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Abstract

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NEW TROPYLIUM SALTS. POLAROGRAPHY OF THE TROPYLIUM ION

Recently Doering and Knox (1) obtained salts of cycloheptatrienylium (tropylium)—a stable seven-membered carbonium ion possessing aromatic properties as a result of the conjugation of six π-electrons:

$$\text{[tropylium ion structure]} \quad X^-$$

The study of derivatives of this new nonbenzenoid aromatic system is undoubtedly of considerable interest.

Until now only a few tropylium salts have been known—tropylium bromide and chloride (1), and, according to a recently published communication (2), tropylium isocyanate. These salts are crystalline high-melting substances, very readily soluble in water and insoluble in nonpolar organic solvents; they are highly hygroscopic and deliquesce in air.

In the present work three new tropylium salts have been obtained: tropylium chloroplatinate $(C_7H_7)_2 \cdot PtCl_6$, tropylium perchlorate $C_7H_7 \cdot ClO_4$, and tropylium tetraphenylborate $C_7H_7 \cdot B(C_6H_5)_4$, and the polarographic reduction of the tropylium ion has been studied.

A distinguishing feature of these three salts is their low solubility in water. Therefore they can be obtained from aqueous solutions of tropylium bromide by the corresponding exchange reactions:

$$2C_7H_7Br + H_2PtCl_6 \rightarrow (C_7H_7)_2PtCl_6 + 2HBr,$$

$$C_7H_7Br + HClO_4 \rightarrow C_7H_7ClO_4 + HBr,$$

$$C_7H_7Br + NaB(C_6H_5)_4 \rightarrow C_7H_7B(C_6H_5)_4 + NaBr.$$

It is essential to note that in tropylium tetraphenylborate the bond of boron with the cycloheptatrienyl residue can only be ionic, since boron is not capable of forming a fifth covalent bond. For the previously known halide salts of tropylium, on the basis of the available data, it was not possible completely to exclude the possibility of formation of a partially covalent bond between the C_7H_7 residue and the anion. Thus, the preparation of stable tropylium salts with the anion $B(C_6H_5)_4^-$ is weighty confirmation that tropylium indeed forms an ionic bond and is a stable organic cation.

Tropylium perchlorate was obtained by adding an excess of 30% $HClO_4$ to a solution of tropylium bromide in a small amount of water; it precipitates in the form of colorless needles (yield above 95%); it is readily soluble in hot water, less readily in cold water, and insoluble in nonpolar organic solvents. Its solubility at 20° is 3.2 g in 100 g of water and 0.26 g in 100 g of absolute alcohol. Boiling or prolonged heating of aqueous solutions causes partial decomposition of the salt and coloration of the solution green. Tropylium perchlorate is nonhygroscopic and quite stable in air.

upon heating to a temperature of about 230° it explodes without melting.

Found, %: C 44.26; 44.09; H 3.87; 3.75
$C_7H_7O_4Cl$. Calculated, %: C 44.11; H 3.71

Tropylium hexachloroplatinate was obtained in quantitative yield by mixing aqueous solutions of chloroplatinic acid and tropylium bromide. An orange precipitate separates; the intensity of its color increases on heating; at temperatures above 175° it darkens and decomposes without melting. The solubility of tropylium hexachloroplatinate at 20° in 100 g of water is 0.35 g, and in 100 g of absolute alcohol, 0.03 g; it is insoluble in ether, benzene, acetonitrile, and acetone.

Found, %: C 28.23; 28.19; H 2.45; 2.36; Cl 36.21; 36.26; Pt 33.06; 33.26
$C_{14}H_{14}Cl_6Pt$. Calculated, %: C 28.49; H 2.39; Cl 36.04; Pt 33.08

Tetraphenylborotropylium, obtained in quantitative yield from tropylium bromide and sodium tetraphenylborate*, is still less soluble in water. Its solubility in water at 20° is of the order of 0.01 g in 100 g of water. It is an orange powder with a melting point of 120–121.5°, insoluble in alcohol and in nonpolar organic solvents.

Found, %: C 91.02; 91.13; H 6.77; 6.94; B 2.47; 2.32
$C_{31}H_{27}B$. Calculated, %: C 90.73; H 6.63; B 2.64

The low solubility in water of tropylium hexachloroplatinate and especially of tetraphenylborotropylium makes it possible to use the corresponding reagents —chloroplatinic acid and sodium tetraphenylborate—for the identification and quantitative determination of the tropylium ion. The determination can be carried out in aqueous solutions or, with still greater accuracy, in alcoholic solutions. The possibility of quantitative precipitation of tropylium from aqueous solutions substantially facilitates work with tropylium salts.

Fig. 1. Polarization and electrocapillary curves

Figure 1: Fig. 1. Polarization and electrocapillary curves

Fig. 2

Figure 2: Fig. 2

As is known, potassium perchlorate, potassium chloroplatinate, and potassium tetraphenylborate are also sparingly soluble compounds and are used for the analytical determination of the potassium ion. Thus there is an evident similarity in the solubility of potassium and tropylium salts. An attempt to obtain tropylium cobaltinitrite (by analogy with potassium cobaltinitrite) was unsuccessful, since the tropylium ion undergoes chemical changes, probably as a result of attack by the NO radical.

Fig. 1. Polarization (1-8) and electrocapillary ($\sigma = f(\varphi)$) (I, II) curves of solutions:
1 –0.1 M LiCl; 2 –0.1 M LiCl + 10^{-4} M $C_7H_7ClO_4$; 3 –0.1 M LiCl + $2 \cdot 10^{-4}$ M $C_7H_7ClO_4$; 4 –0.1 M LiCl + $3 \cdot 10^{-4}$ M $C_7H_7ClO_4$; 5 –0.1 M LiCl + $4 \cdot 10^{-4}$ M $C_7H_7ClO_4$; 6 –0.1 M LiCl + $6 \cdot 10^{-4}$ M $C_7H_7ClO_4$; 7 –0.1 M LiCl + $8 \cdot 10^{-4}$ M $C_7H_7ClO_4$; 8 –0.1 M LiCl + 10^{-3} M $C_7H_7ClO_4$.
I –0.1 M $HClO_4$; II –0.1 M $HClO_4$ + 10^{-2} M $C_7H_7ClO_4$. Mercury dropping cathode, $m = 1.9$ mg/sec, $\tau = 6$ sec in 0.1 M LiCl and $P = 30$ cm Hg ($\varphi = 0$), $t = 25°$.

The absorption spectra in the ultraviolet region of aqueous solutions of the tropylium salts obtained are similar to the previously described spectrum of tropylium bromide ($\lambda_{\max} 275$ mμ, $\lg \varepsilon = 3.64$) (1), which confirms the presence in solutions of all these salts of one and the same tropylium ion.

* We express our deep gratitude to N. S. Kochetkova and V. A. Sazonova for valuable advice on work with sodium tetraphenylborate.

An aqueous solution of $(C_7H_7)_2PtCl_6$ absorbs at $\lambda_{\max} 273$ mμ, $\lg \varepsilon = 3.7$ (calculated for $C_7H_7 \cdot \frac{1}{2} PtCl_6$); upon acidification of the solution, $\lambda_{\max}$ does not change. For tropylium perchlorate in acidified solutions $\lambda_{\max}$ is likewise equal to 273 mμ ($\lg \varepsilon = 3.65$); without addition of acid, $\lambda_{\max}$ is shifted as a result of partial hydrolysis in $1 \cdot 10^{-4} M$ solutions to 256 mμ ($\lg \varepsilon = 3.6$).

Tropylium salts exhibit rather complex polarographic behavior. Depending on the concentration of $C_7H_7ClO_4$ (Fig. 1) or C_7H_7Br (Fig. 2), the polarization curves contain three or four waves, and an increase in current is also observed at about −1.1 V and a decrease in current at −1.25 V. Comparison of Figs. 1 and 2 shows an analogy in the polarographic behavior of solutions of C_7H_7Br and $C_7H_7ClO_4$; this gives grounds to assert that both salts in aqueous solutions dissociate with formation of one and the same ion $C_7H_7^+$.

Fig. 2. Polarization curves of solutions:

1—0.1M LiCl; 2—0.1M LiCl + $1.17 \cdot 10^{-4}M$ C_7H_7Br; 3—0.1M LiCl + $2.63 \cdot 10^{-4}M$ C_7H_7Br; 4—0.1M LiCl + $3.37 \cdot 10^{-4}M$ C_7H_7Br; 5—0.1M LiCl + $4.82 \cdot 10^{-4}M$ C_7H_7Br; 6—0.1M LiCl + $6.44 \cdot 10^{-4}M$ C_7H_7Br; 7—0.1M LiCl + $8.92 \cdot 10^{-4}M$ C_7H_7Br.
$P = 30$ cm Hg, $t = 25°$. The true concentrations of C_7H_7Br in all cases are somewhat lower than those indicated because of partial osmolysis of the preparation.

i_{pr} of the first wave, beginning with $[C_7H_7ClO_4] = 3 \cdot 10^{-4}M$, ceases to depend on $[C_7H_7ClO_4]$ and is proportional to the height of the mercury column (h), which indicates its adsorption nature. At $[C_7H_7ClO_4] < 3 \cdot 10^{-4}M$, i_{pr} of the first wave is proportional to $\sqrt{h}$. Calculation of the diffusion coefficient of $C_7H_7^+$ from the Ilkovič equation using i_{pr} of the first wave gives a plausible value ($0.4 \cdot 10^{-5}$ cm^2/sec), assuming a two-electron process. The surface activity of tropylium salts on the positively charged surface of Hg (Fig. 1, I)* may possibly be attributed to the action of reduction products. The height of the second wave, observed at $[C_7H_7ClO_4] \geq 3 \cdot 10^{-4}M$, does not depend on h and, consequently, is determined by the rate of a chemical transformation whose mechanism has not yet been established. Comparison of the polarization and electrocapillary curves leads to the conclusion that the decrease in current at -1.25 V is caused by desorption of the substance being reduced. The nature of the rise in current at -1.1 V remains unclear.

The wave at -1.55 V corresponds to discharge of H^+ ions appearing as a result of hydrolysis of tropylium salts; it grows upon acidification and disappears upon alkalization of the solution. With stronger alkalization, the remaining waves also decrease and disappear because of conversion of tropylium into nondissociated carbinol:

$$C_7H_7^+ + OH^- \to C_7H_7OH.$$

The small kinetic wave preceding the wave of H^+ ions possibly corresponds to catalytic evolution of hydrogen. The polarographic study of tropylium derivatives is continuing.

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* Curves I and II in Fig. 1 were measured by M. A. Gerovich.

Note: Figure translations are in progress. See original paper for figures.