

THERMODYNAMIC TREATMENT OF DIBENZENECHROMIUM DIRECT-SYNTHESIS REACTION AND ITS RELATION TO DECOMPOSITION REACTION

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(Received March 10th, 1976)

Summary

Thermodynamic studies of the equilibrium in the direct-synthesis reaction of dibenzenechromium from benzene and chromium were carried out. The reaction of gaseous chromium with the solid ligand is shown to be the most probable mechanism of the process. The thermodynamic and kinetic stabilities of dibenzenechromium and their relation to the decomposition reaction resulting in the formation of solid chromium are discussed.

Thermodynamic calculations have been performed previously [1] for the dibenzenechromium decomposition process of reaction 1, within the temperature range 298–1000 K.

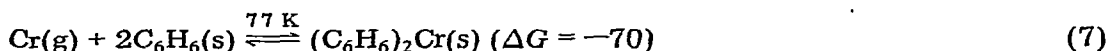
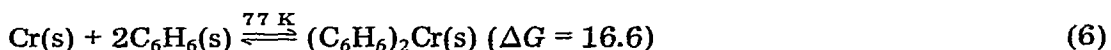
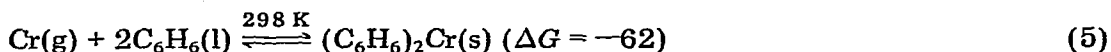
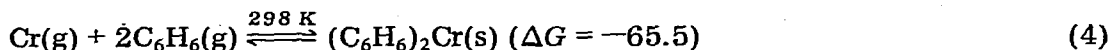
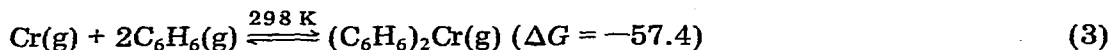
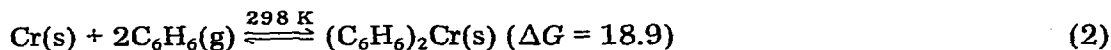
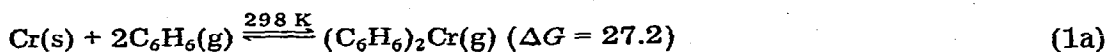


The equilibrium constant value has been shown to increase with rising temperature, and the isobaric-isothermal potential variation has been calculated within the temperature range 298–800 K and at pressures of 10^{-5} – 10^7 atm. Only at pressures of more than 10^7 atm. does the isobaric-isothermal potential variation lead to a reversal of sign, i.e. the equilibrium is shifted largely to the formation of dibenzenechromium.

We have carried out thermodynamic investigations on direct dibenzenechromium synthesis. In recent years much literature on the direct-synthesis of organometallic compounds has appeared. The direct-synthesis reaction conditions differ greatly from traditional ones; direct-synthesis reactions are carried out in a high-vacuum reaction vessel ($P = 10^{-5}$ – 10^{-6} Torr), the walls of which are cooled to liquid nitrogen or liquid helium temperature. Into this the gaseous organic or inorganic compound is introduced, and condensed on the vessel walls with simultaneous metal evaporation from the evaporator and co-condensation of atomic metal with the frozen compound. In the literature there is no completely adequate explanation of the mechanism of these reactions and the given method

is either referred to as, synthesis in vapour or synthesis by co-condensation of atomic metal with a substance condensed on the reaction vessel walls. Using thermodynamic calculations, the mechanism of these reactions, which may be in the gaseous, solid or gas/solid phase etc., can be explained in more detail. The values used for the thermodynamic calculations are listed in Table 1.

We calculated the isobaric-isothermal potential variation (ΔG kcal mol⁻¹) for the following reactions:



Thus, reactions 3, 4, 5, 7, and 8 can be considered thermodynamically possible. The fact that the equilibrium in reactions 1a, 2 and 6 is shifted to the left is explained on the basis of experimental observations. After completing the synthesis, unreacted chromium metal powder which is formed as a result of chromium atom aggregation, remains in the reaction vessel; since chromium powder

TABLE 1
THE THERMODYNAMIC QUANTITY VALUES USED IN THE CALCULATIONS

Substance	State of aggregation	T(K)	H_T° (kcal mol ⁻¹)	S_T° (cal mol ⁻¹ K ⁻¹)	References
Cr	solid	77	0	0.66	2
		298	0	5.7	3
	gas ^a	77	93.7	34.8	2, 4
		298	94.8	41.64	3
		1000	98.3	44.1	4
C ₆ H ₆	solid	77	4.89	8.2	2
	liquid	298	11.72	41.3	3
	gas	298	19.82	63.34	3
		1000	46.58	106.73	5
(C ₆ H ₆) ₂ Cr	solid	77	27.7	15.2	6
		298	35	54.07	6, 7
	gas	298	54.6	92.87	6, 7
		1000	106.5	202.9	1

^a In the calculations gaseous chromium was taken as an ideal gas.

does not react with benzene under ordinary conditions. In order to carry out the pure gas-phase reactions 3, 4, and 8 a termolecular collision is required, the probability of which is extremely small due to the fact that in all reaction vessels used, the distance from the evaporator to the walls does not exceed 10–15 cm, yet the free-path length of the particles under the reaction conditions studied, greatly exceeds this value. The free-path length at pressures 1, 10^{-3} and 10^{-6} Torr are equal to 6.5×10^{-3} , 6.5 and 6.5×10^3 cm, respectively [8]. The termolecular collision probability (Z_3) is related to the bimolecular collision probability (Z_2) for gas-phase reactions, by $Z_3/Z_2 = 10^{-2} \times P$, where P is the gas pressure in atm. in the system at 300 K [9]. When it is considered that the pressure P under direct-synthesis reaction conditions is equal to $10^{-4} - 10^{-6}$ Torr, i.e. $10^{-6} - 10^{-8}$ atm., then the termolecular collision probability, $Z_3 = (10^{-8} - 10^{-10})Z_2$ is seen to be extremely small in magnitude.

Thus it is evident that the direct-synthesis reaction is the gas-solid reaction 7. On this basis, some conclusions relating to the direct-synthesis mechanism can be drawn.

The metal atom, formed by metal evaporation, on striking the condensed ligand surface loses its excess energy, even on collision with the first molecule of the condensed ligand. This conclusion can be made by evaluating the kinetic energy and the weak penetrating ability of the atom. In this case localized overheating of the condensed ligand occurs, which facilitates diffusion of the metal atom and ligands, and this in turn promotes a spatial orientation favourable to interaction in the ligand matrix. By intensive metal evaporation the probability of metal-atom encounter and aggregation increases. Metal in the condensed state does not react. This may explain both the decrease in yield of the organometallic compound formed, and the formation of metal powder. Ligand melting is possible by intensive metal evaporation and the freezing of a thick ligand layer onto the reaction vessel walls, resulting in diminished heat transfer. Reaction 5 of gaseous metal and liquid ligand may occur in this case, but heating the ligand layer would cause its intensive evaporation and rising pressure in the reaction vessel.

For an estimate of metal atom isolation in the ligand matrix, on which the metal aggregation as well as the product yield depends, the ratio M/R can be used, where M is the number of atoms or molecules of the matrix, and R is the number of atoms of the metal. From the spectroscopic study of atoms isolated in a matrix, it was reported [10] that good isolation is reached even at $M/R = 300$, but this is only true for a matrix which is inert to metal. For direct-synthesis such an excess of ligand is evidently not needed as a metal atom reacts with a ligand forming an organometallic compound which itself becomes part of the matrix. $M/R = 6-100$ is usually used in studies on direct-synthesis. Further cooling of the reaction vessel walls (to liquid helium temperatures) makes the ligand matrix more "rigid" and metal atom diffusion is therefore hindered and their aggregation probability is decreased.

The investigations carried out allow us to draw certain conclusions relating to the thermal decomposition of such compounds as bisarenechromium. During thermal decomposition, the phase in which chromium is isolated plays a substantial role in equilibrium displacement. By chromium atom adsorption on solids (substrate) or by aggregation with one another, accompanied by the for-

mation of chromium in the solid phase, the reaction equilibrium must be shifted towards decomposition as a result of the low mobility of chromium atoms at temperatures of decomposition of bisarenechromium compounds. Calculation of the variation of the isobaric-isothermal potential in reaction 8 shows that even at 1000 K the gaseous phase equilibrium is shifted towards dibenzenechromium formation.

Thermodynamic calculations have shown that dibenzenechromium is thermodynamically stable in the absence of solid chromium, even at temperatures above 1000 K (reaction 8). Yet, at high temperatures and in the gaseous phase dibenzenechromium must be kinetically unstable in spite of its thermodynamic stability, as the probability of the reverse unimolecular reaction (dibenzenechromium decomposition (1a)) is greater than the probability of the direct termolecular synthesis reaction (1a). The probability of chromium atom aggregation, to a first approximation, depends upon the probability of bimolecular collision (Z_2) and the synthesis reaction probability depends upon the termolecular collision (Z_3) probability. Consequently, the probability of isolation of solid chromium in the gas-phase reaction is greater than the probability of the termolecular gas-phase synthesis reaction. In turn, traces of solid chromium must shift the equilibrium towards decomposition; the chromium atoms behaving as active centres (autocatalysis).

References

- 1 B.A. Salamatin, S.A. Klinchikova, A.S. Pashinkin and B.G. Gribov, *Metody polucheniya i analiza veshchestv osoboi chistoty*, Nauka, Moscow, 1970, p. 111.
- 2 *Handbook of Chemistry*, B.P. Nickolskiy (Ed.), Khimiya, Moscow, 1962, Vol. 1.
- 3 M.A. Karapet'yants and M.L. Karapet'yants, *Osnovnyye termodynamicheskiye konstanty neorganicheskikh i organicheskikh veshchestv*, M., Khimiya, Moscow, 1968.
- 4 E.A. Guggenheim and J.E. Prue, *Physicochemical Calculations*, Interscience, New York, 1955, Russian translation, IL, Moscow, 1958.
- 5 D.R. Stull, E.F. Westrum and G.C. Sinke, *The chemical thermodynamics of organic compounds*, John Wiley & Sons, New York/London/Sydney/Toronto, 1969, Russian translation, Mir, Moscow, 1971.
- 6 J.T.S. Andrews, E.F. Westrum, N. Bjerrum, *J. Organometal. Chem.*, 17 (1968) 293.
- 7 V.I. Tel'noy, I.B. Rabinovich, *Tr. Khim. Khim. Tekhnol.*, 2 (1972) 12.
- 8 M. Anwärter, *Angew. Chem., Int. Ed.*, 14 (1975) 207.
- 9 V.N. Kondratiev, and Ye. Ye. Nikitin, *Kinetika i mekhanizm gazofaznykh reaktsii*, Nauka, Moscow, 1974, p. 263.
- 10 G.C. Pimentel, *Angew. Chem., Int. Ed.*, 14 (1975) 199.