period of 90 min. Stirring was continued for an additional 6 hr. before it was stopped in order to allow the solids to settle to the bottom of the flask. After 14 hr., the clear supernatant solution was removed by means of a syringe and filtered under vacuum through a fine sintered-glass disk. The residual slurry was washed three times with 30-ml. portions of hexane and filtered into the same flask. After the hexane was replaced by decane by means of the procedure already described, the solution was again filtered, yielding 42 ml. of a clear, nearly colorless solution of β,β-dideuteriobutyllithium in decane. Analysis by the method designated above gave values, for total alkali, 2.41 *N;* lithium alkyl, 1.87 *N;* and per cent of carbon-bound lithium, 77.4.

Pyrolysis Procedure.—The pyrolysis equipment consisted of a thermostated oil bath, a two-necked reaction flask, condenser, stirrer, and gas burets. On the flask were mounted two stopcocks, one of which was covered with a serum cap to allow the introduction of starting material by means of a syringe. The other stopcock was used in order to purge the system with an inert gas. The center of the reaction flask was fitted with the stirrer and the side neck accommodated the condenser through which the evolved gases passed to the mercury-filled gas-collection burets. The temperature of the oil bath was controlled to within 0.2° of the desired pyrolysis temperature.

Before each kinetic run, the flask, stirrer, condenser, syringes, and needles to be used were baked at 110° for at least 24 hr. The bath was brought to the desired temperature (usually 140°), the apparatus was assembled, and the whole system was flushed with prepurified grade nitrogen for approximately 30 min.

Most of the runs were carried out using 12 ml. of butyllithium solution. A calculated amount of decane was introduced into the pyrolysis vessel (stirrer operating) and was allowed to equilibrate for 30 min. The exact amount of solvent added at this point was calculated from the normality of the particular stock solution used and the initial concentration desired for the run in question. The system was then vented briefly to the atmosphere in order to compensate for the solvent vapor pressure.

At time zero, the calculated amount of the stock solution was injected into the flask and as the reaction proceeded, the gas given off was collected in the burets which were leveled continuously to maintain atmospheric pressure. The temperature lag at the time of sample injection was neglected since the volume of the admitted sample was kept small relative to the volume of solvent already present. Volume readings were taken at inter-

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[42] W. L. Everson, *ibid*, **36**, 854 (1964).

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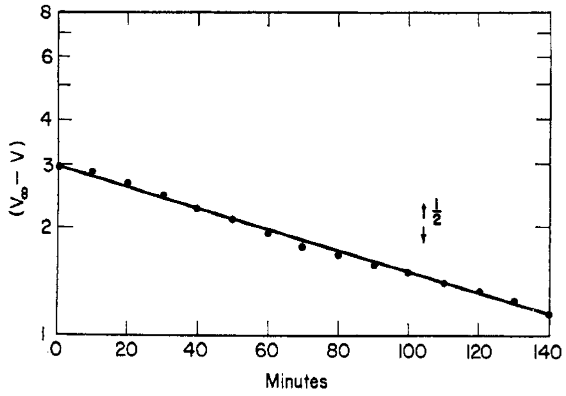

Figure 1.—First-order plot of the pyrolysis of *n*-butyllithium at 140°: initial concentration 1 *N;* 92.4% carbon-bound lithium.

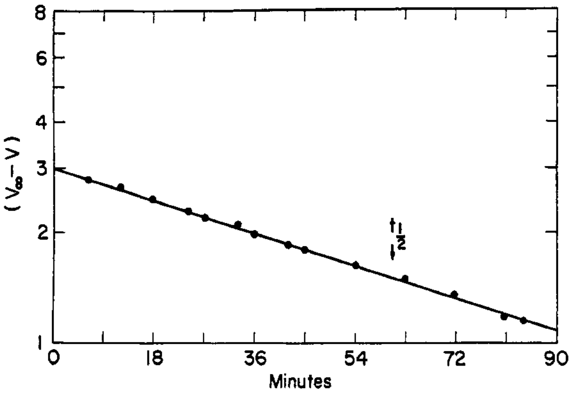

Figure 2.—First-order plot of the pyrolysis of *n*-butyllithium at 140°: initial concentration 1 *N;* 82.4% carbon-bound lithium.

vals appropriate to the speed of the reaction. The four burets were arranged in such a way that each could be individually isolated from the rest of the system. In this way, portions of the gas obtained during different time intervals could be analyzed separately and, if necessary, the buret could be emptied and reused during a run.

Kinetic Treatment.—Plots were prepared of log $(V_\infty - V)$ *vs.* time where V is the volume of gas evolved at a given time (observed volume less the volume of the injected solution) and V_∞ is a theoretical volume calculated from the absolute amount of butyllithium used, assuming 100% decomposition to gaseous products and corrected to the prevailing conditions of atmospheric pressure and room temperature. These plots were very nicely described by straight lines to well over a half-life (*cf.* Figures 1 and 2) and in some cases to between two and three half-lives.[44] From the slopes of these lines were calculated the first-order rate constants. Kinetic runs were usually made in duplicate though not infrequently in triplicate and the maximum deviation from the average value for a set of runs rarely exceeded 5% with an average of under 3%. All the rate constants thus obtained, their averages, as well as the calculated and observed half-lives have been tabulated by Kutta.[40]

Although theory requires the use of an experimentally determined value of V_∞ in the construction of the first-order plot of the data,[45] such a value can not be measured in the present case because of the occurrence of side reactions discussed in the introduction. Indeed, when the pyrolysis was allowed to proceed for an extended period, only about 90–95% of the theoretical quantity of gas was evolved. The use of a theoretical V_∞ is permissible under these circumstances, however, and the error thus introduced into the rate constant probably does not exceed a few per cent[45] over the first one to two half-lives. At longer times, of course, the data deviate markedly upward from linearity indicating a decrease in the reaction rate. This uncertainty, taken with the probably more serious error in determining the initial concentrations, and considering other sources of error such as volume measurements, leads us to estimate an over-all error in the reported rate constants of the order of 5–10%.

The temperature dependence of the rate constant was determined, and from the appropriate plots of this data, which were nicely linear (Figure 3), the enthalpy and entropy of activation were calculated. In view of the probable error in the rate constants, however, the maximum possible error in the derived parameters may be as much as tenfold greater.[46] Accordingly, subsequent discussion of relative reactivity is sensibly limited to comparisons of observed rate constants.

Product Analysis.—The gaseous products were analyzed with an Aerograph Model A-90-P gas chromatograph using helium as carrier gas. Mainly, a dimethylsulfolane column (20% on firebrick, 10 ft. × $^1/_8$ in.) was used for the analyses, although for the detection of hydrogen or methane, a Linde 13× Molecular Sieve column (10 ft. × 0.25 in.) was used. The columns were operated at room temperature or below and the peaks were identified by showing that an authentic sample of the component in question exhibited the same retention time under the conditions of the analysis.

Results and Discussion

Products of the Reaction.—Pyrolysis of decane solutions 1 *N* butyllithium at 130 to 150° provided mainly butene-1 as anticipated from the earlier work of Ziegler and Gellert.[21] The following is typical of the results obtained by gas chromatographic analysis at the completion of a kinetic run: butene-1, 97–98%; butane, 1–2%; *cis*-butene-2, 0.1–0.3%; *trans*-butene-2, 0.0–0.1%; and ethane and ethylene, traces. The nongaseous product, lithium hydride, was identified indirectly by noting the formation of hydrogen after hydrolysis, again by gas chromatographic techniques. The production of butane is somewhat greater at the inception of a run and may be ascribed to one or both of two possible side reactions. In the first place, any protic impurities which may have been retained in the solvent would be immediately scavenged upon introduction of the butyllithium. Secondly, the opportunity for metalation of the product butene by butyllithium with the formation of butane and butenyllithium (eq. 2) is greatest at the outset. The small quantities of butene-2 and C_2 species indicates that side reactions resulting in isomerization or fragmentation are not kinetically significant under the present conditions. Furthermore, our inability to detect methylcyclopropane in the pyrolysis gases tend to rule out the possible occurrence of an α-elimination process resulting in a carbene intermediate (eq. 7).

Evaluation of the Rate Constants.—In accordance with the simple formulation of eq. 1, we presumed to follow the course of the reaction by measuring the rate of gas evolution. When plots were made of log $(V_\infty - V)$ *vs.* time, where V_∞ is the volume of gas anticipated at 100% decomposition as calculated from the initial concentrations of butyllithium and V is the volume of gas observed at a given time, straight line relationships were evident to, on the average, about 65–75% completion of the reaction, thus showing that the process is best described by the first-order rate law.[44] Two such plots are illustrated in Figures 1 and 2 for solutions of different carbon-bound lithium contents (see below). From the slopes of these lines were calculated the first-order rate constants (see Table I.) These determinations were usually carried out in dupli-

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(44) The one-sixth-, one-fourth-, one-half-, three-halves-, and second-order rate laws were found to be inconsistent with the data.

(45) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 31.

(46) R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

TABLE I

KINETIC PARAMETERS FOR THE PYROLYSIS OF *n*-BUTYLLITHIUM[a]

C-bound lithium, %	$k \times 10^3$, min.$^{-1}$ 130°	140°	150°	ΔH^*, kcal. mole^{-1}	ΔS^*_{413}, e.u.
78	4.5	12.2	33.6	34	+5
82	5.9	10.9	28.7	33	+2
96	2.6	6.9	17.1	32	−1
100[b]	2.2	6.0	14.1	31	−1

[a] Initial concentration: 1 *N* in decane solution. [b] Extrapolated.

cate and, in some cases, in triplicate with good reproducibility.

Mechanical Variables.—Since lithium hydride precipitates during the course of the reaction, we felt that a search for possible surface effects was in order. Two types of experiments were, therefore, carried out. Variation of the rate of stirring of the reaction mixture was found to be without effect on the rate constant. Furthermore, since the prior addition of nearly an equivalent of lithium hydride to the reaction mixture again had no effect on the measured rate constant, we concluded that any surface effect caused by the presence of lithium hydride was not significant.

Initial Concentration.—Although the bulk of the work was carried out using 1.0 *N* solutions of butyllithium, it seemed advisable to examine solutions of differing initial concentrations for any possible effects. We concluded from this study that, as expected for a true first-order reaction, the rate constant was indeed constant over the concentration range 0.1 to 1.0 *N*, and that a number of conceivable effects stemming from the aggregate nature of the substrate were not operative, at least in this concentration range.[47] Margerison and Newport[32] have since shown that the degree of association of butyllithium in hydrocarbon solvent is invariant (hexamer) over the concentration range 0.5 to 3.0 *M*. These results were obtained at 25° and although we have no experimental basis for extrapolating them to our pyrolysis temperatures, Margerison and Newport[32] indicate that the degree of association is only slightly dependent on temperature.

Effect of Added Alkoxide.—It is well known that lithium alkyl solutions invariably contain alkali in excess of the carbon-bound lithium. The purest solutions which we were able to prepare contained a maximum of 95–96% of carbon-bound lithium based upon the total alkali content, and our concern with the influence which might be exerted by the excess alkali, presumed to be largely lithium butoxide, was well founded. A brief catalog of such effects (of added Lewis bases) on organolithium reactivity has conveniently been provided by Brown and his collaborators in a recent paper,[48] and we would only add that the literature of sodium and potassium chemistry also contains a number of suggestive analogous examples.

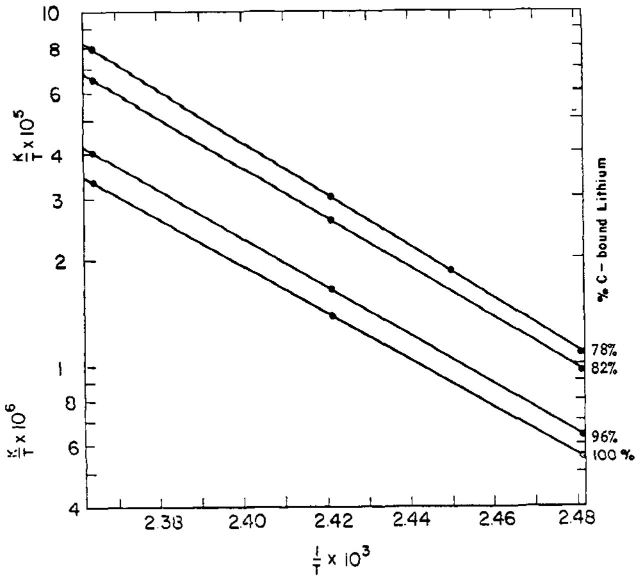

Figure 3.—Arrhenius plots of the pyrolysis of *n*-butyllithium.

A series of experiments were carried out with solutions of differing excess alkali content which were prepared by the addition of lithium butoxide to the butyllithium solutions. A decrease in the per cent of carbon-bound lithium from 96 to 76.5 resulted in a nearly twofold increase in the rate constant. These data, which are illustrated in Figure 4, are reasonably well described by a straight line which allowed extrapolation to 100% butyllithium. Some indication that this curve falls markedly from linearity at lower percentages was obtained; however, these lower percentages were not studied in detail. Similar plots were made from rate constants measured at 130 and 150° with solutions containing 96, 82, and 78% carbon-bound lithium. At each temperature the three points were nicely fit by a straight line.[40] The measured rate constants for these solutions as well as those obtained by extrapolation to pure butyllithium are listed in Table I.

The effect of the added alkoxide is presumed to arise, in common with the effect of other Lewis bases, from coordination with the metal atom, thereby weakening the carbon–metal bond. Whether the alkoxide moiety interacts directly with the butyllithium aggregate or whether it effects disruption and the formation of new aggregates containing both species cannot be decided on the basis of the present work.[49,50] In any event it is clear that discussions of reactivity of lithium alkyl solutions must take into account not only the nature of the solvent but also the effects produced by seemingly extraneous impurities.

Activation Parameters.—Arrhenius plots were constructed, making use of rate constants obtained at three temperatures (in one series, four temperatures) and at three different percentages of carbon-bound lithium. A similar plot was also made from the constants arising from the extrapolations to pure butyllithium described in the preceding section. An

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(47) The previous observation of a marked dependence of apparent first-order rate constants on the initial concentration (R. A. Finnegan, A. W. Hagen, and W. S. Lee, 6th Report on Research under the Sponsorship of the Petroleum Research Fund, Abstracts of Research, 1961, p. 160) is subject to invalidating errors stemming from at least three different sources: the unreliability of the constants measured at very low concentrations; the method of analysis, which was not so accurate as that presently employed; and, the failure to appreciate fully the effects of excess alkali (see below) on the rate constants.

(48) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964).

(49) Compare the ethyllithium–lithium ethoxide interaction studied by T. L. Brown, J. A. Ladd, and G. N. Newman [*J. Organometal. Chem.*, **3**, 1 (1965)].

(50) The matter is further complicated by the realization that the lithium alkoxide–lithium alkyl ratio must change during the course of any given run. Considerably more sophisticated techniques than used here will be required to disentangle these effects.

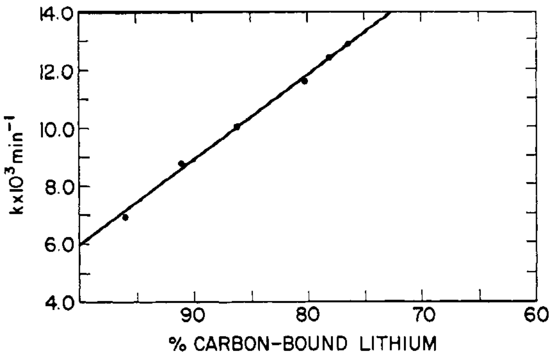

Figure 4.—Plot of *k vs.* per cent carbon-bound lithium for the pyrolysis of *n*-butyllithium (initial concentration 1 *N*) at 140°.

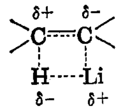

Figure 5.—Model of the transition state for lithium hydride elimination.

excellent fit to a straight line was observed in each case (see Figure 3) and the derived parameters are included in Table I. Although it would appear that the increase in rate caused by the excess of alkali is the result of a more favorable entropy of activation, the large potential error in these figures (see section above on kinetic treatment) casts considerable doubt on the reality of this trend, however suggestive.

Kinetic Isotope Effect.—We have already indicated in the introduction that the most reasonable mechanistic view of this reaction seemed to us to be that outlined in eq. 8. The transition state for this elimination is considered to be of the concerted multicentered type as illustrated for a monomeric species in Figure 5.[51] It will be noted that this transition state is analogous to that depicted for the addition of boron hydrides to olefins,[52] a reaction formally the reverse of the one under study. In addition to the charge-distribution pattern,[53] the model specifically calls for the rupture of the carbon–hydrogen bond in the rate-determining step. We sought to illuminate this point by comparing the rate of thermal decomposition of butyllithium with that of its isotopic analog, β,β-dideuteriobutyllithium. The latter was obtained as indicated in the Experimental Section and pyrolyzed in decane solution (1.0 *N* initial concentration, 77.4% carbon-bound lithium) at 140°. The gas evolution data were very well described by the first-order kinetic expression. Three determinations of the first-order rate constant were made (Table II) which gave an average value of 4.24×10^{-3} min.$^{-1}$ (maximum deviation, 4%). The value for the undeuterated substrate, 12.6×10^{-3} min.$^{-1}$, was obtained from the plot in Figure 4 at a value of the percentage carbon-bound lithium which corresponds to that observed for the deuterated analog.[54] These figures provide the kinetic isotope effect, k_H/k_D, of 2.97 which is offered in support of the proposed model for the transition state. Since the labeled butyllithium could have no more than 76% of the β-position deuterated (see Experimental Section), the value obtained for the isotope effect is undoubtedly a minimum value, the true value being somewhere between 3 and 4.

TABLE II

PYROLYSIS OF DIDEUTERIOBUTYLLITHIUM[a,b]

k_D, min.$^{-1}$
0.00441
0.00409
0.00423
Av. 0.00424

$k_H/k_D = 0.0126/0.00424 = 2.97$

[a] Prepared from butyl chloride 76% deuterated in the β position. [b] 1.0 *N* decane solution, at 140°, 77.4% carbon-bound lithium.

Kinetic isotope effects[55] have been reported for a large number of reactions which involve the cleavage of a carbon–hydrogen bond. The cases in which the hydrogen is lost as hydride, however, are relatively few and invariably occur as part of an oxidation–reduction process[56] in which the electron pair constituting the carbon–hydrogen bond is transferred to some other electrophilic atom. In the present case we have demonstrated, apparently for the first time, an isotope effect for a reaction in which the departing hydrogen preserves the oxidation state of −1.[57]

Previous concern[8,23] with the mechanism of metal hydride elimination from alkali metal alkyls has been directed solely at the mode of carbon–metal bond dissociation. Although the present experiments do not distinguish, *in themselves*, between a polar or a homolytic mechanism, they do rule from further consideration mechanisms in which the carbon–metal bond *alone* is broken in the rate-limiting step.

Acknowledgment.—We are indebted to Mr. A. W. Hagen, undergraduate research assistant supported by Petroleum Research Fund funds, 1961–1963, for valuable technical assistance. We also thank Professors W. N. White, M. A. Schwartz, and C. D. Ritchie and Dr. D. Knutson for helpful discussions about this work.

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(51) Although the model makes use of a monomeric unit, this is done only for illustrative purposes, and is not meant to imply a knowledge of the *molecularity* or the *geometry* of the transition state. The key features, charge distribution, and simultaneity of bond breakage, may readily be applied to higher aggregates of the substrate.

(52) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 121, 145.

(53) The importance of charge distribution as well as the reflectance of product stability in the transition state is indicated, we believe, by the relative rates observed for the decomposition of normal, tertiary, and isobutyllithium, approximately 1:2:8. See ref. 28.

(54) It will be noted that the plot in Figure 4 contains experimental points very near the desired value, so that this extrapolation is quite minimal.

(55) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955); L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960.

(56) (a) C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Am. Chem. Soc.*, **83**, 1945 (1961); (b) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956); (c) K. B. Wiberg, *ibid.*, **76**, 5371 (1954).

(57) *Cf.* ref. 20.