

THE PHOSGENIZATION OF 2,4- AND 2,6-DIAMINOTOLUENE HYDROCHLORIDE*

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In previous publications [1, 2, 3] a number of theoretical and practical questions of the reactions of aromatic amines and phosgene were dealt with. Characterizing the phosgenization of several mono and diamines, and the dehydro-halogenization of the resulting carbamic acid chloride by reaction-kinetic data, conclusions were drawn on the mechanisms of the reactions, and a new "fast-phosgenization method" has been developed for production of isocyanates.

This publication is treating of the phosgenization of tolylene 2,4- and 2,6-diamine hydrochloride. In several industrial processes isocyanate is produced by phosgenization of amine hydrochlorides [4, 5]. Recently the basic phosgenization became general, although amine hydrochlorides can be obtained in the amine-phosgenization reactions too, so the phosgenization of hydrochloride in these processes into consideration must be taken.

The acylation proceeds according to the gross equation:



Because of the poor solubility of diamine hydrochloride, the reaction is heterogeneously phased.

The hydrochloride suspension was phosgenized at various temperatures, made from the solution of tolylene diamine with the aid of hydrochloric acid solution, applying different excesses of solvent and phosgene. The phosgene was given in solution to the suspension adjusted to the required temperature, then closing the vessel, the mixture was shaken with a jolting machine for various times, keeping the temperature constant.

For stopping of the reaction sodium or potassium methyrate or ethylate was used, and in the reaction mixture the content of free amine in non-aqueous medium was determined with perchloric acid in glacial acetic acid. The determination has been described in method [1].

* Dedicated to Prof. Z. Csűrös on the occasion of his 70th birthday.

In the mixture of acetone-glacial acetic acid both amine-groups of diamine can be separately measured with perchloric acid: the curve of the potential change has two inflection points. The titrant, consumed up to the first inflection point, measured the one (the more basic one) of the amine-

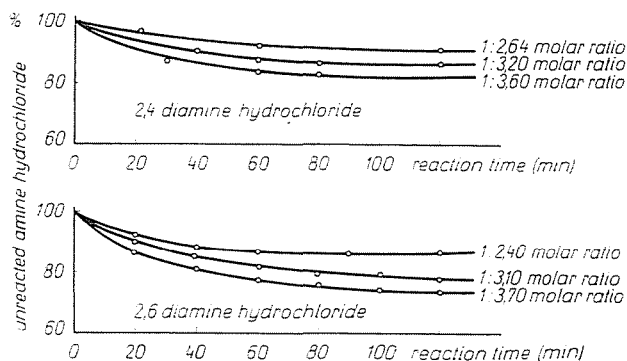


Fig. 1. The phosgenization of 2,4- and 2,6-diaminotoluene-dihydrochloride at 25°C. under various molar ratio of aminehydrochloride: phosgene

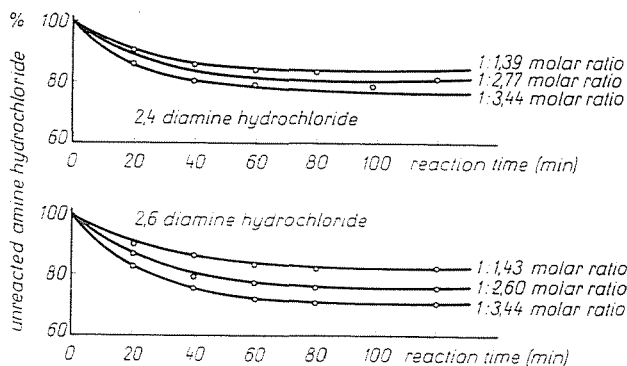


Fig. 2. The phosgenization of 2,4- and 2,6-diaminotoluene-dihydrochloride at 50°C. in toluene, under various molar ratio of aminehydrochloride: phosgene

groups, (in case of 2,4-diamine in the para position), the same quantity of titrant was used up, which titrated the other amine-group. In case of 2,6-diamino-toluene the two amine-groups are in the same position, by the neutralization of the first, the basicity of the second decreased, so it presented a separate wave upon titration in a differentiating solvent. At the alcoholic quenching, the amine-group of the monourethane — monoamine — derivatives, originated from the intermediate products, is equal in basicity to the more

basic amine-group of the diamine, and it appears on titration in the first potential wave.

Thus, from the two inflection points, obtained on titration of the reaction-mixture, with the titrant added up to the first inflection point, the one

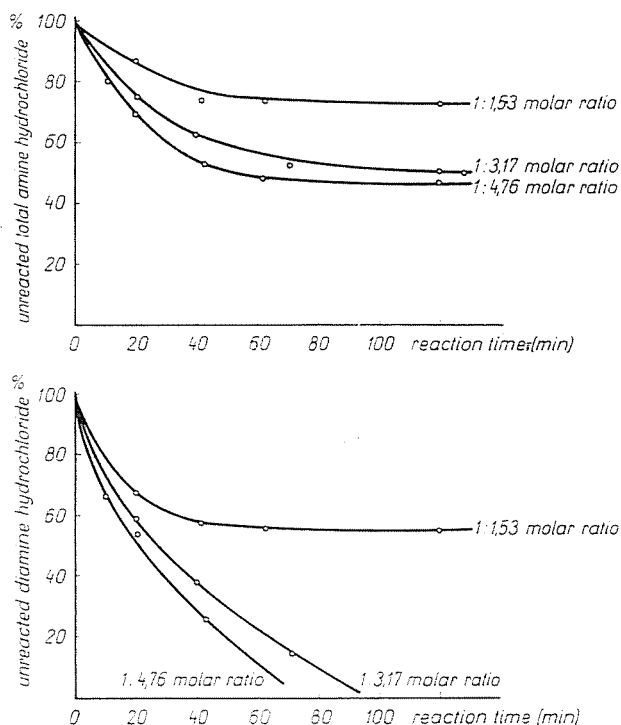


Fig. 3. The phosgenization of 2,4-diaminotoluene-dihydrochloride at 70°C, in toluene, under various molar ratio of aminehydrochloride: phosgene

amine-group of the unreacted diamine, as well as the remained amine-group of the monoacylated compound was titrated. The titrant, added between the two inflection points, measures the second amine-group of the unreacted diamine.

The changes in the content of the total amine-hydrochloride and in the quantity of the diamine-dihydrochloride calculated from the titration results were examined during phosgenization at 25, 50, 70 and 90°C (Figs 1–8).

Comparison of the curve forms, obtained at various temperatures, points to the fact, that after a more or less steep section, all curves tend to flatten, i.e. the reaction is completed. At a given temperature, and with a given amount of phosgene, only a certain transformation is possible.

At 25°C there is a low-rate reaction, even in the case of a large excess of phosgene, the transformation is only 17 and 25 per cent, respectively (Fig. 1).

At 50°C the transformation does not differ considerably from the values at 25°C (Fig. 2).

In case of phosgenization at 70°C (Figs 3, 4, 6, 7), the rate of the reaction is about the double of that at 50°C. A large excess of phosgene reduces

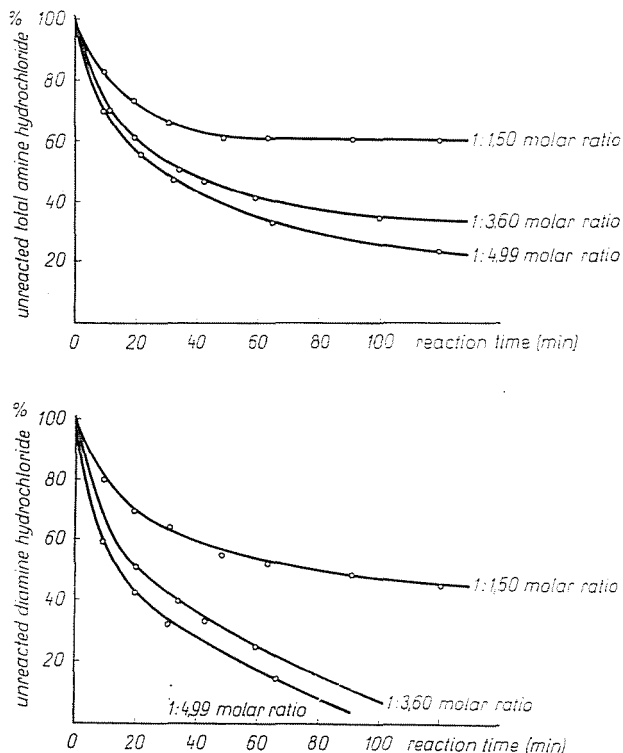


Fig. 4. The phosgenization of 2,4-diaminotoluene-dihydrochloride at 70°C. in orthodichlorobenzene, under various molar ratio of aminehydrochloride : phosgene

the content of the unreacted amine hydrochloride to 48–45 per cent. At 90°C the transformation is even more pronounced (Figs 5, 8).

As regards the change of the content of diamine-dihydrochloride, the two-model-compounds behaved in an essentially different manner.

In case of 2,4 isomer, the amount of the dihydrochloride was zero at the end of the transformation, i.e. the introduction of the first phosgene molecule was complete in all diamine molecules. At the same time the diacylation, i.e. the reaction of the second molecule with phosgene is only low-rate (the content of the total amine-hydrochloride is 40 to 50 per cent).

In case of 2,6 isomer, the acylation of the first amine-group was followed by the introduction of the second phosgene, in spite of the presence of a significant amount of dihydrochloride. During the reaction the diamine-dihydrochloride decreased by slightly more, as the amount of total amine-hydrochloride.

This phenomenon is especially obvious at 70°C, and in case of a reaction with phosgene given in excess, compared to the stoichiometrically required

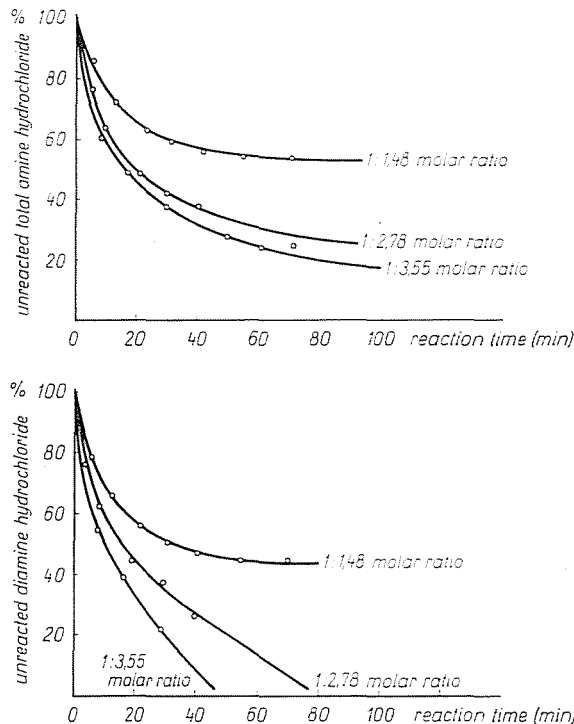


Fig. 5. The phosgenization of 2,4-diaminotoluene-dihydrochloride at 90°C, in orthodichlorobenzene, under various molar ratio of aminehydrochloride : phosgene

amount. In orthodichlorobenzene, as well as for a lower phosgene, addition than required for total diacylation, the difference subsists though it is not so marked.

At lower temperatures (25 and 50°C) 120—150 minutes are required to the transformation under the given circumstances, while at 90°C, 40—60 minutes are enough.

The volume of the solvent did not influence the transformation. Using less solvent (suspending agent), the reaction starts more slowly, but it tends towards the same limits.

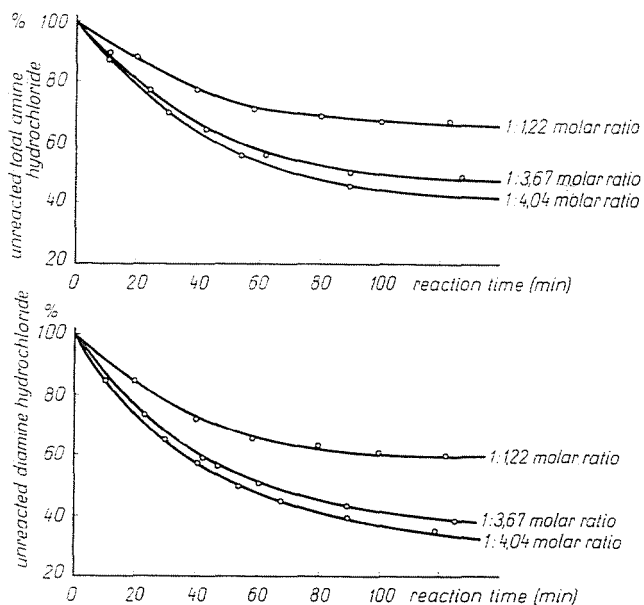


Fig. 6. The phosgenization of 2,6-diaminotoluene-dihydrochloride at 70°C, in toluene, under various molar ratio of aminehydrochloride : phosgene

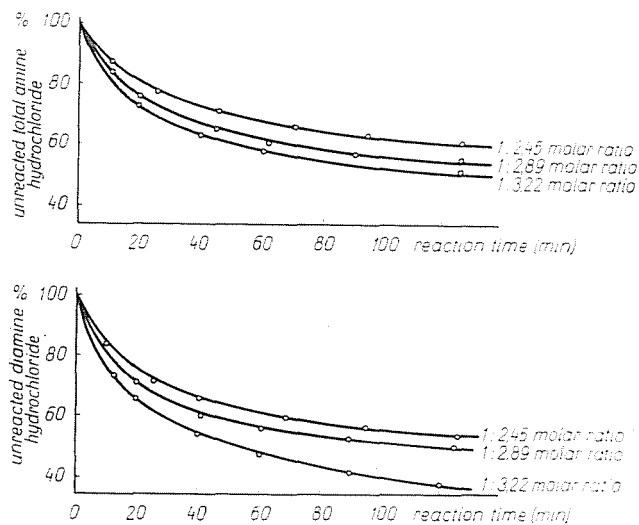


Fig. 7. The phosgenization of 2,6-diaminotoluene-dihydrochloride at 70°C, in orthodichlorobenzene, under various molar ratio of aminehydrochloride : phosgene

The increase of molar ratio of phosgene to diamine hydrochloride increases both the rate of acylation and the reaction.

In some of experiments the amount of hydrochloric acid employed for the preparation of hydrochloride was increased at a 100 per cent excess. The reaction was the same, as for less hydrochloric acid. The excess of hydrochloric

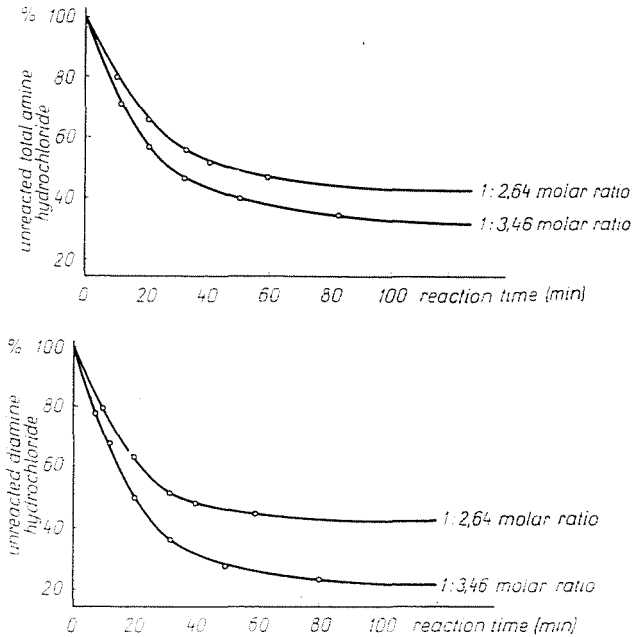
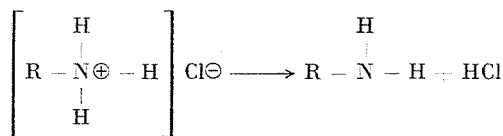


Fig. 8. The phosgenization of 2,6-diaminotoluene-dihydrochloride at 90°C, in orthodichlorobenzene, under various molar ratio of aminehydrochloride : phosgene

acid was probably in the gas-space of the experimental vessel, because of its slight solubility. The hydrochloric acid formed during the acylation leaved the solution in the same way, and the reaction affected a saturated solution.

The different acylation of the two isomer dihydrochlorides can be explained by the electronic structure of molecules and by steric causes. In phosgenization of hydrochloride the acylation must be preceded by thermal dissociation, accounted for by the inert solvent (non-electrolytic dissociation), and by the test temperature.

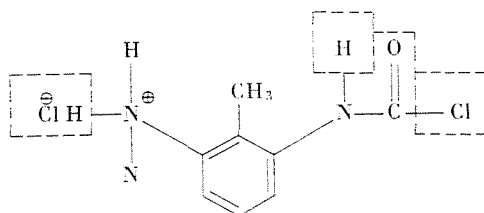
During the dissociation the bond $\ddot{N}-H$ splits and proton is produced:



In case of 2,4 and 2,6 isomers in ortho and para position (thus in positions 2, 4 and 6), the electron density is greater because of hyperconjugational electron-sender effect of the methyl group, consequently the splitting-off of protons is inhibited. In ortho positions (2 and 6), however this effect is reduced, thus, the proton removal goes easier. The elimination of hydrochloric acid is motivated by steric reasons in ortho position.

Therefore in case of 2,4 isomer the hydrochloric acid splits off in the position 2 first, and the molecule is acylated. The acylation being a rapid reaction [3], concerning the reaction time of hydrochloride acylation, the rate depends on the elimination of hydrochloric acid.

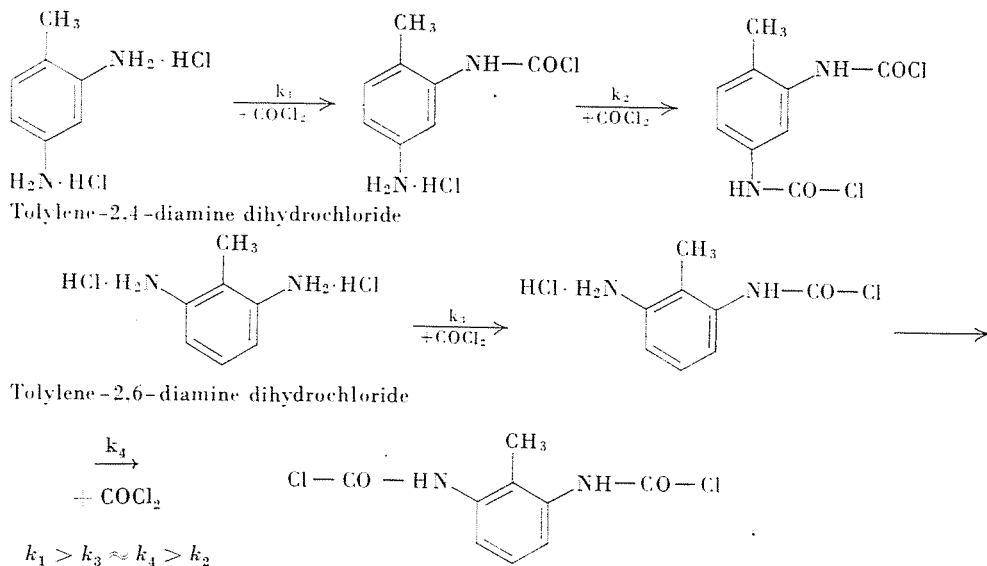
The 2,6 isomer has no marked position for the first acylating group, because the molecule is symmetrical. After the acylation, following the elimination of hydrochloric acid, the electronic structure of the aromatic ring does not change considerably. $-N-H$ group is connected to the ring again, which must lose proton to form isocyanate.



Thus, 2,6 isomers have the same possibility to splitting-off the second hydrochloric acid, as for the first, moreover it can be assumed thermal splitting-off of the second hydrochloric acid is facilitated by the electron-sucking effect of the carbonyl-oxygen, and by the effect of the developed isocyanate-group.

In case of the 2,4 isomer these effects occur also in the 4 (para) position, but these effects do not exceed the relatively easier splitting-off of hydrochloric acid, caused by the steric effect and the effect of the methyl group in the 2 (ortho) position, so instead of splitting-off of second hydrochloric acid, the elimination of hydrochloric acid occurs in another molecule, in position 2.

Order of rates is the following characterizing the processes by relative rate constants:



Summary

The acylation of tolylene-2,4- and 2,6-diamine hydrochloride was examined at temperatures of 25 to 90°C, in toluene and orthodichlorobenzene medium, in the presence of phosgene-excess. Because of the heterogeneous phase no exact reaction-kinetic data could be calculated, the acylation of two-two groups of two isomer was characterized instead by relative reaction rates. From analyses of reaction-mixtures it was concluded, that in case of 2,4-isomer, monoacylation is the first, much slower followed by diacylation, 2,6 isomer is subject to direct diacylation, even the mixture, in conformity with the conditions of reaction, contains much unreacted diamine dihydrochloride.

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