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Abstract

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POLAROGRAPHIC REDUCTION OF CERTAIN CHROMAROMATIC COMPOUNDS OF SANDWICH STRUCTURE

Whereas the polarographic behavior of bis-cyclopentadienyl compounds has been described in sufficient detail ([1]), there is only one paper ([2]) on the reduction of the cation $[(C_6H_6)_2Cr]^+$ at a mercury dropping cathode in an anhydrous solution of $CH_3OH + C_6H_6$ against a background of sodium hydroxide, lithium chloride, and a mixture of a solution of the latter with acetic acid.

Since in our laboratory the iodides of dibenzol-(I), ditoluol-(II), dimesitylene-(III), and bisdiphenylchromium (IV) had been obtained, as well as the iodides, not described in the literature, of dicumol-(V) and di-(cyclohexylbenzene)-chromium (VI), it seemed of interest to study the polarographic reduction of this series of compounds.

The synthesis of the indicated derivatives ((I)–(VI)) was carried out by the method of the so-called reductive reaction (Friedel–Crafts ([3])). A mixture of 23.8 g of anhydrous $CrCl_3$ (0.15 mole), 2.7 g of powdered aluminum (0.10 g-atom), 16 g of freshly sublimed $AlCl_3$ (0.11 mole), and 75 ml of cumene was boiled with stirring for 2 hr in a nitrogen atmosphere, hydrolyzed on cooling first with methanol and then with water, the excess cumene was washed out with cyclohexane, and the aluminum and chromium hydroxides were precipitated with concentrated NH_4OH solution. After heating to 60°, the precipitate was filtered off and washed three times with small portions of warm water. To the filtrate were added an equal volume of benzene and a saturated solution of 35 g of sodium dithionite; the flask was purged with nitrogen and a concentrated solution of 60 g of caustic potash was gradually introduced. On the following day the aqueous layer was separated and discarded. To the dark-orange benzene layer 100 ml of water was added, and air was passed through the system. From the concentrated solution of dicumolchromium hydroxide thus obtained, by addition of a saturated aqueous solution of KI, (V) was precipitated in the form of a cherry-red viscous oil. Attempts to crystallize (V) were unsuccessful.

Found, %: Cr 12.39; J 30.33
$C_{18}H_{24}CrJ$. Calculated, %: Cr 12.41; J 30.31

(V) is readily soluble in lower alcohols, acetone, methylene chloride, dichloroethane, pyridine, and dimethylformamide; it is practically insoluble in ether, CCl_4, cyclohexane, water, and benzene. In an analogous manner (VI) was also synthesized. The heating of the reaction mixture, to which 50 ml of purified n-nonane had been added, was carried out for 1.5 hr at 150°. (VI) was isolated in the form of a dark-red powder.

Found, %: Cr 10.37; J 25.50
$C_{24}H_{32}CrJ$. Calculated, %: Cr 10.42; J 25.45

The behavior of (VI) toward solvents is the same as that of (V).

Polarographic studies of the iodides ((I)−(VI)) were carried out on a visual polarograph manufactured by the Gorky Scientific-Research···

Institute of Chemistry. As the electrode, a capillary was used, for which $m^{2/3}\tau^{1/6}$ was equal to 1.16 $\mathrm{mg}^{2/3} \cdot \mathrm{sec}^{-1/2}$ in an open circuit. The anode was a saturated calomel half-cell, relative to which the half-wave potentials were measured.

Fig. 1. Reduction waves
against a background of 0.5 N LiCl

Fig. 2. Dependence of the limiting current on the square root of the height of the mercury column for (IV).

Reduction was carried out against the background of various 0.5 N aqueous electrolytes: lithium chloride, sodium hydroxide, potassium nitrate, sodium sulfate, hydrochloric acid, and buffer solutions with pH from 2.3 to 11.75.

In almost all the indicated electrolytes, the chromoaromatic compounds give diffusion currents; the exceptions are a 0.5 N hydrochloric acid solution and buffer solutions with pH < 2, in which they precipitate or, as for example (II), do not give reduction waves. All iodides ((I)−(VI)) are reduced in one wave (Fig. 1), whose limiting current has a diffusion character, since its magnitude is proportional to the square root of the height of the mercury column (Fig. 2). For (II), (III), (V), and (VI), a maximum is observed on the wave, which is easily suppressed by a solution of starch glue. For all the chromoaromatic compounds investigated, a direct proportionality is observed between the reduction current and the concentration.

Fig. 3. Dependence between the value of the potential and lg $\frac{i}{i_d - i}$

The half-wave potential of each of the compounds depends neither on the nature of the indifferent electrolyte nor on the concentration of hydrogen ions, but shifts depending on the substituents in the bound aromatic ring. Thus, the half-wave potentials $E_{1/2}$ of the chromoaromatic compounds against a background of 0.5 N LiCl proved to be as follows (in volts):

(IV) -0.66 (I) -0.97
(VI) -0.9 (II) -1.04
(V) -0.98 (III) -1.06

Analysis of individual polarograms of chromoaromatic compounds shows that between the half-wave potential and the value $\lg \frac{i}{i_d - i}$ there is a linear dependence (Fig. 3), in accordance with the Heyrovský-Ilkovič equation:

$$\pi = \pi_{1/2} - \frac{0.058}{n} \lg \frac{i}{i_d - i},$$

where $\pi_{1/2}$ is the half-wave potential, i_d is the limiting diffusion current, and n is the number of electrons participating in the electrode reaction. For the compounds we studied, n, both as found graphically and as deter-

determined by the method of polarographic coulometry (4), is equal to 1. The correspondence of the reduction process to the Heyrovský-Ilkovič equation indicates a reversible process occurring at the dropping mercury cathode. This was also observed in the reduction of the cation $[(C_6H_6)_2Cr]^{4+}$ in an anhydrous medium (2). The reduction mechanism, therefore, consists in the addition of an electron to the cation of the bisarene chromium compound:

$$(\mathrm{Arene})_2\mathrm{Cr}^+ + e^- \rightleftarrows (\mathrm{Arene})_2\mathrm{Cr}^0.$$

From consideration of the data obtained it may be concluded that the introduction of an alkyl (V) or cyclohexyl (VI) substituent into the aromatic ring does not exert a large influence on the magnitude of the half-wave potential, which, in going from (II) to (III), is shifted only slightly toward negative values in comparison with (I). By contrast, introduction of an aromatic substituent (IV) causes a sharp shift of the potential into the region of positive values.

It is still difficult to correlate the polarographic data with data obtained by other methods; however, the polarographic method may play a definite role in elucidating the nature of this class of compounds.

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