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CALORIMETRIC STUDY OF THE LOW-TEMPERATURE COMPLEXATION OF N-8-METHOXYETHYL-0-TOLUIDINE WITH CHLOROACETYL CHLORIDE

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The effect of structural factors on the reactivity of aromatic amines in their acylation of acid chlorides has been studied systematically by Litvinenko [1, 2, 4] and Svetkin [3]. The key step of these reactions has been assumed to be formation of an intermediate complex adduct. However, there has been no experimental evidence for the formation of this complex and the thermodynamic indices for these processes are lacking.

EXPERIMENTAL

A sample of N-8-methoxyethyl-o-toluidine (I) was prepared according to our previous procedure [5]. The calorimetric procedure was described in our earlier work [6]. The samples were prepared as follows: a given amount of the compound was placed in a glass calorimetric ampul, degassed, and sealed at 77 K. The ampul was transferred into the calorimeter cell and thawed to 300 K while recording the observed heat effects.

RESULTS AND DISCUSSION

We initially studied the phase transformations upon warming the samples. Upon cooling to 77 K, (I) forms a transparent glassy mass and a glass melting step was detected at 184 K on the calorimetric thawing curve for this sample (Fig. 1, curve 1) corresponding to transition from the glassy state to the supercooled liquid. Only a melting peak is found for crystalline chloroacetyl chloride (CAC) on the calorimetric thawing curve for this compound (Fig. 1, curve 2, mp 252 K, $\Delta H_m = 0.46 \text{ kJ/mole}$).

A given amount of CAC was frozen in vacuum at 77 K for the preparation of a sample of (I) and (I) + CAC in a degassed sample of (I). Strong heat release was detected on the calor-imetric curve for thawing of the sample after $T_g = 184$ K for (I) in the premelting temperature region of CAC (Fig. 1, curve 3). The amount of heat released depends on the (I)/CAC ratio. For example, $\Delta H_{\text{react}} = 1.62$ kJ/mole for (I)/CAC < 1 (Fig. 1, curves 3' and 3") but $\Delta H_{\text{react}} = 5.08$ kJ/mole for (I)/CAC > 2 (Fig. 1, curve 3).

This difference in the heat effects at different (I)/CAC ratios is apparently related to the complex nature of the chemical reactions. In accord with Litvinenko [7], the reaction of (I) with CAC proceeds as follows:



We may assume that (I) is consumed only in its reaction with CAC when (I)/CAC \leq 1, while this compound when present in excess may react with HCl with the formation of the hydrochloride salt (VII)

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Fig. 1. Calorimetric curves for the thawing of N- β -methoxyethyl-o-toluidine (I) (1) and chloroacetyl chloride (II) (2) and samples of (I) + (II) with (I)/(II) mole ratios of 2 (3) and 1 (3', 3"). The rethawing curve of the sample (3' and 3") after their warming to 300 K and cooling to 77 K (4) and thawing curve for N- β -methoxyethylchloroacetyl-o-toluidine (4').

 $(I) + HCl \rightarrow \underbrace{\bigvee_{(VII)}^{Me} - NHCH_2CH_3OM_e}_{HCl}$

Only the glass melting step at 212 K is detected upon repeated thawing of samples on the calorimetric curve from 77 to 300 K after the reaction (Fig. 1, curve 4).

Intermediate (IV) has a similar thawing curve with glass melting at 215 K. This species is rather stable in the absence of air and no change was noted upon its storage for a week at 300 K, i.e., reaction B does not proceed. Thus, $\Delta H_{react} = 1.62 \text{ kJ/mole released upon the thawing of (I) + CAC with (I)/CAC < 1 is the heat of formation of complex (IV).$

Figure 1 (curves 4 and 4') shows that intermediate complex (IV) and product (V) are converted upon cooling to 77 K to a glassy state with similar glass melting temperatures.

The following findings imply that product (IV) has the indicated complex structure: 1) the IR spectrum has a band at ~2500 cm⁻¹ (Fig. 2, curve 2) characteristic for a quaternary amino group [8] and 2) (IV) dissolves completely in water while starting secondary amine (I) and product (V), which is a tertiary amine, are insoluble in water. We should note that (IV) is stable only in vacuum and decomposes slowly in the air with the disappearance of the IR band at ~2500 cm⁻¹ (amide), 1500-1600 cm⁻¹ (benzene ring C=C), 2840-2940 cm⁻¹ (methylene groups), and 1070-1140 cm⁻¹ (methoxyl group) (Fig. 2, curves 2 and 3 [9]).

Thus, (IV) decomposes in the air through pathway B with the formation of (V).

In previous work [10]1 we noted that solid-phase reactions proceed largely in the vicinity of the phase transitions of the reagents. The glass melting point for (I) at 184 K is much lower than the melting point of CAC (252 K). Nevertheless, complexation in the indicated samples proceeds only upon the melting of CAC. This apparently is a result of the circumstance that glassy(I) is found in the lower part of the ampul, while crystalline CAC is found



in the upper part. Thus, upon thawing of the sample, contact of the molecules of (I) with CAC leading to their reaction is possibly only upon the melting of CAC (Fig. 1, curve 3). Indeed, the complexation reaction begins in ampuls containing crystalline CAC in the lower part and glassy (I) in the upper part much below the melting point of CAC after the softening of (I) (Fig. 1, curve 3").

Thus, the temperature regions for these heterogeneous solid-phase reactions depend on the relative positioning of the reagents.

CONCLUSIONS

A water-soluble complex is formed for equimolar amounts of $N-\beta$ -methoxyethyl-o-toluidine and chloroacetyl chloride in the vicinity of the melting point of one of the components. The decomposition of this complex gives HCl which forms a hydrochloride salt with the excess of the starting amine.

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