Self-Regulating Polycondensations. III. NMR Analysis of Oligomers Derived from Terephthaloyl Chloride and p-Aminobenzhydrazide

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Self-Regulating Polycondensations. III.
NMR Analysis of Oligomers Derived from
Terephthaloyl Chloride
and p-Aminobenzhydrazide

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ABSTRACT

A novel method based on NMR for the characterization of
oligomers formed by the reaction of terephthaloyl chloride
with excess p-aminobenzhydrazide is presented. These
studies have provided significant insight to the "ordering
process" or "self-regulation" involved in corresponding
polymerization reactions.

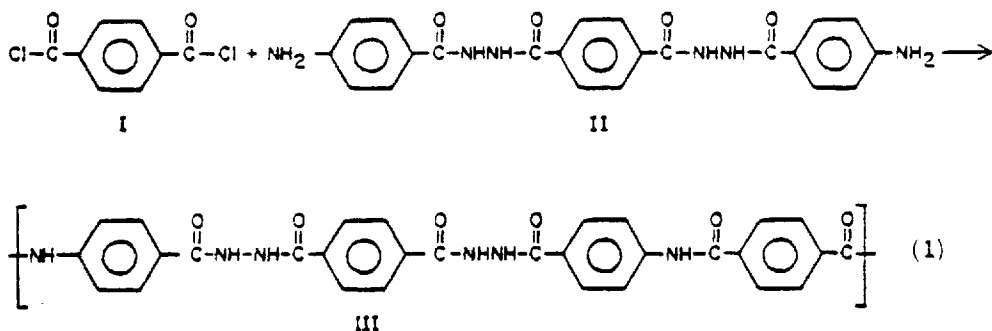## INTRODUCTION

The polyamide-hydrazide prepared from the reaction (Eq. 1) of
terephthaloyl chloride (I) and the symmetrical intermediate, II, in

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(1)

dimethylacetamide (DMAc) is wholly ordered in chemical structure. However, when I is reacted (Eq. 2) with the unsymmetrical monomer IV, it is possible to obtain a copolymer of only "limited order" [1], polyamide-hydrazide V, in which the moiety derived from IV can appear in the polymer chain in either a head-to-head or head-to-tail fashion. Because the hydrazide group of IV is more reactive

(2)
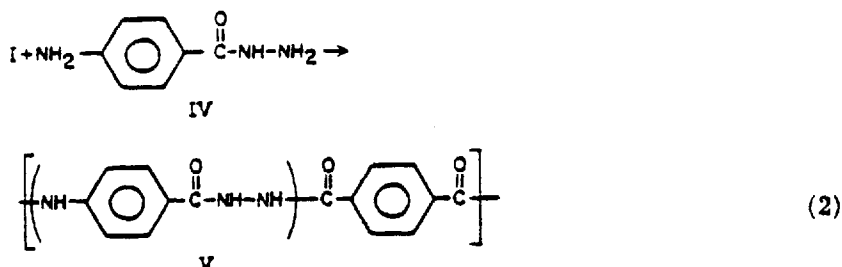
(more basic) than the aromatic amine group toward I, a self-regulating [2] mechanism does exist to a large degree; i.e., the intermediate II is formed in situ and reacts with I to form III. But for reasons previously given [3], the extent to which V approaches III in structural order depends upon the prevailing experimental conditions during polycondensation. Based on the evidence available [3], V might reasonably be referred to as a "partially ordered" copolymer.

The more common methods of characterizing polymers for order or sequence distribution are inadequate for determination of the structure of V because the structural differences between the sequences are only slight at best. Furthermore, electron

diffraction and x-ray methods contain the inherent difficulties of
relating crystallinity differences to differences in chemical order.
The problem is further complicated by the fact that physical order
or crystallinity can exist when small degrees of chemical "disorder"
exist.

A method based on nuclear magnetic resonance spectroscopy
(NMR) for studying the chemical compositions of oligomers formed
by a slow addition of I to a solution of IV has provided insight to
the degree of chemical "ordering" during the polymerization
process. Consequently, a qualitative estimate of the relative
degree of chemical order in a resultant polymer has been made
possible by this NMR analysis [3].

DISCUSSION AND RESULTS
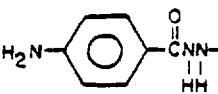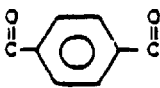
NMR Method—General

The polyamide-hydrazide derived from the stoichiometric
addition of solid terephthaloyl chloride to a solution of p-amino-
benzhydrazide, IV, in a one-step reaction is composed of the
following three structural sequences:
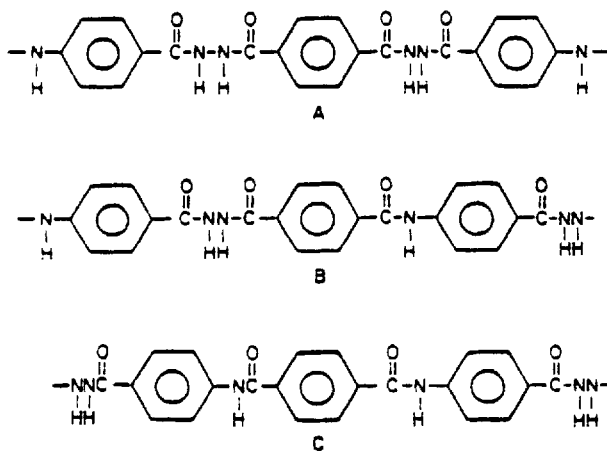
Unfortunately, the chemical shifts of the C—H or NH protons in the
NMR spectrum of 60 MHz of the polymer containing the above sequences

are such that delineating differences cannot be found. Distinct differences in proton chemical shifts are observed, however, for the unreacted aminobenzhydrazide, and both the "mono-" and the "di-" reacted species; the following structural units are expected in a mixture of partially reacted aminobenzhydrazides:

(1) H_2N—⟨◯⟩—$\overset{\overset{O}{\|}}{C}NN$—   hydrazide group reacted only

(2) —$\overset{}{\underset{H}{N}}$—⟨◯⟩—$\overset{\overset{O}{\|}}{C}NNH_2$ amine group reacted only

(3) —$\overset{}{\underset{H}{N}}$—⟨◯⟩—$\overset{\overset{O}{\|}}{C}NN$—   amine group and hydrazide group reacted

(4) H_2N—⟨◯⟩—$\overset{\overset{O}{\|}}{C}NHNH_2$ unreacted aminobenzhydrazide

(5) $\overset{\overset{O}{\|}}{C}$—⟨◯⟩—$\overset{\overset{O}{\|}}{C}$ moiety from reacted terephthaloyl chloride

The NH protons from the above units are subject to chemical exchange and do not represent a reliable source for molecular structure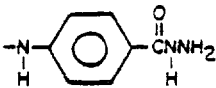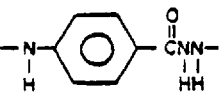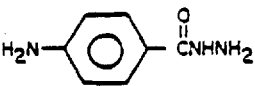 identification. The ring protons of the aromatic units, although not involved chemically, possess chemical shifts that are sensitive to the immediate structural environments. In addition the NMR spectra of the various ring protons are composed of familiar A_4 and A_2B_2 spin systems which greatly simplify the spectral interpretation [4]. Since the line spacings and intensities of the peaks in each half of an A_2B_2 system are identical, it is necessary to have only one-half of an A_2B_2 system isolated for intensity measurements.

The molecular units (1) and (4) above have A_2B_2 systems in which one-half is isolated, thus the total intensity can be measured and compared with that of the entire spectrum of aromatic signals. In each case the protons ortho to the amino groups have relatively high field chemical shifts which are displayed apart from the other aromatic signals. By measuring the areas of these signals and comparing them with the remaining aromatic proton signal areas, one can calculate either the percent unreacted amine groups or percent reacted hydrazide groups. This is done in the following manner. When "a" moles of the aminobenzhydrazide are reacted with "b" moles of the diacyl chloride such that $a > b$ and the diacyl chloride is allowed to react completely, the solution will consist of monomers, dimers, and oligomers composed of the structural units outlined previously. If $x_1 \ldots x_4$ denotes the mole fractions of species $1 \ldots 4$, respectively, then $x_1 a \ldots x_4 a$ will describe the number of moles of aminobenzhydrazide which have reacted accordingly. The aromatic portion of the NMR spectrum can be divided into two parts, X and Y, which have signal areas represented by the following equations:

$$\text{area } X = 2kx_1a + 2kx_4a$$

$$\text{area } Y = 4kb + 2kx_1a + 2kx_4a + 4kx_2a + 4kx_3a$$

Area X contains NMR signals arising from the ring protons ortho to the amino group only. Area Y contains the NMR signals which originate from all of the remaining types of aromatic protons.

Figure 1 gives a typical NMR spectrum of the reaction mixture with assignments of X and Y. It was frequently necessary to add a few drops of trifluoroacetic acid to the sample in order to remove any complicating overlap between the aromatic signals and $-NH_2$ signals. The mole fraction of unreacted amine groups is given by

$$(x_1 + x_4) = \frac{2X}{X + Y}\left(1 + \frac{b}{a}\right)$$

while mole fraction of reacted amine groups is defined as

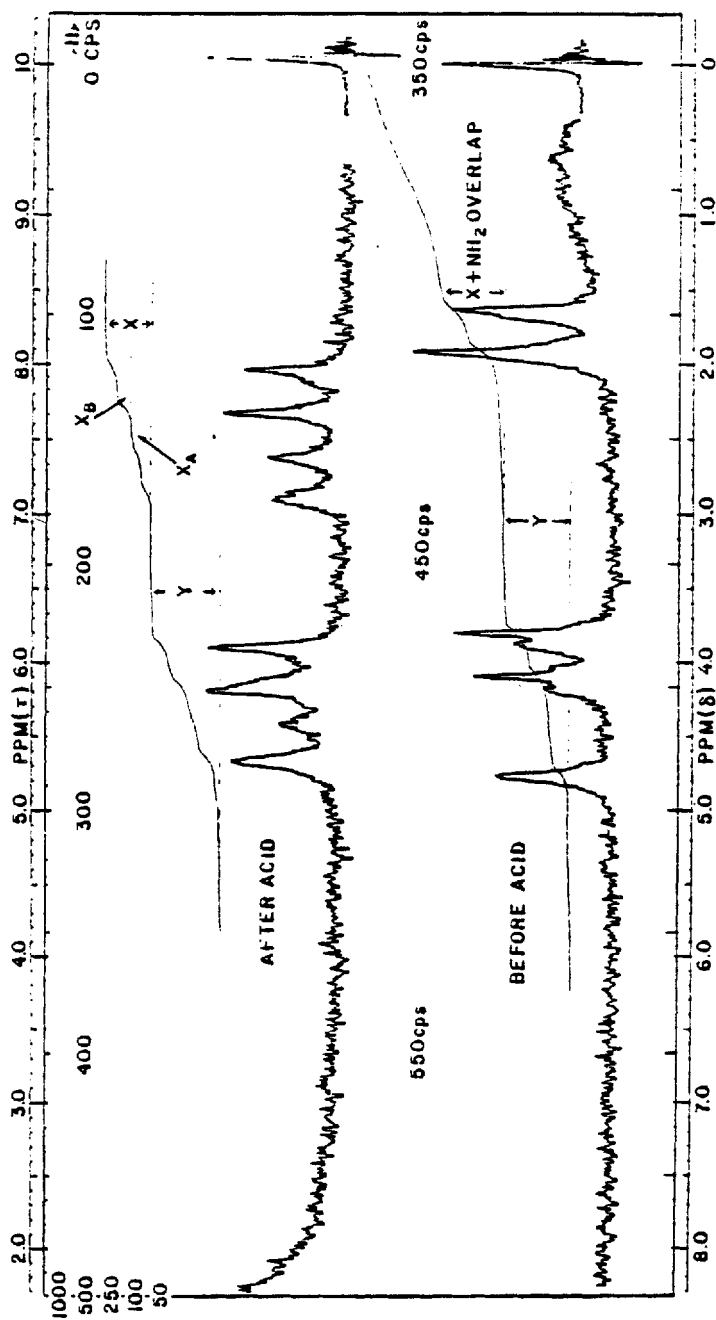$$(x_2 + x_3) = \frac{Y - X}{X + Y}\left(1 + \frac{b}{a}\right) - \frac{b}{a}$$

FIG. 1. NMR spectra of a typical reaction mixture of terephthaloyl chloride and p-aminobenz-hydrazide (b/a = 2).

The NMR area measurements were made with the A-60 integrator and results were obtained from an average of at least 5-10 scans. In Table 1 are the integrals for a run, with duplicates, and the results from a typical experimental run.

TABLE 1. NMR Areas and Calculated Results for a Typical Experiment: The Reaction of Dimethylacetamide Solutions of p-Aminobenzhydrazide (IV) and Terephthaloyl Chloride (I)[a]

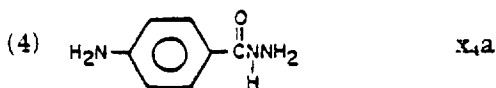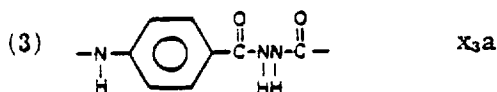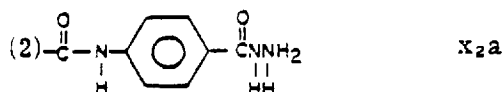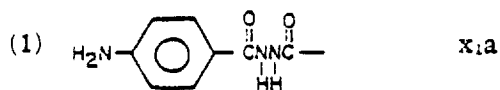| b a	NMR areas (average)		$x_1 + x_4$	$x_2 + x_3$
	X^b	Y^b		
0.10	19_0	23_5	0.98	0.02
0.15	25_5	36_5	0.95	0.05
0.20	11_5	17_5	0.95	0.05
0.20	11_0	17_5	0.93	0.07
0.25	13_0	22_0	0.93	0.07
0.30	24_0	48_5	0.86	0.14
0.39	13_0	36_0	0.74	0.26
0.39	10_0	27_0	0.75	0.25
0.50	16_0	67_0	0.58	0.42

[a] b/a = molar ratio of I to IV: $x_1 \ldots x_4$ = mole fractions of species 1...4.
[b] See Fig. 1.

NMR Analysis—Detailed

The determination of percent reacted or unreacted amine groups in the diacyl chloride-amine reaction mixtures by NMR is quite straightforward. The NMR technique is utilized to its best advantage since only differences in relatively large signal areas are

necessary. However, it is possible through a more tedious analysis to determine the concentration of each of the types of p-aminobenz-hydrazide entities in solution, i.e.,

(1) H_2N—⟨O⟩— C N N C — x_1a
                    ‖ ‖ ‖
                    O O
                    H H

(2) O=C—N—⟨O⟩— C N N H_2 x_2a
        ‖   ‖
                        H H

(3) —N—⟨O⟩— C-N N-C — x_3a
      H   ‖   ‖
              O H H O

(4) H_2N—⟨O⟩— C N N H_2 x_4a
   ‖
                  O H

The reaction between p-aminobenzhydrazide (IV) and terephthaloyl chloride (I) gives, in addition to the adducts (1), (2), and (3) above, a quantity of HCl which is fixed by the b/a ratio. For b/a ratios less than 1, the liberated HCl is neutralized by the excess amines and a state of equilibrium exists between HCl adducts and the free amine groups. The distribution of HCl among the various basic sites will be affected by the relative basicities of the amine groups. This distribution affects the reactions between acyl chloride groups and the various amine groups substantially as discussed earlier [3]. It also significantly alters the appearance or characteristics of the NMR spectra of the reaction mixtures. An amine exchange signal appears at a position defined by the acid concentration and fre-quently overlaps with one or more of the aromatic signals. An addition of trace amounts of trifluoroacetic acid to the NMR sample can remove any complicating overlap by shifting the exchange signal to a lower field value (Fig. 1). A second effect noted was that the addition of acid not only shifted the NH exchange signal but also the aromatic signals. Such a result indicates that the shifting aromatic signals (with addition of acid) represent averages as well, i.e., the aromatic proton finds itself in between an environment

with a protonated NH_2 unit and one with an unprotonated NH_2 unit
during the lifetime of the spectroscopic experiment. The position
of the signal is defined by the population distribution between pro-
tonated and unprotonated sites, i.e.,

$$W_{obs} = pW_{protonated} + (1 - p)W_{unprotonated}$$

($W_{protonated}$ is the chemical shift of the aromatic protons in the
protonated environment, p is the percent protonated molecules, and
$W_{unprotonated}$ is the chemical shift of the aromatic proton in the
absence of protonation [5].) Chemical exchange among active
hydrogen atoms is not unusual behavior and is frequently encountered
in NMR experiments. However, it does appear unusual for the high
field halves of the A_2B_2 systems which appear equivalent and
attributed to species (1) and (4) to shift to lower field positions
by different amounts with the addition of acid. The two distinct
but similar halves of the originally overlapping A_2B_2 systems
have now been separated for quantitative measurements.

The extent of separation of the composite high field A_2B_2
systems was related to the acid concentration. For b/a ratios
greater than 0.25, evidence for incipient separation was present
in the form of a shoulder without the addition of acid. For b/a
ratios of 0.4-0.5, the separation was distinct and further addition
of acid was unnecessary. This behavior was confirmed through
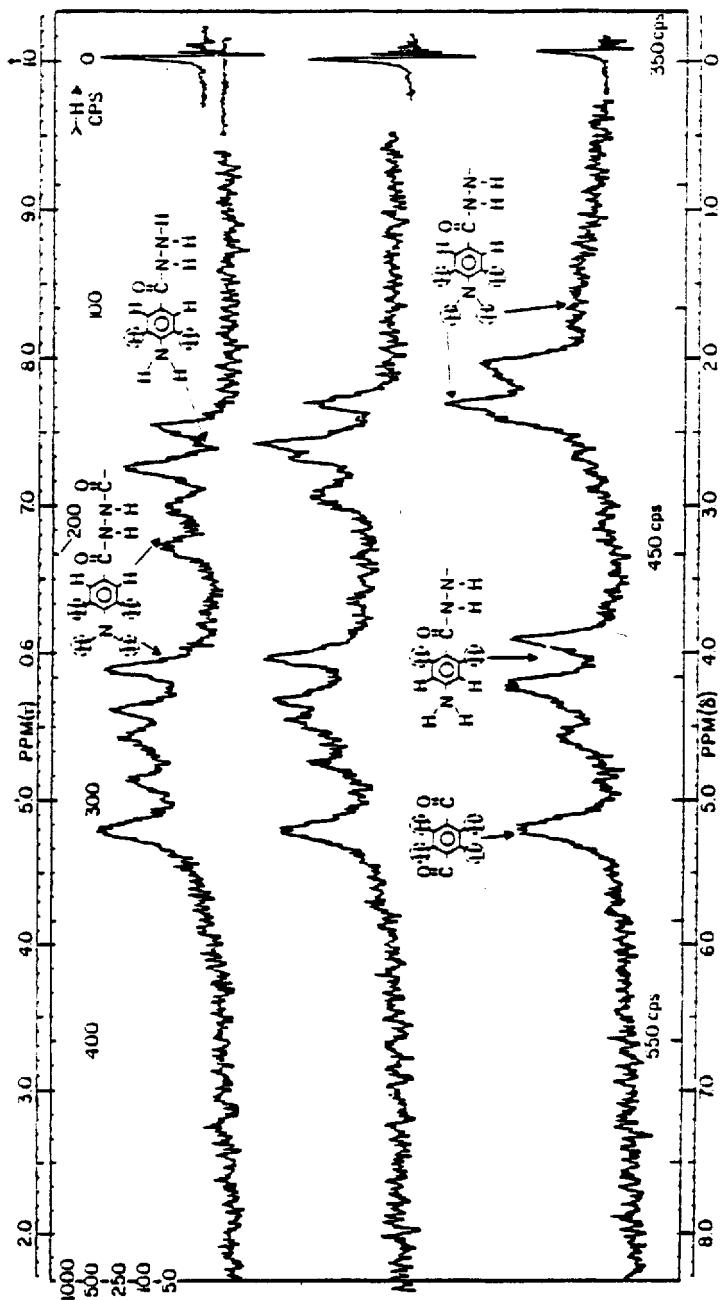examination of a model system:
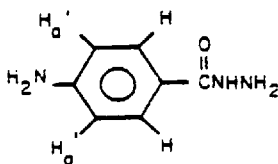
and
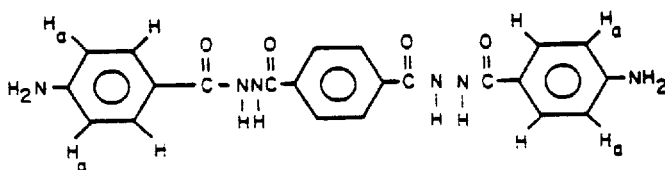
FIG. 2. NMR spectra of a mixture of p-aminobenzohydrazide (IV) and symmetrical diamine II formed from terephthaloyl chloride and IV.

The chemical shifts of the H_a and H_a' were nearly identical prior to the addition of acid. On addition of acid, the H_a signals moved to lower field values at a faster rate than did the H_a'. If sufficient amounts of acid were added, they later merged again at a lower field value. The NMR spectra from this experiment are reproduced in Fig. 2. The ratio of signal areas of the H_a to H_a' proton in the NMR experiment were observed to be 0.94. The calculated ratio based on the known molar concentrations was 0.96. (The 0.94 result was obtained from an average of 10 NMR integrals.)

This unexpected result of achieving separation of the NMR signals from the two types of amine compounds made it possible to calculate x_1 and x_4 independently. The H_a and H_a' signal areas could be measured independently and used in the following equations for the calculation of x_1 and x_4:

$$x_1 = \frac{2x_A}{X + Y} \left(1 + \frac{b}{a}\right)$$

$$x_4 = \frac{2x_B}{X + Y} \left(1 + \frac{b}{a}\right)$$

where x_A = signal area of H_a and x_B = signal area of H_a'. Also, since complete reaction of the diacyl chloride molecules is assumed:

$$2b = x_1a + x_2a + 2x_3a$$

then

$$x_3 = x_4 - 1 + \frac{2b}{a}$$

and the concentrations of all the p-aminobenzhydrazide entities could be determined.

The effects reaction conditions have on mole fractions x_1, x_2, x_3, and x_4 are given in Table 2. The minimum value expected for x_4 is $1 - 2(b/a)$; however, the values obtained for x_4 were sometimes less than the predicted minima. These results were

TABLE 2. The Effects of Reaction Conditions on Intermediate Species[a]

b/a	x_1	x_2	x_3	x_4
Reaction of solid terephthaloyl chloride(I) with a dimethylacetamide solution of p-aminobenzhydrazide(IV)[b]				
0.30	0.21	0.00	0.22	0.62
0.40	0.06	0.00	0.42	0.62
Reaction of a solution of I in tetrahydrofuran (THF) with a solution of IV in dimethylacetamide				
0.10	0.33	0.00	0.00	0.67
0.20	0.47	0.03	0.00	0.50
0.25	0.45	0.04	0.00	0.51
0.25	0.52	0.01	0.00	0.48
0.30	0.54	0.09	0.00	0.37
0.40	0.40	0.14	0.13	0.33
0.50	0.37	0.08	0.28	0.28
Reaction of solid I with a solution of IV in dimethylacetamide/5% LiCl				
0.10	0.15	0.00	0.03	0.83
0.15	0.21	0.00	0.05	0.75
0.20	0.28	0.00	0.06	0.66
0.25	0.28	0.00	0.14	0.64
0.30	0.35	0.00	0.11	0.51
0.40	0.39	0.00	0.23	0.43
0.50	0.42	0.00	0.32	0.32
Reaction of dimethylacetamide solutions of I and IV				
0.10	0.21	0.02	0.00	0.78
0.15	0.24	0.05	0.00	0.70
0.20	0.54	0.05	0.00	0.41
0.20	0.55	0.07	0.00	0.38
0.25	0.43	0.07	0.00	0.50
0.30	0.32	0.02	0.12	0.52
0.39	0.38	0.09	0.16	0.38
0.50	0.23	0.08	0.34	0.34

(continued)

TABLE 2. The Effects of Reaction Conditions on Intermediate Species (Continued)

| b/a	x_1	x_2	x_3	x_4
Reaction of solid I with a solution of IV in N-methylpyrrolidone				
0.10	0.19	0.03	0.00	0.78
0.20	0.31	0.04	0.02	0.62
0.25	0.29	0.00	0.14	0.64
0.30	0.33	0.06	0.11	0.51
0.40	0.29	0.11	0.20	0.40
0.50	0.23	0.09	0.34	0.34
Reaction of solid I with a solution of IV in hexamethylphosphoric triamide				
0.15	0.19	0.01	0.05	0.75
0.25	0.27	0.00	0.13	0.63
0.40	0.30	0.00	0.30	0.50
0.50	0.26	0.00	0.45	0.45

[a]b/a = molar ratio of I to IV; $x_1 \ldots x_4$ = mole fractions of species 1...4.

[b]Separation not achieved on others or too low to detect.

reproducible. There is no readily apparent explanation unless the technique is rather insensitive. The procedure for obtaining the sum $(x_1 + x_4)$ and $(x_2 + x_3)$ did not rely on the small separations and intensity differences the $x_1 \ldots x_4$ procedure required. Thus the precision and accuracy of the former procedure is undoubtedly better, yet the values of $x_1 \ldots x_4$ obtained were certainly revealing as indicators of the effects of reaction conditions. For example, an increase in x_3 suggests an increase in diffusion control of the reaction.

The situation that resulted in the separation of the high field halves of composite A_2B_2 systems into two similar parts as a result of competitive exchange reactions deserves further comment. The populations of protonated and unprotonated species for the aminobenzhydrazide (4) and its hydrazide derivatives (1) under the same acid concentration are certainly different. This observation likely reflects a change in basicity of the $-NH_2$ unit when

the hydrazide group is protonated. Such a possibility explains the
dependence of the incipient separation on acid concentration. At
this point the competing equilibria can be reduced to
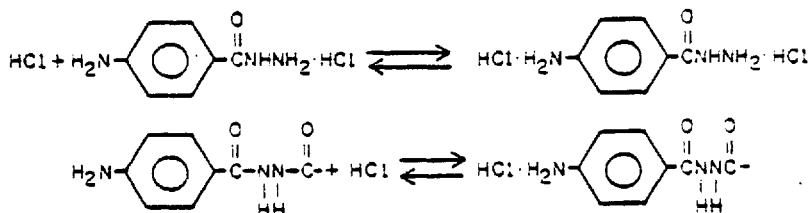
The hydrazide salt may influence the $-NH_2$ group basicity to a
greater extent than the hydrazide derivative. The observed result
is a higher percentage of protonated species among the latter under
competitive conditions, thus giving the different averages necessary
for the NMR separation.

EXPERIMENTAL

The detailed preparation of the samples used in this study were
reported previously [3].

ACKNOWLEDGMENTS

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