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Abstract

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ON THE INFLUENCE OF THE METAL AND THE SOLVENT ON THE FORMATION OF AROMATIC ANION RADICALS–INITIATORS OF POLYMERIZATION

In recent years, much attention has been attracted by the study of anion radicals arising as a result of electron transfer from an alkali metal to an organic molecule. Such anion radicals can initiate polymerization, leading to the formation of so-called "living" polymers ([1]). It is important to know how the conditions of formation of anion radicals and their stability change depending on the metal, and also on the properties and structure of the solvent molecules. This is also of interest for the study of polymerization processes. However, the information available in the literature is sparse and fragmentary ([2,3]).

Until recently, only anion radicals of polycyclic hydrocarbons had been studied; for the initiation of polymerization, usually, following Scott ([4]) and Szwarc ([5]), sodium naphthalene in 1,2-dimethoxyethane or in tetrahydrofuran was used. Recently it was shown ([6,7]) that, in reaction with metallic potassium in dimethoxyethane, anion radicals of benzene and its homologues can be obtained. Monocyclic hydrocarbons have a lower electron affinity than polycyclic hydrocarbons ([8]), and therefore are more suitable for differentiating the influence of various factors on the formation of anion radicals.

Setting ourselves the task of studying the influence of the metal and the solvent on the formation of aromatic anion radicals, in the present communication we chose benzene and toluene as the objects of study, while the solvents used were: 1,2-dimethoxyethane (DME), 1,2-methoxyethoxyethane (MEE), 1,2-diethoxyethane (DEE), tetrahydrofuran (THF), and 1,3-dioxane (DO). To detect the anion radicals and determine their stability, the method of electron paramagnetic resonance was used. Ethylene glycol ethers were synthesized according to ([9,10]), and 1,3-dioxane was obtained according to ([11]). The preparations were fractionated and then boiled for a long time with metallic sodium. To obtain the anion radicals, the following procedure was used. A system of ampoules was attached to a high-vacuum apparatus. After the ampoules had been evacuated while being heated, thoroughly washed with carefully purified nitrogen, and evacuated again, a potassium mirror was deposited on their inner surface. In one of the ampoules there was a frozen solvent (1 ml) mixed with hydrocarbon (0.03 ml). This mixture was several times recondensed from ampoule to ampoule onto a freshly deposited potassium mirror. After such purification, the mixture was distilled into a special ampoule onto the surface of a metallic mirror and the ampoule was sealed off. The ampoule was provided with a side arm for measuring paramagnetic absorption. EPR spectra were measured on the instrument described in ([12]). The character of the EPR spectrum ([8]) did not change when all the solvents and metals studied were used. The relative concentration of anion radicals in solution was determined from the intensity of one and the same component in the spectrum.

Experiments with benzene were carried out at its concentration of approximately 0.4 mole per liter of solution and at a temperature of about -30°. With potassium in DME, the concentration of anion radicals obtained was 4–5 times greater than in DEE. Equilibrium was attained both from the side of higher and from the side of lower temperatures. When sodium was taken instead of potassium, then in DEE the concentration of anion radicals obtained was at least two orders of magnitude lower, which is possibly due in part to the fact that equilibrium is reached with greater difficulty. Parallel experiments carried out at -70° with lithium and sodium in DEE showed that with lithium a considerably higher concentration of benzene anion radicals is formed than with sodium.* It should be noted that solutions of benzenesodium, benzenelithium, and benzenepotassium in DEE are yellow, in contrast to the green solutions of the latter compound in DME. Apparently this depends on the fact that at low temperature potassium is dissolved in DME, and the blue color of its solution is superimposed on the yellow color of the anion radical.

Experiments with toluene, which has a lower electron affinity than benzene, make it possible to characterize more clearly the influence of the above-mentioned solvents on the formation of anion radicals. Table 1 gives approximate data that allow one to judge the relative concentration of toluene anion radicals. The value C expresses the concentration of anion radicals relative to their concentration in a solution of toluenepotassium in DME, which is conventionally taken as 100.

Table 1

Dependence of the concentration of anion radicals on the solvent and metal (0.4 mole of toluene in 1 l of solution at a temperature of about -30°)

Solvent	Metal	C	Color of solution	Solvent	Metal	C	Color of solution
DME	K	100	Blue-green	MEE	Na	1.5	Colorless
MEE	K	30	Green	DEE	Na	0	Colorless

Solvent	Metal	C	Color of solution	Solvent	Metal	C	Color of solution
DEE	K	3	Almost colorless	DO	K	1	Yellow*
THF	K	0.4	Light blue				

* Since toluene anion radicals are formed with difficulty in 1,3-dioxane, the experiment was carried out with benzene. The calculation of C was made taking into account the difference in the number of components in the EPR spectra of benzene and toluene.

Table 1, together with the results presented above concerning the formation of benzene anion radicals, permits the following conclusions to be drawn:

1. Benzene anion radicals can be obtained in reaction with Li, Na, and K; with potassium they are formed in DME, MEE, DEE, THF, and DO.
2. Replacement of the methyl group in ethylene glycol diether by an ethyl group lowers the stability of the anion radicals—it decreases in the series DME, MEE, and DEE.
3. The compound of an aromatic hydrocarbon (benzene) with sodium is formed with greater difficulty than with potassium and lithium.

A comparison of the results we obtained with literature data on the solubility of alkali metals in ethers ([13,15]) shows that there are common features between the processes of dissolution of metals and their interaction with aromatic hydrocarbons. Thus, for example, the solubility of the eutectic alloy K—Na in ethylene glycol ethers, like the stability of the anion radicals, decreases in the series DME, MEE, and DEE ([13]). Apparently, both processes depend on solvation of the metal cation, which—

* In note ([8]) it is indicated that sodium does not add to benzene at all.

due to the enhanced electron-donor ability of the oxygen atoms of the solvent molecule, provided that the atoms in it have a favorable spatial arrangement. Replacement of methyl groups by ethyl groups in ethylene glycol ether may create steric hindrance during solvation of the cation.

As for comparison of the metals, judging from the data available in the literature ([13], [14]), Li and Na do not dissolve even in DME, unlike K, Rb, and Cs. This could be attributed to the larger ionization potential of the first two metals, but, as Caffasso and Sandeim note ([14]),

Fig. 1

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 2

in the sequence of solubilities of alkali metals in different solvents, individual features are observed. In addition, the observations reported in the literature require further verification.*

We carried out a series of experiments on initiating the polymerization of styrene with a solution of benzylpotassium in DME, MEE, and DEE.**

The resulting solutions were colored red and red-violet and in a number of cases exhibited paramagnetic absorption. In the EPR spectrum a narrow singlet was detected against the background of a broad band (Fig. 1). The EPR spectra were obtained at room temperature, when benzylpotassium is unstable and gives no signal. When polymerization was initiated with a solution of potassium in DME without benzene***, in a number of experiments solutions colored green were obtained (at temperatures of about -50 to $-80°$), whose EPR spectrum at low temperature was characterized by the presence of a quintuplet (Fig. 2). This can be associated with the formation of an anion radical arising as a result of addition of an electron to the aromatic ring of polystyrene and similar in structure to the anion radical of monoalkylbenzene. The spectra shown here differ from the EPR spectra of polystyrene anion radicals obtained by Japanese authors under somewhat different conditions ([16]). The work is continuing.

* With very thorough purification of DME we obtained, at low temperature, a blue solution of Li, while E. A. Kovrizhnykh observed a blue coloration upon contact of DME with a sodium mirror at low temperature. Spectral analysis, kindly performed in the laboratory of A. K. Rusanov, showed that the sodium contained less than 0.01% potassium.

** The polymer samples had molecular weights of 350,000–700,000; $[\eta] = 1.0$–2.0 in benzene solution. The measurements were performed by Yu. P. Vyrskii.

*** When these experiments on polymerization with an ethereal solution of the metal had been carried out, we became aware of a brief communication on analogous work by Dainton and co-workers ([15]).

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