The Reaction of Alkyllithium Reagents with Selected Transition Metal Dichalcogenides: Evidence for a One-Electron-Transfer Pathway

Paul L.-K. Hung, Govindarajan Sundararajan, and Joseph San Filippo, Jr.*

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903

Received November 3, 1981

The heterogeneous reaction of selected primary, secondary, and tertiary alkyllithium reagents with various transition metal dichalocogenides (MX_2, M = Ti, Zr, Hf, V, Nb, Ta; X = S, Se, Te) has been examined. The resulting redox reaction (eq 1) occurs readily to yield hydrocarbons derived from the alkyl group. A comparison of product distributions with those obtained from well-defined processes in which the immediate precursor is a kinetically free alkyl radical indicates that similarly behaved intermediates are involved in the reaction of alkyllithium reagents with MX_2. Moreover, the influence of solvent and additives on reaction rate reveal that the rate-determining step is not mass transfer limited and, therefore, is probably not occurring within the interior cavity of the dichalcogenide.

Introduction

Intercalation of alkali metals had been known since 1926.[2] In 1959, Rudorff and Sick reported the observation that an equivalent behavior obtains with certain layered transition metal dichalcogenides.[3] Later still, Gamble et al.[4] showed that some of these intercalates act as low-temperature superconductors. Recently, it was further noted that these same layered transition metal chalcogenides react spontaneously and reversibly with a variety of electropositive elements, e.g., lithium, suggesting their possible application as electrode material in electrical storage devices.[5-7]

Prompted by their unusual properties, a growing interest has developed in the preparation, characterization, and study of the intercalates of layered transition metal chalcogenides. Because of their potential application in electrical storage devices, the lithium intercalates, Li_nMX_2, have received the most extensive study to date and several synthetic procedures for their preparation have been described.[5] Perhaps the readiest of these is that reported by Dines[8a] and later by Murphy et al.,[8c] which involves the reaction of n-butyllithium with an appropriate transition metal chalcogenide.

$$MX_2(\text{solid}) \xrightarrow{n\text{-}C_4H_9RLi} LiMX_2(\text{solid}) \quad (1)$$

$$M = Ti, Zr, Hf, V, Nb, Ta; X = S, Se, Te$$

Two points of interest are to be noted about this reaction. First, whereas intercalation by other procedures is generally nonstoichiometric,[9] the reaction described in eq 1 generally produces the stoichiometric substance $LiMX_2$.[8] Second, since the interlayer bonding in the lamellar transition metal dichalcogenide is of the van der Waals type, it appears that the intercalating lithium centers penetrate between the layers and finally rest in the van der Waals gaps.[10-13]

Our interest in these reactions derives from the fact that a reaction such as eq 1 presents a system that is potentially capable of delineating the nature of an electron-transfer process between a homogeneous reagent and a relatively well-defined heterogeneous system, provided it can be established that a one-electron redox is,in fact, occurring. The work reported here was carried out for the purpose of establishing this last point.

Results and Discussion

The initial reports of the reaction of organolithium reagents with transition metal chalcogenides did not attempt to explore the nature of this unusual process. Thus, our investigation commenced with a careful evaluation of reaction products and relevant parameters.

The product distribution resulting from the reaction of a solution of n-butyllithium with a suspension of various transition metal dichalcogenides in dry, oxygen-free, olefin-free hexane is summarized in Table I. These data reveal several points. First, they show that the principal hydrocarbon product from the reaction with MS_2 (M = Ti, Zr, Hf, Nb, Ta) is the dimer n-octane. Second, the secondary products, viz., n-butane and 1- and 2-butene, constitute the remainder of the product balance with, in general, the production of n-butane equaling about 2-3 times that of the butenes. Third, the reactivity of NbS_2 with n-butyllithium appears anomalous in that n-butane and not n-octane is the principal product.

Table I also illustrates the product distribution observed for the corresponding reaction of n-butyllithium with several transition metal diselenides and ditellurides, MSe_2 and MTe_2. Again, dimerization appears to be a major product, although apparently less so with the tellurides

---

(1) This work was supported by the National Science Foundation, Grant CHE-80-17405, and DOE Contract DE-AS-80ER-1062.

(2) Fredenhagen, K.; Cadenbach, G. *Z. Anorg. Allg. Chem.* **1926**, *158*, 249.

(3) Rudorff, W. *Angew. Chem.* **1959**, *71*, 487. Rudorff, W.; Sick, H. H. *Ibid.* **1959**, *71*, 127.

(4) Gamble, F. R.; Osiecki, J. H.; Cais, M.; Pisharody, R.; Di Salvo, F. J.; Geballe, T. H. *Science (Washington, DC)* **1971**, *174*, 493.

(5) Murphy, D. W.; Trumbore, F. A. *J. Cryst. Growth* **1977**, *39*, 185.

(6) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41.

(7) Proceedings of the International Conference on Layered Materials and Intercalates, Nijmegenn, The Netherlands, August 28-31, 1979. van Bruggen, C. F.; Haas, C.; Myron, H. W. *Physica B+C (Amsterdam)* **1980**, *98*, 1.

(8) (a) Dines, M. B. *Mater. Res. Bull.* **1975**, *10*, 287. (b) Hittingham, M. S.; Gamble, F. R., Jr. *Ibid.* **1975**, *10*, 363. (c) Murphy, D. W.; DiSolvo, F. J.; Hull, G. W.; Waszczak, J. V. *Inorg. Chem.* **1976**, *15*, 17.

(9) Kadijk, F.; Huisman, R.; Jellinek, F. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 768.

(10) Jellinek, F. *J. Less-Common Met.* **1962**, *4*, 9.

(11) Wilson, J. A.; Yoffe, A. D. *Adv. Phys.* **1969**, *18*, 193.

(12) Gamble, F. R. *J. Solid State Chem.* **1974**, *9*, 358.

(13) Huisman, R.; De Jonge, R.; Haas, C.; Jellinek, F. *J. Solid State Chem.* **1971**, *3*, 56.

0276-7333/82/2301-0957$01.25/0

Table I. Product Distributions from the Reaction of Various Early Transition Metal Dichalcogenides with *n*-Butyllithium in Hexane at 40 °C[a]

MX_2	MX_2/ *n*-BuLi	% yield[c]					% of unreacted *n*-BuLi[d]
		n-butane	1-butene	2-butene	*n*-octane[b]	Σ	
		98	0.8		1.2	100	
TiS_2[b]	1.6	22	7.1		72	101	
TiS_2	1.7	19	9	1	74	103	4.9
ZrS_2	1.7	16	6.8		80	103	
NbS_2	1.7	39	6.5		54	100	0.6
TaS_2	1.7	12	4.6		80	97	
HfS_2[b]	1.8	18	5.8		74	98	0.8
$TiSe_2$[b]	1.8	20	9.5		66	96	5.3
VSe_2[d]	1.7	34	5.7		61	101	
$ZrSe_2$[c]	1.7	25	8.1		68	101	
$NbSe_2$	1.7	24.8	5.4	1.2	65	96.4	1.2
$TaSe_2$	1.7	20.9	3.7	0.4	73.2	98.2	1.2
$HfSe_2$	1.6	23.5	6.4		67.3	97.2	
$TiTe_2$	1.7	40.5	9.5		45.7	95.7	
$ZrTe_2$	1.7	46.7	13.5	1	41.8	103	
$NbTe_2$	1.7	53.7	10.8	3.1	33.8	101.4	
$TaTe_2$	1.7	31	15.4		49	95.4	1.2

[a] Unless otherwise indicated a reaction time of 48 h was employed; $[n\text{-}C_4H_9Li]_0 = 0.26$ M; all analyses were preceded by an aqueous quench unless otherwise stated. [b] Commercial material. [c] Yields were determined by GLPC following a methanol quench and are corrected for residual hydrocarbons. [d] Determined by GLPC assay of *n*-butyl bromide formed following 1,2-dibromoethane quench.

Table II. Product Distributions from the Reactions of Metal Dichalcogenides (MX_2) with *n*-Butyllithium in Diethyl Ether at 40 °C[a,b]

MX_2	MX_2/ *n*-BuLi	% yield				
		n-butane	1-butene	2-butene	*n*-octane	Σ
		85	1.9	0.7	2.2	90
TiS_2	1.6	23	6.5		68	98
ZrS_2	1.8	20	9.6		71	101
NbS_2	1.7	38	10		53	101
TaS_2	1.8	25	8		66	99
HfS_2	1.7	19	7.2		74	100
$TiSe_2$	1.7	22	8.4		68	98
VSe_2	1.7	32	8.8		59	100
$ZrSe_2$	1.7	20	10	1.3	67	98
$NbSe_2$	1.7	23	10		64	97
$TaSe_2$	1.7	22	7		68	97
$HfSe_2$	1.8	24	7.5		68	100
$TiTe_2$	1.7	49	10		43	102
$ZrTe_2$	1.8	39	11		47	97
$NbTe_2$	1.8	31	18		47	96
$TaTe_2$	1.8	46	7.8		48	102

[a] All reactions were carried out for a period of 12 h; $[n\text{-}C_4H_9Li]_0 = 0.26$ M. [b] Mixed solvent system: *n*-hexane–ether (5:1).

Table III. Product Distributions from the Reactions of Metal Dichalcogenides (MX_2) with *n*-Butyllithium and TMEDA in Hexane at 40 °C[a]

MX_2	MX_2/ *n*-BuLi	TMEDA/ *n*-BuLi	% yield			
			n-butane	1-butene	*n*-octane	Σ
		1.3	96	0.8	1.3	98
TiS_2	1.7	1.3	31	6.7	65	103
ZrS_2	1.7	1.3	23	8.6	67	99
NbS_2	1.7	1.3	49	9.3	38	97
TaS_2	1.7	1.3	27	8.6	66	102
HfS_2	1.7	1.3	25	6.5	65	97
$TiSe_2$	1.7	1.3	35	11	55	101
VSe_2	1.7	1.3	29	17	52	98
$ZrSe_2$	1.7	1.3	33	18	54	105
$NbSe_2$	1.7	1.3	28	16	55	99
$TaSe_2$	1.7	1.3	31	17	56	104
$HfSe_2$	1.7	1.3	36	11	57	104
$TiTe_2$	1.7	1.3	44	20	40	103
$ZrTe_2$	1.7	1.3	46	22	34	102
$NbTe_2$	1.7	1.3	49	22	29	100
$TaTe_2$	1.7	1.3	47	17	39	103

[a] Unless otherwise indicated, a reaction time of 24 h was employed; $[n\text{-BuLi}]_0 = 0.25$ M. All assays were preceded by an aqueous quench.

than with the sulfides or selenides. Here, too, the lower yields of *n*-octane (and correspondingly higher yields of *n*-butane) produced by VSe_2 and $NbTe_2$ are noted. Finally, increasing the temperature of these reactions from 40 to 70 °C, although substantially increasing the overall rate of reaction, produced no noticeable effect on product distributions.

Because solvent and certain additives can greatly affect the solution structure and reactivity of organolithium reagents,[14] we examined the reaction of *n*-butyllithium with a representative selection of transition metal chalcogenides in (a) diethyl ether and (b) diethyl ether containing 1.6 equiv of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA). The resulting product distributions (Tables II and III) reveal a reactivity profile which closely parallels those of the equivalent reaction carried out in *n*-hexane. Nontheless, it is qualitatively apparent that the presence of 1 equiv of TMEDA during reaction of *n*-butyllithium with MX_2 increases the rate of this reaction.

We turned next to an examination of the reaction of *sec*-butyl- and *tert*-butyllithium with these same substrates (Tables IV and V). These reactions parallel the reaction of *n*-butyllithium. Thus, for *sec*-butyllithium, oxidative coupling is still the generally dominant process, especially with the sulfides and selenides, with *n*-butane being produced in only slightly lesser amounts. Again, however, reaction with the tellurides yields predominantly *n*-butane. The behavior of NbS_2, VSe_2, and $NbTe_2$ is again anomalous. By comparison, the corresponding reactions of *tert*-butyllithium in *n*-pentane reveal that dimerization in this system is a relatively minor process, averaging 15–25% of the total product balance, with isobutane and iso-

---

(14) (a) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807. (b) Russell, G. A.; Lamson, D. W. *Ibid.* **1969**, *91*, 3967. (c) Langer, A. W., Jr. *Adv. Chem. Ser.* **1974**, *No. 130*, 1. Eberhardt, G. g.; Butte, W. A. *J. Org. Chem.* **1964**, *29*, 2928. (d) Mallan, J. M.; Bebb, R. L. *Chem. Rev.* **1969**, *69*, 693. (e) Crettas, C. G.; Eastham, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 3276; **1966**, *88*, 5668. See also: Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press New York, 1974.

Table IV. Product Distributions from the Reactions of Metal Dichalcogenides (MX_2) with *sec*-Butyllithium in Hexane at 40 °C[a]

		% yield[b]				
MX_2	MX_2/*sec*-BuLi	*n*-butane	1-butene	2-butene	3,4-dimethylhexane	Σ
		96	4.8	2.1	0.7	104
TiS_2	1.7	36	23	3.8	38	101
TiS		(36)	(23)	(3.8)		
TiS_2	1.7	35	23	3.4	41	102
		(37)	(25)	(4.2)		
ZrS_2	1.7	34	23	4.3	38	99
		(36)	(24)	(3.4)		
NbS_2	1.7	41	15	3.8	35	95
		(39)	(14)	(3.5)		
TaS_2	1.7	33	22	3.9	43	102
		(35)	(23)	(4)		
HfS_2	1.7	34	22	4.3	41	101
		(37)	(24)	(4.9)		
$TiSe_2$	1.7	38	21	4.7	34	97
		(40)	(19)	(3.2)		
VSe_2	1.7	38	20	4.8	33	96
		(37)	(19)	(4.4)		
$ZrSe_2$	1.7	36	22	4.7	38	101
		(35)	(23)	(4.7)		
$NbSe_2$	1.7	38	24	6.3	35	103
		(38)	(25)	(6.4)		
$TaSe_2$	1.7	38	24	4.6	34	101
		(39)	(26)	(5.1)		
$HfSe_2$	1.7	38	26	4.4	35	103
		(36)	(27)	(4.2)		
$TiTe_2$	1.7	36	21	4.7	33	95
		(36)	(20)	(4)		
$ZrTe_2$	1.7	39	24	5.2	32	100
		(38)	(24)			
$NbTe_2$	1.7	39	20	5	35	99
		(39)	(18)	(4.5)		
$TaTe_2$	1.7	40	20	5.3	33	98
		(38)	(19)	(4.8)		

[a] Unless otherwise indicated, a reaction time of 48 h was employed; $[sec\text{-}C_4H_9Li]_0 = 0.27$ M. [b] Yields were determined by GLPC following methanol quench; yields in parentheses were determined following quench of reaction mixture with 1,2-dibromoethane.

Table V. Product Distributions from the Reactions of Various Metal Dichalcogenides with *tert*-Butyllithium in Pentane at 40 °C[a]

		% yield			
MX_2	MX_2/*t*-BuLi	isobutane	isobutylene	2,2,3,3-tetramethylbutane	Σ
		88	8.8	2.6	99
TiS_2	1.5	49	33	16	98
ZrS_2	1.7	46	29	23	98
NbS_2	1.6	53	26	15	94
TaS_2	1.6	42	33	22	97
HfS_2	1.6	44	31	24	99
$TiSe_2$	1.6	50	28	19	97
$ZrSe_2$	1.6	55	30	18	103
VSe_2	1.7	51	29	16	96
$NbSe_2$	1.6	55	28	17	100
$TaSe_2$	1.7	51	26	19	96
$HfSe_2$	1.7	50	29	17	96
$TiTe_2$	1.7	52	32	13	97
$ZrTe_2$	1.7	56	25	14	95
$NbTe_2$	1.7	59	23	12	94
$TaTe_2$	1.7	53	26	14	93

[a] All reactions were allowed to proceed for 24 h before quenching with methanol; $[t\text{-}C_4H_9Li]_0 = 0.26$ M.

butylene, in an approximately 2:1 proportion, constituting the principal products.

In an effort to establish the origin of the hydrocarbon (*n*-butane and isobutane) component produced in these reactions, we undertook two independent experiments. In one, we examined the reaction of *n*-butyllithium with TiS_2 in both cyclohexane-d_{12} and toluene-d_8 solvents. In either instance the deuterium content of the resulting *n*-butane was found to be insignificant (<6%). Thus, H-atom abstraction from solvent is an unimportant source of *n*-butane.

Adventitious protonolysis is an alternative source of hydrocarbon. To examine this possibility, we investigated the reaction of TiS_2, NbS_2, VSe_2, and $NbTe_2$ with (*n*-butyl-2,2-d_2)lithium. A summary of these results appears in Table VI from which it is clear that the ratio of [*n*-bu-

Table VI. Isotopic Analysis of *n*-Butane Obtained by the Reaction of *n*-Butyllithium-*2,2*-d_2 with MX_2 [a]

reagent	d_0	d_1	d_2	d_3	d_4	[*n*-butane-d_3]/ [butenes]
MeOH	1.2	2.8	95	1.1		
TiS_2	1.1	4.3	48	46	1.1	1.1
NbS_2	4	12	58	25	1.7	1.1
VSe_2	5.1	8.5	53	33	0.6	0.9
$NbTe_2$	3.5	7.7	52	37	0.3	0.82

[a] Corrected for the contributions of ^{13}C and background.

Table VII. Cross-Combination Ratios (ϕ) Observed for the Reaction of 1:1 *n*-Propyllithium–*n*-Butyllithium with Various Metal Dichalcogenides

MX_2	ϕ [a]	MX_2	ϕ [a]
TiS_2	2.03	$ZrSe_2$	1.99
ZrS_2	2.05	VSe_2	2.01
NbS_2	2.03	$NbSe_2$	2.03
TaS_2	1.96	$TaSe_2$	2.01
HfS_2	1.96	$HfSe_2$	1.91
$TiSe_2$	2.01		

[a] The cross-combination ratio ϕ was determined from the product yields of *n*-hexane, *n*-heptane, and *n*-octane according to equation $\phi = [n\text{-}C_7H_{16}]/[n\text{-}C_6H_{14}][n\text{-}C_8H_{18}]^{1/2}$.

Table VIII. Ratios of [R(–H)]/[R–R] Produced by the Reaction of Various Metal Dichalcogenides with *n*-Butyllithium under Differing Conditions

MX_2	[R(–H)]/ [R–R] [a]	[R(–H)]/ [R–R] [b]	[R(–H)]/ [R–R] [c]	[R(–H)]/ [R–R] [d]
TiS_2	0.15	0.15	0.14	0.20
ZrS_2	0.15	0.16	0.22	0.24
HfS_2	0.14	0.15	0.17	0.22
NbS_2	0.21	0.25	0.30	0.45
TaS_2	0.10	0.13	0.19	0.24
$TiSe_2$	0.20	0.16	0.21	0.38
$ZrSe_2$	0.22	0.23	0.27	0.63
$HfSe_2$	0.17	0.22	0.17	0.36
VSe_2	0.16	0.27	0.24	0.63
$NbSe_2$	0.18	0.32	0.26	0.56
$TaSe_2$	0.10	0.22	0.15	0.59
$TiTe_2$	0.40	0.47	0.39	0.93
$ZrTe_2$	0.68	0.78	0.40	1.3
$NbTe_2$	0.86	1.0	0.72	1.5
$TaTe_2$	0.59	0.29	0.26	0.85

[a-d] Solvent, temperature (°C), and time (h) for each ratio are respectively as follows: (*a*) hexane, 40, 48; (*b*) hexane, 70, 48; (*c*) diethyl ether, 40, 12; (*d*) hexane/TMEDA, 40, 24.

Table IX. Comparison of the Product Distributions Produced by the Reaction of Neophyllithium, RLi, with TiS_2 at 70 °C and the Thermal Decomposition of Neophyl(tri-*n*-butylphosphine)copper(I) and -silver(I) at 65 °C

		distrbutn of decompn products	
product	yield [a,b]	RCu^I-PBu_3 [b]	RAg^I-PBu [b]
$C_6H_5C(CH_3)_3$	48	59	56
$C_6H_5CH_2CH(CH_3)_2$	5	7.0	17
$C_6H_5CH_2C(CH_3)=CH_2$	4	6.9	12
$C_6H_5CH_2=C(CH_3)_2$	<1	1.4	1.6
R–R	20	21.2	7.5
R–R′	2	2.3	4.3
R′–R′	<1	2.1	1.6

[a] These yields are corrected for the rearrangement and/or dimerization that occurred during the preparation of the neophyllithium reagent. [b] Taken from ref 27.

tane-d_3]/[butene] ≈ 1.0. Thus, in these instances and presumably in the others listed in Tables I–V, we conclude that ca. half of total yield of *n*-butane produced in these reactions results not from the oxidation of *n*-butyllithium but rather from its protonolysis by adventious proton sources within the transition metal dichalcogenide.

In an attempt to gain additional insight into the mechanism of the oxidative coupling that occurs during the reaction of alkyllithium reagents with MX_2, we examined the reaction of an equilibrated, equimolar mixture *n*-propyl- and *n*-butyllithium in pentane with various metal dichalcogenides. The salient features of these data are (1) the close parallel observed between the reactivity of this mixture and that noted for the individual components, *n*-propyl- and *n*-butyllithium and (2) the essentially statistical distribution of coupling products *n*-hexane, *n*-heptane, and *n*-octane (Table VII).

The data and observations presented above suggest that the oxidation of alkyllithium reagents by various transition metal dichalcogenides is proceeding by a pathway that involves the formation of alkyl radicals. Thus, consider, for example, the olefin/dimer ratio observed in these studies (Table VIII). This ratio is largely independent of solvent but does exhibit a dependence on the nature of the alkyl group R such that [R(–H)]/[R–R] increases according to the order primary < secondary < tertiary. Moreover, for most of the disulfides and diselenides, the value of [R(–H)]/[R–R] for *n*-propyllithium falls within or close to the range of 0.1–0.15 observed for the disproportionation/combination ratios exhibited by *n*-propyl radicals generated from a variety of different radical precursors under varying conditions.[15] Likewise, the [R(–H)]/[R–R] ratios observed for the reaction of most of the metal disulfides and diselenides with *n*-butyllithium lie close to those observed for free *n*-butyl radicals (0.14–0.25) in vapor phase or in solution.[15,16]

The literature values for k_d/k_c for secondary and tertiary radicals exhibit a different behavior than is observed for primary radicals. Thus, for example, a value of k_d/k_c = 2.27 was reported for *sec*-butyl radicals generated by the vapor-phase photolysis of di-*sec*-butyl ketone.[17a] By comparison, corresponding values of 0.77 and 0.63 have been reported for the autodisproportionation/combination ratios of *sec*-butyl radicals in the gas phase.[17b,c] Likewise, k_d/k_c for *tert*-butyl radicals has been found to vary from 2.3, as observed in the photolysis of azo-*tert*-butane,[18] to 3.2, as determined from the photolysis of di-*tert*-butyl ketone and pivaldehyde.[19,20] The values observed for the reaction of *sec*-C_4H_9Li and *t*-C_4H_9Li with representative transition metal dichalcogenides (Table II) exhibit a range of 0.90–1.4 and 2–4, respectively, and as such are reasonably consistent with ratios established for *sec*-butyl and

---

[15] (a) Grotewold, J.; Kerr, J. A. *J. Chem. Soc.* **1963**, 4337. (b) Whiteway, S. G.; Masson, C. R. *J. Chem. Phys.* **1956**, *25*, 233. (c) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.

[16] (a) Morganroth, W. E.; Calvert, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 5387. Stefani, A. P. *Ibid.* **1968**, *90*, 1694. (c) Dixon, P. S.; Stefani, A. P.; Szwarc, M. *Ibid.* **1963**, *85*, 2551. (d) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *Ibid.* **1974**, *96*, 2806.

[17] (a) Kraus, J. W.; Calvert, J. G. *J. Am. Chem. Soc.* **1957**, *79*, 5921. (b) Falconer, W. E.; Sunder, W. A. *Int. J. Chem. Kinet.* **1971**, *3*, 523. (c) Kubin, R. F.; Rabinovitch, B. S.; Harrington, R. E. *J. Chem. Phys.* **1962**, *37*, 937.

[18] (a) James, D. G. L.; Stuart, R. D. *Trans. Faraday Soc.* **1969**, *65*, 175. (b) Terry, J. O.; Futrell, J. H. *Can. J. Chem.* **1968**, *46*, 664. (c) Georgakakos, J. H.; Rabinovitch, B. S.; Larson, C. W. *Int. J. Chem. Kinet.* **1971**, *3*, 535.

[19] Dominguez, J. A. G.; Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1962**, 3357. At 100 °C, the corresponding value of k_d/k_c was found to be 4.59.[18]

[20] Pryor, W. A. "Free Radicals"; McGraw-Hill: New York 1966.

tert-butyl radicals generated by other experimental procedures.

In a similar vein, the cross-coupling ratios established for the reaction of *n*-propyllithium–*n*-butyllithium (1:1) with representative dichalcogenides are completely consistent with the cross-combination ratios observed for processes recognized as involving kinetically free *n*-alkyl radicals.[20]

Reaction of Neophyllithium. Earlier studies established the utility of the neophyl system as a useful diagnostic probe of radical intermediacy in organometallic reactions.[21] In an effort to gain evidence for the intermediacy of free alkyl radicals in the reaction of alkyllithium reagents reactions.[21] metal dichalcogenides, we examined the products from the reaction of neophyllithium $PhCMe_2CH_2Li$, with TiS_2. These results are shown in Table IX. For comparison, the corresponding product distributions produced by the thermal decomposition of neophyl(tri-*n*-butylphosphine)copper(I) and -silver(I) are also given. The similar product distributions observed for these different organometallic precursors suggests that they probably share a common mechanism originating with the neophyl radical.

Conclusions. The central mechanistic distinction to be made concerning the oxidation of alkyllithium reagents by transition metal dichalcogenides revolves on the question of the intermediacy of free alkyl radicals, viz., does the conversion outlined in eq 1 involve kinetically free alkyl radicals or does it occur by an alternative process such as (1) the competition between a concerted carbon–carbon bond formation involving alkyl groups bonded to a common organometallic cluster (yielding dimers) and an elimination process producing olefin, R(–H), and a metal hydride which in a subsequent reaction might possibly yield hydrocarbon, RH, or (2) a process involving homolytic scission of a carbon–metal bond resulting in the formation of an alkyl radical, followed by very rapid reaction of this radical with an organometallic compound to yield combination and disproportionation products.

The evidence outlines in this paper is most readily explained by a single process involving an initial one-electron oxidation of $(RLi)_n$, resulting in the generation of kinetically free alkyl radicals. The principal arguments leading to this conclusion are the following. First, the ratio of disproportionation to combination, [R(–H)]/[R–R], is in good agreement with values reported for free alkyl radicals in a variety of unrelated systems. Second, the cross-coupling ratios show close agreement to values determined for various radical–radical couplings between small *n*-alkyl radicals. Third, the generally increased yield of *n*-butane observed when oxidation of *n*-butyllithium is carried out in ether is also consistent with the acknowledged rapid rate of hydrogen atom abstraction from diethylether by *n*-butyl radicals[22] and the influence which polar solvents and additives have in promoting the rate of electron-transfer from organolithium reagents.[14] Fourth, the conclusion that free alkyl radicals are the immediate precursors to the products observed in eq 1 is strongly supported by the close parallel between the product distribution produced by the reaction of neophyllithium with TiS_2 and the product distributions produced by other organometallic processes known to proceed through the intermediacy of neophyl radicals.

Finally, the results reported here provide one additional aspect of mechanistic insight into the unique redox process described by eq 1. Specifically, they reveal that the rate of this reaction is *not* mass transport limited. This conclusion follows from the fact that the reaction is faster in polar solvents and in the presence of TMEDA. Thus, it can be further concluded that the rate-determining step must not be occurring within the dichalcogenide interior structure since transport of virtually any reagent into the cavity of the dichalcogenide is almost certain to be a mass transport limited process.

Experimental Section

General Materials. High purity sulfur (99.999+%), selenium (99.999+%) and tellurium (99.99+%) were obtained from American Smelting and Refining Co.; titanium granules (99.9%) was purchased from United Minerals and Chemical Corp.; zirconium powder (325 mesh, 99.5%) tantalum powder (325 mesh, 99.9%) were obtained from A.D. Mackay Inc. Hafnium powder (325 mesh, 99.5%), and biobium powder (325 mesh, 99.5%) were purchased from Alfa Inorganics, Inc., along with commercial samples of TiS_2, $TiSe_2$, HfS_2, and $NbTe_2$.

All transfers and manipulations of air-sensitive materials as well as all metal dichalcogenides were carried out in a nitrogen-filled Vacuum Atmosphere glove box. Each dichalcogenide was pulverized (using a mortar and pestle) inside the glovebox.

Solutions of *n*-butyllithium in hexane, *sec*-butyllithium in cyclohexane, and *tert*-butyllithium in pentane were obtained from Aldrich Chemical Co. Pentane (Aldrich, spectrograde), cyclohexane (MCB, spectrograde), and hexane (Mallinckrodt, reagent grade) were purified by stirring over concentrated sulfuric acid for 2 weeks and washing with water, aqueous 10% sodium carbonate solution, and finally water before drying with anhydrous magnesium sulfate prior to distillation from sodium–potassium alloy under nitrogen. Diethyl ether (Fischer) was purified by preliminary distillation from calcium hydride followed by a final distillation from lithium aluminum hydride under nitrogen. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), obtained from Eastman Chemical Co., was distilled from sodium metal under nitrogen. The central fraction boiling at 122 °C was used immediately or stored under nitrogen over 5A molecular sieves for a period of not more than a month. Methanol-*O*-*d* (99% deuterium), cyclohexane-d_{12} (99.5% d_{12}), and toluene-d_8 (99% d_8) were obtained from Stohler Isotope Chemicals. The latter two materials were dried by distillation from sodium metal under nitrogen immediately prior to use.

Solutions of *n*-propyllithium in pentane and *n*-butyllithium in pentane were prepared by reaction of freshly distilled *n*-propyl chloride (Aldrich) and *n*-butyl chloride (Aldrich), respectively, with lithium dispersion (Lithium Corp. of America). The preparation of all organolithium reagents were carried out in pentane under a helium atmosphere according to published procedures.[23]

Analyses of organolithium reagents were performed periodically by the Gilman double titration method[24] using 1,2-dibromoethane which was purified by passage through a short plug of Woelm neutral alumina immediately prior to use.

Analytical gas–liquid partition chromatographic (GLPC) analyses of reaction products were routinely performed on a Hewlett-Packard Model 5750 flame ionization instrument equipped with a Hewlett-Packard Model 3380A electronic integrator. Absolute yields of products were calculated from peak areas using internal standard techniques with response factors

---

(21) Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1971**, *94*, 232.

(22) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2806.

(23) Bryce-Smith, D.; Turner, E. E. *J. Chem. Soc.* **1953**, 861. Linstrumelle, G.; Krieger, J. K.; Whitesides, G. M. *Org. Synth.* **1975**, *55*, 103.

(24) Gilman, H.; Cartledge, F. K.; Sim, S. Y. *J. Organomet. Chem.* **1963**, *1*, 8.

(25) (a) Grenaway, D. L.; Nitsche, R. *J. Phys. Chem. Solids* **1965**, *26*, 1445. (b) Brixner, L. H. *J. Inorg. Nucl. Chem.* **1962**, *24*, 257. (c) Hahn, H.; Ness, P. *Z. Anorg. Allg. Chem.* **1959**, *302*, 136. (d) Clement, R. P.; Davies, W. B.; Ford, K. A.; Green, M. L. H.; Jacobson, A. J. *Inorg. Chem.* **1978**, *17*, 2754.

(26) Brown, T. L. Ladd, J. A. *J. Organomet. Chem.* **1964**, *2*, 373. Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4625.

(27) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

obtained from authentic samples. Hydrocarbons of a four-carbon chain or less were analyzed by GLPC using a 4-ft × $^1/_4$-in. column of 3% Apiezon L on Alumina F-20 (column A). Hydrocarbons of five or more carbon atoms were analyzed by GLPC using a 6-ft × $^1/_4$-in. column of 10% SE-30 silicone oil on Chromosorb W (column B) or a 24-ft × $^1/_8$-in. Hi-Pak (Hewlett-Packard) column of 10% SE-30 on Chromosorb W (column C). *n*-Propyl bromide and *n*-butyl bromide were determined similarly by using either a 12-ft × $^1/_4$-in. column of 20% Carbowax 20M on Chromosorb W (column D) or a 24-ft × $^1/_8$-in. Hi-Pak (Hewlett-Packard) column of 20% Carbowax 20M on Chromosorb W (column E).

GC–mass spectra were obtained by using a Hewlett-Packard 5985 GC–mass spectrometer employing a 12-ft × $^1/_8$-in. column of *n*-octane on Porasil C (100/120 mesh); an ionizing voltage of 12 eV was used for deuterium isotope determinations. In all cases, an average of two spectra was used in calculating the isotopic distributions.

For the preparation of metal dichalcogenides, a high-temperature electrical furnace was fabricated from a 24-in. × $2^3/_8$-in. (i.d.) alumina tube wrapped with nichrome wire, enclosed in a stainless steel jacket packed with insulating materials. Heating was controlled by a Eurotherm temperature control unit, and the temperature was measured by a Pt vs. Pt + 13% Rh thermocouple via a Rubicon potentiometer. A 24-in. × $1^1/_2$ in. (o.d.) thick-walled, appropriately charged and sealed quartz tube, was placed inside the stainless-steel jacket. The two open ends of the furnace were plugged with Fiberflex insulating materials. Temperatures at different positions inside the quartz tube were monitored by means of appropriate thermocouples.

General Procedure for the Preparation of Metal Dichalcogenides.[25] An 18-in. × 1-in. o.d. thick-walled quartz tube with a 35/25 ground-glass male joint at one end and sealed at the other and a 3-in. quartz boat which fitted snuggly inside the quartz tube were soaked for 30 min in a 1:2 (by volume) hydrofluoric acid and concentrated nitric acid, then rinsed for 30 min with running water, three times with deionized water, and then acetone, and finally oven dried at 140 °C overnight. A mixture of 0.05 mol of the metal and 0.1 mol of the chalcogen was mixed well and loaded carefully on the quartz boat which was inserted into the closed end of the tube. When iodine was used as the transporting agent, 4 mg/mL of resublimed iodine was added. The tube was evacuated to 10^{-5} torr and sealed with the aid of a torch. That end of the tube bearing quartz boat was placed near the center of the furnace, and both ends of the furnace were plugged with Fiberflex insulating materials prior to operation. All the metal dichalcogenides were prepared by published procedures.

Reactions of MX_2 with Alkyllithium Reagents. All reactions of metal dichalcogenides with organolithium reagents were carried out in prescored Kimax glass ampules of 10-mL capacity. The glass ampules were prepared by soaking in hot concentrated nitric acid for 2 h and then rinsed thoroughly with distilled water before soaking them in concentrated ammonium hydroxide solution for 2 h. After several rinses with distilled water followed by ethanol, the ampules were dried overnight in an oven at 140 °C.

A Schlenk apparatus was fabricated for accessing reaction mixtures from these ampules at low temperatures.

Reaction of *n*-Propyllithium with Metal Dichalcogenide in Pentane (Typical Procedure). An oven-dried, 10-mL ampule equipped with a Teflon-coated magnetic stirrer bar was charged with 3.3 mmol of the metal dichalcogenide and stoppered with a rubber septum. The ampule was removed from the glovebox and placed in a Dry-Ice/acetone bath. Olefin-free pentane (5.4 mL) and *n*-heptane (160 μL, internal standard) were added by syringe, followed by a solution of *n*-propyllithium (2.0 mL, 1.0 M) in pentane. The ampule was cooled in a liquid nitrogen bath under an atmosphere of nitrogen and sealed with a torch. After it had warmed to ambient temperature, the ampule was placed in a test tube and immersed in a stirred oil bath at 40 ± 1 °C. At the end of 4, h, the ampule was centrifuged and placed in the specially fabricated, flame-dried Schlenk apparatus. After a series of evacuation and fill cycles, the lower portion of the Schlenk apparatus was immersed in a Dry-Ice/acetone bath for 45 min. The ampule was cracked open under a nitrogen atmosphere. The supernatant liquid was transferred by cannula into two, 40-mL centrifuge tubes, each containing 20 mL of pentane which had been cooled in a Dry-Ice/acetone bath. To one tube was added 1 mL of dry methanol and to the other 0.5 mL of 1,2-dibromoethane in 2 mL of ether. The methanol quench and 1,2-dibromoethane quench were stirred at −78 °C for about 30 min and then allowed to warm to ambient temperature and analyzed by GLPC.

A blank experiment was performed in the absence of metal dichalcogenide under the same conditions.

Reaction of *n*-Propyllithium–*n*-Butyllithium (1:1) with Metal Dichalcogenide. A flame-dried, 10-mL ampule equipped with a Teflon-coated magnetic stirrer bat was charged with 3.3 mmol of metal dichalcogenide in the glovebox, stoppered with a rubber septum, removed, and placed in a Dry-Ice/acetone bath. Deolefinated pentane (4.3 mL) and 130 μL of cyclohexane as the internal standard were added by syringe followed by 3.0 mL of an equilibrate[26] 1:1 mixture of *n*-propyllithium–*n*-butyllithium in pentane. The ampule was cooled under nitrogen to a liquid-nitrogen temperature and sealed with a torch. It was then placed inside a long-stemmed test tube and immersed in a stirred oil bath at 40 ± 1 °C. After 48 h, the ampule was centrifuted and the contents were worked-up as described above.

Two blank experiments were performed in the absence of metal dichalcogenide.

Neophyllithium was prepared from dineophylmercury according to published procedure.[21]

Preparation of (*n*-Butyl-2,2-d_2)lithium in Hexane.[27] In a flame-dried, helium-flushed, 250-mL three-necked flask equipped with a Teflon-coated magnetic stirring bar and a 60-mL pressure equalizing dropping funnel and rubber septa was placed in 1.0 g (140 mmol) of lithium dispersion. Freshly distilled hexane (80 mL) was added by syringe. The reaction flask was then cooled in an ice bath and a solution of 8.2 g (59 mmol) of 1-bromobutane-*2,2*-d_2 (isotopic purity 95% d_2) in 12 mL of hexane was added dropwide over 10 min. The resulting mixture was stirred under a static atmosphere of helium for 2 h at 0 °C and then for an additional 12 h at room temperature. The entire reaction mixture was filtered through a plug of glass wool and a 2-cm layer of filter aid into a 150-mL, oven-dried and helium-flushed amber bottle suitably equipped for storage. Assay indicated 0.40 M concentration of *n*-$C_4H_9D_2Li$ (95% d_2).

Acknowledgment. A number of the techniques and early results described in this study were developed by Mr. Jean-Paul Lavalleye; we wish to thank him for his contributions to this work.

Registry No. TiS_2, 12039-13-3; ZrS_2, 12039-15-5; NbS_2, 12136-97-9; TaS_2, 12143-72-5; HfS_2, 18855-94-2; $TiSe_2$, 12067-45-7; VSe_2, 12299-51-3; $ZrSe_2$, 12166-47-1; $NbSe_2$, 12034-77-4; $TaSe_2$, 12039-55-3; $HfSe_2$, 12162-21-9; $TiTe_2$, 12067-75-3; $ZrTe_2$, 32321-65-6; $NbTe_2$, 12034-83-2; $TaTe_2$, 12067-66-2; butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; neophyllithium, 29904-33-4; propyllithium, 2417-93-8.