Carboxylation of Lithium Compounds: Ab Initio Mechanisms

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Received October 17, 1988

Abstract: The model carboxylation reactions of lithium hydride (R = H) and methyllithium (R = CH_3), $RLi + CO_2 \rightarrow RCOOLi$, have been calculated ab initio including electron correlation and zero-point energy (ZPE) corrections. The theoretical levels used were MP2/6-31+G*//MP2-FU/6-31G* + ZPE (R = H) and MP2/6-31G*//HF/6-31G* + ZPE (R = CH_3, d functions omitted from lithium). The initially formed linear RLi·O=C=O complexes between the reactants are bound by 8.4 and 8.6 kcal/mol, respectively. The reactions proceed through highly ionic (charges on lithium, >0.84) four-membered ring transition structures. The activation energies, relative to the complexes, are very small: 1.5 (R = H) and 0.9 (R = CH_3) kcal/mol. The carboxylations of LiH and CH_3Li leading to lithium formate and to lithium acetate are exothermic by 55.7 and 61.7 kcal/mol, respectively. Since these products have structures with R and Li on opposite sides of the CO_2 moiety, considerable movement of the lithium cations is necessary. The transition structures for carboxylation and addition to formaldehyde are compared.

Carboxylation of organolithium compounds, eq 1 (and also of Grignard reagents), is one of the most valuable, generally applicable methods for the synthesis of carboxylic acids.[1,2] Even

$$\begin{gathered} RLi + CO_2 \rightarrow RCOOLi \\ \text{(a) } R = H \qquad \text{(b) } R = CH_3 \end{gathered} \qquad (1)$$

less reactive or sterically hindered lithium compounds give excellent yields. Further addition of an organolithium reagent to the lithium carboxylate intermediate can be used for the preparation of symmetric and unsymmetric ketones.[1,3] Reaction 1 is also well-known in transition-metal chemistry.[4-6] The process is usually called an *insertion* of CO_2 into the metal–R bond in contrast to the organic chemists' view of an *addition* of the organolithium to carbon dioxide. Both insertions into M–C[4,5] and M–H[4,6] as well as into M–O and M–N bonds[4,7] are known. This activation of carbon dioxide by metal complexes has been the subject of experimental[4] and theoretical[8] work. The reverse of reaction 1, the decarboxylation of carboxylates of metals other than lithium, eq 2, is a useful method for the synthesis of organometallic compounds.[9-11]

$$RCOOM \rightarrow RM + CO_2 \qquad (2)$$

The stereochemistry of carboxylation of configurationally stable organolithiums has been shown to proceed with retention.[12] For example, NMR data[12b] show menthyllithium to be conformationally rigid in hydrocarbon solvents. Carboxylation yields only the corresponding menthanecarboxylic acid with only small amounts of the neomenthyl epimer.[12b] Retention of the configuration at the α-carbon also occurs in transition-metal complexes when inserting CO_2 into a metal–alkyl bond.[5a] The reaction obeys second-order kinetics,[5b] first order in metal compound and first order in carbon dioxide. With suitable ligands the reverse decarboxylation reaction has been demonstrated to proceed also with retention at the metal center.[10] Concerted pathways have been proposed for both the carboxylation[5] and decarboxylation reactions.[10]

This paper is a continuation of our theoretical studies on the mechanisms of basic organolithium reactions.[13-16] We provide detailed structural and energetic information for the individual steps of the important organolithium carboxylation reaction. The reaction of CO_2 with LiH as the simplest model for an organolithium has been treated at higher levels to check for the performance of the theoretical method used. In our previous work LiH has been shown to model the behavior of alkyllithiums[14,15] (and also their aggregates)[15] in organolithium reactions quite well. In addition, LiH can be prepared in a finely divided quite reactive state[17] and used for, e.g., metalation reactions. The better model for an organolithium, CH_3Li, also has been treated at reasonably high levels.

Calculational Methods

All geometries were fully optimized within the designated symmetry constraints at the restricted Hartree–Fock (HF) level by using gradient optimization techniques and, in most cases, standard basis sets (3-21G, 6-31G*, 6-31+G*) incorporated in the GAUSSIAN 82 program system.[18,19] Stationary points were characterized by frequency analysis at 3-21G (minima with 0, transition structures with 1 imaginary frequency). The zero-point vibrational energies (ZPE) obtained were scaled by the empirical factor 0.9.[20] Electron correlation was estimated by using

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Table I. Total (–au) and Zero-Point Vibrational (kcal/mol) Energies

species	point group	3-21G//3-21G	6-31G*// 6-31G*	MP2/ 6-31G*// 6-31G*	6-31+G*// 6-31G*	MP2/ 6-31+G*// 6-31G*	ZPE[a]
LiH	$C_{\infty v}$	7.929 84[b]	7.980 87[b]	7.995 96	7.981 01	7.996 15	2.04 (0)
			7.980 87[c]	7.995 96[c]	7.981 00[c]	7.996 15[c]	
$H_2CO/LiCH_3$, TS	C_s	160.008 59[d]	160.904 73	161.355 88			
$H_2CO{\cdot}LiCH_3$	C_s	160.018 56[d]	160.910 96	161.356 76			
C_2H_5OLi	C_s	160.091 19[d]	160.972 53	161.429 20			
CO_2	$D_{\infty h}$	186.561 26[b]	187.634 18[b]	188.102 20[b]	187.638 79	188.112 16	7.45 (0)
			187.628 41[c]	188.107 74[c]	187.633 11[c]	188.117 94[c]	
2	C_s	194.518 48	195.624 48	196.114 52	195.628 92	196.124 23	11.28 (1)
			195.620 37[c]	196.118 50[c]	195.624 37[c]	196.127 59[c]	
1	$C_{\infty v}$	194.523 84	195.632 19	196.116 02	195.636 33	196.123 88	10.86 (0)
			195.626 78[c]	196.121 27[c]	195.631 08[c]	196.129 41[c]	
3	C_{2v}	194.608 66	195.707 34	196.195 13	195.714 41	196.208 95	16.17 (0)
			195.704 10[c]	196.198 36[c]	195.711 21[c]	196.212 43[c]	
			"Li less d"[e]	"Li less d"[e]			
$LiCH_3$	C_{3v}	64.752 48[b]	47.015 03	47.158 37			22.42 (0)
5	C_s	233.341 64	234.653 94	235.274 97			31.34 (1)
4	C_{3v}	233.344 85	234.664 82	235.275 52			30.76 (0)
6	C_s	233.441 07	234.752 13	235.365 75			34.69 (0)

[a] Zero-point energy at 3-21G, number of imaginary frequencies in parentheses. [b] Reference 23. [c] MP2-FU/6-31G* optimized geometries. [d] Reference 15. [e] d functions omitted from lithium, see the text.

Table II. Energies in the RLi/H_2CO and RLi/CO_2 Systems Relative to Isolated Species and Activation Barriers E_a Relative to Complexes (kcal/mol)

species		3-21G// 3-21G	6-31G*// 6-31G*	MP2/ 6-31G*//6-31G*	6-31+G*// 6-31G*	MP2/ 6-31+G*//6-31G*	Δ(ZPE)[a]	final est[b]
R = H								
$H_2CO{\cdot}LiH$[c]		–29.3	–19.8		–19.0	–17.7	+1.6[d]	–16.1[d]
H_2CO/LiH, TS[c]		–22.1	–16.2		–15.1	–14.7	+2.0[d]	–12.7[d]
E_a[c]		7.2	3.6		3.9	3.0	+0.4[d]	3.4[d]
CH_3OLi[c]		–71.5	–52.9		–54.7	–61.6	+7.0[d]	–54.6[d]
$CO_2{\cdot}LiH$	**1**	–20.5	–10.8	–11.2	–10.4	–9.8	+1.2	–8.6
			–11.0[e]	–11.0[e]	–10.6[e]	–9.6[e]	+1.2	–8.4[e]
CO_2/LiH, TS	**2**	–17.2	–5.9	–10.3	–5.7	–10.0	+1.6	–8.4
			–7.0[e]	–9.3[e]	–6.4[e]	–8.5[e]	+1.6	–6.9[e]
E_a		3.3	4.9	0.9	4.7	–0.2	+0.4	0.2
			4.0[e]	1.7[e]	4.2[e]	1.1[e]	+0.4	1.5[e]
HCOOLi	**3**	–73.8	–57.9	–60.8	–59.4	–63.2	+6.0	–57.2
			–59.5[e]	–59.4[e]	–60.9[e]	–61.7[e]	+6.0	–55.7[e]
R = CH_3								
$H_2CO{\cdot}LiCH_3$		–27.7[c]	–18.3	–18.5				
$H_2CO/LiCH_3$, TS		–21.5[c]	–14.3	–18.0				
E_a		6.2[c]	4.0	0.5				
C_2H_5OLi		–73.3[c]	–56.9	–64.0				
R = CH_3			"Li less d"[f]	"Li less d"[f]				
$CO_2{\cdot}LiCH_3$	**4**	–19.5	–9.8	–9.4			+0.8	–8.6
$CO_2/LiCH_3$, TS	**5**	–17.5	–3.0	–9.0			+1.3	–7.7
E_a		2.0	6.8	0.4			+0.5	0.9
CH_3COOLi	**6**	–79.9	–64.6	–66.0			+4.3	–61.7

[a] Difference in zero-point energies, scaled by 0.9.[20] [b] Final estimate evaluated using data from the highest level employed + Δ(ZPE). [c] Reference 15. [d] This work. [e] MP2-FU/6-31G* optimized geometries. [f] d functions omitted from lithium, see the text.

Møller–Plesset theory carried out to second order (MP2)[21] keeping the core electrons frozen. Geometry optimizations at correlated levels included the core orbitals (MP2-FU). In the larger CH_3Li/CO_2 system the d functions were omitted from lithium in the calculations at the 6-31G* level. The omission of polarization functions on lithium does not change the *absolute* energies very much (0.000 51 and 0.003 64 au at the HF and MP2 levels, respectively, in the case of CH_3Li),[22] and the *relative* energies should be influenced very little. Final estimates of relative energies were obtained by adding the differences in zero-point energies to the MP2 results at the highest levels employed. Table I lists the total energies at various levels and the ZPEs. Some reference energies were taken from the Carnegie-Mellon Quantum Chemistry Archive.[23] Relative energies are given in Table II and transition structure geometries in Table III, with key geometrical parameters also in the figures (full geometry information in the form of archive entries[23] is available as supplementary material). Charges and bond orders were obtained by the natural population analysis (NPA) of Reed et al.[24]

Results and Discussion

The carboxylation reactions of lithium hydride and methyllithium proceed in the three stages shown in Figures 1 and 2, respectively. The first step is a complexation between the lithium compound and carbon dioxide. This initial step is characteristic for organolithium reactions.[14-16] The association energies are 8.4 and 8.6 kcal/mol, respectively, about half of the corresponding energy of formaldehyde–LiR complexes.[15] The carbon dioxide complexes adopt linear (end-on bound) structures as expected from electrostatic considerations. They have been characterized as minima by frequency analysis. Whereas in transition-metal chemistry three types of metal bonding to CO_2 are known experimentally (end-on, side-on, and C coordination),[4] theoretical

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Table III. Geometries[a] and Charges of the Transition Structures for the Additions of LiH and CH_3Li to Carbon Dioxide and Formaldehyde

	CO_2			H_2CO	
parameter[b]	3-21G	6-31G*	MP2-FU/ 6-31G*	3-21G	6-31G*
addition of LiH					
$C-O_i$	1.196	1.184	1.206	1.236[c]	1.205[c]
$C-O_0$, C–H	1.149	1.141	1.172	1.076	1.084
H(2)–C–H(2)				116.2	116.7
O–C–O, $M-C-O_i$[d]	162.3	159.1	164.2	176.6	177.7
Li–H	1.710	1.691	1.679	1.708	1.680
Li–O	1.831	1.885	1.944	1.821	1.917
H–C	2.108	1.972	2.220	2.510	2.690
$H-C-O_i$	92.3	96.7	94.1	88.7	88.8
q(C)		+1.239			+0.418
$q(O_i)$		−0.804			−0.762
$q(CO_2)$, $q(H_2CO)$		−0.159			−0.027
q(Li)		+0.846			+0.789
q(H)		−0.687			−0.762
addition of CH_3Li		"Li less d"[e]			
$C-O_i$	1.194	1.188		1.233[c]	1.219[f]
$C-O_0$, C–H	1.149	1.144		1.077	1.083
H(2)–C–H(2)				116.1	116.1
O–C–O, $M-C-O_i$[d]	163.0	156.3		177.0	171.7
$Li-C_n$	2.054	2.055		2.049	2.056
$C_n-H(1)$	1.101	1.103		1.096	1.092
$Li-C_n-H(1)$	92.5	85.3		122.4	132.5
$C_n-H(2)$	1.091	1.088		1.096	1.096
$H(2)-C_n-H(2)$	107.3	107.1		106.5	105.7
$M-C_n-Li$[d]	149.9	158.2		120.2	112.0
Li–O	1.829	1.848		1.838	1.859
C_n-C	2.540	2.349		2.898	2.614
C_n-C-O_i	99.4	105.3		94.2	105.3
q(C)		+1.234			+0.372
$q(O_i)$		−0.810			−0.817
$q(CO_2)$, $q(H_2CO)$		−0.182			−0.119
q(Li)		+0.916			+0.901
$q(CH_3)$		−0.734			−0.782

[a] Distances in Å, angles in degrees. [b] O_i is the oxygen of the four-membered ring, C_n is the methyl carbon. H(1) is the unique, H(2) are the symmetry equivalent hydrogens. q is the NPA[24] charge of the atom or group indicated. [c] Reference 15. [d] M is the H(2)–C–H(2) bisector. [e] d functions omitted from lithium, see the text. [f] This work.

studies[25] show the end-on bonding mode to be preferred with the more electropositive metals. The linear end-on interaction of carbon dioxide is also favored with alkali-metal cations.[26] Nevertheless, the C coordination of LiH to CO_2 was probed here by imposing C_{2v} symmetry, but no association complex was found at 3-21G. The same was true for the complex with the opposite orientation, $O_2C\cdot HLi$, which might have been bound by electrostatic attraction of the positively polarized carbon and the hydride anion. Optimization of a side-on structure led to the linear complex. Thus, the only stationary point is the linear end-on bound complex **1**.

The activation step in the carboxylation reactions is characterized by very small activation energies at all theoretical levels studied. (Unless noted otherwise, the barriers discussed are calculated *relative to the complexes*.) Whereas at the Hartree–Fock level the barriers are ~5 kcal/mol (Table II), inclusion of electron correlation resulted in a modest but significant decrease in energies of the transition structures by about 4–6 kcal/mol. For example, the "barrier" for reaction 1a is −0.2 kcal/mol at the MP2/6-31+G*//6-31G* level (Table II). Consequently, the LiH/CO_2 system also was optimized at the correlated MP2-FU/6-31G* level.[27] The changes in *absolute energies* were relatively large, 2.1–3.6 kcal/mol, mainly due to a lengthening of the C–O bonds by ~0.03 Å upon optimization at correlated levels. For example, the MP2/6-31G*//HF/6-31G* energy of carbon dioxide, corresponding to a C–O distance of 1.143 Å,[23] is higher by 3.5 kcal/mol compared to the MP2/6-31G*//MP2-FU/6-31G* energy (C–O, 1.179 Å). The experimental C–O bond length lies in between (1.16 Å).[28] Other significant geometrical changes occurred for the Li–O separations in the transition structure **2** and in lithium formate **3**, +0.06 and +0.03 Å, respectively. However, the changes in *relative energies* of the individual species of the LiH/CO_2 system did not exceed 1.6 kcal/mol (Table II). Thus, we conclude that the energies of the larger system CH_3Li/CO_2 also should be reasonable although the geometries might be given less accurately. Table III summarizes the geometries of the transition structures **2** and **5** at the various theoretical levels applied.

Our final estimates of the activation energies of the reactions of LiH and CH_3Li with CO_2 are 1.5 and 0.9 kcal/mol, respectively. Despite their variation with the level of theory, we believe the barriers to give products *from the complexes* are much smaller than the initial association energies. This means the carboxylation reactions should proceed readily *without activation from the separated species*, RLi + CO_2, to the carboxylates, RCOOLi, at least under conditions where the energy of the complexation cannot be dispersed. This is in contrast to the significant barriers (>10 kcal/mol) reported in experimental[5] and theoretical studies[8] on CO_2 insertion into transition-metal M–C or M–H bonds. The experimental activation entropies[5] are consistent with a concerted mechanism. However, in the presence of alkali-metal counterions the insertion is enhanced considerably.[5b] The anionic complexes, $M(CO)_5R^-$, may favor an additional complexation of the cations to the "outer" oxygen of the CO_2 moiety in the transition states (structures **2** and **5** with a transition metal instead of Li). If the highly ionic character of the transition structures with M = Li (see below) is the reason for the very low barriers, such complexation is expected to further activate CO_2 by making the transition state more polar.

The last step is the formation of the carboxylates **3** and **6**. These have geometries resembling the usual quadrupole structures of LiX dimers[29] with one of the bridging lithium cations replaced by the positively polarized central carbon of the carboxylic group. In **3**, e.g., the charge is +0.81, according to natural population analysis at 6-31G*. The lithium cation and the oxygens have charges of +0.94 and −0.94, respectively. Since R and Li are on opposite sides of the CO_2 moiety in **3** and **6**, the overall reaction is a *trans addition* of RLi to carbon dioxide. We suspect that there will be no barrier for the considerable movement of the lithium cation from a "cis" location (as in **2** and **5**) to the "trans" position in the products (**3**, **6**), but this has not been checked explicitly. (Indeed, no barrier has been found for this process in an ab initio study[8] on a copper formato complex.) The overall reactions are highly exothermic. The reaction energies are −55.7 and −61.7 kcal/mol for the formation of the carboxylates **3** and **6**, respectively.

For comparison, we have now applied zero-point energy corrections[30] to the addition reaction of LiH to formaldehyde.[15] The

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(30) The 3-21G zero-point energies (in kcal/mol, number of imaginary frequencies in parentheses) involved in the addition reaction of LiH to formaldehyde are: formaldehyde, 18.18 (0); complex, 22.05 (0); transition structure, 22.44 (1); CH_3OLi, 28.02 (0). The complex considered here has a bent C_s structure at both 3-21G and 6-31G*, whereas the linear C_{2v} complex described in our previous paper[15] proved to be a transition structure at 3-21G with ZPE = 21.88 (1). However, the energies of the bent form relative to the linear form were almost zero at higher levels of theory (+0.26 and −0.14 kcal/mol at 6-31+G*//6-31G* and MP2/6-31+G*//6-31G*, respectively). The ZPE of the bent minimum has been used.

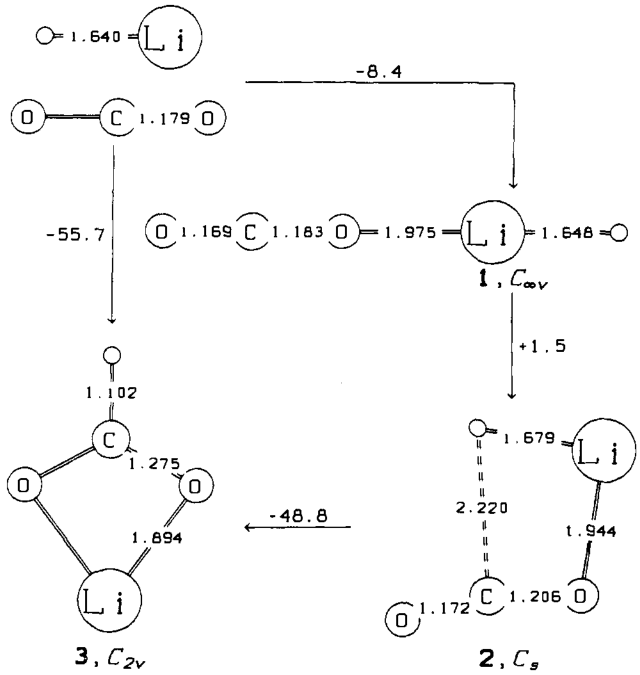

Figure 1. Carboxylation reaction of lithium hydride. Reaction energies (MP2/6-31+G*//MP2-FU/6-31G* + ZPE) are given in kcal/mol, geometrical parameters (MP2-FU/6-31G*) in Å.

addition of methyllithium to formaldehyde[15] also has been recalculated at the higher HF- and MP2/6-31G*//6-31G* levels. The energies are included in Table I. The following discussion refers to the MP2/6-31+G*//6-31G* + ZPE (for LiH) and MP2/6-31G*//6-31G* levels (for CH_3Li). The activation barrier for the LiH addition to formaldehyde is higher by 3.2 kcal/mol compared to the addition to CO_2, but still rather small (3.4 vs 0.2 kcal/mol). In the case of CH_3Li, there is no significant energetic difference between the additions to formaldehyde and carbon dioxide. The barriers are both negligible, 0.5 and 0.4 kcal/mol, respectively.

All four-membered rings of the transition structures are characterized by C=O bonds elongated by 0.3–0.4 Å. The Li–O bond lengths generally are very similar, 1.88 ± 0.04 Å, as are the H–Li and H_3C–Li distances (1.68 ± 0.01 and 2.06 ± 0.01 Å, respectively). Significant differences occur for the distances between the carbonyl carbon and the incoming nucleophile, R. They are much shorter in the additions to CO_2 (1.972 and 2.349 Å for R = H and R = CH_3, respectively) than in the reactions with H_2CO (2.690 and 2.614 Å, respectively), but still considerably larger than a normal C–R bond. Thus, all reactions are dominated by the interaction of the lithium cation with the carbonyl oxygen. The formation of the C–nucleophile bond is of secondary importance. Similar results have been obtained in an ab initio study[8] on CO_2 insertion into the Cu–H bond of $Cu(H)(PH_3)_2$.

In line with the early transition structures are the low activation energies and the high exothermicities of the overall reactions, which are very similar in the additions to formaldehyde and carbon dioxide: about −56 and −65 kcal/mol for R = H and R = CH_3, respectively.

Natural population analysis[24] reveals the various transition structures to be largely ionic. The lithium cations have charges of 0.79–0.92, these being higher for the methyllithium species (Table III). The charge transfer from the lithium reagents, RLi, to the carbonyl components is much larger in the case of CO_2 (0.16 and 0.18 for R = H and R = CH_3, respectively) than for H_2CO (0.03 and 0.12, respectively). This is in line with the more distorted CO_2 moieties (O–C–O angles of ~158°) compared to the almost planar H_2CO units (deviation from planarity, <9°).

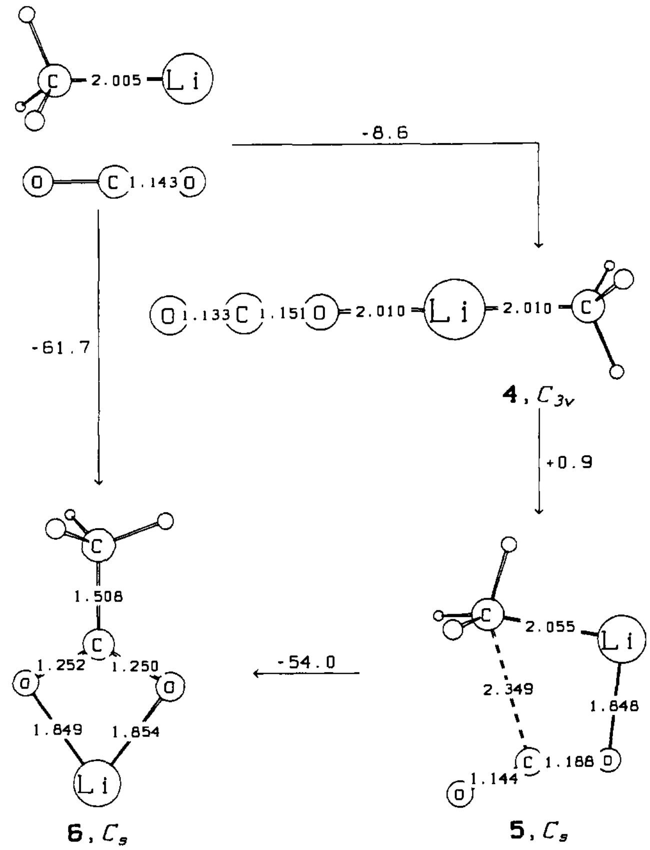

Figure 2. The carboxylation reaction of methyllithium. Reaction energies (MP2/6-31G*//6-31G* + ZPE) are given in kcal/mol, geometrical parameters (6-31G*) in Å. The d functions have been omitted from lithium in all calculations.

Conclusions

As with the addition to aldehydes and ketones[15] our calculations indicate the carboxylation of organolithiums (eq 1) to be a highly ionic reaction, with very early transition states dominated by the lithium cation complexation to oxygen. Several mechanisms for the reverse reaction, decarboxylation of organometallics (eq 2), have been discussed in the literature.[9] They should be of the S_Ei type with carbanion character of the organic group, at least for carboxylates of electropositive metals in nonpolar solvents.

Acknowledgment. Support was provided by Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, and Convex Computer GmbH.

Registry No. LiH, 7580-67-8; CH_3Li, 917-54-4; lithium formate, 556-63-8; lithium acetate, 546-89-4.

Supplementary Material Available: Full geometry information in the form of archive entries (4 pages). Ordering information is given on any current masthead page.