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Structures (I), (II), and (III) for the 2-vinylpyridine complex with proton donors.

Figure 1: Structures (I), (II), and (III) for the 2-vinylpyridine complex with proton donors.

Abstract

Full Text

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On the Possibility of Regulating the Degree of Alternation in the Copolymerization of Styrene with 2-Vinylpyridine

(Presented by Academician V. A. Kargin, October 4, 1963)

In the copolymerization of styrene with 2-vinylpyridine, no effect of monomer alternation is observed ($r_2 > 1$). This is explained by the fact that both monomers have a certain excess of electron density in the double bond, whereas monomers with opposite polarities of the double bonds alternate. In order to create copolymerization conditions ensuring alternation of the indicated monomers, it is necessary to change the polarity of the double bond of one of them to the opposite. We changed the polarity of the double bond of 2-vinylpyridine by forming a complex of the latter with proton-donor substances which, when introduced into the initial monomer mixture, form a hydrogen bond with the nitrogen atom of 2-vinylpyridine. In describing a hydrogen bond by methods of quantum chemistry, the wave function of the complex connected by the hydrogen bond is represented as a linear combination of functions corresponding to the various structures of this complex ([1,2]). Usually one is limited to three structures, taking into account the possible distribution of four electrons over three atoms; for the case under consideration this is the system of atoms $-O..H : N\leq$. Let us consider these structures for the complex of 2-vinylpyridine with proton-donor substances, the latter denoted by R—OH. From comparison of these structures it is seen that in structure (III) 2-vinylpyridine exists in the form of a 2-vinylpyridinium ion.

It is known ([3]) that the pyridinium ion differs from pyridine by a sharp displacement of the electron density of the ring in the direction of the positively charged nitrogen atom. Similarly, the electron density of 2-vinylpyridinium should also be displaced through the system of conjugated bonds in the direction of the positively charged nitrogen atom. As a result, the double bond acquires a considerable positive charge. But the real structure of the complex includes, to one degree or another, elements of all three structures. Therefore the contribution of structure (III) will lead to a decrease in the electron density of the double bond of 2-vinylpyridine. The overall effect is shown in the following scheme:

Scheme showing displacement of electron density in the hydrogen-bonded 2-vinylpyridine complex.

Figure 2: Scheme showing displacement of electron density in the hydrogen-bonded 2-vinylpyridine complex.

Fig. 1

Figure 3: Fig. 1

The displacement of the electron density of the double bond should be significant, since the effect is transmitted from atom to atom through the system of conjugated bonds.

It is obvious that the weight of structure (III) in the real structure of the complex increases with an increase in the proton-donor properties of R—O—H. These properties can be estimated from the dissociation constants of R—O—H in aqueous

solutions. From this it may be assumed that, when complexes of 2-vinylpyridine with proton-donor substances are formed, the electron density of its double bond decreases the more, the higher the dissociation constant of the indicated substances. At the same time, the difference between the polarities of the double bonds of styrene and 2-vinylpyridine increases more and more, which should lead to an increase in the degree of their alternation and, correspondingly, to a decrease in the product $r_1 \cdot r_2$.

Fig. 1. Composition curves of the styrene—2-vinylpyridine copolymer obtained in the presence of various additives and in bulk: 1 —acetic acid, 2 —phenol, 3 —methanol, 4 —ethanol, 5 —copolymerization without additives. m_2, M_2 —mole fractions of 2-vinylpyridine in the copolymer and in the monomer mixture

To verify this proposition, we carried out copolymerization of styrene with 2-vinylpyridine in the presence of additives having different dissociation constants of the —O—H bond. Figure 1 presents the composition curves; the corresponding values of r_1, r_2, and $r_1 \cdot r_2$, calculated by the Joshi–Kapoor method ([4]), are given in Table 1. It is seen from the figure that, during copolymerization in the presence of the mentioned additives, the composition curves acquire an S-shaped form characteristic of monomer alternation during copolymerization. The corresponding values of the relative activities are less than unity, which is also characteristic of the effect of monomer alternation in copolymerization. The greater the dissociation constant of the additive, the smaller the values of r_1, r_2, and $r_1 \cdot r_2$, and, consequently, the better the alternation.

A quantitative treatment of the results obtained was carried out using the Hammett equation: $\lg \dfrac{k}{k_0} = p\sigma$, where k and k_0 are the rate or equilibrium constants of the reaction of a functional group of a substituted and an unsubstituted ben-

Fig. 2

Figure 4: Fig. 2

zene nucleus, σ is the constant referring to the substituent, and p is a constant determined by the type of reaction. This equation reflects the fact that, in aromatic systems, a substituent can influence the reactivity of another group through the system of mobile conjugated bonds. In the case considered by us, in principle the same phenomena occur. A local change in the electron density of the aromatic pyridine nucleus, caused by the different polarization of nitrogen, affects the reactivity of the double bond conjugated with it or of the free radical. Consequently, we compare the substituents $R_1, R_2, \ldots, R_n \ldots$ in the benzene nucleus with complex

Table 1

Values of the relative activities and their products in the copolymerization of styrene and 2-vinylpyridine in the presence of additives

Additive	pK of additive	r_1	r_2	$r_1 \cdot r_2$
Copolymerization in bulk		$0,57 \pm 0,05$	$1,33 \pm 0,08$	$0,758$
Acetic acid	$4,75$	$0,16 \pm 0,04$	$0,36 \pm 0,07$	$0,0576$
Phenol	$9,95$	$0,253 \pm 0,06$	$0,549 \pm 0,07$	$0,139$
Methyl alcohol	16	$0,426 \pm 0,05$	$0,607 \pm 0,06$	$0,258$
Ethyl alcohol	18	$0,486 \pm 0,07$	$0,862 \pm 0,08$	$0,418$

by groups R_1—O—$H \ldots N <$, R_2—O—$H \ldots N <, \ldots$

R_n—O—$H \ldots N <$, i.e., with the nitrogen atoms in the complex with additives of different acidity in the pyridine ring. As applied to our case, $k = k_{12}$, $k_0 = k_{12}^0$, where k_{12} and k_{12}^0 are the constants of interaction of 2-vinylpyridine, in the form of a complex and in the free form, with the styrene radical. As σ it is logical to take a quantity proportional to $\lg K_{\text{diss}}$ of the additive R—O—H, since precisely this quantity determines the fraction of structure (III) in the real structure of the complex and, consequently, the change in the polarity of the double bond of 2-vinylpyridine.

Fig. 2. Dependence of $\lg \dfrac{r_1^0}{r_1}$ and $\lg \dfrac{r_2^0}{r_2}$ on the pK of the additive

Fig. 3. Dependence of $\lg \dfrac{r_1^0 \cdot r_2^0}{r_1 \cdot r_2}$ on the pK of the additive

Fig. 3

Figure 5: Fig. 3

Hammett' s equation will have the form: $\lg \frac{k_{12}}{k_{12}^0} = pa \lg K_{\text{diss}}$. But $k_{12} = \frac{k_{11}}{r_1}$, $k_{12}^0 = \frac{k_{11}^0}{r_1^0}$, where $k_{11} = k_{11}^0$, since the formation of a complex of 2-vinylpyridine with the additive is not reflected in the rate of homopolymerization of styrene. Consequently, $\lg \frac{k_{12}}{k_{12}^0} = \frac{r_1^0}{r_1} = \lg \frac{r_1^0}{r_1} = pa \lg K_{\text{diss}}$. Denoting $p \cdot a = p_1$ and taking into account that $\lg K_{\text{diss}} = -\text{pK}$, we finally obtain:

$$\lg \frac{r_1^0}{r_1} = -p_1 \text{pK}. \tag{1}$$

An analogous relation can be derived for r_2. But in this case the replacement of $\lg \frac{k_{21}}{k_{21}^0}$ by $\lg \frac{r_2^0}{r_2}$ will be a cruder approximation, for k_{22} is not equal to k_{22}^0. However, there is reason to think that they differ only slightly, since the rates of homopolymerization of the monomers are determined mainly by their ideal radical reactivity, and not by the polarities of the double bonds. In any case it is clear that r_1 and r_2 decrease owing to the sharp change in k_{12} and k_{21}, i.e., the constants of alternate addition of monomers, since their magnitude will be affected primarily by the change in the polarity of the double bonds of the monomers. Therefore for r_2 we shall also write:

$$\lg \frac{r_2^0}{r_2} = -p_2 \text{pK}. \tag{2}$$

In Fig. 2, $\lg \frac{r_1^0}{r_1}$ and $\lg \frac{r_2^0}{r_2}$ are plotted as functions of the pK of the corresponding additives. The expected linear dependence is well obeyed for

$\lg \frac{r_1^0}{r_1}$ and worse for $\lg \frac{r_2^0}{r_2}$. In light of the foregoing, the latter is not unexpected.

From the derived relations one can easily obtain an expression for the dependence of the product $r_1 \cdot r_2$ on the pK of the additive. Adding (1) and (2) term by term, we obtain $\lg \frac{r_1^0}{r_1} + \lg \frac{r_2^0}{r_2} = -p_1 \text{pK} - p_2 \text{pK}$. This expression is reduced to the form

$$\lg \frac{r_1^0 \cdot r_2^0}{r_1 \cdot r_2} = -(p_1 + p_2)\, \text{pK}. \tag{3}$$

From Fig. 3 it is seen that a straight-line dependence between $\lg \frac{r_1^0 \cdot r_2^0}{r_1 \cdot r_2}$ and the pK of the additive is indeed observed. This graph makes it possible to find conditions for obtaining a copolymer of styrene and 2-vinylpyridine with a predetermined degree of alternation. Indeed, a definite value of the product $r_1 \cdot r_2$ corresponds to it. Having specified the desired value of this product, one should calculate the value $\lg \frac{r_1^0 \cdot r_2^0}{r_1 \cdot r_2}$ and, from the graph in Fig. 3, determine the pK of the corresponding "acidic" solvent. By carrying out the copolymerization in its medium, one can obtain a copolymer of the required structure.

Experimental Part

The monomers were purified by vacuum fractional distillation; their physicochemical constants are given below: styrene n_d^{20} 1.5462, d 0.909 g/cm^3; 2-vinylpyridine n_d^{20} 1.5495, d 0.982 g/cm^3. Copolymerization was carried out under ultraviolet light at 22° to 5–7% conversion of the monomers. To accelerate the process, benzoyl peroxide was added in an amount of 0.5% by weight of the monomers. Acetic acid, phenol, methyl and ethyl alcohols were used as additives. Acetic acid and phenol were introduced in an amount of 1.4 mol, and the alcohols in an amount of 2.5 mol per mol of 2-vinylpyridine. The copolymer was precipitated twice from pyridine to remove the additives and then four times from benzene. Petroleum ether served as the precipitant. Analysis of the copolymer was carried out by titration of the pyridine groups of the copolymer with a solution of hydrochloric acid in glacial acetic acid. The procedure used is analogous to that described in work (5). Relative activities were determined from five points by the Joshi-Kapur method. The values of the dissociation constants of the compounds used as additives were taken from the literature data (6). Additives with a dissociation constant greater than the dissociation constant of acetic acid were not used, since they cause ionic oligomerization of 2-vinylpyridine.

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