Journal of Organometallic Chemistry, 375 (1989) C17–C19
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20187PC

Preliminary communication

The extent of aggregation of air-sensitive alkyllithium compounds as determined by fast-atom-bombardment mass spectrometry

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(Received June 23rd, 1989)

Abstract

Fast-atom-bombardment mass spectrometry provides direct experimental evidence for the degree of aggregation of alkyllithium compounds in solution: 2-(2-methylpropyl)lithium is tetrameric in Nujol, whereas butyllithium is hexameric.

Although alkyllithium compounds are widely used as synthetic reagents, their nature (in particular, the degree of aggregation) in solution is still poorly defined [1]. The majority of studies rely on either calorimetry [2,3] or multinuclear NMR spectroscopy [4,5] as the primary experimental probes. We demonstrate here that fast-atom-bombardment mass spectrometry (FAB-MS) can be used as a direct means of detecting which molecular species are present in solution.

Previous studies of alkyllithium (RLi) compounds by mass spectrometry have been primarily by electron-impact mass spectrometry (EI-MS) [5–7]: no molecular ions were detected, but it has been generally accepted that an n-mer $(RLi)_n$ will produce the cation $[(RLi)_{n-1}Li]^+$, which then exhibits sequential loss of neutral RLi species. The only published FAB-MS study of alkyllithium compounds [8] failed to detect any alkyllithium species.

As many alkyllithiums are involatile, thermally unstable, and extremely air-sensitive, we have specially designed and constructed an anaerobic direct-insertion probe for use with the "soft" ionization technique of FAB. By use of this probe, solutions of 2-(2-methylpropyl)lithium (Me_3CLi) and butyllithium (BuLi) in Nujol were inserted into the mass spectrometer, and their positive-ion FAB mass spectra obtained using a xenon atom beam at 7 kV: the experimental spectrum for the former sample is illustrated in Fig. 1, and the spectra of both samples are assigned in Table 1. It has been observed [9], for a wide range of halometallate salts $A_x[MX_n]$ ($X = Cl$ or Br; x, n = integers), that the "molecular ion" in the FAB mass spectrum is stabilized by the addition of an extra cation, producing $[A_{x+1}(MX_n)]^+$ as the highest observed species. The same phenomenon is noted for the alkyllithium

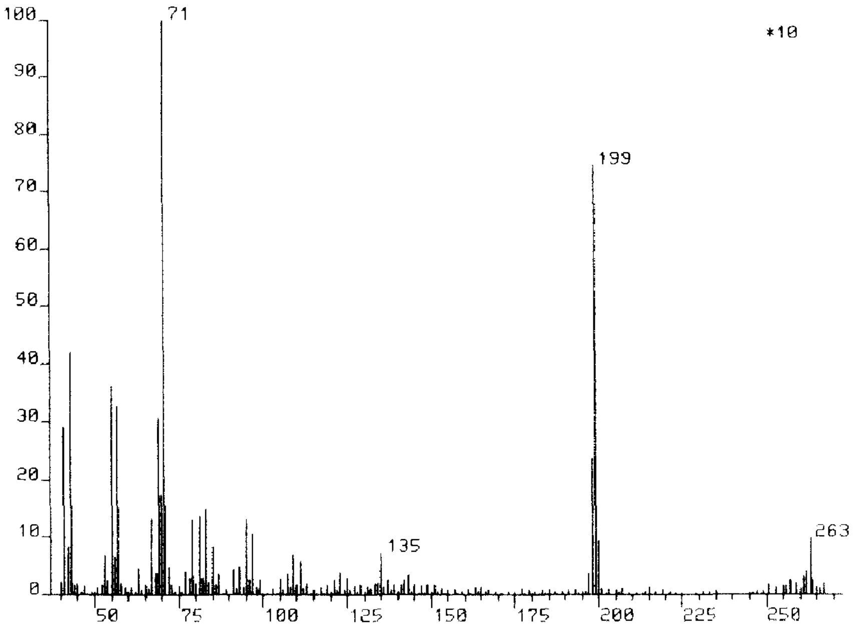

Fig. 1. The experimental FAB mass spectrum (uncorrected) of 2-(2-methylpropyl)lithium in Nujol.

Table 1

Assignments of the FAB mass spectra for two alkyllithium compounds dissolved in Nujol

m/z	Ion	Relative intensity (%)	
		R = Bu	R = CMe_3
392	$[(RLi)_6Li]^+$	8	–
327	$[(RLi)_5Li]^+$	8	–
263	$[(RLi)_4Li]^+$	7	1
199	$[(RLi)_3Li]^+$	35	75
135	$[(RLi)_2Li]^+$	14	8
71	$[(RLi)Li]^+$	100	100

compounds, *n*-mers producing ions corresponding to $[(RLi)_nLi]^+$, which then exhibit sequential loss of RLi. In contrast to observations in the EI-MS studies [5–7], no initial loss of an alkyl radical was observed. Thus, 2-(2-methylpropyl)lithium exists as a tetramer in Nujol, whereas butyllithium exists as a hexamer.

Acknowledgements. We are indebted to the Iraqi government for the award of a research scholarship (A.K.A.-S.), and to the Venture Research Unit (BP) for their support.

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