plane of the ion, which may then be occupied by the anion of the acid residue. The parameters observed for complex (III) are in accord with the hypothesis of the entry of an oxyacid anion into the equatorial environment of the copper.

The ESR parameters of complex (IV), which is formed during the oxidation reaction or by hydroperoxide treatment of PBC, are not very much different from the parameters of complex (III). It is possible that complex (IV) has a similar structure to complex (III), the only difference being that an OH group is probably coordinated to the Cu(II) ion in the equatorial plane and the N atom becomes attached to one of the R' or RO' radicals formed by decomposition of the HP.

CONCLUSIONS

1. On the basis of an analysis of the ESR parameters of Cu(II) ions stabilized in polymers derived from substituted chrysoidines and an examination of the effect of various reagents, a model is proposed for the copper-containing centers.

2. The data obtained indicate the high lability and reactivity of the copper-containing centers in polymers which are catalytically active with respect to the liquid-phase oxidation of hydrocarbons.

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INFLUENCE OF SOLVENTS ON THE KINETICS OF THE REACTION

OF BENZYL CHLORIDE WITH METHACRYLIC ACID

IN THE PRESENCE OF TERTIARY AMINES

UDC 541.12.038.2:541.127:547.539.211.3:547. K. A. Charushnikov, M. A. Bulatov, 391.3 and L. G. Surovtsev

Benzyl methacrylate and other methacrylates of benzyl alcohols are synthesized from the corresponding chloromethyl compounds by nucleophilic substitution of the chlorine atom under the action of methacrylic acid (MAA) in the presence of a tertiary amine [1, 2]

$$\begin{array}{c} CH_{3} & CH_{3} \\ \downarrow \\ ArCH_{2}Cl + CH_{2} = CCOOH + R_{3}N \rightarrow ArCH_{2}OCOC = CH_{2} + R_{3}N \cdot HCl \end{array}$$
(1)

We investigated the influence of the nature of the solvent on the rate and mechanism of the formation of benzyl methacrylate from benzyl chloride (BC). Only the ester forms in the presence of highly basic triethylamine (TEA), and quaternization of the amine occurs in the case of less basic pyridine, quinoline, and diethylaniline [3]. The acid-base reaction of MAA with amines results in the formation of the complex MAA amine. The IR spectrum of the complex MAA.TEA, unlike that of the complex MAA.pyridine, shows strong absorption bands in the $2400-2700-cm^{-1}$ region, which are characteristic of the stretching vibrations of NH

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Solvent	ε [8, 9]	Т., °С]g k4	Relative re- action rate at 20°C	Overall reaction order	Activation energy, kJ/mole	Logarithm of preex- ponential factor
Toluene	2,38	90 75 60 20	4,50 4,97 5,34 6,77 *	1,00	3,0 3,3 3,2 -	65,3	4,89
Anisole	4,30	90 75 60 20	4,08 4,41 4,82 6,12 *	4,44	2,4 2,5 2,3	59,4	4,54
DMFA	36,70	75 46 24 20	$3,66 \\ 4,41 \\ 5,26 \\ 5,38 *$	24,56	1,2 1,2 0,8	61,6	5,67
Acetonitrile	37,50	50 35 23 20	4,45 4,86 5,12 5,23 *	34,74	1,5 2,2 1,7 -	45,6	2,94
DMSO	48,90	$50 \\ 35 \\ 22 \\ 20$	3,61 4,06 4,66 4,73 *	108,77	0,9 0,8 0,7	59,4	4,54

TABLE 1. Influence of the Nature of the Solvent on the Kinetics of the Formation of Benzyl Methacrylate

*The values of $-\log k_4$ at 20°C were calculated from the Arrhenius equation.



Fig. 1. Influence of the methacrylic acid:benzyl chloride (1) and (methacrylic acid.triethylamine):benzyl chloride (2) ratios (A) on the rate of formation of benzyl methacrylate in toluene at 75°C.

Fig. 2. Dependence of the rate constant for the formation of benzyl methacrylate at 20°C on ε of the solvent according to the Kirkwood (a) and Amis (b) equations: 1) toluene; 2) anisole; 3) DMFA; 4) MeCN; 5) DMSO.

[4], as well as bands at 1400 and 1570 cm^{-1} , which are characteristic, respectively, of the symmetric and antisymmetric stretching vibrations of the carboxyl anion [4, 5]. Apparently, the complex MAA·TEA is an ion pair, which is similar to those that, according to [6], are formed by TEA with PhCOOH and AcOH, the latter being similar in strength to MAA [3, 7].

When the acid-base interaction of MAA with the amine and the quaternization of the amine by BC are taken into account, the conversions of the components of reaction (I) may be represented by the scheme

+ PhCH₂Cl \downarrow (III) [PhCH₂NR₃]+Cl-

+PhCH₂C1 \downarrow (IV) $PhCH_2OCOR' + R_3N \cdot HCl$

A highly basic amine shifts equilibrium (II) to the right, and the reaction proceeds with the formation of an ester [reaction (IV)]. In the case of weak bases, equilibrium (II) is shifted to the left, and the amine is alkylated by BC [reaction (III)]. The use of an amine of moderate basicity, for example, triethanolamine, results in both reactions. Therefore, the further investigations were carried out with highly basic TEA. An excess of the carboxylic acid performs the role of a protonic polar solvent in reaction (IV). Increasing the MAA concentration above the equivalent level with respect to the amine lowers the reaction rate (Fig. 1). In the case of a bimolecular substitution mechanism, this may be attributed to the specific solvation of the attacking anion by the molecules of the protonic solvent [8]. At the same time, increasing the concentration of the MAA.TEA complex relative to the BC concentration results in sharp acceleration of the substitution. The lowering of the rate in the protonic solvent and the strong dependence of the rate of substitution on the concentration of the nucleophile indicate a bimolecular S_N^2 mechanism for reaction (IV).

Since bimolecular nucleophilic substitution reactions proceed rapidly in aprotonic polar solvents [8], to investigate the influence of the polarity of the solvent on reaction (IV) we selected toluene, anisole, DMFA, MeCN, and DMSO, which differ greatly with respect to their dielectric constants ε .

As we see from Table 1, as arepsilon increased, the rate of reaction (IV) increases. Since the MAA.TEA complex is an ion pair, and the BC molecule is a polarized dipole, the substitution reaction is realized during an interaction between two dipoles.

The dependence of the rate of a dipole dipole interaction on ε of the solvent can be expressed by the Kirkwood (1) and Amis (2) equations [10, 11]

$$\lg k = \lg k_0 - \frac{1}{2,3kT} \frac{\varepsilon - 1}{2\varepsilon + 1} \left(\frac{\mu_1^2}{r_1^3} + \frac{\mu_2^2}{r_2^3} + \frac{\mu_{\neq}^2}{r_{\neq}^3} \right)$$
(1)

$$\lg k = \lg k_{\infty} - \frac{1}{2,3kT} \frac{2\mu_{1}\mu_{2}}{d^{3}} \frac{1}{\epsilon}$$
(2)

where k_0 and k_{∞} are the reaction rate constants in the gaseous phase and in a medium with an infinitely large value of ε , respectively; k is the Boltzmann constant; T is the absolute temperature; μ_{\neq} , μ_1 , and μ_2 and r_{\neq} , r_1 , and r_2 are, respectively, the dipole moments and radii of the activated complex and the reacting dipoles; and d is the distance to which the molecules must approach in order to react.

The treatment of the experimental data showed that there is a linear dependence of the logarithm of the rate constant of reaction (IV) (k₄) both on the parameter $(\epsilon - 1)/(2\epsilon + 1)$ and on the parameter $1/\epsilon$ (Fig. 2). The experimental points correlate well (r = 0.96) with the equations of straight lines (3) and (4), which were calculated according to the leastsquares method:

$$lg k_4 = -8,49 + 7,01 \frac{\varepsilon - 1}{2\varepsilon + 1}$$
(3)
$$lg k_4 = -5,02 - 4,29 \varepsilon^{-1}$$
(4)

The positive sign in Eq. (3) is evidence that the polarity of the activated complex is higher than the polarity of the original reactants, since the term in Eq. (1)

$$\left(\frac{1}{2,3kT}\cdot\frac{\varepsilon-1}{2\varepsilon+1}\sum\frac{\mu^2}{r^3}\right) < 0$$

only under the condition that

 $\left|\frac{\mu_{\neq}^{2}}{r_{\neq}^{3}}\right| > \left|\frac{\mu_{1}^{2}}{r_{1}^{3}} + \frac{\mu_{2}^{2}}{r_{2}^{3}}\right|$

The dipole moment of the activated complex calculated according to the method in [12] is equal to $7.07 \cdot 10^{-18}$ esu, which is significantly greater than the dipole moments of BC $(1.85 \cdot 10^{-18} \text{ esu } [13])$ and the complex MAA·TEA $(4.66 \cdot 10^{-18} \text{ esu in toluene*})$. The higher polarity of the activated complex confirms the participation of the ion pair in the rate-limiting step of the reaction. The structure of the transition state in this case may be represented by the scheme (V)



The attack of the nucleophilic reagent on the carbon atom of BC is realized with the simultaneous drawing off of the Cl atom by the ammonium cation in accordance with a push-pull mechanism [14].

As ε is increased, the interaction between the charges in the ion pair decreases. The distance between the charges in the ion pair then increases, causing an increase in its dipole moment and the polarity of the transition state. This results in an increase in the reaction rate with increasing ε of the medium. Such a picture totally corresponds to a substitution reaction mechanism in media with a relatively low ε . The kinetic order of the reaction in toluene and anisole is equal to 2.5-3.0, which fit the molarity of the reaction and the proposed mechanism.

As we see from Fig. 2, in strongly polar aprotonic solvents such as DMFA and DMSO, there are appreciable positive deviations from the linear dependence. The kinetic order of the reaction decreases from 3 to 1. The observed decrease in order may indicate a change in the reaction mechanism. As ε is increased, there is more complete separation of the charges in the ion pair until complete dissociation in strongly polar media owing to the ability of DMFA and DMSO to effect specific solvation of the cations [8]. In that case, the free anion becomes the attacking particle. In addition, in strongly polar solvents the G-Cl bond in BC probably undergoes ionization, which is promoted by the possibility of the stabilization of the carbocation by delocalization of the charge in the π orbitals of the phenyl ring [14]. Benzyl methacrylate forms as a result of the rapid reaction of two ions:

The rate-limiting step of the reaction is then the ionization of the C-Cl bond, which corresponds to a first-order reaction, i.e., transition to an S_Nl mechanism occurs in media with a high value of ε .

EXPERIMENTAL

All the chemically pure and pure reagents were additionally purified by redistillation. The DMSO was purified by repeated freezing, and the remaining solvents were purified according to [15]. The reaction was carried out in a thermostatted $(\pm 0.5^{\circ})$ three-necked glass reactor with a stirrer and a reflux condenser. The components were mixed with cooling in the following order: solvent, acid, amine, benzyl chloride. In the experiments designed to study the influence of an excess of MAA on the substitution rate, the initial BC:TEA ratio was 0.95:1.00, and in all the other experiments the MAA:TEA:BC ratio was 1.05:1.00: 0.95. The initial BC concentrations were 0.9, 1.4, 1.9, and 2.2 moles/liter. The preliminary experiments showed that the rate of conversion of TEA coincides in time with the rate of formation of benzyl methacrylate. The course of the reaction was monitored by collecting samples, in which the unreacted TEA was determined on a TB-6L high-frequency titrator in a water—isopropanol medium (1:1) by 0.1 N aqueous HCl. The rate of the substitution reaction vo was determined by the differential method in [16] from the slope of the tangent to the TEA-concentration—time curve at the initial moment in time. The least-squares method was used to find the dependence of the logarithm of the initial reaction rate on the logarithm

*Measured by V. I. Kodolov on a Tangens instrument.

of the original concentration of the reactant (log C). The slope of the straight line obtained was used to determine the reaction order, and the logarithm of the rate constant log k₄, which is numerically equal to log v₀ under conditions under which the concentrations of all three reactants are equal to unity, was determined by extrapolation of the straight line to the zero value of log C. The activation energy and the preexponential factor were found from the dependence log k₄ = f(1/T).

The IR spectra were recorded in liquid films on a UR-10 spectrometer.

CONCLUSIONS

1. The direction of the reaction of benzyl chloride with methacrylic acid in the presence of tertiary amines depends on the basicity of the amine. In the presence of highly basic amines, benzyl methacrylate is formed. Weakly basic amines are alkylated by benzyl chloride.

2. Aprotonic polar solvents accelerate the formation of the ester. The reaction rate constant correlates with the dielectric constant ε of the solvent according to the Kirkwood and Amis equations for the reaction of two dipoles.

3. An hypothesis of a push-pull $S_N 2$ mechanism in media with a low or moderate value of ϵ and replacement of this mechanism by an $S_N 1$ mechanism in media with a high value of ϵ has been advanced.

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