

THERMAL DECOMPOSITION OF TOLYLENE 2,4- AND 2,6-DICARBAMIC ACID CHLORIDE

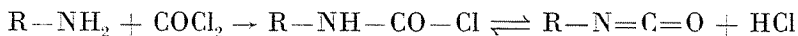
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Isocyanates are used by the organic chemical industry as basic materials: e.g. tolylene diisocyanates are the basic materials of polyurethane foams. They are produced by phosgenizing the corresponding amine or amine salt, and dehydro-halogenation of carbamic acid chloride by acylation produces the isocyanate [1, 2].



and



In a previous study on the equilibrium elimination reaction of the transformation of carbamic acid chloride to isocyanate [3], it has been stated that in solution the equilibrium is considerably shifted towards the isocyanate, even at room temperature. The thermal decomposition of solid acid chlorides was investigated by measuring the forming hydrochloric acid, and the process was characterized by reaction-kinetic data.

The follow-up of the decomposition by means of derivatograph has furnished further data on the thermal decomposition of dicarbamic acid chlorides, to be presented below.

The decomposition was investigated by means of a MOM type derivatograph, at about 70 °C, permitting check-ups at intervals of 100 to 200 minutes, and the sample could be heated to the reaction temperature rapidly enough in comparison with the total reaction time. At a lower temperature the reaction was slow, while a higher temperature lasted long to reach, and meanwhile the decomposition made considerable progress.

In case of the two model compounds the processes go ahead differently. In case of 2,6-dicarbamic acid chloride (Figs 1, 2), the decomposition rate shows a maximum (curve T-G an inflexion, curve DTG a minimum, curve DTA a minimum), and this does not appear immediately at constant temperature (namely the decomposition starts at the original temperature), but later, at about 40 to 50 per cent of decomposition. This is different from the decomposition curve of the 2,4-isomer (Figs 3, 4).

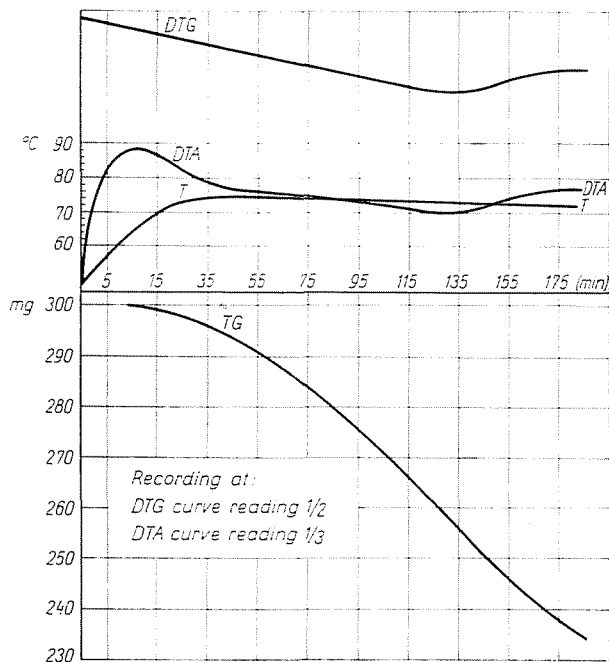
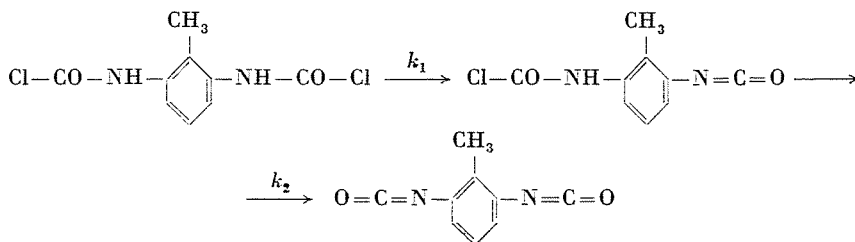


Fig. 1. Derivatogram of tolylene 2,6-dicarbamic acid chloride at 73 °C

The maximum of the decomposition rate curve is explained as follows: the decomposition of dicarbamic acid chloride can be reduced to two successive steps, consequently it can be realized as a consecutive first order reaction:



where k_1 and k_2 are rate constants of the reaction. Rate equations of the two reactions:

$$1. \quad \frac{dA}{dt} = -k_1 \cdot (A_0 - B)$$

$$\frac{dB}{dt} = +k_1 \cdot (A_0 - B)$$

$$\text{hence } B = A_0(1 - e^{-k_1 t})$$

where A concentration of dicarbamic acid chloride

A_0 initial concentration of dicarbamic chloride

t time

B concentration of monocarbamic acid chloride

$$2. \quad \frac{dC}{dt} = k_2 \cdot (B - C) \quad \text{where } C \text{ concentration of diisocyanate}$$

$$\frac{dC}{dt} = k_2 \cdot [A_0(1 - e^{-k_1 t}) - C]$$

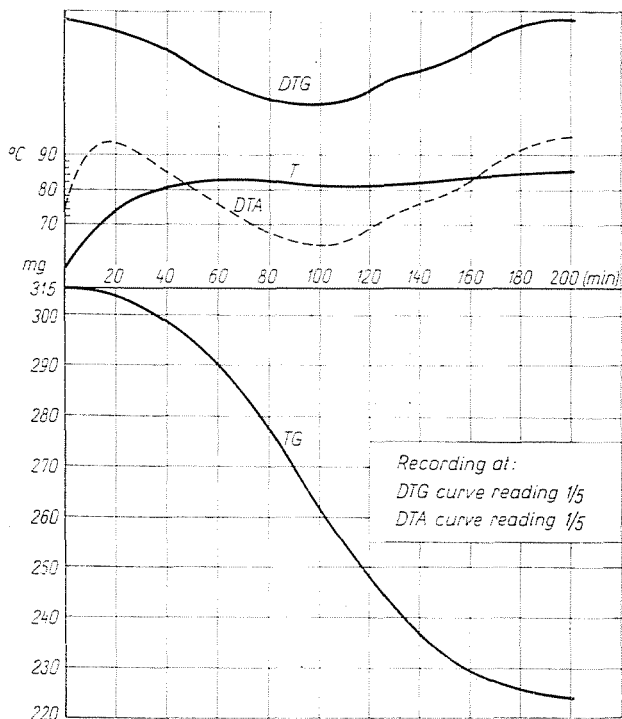


Fig. 2. Derivatogram of tolylene 2,6-dicarbamoyl chloride at 83 °C

The solution of the linear differential equation of first order for $B_0 = 0$ and $C_0 = 0$.

$$C = A_0 \cdot \left(1 + \frac{k_2}{k_1 - k_2} \cdot e^{-k_1 t} - \frac{k_1}{k_1 - k_2} \cdot e^{-k_2 t} \right)$$

The loss of weight during the decomposition (Δm) can be computed from the molar numbers of the forming products:

$$\Delta m = (B + C) \cdot M \quad \text{where } M \text{ molecular weight of hydrochloric acid.}$$

Substituting:

$$\Delta m = M \cdot A_0 \left[2 + \left(\frac{k_2}{k_1 - k_2} - \frac{k_1 - k_2}{k_1 - k_2} \right) \cdot e^{-k_1 t} - \frac{k_1}{k_1 - k_2} \cdot e^{-k_2 t} \right]$$

This is the equation of curve T—G, convertible to molar conditions:

$$\frac{\frac{\Delta m}{M}}{A_0} = 2 + \frac{2k_2 - k_1}{k_1 - k_2} \cdot e^{-k_1 t} - \frac{k_1}{k_1 - k_2} \cdot e^{-k_2 t}$$

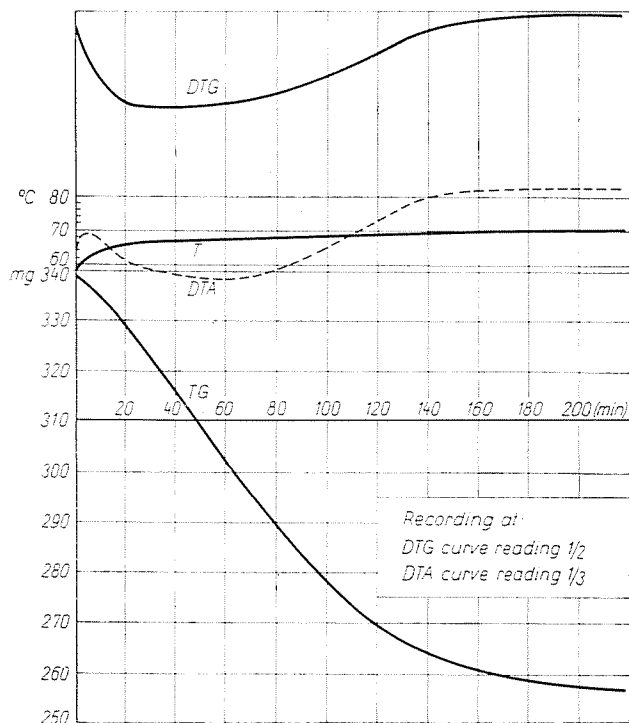


Fig. 3. Derivatogram of tolylene 2,4-dicarbamoyl chloride at 69 °C

In the place of rate maximum, at the point of inflexion of curve T—G, the second derivative is zero.

$$\frac{d^2 \left(\frac{\Delta m}{M \cdot A_0} \right)}{dt^2} = \frac{2k_2 - k_1}{k_1 - k_2} \cdot k_1^2 \cdot e^{-k_1 t} - \frac{k_1}{k_1 - k_2} \cdot k_2^2 \cdot e^{-k_2 t} = 0$$

from which, for $k_1 \neq k_2$ and $k_1 \neq 0$, substituting $k_1/k_2 = K$

$$t = \frac{2,303}{k_2} \cdot \frac{\lg K \cdot (2 - K)}{K - 1} \quad \text{where } t \text{ is the time datum of inflexion.}$$

This is explainable only in case of $0 < K < 2$ and $K \neq 1$. If $1 < K < 2$, because of the positive sign of fraction, $\lg [K \cdot (2 - K)] > 0$. This is valid only for $K(2 - K) > 1$. Because the tangent of parabola $y = 1 + K^2$ is the straight $y = 2K$, $1 + K^2 \geq 2K$ whence $K(2 - K) \leq 1$. Consequently the supposition of $1 < K < 2$ is wrong.

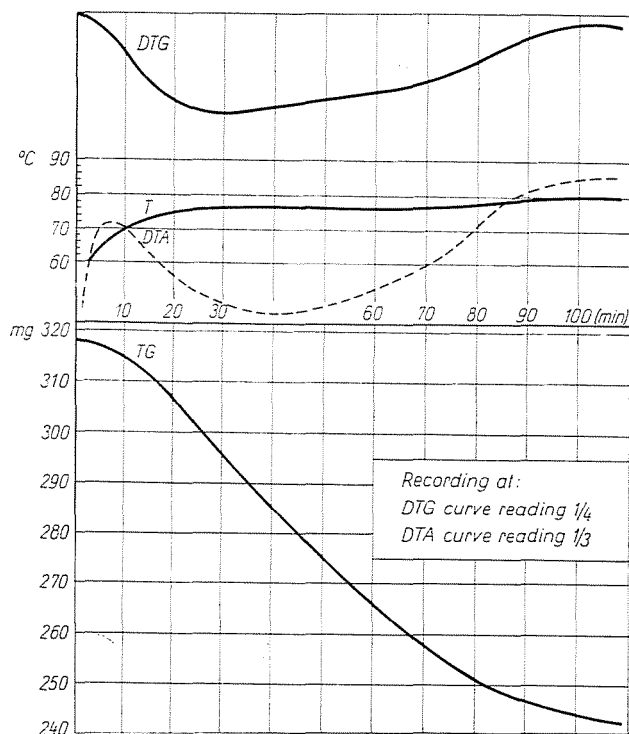


Fig. 4. Derivatogram of tolylene 2,4-dicarbamic acid chloride at 77 °C

If $0 < K < 1$ then $(2 \lg [2 - K]) < 0$ and $K(2 - K) < 1$, namely this is the correct solution.

Consequently, the rate maximum has explanation only for $k_2 > k_1$, the second step of decomposition being the faster. Numerical values of the rate constants could not be exactly computed, because the loss of weight vs. time curve does not directly show the decomposition, but it diverges a little. The developing hydrochloric acid cannot leave the measuring vessel exactly at the rate of decomposition, because of diffusion and adsorption processes. The reaction results in an uncertain and ever-changing equilibrium, rather than in a pure, kinetic first-order decomposition.

However, the above mentioned order of the rate constants was supported by the minimum of the DTA curve as result of the chemical reaction.

independently of the small deformations of the T—G and DTG curves. The two rate constants might not differ considerably, and the slight difference was truly recorded by the derivatograph.

The deviations of the rate constants in the above mentioned order are supported by experimental evidence, namely in the case of 2,6-isomer no

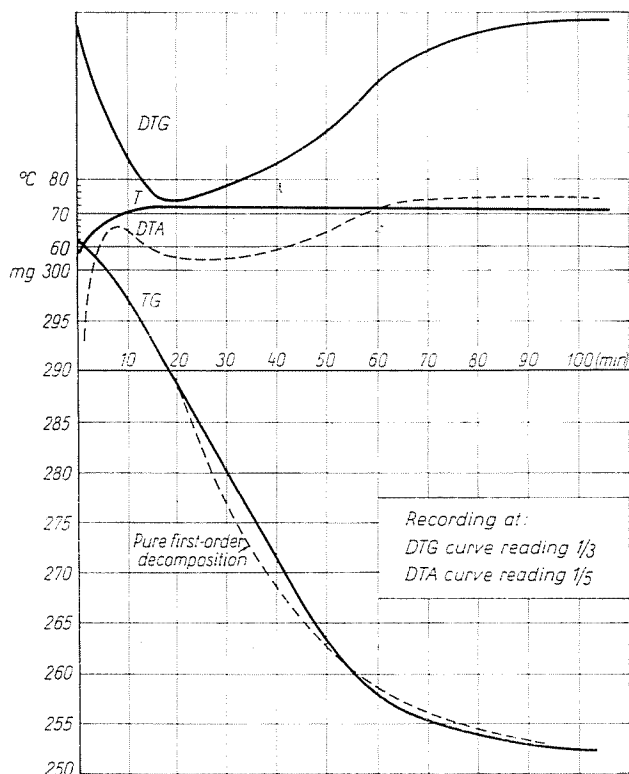


Fig. 5. Derivatogram of tolylene-2-isocyanate-4-carbamic acid chloride at 72 °C

monoisocyanate-monocarbamic acid chloride developed, while in case of 2,4-isomer the analogous intermediate could be produced by supplying hydrochloric acid gas in solution of isocyanate.

The thermal decomposition of monocarbamic-acidchloride-monoisocyanate, made from 2,4-diisocyanate (Fig. 5) was studied in a thermo-balance. In this case the measured loss of weight (curve T—G) differed from the loss of weight curve corresponding to the exponential, kinetic first-order decomposition, but the difference was less than in case of dicarbamic acid chlorides. The monoacid chloride was much finer grained, and so less hydrochloric acid was left over during decomposition. The rate constant computed from the decomposition well agreed with the rate constant of 2,4-dicarbamic acid chlo-

ride determined by the nitrogen-flow method, presented in our previous publication [3].

The decomposition curves of 2,4-dicarbamic acid chloride differ from those of the first-order decomposition (Figs. 3, 4), due to the retention of hydrochloric acid. If a distinction is made between the rate constants of the two elementary steps, then $k_1 > k_2$ order can be proposed for this case, because the decomposition rate showed no maximum in the later phase of decomposition, as in case of 2,6-isomer. This is supported by the fact that a very pure monoacid chloride-monoisocyanate could be prepared (on the basis of analogous reactions [4], it can be considered as 2-isocyanate-4-carbamic acid chloride).

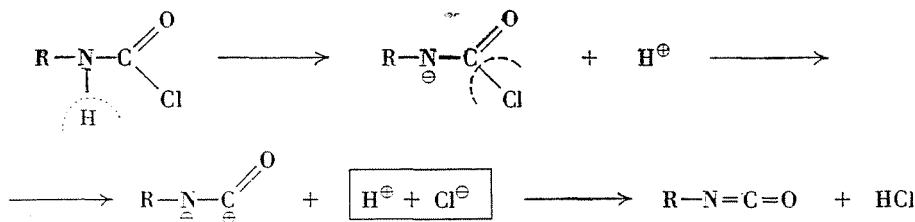
The different decomposition rates of the two isomer acid chlorides can be attributed to the electronic structures of molecules and to steric causes. The decomposition of the acid chloride starts by proton splitting-off according to the mechanism previously described (N—H bond splits) [3]. In case of tolylene 2,4- and 2,6-dicarbamic acid chloride in ortho and para positions (in positions 2,4 and 6), the electron density is larger because of the hyperconjugational electron-sender effect of the methyl group, consequently the proton splitting-off is slightly inhibited. However, in the ortho positions (2 and 6) this effect is less pronounced, consequently the proton is relatively easier to remove. The elimination of hydrochloric acid is accounted for, — rather in ortho position — by steric reasons. The first molecule hydrochloric acid is splitt-off in ortho position in case of 2,4-isomer too (in case of 2,6-isomer only ortho position exists).

The forming isocyanate group facilitates the second elimination in position 6, exerting a sucking on the electron system of the ring. This effect is, however, not so great as it could ease hydrochloric acid and proton to leave in position 4, by counteracting the steric effect and the hyperconjugational effect of the methyl group.

Therefore, in case of 2,4-isomer, the hydrochloric acid can easier be eliminated in position 2 of another molecule, than hydrochloric acid in position 4, while in case of 2,6-isomer the hydrochloric acid splitts-off a little faster in the same molecule in position 6 than the first hydrochloric acid.

In case of decomposition of dicarbamic acid chlorides the responses of the two isomers are found to be identical with those observed during the phosgenization of amine hydrochloride [5], where the acylation was preceded by hydrochloric acid elimination. Although in case of the decomposition of acid chlorides the non ionic bound chlorine is splitt off, the proton splitting-off — the rate-limiting step in both cases — goes ahead in the same way as the decomposition of hydrochloride: N—H bond decomposes. Otherwise the analogy demonstrates, that, similarly to the thermal decomposition of acid chloride, the hydrochloride thermally decomposes in case of phosgenization in suspen-

sion, thus, it supports the schema previously determined [3] for the decomposition mechanism of acid chloride.



Summary

Derivatograph testing of the thermal decomposition of tolylene 2,4- and 2,6-dicarbamic acid chloride showed the behaviour of the two isomers to be different. By comparison of the decomposition curves, in the light of the adequate reaction-kinetic relations, considering the decomposition of the two functional groups as consecutive reactions, in case of 2,4-isomer and 2,6-isomer the first and the second hydrochloric acid splitt-off were found to be faster, respectively. So in case of 2,4-isomer the monoacid-chloride-monoisocyanate can be prepared from isocyanate, at a difference from 2,6-isomer.

Our results furnish further data for the investigation of the decomposition of dicarbamic acid chloride, besides, they prove the reaction mechanism previously stated on the basis of analogy to the differential behaviour of the functional groups of isomers obtained by phosgenizing diamine hydrochloride.

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