The Radical and Ion-Radical Mechanism of Polymerization of 2,6-Xylenol. III. Phenoxonium Ions

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> > Received December 20, 1969

In revised form June 9, 1970

This cansfer of an electron from tri-tert-butyl-phenoxy radicals to Cu(II) ions v. s proved by means of a parallel study of EPR and NMR spectroscopy and electric conductivity. During the "titration" of an ethanol solution of CuCl₂ with benzene solution of the free radical, by elimination of oxygen, the intensity of the EPR signal of the unpaired $3d^9$ electron of Cu(II) ions decreases and, after attaining the equilibrium state, the signal of free radical (g = 2.006) can be observed. The simultaneously measured direct conductivity travels through a maximum. In deuterated solvents at a molar ratio of 1 : 1 the broadening of the NMR lines primarily caused by paramagnetic properties of both components [Cu(II) and free radical], will be eliminated. Under these conditions a high resolved spectrum can be observed. The transfer of an electron from the radical to the Cu(II) ion is connected with an expressive chemical shift. Unambiguous interpretation of NMR spectra is made difficult by secondary reactions following the charge transfer effect.

Interpreting the radical-ion mechanism of polymerization by oxidative synthesis of 2,6-xylenol catalyzed by Cu(II)-amine complexes, the origin of positive phenoxonium ions was assumed [1] as a result of electron transfer from the aryloxy radical to Cu(II). On the basis of kinetic analysis an analogous electron transfer from aryloxy radicals to $IrCl_4$ and a simultaneous reduction of iridium has been reported [2]. From the chemical analysis of the products of the phenol oxidation by dichlorcyanobenzoquinone, *Becker* [3] suggests that during this reaction passing through the radical-ion mechanism, intermediately positive phenoxonium ions are formed. A direct evidence of these ions at the oxidation of 2,6-xylenol by copper complexes has not yet been done. Stable phenoxonium ions prepared by *Dimroth* [4] by the oxidation of tris-phenyl substituted phenols were identified from their infrared spectra. As the primary radicals generated by initiation are of relatively short life-time [5], for the model study of electron transfer the stable tri-*tert*-butyl-phenoxy

Presented at the III^{ème} Réunion Franco-Tchécoslovaque, Mürbach, October 27-31, 1969.

radical was used. The reactions of this radical dissolved in benzene, with $CuCl_2$ in ethanol at different molar ratios were studied simultaneously by EPR and NMR spectroscopy as well as by direct and alternate electric conductivity.

Experimental

EPR technique

EPR spectrometer Varian E-3 with 100 KHz modulation was used. Solutions were prepared in the absence of oxygen and humidity. All measurements were carried out in inert atmosphere in cells of 4 mm diameter closed by a three-pass stop-cock placed in a resonance cavity of the modus H_{011} . In order to follow the changes of the electric conductivity parallelly with the changes of EPR signals in an inert atmosphere, a special cell developed for this purpose, was used. The reaction of copper(11) ions with stable free radicals was carried out by "titration" technique. A 0.1 mole l^{-1} solution of tri*tert*-phenoxy radical (TTBP) in benzene was gradually added to 0.1 mole l^{-1} ethanol solution of CuCl₂ while intensive mixing by magnetically driven rotor. The direct conductivity was defined by measuring the electric current (with milliammeter) given by the resistance of the system at a constant potential (6 V). The determination of the current was done always one minute after joining the potential to the electrodes. The alternating conductivity was calculated from the resistance measured with a conductoscope.

By turning the double cell, the measured solution was poured into the cylindric tube placed into the resonance cavity of the spectrometer. The quantitative data were corrected for the dilution.

NMR technique

The NMR spectrometer Tesla BS 487 operating at 80 MHz was used. The closed glass cells of 5 mm diameter were filled with the solutions under investigation in the manipulator in a highly purified nitrogen atmosphere. The sweeping rate of the spectra was 2 Hz s⁻¹. The calibration for the chemical shift determination was done by the "sideband" technique on the basis of modulation frequency of 640 Hz (8 p.p.m.) controlled by the universal computer of vibrations Tesla 445 E with a precision of 10^{-6} . 1-2% of HMDS hexamethylene disiloxan used as calibration standard, was added to the samples.

Hexadeuterated benzene (98.9%) and completely deuterated methanol (CD₃OD) (VEB Chemie, Berlin-Adlershof) were used as solvents.

The experiments were carried out in the concentration range of 1 to 0.1 mole l^{-1} phenoxy radical and waterless CuCl₂.

At paramagnetic solutions a phase shift, individually corrected for all NMR spectra, was observed.

The free radical was prepared by the oxidation of chromatographically pure tri-tertbutylphenol in benzene-water solution [6]. The purity of the radical was controlled by the IR and NMR spectra. Since in a perfectly inert atmosphere at laboratory temperature the radical changes with time (half-life time about 7 days), the measurements were carried out with freshly prepared samples. CuCl₂ was used without water, dried at 110°C to constant weight. The other chemicals were p.a. and before use they were purified from traces of oxygen by blowing through highly purified nitrogen or argon.

Results and Discussion

During the titration of the ethanol solution of CuCl_2 by benzene solution of the TTBP free radical the intensity of the EPR signal belonging to the $3 d^9$ unpaired electrons of Cu(II) (g = 2.16) gradually decreased and after reaching the equimolar ratio of 1:1 an increase of the EPR signal intensity of the free radical (g = 2.006) (Fig. 1) was observed. With the electron transfer from the radical to the copper



Fig. 1. Change of the number of unpaired electrons during the titration of 1 ml ethanol—benzene solution of waterless CuCl₂ (0.1 mole l^{-1}) by a 0.1 mole l^{-1} solution of TTBP radical. The amount of the samples in the EPR cell was 0.3 ml.



Fig. 2. Change of the number of unpaired electrons of Cu(II) ions at g = 2.16 (1) and TTBP radicals at g = 2.006 (2) expressed by the area of the respective EPR signals ($S_{\rm EPR}$), and of the direct conductivity \varkappa (3) at the variation of the molar fraction of Cu(II) during the titration of ethanol 0.1 mole 1^{-1} solution of phenoxy radical. All quantities were corrected for the volume difference ($\varkappa_{\rm corr.} = (v/v_0) \varkappa_{\rm exp}$, v — the total volume of the mixture, v_0 — the initial volume).

the originally paramagnetic ions of Cu(II) change to EPR inactive ions of Cu(I) whereby the original level of unpaired electrons decreased from 10^{19} to 10^{16} (for 0.3 ml of the sample), it means by about 3 ranges. The number of unpaired electrons belonging to Cu(II) and of free radicals on the molar fraction are shown in Fig. 2. This diagram also shows the simultaneously measured direct electric conductivity of the mixture considered. With the successive decrease of the amount of Cu(II) ions indicated by the EPR method the direct current conductivity corrected for the dilution by benzene does not fall monotonously but passes through a maximum before reaching the equimolar ratio of CuCl₂ and of the TTBP free radicals.

For the unambiguous interpretation of the increased direct conductivity it was necessary to examine the effect of $CuCl_2$ dilution in the absence of the radical by both solvents used in the reaction system (ethanol—benzene). As it is seen in the diagram (Fig. 3), the dilution by ethanol causes no change either of the corrected direct or the alternating current conductivity. The dilution by benzene, however, causes a decrease of the corrected current conductivity, especially at higher dilution. This effect is probably connected with a decrease of the dissociation grade of $CuCl_2$ owing to the decrease of the dielectric constant of the solution. In the absence of the free radical, however, in none of the mentioned cases the maximum was observed. In the presence of the free radical, on the other hand, in the benzene solution the steep decrease of conductivity is more expressive than the decrease observed for the dilution with pure benzene.

It follows from these results and EPR measurements that between Cu(II) and the free radical a reaction connected with electron transfer takes place leading to an increase of direct conductivity. On the other hand, the alternating conductivity



Fig. 3. Influence of dilution on the corrected conductivity $(v - \text{total volume}, v_0 - \text{initial volume})$. 0.1 mole l^{-1} ethanol solution of CuCl₂.

The alternating conductivity at 50 Hz, dilution by ethanol (1); dilution by 0.1 mole 1^{-1} benzene solution of TTBP radical (2); direct conductivity, dilution by ethanol, inside electrode negative (3); dilution by benzene, inside electrode negative (4); dilution by 0.1 mole 1^{-1} TTBP radical, inside electrode negative (5); dilution by 0.1 mole 1^{-1} benzene solution of TTBP radical, inside electrode positive (6).



Fig. 4. Dependence of electric conductivity upon the molar fraction of copper $X_{\rm Cu}$ during the titration of 0.1 mole l^{-1} ethanol solution of TTBP radical $X_{\rm Cu}$ + + $X_{\rm Ro.} = 1$. The quantities were corrected for the volume difference.

The alternating conductivity at the frequency 1000 Hz (1); direct conductivity — the inside electrode connected to the negative pole (2); direct conductivity — the inside electrode connected to the positive pole (3). decreases during the titration already from its origin. As the conductivity cell in use is cylindrical (a platinum spiral with a concentrically placed platinum wire) an expressive polarization effect on the direct conductivity may be expected in contrast to the alternating one, according to the choice of polarity on the electrodes. When the platinum wire is negative and the cylindrical electrode positive, the maximum observed is higher than in the case of the opposite polarity. According to this fact it is possible to conclude that the conductivity calculated from the current measured 1 minute after the connection of the potential, is a result of polarization effects — by the formation of volume charge before the electrodes, because it depends on the shape of the electrodes and their polarity. The more expressive maximum is probably caused by the formation of a more voluminous ion, a product of the reaction. At the alternating conductivity the motion of voluminous ions, which do not take part in the conductivity defined only by the icns of Cu(II) and Cl⁻, practically does not take place, and so during the titration by free radicals the alternating conductivity falls (Fig. 4).

According to the proposed reaction [1] formation of the positive phenoxonium ions can be expected. The scheme A supposes a rising of conductive particles to



equimolar ratio at keeping the electroneutrality of the system. According to the previous consideration the maximum observed at the direct conductivity may be attributed to the more voluminous positive phenoxonium ions, while the smaller Cu(II), Cu(I), Cl⁻ ions form the volume charges before the electrodes practically in the same time at the connection of the potential. The next decrease of the conductivity is caused by the dilution with non-polar benzene, what can lead to a decrease of the dissociation (Scheme B). The associated chlorinated derivatives were proved also by the infrared spectroscopy [7].

$$t-Bu + Cl^{-} \underbrace{benzene}_{t-Bu} + Cl^{-} \underbrace{benzene}_{t-Bu} (B)$$

$$t-Bu = C(CH_{3})_{3}$$

The problem of an electron transfer and the formation of phenoxonium ions was parallelly studied also by NMR spectroscopy. In Fig. 5 three NMR spectra are mutually compared: 0.2 mole l^{-1} solution of TTBP free radical in hexadeuterated benzene (c), 0.4 mole l^{-1} solution of tri-*tert*-butylphenol in hexadeuterated benzene (b), mixture of 0.52 mole l^{-1} TTBP free radical in hexadeuterated benzene with 0.2 mole l^{-1} CuCl₂ in CD₃OD in the ratio 2:5 (a), which corresponds to the molar ratio of free radical : CuCl₂ = 1:1 (calculated with a lower capacity of radical than

100%). The additionally shown chemical shifts are the average values of four experimentally measured spectra. The whole spectrum of the TTBP free radical lies in a wide frequency region [8]. In the region measured we could observe only the lines of the protons of the tri-*tert*-butyl groups in *ortho* position, which are extraordinarily broad and visible only at relatively high concentration (1 mole l^{-1}).



Fig. 5. NMR spectra (80 MHz). a) mixture of 0.52 mole l^{-1} solution of TTBP radical in deuterated benzene and 0.2 mole l^{-1} solution of CuCl₂ in deuterated chloroform in the molar ratio of 1:1; b) 0.4 mole l^{-1} solution of tri- *-tert*-butylphenol in hexadeuterated benzene; c) 0.2 mole l^{-1} solution of TTBP radical in hexadeuterated benzene.



Fig. 6. ERP spectrum of the equimolar mixture of $CuCl_2$ and TTBP radical in deuterated solvents under the same conditions as in the case of the NMR spectrum according to Fig. 5a.

The lines in the spectrum belong therefore to the phenolic products (nonreacted tri-*tert*-butylphenol, dimer of the free radicals, products of consecutive reactions), which, in any case, are present in low concentration in the sample of the TTBP free radical.

The paramagnetic nature of a free radical is expressed by considerable broadening of lines that causes the rubbing of the hyperfine structure of the tri-*tert*-butylphenol. The distinction of lines is a function of the concentration; at raised concentration a higher phase shift was observed. The aliphatic part of the spectrum is in the range of 1.2-1.3 p.p.m., and at concentrations lower than 0.4 mole l^{-1} a till now undefined band has been observed at 0.73 p.p.m. The protons on the aromatic ring are blended with those of not deuterated benzene (7.1-7.2 p.p.m.) partially present in the mixture (b).

The spectrum of tri-*tert*-butylphenol is formed of four types of protons with different values of shading. In the range of 1.20-1.30 p.p.m. two lines belonging to ortho and para tri-*tert*-butyl groups in the assumed ratio 2:1 may be observed. The hydroxylic proton is found at 4.67 p.p.m. and two ring protons absorb at 7.23 p.p.m. (5% of the remaining not deuterated protons of benzene which gives the line at 7.03 p.p.m.). Little deviations from the values of chemical shifts published by Gibbons and Gil [9] are caused by solvent effects because the NMR spectra of tri-*tert*-butylphenol were measured in a CCl₄ solution.

The equimolar mixture of two originally paramagnetic components, namely the phenoxy free radical and CuCl_2 gives a well distinguished NMR spectrum (a). The narrowing of the NMR lines is due to the considerable decrease of concentration of the paramagnetic components. The simultaneously measured proper EPR spectrum (Fig. 6) shows that the original concentration of the free radicals as well as the paramagnetic ions of Cu(II) have decreased to the value of about 10^{-4} mole l^{-1} . This low level of paramagnetic components has no influence on the quality of NMR spectra.

In comparison with 2,4,6-tri-tert-butylphenol, the equimolar mixture shows a higher number of lines in the aliphatic region (0.73-1.37 p.p.m.). This spectral region is characterized by five lines of different intensity. The chemical shift of lines 1.22 and 1.37 p.p.m. corresponds with its value to the protons of the tri-tert-butyl groups of 2,4,6-tri-tert-butylphenol defined in the presence of CuCl₂. At equal splitting (of about 0.16 p.p.m.) only the width of both lines is changed.

At this time it is not possible to interpret the lines unambiguously because the structure of NMR spectra is simultaneously dependent in various degrees on several other factors; e.g. on the effects caused by a solvent, by dissociation, by traces of oxygen and by products formed at the successive decay of the free radical. Also at relatively low temperature even in inert atmosphere the products of phenolic character are formed [10] as a result of the gradual change of the radical with a half-time decay of 7 days. If a free radical is used directly after its preparation, the relatively most intensive lines are with the 0.9 and 1.1 chemical shift. These lines do not appear in the NMR spectrum of tri-*tert*-butylphenol, they change parallelly by modification of the conditions and they are followed by intensity changes of the lines belonging to protons on the aromatic ring at 6.61 p.p.m. The electron transfer leads directly to the decrease of paramagnetism of the components, where new types of alkyl as well as aromatic protons are formed. The variations in the shading effect in forming phenoxonium ions and total analysis of the proper NMR spectra remain of permanent interest in our study.

As in the final products of polymerization of 2,6-xylenol by $CuCl_2$ -amine complexes no chlorinated derivatives are observed, it must be assumed that in the presence of amines and xylenol as monomers the positive phenoxonium ion indicated by EPR and NMR spectroscopy as well as by direct and alternate electric conductivity reacts before all with xylenol to polymer.

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Translated by M. Tkáčová