# THERMAL DECOMPOSITION OF BIS(PHENYL-

# CHROMIUM TRICARBONYL)MERCURY

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Organometallic compounds with weakly polar metal-carbon bonds decompose at high temperatures to give the corresponding radicals and metal. In particular, this direction of the decomposition is characteristic for most organomercury compounds. The behavior of the thus formed radicals depends both on their nature and on the medium in which reaction occurs.

We used the DTA method to study the thermal decomposition of bis(phenylchromium tricarbonyl)mercury (I) [1] in order to ascertain the effect of  $\pi$ -complex formation on the tendency of the C-Hg bond to undergo homolytic cleavage, and also to compare the reactivity of the practically unstudied phenylchromium tricarbonyl radical [2, 3] with the phenyl and ferrocenyl radicals, which are formed during the decomposition of the corresponding organomercury compounds.

The DTA diagram of (I) (Fig. 1, curve 1a) contains two exothermic signals and one endothermic signal. Practically no gaseous products are evolved (curve 1b) in the temperature range of the first exothermic signal (maximum at 215°C). When (I) is heated for 17 h at 200° in a sealed evacuated system, with freezing of the volatile products, mercury is deposited and a mixture of products is formed, from which were isolated benzenechromium tricarbonyl (II) and diphenylbis(chromium tricarbonyl) (III) in respective yields of 25 and 51%. The composition of the decomposition products of (I) at 200° indicates that the signal with a maximum at 215° corresponds to the homolytic cleavage of the Hg–C bond with the deposition of Hg and the formation of the radical  $\cdot PhCr(CO)_3$ . For comparison we will mention that  $Ph_2Hg$  decomposes at 200° to the extent of only 9.7% in 24 h [4] and the sole reaction product is diphenyl. In contrast to the phenyl radical, which is formed during the decomposition of  $Ph_2Hg$ , the  $\cdot PhCr(CO)_3$  radical is capable not only of recombination, but also either of disproportionation or the cleavage of hydrogen from the surrounding molecules to give (II).



This makes it similar to the ferrocenyl radical, whose behavior was studied while studying the thermal decomposition of differocenylmercury [5]. The latter decomposes at 265° in 17 h to give ferrocene (68%) and diferrocenyl (13%). However, the tendency of the  $\cdot$ PhCr(CO)<sub>3</sub> radical to cleave hydrogen is expressed less clearly than for the ferrocenyl radical. Besides these products, the other products detected in the thermal decomposition of (I) were Cr metal and CO, and also Cr(CO)<sub>6</sub> and Ph<sub>2</sub>Hg, whose formation was caused by the partial decomposition of the  $\pi$ -arenechromium tricarbonyl structure.

The exothermic signal with a maximum at  $215^{\circ}$  (see Fig. 1) changes to a quite broad endothermic signal with a maximum at  $245^{\circ}$ , which is probably superimposed on the peak that corresponds to the decomposition of (I) at the C-Hg bond. This can be caused by a sublimation of the volatile decomposition products of (I) and a fusion of the starting compound in the mixture with the thermal decomposition products. To verify this

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Fig. 1. DTA diagrams of bis(phenylchromium tricarbonyl)mercury: 1) at atmospheric pressure; 2) 150 torr; 3) 0.01 torr; 4) in presence of Pd black; 5) in presence of Cr metal; 6) diphenylmercury in presence of Pd black (a = thermograms, b = gas evolution curves).

assumption we took the DTA diagrams of (I) at various residual argon pressures in a measuring cell: 760, 150, and 0.01 torr. As can be seen from the presented diagrams 1-3, a decrease in the pressure leads to a splitting of the endothermic signal into two dignals with maxima at 245 and 260°, which were respectively assigned to the sublimation of the volatile decomposition products and the fusion of (I).

The endothermic signal with a maximum at  $260^{\circ}$  changes sharply to a narrow, very intense exothermic signal with a maximum at  $264^{\circ}$ . The intense evolution of gaseous products (Fig. 1, curve 1b) corresponds to the process that proceeds at this temperature; as a result, the complete decomposition of the organometallic compound occurs here. The heating of (I) in a sealed ampul for 5 h at  $260^{\circ}$  gives benzene, diphenyl, CO and  $CO_2$ , and metallic Cr and Hg. The ratio of benzene and diphenyl in the products corresponds approximately to the ratio of (II) and (III), obtained during the thermal decomposition of (I) at  $200^{\circ}$ , i.e., these products are probably the decomposition result of the arenechromium tricarbonyl complexes that are formed during the transformations of the •PhCr(CO)<sub>3</sub> radical.

In [4, 6] it was shown that metals catalyze the decomposition of organomercury compounds and that Pdblack is one of the most active catalysts. Thus,  $Ph_2Hg$  in the presence of Pd decomposes at 25° to the extent of 90% in 24 h, and the sole product, the same as without a catalyst, is diphenyl. We studied the thermal behavior of (I) and  $Ph_2Hg$  in the presence of Pd by the DTA method.

The DTA diagram of (I) (curves 4a and b) testifies to a two-step process. We assigned the broad exothermic signal with a maximum at 168° to the decomposition of (I) at the Hg-C bond. The main chromium tricarbonyl products, corresponding to this process, are (II) (22% yield) and (III) (44% yield). The maximum evolution rate of the gaseous products is observed above 200° (curves 4a and b), which corresponds to the second step of the process, which leads to a complete decomposition of organometallic compounds. As can be seen from the presented data, metallic Pd catalyzes the decomposition of (I) not only at the Hg-C bond, but also the decomposition of the arenechromium tricarbonyl structure.

When compared with diphenylmercury, a characteristic trait of the decomposition of (I) is the fact that, parallel with cleavage of the C-Hg bond, a more profound decomposition of the compound takes place, which is accompanied by the deposition of metallic Cr, which, in turn, can catalyze the decomposition of (I) and the products formed it. As a result, the reaction bears an autocatalytic character. Actually, the addition of finely dispersed Cr to the reaction mixture substantially lowers the decomposition temperature of (I) (see Fig. 1, curves 5a and b), while the general form of the thermogram of (I) in the presence of Pd and Cr becomes quite similar, although chromium, when compared with Pd, is a somewhat less active catalyst. However, the activity of the metal at the moment of formation is probably much higher.

From the above said it follows that the thermal decomposition of (I), both in the presence of a catalyst and without it, proceeds by the same mechanism, which includes the homolytic decomposition of the C-Hgbond and the formation of the  $\cdot PhCr(CO)_3$ , radical, which, in contrast to the phenyl radical, is capable of disproportionation to give (II). This makes it similar to the ferrocenyl radical. The decomposition of diferrocenylmercury in the presence of Pd at 115-250° leads to the formation of 46% of ferrocene and 6% of diferrocenyl [7].

#### EXPERIMENTAL

Thermal Decomposition of Bis(phenylchromium tricarbonyl)mercury (I). An ampul, containing 0.626 g (1 mmole) of (I), was evacuated, sealed, and heated for 17 h at 200°. At the end of reaction the ampul was opened and the very volatile reaction products were sublimed into a trap, cooled with liquid nitrogen, at  $40^{\circ}/0.02$  torr. The benzene-soluble arenechromium tricarbonyl complexes were extracted from the reaction mixture with benzene. We obtained 0.2 g of a yellow substance, which, based on the TLC data, is a mixture of benzenechromium tricarbonyl (II) and diphenyl-bis(chromium tricarbonyl) (III). We separated (II) by sublimation at  $80^{\circ}$  (0.01 torr). The residue was chromatographed on an  $Al_2O_3$  column using acetone as the eluant. We isolated (III) from the yellow zone. Both compounds were identified via the melting points and the IR and NMR spectra.

<u>Thermal Decomposition of (I) in Presence of Pd.</u> A mixture of 0.626 g of (I) and 2 g of Pd black was heated in an ampul for 5 h at 145°. The reaction products were isolated the same as in the preceding experiment.

### CONCLUSIONS

1. The DTA method was used to study the thermal behavior of diphenylmercury and bis(phenylchromium tricarbonyl)mercury in the presence of finely dispersed Pd and Cr, and also without a catalyst.

2. The thermal decomposition of bis(phenylchromium tricarbonyl)mercury bears an autocatalytic character.

3. The behavior of the phenylchromium tricarbonyl radical, which is formed during the decomposition of the bis(phenylchromium tricarbonyl)mercury, was studied.

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