

AGGREGATION OF α -LITHIO ESTERS OF CARBOXYLIC ACIDS

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The degree of aggregation of the α -lithio esters of carboxylic acids in solutions was determined by vapour phase osmometry. These compounds were found to form oligomeric aggregates whose size depends on the structure of the ester and on the solvent, similarly to the other organolithium compounds.

Lithium forms readily coordination bonds, most frequently having the coordination number four. This tendency is reflected in the case of alkyllithium compounds in the formation of oligomeric aggregates by means of electrondeficient bonds¹. Aggregation also occurs in lithium alkoxides; in this case however free electron pairs of oxygen participate in the coordination^{2,3}. Recently, some α -lithio esters of carboxylic acids have been prepared in pure state⁴; these compounds are intermediates of a number of important synthetic⁵ or polymerization⁶ reactions. This paper is an attempt to answer the question whether aggregation takes place also in the above compounds, which contain the donor atom of a different type.

Molecular weights of the organolithium compounds used in this work were determined by vapour phase osmometry at 25°C in benzene and tetrahydrofuran solutions. Since these compounds are very sensitive toward the atmosphere, an apparatus for measurements in an inert medium was used³; the other operations were also carried out in argon atmosphere. The measurements were made as described in ref.³, each time 10 minutes after dissolution at the utmost. As in most cases the autocondensation half-times of the lithio esters used considerably exceeded one hour⁷, the effect of this reaction in the measurements of their molecular weights can be neglected. The degree of aggregation as the ratio of the determined and calculated molecular weight (error ± 0.1) was determined for six different concentrations of the solutions (the range is given in Table I).

It follows from the results (Table I) that the esters of α -lithioisobutyric acid are aggregated in their solutions to a various degree. The degree of aggregation found in weakly solvating benzene was higher than that found in strongly solvating tetrahydrofuran. Compared to other esters of α -lithioisobutyric acid, the sterically bulkier tert-butyl ester showed a lower degree of aggregation. In the concentration range examined here the degree of aggregation varied within the limits of experimental error only. In these respects the aggregation of the lithio esters resembles that of the alkyllithium compounds or of the alkoxides of alkaline metals.

Compared to the parent ester, the infrared spectrum of the respective lithio ester exhibited, among others, also frequency shifts of the carbonyl vibrations (decrease), combination vibrations of the $(O)=C-O$ bond (increase), and similar vibrations of the $(C=O)-O-C$ bond (decrease)⁴. Qualitatively similar shifts were observed by Lappert⁸ for adducts of the esters of carboxylic acids with metal halides; he inferred therefrom that the carbonyl group takes part in the coordination. Although the comparison is more difficult for the lithio esters, we believe that in this case too the coordination of the alkoxy oxygen is less likely.

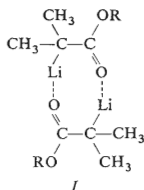


TABLE I

Degree of Aggregation (r_a) of Some Organolithium Compounds

(r_a = mol. weight found/mol. weight calculated; determined for at least six concentrations (mol/kg solvent)).

| Compound | Benzene | Tetrahydrofuran |
|--|--------------------|---------------------------------|
| $(CH_3)_2CLiCOOCH_3$ | insoluble | 3.5 (0.07–0.34) |
| $(CH_3)_2CLiCOOC_2H_5$ | 6.6 (0.10–0.42) | 3.5 (0.05–0.31) |
| $(CH_3)_2CLiCOOC(CH_3)_3$ | insoluble | 2.3 (0.05–0.26) |
| $(CH_3)_2C \begin{array}{c} \\ COOC(CH_3)_3 \end{array} - CH_2 - CH_2 - C(CH_3)_2 \begin{array}{c} \\ COOC(CH_3)_3 \end{array} Li \cdot THF$ | — | 1.7 ^a (0.06–0.07) |
| $[(CH_3)_2CLiCOOC(CH_3)_3 \cdot (CH_3)_3COLi]$ | 2.8 (0.06–0.30) | 1.8 (0.03–0.30) |
| $[C_4H_9Li \cdot (CH_3)_3COLi]$ | 3.7 (0.10–0.40) | 1.8 (0.05–0.25) |

^a Determined at two concentrations only.

Some more information is certainly needed to determine the structure of even the simplest aggregate of lithio esters, namely, a dimer, which is obviously present, e.g., in a tetrahydrofuran solution of tert-butyl α -lithioisobutyrate. One of the possible structures may be adequately represented by I (R = tert-butyl), from which other forms may be derived by electron shifts.

The problem of aggregation of the lithio derivatives of β -dicarboxylic esters was interesting because of their structure. It was deduced from the spectral data on di-tert-butyl- α -lithio- α,α',α' -trimethylglutarate that lithium reacts not only with the adjacent carbalkoxyl group, but with both of them⁴. It follows from the molecular weight found for this lithio ester that it is aggregated in solution, at least in part (Table I), and that lithium is therefore coordinated both intra- and intermolecularly.

Lithium alkoxides form adducts with the organolithium compounds, as has been described for lithio esters⁴ or for alkylolithium compounds⁹. Now it has been demonstrated for both these cases that the adducts form aggregates of a higher order (Table I), so that the coordination power of lithium is not fully exhausted by the formation of an adduct.

REFERENCES

1. Coates G. E., Green M. L. H., Wade K.: *Organometallic Compounds*, Vol. I, p. 35. Methuen, London 1967.
2. Golovanov I. B., Simonov A. P., Piskunov A. K., Talalajeva T. V., Careva G. V., Kočeškov K. A.: *Dokl. Akad. Nauk SSSR* 149, 835 (1963).
3. Halaška V., Lochmann L., Lím D.: *This Journal* 33, 3245 (1968).
4. Lochmann L., Lím D.: *J. Organometal. Chem.* 50, 9 (1973).
5. Plešek J., Zobáčková A.: *Preparativní reakce v organické chemii*, Part V, p. 646. Published by Nakladatelství ČSAV, Prague 1960.
6. Reich L., Schindler A.: *Polymerization by Organometallic Compounds*, p. 569. Interscience, New York 1966.
7. Lochmann L., Rodová M., Petránek J., Lím D.: Unpublished results.
8. Lappert M. F.: *J. Chem. Soc.* 1961, 817.
9. Lochmann L., Pospíšil J., Vodňanský J., Trekoval J., Lím D.: *This Journal* 30, 2187 (1965).

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