In recent years, numerous papers have appeared on the use of dithiocarbamates as analytical reagents. As has been known for some time, these compounds possess the important property of being able to form complexes with many metal ions. These reactions, the basis of the analytical application of dithiocarbamates, have been the subject of a recent comprehensive review.

The purpose of the present review is to discuss recent contributions to our knowledge of the other important physical and chemical properties of dithiocarbamates (I). Nearly all the papers on these compounds have dealt solely with the properties of dialkyldithiocarbamates and little mention has been made of the properties of monoalkyldithiocarbamates. This is perhaps because of the general instability of monoalkyldithiocarbamates and their complexes, as a result of which they have found little use analytically. In this review, it is intended, wherever possible, to compare the properties of mono- and dialkyldithiocarbamates.

* Present Address: Analytical Chemistry Department, University of Chemical Industries, Veszprém, Hungary.
Dithiocarbamates are formed by the exothermic reaction between carbon disulphide and either ammonia or a primary or secondary amine in the presence of a base. The base may be an alkali such as sodium hydroxide or excess of the amine. The kinetics and mechanism of the formation of dithiocarbamates have been studied. The rate of formation is inversely proportional to the pH and it is believed to follow a mechanism that is the reverse of the decomposition in acid media.

Ammonium dithiocarbamate is produced by the reaction of ammonia and carbon disulphide. The free dithiocarbamic acid can be obtained by treatment of the ammonium dithiocarbamate with cold acid. It is, however, unstable and decomposes to thiocyanic acid and hydrogen sulphide.

Monoalkyl dithiocarbamates are formed from the exothermic reaction between carbon disulphide and a monoalkylamine; they decompose, however, on long standing in alkali. No such difficulty is experienced in the preparation of dialkyl dithiocarbamates.

If a diamine such as ethylene diamine is used, a molecule with dithiocarbamate groups at either end can be obtained [e.g. disodium ethylenedibisdithiocarbamate (IV)].

The preparation of many dithiocarbamates from more complicated amino-compounds has been described; for these, special conditions are often necessary.

The sodium salts are extremely soluble in water and quite soluble in ethanol, but relatively insoluble in non-polar solvents such as ether and chloroform. Most of the sodium salts are hydrated.

Stability in acidic and alkaline solution

The free acids, which are formed from dithiocarbamates in acidic media, are generally unstable; diphenyldithiocarbamic acid is, however, said to be stable. Martin first showed the importance of the decomposition of diethyldithiocarbamic acid in the development of methods based on diethyldithiocarbamate as an analytical reagent; previously methods had been published which advocated the use of diethyldithiocarbamate at low pH. However, Bode was the first to examine quantitatively the acid decomposition of sodium diethyldithiocarbamate. He found that the decomposition at constant pH was first order and that the rate