

**THE REACTIVITY OF LINEAR ALKYL
CARBONATES TOWARD METALLIC LITHIUM:
INFRARED REFLECTION ABSORPTION
SPECTROSCOPIC STUDIES IN ULTRAHIGH
VACUUM**

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Introduction

The reactivity of clean Li foils toward dimethyl-, diethyl-, and ethyl-methyl carbonates (DMC, DEC and EMC, respectively) has been examined by infrared reflection absorption spectroscopy (IRAS) in UHV. This work complements an analogous investigation reported recently involving propylene carbonate (PC). A rather general reaction mechanism for the Li metal-induced decomposition of both linear and cyclic carbonates has been deduced, which may be of relevance to Li passive films formed in electrochemical environments.

Results and Discussion

A. Diethyl carbonate - The $-\Delta R/R$ IRAS spectrum obtained after dosing diethyl carbonate (DEC) onto a clean Li foil surface, using the spectrum of the clean Li surface as a reference, is shown in curve A, Fig. 1. The peaks in the regions 800 - 1500 cm^{-1} and 2700 - 3000 cm^{-1} can be ascribed to C-O stretching (1065 and 1125 cm^{-1}), C-H bending (886 and 1384 cm^{-1}), and C-H stretching modes (2703, 2818, 2849, and 2953 cm^{-1}), whereas the somewhat less intense features at 1320 and 1650 cm^{-1} are associated with CO_2 symmetric and asymmetric stretching typically attributed to Li alkyl carbonate-type species. Prominently absent from this spectrum are peaks attributed to intact DEC, indicating the absence of unreacted material on the surface, and also the rather strong bands at 875 and 1530 cm^{-1} , characteristic of Li_2CO_3 . Insight into the identity of the species formed by the reaction of DEC with Li was obtained from results obtained in similar experiments in which either a clean Li film or foil was dosed with gas-phase ethanol (as opposed to DEC) shown in curve C, Fig. 1 to yield the corresponding Li alkoxide according to the mechanism:



B. Dimethyl Carbonate - Li foils exposed to DMC (see curve A and B, respectively, in Fig. 2) and Li films supported on Ni(poly) exposed to methanol (see curve C in Fig. 2) yielded virtually identical IRAS spectra consistent with the formation of Li methoxide as the only detectable product.

C. Ethyl-methyl Carbonate - Evidence for a rather general reaction pattern could be gleaned from the data obtained with ethyl-methyl carbonate (EMC), the only asymmetric alkyl carbonate examined in this study. Li foils exposed to EMC yielded IRAS spectra (see curve A, Fig. 3), displaying features consistent with a mixture of Li ethoxide (see Curve D), Li ethyl carbonate, and Li methoxide (see curve C), as judged by the broadening of the feature at 1068 cm^{-1} , and also by the assignment of the series of bands in the C-H and C-O stretching, as well as the C-H bending regions. As was the case with DMC and DEC, no spectral evidence could be found for the

presence of neat material, Li alkyl carbonates or Li_2CO_3 upon dosing thin Li films with EMC (Curve B Fig. 3).

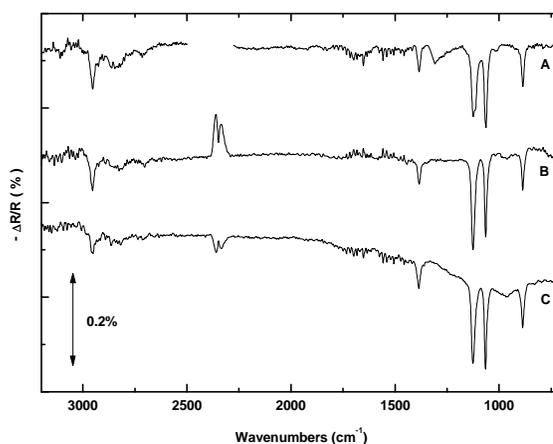


Fig. 1. IRAS spectra of both Li foil (curve A) and Li/Ni (curve B) surfaces exposed to DEC and of a Li/Ni surface exposed to ethanol (curve C). (See text for details)

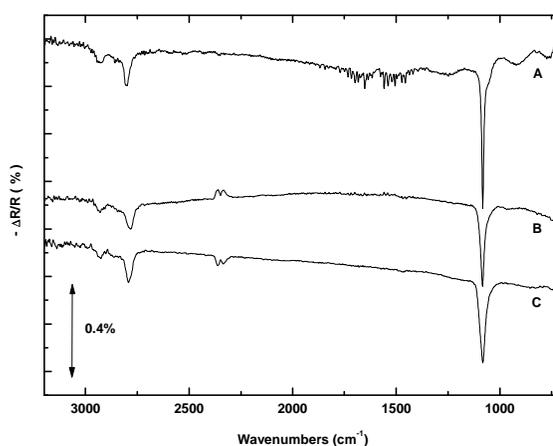


Fig. 2. IRAS spectra of both Li foil (curve A) and Li/Ni (curve B) surfaces exposed to DMC and of a Li/Ni surface exposed to methanol (curve C).

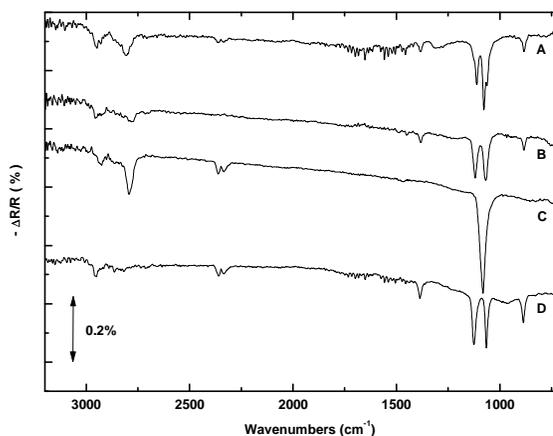


Fig. 3. IRAS spectra of both Li foil (curve A) and Li/Ni (curve B) surfaces exposed to EMC and of a Li/Ni surface exposed to methanol (curve C) and ethanol (curve D).

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References

- Rendek, L. J.; Chottiner, G. S.; Scherson, D. A. *Langmuir* **2001**, *17*, 849-851.