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CYCLIZATION OF AROMATIC POLY(AMIC ACIDS) TO POLYIMIDES. CYCLIZATION KINETICS OF A MODEL COMPOUND OF N-PHENYLPHTHALAMIC ACID*

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A kinetic study of the thermal cyclization of N-phenylphthalamic acid to N-phenylphthalimide has been carried out in various solvents; the reaction is described by a second order equation and is catalyzed by acids. At 40–60% conversion the rate constant is reduced as a result of side-reactions taking place. It was found that as the basicity of the solvent increases the rate constant is reduced, and the relative contribution of side reactions increases. The experimental results were used to interpret data on the cyclization kinetics of aromatic polyamic acids.

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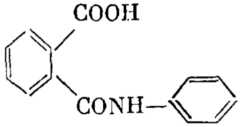
ALTHOUGH a relatively large number of papers [1–7] have appeared in connection with kinetic investigations of the thermal cyclization of aromatic polyamic acids to polyimides, no definite conclusions have as yet been reached in regard to regularities of formation of the imide ring. This may be because the cyclization reaction takes place in the solid phase, in the polymer chains, and both of these factors may distort the true character of the process of imide ring formation. In view of this our aim in the present work was to investigate kinetic parameters of the cyclization of a low molecular model compound, namely N-phenylphthalamic acid



Cyclization of the N-phenylphthalamic acid was carried out under a variety of conditions, varying the concentration, temperature, and solvent.

N-phenylphthalamic acid was prepared by reacting phthalic anhydride with aniline in chloroform. The precipitate was filtered, washed with chloroform and recrystallized from ethanol; m.p. 170°. N-Phenylphthalimide was prepared by heating N-phenylphthalamic acid at 170° for 3 hr and was recrystallized from ethanol; m.p. 210°. N,N-Dimethylphthalamic acid was prepared by passing gaseous dimethylamine through a solution of phthalic anhydride in benzene. The precipitate was filtered, washed with benzene, and recrystallized from ethanol; m.p. 124·5–125°.

Phthalic anhydride was recrystallized from benzene, and phthalic acid, from water. *o*-Chlorobenzoic acid was sublimed in vacuum at 100°. Aniline was distilled at reduced pressure.

DMF, DMAA and *m*-cresol were dried over CaH_2 and distilled *in vacuo*. Dimethyl ether of diethylene glycol (diglyme) was boiled and distilled over KOH, and then boiled and distilled over sodium wire; the fraction with b.p. 160·5–161° was collected. Chloroform was washed repeatedly with water, dried over $CaCl_2$ and CaH_2 and distilled. Benzene was distilled over sodium wire. Ethanol and ethyl acetate underwent distillation.

The melting (boiling) points of the reagents and solvents agreed with published information.

The kinetics of N-phenylphthalimide formation were investigated by IR spectroscopy through changes in the optical density of solutions at 721 cm^{-1} (1780 cm^{-1} when *m*-cresol was used as solvent). The reaction was run in glass ampoules in an argon current; the ampoules were placed in a thermostat, and the temperature was maintained to within $\pm 0{\cdot}2°$. The time for the commencement of reading was the moment when the temperature of the ampoule contents reached a level 5° below the required temperature. Sampling was carried out after specified intervals of time. The spectra were recorded on a UR-10 instrument. The N-phenylphthalimide concentration in solution was determined from a calibration plot of the optical density of N-phenylphthalimide solutions versus concentration (the dependence is a linear one, i.e. the Lambert–Beer law is satisfied).

The amount of unreacted acid was determined by potentiometric titration on a pH-340 instrument. Collected samples were diluted with DMF and titrated with a 0·1 N solution of KOH in absolute ethanol; the working electrode and comparative electrode were respectively of glass and silver chloride.

The amount of N-phenylphthalimide formed was also determined by a gravimetric method [1] by fractionating the products according to their solubility.

The composition of the reaction products was determined by thin-layer chromatography "with a witness". Plates with a "Silufol" layer attached were used; a benzene-ethyl acetate mixture (2 : 5) was used as the eluent. Specimens intended for chromatography were prepared as follows. A solution of N-phenylphthalamic acid (phthalic anhydride or phthalic acid) in DMF was heated for 2 hr at 145°, DMF was distilled off under vacuum, and the dry residue was dissolved in ethyl acetate.

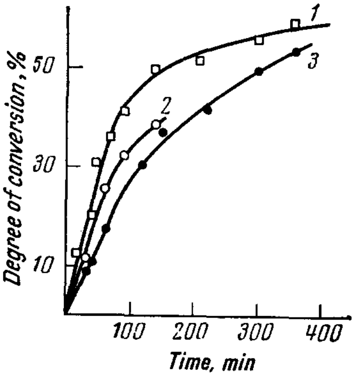


FIG. 1. Degree of conversion of N-phenylphthalamic acid to N-phenylphthalimide vs. time: *1* — determined by potentiometric titration of the acid; *2* — determined gravimetrically; *3* — by IR spectroscopy. Solvent — DMF, temperature 145°, initial concentration 0·14 mole/l.

Figure 1 shows the kinetic curves for the cyclization of N-phenylphthalamic acid in solution in DMF at 145°, concentration 0·14 mole/l. plotted by means of the various methods. Maximum values for the cyclization rate were obtained when the N-phenylphthalimide concentration was determined by IR-spectroscopy. The underestimated values obtained gravimetrically may be the result of the inevitable losses occurring during fractionation of the reaction products. The lowest rate of cyclization was obtained by the method of titration of the unreacted N-phenylphthalamic acid, i.e. it was formally found that the rate of disappearance of N-phenylphthalamic acid is lower than the rate of N-phenylphthalimide formation. Since it was thought that the underestimated results obtained by potentiometric titration were due to the formation of carboxyl-containing products in solution, the method of IR spectroscopy was used by us to investigate the kinetics of the imidization reaction.

It can be seen that an inflexion appears on the kinetic curves in Fig. 1 at 40% conversion. This inflexion is particularly evident if the kinetic data are plotted as curves of $2{\cdot}3 \log [a/(a-x)]$ and $x/a\ (a-x)$ versus time, where a is the initial concentration of the N-phenylphthalamic acid, and x is the current concentration of N-phenylphthalimide (Fig. 2*a*). It seems that at a definite degree of conversion there is a marked reduction in the rate constant, apparently as a result of a change in the mechanism of the process. The plot of 2·3 log $[a/(a-x)]$ versus time is a straight line only in the initial portion prior to the point of inflection. At the same time, if we plot the curve of $x/a(a-x)$ versus time, we obtain two intersecting straight lines with different slopes, i.e. the process is described by two second order equations with different rate constants. Since no conclusion as to the order of the reaction can be reached through the data in Fig. 2*a* on the basis of initial portions of the curves, we measured the initial rates of the reaction with different initial concentrations of N-phenylphthalamic acid (Fig. 2*b*); the slope of the curve is 1·87. This means that the cyclization reaction of N-phenylphthalamic acid is described by a second order equation both in the initial stage of the process and in subsequent stages. The rate constants for a second order reaction of cyclization of N-phenylphthalamic acid in DMF at 145°, determined from the slope of the $x/a\,(a-x)$ versus time curve are 0·0487 l./mole·min in the initial stage of the process and 0·0122 l./mole·min in subsequent stages, i.e. there is approximately a fourfold difference in the rate constants.

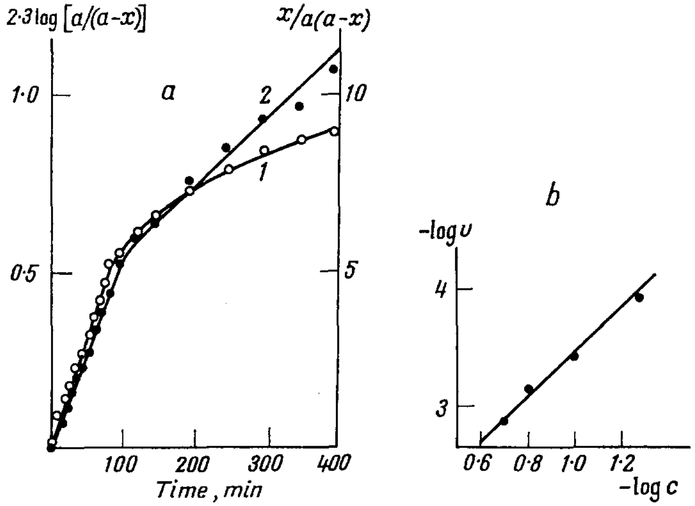


FIG. 2. *a* — Plots of 2·3 log $[a/(a-x)]$ (*1*) and $x/a(a-x)$ (*2*) vs. time, using the IR spectroscopic data in Fig. 1; *b* — logarithm of the rate (log *v*) of cyclization (mole/l.·min) of N-phenylphthalamic acid vs. the logarithm of the initial DMF concentration log *c*.

The bimolecular character of the cyclization reaction may be due to a protonated form of N-phenylphthalamic acid, or of a dimer of the latter, undergoing cyclization. The formation of dimers in highly polar basic solvents such as DMF is considered doubtful [8]. It appears more probable that an intermediate auotoprotonated product may be formed. This supposition is borne out by the fact that the reaction is catalysed by carboxylic acids. It was found that additions of *o*-chlorobenzoic acid within the concentration interval 0·01–0·15 mole/l. leads to a marked increase in the reaction rate; in addition, the initial rate of the reaction is a linear function of the amount of acid added (see Fig. 3).

To shed light on the factors underlying the reduced rate of the cyclization reaction at ~40% conversion, we investigated the composition of reaction products formed on heating N-phenylphthalamic acid for 90 min in solution in DMF.

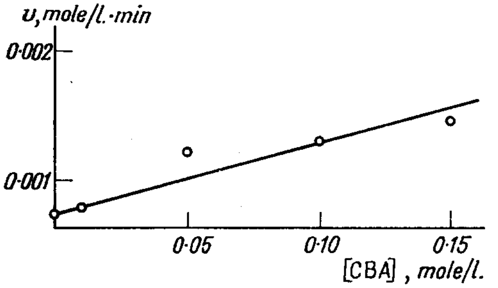


FIG. 3

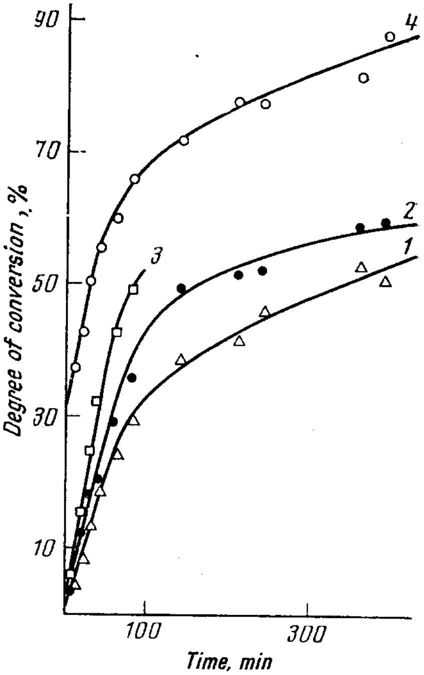


FIG. 4

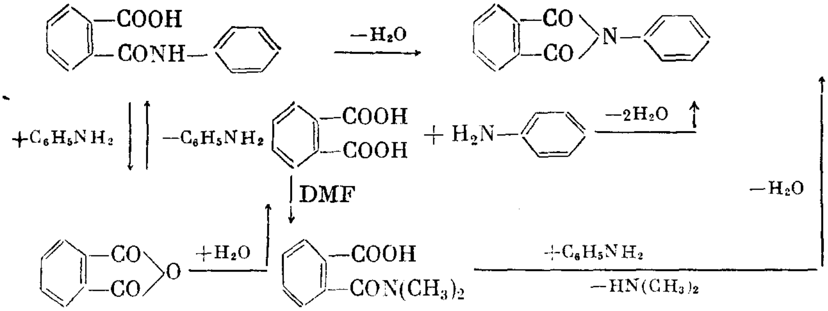
FIG. 3. Initial rate of cyclization of N-phenylphthalamic acid vs. the concentration of *o*-chlorobenzoic acid (CBA) added. DMF, initial concentration 0·14 mole/l.

FIG. 4. Degree of conversion of N-phenylphthalamic acid to N-phenylphthalimide vs. time in different solvents: *1* — DMAA, *2* — DMF, *3* — diglyme, *4* — *m*-cresol.

Aniline, phthalic acid and N,N-dimethylphthalic acid were detected by thin layer chromatography. Aniline and phthalic acid are apparently formed through intramolecular dissociation of N-phenylphthalamic acid together with subsequent hydrolysis of phthalic anhydride by water evolved during imidization. Possible factors giving rise to the formation of N,N-dimethylphthalamic acid could be reactions of phthalic anhydride, that is at equilibrium with N-phenylphthalamic acid, or of phthalic acid with DMF. Such a view is supported by other results [10, 11] relating to the interaction of anhydrides with DMF. In addition, we found that the heating of solutions of phthalic acid or its anhydride in DMF for 1–3 hr at 145° leads to the formation of N,N-dimethylphthalamic acid.

Thus a complex mixture of products appears in the cyclization of N-phenylphthalamic acid. At the same time with prolonged heating of the reaction mixture (~70 hr) the N-phenylphthalamide yield determined by IR-spectroscopy is close to 100%, i.e. the products formed during the reaction are nevertheless converted to N-phenylphthalamide.

Certainly, on heating equimolar mixtures ($c=0{\cdot}15$ mole/l.) of phthalic acid with aniline in DMF at 145° it was found that N-phenylphthalimide is formed. The rate constant for the latter reaction is 0·019 l./mole·min, which is only insignificantly higher than the rate constant for the slow stage of cyclization of N-phenylphthalamic acid ($k=0{\cdot}012$ l./mole·min). Similar results were also obtained on heating a mixture of N,N-dimethylphthalamic acid and aniline ($c=0{\cdot}15$ mole/l.) in DMF at 145°. The rate constant for N-phenylphthalamide formation in the latter case is 0·032 l./mole·min, i.e. it is slightly lower than the rate constant in the initial stage of the cyclization of N-phenylphthalamic acid, and considerably higher than in the slow stage. This means that the change in the rate constant during the cyclization reaction of N-phenylphthalamic acid is mainly due to the formation of phthalic acid, the interaction of which with aniline takes place at an appreciably lower rate. In view of the experimental results, the processes occurring during the cyclization of N-phenylphthalamic acid may be represented by the following scheme:



It should be noted that under the conditions adopted in this investigation the cyclization reaction of N-phenylphthalamic acid is an irreversible one. No change in the N-phenylphthalimide concentration appears on heating the latter in DMF solution ($c=0{\cdot}12$ mole/l.) in the presence of 2% water at 145° for 7 hr.

Phthalic acid formation enables one to account for differences in the results obtained by the methods of potentiometric titration and IR spectroscopy. The absence of agreement is due to the fact that the forming phthalic acid is titrated as a dibasic acid, which leads to overestimated results in determinations of the unreacted acid, which in turn leads to errors in determining the N-phenylphthalimide concentration.

Starting with the temperature depedence of the cyclization rate constant in the initial stages of N-phenylphthalamic acid formation in DMF solution determined at 130, 135, 140 and 145°, we found that the activation energy for the process is 30·5 kcal/mole.

Figure 4 shows the kinetic curves for the cyclization of N-phenylphthalamic acid in the different solvents at 145°. It can be seen that the cyclization rate decreases in the order *m*-cresol>diglyme>DMF>DMAA as the basicity of the solvent increases. The shape of the curves is identical for all the solvents. The $x/a(a-x)$ versus time plots appear as two intersecting straight lines; in addition, the degree of conversion at which the discontinuity appears varies with the nature of the solvent, and rises in the order DMAA<DMF<*m*-cresol. The Table gives the rate constants for the reaction in the different solvents. It appears that the rate constant largely depends on the basicity of the solvent; the maximum rate is obtained in the acidic *m*-cresol. Moreover, there is at the same time a reduction in the relative contribution of the reaction of N-phenylphthalamide formation via a stage of phthalic acid formation.

CYCLIZATION RATE CONSTANTS FOR N-PHENYLPHTHALAMIC ACID IN DIFFERENT SOLVENTS AT 145° (k_1 AT THE START OF THE REACTION, k_2 IN THE SUBSEQUENT SLOW STAGE)

Solvent	k_1, l./mole·min	k_2, l./mole·min
DMAA	0·0408	0·0001
DMF	0·0487	0·0122
Diglyme	0·1010	—
m-Cresol	0·1606	0·0010

The results of kinetic investigations of the cyclization of N-phenylphthalamic acid to N-phenylphthalimide may be used to interpret data on the cyclization kinetics of polyamic acids. In particular, the change in the rate constant in the cyclization of polyamic acids [1–3, 5, 7] is apparently similar in character to that occurring in the case of the model compound. However, the mobility of the polymer chains decreasing in the course of the reaction impedes interaction between terminal carboxyl groups and amino-groups, and results in a continuous reduction in the cyclization rate constant after a definite degree of conversion has been reached [7].

The influence of the nature of a solvent remaining in polyamic acids [7, 8] is similar to the influence which a solvent has upon the cyclization of N-phenylphthalamic acid. In either case this is related to the fact that autoprotonation of amic acid groups is facilitated when the basicity of the solvent is reduced. In view of this we have, of course, the acid catalysis occurring in the cyclization of the model compound and of polyamic acids [6].

Translated by R. J. A. HENDRY

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THE POLYMERIZATION OF BENZYL THIOCYANATE*

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(*Rceeived* 12 *September* 1976)

A polymer containing —C=N— conjugated bonds has been synthesized from benzyl thiocyanate. The kinetics and mechanism of the polymerization reaction have been investigated. In the light of the results of IR, NMR and chemical analyses the structure of the polybenzylthiocyanate has been elucidated. Some properties of the polymer have been investigated.

On an earlier occasion [1] we showed that the formation of polymers from organic thiocyanates is feasible.

In a comparative analysis of the reactivity of aromatic, fatty aromatic and aliphatic thiocyanates [2] it was found that the presence of a labile H atom in the

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