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Review

Mercarbide: An unusual organomercury polymer

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Contents

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ABSTRACT

Mercarbide $[CHg_4O_2](OH)_2$, is a mercury derivative of ethane in which all of the ethane hydrogen atoms are substituted by mercury atoms. Mercarbide exhibits basic and anion exchange properties in addition to showing unique stability towards mineral acids as well as oxidizing and reducing agents. The selectivity of mercarbide towards organic anions shows selectivity dependence on the size and configuration of the pendant hydrocarbon group. Titration of mercarbide with Hammett indicators shows that mercarbide in its hydroxide form is a solid base with sites allocation $7.2 < H_0 < 26.5$. Studies of the catalytic activity of mercarbide towards alcohol oxyethylation and aldol condensation show that it functions as a homogeneous basic catalyst, but with increased activity owing to the higher basicity of its active sites. The present paper reviews the synthesis, structure, physicochemical, and catalytic properties of mercarbide.

1. Introduction

Mercarbide is a unique example of a completely mercurated polymeric organic compound with a venerable scientific history dating back to the middle of 19th century. Since that time it has been a subject of research for many scientists, especially Hofmann [1], in honor of whom mercarbide is frequently called "Hofmann's base". A 1921 review [2] stated that mercarbide was the most studied mercury derivative. However, for the next nearly half century, almost nothing further was published on mercarbide. Then in the 1960s papers devoted to the ion exchange properties of mercarbide began to appear [3,4]. These ion exchange properties motivated structural studies on mercarbide [5,6]. Another hiatus in mercarbide publications then occurred. During the last two decades, mercarbide structure has received much attention and a number of reviews were published [7,8]. Today the main interest in mercarbide is its use as a marker in biological research for the statistical processing of electron micrographs of molecular objects modified by electron-dense labels containing mercury. This provides a method for the study of the size, degree of modification, and heterogeneity of objects [9,10].

The scientific interest in mercarbide arises from its unique properties and amazing stability. Thus mercarbide does not undergo changes in the presence of acids and bases and is stable towards oxidizing and reducing agents. Even long heating in HNO_3/HCl does not result in visible changes in its structure. However, the mercury present in mercarbide limits its development for industrial applications, especially with the present-day ecological limits.

The present paper discusses applications of mercarbide as a sorbent and a solid basic catalyst including the adsorption properties; the concentration, intensity, and origin of surface basic sites; and the catalytic activity and selectivity in oxyethylation and aldol condensation reactions.

2. Formation of mercarbide: the polymercuration of organic compounds

The mechanism for mercarbide formation by polymercuration of alcohol involves stepwise replacement of protons by hydrox-

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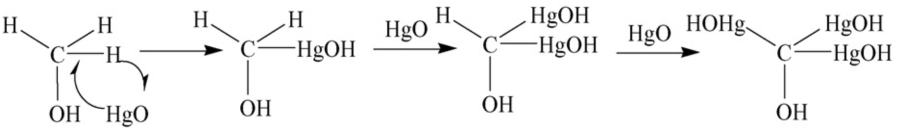
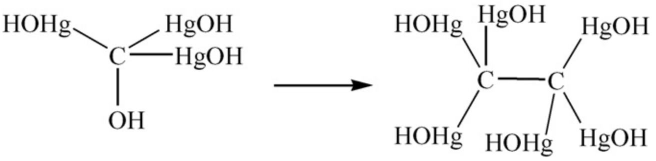
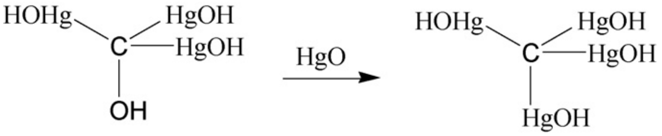
ymercuri groups according to Eq. (1).


(1)

The trimercurated product then undergoes still further mercuration resulting in tetramercurimethane as well as hexamercuriethane (Eqs. (2a) and (2b)).

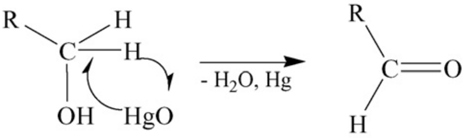

(2a)


(2b)

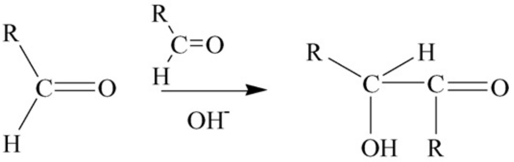
The concurrent formation of ethane and methane derivatives suggest the possibility of different structures for mercarbide [3–6]. However, formation of a polymer containing predominantly a tetrahedral arrangement of four mercury atoms around a carbon atom is observed.

Formation of the polymeric carbon—mercury framework of mercarbide may be observed using a variety of organic substances as starting materials for the polymercuration reaction. Table 1 shows the yields of mercarbide from the reaction of red mercury oxide with various organic substrates.

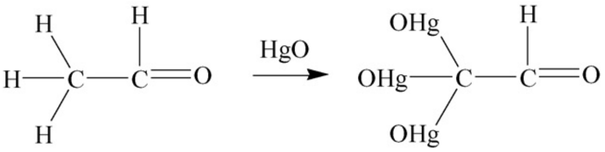
Rather low conversion for alcohols and significantly low conversion for aldehydes can be explained through the side reaction of the aldol condensation. In the initial moment of the reaction the conversion of an alcohol into an aldehyde takes place (Eq. (3)).


(3)

Subsequent base-catalyzed aldol condensation of the aldehyde or ketone (Eq. (4)) then prevents mercarbide formation since aldol condensation is much faster than mercuration. The lowest selectivity is observed for formaldehyde.


(4)

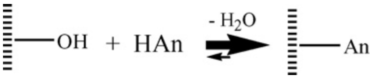
Mercuration of acetaldehyde proceeds through the triply mercurated derivative (Eq. (5)).


(5)

The formation of the corresponding aldehydes and their subsequent aldol condensation, oligomeriazation and resinification are observed for the alcohols. Thus, the selectivity of mercarbide formation via various organic substrates is determined by the rates of the parallel reactions of mercuration and carbonyl group formation as well as by the rates of successive condensation reactions.

3. Ion exchange properties of mercarbide

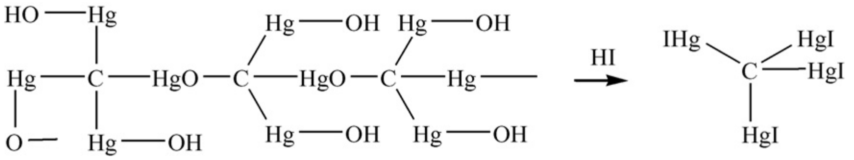
Mercarbide in its hydroxide form is a solid polymeric base with a positive charge, which is localized on the Hg atoms. The positive charge is balanced by the negatively charged hydroxyl ions. In the titration of solid bases it is necessary to consider whether the basic sites located in interior cavities of the polymeric solid can be reached by the acid molecules. If the anion of the acid is bulky then it cannot penetrate the interior of the polymer. For the studied mercarbides the equilibrium in titration is shifted towards the salt form formation (Eq. (6)).


(6)

The selectivity of hydroxymercarbide towards inorganic anions increases in the following sequence:

$NO_3^- < Cl^- < Br^- < OH^- < CN^- \ll I^-$

This anion sequence of selectivity for mercarbide differs from such sequences for other solid bases, for which the selectivity is correlated with the anion radius [11–13]. The selectivity of mercarbide is especially high for iodide ions. This relates to total replacement of hydroxide ions with iodine ions thereby destroying the polymeric mercarbide framework to give the molecular tetramercurated methane derivative $C(HgI)_4$ (Eq. (7)).


(7)

The formation of $C(HgI)_4$ occurs in the presence of HI acid as well as in the presence of the iodide ions. For comparison, for destruction of polymer and obtaining of completely substituted chloride product the solution of hydrochloric acid, with concentration not less than 5 mol/l, is required.

The following tetramercurated methane fragment $CHg_4O(OH)_2$ is found in the polymeric structure of mercarbide:

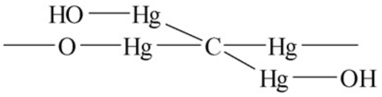
Table 1
The conversion of mercury oxide to mercarbide, %.

Alcohols

CH_3OH	C_2H_5OH	C_3H_7OH	i-C_3H_7OH	C_4H_9OH	$C_7H_{15}OH$	3-$C_7H_{15}OH$	$C_{12}H_{25}OH$
<0.5	55.11	34.87	41.01	14.96	2.43	4.62	<0.5

Aldehydes and ketones

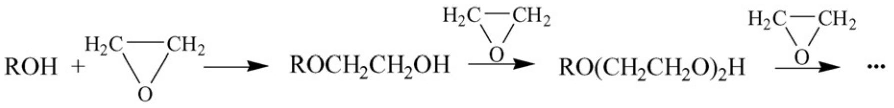
HCHO	CH_3CHO	CH_3COCH_3	$CH_3COC_2H_5$	CH_2CHCHO
<0.5	11.27	21.58	12.67	8.16



The selectivity dependence of mercarbide towards alkoxide anions differs greatly from that of inorganic anions and follows the sequence

$$CH_3OH \approx C_2H_5OH \approx C_3H_7OH < C_5H_{11}OH \approx C_7H_{15}OH < i\text{-}C_3H_7OH < C_{12}H_{25}OH \tag{7}$$

Some ion exchange can be observed even for C_{18-23} alkoxides. This suggests, that long hydrocarbon radicals can penetrate into the interior of mercarbide. Internal ionic exchange does not occur for the branched hydrocarbon radicals like 3-propyoheptanol or 2-octadecanol due to the impossibility of such radical to penetrate to the basic active sites at the inner space of the mercarbide. Ionic exchange takes place on external surface only. This fact gives an opportunity to estimate the amount of the basic sites located on the external surface of the mercarbide which appeared to be less than 5% of total.



(8)

The titration of hydroxymercarbide with sulphuric and hydrochloric acids gave similar values of ion exchange capacity (E = 1.35–1.37 mequiv./g). The same result was reached during the study of ion exchange with chlorides. However, using iodides to determine the mercarbide exchange capacity was found to give higher results (Table 2). For the complete replacement of hydroxide ions with iodide anions, the theoretical value of ion exchange capacity for tetramercurmethane is E = 2.2 mequiv./g.

The results of basic site determination through different alkoxides are shown in Table 3. These results indicate the inaccessibility of basic sites in mercarbide to larger hydrocarbon radicals. It is also shown that for the blocking single active site the hydrocarbon radical of length not less than 3 $-CH_2-$ groups is required.

The determination of the concentration of basic sites in mercarbide was carried out using the Hammett indicators method [12]. Since the hydroxyl form of the mercarbide has a yellow color, the measurements were carried out in the presence of the white color, comparison standard. It is necessary to mention that although the internal sites are absolutely inaccessible for such indicators as bromthymol blue, that does not affect the results of the titrations since those sites are accessible for the molecules of an acid.

The Hammett titration showed that in presence of bromthymol blue (pK_a = 7.2) or 2,4-dinitroaniline (pK_a = 15.0) the concentration of basic sites is E = 1.5 mequiv./g. However, using 4-chloro-2-nitroaniline (pK_a = 17.2) gave a basic site concentration of only E = 0.8 mequiv./g. The sites of the strength of H_0 = 26.5 were not detected (indicator: 4-chloraniline) [12].

Table 2
The concentration of mercarbide basic sites determined in HI solution.

C_{HI}, mol/l	0.001	0.01	0.05	0.1	0.2
E, mequiv./g	1.35	1.45	1.56	1.59	1.68

Table 3
The concentration of mercarbide basic sites according to ion exchange with alkoxides.

Alcoholate	CH_3O^-	$C_2H_5O^-$	$C_3H_7O^-$	$C_7H_{15}O^-$	$C_{12}H_{25}O^-$
E, mequiv./g	1.35	1.38	1.22	0.95	0.11

4. Mercarbide as a solid base catalyst: applications for alcohol oxyethylation and the aldol condensation

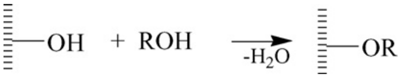
The activity of mercarbide as a basic heterogeneous catalyst was studied using the oxyethylation of alcohols (Eq. (8)) [14,15] as well as the aldol condensation of acetone (Eq. (9)).

$$CH_3COCH_3 + CH_3COCH_3 \rightarrow CH_3COCH_2C(OH)(CH_3)_2 \tag{9}$$

The catalityc activity of mercarbide in the oxyethylation reaction were studied using manometric unit which allows to measure the concentration of the ethylene oxide in liquid phase through the measurement of partial pressure in gas phase.

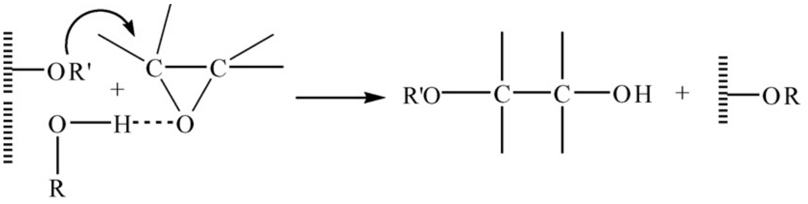
For such experiments mercarbide was first converted to the OH^- form. Kinetic studies indicated that the alcohol oxyethylation reaction is first order in mercarbide, alcohol, and ethylene oxide. A comparison of kinetic factors for the oxyethylation reaction catalyzed by mercarbide with those for other basic heterogeneous catalysts indicated greater activity of mercarbide apparently because of the high basicity of the mercarbide basic sites. Similar results were obtained during the study of the oxyethylation of methanol, but the activation energy was considerably less than for other alcohols because of the relatively high methanol acidity and the high basicity of the mercarbide basic sites.

After the catalytic reaction, the mercarbide used in the reaction was separated and then treated with hydriodic acid to remove the anions remaining on the catalyst. This indicated that mercarbide in its alkoxide rather than the hydroxide form participates in the catalytic reaction. This indicates that the hydroxymercarbide first exchanges OH^- for OR^- (Eq. (10)) before onset of the catalytic reaction.



(10)

Subsequent oxyethylation occurs through a trimolecular intermediate with ring opening in a process resembling an SN2 reaction (Eq. (11)).



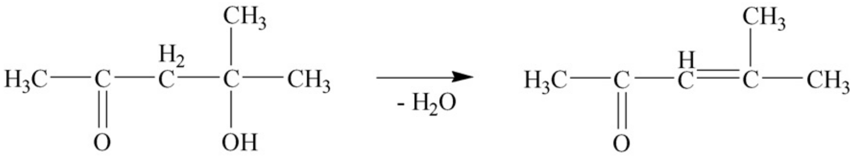
(11)

The mercarbide catalyst retained its catalytic activity throughout the alcohol oxyethylation reaction.

The kinetics of the aldol condensation reaction in presence of mercarbide in its hydroxyl form has also been studied. The kinetics parameters were found to be similar to those for homogeneous base catalysis. The similar research of the mercarbide catalytic stability in the aldol condensation reaction did not show the drop in catalyst activity.

The absence of the drop in catalytic activity in the reaction can be explained only through the high rate of strong basic sites deactivation during the reaction. The direct catalytic process takes place on the basic sites of the medium strength.

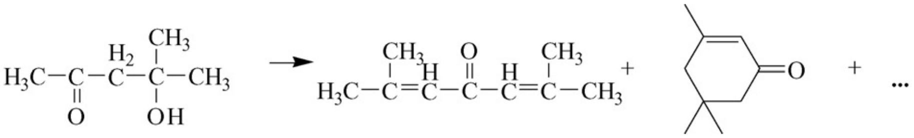
We conclude that the deactivation of the strongly basic sites can occur by two processes. Thus the catalytic sites for oxyethylation become deactivated by the alcohol molecules showing insignificant acidic properties. However, water molecules generated by side dehydration reactions (Eq. (12)) poison the active mercarbide sites for aldol condensation.



$$H_3C-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow[-H_2O]{} H_3C-\underset{\underset{O}{\|}}{C}-\overset{H}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3 \qquad (12)$$

In other words, the real values of reaction rate real constants are considerably higher, since the concentration of the active sites, which participate in the catalytic process, is lower due to the fact that the sites of the strong strength are removed from the process.

Heterogeneous catalysts are characterized not only by high concentrations of active centers in the reaction mixture but also by selectivity combined with penetration of the bulky substrate molecules into the interior of the solid catalyst. The molecular sieve properties of mercarbide hydroxide were studied in oxyethylation and aldol condensation reactions. Both of these processes consist of consecutive reactions which cause formation of high molecular weight products. Alcohols form in oxyethylation reaction (8), while the aldol condensation reaction gives the following products of successive conversion:



(13)

The reaction products were analyzed by gas–liquid chromatography after completion of the reaction. The studies of the products which forms during the reaction of ethylene oxide with butanol has shown that with the increase in oligomers molecular weight the rate of the reaction increases. The relation of rates constants of consecutive stages of ethylene oxide polyaddition to alcohol k_1/k_o and k_2/k_o are equal to 2.3 and 4.3, respectively.

These results are very close to those with homogenous basic catalysts, which of course have no problems of substrate access to the active sites. The distribution of reaction products is also similar to those from basic homogenous catalysis in aldol condensation reactions. These results indicate the presence of wide pores in the mercarbide solid structure which provide substrate access to the interior active sites.

5. Conclusion

The formation of mercarbide by polymercuration of various organic substrates is shown to depend on concurrent condensation and polymerization reactions. Mercarbide in its hydroxyl form is a solid base and anion-exchanger showing high selectivity towards halides. The basic sites in the internal space of mercarbide are accessible to organic molecules, but substances with long hydrocarbon radicals block basic sites. Determination of the basic properties of mercarbide show medium to high concentration of its basic sites. This determines the catalytic activity of mercarbide for base-catalyzed oxyethylation and aldol condensation reactions. In the base-catalyzed reactions mercarbide performs as an active basic heterogeneous catalyst with high basicity of active sites and does not display any sieving properties against to initial compounds.

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