



**Table I. Formation of Carbamates from CO<sub>2</sub>, Acetylene, and Secondary Amines<sup>a</sup>**

entry	secondary amine	products (isolated yield, %) <sup>b</sup>	
		2a (46)	3a (2)
1	pyrrolidine (1a)	2a (46)	3a (2)
2	piperidine (1b)	2b (34)	3b (4)
3	morpholine (1c)	2c (20)	not analyzed
4	diethylamine (1d)	2d (10)	3d (2)

<sup>a</sup> CH<sub>3</sub>CN (50 mL), RuCl<sub>3</sub>·3H<sub>2</sub>O (2 mmol), amine (100 mmol), acetylene (320 mmol), CO<sub>2</sub> (15 atm), 90 °C, 20 h. <sup>b</sup> Based on amines. The yield of 3 was determined by GLC analysis of the distillate of high boiling point which mainly consisted of 3. High molecular weight products were not analyzed.

ditions lead to the vinyl carbamates 2b, 2c, and 2d, respectively, with a small amount of derivatives 3 as shown in Table I.

Little of the unreacted amines were recovered and a substantial amount of polymeric products were obtained as residue in all the cases. This may be caused by the polymerizations of acetylene, the carbamate monomers, and/or some monomers formed by reactions of acetylene with amines.

Although the reaction conditions are not determined as optimum for each of the secondary amines, those of low steric hindrance and high basicity seem to be favorable for the formation of carbamates. Primary amines did not undergo this reaction.

The reaction mechanism may involve a nucleophilic attack of the ammonium carbamate to acetylene coordinated on ruthenium. 1-Methylene-2-propenyl carbamates are considered to be formed via vinylacetylene resulting from the in situ dimerization of acetylene catalyzed by RuCl<sub>3</sub>·3H<sub>2</sub>O. Vinylacetylene is known to react with carboxylic acids to give 1-methylene-2-propenyl carboxylates.<sup>7</sup>

This novel synthesis of simple vinyl carbamates presents the advantage over the multistep synthesis based on phosgene, to result in one step from the nontoxic reagent CO<sub>2</sub>.

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(7) Wertz, J. H. *J. Am. Chem. Soc.* 1935, 57, 204. Klebanski, A. L.; Chevuichalova, K. K. *Sint. Kauch.* 1935, 4, 5.

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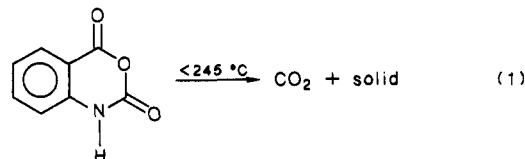
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### Decarboxylation of Isatoic Anhydride in the Crystalline State

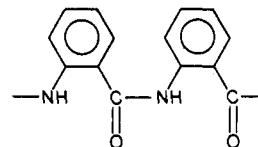
**Summary:** Isatoic anhydride when heated below its melting point decarboxylates to form a thermally stable polyamide. Gel permeation chromatography, kinetics, microscopy, dopant studies, etc. were carried out to characterize the reaction.

*Sir:* Sometimes one pursues a laboratory observation that is unrelated to any personal interest or experience of the past. Intuition, memory, analogy, and testimony play no role; mere curiosity motivates the decision to experiment further. Thus we were curious about an unexpected observation made during the course of our work: Isatoic anhydride decarboxylates when heated at temperatures below its melting point of 245 °C (eq 1). Crystals eject



CO<sub>2</sub>, often shattering in the process. What is the main product of this solid-state reaction? What are the mechanistic details? Is the solid-state reactivity<sup>1,2</sup> different from that in solution? These and other questions are addressed herein.<sup>3</sup>

**Product.** The product is a high-melting amorphous material. It is insoluble in all common organic solvents; appreciable solubility was noticed only in concentrated H<sub>2</sub>SO<sub>4</sub>. Elemental analyses correspond closely to that of isatoic anhydride minus CO<sub>2</sub>.<sup>4</sup> Gel permeation chromatography (column = micro Bondagel; solvent = hexafluoro-2-propanol)<sup>5</sup> gave a weight-average molecular weight *M<sub>w</sub>* equal to five times that of isatoic anhydride. These facts, plus IR data and flame tests,<sup>6</sup> all point strongly toward an oligomeric polyamide:



**Kinetics.** Reaction rates were monitored gravimetrically and by gas volume measurements; the two methods agree. Plots of "percent conversion vs. time" are sigmoidal, displaying an induction period prior to a steep rise in rate. Perhaps when a crystal defect appears at a reaction site, further reaction is facilitated at that location; the process is thereby autocatalytic. Curiously, the yield at "infinity" was always a few percent less than theoretical. A small amount of isatoic anhydride, which could be leached from the product by a DMF wash, resists decarboxylation. Rates of decarboxylation depend upon the purity of the isatoic anhydride. Thus, 4× recrystallized isatoic anhydride (EtOH + activated carbon) reacts 2-3 times more slowly than once recrystallized material. All work was carried out on highly purified isatoic anhydride. Reaction times are also sensitive to temperature. For example, about 90% of the isatoic anhydride was unreacted after 60 min at 210 °C, whereas only 12% remained after 60 min at 220 °C. Particle size is, on the other hand, not a factor.

(1) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* 1973, 6, 217.

(2) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* 1982, 82, 1.

(3) For full details, see: Kaiserman, H. B. "Part I. A Proton Transfer Trajectory Study Utilizing a System of Known Angularity. Part II. Characterization of Phenyl Phosphonate as a Micellar Counterion. Part III. The Solid State Thermal Decomposition of Isatoic Anhydride" Ph.D. Thesis, Emory University, Atlanta, 1984; pp 87-179.

(4) The elemental analysis of product was found to be 69.15% C, 4.09% H, and 11.38% N compared to values calculated for "isatoic anhydride minus CO<sub>2</sub>" of 70.58% C, 4.23% H, and 11.76% N.

(5) Performed by Modchrom, Inc., Mentor, OH.

(6) Urbanski, J.; Czerwinski, W.; Janicka, K.; Majewska, F.; Zowall, H. *Handbook of Analysis of Synthetic Polymers and Plastics*; Halsted: New York, 1977; pp 21-22.