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Abstract

Full Text

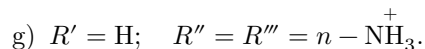
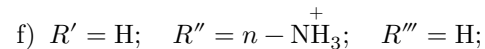
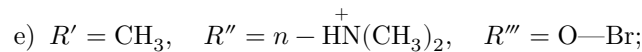
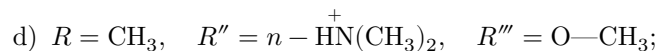
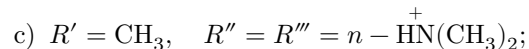
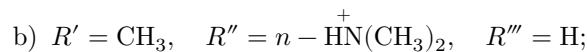
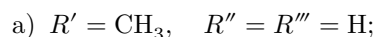
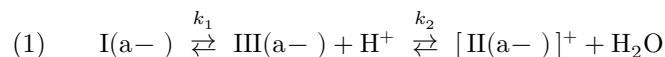
Chemistry

N. G. BELOTSEKOVSKAYA, O. F. GINZBURG

ON QUASITAUTOMERIC TRANSFORMATIONS OF AMINOTRIPHENYLCARBINOLS

(Presented by Academician M. I. Kabachnik on XII 6, 1963)

In solutions of aminotriphenylcarbinols in sulfuric acid, as the concentration of the latter increases, the ratio changes between ammonium and conjugated carbonium ions of one and the same charge; namely, the content of colorless ammonium ions (I) decreases, while the concentration of conjugated carbonium ions (II) increases, and in 50-70% sulfuric acid only conjugated carbonium ions (II) are present. The transformation of ammonium ions (I) into conjugated carbonium ions apparently proceeds through the stage of formation of the base (III), which, however, at the given acidities can be present in solution only in negligible amounts.



Equilibrium (1) is a triple buffer system and in this respect is similar to tautomeric equilibria⁽³⁾. It should be noted, however, that the "tautomers" in the present case are not neutral molecules, but ions identical in charge yet different in chemical composition. The ratio of conjugated carbonium and ammonium ions, derived taking into account the values of the ionization constants K_1 and K_2 , has the following form:

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

$$\frac{[\text{II}]}{[\text{I}]} = \frac{K_1}{K_2} \frac{f_{\text{BH}^+} f_{\text{ROH}}}{f_{\text{R}^+} f_{\text{B}} a_{\text{H}_2\text{O}}}, \quad (2)$$

where f_{BH^+} , f_{R^+} are the activity coefficients of the ammonium and conjugated carbonium ions, and f_{B} and f_{ROH} are the activity coefficients of the corresponding bases.

Table 1

Values of the ionization constants of dimethylamino groups of conjugated carbonium ions of aminotriphenylcarbinols

Compounds II	K
a	$3.89 \cdot 10^5$
b	$2.57 \cdot 10^7$
c	$1.20 \cdot 10^9$
d	$1.07 \cdot 10^7$
e	$2.29 \cdot 10^8$

The different changes in the activity coefficients of the conjugated carbonium and ammonium ions and their corresponding bases in solutions of strong acids are reflected in the difference between the acidity scales H_0 and H_R . If equation (2) is compared with the expression for the difference of the acidity functions H_0 and H_R (⁴), it is not difficult to see that

$$\lg \frac{[\text{II}]}{[\text{I}]} = \lg \frac{K_1}{K_2} + H_0 - H_R. \quad (3)$$

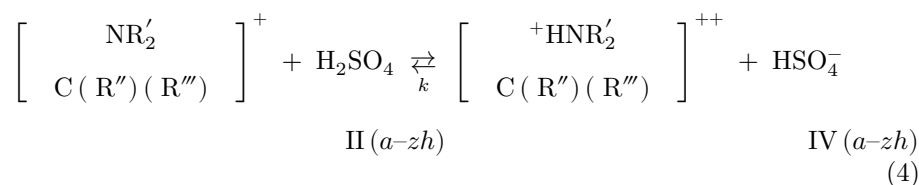
The experimental data obtained by us show that the dependence between $\lg \frac{[\text{II}]}{[\text{I}]}$ and the difference of the acidity functions is indeed linear; however, the tangent of the angle of inclination of the straight line is not equal to 1, but varies within the limits from 0.70 to 0.75 (Fig. 1).

Fig. 1. Dependence of \lg of the ratio of the concentrations of conjugated carbonium and ammonium ions on the difference of the acidity functions H_0 and H_R : 1 –IIa/Ia; 2 –IIb/Ib; 3 –IIv/Iv; 4 –IIe/Ie; 5 –IIzh/Izh

Fig. 2. Dependence of the percentage content of 4-dimethylaminotriphenylcarbinol and its ionized forms on the acidity of the medium. 1 –(IIIa); 2 –(Ia); 3 –(IIa); 4 –(IVa)

Recently, the question of the validity of applying the acidity scales H_0 and H to various compounds has repeatedly been raised in the literature (⁵⁻⁸). Apparently, in the case of aminotriphenylcarbinols, the use of these acidity functions also requires certain corrections.

In more concentrated solutions of sulfuric acid, salt formation of amino groups in the conjugated carbonium ions (II) occurs



On the basis of spectral data, the ionization constants of the dimethylamino group of the conjugated carbonium ions of aminotriphenylcarbinols were calculated (Table 1).

The data obtained make it possible to determine the percentage content of one or another form of aminotriphenylcarbinols at various values of the acidity of the medium. As an example, Fig. 2 presents the dependence of the percentage content of 4-dimethylaminotriphenylcarbinol and its ionized forms on the acidity of the medium.

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

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