INDUSTRIAL APPLICATIONS OF THE ORGANOMETALLIC COMPOUNDS

J.H. HARWOOD

Industrial Applications of the Organometallic Compounds

A LITERATURE SURVEY

J. H. Harwood

Research Manager, Peter Spence
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PREFACE

THIS WORK originated in a series of fourteen articles contributed to *The Industrial Chemist* in 1959–60. The interest taken in them and the correspondence which followed led to several suggestions that the subject matter ought to be expanded, more completely referenced and put into book form. After pressure from various sources this has been done. The literature information has been brought as up to date as possible and the articles completely rewritten and expanded to many times their original size. Mention is made of some of the more important literature references that have arisen while the work has been going through the Press (Appendix II). The background of organometallic chemistry is growing so rapidly that it was considered advantageous to give, as far as possible, complete coverage to three major groups of compounds, the metal alkyls, alkoxides and chelated compounds. The original articles included other groups of compounds such as carboxylates, nitrogen and phosphorus derivatives.

The book has been compiled and indexed primarily for the industrialist. Theoretical discussion and complete surveys of all the compounds of an element have not been attempted since several excellent books already give very adequate coverage:

Rochow, E. G., Hurd, T. D., Lewis, R. N., *The Chemistry of Organometallic Compounds*, 344 pp.; John Wiley & Sons Inc., N.Y. (1957).

Zeiss, H., (editor), *Organometallic Chemistry*, 549 pp.; Reinhold Publishing Corp., N.Y. (1960).

Coates, G. E., *Organometallic Compounds*, 366 pp.; Methuen & Co. Ltd., London (1960).

Mortell, A. E., Calvin, M., *Chemistry of the Metal Chelates*, 613 pp.; Prentice Hall Inc., N.Y. (1959).

Metal Organic Compounds, Advances in Chemistry Series No. 23, 371 pp.; American Chemical Society (1959).

Critical discussion of periodical and patent information has only been undertaken in those sections in which personal knowledge and background is adequate to justify a reasoned judgement. As complete as possible assessment of the literature and patents of the last ten years has been provided in order that the reader can rapidly assess whether organometallic compounds are likely to provide a solution to any particular problem and to enable him to determine the 'state of the art' with extensive literature references in one volume. For the reader's convenience, addresses of companies referred to in the text have been collected in Appendix I.

The Periodic Group system has been used as a convenient method of systematisation. In three main sections, the alkyls, alkoxides and chelates are discussed following the Periodic classification. The decision on which elements should be omitted as non-metals caused considerable thought. It was eventually decided to make the scope as wide as possible and to include all the elements with the exception of the permanent gases, boron, carbon, silicon, phosphorus and the halogens.

References have been given as fully as possible with the date of publication of patents. Where corresponding patents in different countries were located they have been given, but the absence of corresponding patents should not be presumed if none are listed. The labour involved in checking each patent quoted for corresponding ones in other countries would obviously be enormous and it is only where the literature survey work has brought the correspondence out that they have been quoted. Temperatures throughout the book are given in degrees Centigrade.

The system of nomenclature to be adopted presented several problems. The majority of names used for the compounds follow the *Handbook for Chemical Society Authors* (The Chemical Society, London, 1961) based on the current recommendations of the International Union of Pure and Applied Chemistry. In many instances this nomenclature differs from accepted commercial practice but is not likely to cause confusion. The only notable exception is in the case of the acetylacetone derivatives in which the acetylacetonate terminology has been retained.

This book is the first attempt to describe the industrial applications of a rapidly growing new field of chemistry. Although every care has been taken to ensure accuracy the author would be grateful to hear of any errors which may have passed unnoticed, and would be very pleased to supply any additional information at his disposal to readers interested in a particular problem.

A useful survey of current information subsequent to this work may be found in the abstracts on Organometallic Compounds published monthly by Translation and Technical Information Services, 32 Manaton Road, London, S.E.15.

The assistance of a colleague, Mr. L. Williams and of former colleagues Mr. R. Sidlow and Mr. J. L. Ireland, and of Dr. A. Ledwith of the University of Liverpool in checking and correcting the manuscript and proofs, and for offering valuable suggestions on the contents and format is gratefully acknowledged. Dr. J. Hoy Robertson, editor of *The Industrial Chemist*, commissioned the original articles and put forward the suggestion that they ought to be expanded into book form.

J. H. HARWOOD

Peter Spence & Sons Limited,
Widnes, Lancs.

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SECTION ONE

Compounds containing a direct metal–carbon link

INTRODUCTION

To the purist, these are the true organometallic compounds and contain an alkyl or aryl group directly linked through a carbon bond to the metal. Typical compounds are n-amyl sodium, $C_5H_{11}Na$, and triethyl aluminium $(C_2H_5)_3Al$. Many such compounds exist and recently a great deal of interest has been focused on the cyclopentadiene compounds. The recommended standard nomenclature is to place the organic radical first, but in the industrial literature it is almost more frequent to find this reversed, that is sodium amyl instead of amyl sodium. Throughout this section standard nomenclature has been adopted.

Early industrial interest in these compounds was centred round the development in 1923 of tetraethyl lead as an antiknock additive for petrol. Until the Ziegler–Natta discovery of their application as catalysts for the low pressure polymerisation of olefins, there was no other commercial production. A vast number of patents now covers all types of combinations of alkyl and aryl compounds and metal salt co-catalysts. Should any new system prove to have substantial advantages over the established alkyl aluminium–titanium tetrachloride combination, the potential is obviously very large. The alkyl metals are often readily prepared but many are spontaneously inflammable or even explosive, and their production on a large scale has been delayed until the handling techniques had developed to the extent that they could be prepared and transported in safety.

Grignard compounds or organomagnesium halides have been known for over 50 years but have normally been prepared on site for immediate use. Of recent years increasing industrial demand has led to their appearance on the market in special packs.

The remarkably stable cyclopentadiene (ferrocene) type compounds are the most recent discovery and within a few years of the discovery of the parent compounds, the number of derivatives is enormous and the compounds are likely to have widespread application in the industrial chemistry of the future. Methylcyclopentadienyl manganese tricarbonyl is now in commercial production as an antiknock supplement. Other cyclopentadienyl metal compounds are being developed as catalysts and as a means of depositing the metal on suitable surfaces such as other metals, resin, glass or plastics to form metallic mirrors, printed electrical circuits and protective coatings.

The objective has been to provide as complete as possible information about recent developments in the field. The literature relating to the alkyl aluminium compounds in particular as polymerisation catalysts is, however, so extensive that it has been impossible to do more than present a summary with reference to the major reviews available. Adequate treatment would demand a separate book.

1.1. GROUP IA

Lithium, Sodium, Potassium, Rubidium, Caesium

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Introduction

All the alkyl and aryl compounds of the alkali metals are highly reactive compounds; their methods of preparation, chemical reactions, and industrial applications are very similar. Simple alkyls and aryls are solids, soluble in organic solvents, which cannot be melted without decomposition. In many ways the alkyl alkali metal compounds behave as salts owing to the ionic character of the metal–carbon bond. This ionic character increases from lithium to caesium; their chemical reactivity also increases in the same order. Complex salts can be formed; these dissociate to form conducting solutions in some special solvents.

Preparation is relatively straightforward provided that a dry, inert atmosphere is used. The finely dispersed metal is reacted with the alkyl chloride in benzene or petroleum ether:

$$RCl + 2M \rightarrow RM + MCl.$$

This reaction represents an intermediate stage in the well-known Wurtz reaction and the secondary reaction:

$$RM + RCl \rightarrow RR + MCl$$

may greatly decrease the yield of alkyl metal.

Both the alkyl chloride and the alkyl metal are soluble in the solvents used and separation is difficult, but frequently unnecessary, since the products are generally made as intermediates in organic synthesis. An extensive range of alkyls is known and there is a considerable literature covering their preparation, properties, and industrial applications.

Lithium

Organolithium compounds have been known for many years and a very wide range of them has been prepared. Apart from the lithium soaps it is only recently that any commercial processes for their utilisation have been developed; for example, alkyl lithiums were first offered on a production scale in 1958.

Several general articles and information summaries are available. Lithium Corporation of the U.S.A. have published a book *Organolithium Compounds in Organic Synthesis*, to which a series of supplements has been added. Foote Mineral Co. cover the industrial uses of lithium organic compounds in a series of publications (1). The preparation of a wide range of lithium derivatives is described (2), and developments up to 1950 (3) and 1955 (4) are reviewed.

ALKYL COMPOUNDS

Preparation

Alkyl compounds of the alkali metals are considerably different in character from the covalently-bonded alkyl compounds of the majority of the other elements. Alkyls of alkali elements of greater atomic weight are salt-like in character, with the alkyl lithiums representing an intermediate stage.

Preparation of alkyl lithiums is relatively easy if care is taken to carry out the reactions in a dry, inert atmosphere. The most generally applicable method is to treat lithium metal with the corresponding alkyl chloride in a suitable solvent. Ether is generally used, with benzene and cyclohexane available as useful alternatives when it is desired to slow down the rate of reaction. As both the alkyl lithium (with the exception of the higher compounds) and lithium chloride are insoluble in the solvents used, separation is difficult, but in many cases, and when they are used for the synthesis of other compounds, it is not necessary. If it is desired to isolate the alkyl compound, reaction between lithium metal and the alkyl of a less reactive metal such as mercury, or with a Grignard reagent is a useful process.

Preparations of n-butyl, n-propyl, n-amyl and n-hexyl lithium in about 80% yield (5) and of pure crystalline ethyl lithium (6) are described. Manufacture is relatively simple in the case of the n-butyl derivative, butyl chloride is added to a suspension of finely divided lithium metal in an inert solvent over a 4 to 8 hour period. Reaction is vigorous and the mixture must be cooled; a yield of 75–85% is obtained. n-Heptane is normally used as the solvent to avoid the disadvantages of using ether. The solution (2·5 M) is very stable and can be stored at room temperatures for indefinite periods without decomposition, and handled without difficulty in a nitrogen, argon, or helium atmosphere.

n-Butyl lithium is now being produced by Lithium Corporation in a specially blended paraffin wax medium instead of in hydrocarbon solutions. The product is non-inflammable and more convenient to store, transport and use, and is sold as cast sticks 5 inches long and 1 inch diameter, containing 20 or 30% by weight of n-butyl lithium. The sticks can be cut and handled in air for up to 2 hours without significant loss of activity, are non-pyrophoric and will not ignite even when immersed in liquid water. They are shipped under an inert gas in hermetically sealed drums. Foote Mineral Co. offer both n-butyl and s-butyl lithium as 15% solutions in a solvent. At this concentration the solution is safe to handle and store (125).

Commercial Availability

When n-butyl lithium was initially offered at the end of 1958 in pilot plant quantities by the Lithium Corporation of U.S.A., the price was $100 a lb., but it was announced in August 1959 that the price in production quantities in 500 lb. returnable containers had been cut to $18.50 a lb.

In March 1960 the price was reduced to $12.00 a lb., and in September 1960 to $9.00 a lb. It is sold as a 22% solution in commercial heptane or in pure n-heptane at an extra $2.50 a lb. The rapid drop in price is due to the growing demand as a catalyst; the present cost is considerably below the original figure of $30.00 a lb. envisaged for bulk production.

Lithium Corporation started up a second unit in February, 1961, bringing their total capacity to 150,000 lb. a year. Foote Mineral Co. are constructing a 100,000 lb. a year unit and American Potash & Chemical Co. has a 75,000 lb. a year plant. Production of other alkyl and aryl compounds is intended. In the U.K. n-butyl lithium has been offered by Pfizer Ltd., and by Borax and Chemicals Ltd.

COMMERCIAL APPLICATIONS

Polymerisation Catalysts

This represents the main industrial development of alkyl and aryl lithiums. Prior to 1958 there was little use of these compounds (7), the table shows how rapidly interest has developed.

Year	*Major articles*	*Patents*	*Total*
1958	3	4	7
1959	9	13	22
1960	14	36	50

Various organolithium compounds such as the methyl, ethyl, butyl, dodecyl, phenyl, *p*-tolyl, mesityl, 1-naphthyl and benzyl were treated with titanium tetrachloride in equal weight ratios giving a series of catalysts which made it possible to carry out the polymerisation of ethylene at temperatures between −75° and +55° (8). Low and atmospheric pressure polymerisation of ethylene using catalysts prepared from n-butyl or iso-amyl lithium and titanium tetrachloride has been studied; efficiency depends on the molecular ratio of the alkyl to titanium tetrachloride (9). In the patent literature a number of different combinations of catalysts are claimed.

$nBuLi + TiCl_4$ Brit. 797,344 (Imperial Chemical Industries Ltd.), 9.4.54.

nBuLi + dicyclopentadienyl zirconium dichloride U.S. 2,924,593 (Hercules Powder Co.), 9.2.60.

Alkyl lithiums + (Co, Al, Mg, Pb or Zn) acetylacetonate U.S. 2,921,060 (Sun Oil Co.), 12.1.60.

nBu, benzyl or phenyl $Li + TiCl_3$ Brit. 829,098 (Distillers Co. Ltd.), 10.8.55.

$AmLi + FeCl_3$ Brit. 826,638 (K. Ziegler), 7.11.55.

Efficiency of a mixed catalyst of n-butyl lithium and titanium tetrachloride in the low pressure polymerisation of propylene is at a maximum at molecular ratios from 2·5 to 1·8 with sharp drops on both sides. There was another peak at the ratio of 1·1 but this polymer was largely atactic; in the range 2·5 to 1·8 the polymer was 60% isotactic. Using the optimum ratio the polypropylene had a molecular weight of 215,000; the molecular weight of the isotactic fraction was 141,000 (10). The proportion of isotactic polypropylene obtained is much greater than that with amyl sodium (11). Patents claim the use of a C_3–C_5 alkyl lithium with titanium tetrachloride (12) and also a mixture of butyl lithium, ethyl aluminium and titanium tetrachloride (13), both yielding crystalline polypropylene.