Structural Effects on the Rates of Formation of Amic Acids and Imides

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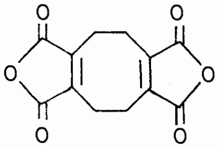
The reaction of amines with maleic anhydride (MA), pyromellitic anhydride (PMDA), dimethylmaleic anhydride (DMMA), and cyclo-octa-1,5-diene-1,2,5,6-tetracarboxylic dianhydride (CODA) was followed by titration. MA and PMDA give the amic acids very readily and cyclize to the imides only at high temperatures, while DMMA and CODA react slowly to yield a mixture of the amic acids and imides even at ambient temperatures. The structural factors affecting the reaction are discussed.

A NEW dianhydride cyclo-octa-1,5-diene-1,2,5,6-tetracarboxylic dianhydride (1) (CODA) prepared by photodimerization, in the solid state, of *trans,trans*-muconic acid was reported recently.[1] We have used this anhydride for the preparation of high temperature resistant polyimides which have physical characteristics different from polyimides based on aromatic dianhydrides.



(1)

Polyimides are normally prepared in two stages.[2] The first consists of treating a solution of the dianhydride with a diamine at room temperature, or at a temperature not higher than 75°, to give the polyamic acid, which is soluble and can be cast into a film. The second stage consists of heating the film up to 300°, eliminating a water molecule, to give the polyimide which is insoluble in any common solvent.

We have tried to obtain the polyamic acid derived from CODA by the method mentioned above. However, no increase in the viscosity of the solution was observed at temperatures up to 50° and no polyamic acid could be isolated. Upon raising the temperature to *ca.* 100°, a polymer was obtained, consisting essentially of a polyimide chain with possibly some free acidic groups.

In order to understand this unusual behaviour we have carried out a comparative kinetic study of the reaction of CODA and related anhydrides with aliphatic and aromatic amines.

EXPERIMENTAL

Materials.—Aniline (Fluka) was distilled under reduced pressure under argon. n-Butylamine was Fluka puriss grade. Maleic anhydride (MA) was crystallized three times from chloroform. Dimethylmaleic anhydride (DMMA) was from Fluka. Pyromellitic dianhydride (PMDA) (EGA-Chemie KG) was sublimed in the presence of dry silica. CODA was prepared from *trans,trans*-muconic acid [1] and was purified in the form of the tetrasodium salt in aqueous solution with activated charcoal, precipitated with hydrochloric acid, and finally crystallized from glacial acetic acid.

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[1] B. S. Green, M. Lahav, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1971, 1552.

[2] C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, *J. Polymer Sci. A*, 1965, **3**, 1373.

Dimethylformamide (DMF) (Fluka; puriss) was stirred overnight with anhydrous copper(II) sulphate and then distilled under reduced pressure under argon. Dimethyl acetamide (DMA) (Fluka; puriss) was distilled under reduced pressure over phosphorus pentaoxide under argon. 1,4-Dioxan was refluxed over sodium overnight and then distilled. Perchloric acid was B.D.H. AnalaR grade.

Procedure.—The reactions were normally carried out in a volumetric flask (25 cm³). The required volumes of solutions of the amine and the anhydride in DMF were mixed and diluted with DMF to a concentration of *ca.* 0·3M in reactive groups. At chosen intervals portions (4 cm³) of the reaction mixture were withdrawn and quenched with dioxan (50 cm³).

Titrations.—The progress of the reaction was followed by the method of nonaqueous titration described by Patchornik and Rogozinski [3] using an automatic titrator TTT 1C Titrigraph SBR 2c (Radiometer) with a glass electrode and an Ag–AgCl reference electrode. Portions of the quenched solutions were further diluted three times with absolute ethanol and then titrated with 0·25N-perchloric acid in dioxan and 0·25N-sodium methoxide in benzene–methanol (7 : 3). Each titration was repeated 2—3 times. The concentrations of the amine and anhydride solutions and the purity of the reagents were also verified by titration.

Calculations.—The unchanged amine was titrated with $HClO_4$ in dioxan thus allowing estimations of the reacted anhydride [equation (1)]. A further titration with NaOMe

$$[\text{reacted anhydride}]_t = [\text{amine}]_0 - [\text{amine}]_t \quad (1)$$

gave the total acid fraction [equation (2)] since it is known [3]

$$[\text{total acidity}]_t = [\text{amic acid}]_t + (\text{anhydride}]_t \quad (2)$$

that one mole of anhydride reacts with one equivalent of methoxide only. Thus from (1) and (2) it is possible to find the concentrations required [equations (3)—(5)].

$$[\text{anhydride}]_t = [\text{anhydride}]_0 - ([\text{amine}]_0 - [\text{amine}]_t) \quad (3)$$

$$[\text{amic acid}]_t = [\text{total acidity}]_t - [\text{anhydride}]_t \quad (4)$$

$$[\text{imide}]_t = [\text{anhydride}]_0 - [\text{total acidity}]_t \quad (5)$$

RESULTS

MA in DMF reacts instantaneously with n-butylamine to yield butylmaleamic acid and with aniline to yield maleanilic acid. On heating the solution of butylmaleamic acid for 14 h at 150° a change of only 12% in the titration of the free acid was observed. The maleanilic acid under the same conditions did not show any change. PMDA in DMA reacts very fast with n-butylamine and with aniline, at room temperature, to yield the corresponding amic acids. No change in the titration of the free acid was observed when the solutions were left at room temperature for a few days. Cyclization occurred only on heating the solutions to 150°. The rate of cyclization is shown in Figure 1. DMMA and CODA react fairly rapidly with n-butylamine at 30° (Figure 2). However, unlike the previous cases, a mixture of amic acids and imides is obtained from both DMMA and CODA. It can be seen from Figure 2 that the addition of Bu_3N as catalyst does not accelerate amidation and even slows down cyclization to the imide. The reaction of aniline with both anhydrides is very slow but it is considerably accelerated by the addition of Bu_3N (Figure 3). The rate of cyclization follows closely the rate of amidation and therefore a mixture of amic acid and imide is obtained.

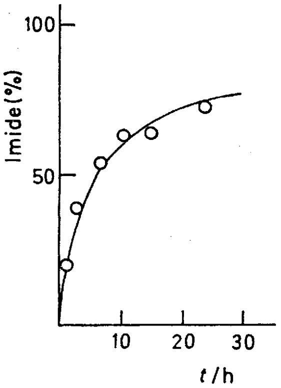

FIGURE 1 Rate of conversion of the amic acid derived from PMDA and aniline into the imide: solvent, DMA; temperature, 150°

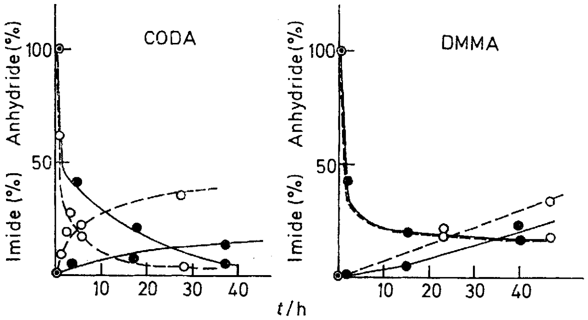

FIGURE 2 Rates of reaction of $BuNH_2$ with CODA and DMMA: ● in the presence of Bu_3N; ○ in the absence of Bu_3N: solvent, DMF; temperature, 30°

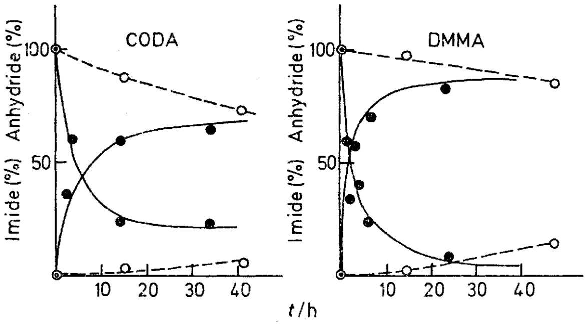

FIGURE 3 Rates of reaction of aniline with CODA and DMMA: ● in the presence of Bu_3N; ○ in the absence of Bu_3N: solvent, DMF; temperature, 30°

DISCUSSION

The fact that MA reacts so readily with amines is well known and fairly well understood. It is also known that maleamic acids can be cyclized to the imides only by heating to high temperatures and even then only very low yields are obtained.[4]

PMDA is the most common anhydride used for the manufacture of polyimides, *e.g.* DuPont's H-film is made from PMDA and 4,4′-diaminodiphenyl ether.[5] Kreutz

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[3] A. Patchornik and S. Ehrlich-Rogozinski, *Analyt. Chem.*, 1959, **31**, 985.

[4] N. B. Mehta, A. P. Phillips, F. F. Lui, and R. E. Brooks, *J. Org. Chem.*, 1960, **25**, 1012.

[5] (*a*) C. E. Sroog, *J. Polymer Sci. C*, 1967, **16**, 1191; (*b*) Technical Information Bulletin, H-2, DuPont, Kapton.

et al.[6] have studied the kinetics of H-film formation. They showed that whereas the polyamic acid is formed at room temperature, cyclization to the imide can be carried out only at temperatures of 150° or higher. This is in agreement with our titration results showing that monoamines react quantitatively with PMDA at room temperature, to yield the amic acids, while cyclization to the imide is slow even at 150° (Figure 1).

One can conclude therefore that MA and PMDA show essentially the same behaviour pattern, namely, very fast amidation reaction at room temperature and slow cyclization to imide at high temperatures.

DMMA and CODA, on the other hand show a completely different pattern, a relatively slow amidation reaction with cyclization to imide occurring even at room temperature (Figures 2 and 3). The similarity between DMMA and CODA is also manifested by the fact that in both cases the corresponding free acid cannot be obtained as it cyclizes to the anhydride even in aqueous solution at room temperature.

Eberson [7] has shown that in equilibrium (6) $k_1/k_{-1} = 5{\cdot}3$. Koskikallio [8] suggested that the energy and the

$$\text{Dimethylmaleic acid} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{DMMA} + H_2O \qquad (6)$$

entropy of hydrolysis of DMMA are very similar to that of other anhydrides, whereas the entropy of cyclization of dimethylmaleic acid is much greater than for other acids. The same conclusion was also reached by Wheeler,[9] who suggested that the easy cyclization could be explained by the mutual repulsion of the methyl groups which brings the two carboxy-groups closer together. This seems more likely than the speculation of Bartlett [10] that stronger dipole–dipole interactions between the carboxy-groups in dimethylmaleic acid are the reason for the easy cyclization.

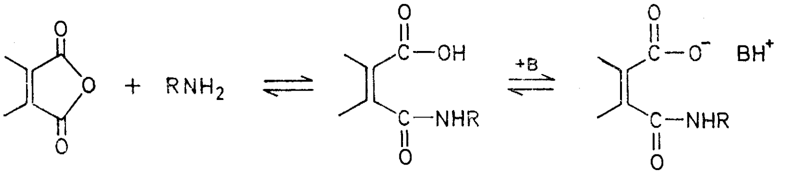
Two recent papers dealing with conformations around carbon–carbon double bonds, seem to support Wheeler's suggestion. Kondo *et al.*[11] carried out a microwave study of *cis*-but-2-ene. They showed that the C–C=C angle is increased to 126·7° in this compound. Calculations carried out by Ermer [12] with a consistent force field showed that a lower minimum energy conformation is obtained by opening the bond angles of *cis*-but-2-ene than by a twist around the double bond. Unfortunately, there is no published crystal structure analysis of DMMA. Yet, by analogy to the *cis*-but-2-ene it is reasonable to assume that the C=C–CH_3 angles in DMMA will also be considerably larger than 120°.

A recent crystal structure analysis of 4,8-dimethylcyclo-octa-1,5-diene-3,7-dicarboxamide (having the same ring structure as CODA) was carried out by Leizerowitz.[13] He has shown that the C–C=C bond angles in this compound are *ca.* 130°. Therefore, substituents on such a C=C bond will have a considerable tendency to come closer to each other than in normal olefins.

It is reasonable to regard CODA as the cyclic dimer of DMMA. From all the information cited above, we can assume that in both cases the strain in the molecule can be the driving force for the cyclization of the acid to the anhydride. Consequently the reaction of the anhydride with an amine to yield the amic acid can be expected to be slow.

Tributylamine has a very pronounced effect on the reaction of aniline with DMMA as well as with CODA (Figure 3). There is a very remarkable enhancement of the rate of formation of the amic acid by about an order of magnitude. The cyclization is also much faster, but this is probably due to the fact that the rate-determining step is the amic acid formation, both in the presence or absence of catalyst. The reaction with butylamine, on the other hand is hardly affected and in the case of CODA the cyclization is even slowed down.

A possible explanation for the acceleration of the reaction with aniline can be found by assuming equilibrium (7). Any strong enough base will shift the equilibrium to give the salt. Indeed when one adds two equivalents of butylamine, or one equivalent of butylamine and one of Bu_3N, a crystalline salt precipitates, which was shown by microanalysis and i.r. spectra to be the salt of the amic acid. In the case of butylamine amidation is fast enough so that the catalytic effect is not noticeable. However, the reaction with aniline is very slow and its effect is much more meaningful.



(7)

From the kinetic results reported above one could hope to be able to prepare polyimides from CODA and a diamine at 30 or 50° in DMF; however, this was not the case even after very long reaction periods. On closer inspection of the titration results we see that 100% conversion was never attained. This is due to the fact that

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[6] J. A. Kreuz, A. L. Endrey, F. P. Gay, and C. E. Sroog, *J. Polymer Sci. A*, 1966, **4**, 2607.

[7] L. Eberson, *Acta Chem. Scand.*, 1964, **18**, 1276.

[8] J. Koskikallio, *Acta Chem. Scand.*, 1956, **10**, 822.

[9] O. H. Wheeler and E. E. Granell Rodriguez, *J. Org. Chem.*, 1961, **26**, 4763.

[10] P. D. Bartlett, *J. Chem. Educ.*, 1953, 22.

[11] S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectroscopy*, 1970, **34**, 231.

[12] O. Ermer and S. Lifson, *J. Mol. Spectroscopy*, in the press.

[13] L. Leizerowitz, personal communication.

there are some minor side reactions taking place in DMF. In polymerization reactions the degree of polymerization is determined by the percentage of conversion; this can therefore account for our failure to obtain polymers in DMF. By changing the solvent to *m*-cresol, high molecular weight polymers were obtained after 30 h at 110°. The results will be reported in a forthcoming publication.

We thank Mrs. S. Ehrlich-Rogozinski for her help and valuable advice in connection with the titration procedures.

[4/474 *Received*, 11*th March*, 1974]