# Use of Fourier Transform Infrared Spectroscopy to Follow the Heterocumulene Aided Thermal Dehydration of Phthalic and Naphthalic Acids

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Fourier transform infrared (FT-IR) spectroscopy has been successfully employed to follow the formation of phthalic anhydride and 1,8naphthalic anhydride on heating their corresponding acids. The effects of three heterocumulenes, cyanamide, dicyandiamide, and sodium cyanate, on the temperature of formation of the anhydrides were also investigated using this method. It was found that the carbodiimides cyanamide and dicyandiamide dramatically lowered the temperature at which thermal dehydration of the acid led to anhydride formation. It was noted that cyanamide had a stronger catalytic effect than dicyandiamide, presumably due to the electron-withdrawing effect of the amidine group. Sodium cyanate was also found to promote the thermal dehydration of the acids to form the corresponding anhydrides. Under more severe conditions, phthalic acid anhydride formed is seen to react further, leading to the formation of phthalimide. The discrepancy between the products obtained with cyanamide and sodium cyanate leads to the conclusion that, unlike earlier claims, imide formation is not due to the reaction of the anhydride with the urea formed but with sodium cyanate itself. However, only the phthalic anhydride five-membered ring system is sufficiently reactive towards the CNO<sup>-</sup> nucleophile to form the imide; the six-membered 1,8-naphthalic anhydride system does not react in this way. Index Headings: Fourier transform infrared spectroscopy; FT-IR spectroscopy; Dehydration of carboxylic acids; Carboxylic acid; Carboxylic acid anhydride; Thermal dehydration; Carbodiimide aided dehydration.

#### INTRODUCTION

Carboxylic acid anhydrides are highly valuable as acylating agents, since they can undergo a wide range of nucleophilic addition reactions under relatively mild conditions. Their formation reactions are thus of high interest, and although many routes for their synthesis are known, new catalytic pathways can prove invaluable for specific applications. It is widely known that carboxylic acids can be thermally dehydrated to yield their corresponding anhydrides. This is particularly true for di-acids that form five- and six-membered ring anhydrides, which are thermodynamically favored due to the low ring strain. In addition, the elimination of water molecules provides a strong driving force for the reaction. Thus, cyclic anhydrides are relatively easily formed by hightemperature dehydration of the corresponding di-acid, while carboxylic acids not capable of forming cyclic anhydrides seldom undergo purely thermal dehydration.<sup>1</sup> During the course of a multi-step synthesis process, it was required that a cyclic anhydride should be formed from the corresponding di-acid. Since the temperature to achieve the above had to be relatively low (below 190 °C), due to the thermosensitive nature of other compounds present, a number of investigations were carried out. In order to facilitate the formation of both

cyclic and acyclic anhydrides, appropriate reagents are often added. Many have been described in the literature;<sup>2-12</sup> most add to the carboxylic acid group, forming an activated derivative of the starting acid. The activated acid derivative is then susceptible to attack by the weakly nucleophilic oxygen of a free acid molecule, resulting in the formation of the anhydride. A particular group of potential dehydrating agents are the heterocumulenes. In this paper three heterocumulene dehydrating agents, cyanamide, dicyandiamide, and sodium cyanate, have been studied. To compare the effectiveness of the above agents, anhydride formation upon thermal dehydration of the di-acids phthalic and 1,8-naphthalic acids was studied in the absence and in the presence of these agents. Fourier transform infrared (FT-IR) spectroscopy has been found by previous workers<sup>13–24</sup> to be useful for monitoring anhydride formation and was thus used in this case.

### **EXPERIMENTAL**

Materials. Phthalic acid (1,2-benzenedicarboxylic acid, 98%), cyanamide (99%), sodium cyanate (96%), and HCl (37%) were purchased from Aldrich Chemicals. Phthalic anhydride (1.2-benzenedicarboxylic anhydride, 99%), 1.8naphthalic anhydride (1,8-naphthalenedicarboxylic anhydride), and dicyandiamide (99%) were obtained from Avocado. NaOH (>97%) was provided by Fisher Scientific. 1,8-Naphthalic acid (1,8-naphthalenedicarboxylic acid) was obtained from the hydrolysis of the corresponding anhydride. 1,8-Naphthalic anhydride was suspended in 0.03 M NaOH solution. The temperature was then maintained at 50 °C for 5 hours, after which time 1,8-naphthalic anhydride had hydrolyzed to the water-soluble sodium di-carboxylate salt. The solution was subsequently filtered in order to remove any un-hydrolyzed anhydride. 1,8-Naphthalic acid was precipitated by adding dilute HCl, filtered under vacuum, then washed in dilute HCl. The purity of the sample obtained was monitored by FT-IR spectroscopy.

**Thermal Dehydration.** One gram (1.00 g) of carboxylic acid was ground in a pestle and mortar with an appropriate amount of dehydrating agent (1:1 molar ratio). Typically, 0.025 g of the mix was placed in aluminum foil and sealed. The sample was subsequently heated in a heat press (transfer press model BMSI.20, A. Adkins and Sons Ltd, Leicester, UK), the accuracy of the temperature being controlled via the use of a thermocouple (Electronic Thermometer type 1602, Comark Electronics Ltd, Sussex, UK).

**Fourier Transform Infrared Analysis.** Fourier transform infrared analysis was performed on a PerkinElmer Spectrum One Spectrometer (PerkinElmer Instruments, UK) using the PerkinElmer Diamond Golden Gate sampling attachment, which obtains attenuated total reflectance (ATR) spectra.

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FIG. 1. Anhydride formation upon thermal dehydration of phthalic acid.

Spectra were recorded at 4 cm<sup>-1</sup> resolution using 100 scans per spectrum, at a scan speed of 0.50 cm s<sup>-1</sup>. Data was collected and processed with Spectrum 5.0.1 software (PerkinElmer Instruments, UK). For some of the peaks of weakest intensity, and for those appearing as shoulders on other peaks, the second-derivative plot of the spectrum was used to accurately determine the wavelength of absorption.

**Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) was performed using a DSC 2010 (TA Instruments Ltd) under a nitrogen atmosphere, from room temperature. Typically, 5 to 10 mg of sample was heated at a rate of 10 °C min<sup>-1</sup> with a purge gas flow of 200 cm<sup>3</sup> min<sup>-1</sup>. Data was recorded using Thermal Advantage software (TA Instruments Ltd).

### **RESULTS AND DISCUSSION**

Anhydride Formation in the Absence of a Dehydrating Agent. The thermal dehydration of phthalic acid to form phthalic anhydride in the absence of any dehydrating agent, as illustrated in Fig. 1, was first considered.

The FT-IR spectra of phthalic acid and phthalic anhydride are presented in Fig. 2. The vibrational assignments of the bands observed are summarized in Table I. The antisymmetrical carbonyl stretch band for the acid, at 1662  $cm^{-1}$ , is of strong intensity and, as seen in Fig. 2, is in a region where the anhydride hardly absorbs. The monitoring of the decrease in intensity of this particular band can thus give clear information regarding the amount of phthalic acid present, while being relatively free of interference from the absorption bands of the anhydride that might eventually form. Similarly, the absorbance values of the symmetrical and anti-symmetrical carbonyl stretches of phthalic anhydride, at 1849 and 1755  $cm^{-1}$ , respectively, can be successfully used in order to assess the amount of phthalic anhydride present, regardless of the presence of phthalic acid.

Some of the spectra recorded, from the heating of phthalic acid alone for 30 seconds at various temperatures, are shown in Fig. 3. Anhydride formation, as seen by the appearance of peaks at 1849 and 1755 cm<sup>-1</sup>, is detected at and above 190 °C. The percentage of phthalic anhydride present at each temperature, listed in Table II, was calculated from the absorbance of the anti-symmetrical carbonyl stretch bands of phthalic acid and anhydride. For this purpose, the spectra of an equimolar sample of acid and anhydride were first recorded, and all subsequent anhydride percentages were calculated from the ratio of absorbance of the carbonyl anti-symmetrical stretch bands thus obtained (thereby accounting for the difference in intensity of the bands of acid and anhydride).

The FT-IR spectra of 1,8-naphthalic acid and anhydride are shown in Fig. 4. Vibrational assignment of the bands observed, summarized in Table III, have been extensively reported in the



Fig. 2. Infrared spectra of (A) phthalic acid and (B) anhydride. The carbonyl symmetrical and anti-symmetrical stretches are also labeled.

literature.<sup>26–29</sup> As for phthalic acid, anhydride formation can be assessed by monitoring the anhydride symmetrical and antisymmetrical carbonyl stretches at 1769 and 1734 cm<sup>-1</sup> and the acid carbonyl stretch at 1680 cm<sup>-1</sup>, free from interference from

TABLE I. Vibrational assignments of phthalic acid and anhydride.<sup>a</sup>

Phthalic acid		Phthalic anhydride		Assignment		
3064	w	3094	w	v(PhH)		
2961	w	3053	w	v(PhH)		
2862	s br			v(OH)		
2645	w			overtone and combination $v(C-OH)$ and $\delta(COH)$		
2519	w					
1978	vw	1985	vw	overtone and combination ω(PhH)		
1940	vw	1931	vw	(summation bands)		
1867	vw	1902	VW			
		1849	S	$v_s(C=0)$		
		1807	vw	overtone v(C–O)		
		1790	m	Fermi resonance splitting of $v_{as}(C=O)^a$ overtone and combination $\omega(PhH)$		
1782	vw					
		1755	vs	$v_{as}(C=O)$		
1662	S			$v_{as}(C=O)$		
		1650	VW			
1585	m	1599	m	$\delta(CCC)$ (quadrant stratch)		
1538	VW	1572	W	o(eee) (quadrant stretch)		
1496	W	1518	W	$\delta(CCC)$ (semicircle stratch)		
1455	W	1471	m	o(eee) (semicinene stretch)		
		1423	W			
1399	m			δ(C–O–H)		
		1384	W			
		1360	m	Earmi reconcise splitting of $\delta(CCC)^b$		
		1336	m	remin resonance spinning of 0(eeee)		
		1288	W			
1262	m			v(C-OH)		
		1257	VS	v(C–O)		
1211	m	1213	W	δ(CCC)		
1154	W	1170	m	δ(PhH)		
1140	W	1110	S	δ(PhH)		
1070	m	1072	W	δ(PhH)		
1005	W	1007	W	ω(PhH)		
974	W			ω(PhH)		
		904	S	v(C–O)		
894	m, br			$\omega_{oop}(OHO)$		
		888	VW	ω(PhH)		
830	W	839	m	ω(PhH)		
795	W	800	m	$\omega(C=O)$		

<sup>a</sup> All frequencies are given in cm<sup>-1</sup>. Relative intensities: s, strong; m, medium; w, weak; vw, very weak; vs, very strong; and br, broad. Vibrational modes: v, stretching;  $\delta$ , deformation (all kinds of); and  $\omega$ , wagging; subscripts: s, symmetrical; as, anti-symmetrical; and oop, out-of-plane.

<sup>b</sup> Assignment from Ref. 25.



Fig. 3. Selected infrared spectra of phthalic acid heated for 30 s at (A) 180 °C, (B) 190 °C, and (C) 200 °C. All conditions as described in the Experimental section. The carbonyl symmetrical and anti-symmetrical stretches are also labeled.

other bond vibrations. Significant amounts of 1,8-naphthalic anhydride are thus first observed to form upon dehydration of the acid after 30 seconds at 180 °C. Again, the percentages of anhydride present, listed in Table II, were calculated from the relative intensities of the acid and anhydride carbonyl stretch bands.

Differential scanning calorimetry was performed on 1,8naphthalic acid and phthalic acid and their corresponding anhydrides. The thermograms recorded are shown in Fig. 5. Also shown in Fig. 5 is the thermogram of the phthalic acid heated to 200 °C and then reheated. The thermogram of 1,8naphthalic acid shows two endothermic processes, the first one at 185 °C and the second at 275 °C. The enthalpy change that takes place at 275 °C can be attributed to the melting of the anhydride, as confirmed by the thermogram of 1,8-naphthalic anhydride produced independently. It is thus presumed that the endothermic process at 185 °C corresponds to the thermal dehydration of 1,8-naphthalic acid to form the corresponding anhydride. These results seem to be in good accordance with the temperatures at which anhydride formation was previously observed.

In the case of phthalic acid, interpretation of the thermogram is not as straight forward. While the anhydride is seen to melt at 135 °C and boil at 247 °C, the thermogram of phthalic acid shows an endothermic process taking place at 195 °C only. However, heating the acid to 200 °C and repeating the DSC process shows two important points: (1) weighing the sample revealed that considerable mass loss occurred during the first DSC process; (2) no enthalpy changes are observed. It may



Fig. 4. Infrared spectra of (A) 1,8-naphthalic acid and (B) 1,8-naphthalic anhydride. The carbonyl symmetrical and anti-symmetrical stretches are also labeled.

TABLE II. Percentage of anhydride formed through thermal dehydration of the corresponding acid.

Temperature	No dehydrating agent	Cyanamide as dehydrating agent	Dicyandiamide as dehydrating agent	ide Sodium cyanate ng as dehydrating agent				
Phthalic acid/anhydride								
90 °C		0%	0%					
100 °C	$^{\circ}C$ $0\%$ (8% <sup>a</sup> ) 0		0%					
110 °C		18%	0%	0%				
120 °C		36%	0%	22%				
130 °C		56%	98%	22%				
140 °C		85% <sup>b</sup>	94% <sup>b</sup>	24%				
150 °C	0%ь			20%				
160 °C	0% <sup>ь</sup>			0%				
170 °C	0% <sup>ь</sup>			0%				
180 °C	0% <sup>ь</sup>			0%				
190 °C	11% <sup>b</sup>							
200 °C	38% <sup>ь</sup>							
1,8-Naphthalic acid/anhydride								
90 °C		0%	0%	0%				
100 °C		0%	0%	0%				
110 °C		25%	0%	9%				
120 °C		42%	17%	16%				
130 °C	0%	86%	33%	31%				
140 °C	0%	100%	100%	35%				
150 °C	13%	100%	100%	37%				
160 °C	17%			44%				
170 °C	27%			53%				
180 °C	81%			89%				

<sup>a</sup> In the presence of hydrochloric acid.

<sup>b</sup> Percentages must be taken as approximations due to the volatile nature of phthalic anhydride at temperatures above 130 °C, which is likely to result in some anhydride being lost previous to analysis.

therefore be deduced that the endothermic process observed in the thermogram of phthalic acid corresponds to the thermal dehydration of the acid, leading to anhydride formation. The temperature is indeed in good accord with the temperature at which anhydride formation was first observed in the heating of phthalic acid in the heat press, as described above. Since this temperature is above the anhydride melting point, it is presumed that the small amount of anhydride thus formed is subsequently lost through vaporization, leading to the results observed in the thermogram produced in the second heating step.

**Cyanamide as a Dehydrating Agent.** Carbodiimides have been found previously to have a catalytic effect on the thermal dehydration of carboxylic acids.<sup>1,2,30–32</sup> Cyanamide in particular has been successfully employed in the past.<sup>13,33</sup> Its relative stability compared to other carbodiimides<sup>32</sup> makes cyanamide the dehydrating agent of choice. However, confusion still remains as to its reactivity, and the mechanism of its dehydrating effect with carboxylic acid to form anhydrides has not been fully established.<sup>34</sup>

Cyanamide is known to exist, as illustrated in Fig. 6, in equilibrium with its carbodiimide tautomer. The equilibrium constant for this particular tautomeric equilibrium has been calculated and found to be  $10^{19}$  at 300 K in the gas phase,<sup>32</sup> which accounts for the relative stability of cyanamide compared to other carbodiimides. However, it is thought that a very small amount of the carbodiimide tautomer is sufficient to catalyze reactions.

Carbodiimides have two centers of reactivity: the electrophilic central carbon atom and the nucleophilic terminal

TABLE III. Vibrational assignments of 1,8-naphthalic acid and anhydride.<sup>a</sup>

1,8-Naphthalic acid		1,8-Naphtalic anhydride		Assignment		
		3098	w	v(PhH) <sup>b,c</sup>		
3054	w	3075	W	v(PhH) <sup>b,c,d,e</sup>		
2964	w	3038	W	v(PhH) <sup>b,c,e</sup>		
2873	s, br			v(OH) <sup>d,e</sup>		
2695	W			overtone and combination $v(C-OH)$ and $\delta(COH)^d$		
2640	w					
2546	w					
2487	vw					
1954	VW	1983	W	overtone and combination ω(PhH) (summation bands)		
1907	vw	1938	W			
1858	vw	1897	W			
1778	vw	1799	W			
		1769	S	v <sub>s</sub> (C=O) <sup>d,e</sup>		
		1734	vs	$v_{as}(C=O)^{d,e}$		
1680	vs			v <sub>as</sub> (C=O) <sup>d,e</sup>		
1612	m	1629	W	v(CC) <sup>d,e</sup>		
1595	w					
1576	s	1579	Μ	v(CC) <sup>b,e</sup>		
1509	m	1511	Μ	$v(CC)^{b,e}$		
		1477	vw			
1457	vw	1460	vw	v(CC) <sup>b</sup>		
1433	m	1438	Μ	δ(CCC) <sup>e</sup>		
1417	m	1406	Μ	ω(PhH) <sup>e</sup>		
1370	W	1385	W	$\delta_{ip}(PhH)^{b}$		
1357	w	1368	vw	v(CC) <sup>b</sup>		
1358	w	1355	W	v(CC) <sup>b,e</sup>		
1281	s	1301	S	ω(PhH) <sup>e</sup>		
1268	vw	1265	W	$\delta_{ip}(PhH)^b$		
		1231	Μ			
1213	vw	1214	Μ	$\delta_{ip}(PhH)^{b,e}$		
1200	m	1191	Μ	ω(PhH) <sup>e</sup>		
		1173	Μ	$v(C-O)^e$		
1156	m					
		1120	S	v(C–O) <sup>e</sup>		
1092	vw					
1077	w	1076	Μ	δ(CCC) <sup>e</sup>		
1020	W	1006	S	$\delta(CCC)^b$		

<sup>a</sup> All frequencies are given in cm<sup>-1</sup>. Relative intensities: s, strong; m, medium; w, weak; vw, very weak; vs, very strong; and br, broad. Vibrational modes: v, stretching;  $\delta$ , deformation (all kinds of); and  $\omega$ , wagging; subscripts: s, symmetrical; as, anti-symmetrical; and ip, in-plane.

<sup>b</sup> Assignment from Ref. 28.

<sup>c</sup> Assignment from Ref. 29.

<sup>d</sup> Assignment from Ref. 26.

<sup>e</sup> Assignment from Ref. 27.

nitrogen. It has been proposed that the driving force for most of the reactions involving the use of carbodiimides is the very powerful saturating ability of the C=N bond, joined to, in the case of dehydration, the very stable product.<sup>32</sup> In this instance, the suggested catalytic pathway involving cyanamide, as illustrated in Fig. 6, results in the formation of a urea.

The stability of aqueous solutions of cyanamide has aroused the interest of many workers.<sup>14,35–46</sup> However, its stability in crystalline form has been less extensively studied.<sup>47–50</sup> Golov et al.<sup>47</sup> reported the stabilizing effect of some acids and solvents when heating cyanamide. They reported times of polymerization, leading to both melamine and dicyandiamide formation, from 5 hours at 80 °C to just 12 minutes at 110 °C; Baughen,<sup>48</sup> however, indicates that cyanamide polymerizes when heated to 150 °C. Differential scanning calorimetry analysis performed in this study, and shown in Fig. 7, confirms cyanamide's stability over the temperature range required and under the short heating times employed; this thus indicates its suitability as a potential dehydrating agent. It must, however, be noted that the cyanamide sample used in this study is known to contain an acidic stabilizing agent. It is, however, expected that such an agent will not interfere with the dehydrating properties of cyanamide, due, in part, to its very low concentration.

Assignments of the FT-IR vibrational bands of cyanamide are summarized in Table IV. Since cyanamide residues show no vibrations in the region 1850 to 1650 cm<sup>-1</sup>, the clear identification of the carboxylic acid and eventual anhydride carbonyl stretch bands is possible.

When heating a sample of phthalic acid in the presence of cyanamide for 30 seconds at various temperatures, formation of phthalic anhydride, as determined by the presence of the carbonyl symmetrical and anti-symmetrical stretch bands at 1849 and 1755 cm<sup>-1</sup>, respectively, is evident at 110 °C and above (190 °C in the absence of dehydrating agent), thus confirming the catalytic dehydrating action of cyanamide leading to anhydride formation.

The reaction of carboxylic acids with carbodiimides, illustrated in Fig. 6, is believed to initially involve the protonation of the carbodiimide, followed by the subsequent attack of the acid anion to form the O-acylisourea derivative (Fig. 6, I). The latter may either rearrange to form the corresponding N-acylurea (Fig. 6, II), or may be further protonated, leading to a subsequent attack by a second carboxylate ion, resulting in the simultaneous formation of both the corresponding N'-substituted urea (Fig. 6, IV) and acid anhydride (Fig. 6, V). Which product is formed is known to depend on the nature of the reagents and the conditions employed.<sup>2,30,31</sup> The formation of N-acylurea (II) from the Oacylisourea (I) is thought to take place via a cyclic electronic displacement, leading to the migration of the acyl group from the oxygen to the nitrogen.<sup>2,31</sup> However, in the cases where the attachment of the second proton to form the intermediate form III overtakes the oxygen to nitrogen migration, the formation of the anhydride results.<sup>30</sup> Thus, the ease of cyclization and the nucleophilicity of the acid anion are predominant factors in dictating the nature of the final product.<sup>30,31,51,53</sup> The reaction of phthalic acid, for which the carboxyl groups are so placed as to facilitate intramolecular anhydride formation, has been reported to result, with a variety of carbodiimides, in anhydride formation solely.<sup>2,30</sup> Results presented here indeed confirm the formation of the anhydride, while no trace of N-acylurea (Fig. 6, II) can be detected.

It was found that addition of a small amount of hydrochloric acid to the phthalic acid-cyanamide mix resulted in the lowering of the temperature at which anhydride formation was first observed, as can be seen from the band intensities tabulated in Table II. This effect was not observed upon addition of a small amount of deionized water to the mix, thus refuting the possibility of increased reactivity, as indicated by the lower anhydride formation temperature, being linked to the presence of a greater amount of moisture in the mix. The increased acidity is expected to have an influence on steps where a proton is involved, i.e., in the steps leading to the formation of compounds I and III (Fig. 6), via the increase in concentration of the reactive protonated carbodiimide derivatives. Results presented here thus confirm that the protonated cyanamide species is indeed involved in the reaction mechanism.



Fig. 5. Thermograms of (A) 1,8-naphthalic acid, (B) 1,8-naphthalic anhydride, (C) phthalic anhydride, (D) phthalic acid, and (E) phthalic acid reheat. All conditions as described in the Experimental section.

The effects of cyanamide on the thermal dehydration of 1,8naphthalic di-carboxylic acid were also investigated. As for the case of phthalic acid, it was found that cyanamide did act as a dehydrating agent and lowered the temperature of anhydride formation; in this case, 1,8-naphthalic anhydride was detected to form significantly from 30 seconds at 130  $^{\circ}$ C (compared to 180  $^{\circ}$ C in the absence of cyanamide).

**Dicyandiamide as a Dehydrating Agent.** As for cyanamide, dicyandiamide is known to exist in two tautomeric forms, in equilibrium with each other.<sup>30</sup> The suggested



FIG. 6. Carbodiimide aided thermal dehydration of a di-carboxylic acid.



FIG. 7. Thermograms of (A) cyanamide, and (B) dicyandiamide. All conditions as described in the Experimental section.

dehydrating action of dicyandiamide, as illustrated in Fig. 6, is thus similar to that of cyanamide.

Differential scanning calorimetry analysis of dicyandiamide, shown in Fig. 8, confirms its stability over the temperature range required and thus refutes polymerization, which might have hindered its dehydrating action.

Vibrational assignments of the FT-IR bands are summarized in Table IV. Since dicyandiamide does not give rise to significant absorbance in the 1850 to  $1750 \text{ cm}^{-1}$  region, any acid anhydride bands can be clearly identified.

Upon heating a sample of phthalic acid in the presence of dicyandiamide for 30 seconds at various temperatures, formation of phthalic anhydride from dehydration of phthalic acid, as determined by the presence of the carbonyl symmetrical and anti-symmetrical stretch bands at 1849 and 1755 cm<sup>-1</sup>, respectively, is evident at and above 130 °C.

The temperature at which, in the presence of dicyandiamide, anhydride first forms (130  $^{\circ}$ C) is higher than that in the presence of cyanamide (110  $^{\circ}$ C). Presumably, this effect can be attributed to the difference in reactivity of the corresponding carbodiimides of both additives. Indeed, the presence of an

TABLE IV.	Vibrational	assignments	of cy	anamide	and	dicvand	liamide.	5
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Cyanamide		Dicyandiamide		Assignment
		3368	w	v(NH)
3318	S	3327	m	$v_{as}(NH_2)$
		3238	w	overtone $\delta(NH_2)$
3238	S	3138	8	$v_a(NH_2)$
3104	М			overtone $\delta(NH_2)$
2723	М			
2215	S	2202	s	
		2161	s	V(C=N)
		1862	w	overtone $v_s(N-C-N)$
1568	S	1627	s	$\delta(NH_2)$
		1583	m	
		1564	m	V(C=N)
		1501	s	$v_{as}(N-C-N)$
		1252	m	W(C NIL)
1136	W	1140	w	$V(C-INH_2)$
		1070	m	$v_{as}(C-N-C)$
		1005	w	$v(C-NH_2)$
		928	s	$v_{s}(N-C-N)$
864	Vw			$\omega(NH_2)$
		795	m	v(C-N-CN)
		735	m	
		720	m	$\omega(NH_2)$ and $\omega(NH)$
667	Vw	668	m	$\delta_{ip}(N-C=N)$
563	W	548	w	$\delta_{oop}(N-C=N)$

<sup>a</sup> All frequencies are given in cm<sup>-1</sup>. Relative intensitis: s, strong; m, medium; w, weak; and vw, very weak. Vibrational modes: v, stretching;  $\delta$ , deformation (all kinds of); and  $\omega$ , wagging; subscripts: s, symmetrical; as, anti-symmetrical; oop, out-of-plane; and ip, in-plane.

electron-withdrawing or -donating substituent on the carbodiimide results in a lesser or greater concentration of the active protonated forms.<sup>31,54</sup> Furthermore, the efficiency of the respective carbodiimides at aiding anhydride formation is dependent on the concentration of the protonated species. Therefore, the reactivity of the carbodiimides is linked to the electron density on the nitrogen atoms. It is assumed that, in the case of dicyandiamide, the dipole of the amidine group leads, due to its latent polarity, to its central carbon atom bearing a slight positive charge. This, in turn, leads, through inductive effects, to the amidine group being electron withdrawing. Hence, the electron density on the amidine substituted nitrogen of dicyandiamide is lower than that found on either nitrogens in cyanamide. As a result, it is presumed that dicyandiamide's amidine substituted nitrogen is less prone to protonate. It is interesting to note that cyanamide and dicyandiamide have similar pKa values (-0.6 for cyanamide<sup>55</sup> and -0.3 for dicyandiamide<sup>56</sup>). It is presumed that, due to the high equilibrium constant for tautomerization, the pKa values are those of the cyano tautomer rather than the carbodiimide tautomer. However, it suggests that the presence of the amidine substituent does not greatly influence the electron density on the cyano nitrogen. Thus, in their carbodiimide form, the pKa values of the primary imino group of cyanamide and dicyandiamide could also be expected to be similar. It would therefore be expected that both compounds should exhibit similar reactivity. Furthermore, in the case of dicyandiamide, the unsubstituted nitrogen would be expected to be less sterically hindered and more basic than that bearing the amidine group. It would thus be expected that this particular nitrogen would be involved in the formation of the reactive protonated carbodiimide derivative. Therefore, it would be



Fig. 8. Infrared spectra of (A) cyanamide and (B) dicyandiamide in the 3500 to  $1400 \text{ cm}^{-1}$  region.



FIG. 9. Representation of the nucleophilic attack of a carboxylate anion on the carbodiimide central carbon atom; the pi-orbitals are shown in order to illustrate charge delocalization and thus the stabilizing effect through pi-orbital conjugation in the carbodiimide molecule.

expected that both cyanamide and dicyandiamide should exhibit similar reactivity.

Mock et al.,<sup>54</sup> who studied the substituent effect in the addition of carboxylic acids to arylcarbodiimides, also observed that the carbodiimide reactivity was influenced by substituent effects. They found that mono-aryl-substituted carbodiimides bearing either indifferent or electron-donating substituents are more reactive than those possessing inductively electron-withdrawing substituents. They explained these findings in terms of stereoelectronic effects and orbital orientation. They suggested that, for strictly kinetic reasons, and so that the O-acylisourea may experience continuous pi bonding as the central carbon atom changes configuration from sp to sp<sup>2</sup> hybrid, approach of the nucleophile towards the protonated carbodiimide must be focused on the central carbon atom's p-orbital, which suffers extended conjugated overlap with the nitrogen substituents, as represented in Fig. 9. Others have also found that the substituents on the carbodiimides have important repercussions on the electron density localized on the carbodiimide moiety. Glaser et al.<sup>57,58</sup> found this was apparent when studying the dipole and quadrupole moments of carbodiimides. They found that for cyanamide itself (in the carbodiimide tautomeric form), the dipole and quadrupole moments were related to the N-H bond polarity. Thamassebi,<sup>60</sup> in his study of the substituent effects on the stability of carbodiimides, found that the substituents were able to stabilize or destabilize the carbodiimides through an electronic effect. Effectively, he found that substituents that have unsaturated bonds conjugated with the carbodiimide moiety can serve as pi acceptors and thus delocalize the carbodiimide pi-electron density. Others also confirmed through their findings delocalization of the electron density over the whole molecule.<sup>35,42</sup> The difference in reactivity between cyanamide and dicyandiamide observed here is presumably due to one of the following: (1) the amidine substituted nitrogen is the nitrogen atom from which, following protonation, the reactive species forms; in accordance with Mock et al.,<sup>54</sup> the amidine substituent on dicyandiamide can be alleged to be of stabilizing effect on the O-acylisourea formation, and this also implies that protonation must take place on the sterically hindered amidine substituted nitrogen; (2) the electron density on the unsubstituted nitrogen is affected by the inductive effect of the amidine substituents and thus this substitution has a deactivating effect. In either case, the ability of the amidine group to disperse charge through resonance forms leads to its having an electron-withdrawing effect, to which the observed difference in reactivity between cyanamide and dicyandiamide can be attributed. Due to the electron-withdrawing nature of the



Fig. 10. Tautomerism of the cyanate ion;  $(\mathbf{I})$  cyanate form;  $(\mathbf{II})$  isocyanate form.

amidine group of dicyandiamide, cyanamide more readily forms the reactive protonated species; therefore, cyanamide is subsequently found to be more reactive, and thus promotes anhydride formation at lower temperatures.

The same effect was observed when heating 1,8-naphthalic acid in the presence of dicyandiamide; in this particular case, significant anhydride formation was detected from 140 °C, compared to 130 °C in the presence of cyanamide and 180 °C in the absence of dehydrating agent.

**Sodium Cyanate as a Dehydrating Agent.** The reaction of carboxylic acids with isocyanates to form acid anhydrides, and the dehydrating properties of the aforementioned isocyanates leading to the formation of anhydrides otherwise difficult to prepare, was reported early on in the literature.<sup>60–62</sup> Isocyanates have also been proposed as heterocumulenes, which are more reactive than their carbodiimides counterparts.<sup>32</sup> They thus have the potential of being dehydrating agents of choice when considering the thermal formation of anhydrides from carboxylic acids.

Cyanates are known to isomerize readily to their isocyanate form, as illustrated in Fig. 10. It is presumed that the isocyanate tautomer, rather than the cyanate tautomer, is involved in reported cyanate reactions, due to its high reactivity. It must also be noted that, due to the instability of cyanic acid (and its tautomer isocyanic acid), the sodium salt was used in this study.

The isocyanate-aided dehydration of carboxylic acids to yield anhydrides, as illustrated in Fig. 11, is known to proceed through the addition of the isocyanate to the acid, forming a mixed anhydride (Fig. 11, I) of the carbamic and carboxylic acid. This derivative is then thought to disproportionate into two pure anhydrides, with the carbamic anhydride eliminating carbon dioxide to yield urea (Fig. 11, IV). Alternatively, carbon dioxide can be eliminated from the mixed anhydride, forming the corresponding amide (Fig. 11, II).<sup>61,62</sup>

Differential scanning calorimetry performed on sodium cyanate confirms its stability over the temperature range required. Furthermore, FT-IR analysis shows that no vibrations of sodium cyanate give rise to significant absorbance in the 1900 to 1600 cm<sup>-1</sup> range, thus allowing for the carbonyl symmetrical and anti-symmetrical stretches of the anhydride (1849 and 1755 cm<sup>-1</sup>, respectively) and the acid (1662 cm<sup>-1</sup>) to be clearly identified in the mix. Extensive assignments of cyanate vibrations have been published in the literature<sup>63–71</sup> and are thus not reiterated here.

Upon heating phthalic acid in the presence of sodium cyanate, anhydride formation is detected after 30 seconds at or above 120 °C (refer to Table II). However, the intensity values of the bands at 1849 and 1755 cm<sup>-1</sup> associated with the presence of phthalic anhydride are relatively weak, suggesting that only a small amount of anhydride is formed. Heating to 130, 140, and 150 °C (30 seconds) does not result in an increase in the intensity of those particular bands, thus suggesting that no further anhydride was formed. At higher temperatures (160 °C and above), the anhydride carbonyl stretch bands are seen to disappear altogether. This disappearance is associated with the appearance of bands notably at 1773



FIG. 11. Isocyanate-aided dehydration of a di-carboxylic acid.

and 1717 cm<sup>-1</sup>. It has been reported in the literature that, at higher temperatures, the anhydride previously formed may react with the resulting urea, yielding the amide.<sup>61</sup> Furthermore, the reaction of phthalic anhydride with urea, leading to the formation of phthalimide, is well documented in the literature.<sup>72-91</sup> The bands observed at 1773 and 1717 cm<sup>-1</sup> are thus presumably associated with vibrations of phthalimide (Fig. 12); the imide carbonyl symmetrical and anti-symmetrical stretches at 1773 and 1717 cm<sup>-1</sup>, respectively, are indeed in good accordance with vibrations reported in the literature.<sup>92</sup> It is, however, interesting to note that urea was also formed as part of the dehydration mechanism when using cyanamide as the dehydrating agent. However, no phthalimide can be detected under the conditions employed in that particular instance. It must therefore be presumed that phthalimide formation, as observed in the presence of sodium cyanate, results from a different mechanistic pathway than simple addition of urea to the anhydride previously formed, as proposed in the literature. This is also further supported by the fact that little phthalic anhydride is seen to form, yet significant conversion of the acid to phthalimide is observed from just 30 seconds at 160 °C. Therefore, phthalimide formation must result from one of the following: (1) dehydration of the amide II; (2) reaction of the anhydride formed with sodium cyanate itself; or (3) reaction of sodium cyanate or urea with the mixed anhydride intermediate.

Sodium cyanate assisted the thermal dehydration of 1,8naphthalic acid as expected. Anhydride formation was detected from 30 seconds at 110 °C (150 °C in the absence of a dehydrating agent), while no imide formation was observed. Six-membered ring anhydrides, such as 1,8-naphthalic anhydride, have been reported as being less reactive than their fivemembered ring counterparts, presumably due to the lower ring strain.<sup>93,94</sup> Therefore, the difference in reactivity between 1,8naphthalic and phthalic acids further confirms the involvement of the anhydride species in the formation of the cyclic imide. Presumably, the electron-rich nitrogen of the cyanate anion



Fig. 12. Proposed formation of phthalimide from carboxylic acid and isocyanate derivatives.

adds onto one of the anhydride's carboxyl carbon atoms, while, most probably in a concerted manner, the anhydride oxygen adds onto the electron-deficient cyanate central carbon atom. Oxygen to nitrogen migration then follows, associated with carbon dioxide elimination, resulting in the formation of phthalimide (Fig. 12).

# **CONCLUSION**

The heterocumulenes cyanamide and dicyandiamide have proven to be effective activating agents in lowering the temperature at which thermal carboxylic acid dehydration leads to cyclic anhydride formation. It was observed that cyanamide lowered anhydride formation temperature to a greater extent than dicyandiamide. It is presumed that this difference can be attributed to electronic effects by which the amidine group deactivates, through the inductive effect, and lowers the electron density on the nitrogen atom(s), changing the availability of the carbodiimide moiety to nucleophilic attack. However, the actual mechanistic implications are still unclear; two possible mechanisms have been presented, involving either of the carbodiimide nitrogen atoms.

Sodium cyanate was seen to have poor catalytic effects on phthalic acid under the conditions used. Presumably, its high reactivity leads to its adding onto the anhydride first formed, resulting in the formation of phthalimide. However, in the case of 1,8-naphthalic acid, for which the anhydride is less reactive due to the lower ring strain, no cyclic imide forms and sodium cyanate acts as an efficient dehydrating agent, leading to a decrease in the temperature at which thermal dehydration of the acid leads to anhydride formation.

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