Amic Acid Redistribution Reactions: Substituent Effects

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ABSTRACT: The amide redistribution reaction was used to determine the rate of anhydride formation from substituted amic acids. Solutions of monoamic acid or diamic acid were prepared and an equimolar quantity of free amine was added. Exchange of the free amine into the amic acid was observed at ambient temperature and monitored by ^{13}C NMR spectroscopy. The reaction kinetics are pseudo first order in amic acid. Acid catalysis by the amic acid causes the reaction rate to be concentration dependent; thus the true rate constants are second order. The rate of anhydride formation is accelerated in less-polar solvents. Electron donating substituents on either the anhydride or amine-derived portions of the amic acid accelerate the rate of anhydride formation. A detailed mechanism consistent with the kinetic evidence involves a reversible reaction of amic acid to anhydride and amine.

Introduction

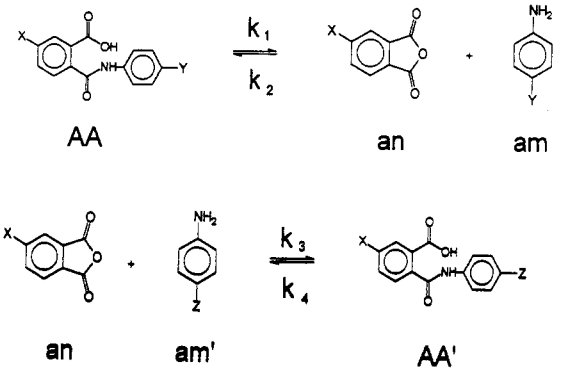
Aromatic polyimides have found widespread use in microelectronics and aerospace applications because of their high thermal stability[1] but often are sold and used as solutions of the precursor amic acid. Polyamic acid solutions have been reported to undergo a redistribution reaction which can affect molecular weight distribution,[2–5] randomize a mixture of polyamic acids,[6–8] or alter block sequence distribution in block copolyamic acids.[9] These changes occur not only during thermal curing but also under ambient conditions in solution. The redistribution reaction is generally thought to occur via formation of anhydride and amine from amic acid.[3–14] The present study addresses the effect which substituents on either the amine or the anhydride have on the amic acid redistribution rate at ambient conditions, as well as an examination of the effects of solvent and concentration. We reported the effects of solvent and polyamic acid structure on the rate and extent of anhydride formation during thermal imidization previously.[10] Amic acid redistribution was proposed to occur by reversion of amic acid to anhydride and amine, although mechanistic details were not addressed. Anhydride and free amine have also been directly observed by others during the thermal curing of amic acids, supporting that mechanism.[10,11] It has been reported that amic acids containing electron-rich amines exchange at a rate faster than those containing electron-deficient amines.[6] No reports on the relative effects of anhydride substituents are available.

Experimental Section

Amic Acid Preparation. Reagents were purchased in high purity from commercial sources and used as received. *N*-Methylpyrrolidone (NMP) and 2-methoxyethyl ether (diglyme) were purchased from Burdick and Jackson, 2-(2-ethoxy)ethoxyethanol (ethyl carbitol) was purchased from Aldrich. Reactions were run at a concentration of 0.075 mol amic acid per 100 g of solution, with the exception of those reactions investigating the effect of concentration. Amic acids were formed by weighing the anhydride and initial amine into a 125-mL HDPE bottle, adding the solvent, and agitating the solution overnight. An equimolar amount of a different amine was added to the solution and the exchange reaction was followed by ^{13}C NMR. The solutions were stored at ambient temperature, approximately 21 ± 1 °C. All manipulations were performed under nitrogen in a glovebox.

^{13}C NMR Spectroscopy. Quantitative ^{13}C NMR data were collected using a Varian VXR-300S spectrometer at ambient temperature using a 30-s pulse delay, gated decoupling (decoupler on only during acquisition), 90° pulse width, spectral width of 30 000 Hz, and an acquisition time of 0.533 s. The nuclear Overhauser effect was suppressed by gating the decoupler on during acquisition and then off during relaxation. The pulse relaxation delay was chosen to allow complete relaxation between scans. The internal consistency of the integrals verifies that the data are quantitative. Total acquisition time was 2 h. The experiments were run unlocked since proteo-solvents were used. Chemical shifts were referenced to the furthest downfield solvent peak at 174.4, 72.3, and 72.8 ppm, respectively, for NMP, diglyme, and ethyl carbitol.

Scheme I. Amic Acid Redistribution Model



Redistribution Studies. The initial amic acid solution contains equimolar amounts of amic acid and free amine. All peaks in the ^{13}C NMR spectrum are assigned without ambiguity to one of these two species using substituent constants and have the proper integrated intensity.[15] As the redistribution occurs, two additional sets of peaks appear from the new amic acid and new free amine. A pair of peaks free from interference was selected for each model system and the relative concentration of the amic acid originally present was calculated to be equal to $a/(a + a')$, where a is the integral of the peak originally at 100% and a' is the integral of the complementary peak resulting from displacement of a. The peaks a and a' were selected to both be either free amine or amic acid. Equilibrium values for the exchange reaction were determined by heating samples at 65 °C until no further relative intensity change was observed.

Results and Discussion

Kinetic Analysis of the Redistribution. Reaction kinetics were modeled with a reaction mechanism consisting of reversible formation of anhydride and amine from amic acid, followed by reaction of anhydride with free amine to form a new amic acid (Scheme I). The initial amic acid forming reaction to produce the amic acid (AA) is reversible to the starting amine (am) and anhydride

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(an). When a second amine (am′) is added to the amic acid solution containing AA, a new amic acid forms (AA′) which is the reaction product of am′ and an. An equilibrium develops between AA and AA′ which depends on the relative reactivity of am and am′. A kinetic analysis based on these equations gives a value for the rate of anhydride formation from AA, k_1, that is first order in amic acid.

The kinetic analysis based on Scheme I treats anhydride formation as a first-order process since the amic acid concentration is constant throughout. The amic acid AA reverts to anhydride and amine at a rate k_1, independent of the free amine. The rate of consumption of [AA] is given in eq 1

$$-\mathrm{d[AA]}/\mathrm{d}t = k_1[\mathrm{AA}] - k_2[\mathrm{an}][\mathrm{am}] \quad (1)$$

The concentration of anhydride is small and cannot be measured directly since the equilibrium k_2/k_1 is large, heavily favoring amic acid formation. Thus, the contribution of free anhydride to the concentration of amic acid can be neglected. The rate of anhydride formation is expressed by eq 2

$$\mathrm{d[an]}/\mathrm{d}t = k_1[\mathrm{AA}] - k_2[\mathrm{an}][\mathrm{am}] - k_3[\mathrm{an}][\mathrm{am'}] + k_4[\mathrm{AA'}] \quad (2)$$

which can be set equal to zero at the steady-state condition. The rate constant values k in eq 2 can be consolidated and expressed in terms of k_1 and k_2 by making the substitutions

$$k_2/k_3 = k_4/k_1 = K_{eq} = 10^{\sigma\rho} \quad (3)$$

where σ refers to the substituent constant and ρ is the reaction constant for linear free energy relationships as described by Hammett ($\sigma = \sigma_{am} - \sigma_{am'}$).[16] Additionally, the concentration of AA = am′ and of AA′ = am and the concentrations of amic acid (AA + AA′) and free amine (am + am′) are constant. After making these substitutions into eq 2 the expression for steady-state concentration of anhydride becomes

$$[\mathrm{an}] = K_{eq}k_1/k_2 \quad (4)$$

Substituting eq 4 into eq 1 and integrating gives the rate equation for the amic acid exchange process which expresses k_1, the rate of anhydride formation from amic acid, in terms of the measurable quantitites [AA] and time and the constant K_{eq}.

$$k_1t = \{-1/(1 + K_{eq})\} \ln\{(1 + K_{eq})[\mathrm{AA}] - K_{eq}\} \quad (5)$$

Cyclization of amic acid to anhydride is much faster than cyclization to imide. Even during reactions run to 80% approach to equilibrium, only a trace amount of imide formation was observed. During thermal curing of amic acids anhydride formation has also been observed to precede imide formation.[10]

Effect of Amic Acid Concentration. The kinetic analysis above treats anhydride formation as a first-order process. Since the amic acid concentration is constant in this experiment the assumption is valid. However, when the concentrations of the amic acid/amine reaction solutions were varied, the first-order rates of anhydride formation increased with increasing concentration. The redistribution reaction is concentration dependent, inconsistent with a first-order process. The experiments summarized in Tables II–IV were all run at a constant 0.75 mol/kg concentration of amic acid (vide infra); most of these were also run at 0.5 mol/kg. A plot of the first-order rates of anhydride formation at 0.5 versus 0.75 mol/kg in Figure 1 gives a fitted line with slope = 0.66, consistent

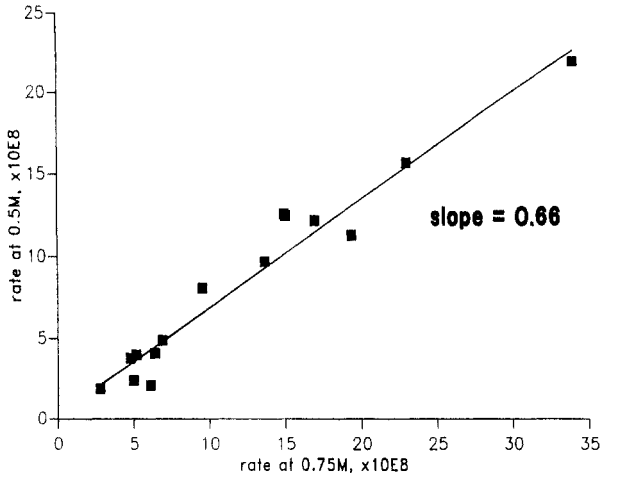


Figure 1. Rates of anhydride formation at 0.75 and 0.5 M.

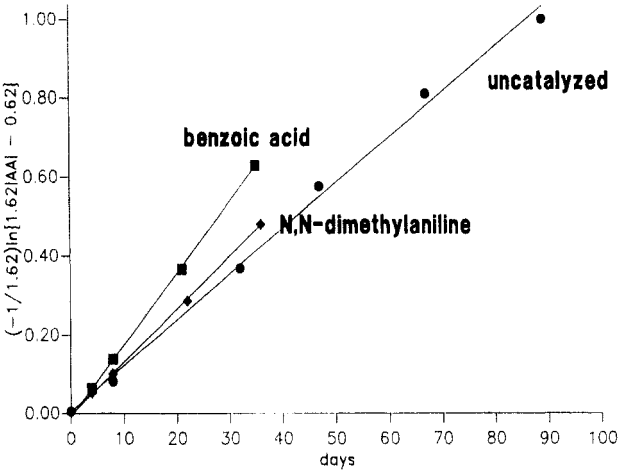


Figure 2. Exchange of IPAN/*p*-bromoaniline amic acid with aniline in the presence of added catalyst.

with a second-order dependence on amic acid concentration. The weight percent amic acid for the experiments represented in Figure 1 ranges from 11.5 to 29.6 wt %. It can be concluded that the amic acid redistribution reaction is second order in amic acid in this concentration range.

The accelerated rate of anhydride formation at higher concentration is probably caused by catalysis by the acid group of the amic acids. Catalysis of substitution reactions of carbonyl compounds by both acids and bases is a well-known phenomenon and is important in the aprotic solvents typically used to synthesize polyamic acids.[12,17–20] This is a rate effect only, and the exchange equilibria are not affected by concentration.

The hypothesis of acid catalysis was further probed by forming the isopropylidene bis(phthalic anhydride)/*p*-bromoaniline amic acid at 0.75 mol/kg, then adding an equivalent amount of aniline and half equivalent of either benzoic acid or (*N*,*N*-dimethylamino)aniline. Figure 2 is a plot of eq 5, for this experiment, with $K_{eq} = 0.62$ for the amine couple of *p*-bromoaniline/aniline.

Increasing the acid concentration 50% by adding benzoic acid increased the rate of anhydride formation by 50%, so the measured rate k_1 depended on the concentration of added benzoic acid to the 1.0 power. Adding the base (*N*,*N*-dimethylamino)aniline to the amic acid solution very slightly increased the rate of exchange; the observed rate increase depended on the concentration of added base to the 0.3 power.

The redistribution reaction is concentration dependent and is pseudo first order under the reaction conditions.

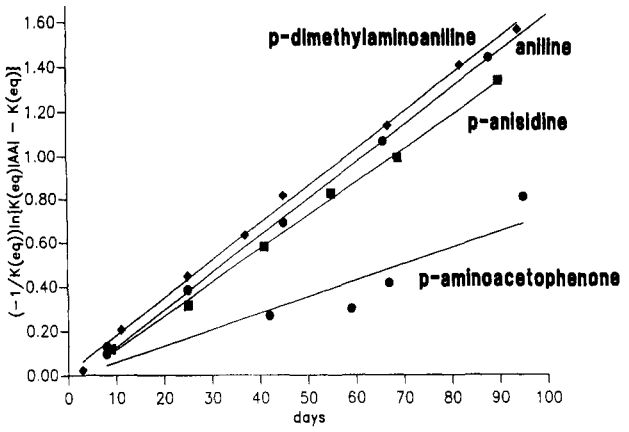


Figure 3. Exchange of phthalic anhydride/*p*-bromoaniline amic acids with substituted amines.

Table I. Rate of Anhydride Formation from Phthalic Anhydride/*p*-Bromoaniline Amic Acid in the Presence of Substituted Anilines

substituent	K_{eq}	k_1, s^{-1}
p-C(O)CH$_3$	3.5	8×10^{-8}
p-Br	1.00	
-H	0.62	1.97×10^{-7}
p-OCH$_3$	0.158	1.74×10^{-7}
p-N(CH$_3$)$_2$	0.047	1.97×10^{-7}

All subsequent discussions in this paper comparing substituent effects refer to reactions run at a constant amic acid concentration of 0.75 mol/kg of solution. This concentration corresponds to weight percent amic acids between 17.3 and 29.6 wt %.

Effect of the Free Amine. The amic acid model system in this study contains an equivalent amount of free amine, in contrast to polyamic acid solutions which would typically contain only a small amount of amine end groups or none at all. To ensure that amide exchange caused by attack of the free amine at the amide carbonyl (transamidation) was not occurring under our experimental conditions, a series of reactions was run between phthalic anhydride/*p*-bromoaniline amic acid and differentially substituted anilines. If the anhydride formation is the rate-determining step, the reaction rate k_1 will be independent of the identity of the free amine. In the preceding section, it was shown that added (*N*,*N*-dimethylamino)aniline had minimal effect on the rate of anhydride formation. The results from eq 5 for these reactions are plotted in Figure 3, and first-order rate constants are listed in Table I. K_{eq} varies with the different amine couples. The rate of anhydride formation from phthalic anhydride/*p*-bromoaniline amic acid is independent of the identity of the free amine in the presence of amines having a σ value more negative than bromine. {There is an apparent rate change for the reaction with *p*-aminoacetophenone, although the data are poor.} The independence of the rate of anhydride formation from the free amine verifies that the model system is well behaved for amine substituents with σ more electropositive than bromine.

Anhydride Substituent Effects. The structure of an anhydride is expected to affect its reactivity with amines and the propensity of the amic acid to re-form anhydride. Dianhydrides typically have one substituent (the bridging group) located in the meta or para position relative to the anhydride carbonyls. Bridging groups of common anhydrides range from strongly electron donating (isopropylidene in IPAN, ether in ODPA) to strongly electron accepting (carbonyl in BTDA, hexafluoroisopropylidene in 6FDA). Pyromellitic dianhydride is by far the most

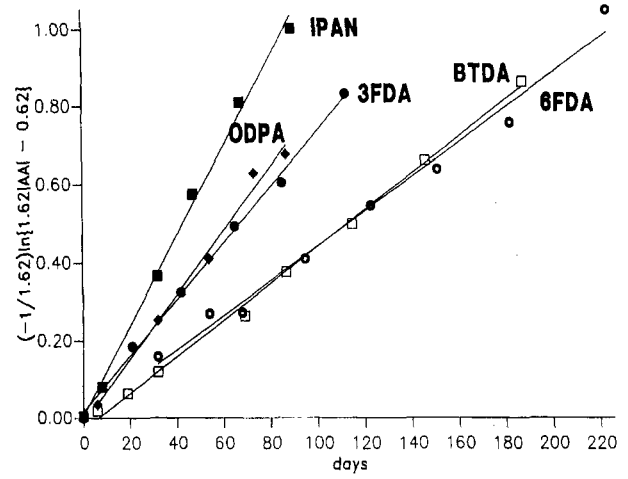
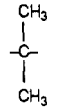
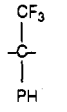
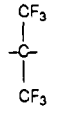


Figure 4. Exchange of dianhydride/*p*-bromoaniline amic acids with aniline.

Table II. Rate of Anhydride Formation from Dianhydride/*p*-Bromoanilide Amic Acid

anhydride	bridging group	rate, s^{-1}	σ (av)
IPAN		1.37×10^{-7}	−0.15
ODPA	–O–	9.57×10^{-8}	−0.01
phthalic	–H	1.94×10^{-7}	0.00
3FDA		8.39×10^{-8}	
BTDA		5.17×10^{-8}	+0.43
6FDA		4.78×10^{-8}	

electrophilic common dianhydride because of its tetracarbonyl substitution.

Diamic acids were formed from a bridged dianhydride and *p*-bromoaniline, then an equivalent amount of aniline was added. All reactions went to the same equilibrium ratio of *p*-bromoaniline/aniline. Results of the kinetic analysis based on eq 5 are presented in Figure 4 and Table II.

The rate of anhydride formation k_1 increases with the increasing electron-donor character of the anhydride bridge, in the order expected from Hammett σ values for substituent constants (with the exception of phthalic anhydride).[21] The observed rates are actually weighted averages of the redistribution rates for the two amic acid isomers having *m*- and *p*-amide moieties. By using literature σ values for analogs (*tert*-butyl for IPAN, methoxy for ODPA, acetyl for BTDA) and the observed equilibrium values for *m*-/*p*-amic acid, averaged σ values can be estimated for several of the dianhydrides. A plot of log (k_1) versus σ (av) gives a line with slope equal to ρ. The reaction constant ρ for bridging anhydride substituents is −0.75. σ (av) values for 6FDA and 3FDA can be calculated for 6FDA (+0.46) and for 3FDA (+0.11) based on this ρ value.[22] The rate of anhydride formation from 6FDA amic acid indicates the σ (av) value for the 6F group is very similar to that for carbonyl. This makes an interesting comparison between 6FDA and BTDA since they are electronically similar and differ primarily in the

steric requirements of the bridging group. The observed rate of anhydride formation from 3FDA indicates that the 3F group (1-phenyl-2,2,2-trifluoroethylidene) is moderately electron withdrawing. Pyromellitic dianhydride and biphenyltetracarboxylic dianhydride could not be tested with the group of bridged dianhydrides because of limited solubility of the *p*-bromoanilide amic acids.

The rate of anhydride formation from phthalic anhydride/*p*-bromoaniline amic acid is approximately twice that expected based on substituent effects of the other amic acids. Although this is not presently understood, a similar trend is seen in the amine substituent effects presented below. It is perhaps related to intramolecular hydrogen bonding or a solvent effect caused by differential hydrogen bonding of mono- and diamic acids. Thus, in order to compare substituent effects, it is necessary to maintain strictly similar geometry.

Amine Substituent Effects. Reactivity of aromatic amines is affected by substituents on the aromatic ring. The nucleophilicity of the amine is increased by electron-donating groups and decreased by electron-withdrawing groups. Thus, electron-rich amines such as *p*-phenylenediamine or 4,4′-oxydianiline react faster with anhydrides than electron-poor amines substituted by fluorine or carbonyl. In a competitive situation, such as the amic acid redistribution reactions, formation of the amide with the more nucleophilic amine is favored. However, it is not obvious how a substituent on the amine portion of an amic acid will affect the rate of anhydride formation from that amic acid.

Amic acids were formed from substituted amines and phthalic anhydride, then an equivalent amount of aniline was added. The equilibrium concentrations of the two amic acids always favored the amic acid containing the more nucleophilic amine. However, electron-donating substituents on the amine portion of the amic acid accelerated the rate of anhydride formation. Thus even though the amic acid formed with the more nucleophilic amine is thermodynamically favored, it is kinetically less stable toward the back reaction to anhydride and amine.

Results of the kinetic analysis are presented in Table III, grouped by similar geometry to facilitate comparison of substituent effects. There is a significant effect of amine geometry on rate of anhydride formation, as observed with the anhydrides. In all cases the amic acids from amines with more electropositive substituents (more negative sigma) have the highest rate of anhydride formation, given that they are in the same "geometry group". In diamic acids derived from diamines and monoanhydrides, acylation of the first amino group may decrease reactivity of the second amino group.[23] The rates of anhydride formation qualitatively appear in order of the literature σ values for analogous aliphatic groups and indicate that the Hammett ρ value for amine substituents is negative. A fit of the data gives $\rho = -0.62$. The 1-phenyl-2,2,2-trifluoroethylidene (3F) group in the diamine BA3F (Table IIIb) is moderately deactivating, consistent with the result on the 3F dianhydride. The hexafluoroisopropylidene group (6F) in the diamine BAAF is strongly deactivating and has the lowest rate of anhydride formation among the diamines tested in its "geometry" group.

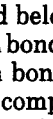
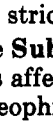
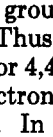
Placing a trifluoromethyl group directly on the aromatic ring has a very strongly deactivating effect. The rate of anhydride formation decreased four-fold from ODA to OBABTF (2,2′-bis(trifluoromethyl)-4,4′-diaminodiphenyl ether). The effect of trifluoromethyl is also strongly deactivating as a substituent on *m*-phenylenediamine (parts b and c of Table III).

Table III. Rate of Anhydride Formation from Amine/Phthalic Anhydride Amic Acid (IIIa) and Diamine/Phthalic Anhydride Diamic Acid (IIIb, IIIc)

IIIa. Monoamines

amine	rate, s^{-1}	σ
p-phenoxyaniline	3.6×10^{-7}	−0.27
p-(*tert*-butyl)aniline	3.2×10^{-7}	−0.20
p-bromoaniline	2.0×10^{-7}	+0.23

IIIb. Singly Bridged Diamines

diamine	bridging group	rate, s^{-1}	σ
ODA	–O–	2.3×10^{-7}	−0.27
BAA		1.7×10^{-7}	−0.20
BA3F		1.4×10^{-7}	+0.13
1,2,4-OBABTF	–O–	6.4×10^{-8}	
BAAF		6.9×10^{-8}	+0.52

IIIc. 5-Substituted 1,3-Phenylenediamine

diamine	rate, s^{-1}	σ
3,5-diamino-*tert*-butylbenzene	1.5×10^{-7}	<0
3,5-diaminobenzotrifluoride	2.8×10^{-8}	>0

Table IV. Rates of Anhydride Formation from Various *p*-Phenoxyanilines

diamine	rate, s^{-1}	σ
p-phenoxyaniline	3.6×10^{-7}	−0.27
4,4′-bis(*p*-aminophenoxy)biphenyl (APBP)	3.4×10^{-7}	−0.27
2,2-bis(*p*-(*p*-aminophenoxy)phenyl)propane (BAPP)	2.7×10^{-7}	−0.27
4,4′-oxydianiline (ODA)	2.3×10^{-7}	−0.27

The monoamic acids (Table IIIa) and singly bridged diamic acids (Table IIIb) having nominally the same substituent differ in their rate of anhydride formation, as was observed with the dianhydrides. The rate of anhydride formation from ODA diamic acid is 65% that of the rate from *p*-phenoxyaniline; the rate of anhydride formation from the BAA diamic acid is also about 65% that of *p*-(*tert*-butyl)aniline. This geometry effect is probably caused by intramolecular hydrogen bonding in the diamic acid or a solvent effect caused by proximity of the amic acid moieties.

The effect of diamine geometry on the rate of anhydride formation from several *p*-phenoxyaniline amic acids is shown directly in Table IV. These diamines all have a similar electronic contribution from the *p*-phenoxy substituent yet display different rates of anhydride formation, illustrating the effect that the specific geometry of the amine has on rate of anhydride formation. The monoamic acid based on *p*-phenoxyaniline has the highest rate of anhydride formation. However, an extended diamic acid based on APBP had nearly the same rate of anhydride formation as observed in the monoamic acid. The rigidity of the APBP structure effectively prevents any interaction between the two amic acid groups, making the rate of anhydride formation nearly equal to that of free *p*-phenoxyaniline. The rate of anhydride formation drops significantly when the flexible isopropylidene spacer group is added to form BAPP from APBP, even though it is a four-ring system as is APBP; the added flexibility apparently gives the two amides freedom to interact and

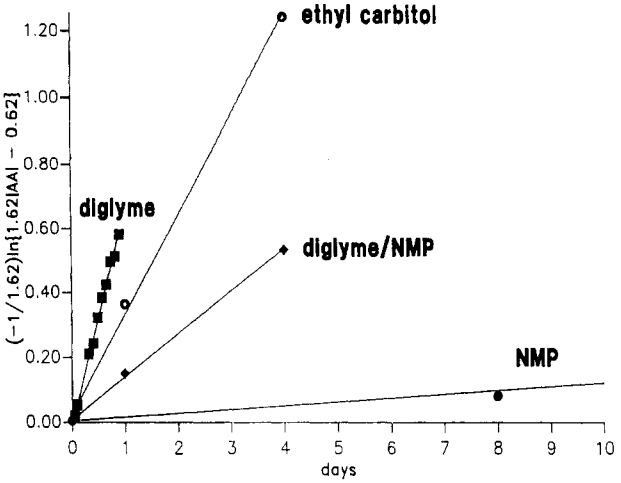


Figure 5. Solvent effect on the redistribution reaction rate.

Table V. Rate of Anhydride Formation from IPAN/ *p*-Bromoaniline Amic Acid

solvent	rate, s^{-1}	relative rate
NMP	1.37×10^{-7}	1
50% NMP/50% diglyme	1.54×10^{-6}	11
ethyl carbitol	3.59×10^{-6}	26
diglyme	7.64×10^{-6}	66

stabilizes the diamic acid. The ODA diamic acid has an even lower rate of anhydride formation, only 65% that of the monoamic acid of *p*-phenoxyaniline. A rate effect of similar magnitude was observed between monoanhydrides and singly bridged dianhydrides.

Solvent Effects. The solvent often has a significant role in the reaction rate and mechanism. Two different types of solvents, other than NMP, were used to monitor the amic acid redistribution reaction between IPAN/*p*-bromoaniline and aniline: diglyme (2-methoxyethyl ether), a polyalkyl ether; ethyl carbitol (2-(2-ethoxy)ethoxyethanol), a polyalkyl ether alcohol. The rate of anhydride formation from amic acids is substantially accelerated in ethyl carbitol and even further in diglyme, relative to NMP. The rates of amic acid exchange in these three solvents and a blend of 50% NMP/50% diglyme are illustrated in Figure 5 and Table V. The enormous rate increase in diglyme over NMP may be caused by the inability of the solvent to effectively hydrogen bond with the amic acid. The lack of hydrogen bonding destabilizes the amic acid relative to NMP and lowers the activation barrier to anhydride formation. The rate of anhydride formation in the NMP/diglyme cosolvent is intermediate between the two pure solvents.

Hydrogen bonding alone does not adequately explain the rate differences, however. Ethyl carbitol is structurally similar to diglyme but is an alcohol; thus it would be expected to have good hydrogen bonding ability. But the rate of anhydride formation is only a factor of 3 lower in ethyl carbitol than in diglyme, while remaining 26 times faster than in NMP. One possible explanation is that the protic solvent has a catalytic effect, accelerating the rate of anhydride formation. A similar effect has been observed by Denton where water was observed to catalyze imidization.[24] The equilibrium constant for amic acid formation has been correlated to solvent basicity.[25]

Mechanistic Implications. Two basic mechanisms for the amic acid redistribution are illustrated in Figure 6 and can be distinguished based on the information contained in this study. Transamidation is the direct attack of an amine on an amide carbonyl and does not involve anhydride formation (Figure 6a). An alternative

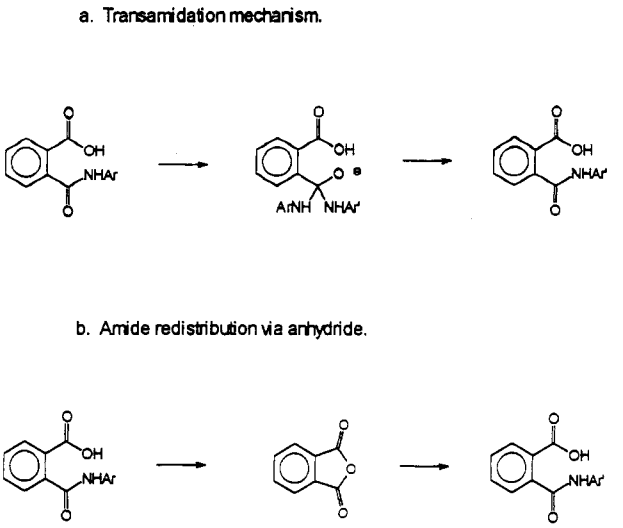


Figure 6. (a) Transamidation mechanism. (b) Amide redistribution via anhydride.

mechanism uniquely available to *o*-amic acids is intermediate anhydride formation from the amic acid followed by reaction of the anhydride with free amine (Figure 6b).

The transamidation mechanism involves a nucleophilic attack at the amide carbonyl by the free amine (Figure 6a). This mechanism would be expected to have a positive Hammett ρ value since electronegative anhydride substituents would accelerate the redistribution reaction by decreasing electron density on the amide carbonyl. The rate acceleration observed with electropositive anhydride substituents implies a negative ρ value for the amic acid redistribution. (A plot of log (k) vs σ (av) gives $\rho = -0.75$ for the reaction of amic acid to give anhydride and amine, based on BTDA, ODPA, and IPAN.) The independence of the rate of anhydride formation from the identity of the free amine confirms that attack of free amine on the amide is not a major contributor to amide interchange.

An alternate mechanism uniquely available to *o*-amic acids offers a low energy pathway to amide interchange (Figure 6b). Formation of anhydride and amine from amic acid is an entropically favored process. Anhydride formation via elimination of aromatic amine from the amic acid has been directly observed during thermal curing. The evidence in this study suggests that anhydride formation is a rapid process in amic acid solutions at ambient temperature, although equilibrium lies heavily toward amic acid.

A rate-determining step for anhydride formation involving protonation of the amide carbonyl is consistent with the substituent and concentration effects. The acceleration of the rate of anhydride formation with increasingly basic amines runs counter to what one would expect based on leaving group effects. However, favorable protonation of a more basic amide carbonyl could explain the amine substituent effects. The small value of ρ for both amine and anhydride substituents is also consistent with an early transition state with minimal charge separation.

Conclusions

Amic acids undergo a redistribution reaction at ambient conditions. Analysis of substituent effects rules out direct attack of free amine on amide carbonyl as the major redistribution mechanism. A mechanism consistent with the data is cyclization of the amic acid to form anhydride followed by condensation of the anhydride with a different amine. Anhydride formation from amic acid is accelerated

by electron-donating substituents on either the amine or anhydride portions of the amic acid. A rate-determining step consistent with the evidence is protonation of the amide carbonyl followed by intramolecular attack of the acid group.

The solvent for the amic acid has a significant effect on the rate of anhydride formation. Polar solvents such as NMP retard the redistribution reaction perhaps either by stabilizing the amic acid through hydrogen bonding or by lowering the acid strength of the solution. Less polar solvents such as diglyme, which also has poorer hydrogen-bonding ability, accelerate the redistribution reaction. A polyether alcohol, ethyl carbitol, had a rate effect intermediate between NMP and diglyme.

The rate of anhydride formation depends on the amic acid concentration and can also be affected by added acid catalysts. Bases have a minimal effect on the reaction rate. The rate of anhydride formation is higher at higher concentrations of amic acid.

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Glossary

IPAN	1,3-isobenzofurandione, 5,5′-(1-methylethylidene)bis-
ODPA	1,3-isobenzofurandione, 5,5′-oxybis-
3FDA	1,3-isobenzofurandione, 5,5′-(1-phenyl-2,2,2-trifluoroethylidene)bis-
BTDA	1,3-isobenzofurandione, 5,5′-carbonylbis-
6FDA	1,3-isobenzofurandione, 5,5′-{2,2,2-trifluoro-1-(trifluoromethyl)ethylidene}bis-
ODA	benzenamine, 4,4′-oxybis-
BAA	benzenamine, 4,4′-(1-methylethylidene)bis-
BA3F	benzenamine, 4,4′-(1-phenyl-2,2,2-trifluoroethylidene)bis-1,2,4-
OBABTF	4,4′-oxybis(3-trifluoromethyl)benzeneamine)
BAAF	benzenamine, 4,4′-{2,2,2-trifluoro-1-(trifluoromethyl)ethylidene}bis-
APBP	benzenamine, 4,4′-{(1,1′-biphenyl)-4,4′-diylbis(oxy)}bis-
BAPP	benzenamine, 4,4′-{1-methylethylidenebis(4,1-phenyleneoxy)}bis-

References and Notes

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