INVESTIGATION OF THE REACTION OF THIONYL CHLORIDE WITH DIMETHYLFORMAMIDE

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Thionyl chloride forms a complex with dimethylformamide (DMF). In view of its great polarization, this complex is more reactive than the original thionyl chloride. Thus, the complex of DMF with thionyl chloride is successfully used for the production of chlorides of sulfonic acids, benzoic acids with negative substituents in the p-position, and in a number of cases, when the acid chlorides cannot be produced directly by the action of thionyl chloride alone on the acids, or when it is necessary to conduct the synthesis under mild conditions (at room temperature or lower [1-3]). The complex can also be used for the dehydration of amides of acids to nitriles at comparatively low temperatures (0-60°) [4-6], for formylation [7, 8], and in other reactions.

Bosshard and Zollinger, who used a complex of DMF with thionyl chloride to synthesize chlorides of sulfonic acids [2] and ketones according to the Witsmayer reaction [9], have proposed that the active reagent is an immonium chloride (I), formed in the reaction of thionyl chloride with DMF

\[(\text{CH}_3\text{N} = \text{C} - \text{SO}) + \text{Cl} \rightarrow \text{Cl}^+ \cdot \text{SO}^- \cdot \text{C} - \text{N} \cdot \text{CH}_3\]  (I)

At the same time, these authors do not exclude the possibility of participation of the initially formed unstable adduct of thionyl chloride with DMF

\[\left(\text{CH}_3\text{N} = \text{C} - \text{SO} \cdot \text{Cl} \right) \cdot \text{Cl}^- \]  (II)

in the indicated reactions.

To study the dehydration of the diamide of terephthalic acid by a complex of DMF with thionyl chloride [6], under definite conditions we detected the formation not only of the dinitrile of terephthalic acid, but also terephthalyl dichloride. In particular, we observed this anomalous phenomenon when the reaction was conducted under comparatively rigorous conditions (80° and above), when DMF and thionyl chloride were taken in an equimolar ratio, or in the presence of excess thionyl chloride.

Since there is no information in the literature on the behavior of the complex of thionyl chloride with DMF during the dehydration of amides of acids and on changes in the complex at increased temperatures, it seemed interesting to us to investigate the possible conversions of this complex at various temperatures and certain side reactions that occur during its decomposition.

EXPERIMENTAL METHOD

The analysis of the mixtures and identification of the products obtained with known samples were performed by the method of gas-liquid chromatography (GLC) on no less than two columns with various stationary phases on a "Khrom-3" instrument. The IR spectra were recorded on a UR-10 spectrophotometer in a KBr cuvette.
Samples of mixtures of DMF with thionyl chloride in various molecular ratios were prepared for taking the IR spectra by pouring together the components, preliminarily cooled to 0-5\(^\circ\)C, in a stream of argon and then exposing them at 20\(^\circ\)C for 1 h. No loss in mass of the reaction mixture was observed in this case.

Thionyl chloride was purified by distillation on a column, collecting the fraction boiling at 75.7\(^\circ\)C. Grade "pure" DMF was dried by azeotropic distillation with benzene, collecting the fraction with bp 153\(^\circ\)C. The redistilled DMF was stored in a dark bottle over Na\(_2\)A zeolite.

**Interaction of Dimethylformamide with Thionyl Chloride.** Synthesis a: into a flask equipped with a mixer, thermometer, reflux condenser with calcium chloride tube, inlet for argon, and dropping funnel with bypass tube, we loaded 18.25 g DMF, cooled it to -5\(^\circ\)C and gradually added 29.85 g of preliminarily cooled thionyl chloride, so that the reaction mixture was not heated above -5\(^\circ\)C. The dropwise addition of thionyl chloride was carried out in a stream of argon.

The reaction mixture was exposed for 30 min at room temperature. Then the reaction flask was added through a trap for gases, placed in a Dewar flask with a mixture of acetone and dry ice, to a rotary evaporator and evacuated with a water jet pump (8-9 mm) at 40\(^\circ\)C. After 2 h the entire reaction mass crystallizes – white, highly hygroscopic crystals are formed. The loss of mass by the reaction mixture in this case is 9.58 g. A total of 9.2 g of SO\(_2\) condenses in the trap for gases. For the crystals obtained, found: C 24.08, 24.12; H 4.94, 4.85; N 10.62, 10.77%. \(\text{C}_3\text{H}_7\text{Cl}_2\text{N}\) (I); calculated: C 28.14; H 5.52; N 10.94; Cl 70.92%. \(\text{C}_3\text{H}_7\text{Cl}_2\text{NO}_2\text{S}\) (II); calculated: C 18.75; H 3.68; N 7.29; Cl 36.82. The crystals, washed with abs. ether melt with decomposition at \(\sim130\)^\circ\)C with a rapid rise in the temperature.

When the crystals were treated with water, turbidification of the solution was observed. After this solution was filtered, DMF was detected in it by the GLC method. In the filtrate \(\text{Cl}^-\) and \(\text{SO}_2^-\) ions were found with the aid of a solution of \(\text{AgNO}_3\) and a dilute solution of \(\text{HNO}_3\). The precipitate on the filter \((\sim0.05\) g\) was washed with water and dried; mp 115-117\(^\circ\)C; it is soluble only in \(\text{CS}_2\) and a mixture of \(\text{HNO}_3\) and \(\text{HCl}\) Found: S 98%. The IR spectrum of the precipitate is analogous to the spectrum of elemental sulfur.

Synthesis b: analogously to the procedure described in synthesis a, equimolar amounts of DMF (18.25 g) and thionyl chloride (29.85 g) were mixed. The reaction was conducted at 80\(^\circ\)C in a stream of argon with absorption of the liberated gases with water. The reaction mixture was heated for 10 h, and after 1 h samples were collected to take the IR spectra of the reaction mass. After the first hour of the reaction, turbidification of the reaction mass was observed – a yellow crystalline precipitate (1) separated out. At the end of the reaction, the precipitate (1) was filtered off and the filtrate redistilled under vacuum. We obtained 12 g of the liquid (2) with bp 46-50\(^\circ\)C (3 mm). The residue in the distillation flask (1.5 g) consisting of dark yellow crystals (3). The precipitate 1 was washed with water to a neutral pH and dried under vacuum. Weight of the precipitate 1.95 g; mp 115-117\(^\circ\)C. Found: S 98%.

The presence of \(\text{Cl}^-\) and \(\text{SO}_2^-\) ions was detected in the absorbing bottles with the aid of qualitative reactions. The formation of an incrustation of sulfur was observed on the bubbler of the first absorbing bottle. Fraction (2) was redistilled again at atmospheric pressure; bp 166-167\(^\circ\)C; \(n_\text{D}^20\) 1.4519. Found: C 33.43, 33.52; H 5.60, 5.53; N 13.10, 12.90; Cl 32.69, 32.56%. \((\text{CH}_3)_2\text{NCOCl(C}_3\text{H}_7\text{Cl}_2\text{NO})\). Calculated: C 33.50; H 5.63; N 13.03; Cl 32.97%.

According to the data of [10], for \((\text{CH}_3)_2\text{NCOCl}\): bp 167-167.5\(^\circ\)C (754 mm); \(n_\text{D}^21\) 1.45196. The residue after redistillation (3) was washed with abs. ether; mp \(-14\)^\circ\)C. Found: V 28.50, 28.30; H 5.60, 5.20; N 11.05, 10.70%. \(\text{C}_3\text{H}_7\text{Cl}_2\text{N}\). Calculated: C 28.14; H 5.52; N 10.94%.

**DISCUSSION OF RESULTS**

First we investigated the mixtures of DMF with thionyl chlorides in various mole ratios, obtained under mild conditions (see "Experimental Method" section), by the method of IR spectroscopy.

From the IR spectra of the initial DMF and thionyl chloride, as well as their mixtures (Fig. 1), it is evident that when the mole ratio of thionyl chloride to DMF is increased from 0.25:1 to 5:1, the nature of the spectrum changes greatly. At a thionyl chloride:DMF ratio equal to 1:1, most of the bands characteristic of both components are entirely absent, and actually a new compound is formed, which is a complex of DMF and thionyl chloride. A narrow intense band in the region of 1660 cm\(^{-1}\) is observed in the