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Mechanism of the Ziegler Dilithiomethane Synthesis. An ab Initio Study of Methyllithium Pyrolysis

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Abstract: Ziegler's disproportionation reaction of methyllithium to give dilithiomethane and methane upon heating to 225 °C is predicted by ab initio theory (MP2/6-31+G*//6-31G*) to proceed endothermically through a polar hydrogen-transfer mechanism within a tetrameric methyllithium aggregate, $(CH_3Li)_4 \rightarrow CH_2Li_2\cdot(Li/CH_3)_2 + CH_4$. A free energy of reaction of +19.6 kcal/mol and an activation barrier ($\Delta G^{\ddagger}$) of 53.8 kcal/mol at 500 K are computed. The alternative reactions within dimeric and trimeric aggregates are endothermic by 31.1 and 21.4 kcal/mol at MP4SDTQ/6-31+G*//6-31G* with activation barriers of 64.3 and 58.2 kcal/mol, respectively. Under the reaction conditions, methyllithium trimers should be in equilibrium with tetramers, but tetramers are still expected to be the predominant species.

Introduction

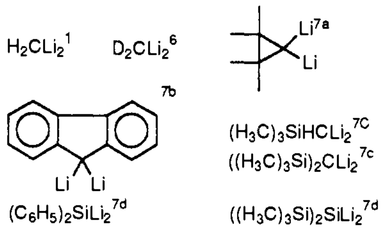
In 1955, Ziegler, Nagel, and Patheiger reported the preparation of dilithiomethane by pyrolysis of methyllithium (eq 1).[1] The product, a highly pyrophoric insoluble powder, showed erratic behavior: Its reactions were reported to proceed explosively or, in other experiments, very sluggishly with the same reagent under the same conditions.[2] Apart from a few IR signals,[3] no information concerning the molecular structure was available until the first computational studies by Schleyer and Pople et al.[4] 20 years later. They discovered that dilithiomethane, as well as some other geminal dilithio compounds, have a remarkably small energy difference between the planar and the usual "tetrahedral" geometries. The same was found to be true for the dilithiomethane triplets, which have nearly the same energies as the singlets. These results not only stimulated much theoretical work[5] but also revived the experimental interest in this class of compounds.[6-9] Lagow and his group optimized the Ziegler pyrolysis[6] and developed it into a general method for the preparation of a large variety of geminal dilithiated compounds (Chart I).[7] The dilithiated products are obtained in moderate to good yields and can be useful intermediates in the synthesis of other organometallic compounds.[8d]

$$2n\mathrm{H_3CLi} \rightarrow (\mathrm{H_2CLi_2})_n + n\mathrm{CH_4} \qquad (1)$$

Detailed investigations of dilithiomethane and its dideuterio derivative[6,10] culminated recently in the successful determination of the powder neutron diffraction structure of dideuteriodilithiomethane.[11] The structure proved to be much more complex than that anticipated by model ab initio calculations on small aggregates:[5b] In the three-dimensional polymeric network, each methylene "dianion" is surrounded by no fewer than *eight* lithium cations!

The mechanism of the Ziegler disproportionation reaction is unknown. Prolonged heating and careful removal of the gaseous products are required.[6] This suggests that the reaction is endothermic and is driven by the loss of the volatile byproducts.

Chart I



Furthermore, the use of halide-free monolithium compounds is essential;[8b] e.g., the use of commercial methyllithium, which

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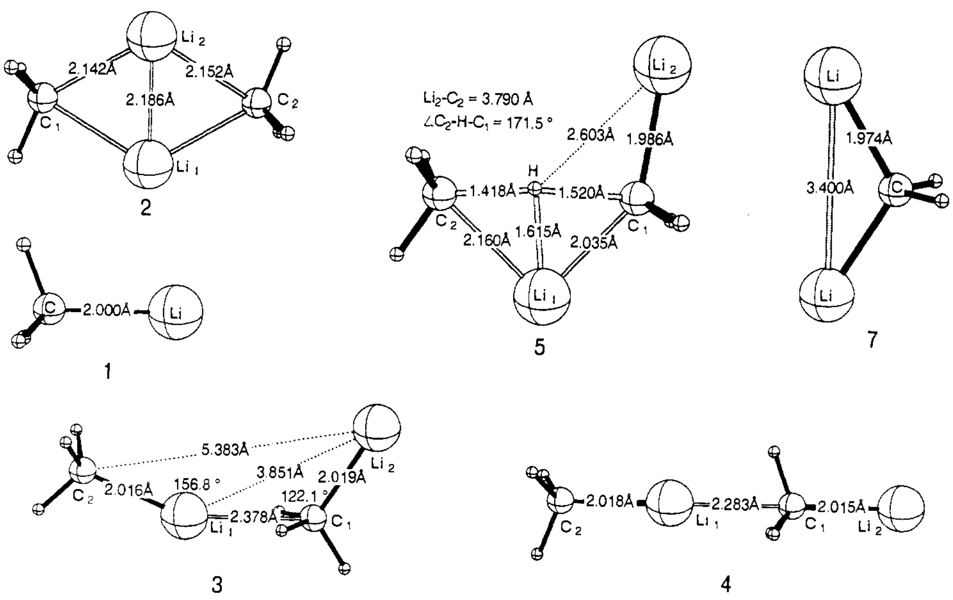

Figure 1.

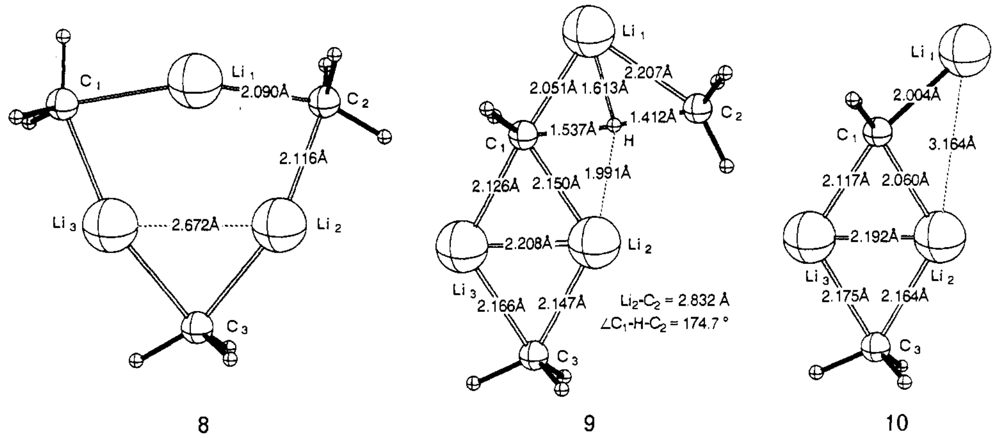

Figure 2.

Table I. Thermochemical Data for Dissociation of Methyllithium Oligomers at 500 K

equation	ΔE	ΔH^a	$-T\Delta S$	ΔG
$(CH_3Li)_4 \rightarrow 2(CH_3Li)_2$ (2)	49.3	-2.6	-30.9	15.8
$(CH_3Li)_4 \rightarrow {}^4/_3(CH_3Li)_3$ (3)	20.6	-0.9	-18.6	1.1
$(CH_3Li)_4 \rightarrow {}^1/_2(CH_3Li)_2 + (CH_3Li)_3$ (4)	27.8	-1.4	-21.7	4.7
$(CH_3Li)_2 \rightarrow 2CH_3Li$	44.0	-2.1	-13.2	28.7
$(CH_3Li)_3 \rightarrow 3CH_3Li$	87.9	-4.4	-30.2	53.3
$(CH_3Li)_4 \rightarrow 4CH_3Li$	136.8	-6.8	-57.3	72.7

[a] Translational, rotational, and vibrational contributions to enthalpy.

contains an equimolar amount of lithium halide, gives unsatisfactory results. As a part of our theoretical investigations of the reactions of organolithium compounds,[12] we have now studied the mechanism of this reaction by means of high-level ab initio calculations.

Computational Details

Calculations were performed using the GAUSSIAN[13] and CADPAC[14] program packages. Geometries were first optimized using the 3-21G[15] basis set and analytical gradient techniques.[16] Transition structures **5**, **8**, and **11** for the disproportionation within dimeric, trimeric, and tetrameric aggregates were located using the eigenvector following (EF) method of Baker.[16b] Subsequently, all stationary points were refined using the 6-31G*[17] basis set and characterized as minima, saddle points, etc., by calculation of vibrational frequencies. These were scaled by the empirical factor of 0.89[18] in the calculation of zero-point vibrational

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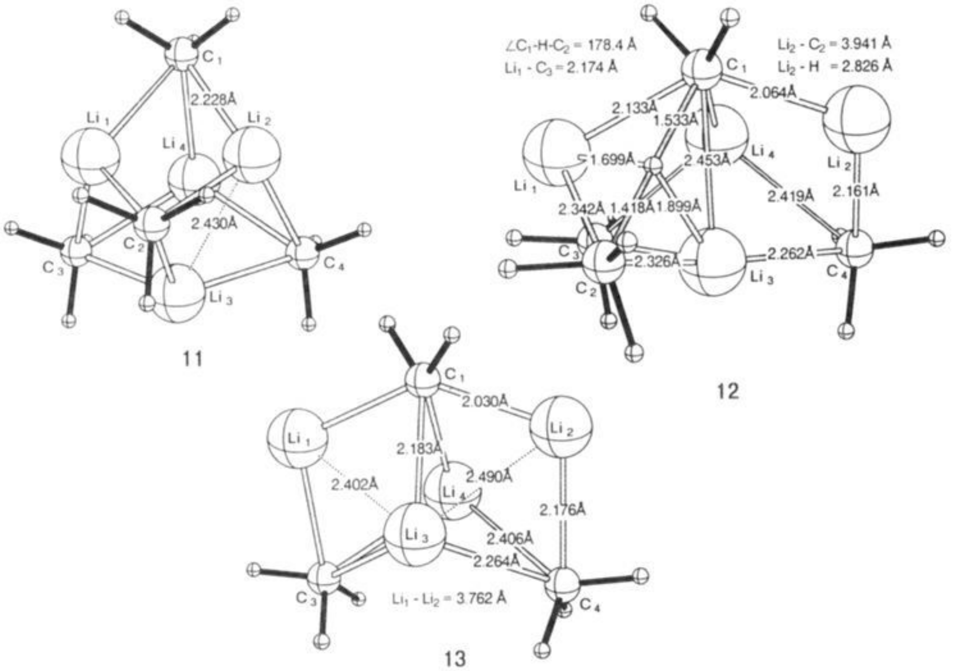

11

12

13

Figure 3.

energies (ZPE) and vibrational contributions to enthalpy. Thermochemical values were computed for a temperature of 500 K and a pressure of 1 atm using the standard statistical formulas.[19] It is important to note that low-lying vibrational frequencies are treated in these calculations as genuine vibrations, although they often correspond to internal rotations. This leads to errors in the absolute entropy values, but relative values are usually assumed to be reliable.

The 6-31G* optimized geometries were used to calculate energies with the 6-31+G*[20,21] basis set, which contains additional diffuse functions on the heavy atoms. Influence of electron correlation was estimated using Møller–Plesset theory[22] carried out to full fourth order (MP4SDTQ) or only to second order (MP2) for the larger $(CH_3Li)_4$ systems. Core electrons were kept frozen (FC) in these calculations. Atomic charges and bond orders were calculated using the natural population analysis (NPA) method by Reed et al.[23] A few of the geometries and total energies were taken from the Carnegie-Mellon[24] and Erlangen[25] Quantum Chemistry Archives. Some of the data on methyllithium oligomers have been published before.[26]

Results and Discussion

Calculated structures for the $(CH_3Li)_2$, $(CH_3Li)_3$, and $(CH_3Li)_4$ systems are shown in Figures 1–3, respectively.

Aggregation State of Methyllithium at 500 K. The first question to be answered concerns the aggregation state of methyllithium under the conditions of the Ziegler thermolysis reaction, i.e., a reaction temperature of 225 °C. At room temperature, methyllithium is tetrameric in the solid state.[27] The tetrameric aggregates are very stable: They persist in the presence of strong ligands like TMEDA[28] and under flash vaporization conditions.[29] On the other hand, it was shown in previous computational work[26] that trimeric aggregates could be the most stable species at elevated temperatures. Signals are seen in the mass spectrum of methyllithium which may originate both from tetramers and from trimers.[29] Even dimers may be present.

$$(CH_3Li)_4 \rightarrow 2(CH_3Li)_2 \qquad (2)$$

$$(CH_3Li)_4 \rightarrow \tfrac{4}{3}(CH_3Li)_3 \qquad (3)$$

$$(CH_3Li)_4 \rightarrow \tfrac{1}{2}(CH_3Li)_2 + (CH_3Li)_3 \qquad (4)$$

Table I summarizes the free energies for the various dissociation modes of methyllithium oligomers at the reaction temperature 225 °C. Energies for dissociation into monomers are included for comparison. These data indicate that trimeric aggregates are likely to be present in equilibrium with tetramers (eq 3), which should still be the predominant species. Dissociation into dimeric aggregates (eq 2) requires considerable energy. Even if formed via the most favorable route, eq 4, dimers will certainly recombine to tetramers.

Reaction Energies. Methyllithium dimer **2** could disproportionate to methane and monomeric dilithiomethane **7** (eq 5a), but the latter product is unlikely to persist as a monomer. Aggregation to a polymer $(\mathbf{7})_n$ will take place (eq 5b). Likewise, methane and

$$\underset{\mathbf{2}}{(CH_3Li)_2} \rightarrow CH_4 + \underset{\mathbf{7}}{H_2CLi_2} \qquad (5a)$$

$$\underset{\mathbf{7}}{nH_2CLi_2} \rightarrow \underset{(\mathbf{7})_n}{(H_2CLi_2)_n} \qquad (5b)$$

a "mixed-dimer" **10** of dilithiomethane **7** and methyllithium **1** are the initial products of methyllithium trimer **8** disproportionation (eq 6a). Tetrameric methyllithium **11** will first give rise to a

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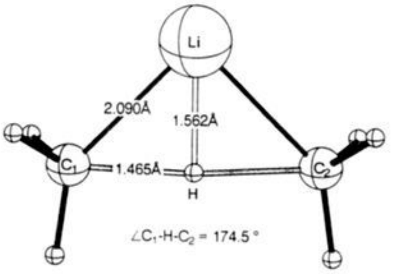

Figure 4.

"mixed-trimer" **13** comprised of dilithiomethane **7** and two methyllithium **1** units (eq 7a). These initial aggregates undergo interaggregate exchange to polymeric dilithiomethane and new methyllithium oligomers (eqs 6b and 7b). In all cases, the

$$\underset{\mathbf{8}}{(CH_3Li)_3} \rightarrow CH_4 + \underset{\mathbf{10}}{H_2CLi_2{\cdot}LiCH_3} \qquad (6a)$$

$$n\underset{\mathbf{10}}{H_2CLi_2{\cdot}LiCH_3} \rightarrow \underset{(\mathbf{7})_n}{(H_2CLi_2)_n} + (n/3)\underset{\mathbf{8}}{(CH_3Li)_3} \qquad (6b)$$

$$\underset{\mathbf{11}}{(CH_3Li)_4} \rightarrow CH_4 + \underset{\mathbf{13}}{H_2CLi_2{\cdot}(LiCH_3)_2} \qquad (7a)$$

$$n\underset{\mathbf{13}}{H_2CLi_2{\cdot}(LiCH_3)_2} \rightarrow \underset{(\mathbf{7})_n}{(H_2CLi_2)_n} + (n/2)\underset{\mathbf{11}}{(CH_3Li)_4} \qquad (7b)$$

disproportionation steps are calculated to be endothermic. Reaction energies are 43.8 kcal/mol for the dimer, 37.2 kcal/mol for the trimer, and 39.3 kcal/mol for the tetramers. The energies are relatively insensitive to the level of theory employed: The use of larger basis sets or inclusion of electron correlation at various levels has only a modest influence.

Entropy is particularly important: The reaction involves loss of a molecule of methane and considerable reduction of symmetry with the tetramer. The resulting free energies of reaction are +31.1 kcal/mol for the disproportionation of the dimer, +21.4 kcal/mol for reaction for the trimer, and +19.6 kcal/mol for the tetramer. The endothermicity of the reaction is in line with the experimental observations.[8f] Geminal dilithioalkanes are very strong metalating agents. Hence, they are not likely to be present in equilibrium, unless a gaseous product (like methane) escapes by diffusion from the solid material.[6]

Transition Structures. The disproportionation of methyllithium involves the metalation of one methyllithium molecule by another. A related reaction has been studied previously: the degenerate hydrogen transfer between methane and methyllithium.[12f] We expected a similar polar mechanism to be operative here, although an alternative pathway, involving homolytic bond cleavage leading to radical intermediates, cannot be ruled out a priori.

In the transition structure for hydrogen exchange between methyllithium monomer and methane[12f] (Figure 4), the lithium cation is bridging between the anionic carbon centers and also is remarkably close to the migrating hydrogen (the Li–H separation in lithium hydride monomer is 0.08 Å longer). We first expected the involvement of the second lithium might lead to transition structures with the lithium cations in a favorable doubly bridging arrangement between the anionic carbons. We explored several candidates of this type for the reaction within $(CH_3Li)_2$ (the most favorable one is structure **6** shown in Figure 5), but all were found to have at least two imaginary vibrations. The true transition structure **5** for the disproportionation reaction within the dimer is shown in Figure 1. Li(1) bridges between the carbon atoms, while Li(2) appears to be not involved at all! The imaginary vibration corresponds to a nearly linear movement of the migrating hydrogen. The resemblance of **5** to the transition structure for hydrogen transfer between methyllithium and methane[12f] (shown in Figure 4) is striking. This strong similarity suggests that both reactions have similar mechanisms.

There is, however, a considerable difference in activation energy. Transition structure **5** is 66.7 kcal/mol less stable than methyllithium dimer **2** (MP4SDTQ/6-31+G*//6-31G*; the MP2 value is 65.5 kcal/mol), whereas a barrier of 32.9 kcal/mol (MP2/6-31+G*//6-31G*) was calculated for degenerate hydrogen transfer between methyllithium and methane.[12f] The free energy of activation for the disproportionation reaction (eq 5a) is calculated to be 64.3 kcal/mol.

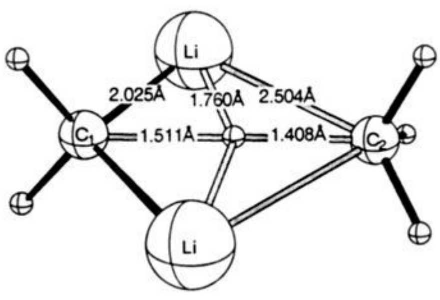

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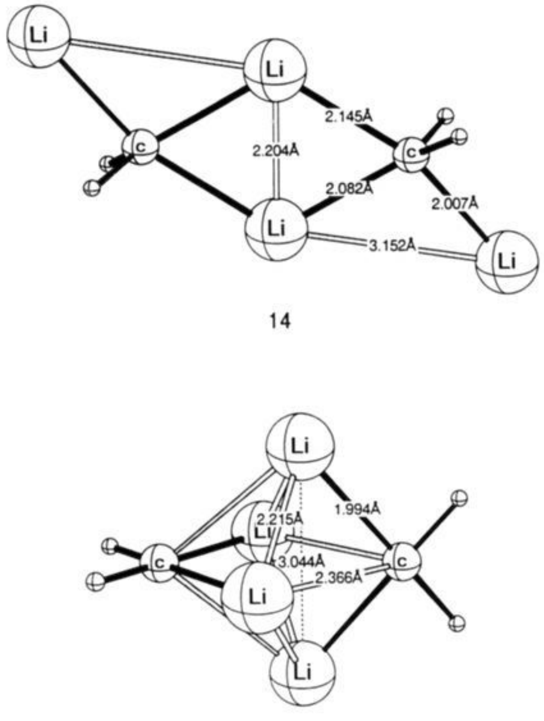
Figure 5.

Table II. NPA Charges and NLMO/NPA Bond Orders

	2	8	11
C	−1.49	−1.48	−1.47
Li	0.89	0.86	0.88
H (av)	0.20	0.20	0.20
C(1)–Li(1)	0.061	0.073	0.037
C(1)–Li(2)	0.054	0.061	0.037
	5	**9**	**12**
C(1)	−1.83	−1.84	−1.87
C(2)	−1.20	−1.20	−1.20
C(3, 4)		−1.47	−1.49
Li(1)	0.93	0.95	0.92
Li(2)	0.87	0.89	0.88
Li(3, 4)		0.88	0.88
H	0.26	0.21	0.23
H(C1 av)	0.19	0.18	0.20
H(C2 av)	0.20	0.21	0.21
H–C(1)	0.281	0.278	0.272
H–C(2)	0.375	0.413	0.403
H–Li(1)	0.024	0.017	0.021
H–Li(2)	0.007	0.008	0.001
H–Li(3)			0.018
Li(1)–C(1)	0.053	0.045	0.031
Li(1)–C(2)	0.006	0.022	−0.002
	7	**10**	**13**
C(1)	−2.07	−2.02	−2.10
C(3, 4)		−1.47	−1.49
Li(1, 2)	0.84	0.84	0.86
Li(3, 4)		0.88	0.89
H(Cl)	0.19	0.17	0.19
H(C3, 4 av)		0.19	0.20
C(1)–Li(1)	0.156	0.160	0.067
C(1)–Li(2)	0.156	0.091	0.067

Natural population analysis[23b,f,g] indicates that partial bonds between the migrating hydrogen and the carbon atoms are largely covalent (Table II). The stronger bonding to C(2) than to C(1) indicates a late transition state, in line with the endothermicity of the reaction. Despite the small distance between Li(1) and the migrating hydrogen (1.615 Å), covalent bonding is very weak. Instead, Li(1), which is slightly more positive than the lithium in a methyllithium dimer, interacts mainly with the negatively charged carbons. The NPA charge on C(2) (−1.20) is intermediate between the charge on carbon in methyllithium dimer (−1.49) and in methane (−0.84). The charge on the migrating hydrogen atom (+0.26) is only slightly higher than that on the carbon-bound hydrogens (average +0.20). As a consequence, the electrostatic interaction with Li(1) is repulsive. This may explain why a doubly bridged transition structure, like **6**, is unfavorable: Two repulsive Li–H interactions would be present.

The reaction is thus best considered to be a hydrogen atom transfer process. However, it does not involve biradical character: Configuration interaction calculations (QCISD/6-31+G*//6-



14

15

Figure 6.

31G*) do not indicate significant contributions of configurations other than the closed-shell ground state.

The large distance between Li(2) and C(2), the carbon atom of the methane molecule being formed, suggests that the disproportionation proceeds in two stages and begins with the elongation of a C–Li bond within the aggregate. Note that the breaking of a carbon–lithium bond within an aggregate is not comparable to homolysis of the carbon–lithium bond in methyllithium monomer. Bonding within aggregates is largely ionic (see Table II). Thus, intraaggregate bond breaking involves the separation of a cation and an anion. We investigated this in more detail for $(CH_3Li)_2$. Breaking a carbon–lithium bond within this aggregate leads, via transition structure **3** (with an activation barrier ($\Delta E^{\ddagger}$) of 25.9 kcal/mol), to the metastable linear dimer **4**, which is 22.1 kcal/mol less stable than **2**. (The corresponding free energy values are 26.2 and 21.2 kcal/mol, respectively.) These values are considerably lower than the dissociation energy of the carbon–lithium bond in methyllithium, for which 43.7[30] and 46.4[26] kcal/mol have been computed.

The transition structures **9** and **12**, for reaction within a trimeric and a tetrameric aggregate, respectively, show the same basic features as **5**. Here, too, the first step appears to be breaking of a carbon–lithium bond within the aggregate. The hydrogen transfers occur along almost linear reaction paths, as is confirmed by the imaginary vibration. The positively charged migrating hydrogens are covalently bound to C(1) and C(2), while only weak covalent interactions with Li(1) exist in addition to the electrostatic repulsions. Covalent bonding to Li(2), in **9**, or to Li(3), in **12**, is negligible. As in **5**, the partial bonds to C(2) are stronger than to C(1) in both **9** and **12** (Table II).

For the trimer, an activation energy of 61.8 kcal/mol (MP4SDTQ/6-31+G*//6-31G*) and a free energy of activation of 58.2 kcal/mol are calculated. At the same level of theory, the barrier calculated for reaction within a tetrameric aggregate is even lower. The activation energy is 58.7 kcal/mol (MP2/6-31+G*//6-31G*); the free energy of activation is 53.8 kcal/mol. The entropy contributions in the trimer and especially in the tetramer are more significant, due to the larger reductions in symmetry on going from **8** (C_{3h} symmetry) to **9** (C_s symmetry) or from **11** (T_d symmetry) to **12** (C_1 symmetry).

These activation barriers for dimer, trimer, and tetramer are noteworthy in another context. Usually, the smaller aggregates of lithium compounds are expected to be more reactive.[31] Here, the reverse is found: The lowest activation barrier corresponds to reaction within a tetramer.[32] However, this is easily understood from the nature of the transition structures. In dimeric methyllithium, the initial breaking of the C(2)–Li(2) bond leads to the maximum possible reduction in coordination of Li(2). This unfavorable monocoordination persists in the transition structure **5**. The trimer transition structure **9** is more favorable in this respect, as Li(2) can bind to another carbon, C(1). Hence, the activation barrier for the trimer is lower than that for the dimer. In the tetramer, several factors are important. First, breaking of the bond between C(2) and Li(2) reduces the Li(2) coordination number to a lesser extent, from 3 in **11** to 2 in **12**. In addition, Li(1) is coordinated by C(3) and a new bond is being formed between C(1) and Li(3) in **12**.

Subsequent Steps. Once the disproportionation reaction has taken place, the mixed aggregates formed can undergo interaggregate exchange to yield methyllithium aggregates and polymeric dilithiomethane.[11] For the case of reaction within the tetrameric aggregate, the hypothetical initial stage of this interaggregate exchange, eq 7b (between two mixed trimers **13** to give a dilithiomethane dimer **14** (Figure 6) and methyllithium tetramer **11**) is almost thermoneutral (ΔE = +0.7 kcal/mol, ΔG = 2.0 kcal/mol). For the reaction within the trimer, the formal exchange between two mixed dimers **10**, to give **14** and two-thirds of a trimer **8**, eq 6b, is exothermic (ΔE = −12.9 kcal/mol, ΔG = −6.6 kcal/mol). Note that the previously published D_{2d} structure **15** for $(CH_2Li_2)_2$,[5b] with four lithiums bridging between the carbon atoms, is 15.0 kcal/mol less stable than **14**, which has only two bridging lithiums. The aggregation energy of dilithiomethane **7** is large: Dimerization of **7** to give **14** is more exothermic (ΔE = −55.2 kcal/mol, ΔG = −34.5 kcal/mol) than dimerization of methyllithium **1** to give **2** (ΔE = −44.0 kcal/mol, ΔG = −28.7 kcal/mol). Subsequent polymerization to give $(\mathbf{7})_n$ will certainly be considerably exothermic as well. Therefore, we expect interaggregate exchange to be more likely than the alternative, H-exchange within the mixed aggregate **13** to give **14**. Other reactions of dilithiomethane, or mixed aggregates with methyllithium, are also possible. Especially at higher temperatures, species like C_3Li_4, LiH, and, finally, C_2Li_2 are obtained,[6] but the reactions leading to these products are beyond the scope of the present study.

Conclusions

The Ziegler pyrolysis of methyllithium is an autometalation reaction, with a mechanism similar to the metalation of alkanes.[12f] The hydrogen transfer is preceded by the breaking of an intraaggregate carbon–lithium bond. The disproportionation takes place within tetrameric methyllithium aggregates, which are indicated to be the predominant species under the reaction conditions. The reaction is slow. We find it to be endothermic and to require considerable activation energy. The loss of methane and, to a lesser extent, the polymerization of the product, dilithiomethane, are the "driving forces". Reactions within methyllithium trimers, present to a lesser extent, or dimers, only present in very small quantities, are less important. These reactions are even more endothermic and, especially in the case of the dimer, have significantly higher activation barriers.

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J. Am. Chem. Soc. **1992**, *114*, 1151–1156

on the Convex C220-256s of the Institut für Organische Chemie, on the Cray Y-MP4/464 of the Leibniz Rechenzentrum München, and on the Cray Y-MP8/832 of the Kernforschungsanlage Jülich. N.J.R.v.E.H. thanks the Alexander von Humboldt Foundation for a research fellowship.

Registry No. 1, 917-54-4; **2**, 74309-22-1; **7**, 21473-62-1; **8**, 74316-42-0; **11**, 20670-26-2.

Supplementary Material Available: Tables of total and relative energies, zero-point vibrational energies, thermochemical corrections, and 6-31G* optimized structures in the form of "archive entries" (7 pages). Ordering information is given on any current masthead page.

Ionized Methyl Formate ($CH_3OCHO^{\cdot+}$) and Its Distonic Isomer (${}^{\cdot}CH_2OC^+HOH$)

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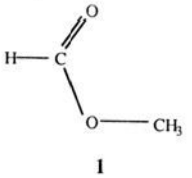
Abstract: Ab initio molecular orbital calculations have been carried out for ionized methyl formate ($CH_3OCHO^{\cdot+}$) and its distonic isomer (${}^{\cdot}CH_2OC^+HOH$). The ground state of ionized methyl formate is ${}^2A'$ (σ) and the lowest energy structure has COCO syn and a staggered methyl group (**2a**). The ${}^2A''$ (π) state (**3**) lies 74 kJ mol^{-1} above the ${}^2A'$ state (**2a**); its preferred conformation also has COCO syn but in this case the methyl group is eclipsed. The two structures of the distonic isomer (**4**) of lowest energy are both asymmetric but may be described approximately as COCO syn and OCOH anti (**4a**) and COCO anti and OCOH syn (**4b**); **4a** lies 62 kJ mol^{-1} *lower* in energy than **2a**. Rearrangement of **2a** to **4** requires 41 kJ mol^{-1}. Vertical ionization of methyl formate produces an ion lying 35 kJ mol^{-1} above **2a**; consequently, rearrangement to the distonic ion **4** only requires a further 6 kJ mol^{-1}. The calculations thus predict that ionization of methyl formate initially produces the σ state of the methyl formate radical cation (**2a**) which may rearrange with a small barrier to the distonic isomer **4**.

Introduction

In recent years, electron spin resonance (ESR) spectroscopy in conjunction with matrix isolation techniques has provided an attractive method for the investigation of organic radical cations.[2] Irradiation at low temperature of dilute solutions of neutral substrates having ionization energies smaller than that of the solvent (typically a freon such as trichlorofluoromethane) gives the corresponding cations. The resulting spectral data can yield valuable information on the molecular and electronic structures of the radical cations, which is not readily attainable from other experimental procedures. Complications can arise, however, because of complexation with the solvent matrix or because of unimolecular rearrangement of the species under examination.[3] A case in point involves ionization of matrix-isolated methyl formate (**1**), the simplest ester, for which agreement has yet to be reached as to the nature of the observed ions.



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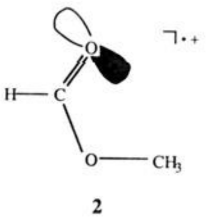

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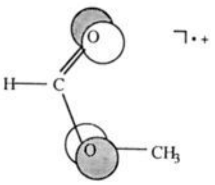
In 1983, Sevilla[4] and Symons[5] and co-workers independently reported that the methyl formate radical cation (**2**) in trichlorofluoromethane forms a stable σ^* complex with a solvent molecule at 77 K and that the complex decomposes on annealing at 140 K, yielding an isolated π-type cation **3**. Evidence in support of **3** was provided by INDO calculations of the spin density.[4]



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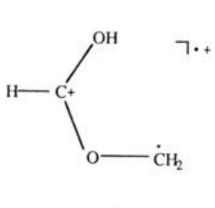
In a subsequent paper, Iwasaki and co-workers[6] also proposed that the primary radical cation has the π structure (**3**) but argued that it is produced directly from the σ radical (**2**) at 4 K without the intervention of a σ^* complex with the matrix. In addition, these authors argued, on the basis of proton hyperfine coupling constants, that **3** readily converts into the carbon-centered radical ion **4** via a McLafferty-type rearrangement upon warming from 4 K to 77 K.



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There has been vigorous discussion[7] of the reasons for the differing interpretations of the experimental data. The most recent

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