02-8; (*E*,*S*)-**16c**, 103980-99-0; (*Z*,*S*)-**16c**, 103981-00-6; (*E*,*S*)-**17c**, 103981-01-7; **19**, 1192-04-7; **20**, 103981-04-0; **21**, 103981-10-8; (*S*)-**22**, 83972-44-5; (*R*)-**23**, 83972-40-1; (*S*)-**24**, 83972-41-2; (*S*)-**25**, 83972-42-3; (*S*)-**26**, 22148-86-3; (*S*)-**27**, 103981-11-9; (*S*)-**28**, 6033-23-4; (*S*)-**29**, 103981-12-0; (1*R*,2*S*,3*S*)-**30**, 88076-44-2; (1*S*,2*R*,3*R*)-**30**, 88155-41-3; **31** (isomer 1), 104033-86-5; **31** (isomer 2), 104111-04-8; **32**, 104111-03-7; (*E*,3*R*,4*S*)-**33**, 103981-13-1; (2*R*,3*R*)-**34**, 92999-39-8; (*E*,*R*)-**35**, 104068-39-5; (*Z*,*R*)-**35**, 104068-40-8; (*R*,*S*)-PPFA, 55700-44-2; (*S*)-Valphos, 74492-09-4; $PdCl_2$[1*R*,*S*)-PPFA], 76374-09-9; $PdCl_2$[(*R*,*S*)-BPPFA], 79723-33-4; $PdCl_2$[(*S*)-Valphos], 104013-74-3; $NiCl_2$[(*S*)-prophos], 104069-06-9; $NiCl_2$[(−)-DIOP], 41677-72-9; $NiCl_2$, 7718-54-9; (*Z*)-*β*-bromostyrene, 588-73-8; (1-chloroethyl)trichlorosilane, 7787-82-8; crotonaldehyde, 4170-30-3; (*S*)-1-phenyl-1-(trifluorosilyl)propane, 103980-93-4; (*S*)-1-phenyl-1-(trifluorosilyl)butane, 103980-94-5; 1-(trimethylsilyl)ethyl chloride, 7787-87-3; 1-(dimethylphenylsilyl)ethyl chloride, 17877-00-8; 1-(triethylsilyl)ethyl chloride, 18279-74-8; 1-(triphenylsilyl)ethyl chloride, 103981-16-4; 1-(trichlorosilyl)ethyl chloride, 7787-82-8; 1-(phenyldichlorosilyl)ethyl chloride, 18236-52-7; trimethylacetaldehyde, 630-19-3.

Supplementary Material Available: Preparation of 1-(trimethylsilyl)ethyl chloride, 1-(dimethylphenylsilyl)ethyl chloride, 1-(triethylsilyl)ethyl chloride, and 1-(triphenylsilyl)ethyl chloride (2 pages). Ordering information is given on any current masthead page.

Studies of Methyl Isocyanate Chemistry in the Bhopal Incident†

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Received February 19, 1986

Following the methyl isocyanate leak from Tank 610 at the Bhopal plant, the residual material from the tank was analyzed for its contents. Approximately 70% of the residue was comprised of three cyclic materials: 1,3,5-trimethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione or methyl isocyanate trimer (**5**), 1,3-dimethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione or dimethyl isocyanurate (**6**), and dihydro-1,3,5-trimethyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione or dihydrotrimethyltriazinedione (**7**). Minor quantities of methyl-substituted ureas, biurets, and amine hydrochlorides were also found. The composition of the residue was replicated very closely by the products obtained when a mixture of methyl isocyanate (84.4%), chloroform (12.0%), and water (3.6%) was heated at 225 °C under pressure in a stainless steel reactor. Experimental results are consistent with the view that under these conditions methyl isocyanate reacts initially with water to form 1,3-dimethylurea (**1**) and 1,3,5-trimethylbiuret (**2**). At temperatures between 100 °C and 225 °C these products decompose to reactive intermediates which further react exothermically to form the aforementioned cyclic materials, trimethylurea, and mono-, di-, and trimethylamine hydrochlorides. The decomposition of **1** and **2** is facilitated by the presence of chloroform and metals. Other experiments involving ^{13}C-enriched chloroform have given support to the proposed mechanisms for formation of **6** and **7**.

The investigation of the methyl isocyanate incident in Bhopal, India, required not only understanding what residues or products were formed during the reaction(s) which occurred in Tank 610 but also developing an understanding of the probable chemistry which could result in such a mixture. Thus, this aspect of the total investigation addressed the following issues: (1) What starting materials and reaction conditions could lead to product mixtures qualitatively and quantitatively like that found in Tank 610? (2) What are the likely mechanisms by which these starting materials lead to the observed product mixture?

This paper presents the results of these experiments directed to the aforementioned issues but does not address in any way the possible events which led to the incident.

Basic Methyl Isocyanate Chemistry. The electrophilic nature of isocyanates as indicated by their reactivity with a variety of nucleophilic reagents is well-recognized.[1-3] The most characteristic reactions of isocyanates, and methyl isocyanate (MIC) in particular, are those involving compounds with an active hydrogen. These include hydroxylated compounds such as water, alcohols, phenols, and oximes, and also amino compounds, among others.

Water reacts exothermically with MIC to form 1,3-dimethylurea (**1**) and 1,3,5-trimethylbiuret (**2**) with evolution of carbon dioxide. Excessive water leads to predominantely **1** and limited amounts of water (excess MIC) to **2**.

excess water

$$\underset{\text{MIC}}{CH_3N{=}C{=}O} + H_2O \rightarrow [CH_3NHCOOH] \rightarrow CH_3NH_2 + CO_2$$

$$CH_3NH_2 + CH_3N{=}C{=}O \rightarrow \underset{\mathbf{1}}{CH_3NHCONHCH_3}$$

excess MIC

$$\underset{\mathbf{1}}{CH_3NHCONHCH_3} + CH_3N{=}C{=}O \rightarrow \underset{\mathbf{2}}{CH_3NHCONCH_3CONHCH_3}$$

Methyl isocyanate is also known to react with itself under a variety of conditions to form cyclic dimer and trimer, as well as linear polymers, with cyclotrimerization being the most common.[1-3] Metal salts[4,5] and bases[6] are

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† Certain aspects of this work have appeared: D'Silva, T-D. J.; Lopes, A. *J. Chem. Soc., Chem. Commun.* **1986**, 795.

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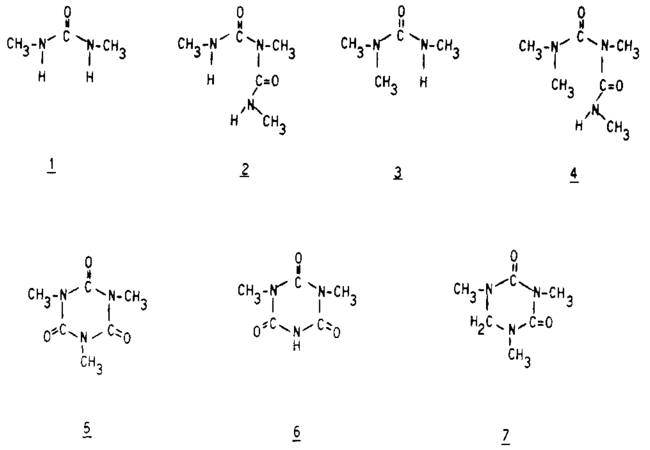

Figure 1. Structures of seven major MIC derived products and their levels analyzed in the residue from Tank 610: **1** (1–2%); **2** (4–8%); **3** (2–4%); **4** (3–6%); **5** (40–55%); **6** (13–20%); **7** (5–7%).

known to be excellent catalysts to effect trimerization. Although linear polymers of isocyanates are formed at very low temperatures,[7,8] methyl isocyanate does not normally polymerize under these conditions. Hexamethylenetetramine is claimed[9] to be a unique catalyst to effect the polymerization of MIC, even at ambient temperatures. Highly purified MIC, however, has been observed to polymerize.[10] Iron has been found to inhibit polymerization.[9]

Characterization of the Residue in MIC Tank 610. Core samples of the residue in the tank were obtained 17 days after the incident through a thermowell nozzle using a section of stainless steel pipe. The results of these analyses were made public in a report released by Union Carbide in March 1985.[11] Details of this analytical investigation will be published elsewhere.[11a]

About 70% of the residue is comprised of three cyclic materials: 1,3,5-trimethyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (MIC trimer) (**5**), 1,3-dimethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**6**), and dihydro-1,3,5-trimethyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione (**7**). 1,3,5-trimethylbiuret (**2**) and 1,1,3,5-tetramethylbiuret (**4**) ranged from 4% to 8%, with slightly higher concentrations in the upper zones of the core samples. Dimethylurea (**1**), trimethylurea (**3**), hydrochloride salts of mono-, di-, and trimethylamine, in varying proportions, about 1.5% chloroform, and less than 0.1% each of the dimer of methyl isocyanate and tetramethylurea were also detected. The residue also contained 800–3000 ppm of iron, 140–400 ppm of chromium, and 50–150 ppm of nickel. These concentration ranges approximate the ratio of these metals in type 304 stainless steel. Subsequent analyses of residues from other locations in the tank have also shown the same products in similar concentrations except for lesser amounts of the biurets.[11a] Structures of the significant components and the ranges of concentrations found in the residue from Tank 610 are shown in Figure 1.

Results

Nature of Starting Materials. The absence of linear polymers in the residue indicated that the reaction could not be characterized as a low temperature polymerization. The formation of **1** and **2**, although in small quantities, indicated the probable presence of water. The presence of chloride ion suggested the presence of a chlorine source; chloroform, as mentioned above, had been found in the tank residue. In addition to chloroform, phosgene and methylamine (the raw materials used in the manufacture of MIC), and other process intermediates and/or byproducts such as methylcarbamoyl chloride (MCC), dimethylallophanyl chloride (DMAC), and hydrogen chloride could also be contaminants. The low concentration (less than 40 ppm)[11a] of sodium ion in the residue precluded a role for sodium hydroxide or other sodium salts. The presence of substantial quantities of MIC trimer **5**, **6**,[12-16] and dione (**7**)[17] suggest a more complex situation.

Table I. Effect of Chlorinated Compounds on Reaction Products

	expt				
	1	2	3	4	5
time at 225 °C (h)	4	4	1	1	4
reagents (wt %)					
MIC	82.0	90.1	92.0	92.0	84.4
water	5.7		3.0	3.0	3.6
chloroform	12.3				12.0
hydrogen chloride		9.9[b]			
phosgene			5.0		
MCC				5.0	
total charge (g)	3.7	3.3	5.0	5.0	5.0
product composition[a] (area %)[c]					
3 (2–4)	1.1	3.2	0.6	2.3	0.5
1 (1–2)	6.9	60.4	1.6	3.8	1.9
5 (40–55)	53.5	30.4	86.8	70.0	59.6
6 (13–20)	18.2	1.9			16.9
2 (4–8)	0.2	0.9	8.8	20.8	0.4
7 (5–7)	6.7	0.2	0.5	0.4	4.7

[a] Only selected products shown. [b] Added as concentrated hydrochloric acid; therefore reagents consisted of 90.1 wt % MIC, 6.6 wt % water, and 3.3 wt % hydrogen chloride. [c] Product composition analyzed in the residue from Tank 610.[11]

A methodical evaluation (described below) of these various possible contaminants showed that chloroform and water were necessary ingredients to produce the major components in the residue and the others (HCl, MCC, phosgene, DMAC) apparently played no significant role.

Experiments 1–5 (Table I) show the composition of the reaction products when either chloroform, hydrogen chloride, phosgene, or methylcarbamoyl chloride (MCC) is added separately to MIC–water mixtures and heated to 225 °C for up to 4 h in type 316 stainless steel reactors. With 12% chloroform and 3.6% to 6% water in MIC (expt 1 and 5), approximately 17–18% of **6** and 5–7% of **7** (both produced in the desired range) were formed. (As described later, comparable product composition was obtained in the presence of 304 stainless steel.) When chloroform was replaced by aqueous hydrogen chloride (expt 2), or phosgene (expt 3), or MCC (expt 4), little or none of **6** and **7** were produced. Higher concentrations of phosgene and MCC and longer reaction times also failed to produce these materials in significant quantities.

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Table II. Effect of Chloroform and Water Concentrations on Reaction Products[a]

	expt				
	6	7	8	9	10
reagents (wt %)					
MIC	96.4	91.4	84.4	77.0	81.0
chloroform		5.0	12.0	18.0	12.0
water	3.6	3.6	3.6	5.0	7.0
total charge (g)	5.0	5.0	5.0	5.0	5.0
product composition (area %)[b]					
3 (2–4)		2.7	5.3	0.5	4.3
1 (1–2)	3.5	4.6	2.1	4.3	25.9
5 (40–55)	63.4	68.8	51.4	52.5	26.5
6 (13–20)		2.6	17.3	16.8	11.8
2 (4–8)	30.0	13.8	1.4	0.3	3.4
7 (5–7)	0.1	4.6	2.6	5.7	9.7

[a] Experimental Conditions: expts 6–8 at 25 °C for 17 h and 225 °C for 1 h; expts 9 and 10 at 225 °C for 4 h, and 1 h respectively. [b] Product composition analyzed in the residue from Tank 610.

Table III. Low Temperature Reaction Products

	expt					
	11	12	13	14	15[a]	16[a]
temperature (°C)	25	25	80	80	100	100
hold time (h)	17	17	4	4	48	48
reagents (wt. %)						
MIC	96.4	84.4	97.5	81.5	74.1	78.1
water	3.6	3.6	0.5	6.3	7.4	2.4
chloroform		12.0	2.0	12.2	18.5	19.5
total charge (g)	5.0	5.0	5.1	3.7	10.1	9.6
product composition (% area)						
MIC	59.6	50.3	91.9	2.6	0.8	0.9
3						
1	8.1	3.0	0.2	3.2	14.6	2.0
5			0.2	0.1	0.7	48.5
6						
2	32.1	37.8	5.6	92.1	69.3	41.2
7						0.9

[a] With 304 SS coupons in the reactor.

The small quantities of the dione **7** (0.2–0.5%) detected in experiments 2–4 are partly attributed to the trace amounts of chloroform present in commercial grade MIC.

Reaction Conditions. Having established that chloroform, water, and MIC are necessary to produce the desired materials in the core residue, additional experiments were conducted which examined the effects of varying the amounts of chloroform and water. The results are shown in Table II. The composition of the tank residue was closely approximated by the product mix obtained by heating mixtures of MIC with 12–18% chloroform and 3.6–5.0% water (expt 8 and 9). There was considerably less of **6** (expt 7) when the amount of chloroform was reduced to 5% and more **1** (expt 10) when the amount of water was increased to 7%.

The product profile of MIC–water–chloroform reactions carried out at 25 °C, 80 °C, and 100 °C is shown in Table III. It is noteworthy that when the mixture of MIC containing 0.5% water and 2% chloroform was heated at 80 °C (expt 13), less than 6% of MIC reacted to form mainly trimethylbiuret (**2**). Less than 1.0% of **7** was detected with the highest concentration of chloroform (expt 16), but none of **3** or **6** was formed at these temperatures.

The above experiments demonstrate that when mixtures of MIC and water are allowed to react either in the presence or absence of chloroform at ambient temperatures, only the expected water–MIC products **1** and **2** are formed, and the addition of chloroform has little effect on the reaction products up to 80 °C. At 100 °C (expt 16), significant trimerization was evident and little or none of **6** or **7** was formed, even when most of the MIC was consumed.

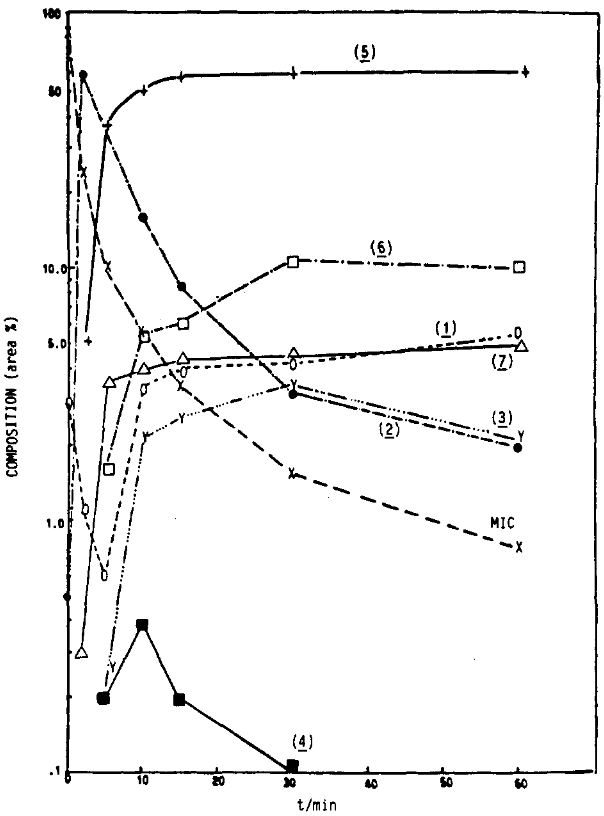


Figure 2. Kinetic profile of products from MIC (84.4%) + chloroform (12.0%) + water (3.6%) when heated at 225 °C in 316 stainless steel reactors.

Since the mix of products at 100 °C or below was totally different from that at 225 °C, the kinetics of the MIC–chloroform–water mixture was studied by placing appropriate mixtures of reactants in a series of reactor vessels, heating them at 225 °C, and removing and quickly cooling individual reactors at short intervals. The profiles of products at various reaction times are presented in Figures 2 and 3. There is rapid formation of **2** within 5 min with concomitant decrease in the concentration of MIC and continued gradual decrease of MIC and **2** on further heating. The disappearance of MIC and **2** coincides with the appearance of the three cyclic materials—MIC trimer **5**, **6**, and **7**, as well as **3**. The concentration of the cyclic materials changed very little on further heating. The thermally unstable **4** was also detected within 5 to 10 min but had virtually disappeared by 30 min.

The internal temperature profiles corresponding to the experiments in Figures 2 and 3 are plotted in Figures 4a and 4b, respectively. The significant and brief exotherm detected between 5 and 15 min also coincides with the appearance of the cyclic materials. The exotherm is more pronounced (Figure 4b) when 304 stainless steel (SS) coupons are introduced inside the 316 SS reactors. The 304 SS coupons which are slightly more susceptible to corrosion appear to have a slight rate-accelerating effect which is apparent during the first few minutes of heating. Whereas it takes 10 to 15 min for the three cyclic materials to be formed in 316 SS reactors without the 304 SS coupons (Figure 2), the same products are formed within 5 and 10 min with 304 SS coupons inserted in the reactors (Figure 3). It is noteworthy that in both series the composition of the product mix is similar after heating for 1 h.

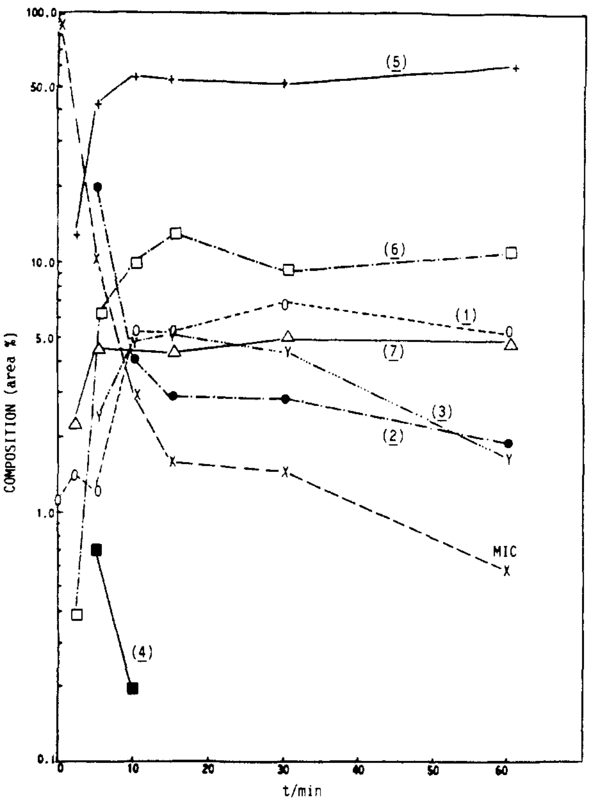


Figure 3. Kinetic profile of products from MIC (84.4%) + chloroform (12.0%) + water (3.6%) when heated at 225 °C in 316 stainless steel reactors with 304 SS coupons.

Thermal Stability of the Products. Because the kinetic studies at 225 °C indicated the formation and decomposition of some products, thermal stability studies were undertaken by heating synthetic mixtures of the products simulating the composition of the tank residue at 80 °C, 120 °C, and 225 °C. The results are shown in Table IV (see paragraph at the end of paper about supplementary material).

All the products are stable when heated to 80 °C for 4 h. Biuret **4** partially decomposed at 120 °C and both biurets **2** and **4** totally decomposed at 225 °C, while the cyclic materials **5**, **6**, and **7** changed very little at these temperatures. Small amounts of MIC were also detected at 80 °C and 120 °C, presumably produced by the decomposition of biurets.

It was also demonstrated in separate experiments that **2** was formed again at 120 °C and 80 °C but **4** was formed only at or below 80 °C when the urea precursors were exposed to MIC.

Discussion

Reaction Pathways and Mechanisms. The results of experiments carried out by heating mixtures of MIC–chloroform–water at various temperatures and reaction times and a study of the relative stabilities of the various products may be summarized as follows: 1. MIC reacts initially with water to form **1** and **2**. The amount of **2** formed depended on the concentration of water. 2. Chloroform is an essential ingredient necessary to produce the composition of the Tank 610 residue, but it is unreactive below 100 °C. 3. Minimal trimerization of MIC occurs below 100 °C. 4. When the three-component mixture is heated in appropriate ratios at 225 °C, the cyclic products—MIC trimer **5**, **6**, and **7**—are formed within 5 to 15 min and their concentrations remain relatively constant on further heating. 5. The formation of cyclic materials is accompanied by a brief exotherm which is also observed between 5 and 15 min of heating. 6. Trimethylurea (**3**) is also produced during this period but the concentrations of **1** and **2** are reduced sharply. 7. Biurets **2** and **4** can be formed again at or below 80 °C by heating **1** and **3**, respectively, with MIC.

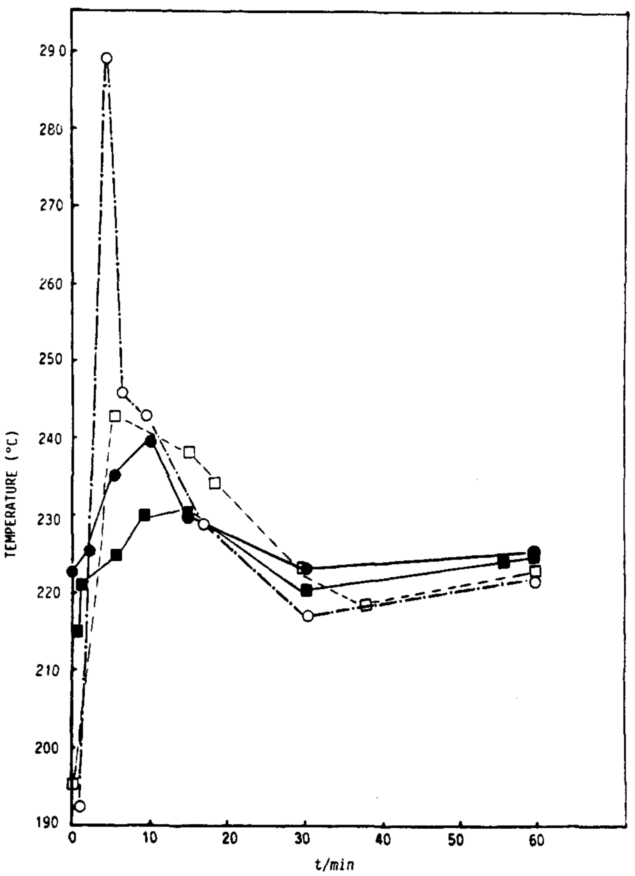


Figure 4. Reaction temperature profile (a) without 304 stainless steel coupons: (□) temperature inside the reactor, (■) temperature of oil bath; (b) with 304 SS coupons: (○) temperature inside the reactor, (●) temperature of oil bath.

These data suggest the following sequence of reactions occurring at various temperatures:

below 100 °C

$$\mathrm{MIC} + \mathrm{H_2O} \rightarrow \mathbf{1} + \mathrm{CO_2} \tag{1}$$

$$\mathrm{MIC} + \mathbf{1} \rightarrow \mathbf{2} \tag{2}$$

above 100 °C

$$\mathbf{2} + \mathrm{CHCl_3} \rightarrow \mathbf{1} + \mathbf{3} + \text{cyclic products } \mathbf{5}, \mathbf{6}, \mathbf{7} \tag{3}$$

cooling period (reaction with residual MIC, if any)

$$\mathrm{MIC} + \mathbf{1} \rightarrow \mathbf{2} \tag{4}$$

$$\mathrm{MIC} + \mathbf{3} \rightarrow \mathbf{4} \tag{5}$$

Reactions 1 and 2 are well-known—producing the normally expected products. Reactions 4 and 5 are the same or similar to reaction 2. Reaction 3, which is indicated to be occurring from the results of our experiments, has not been previously reported.

Trimethylbiuret–Chloroform Mixtures. To demonstrate the validity of eq 3, mixtures of trimethylbiuret (**2**) and chloroform (37.6:62.4) were heated in 316 SS reactors at 225 °C for 1 h with and without the introduction of 304 SS coupons in the reactors. The results of these experiments are profiled in Figures 5 and 6, respectively.

In both sets of experiments there was a rapid decrease in the concentration of **2**, and formation and subsequent decomposition of **1**, with concomitant formation of MIC

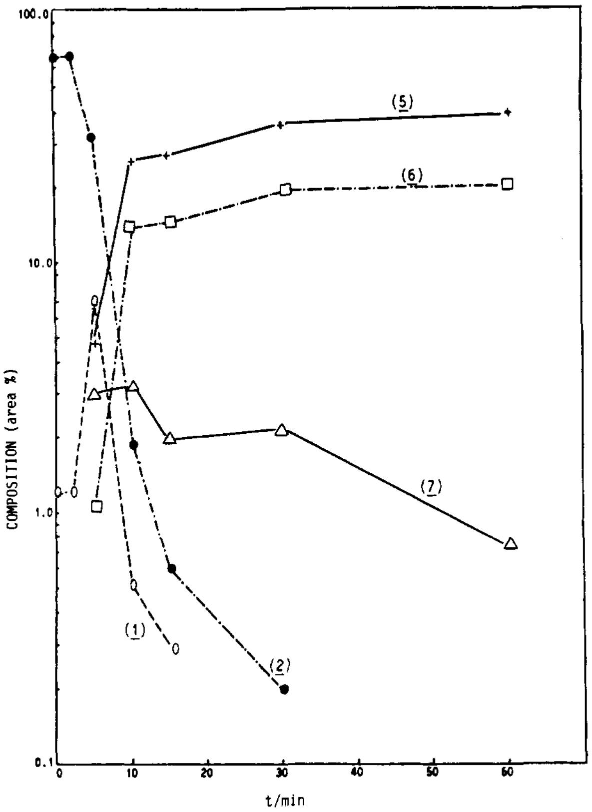


Figure 5. Kinetic profile of **2** (37.6) + chloroform (62.4%) – (total charge = 4.81 g) when heated at 225 °C in 316 stainless steel reactor with 304 SS coupons.

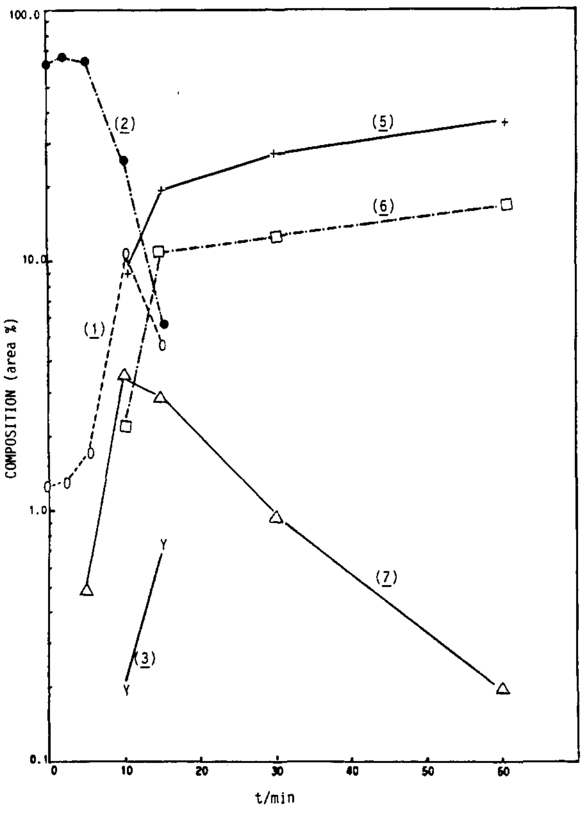
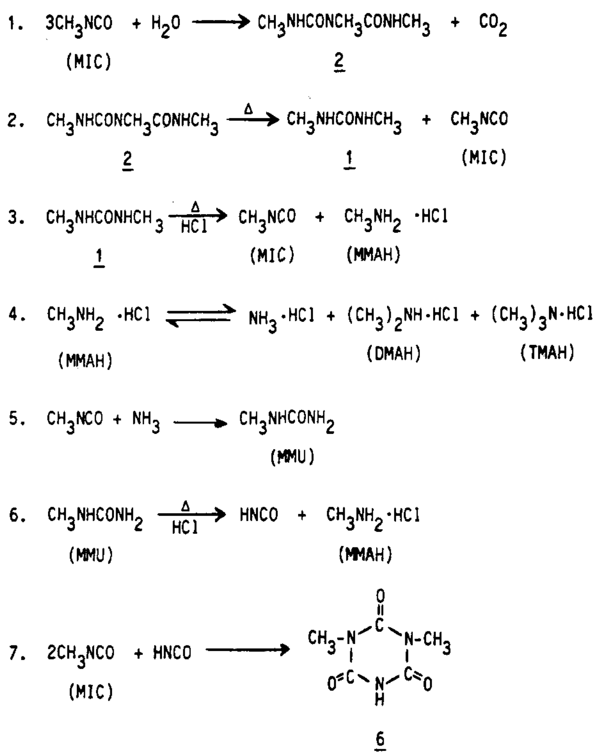


Figure 6. Kinetic profile of **2** (37.6%) + chloroform (62.4%) – (total charge = 4.81 g) when heated at 225 °C in 316 stainless steel reactors.

Scheme I. Pathway for Formation of 6



trimer **5** (35–40%), **6** (16–20%), and **7** (0.2–0.7%). Dichloromethane (5–8%) was also detected. The concentration of dione **7** peaked to approximately 3–5% within a period of 10 min and partially decomposed with continued heating. All of **1** and **2** decomposed within 15–30 min.

In analogy with MIC–chloroform–water reactions, the brief exotherm observed in these reactions also coincided with the appearance of the cyclic products. Moreover, the presence of 304 SS coupons also caused a slight rate enhancement and a more pronounced exotherm.

Dimethylurea–Chloroform Mixtures. Heating dimethylurea (**1**) and chloroform (20.9:73.1) mixtures under similar conditions as with the trimethylbiuret/chloroform reaction also produced the same product mixture as obtained from the biuret reaction but in different ratios: MIC trimer **5** (5%), **6** (27.3%), **7** (1%), and dichloromethane (6.9%), with complete disappearance of dimethylurea.

The formation of only 5% MIC trimer is not surprising because less MIC would be produced from decomposition of dimethylurea relative to trimethylbiuret.

The decomposition of **2** and **1** to produce MIC is apparently facilitated[18] by hydrogen chloride generated from chloroform.[19-22] MIC and methylamine hydrochloride, the transient products of decomposition, have also been detected in these experiments.

Trimethylbiuret–Dichloromethane Mixtures. The same array of products as in chloroform was also produced by heating **2** (63%) and CH_2Cl_2 (37%) at 225 °C for 4 h. The crude product consisted of 40–55% MIC trimer **5**, 11–12% of **6**, 6–7% of **7**, 0.5–1.1% of **1**, and 0.5% of **3** besides the methylated amine hydrochlorides. There was considerably more dione **7** produced in these reactions compared to TMB–chloroform reaction.

Mechanisms

Pathway to Formation of 6. A plausible pathway leading to the formation of **6** is depicted in Scheme I.

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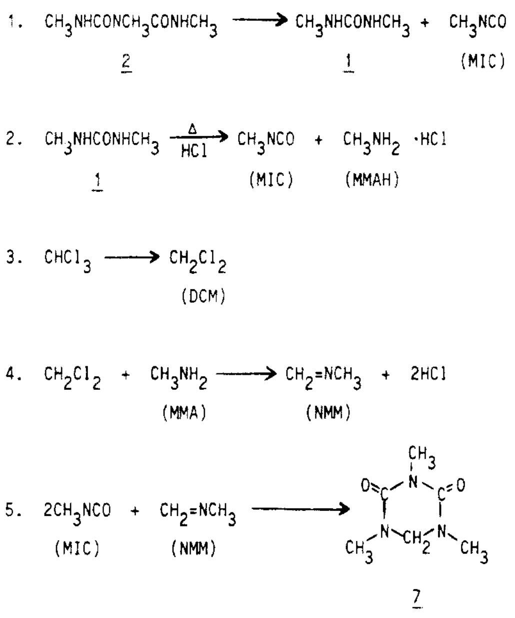
Scheme II. Pathway for Formation of Dione 7



High temperatures ranging from between 200 °C to 225 °C for a brief period, and the presence of chloroform or methylene chloride (as generators of hydrogen chloride), appear to be critical to cause the efficient decomposition of **2** and **1** as depicted in eq 2 and 3.

Methylamine hydrochloride (MMAH) is known[23] to disproportionate (eq 4) to an equilibrium mixture of ammonium chloride, dimethylamine hydrochloride, and trimethylamine hydrochloride, all of which have been identified in the core samples and in the laboratory produced reaction products.

The intermediacy of methylurea (MMU) (eq 5) was demonstrated independently when a mixture of ammonium chloride (23.2%), MIC (24.7%), and chloroform (52.1%) was heated at 225 °C for 4 h to product 10% of **6**, 34.6% MIC trimer, and 4.2% dichloromethane. Moreover, when a mixture of methylurea (56.1%) in MIC was heated at 150 °C for 17 h, it produced 15.2% of **6**, 7.0% of methyl isocyanurate,[24] a trimer resulting from two molecules of isocyanic acid and MIC, small quantities of **1** and **2**, and unreacted methylurea.

Pathway to Formation of Dione 7. The earlier experiments have indicated the importance of either chloroform or dichloromethane in the formation of dione. Chloroform is known to undergo reduction or hydrodechlorination to produce dichloromethane when heated with a variety of metal catalysts.[25-27] The exact nature of the "metal catalyst" in these investigations has not been defined but the fact that dichloromethane is formed in substantial quantities suggests that such a system is operative. A plausible pathway to dione is shown in Scheme II.

The experimentally determined heat of reaction for the trimerization of MIC is −54 kcal/g/mol of MIC[6] and the estimated[28] values for the cyclization reactions leading to **6** (Scheme I, eq 7) and dione **7** (Scheme II, equation 5) are −54 kcal/g/mol and −73 kcal/g/mol, respectively. These highly exothermic reactions would explain the brief exotherm observed within 5 to 15 min of heating the mixtures of MIC–chloroform–water at 225 °C.

The observed simultaneous formation of MIC trimer **5**, **6**, and **7** within a short period, all arising through trimerization of various combinations of reactive species such as MIC, isocyanic acid, and *N*-methylenemethanamine (NMM), received further support when the desired cyclic materials were produced by heating trimethylbiuret (**2**), methylurea (MMU), and hexahydro-1,3,5-trimethyl-1,3,5-triazine (HTMT) in the presence of gaseous hydrogen chloride. HTMT was used as a source of *N*-methylenemethanamine.[29] When a mixture of **2** (80.9%), MMU (16.5%), HTMT (1.2%), and HCl (1.4%) was heated at 225 °C for 15 min there resulted a product mixture containing 0.4% **3**, 57.7% **1**, 10.8% MIC trimer **5**, 13.8% **6**, and 6.6% dione **7** with about 5.0% of unreacted **2**. In the absence of hydrogen chloride, there was no dione or only trace amounts (less than 0.1%) were produced.

Implicit in the reactions described in Scheme I and II is the cyclotrimerization of MIC to **5** (not depicted). Compounds **3** and **4** are produced by the reactions of dimethylamine with 1 and 2 equiv of MIC, respectively.

Studies with Stable Isotope of Chloroform ($^{13}CHCl_3$). To further verify the postulated mechanism leading to the formation of the dione, and specifically, in order to determine the role of chloroform, two experiments were conducted. In one, chloroform (10 atom % ^{13}C) was heated with methyl isocyanate and water using the ratios of expt no. 10, Table II, at 225 °C for 0.5 h. In the second, the chloroform was enriched to the extent of 50 atom % ^{13}C. The dione produced in these reactions was isolated and analyzed by ^{13}C NMR spectroscopy. The crude reaction products were also analyzed by GC–MS.

The NMR spectra of the dione from unenriched chloroform (C) and that from the enriched chloroform experiments (A and B) are shown in Figure 7 (supplementary material). The chemical shifts with the normalized peak heights are shown in Table V (in supplementary material).

Figures 8a, 8b, and 8c (supplementary material) show the mass spectra of dione (MW 157) when unenriched chloroform, 10% $^{13}CHCl_3$ and 50% $^{13}CHCl_3$ were used as starting materials. Tables VI and VII (supplementary material) show comparisons of M − 1, M, and M + 1 ions when unenriched $CHCl_3$, 10% $^{13}CHCl_3$, and 50% $^{13}CHCl_3$ were used. Although the peak intensities of M and M + 1 (Figure 8c) are higher than those from 10% $^{13}CHCl_3$, the reasons for greater differences between the calculated and experimental values (Table VII) are not clear.

The enhancement of the NMR absorption peak due to C-2 of the dione and the mass spectral analyses have unequivocally established that the carbon atom from chloroform was incorporated into the dione molecule via dichloromethane (DCM) as an intermediate. GC–MS analyses of the unreacted DCM in the reaction products also indicated complete incorporation of ^{13}C from enriched chloroform (see Table VIII and Figures 9a, 9b, supplementary material).

GC–MS–EI analyses of the other materials indicated that there was some incorporation in trimethylurea but none in **1**, **2**, **6**, and MIC trimer **5**.

Corrosion Studies and Effect of Metals on Reaction Rates. The slight rate effect on introduction of 304 SS

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coupons in the reactors was described in the earlier discussion.

Ambient temperature experiments wherein 304 SS coupons were immersed in MIC containing 16% chloroform, and left standing for a period of 15 to 28 days, showed corrosion rates which ranged from 0.02 to 0.3 mils/year. With 2.5% chloroform, the rates ranged from 0.02 to 0.05 mils/year. These corrosion rates are not considered sufficient to generate the concentration of metals found in the core samples. At higher temperatures, however, the corrosion rates increased dramatically. During the first 5 min after immersion of the reactors containing 304 SS coupons into a 225 °C bath, corrosion rates as high as 20 000 mils/year were measured.

A few experiments run in tantalum-lined reactors also produced the same mixture of products but at a slower rate than in 316 SS reactors.

Conclusions

This investigation has established the following:

All of the materials found in the core samples from Tank 610 have been produced by heating mixtures of MIC, chloroform, and water in stainless steel reactors.

Approximately 12 wt % of chloroform and 4 wt % of water are required to produce the relative proportions of the major components in the residue, with complete conversion of MIC to the products.

Water alone or chloroform alone when heated with MIC does not yield the major products in the residue.

Reaction temperature exceeding 200 °C, lasting for a brief period, is necessary to produce the observed quantities of dimethylisocyanurate (**6**).

At elevated temperatures chloroform generates hydrogen chloride and is converted to dichloromethane which is incorporated in the dione **7**.

Lower than expected concentrations of dimethylurea and trimethylbiuret are explained through their decomposition at higher temperatures which lead to the formation of MIC trimer, **6**, and **7**.

Trimethylbiuret and tetramethylbiuret (concentrated in the upper portion of the tank residues) are formed from ureas reacting with residual MIC during the cooling period.

Corrosion occurring during the high temperature period can account for the concentration of metals found in the core samples.

Experimental Section

Melting points are uncorrected. NMR spectra were obtained with a Varian EM 360L spectrometer using Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. IR spectra were taken on an IBM IR/32 FTIR spectrophotometer. Gas chromatograms were recorded on a Hewlett-Packard Model 5880A gas chromatograph. Mass spectra were obtained through contract services using a Hewlett-Packard Model 5985B quadrupole mass spectrometer and an AEI Model 902 double-focusing mass spectrometer (static resolution 10 000). All measurements were made in the EI mode at 70 eV.

Apparatus. High-temperature and high-pressure reactions were conducted in cylinders constructured of type 316 stainless steel (manufactured by Hoke Inc.) with openings at both ends fitted with plug-screws which could withstand pressures of 1800–3200 psig. The cylinders measured 4.75 in. in length with an external diameter of 1.0 in. and an internal diameter of about 0.5 in. The volume of each cylinder was exactly 32 mL. Some cylinders were also fitted with thermocouples. To minimize leaks, the cylinders were not connected to pressure gauges. The 304 SS cylinders of similar design and custom-made, measured 4.25 in. in length, 1.25 in. external diameter, and 0.75 in. internal diameter.

The dimensions of 304 SS coupons used in the experiments measured 3.5 in. or 1.0 in. long, 0.375 in. wide, and 0.0625 in. thick.

Materials. Chloroform was MCB reagent-grade (99.7%) stabilized with nonpolar hydrocarbon; dichloromethane, OmniSolv (99.9%), was obtained from EM Industries; methyl isocyanate was a commercial product of Union Carbide Corporation; acetonitrile, used as a solvent for GC analyses, was OmiSolv reagent (99.9%) obtained from EM Industries, Inc.

Other reagents used in this study, and as starting materials in the independent syntheses of specific compounds required for identification purposes, were all produced from commercial sources.

Procedure for High-Pressure and High-Temperature Reactions. The following procedure is typical for the high-pressure and high-temperature reactions. With one end of the Hoke cylinder closed, the reactants were charged into the cylinder in a well-ventilated hood. Solid reactants were weighed accurately prior to transferring into the cylinders. The materials were charged into the cylinders by volume using pipets or microsyringes to minimize the handling hazards of volatile reactants and liquids such as methyl isocyanate, chloroform, and water. In a typical experiment, methyl isocyanate was introduced into the cylinder, followed by addition of chloroform and water. The other opening was then quickly closed with the plug-screw. The cylinder was then immersed into an electrically heated oil (Therminol) bath at designated temperatures and times. The cylinder was pulled out from the heating bath and chilled immediately for 30 min at 0 °C and then opened in a well-ventilated hood. The reaction mixture was then sampled for analysis.

Sample Preparation of Solids for Capillary Gas Chromatographic Analyses. Approximately 0.1 g of solid material was dissolved in acetonitrile (10 mL) and filtered. No sample preparation was necessary for liquids. One microliter of the liquid or solution was then injected into the gas chromatograph.

Gas Chromatographic Analyses. A Hewlett-Packard Model 5880A gas chromatograph equipped with split-splitless capillary injector, Hewlett-Packard Model 7672A automatic sampler, and flame-ionization detector was employed for this study. The components in the mixture were separated on a 25 m × 0.32 mm I.D., 1.0 μm film thickness, OV-1701 fused silica capillary column (Quadrex Corporation). The helium carrier gas was adjusted to a linear velocity between 25 to 30 cm per s (column head pressure at $\simeq$10 psi). A 1-μL sample was introduced via automatic sampler in the split injection mode with a split ratio of ~25:1 and injection port temperature at 250 °C. The oven temperatures were programmed from 40 to 190 °C at 10° per min and 190 to 270 °C at 6° per min with isothermal periods of 5 min at 40 °C, 10 min at 190 °C, and 15 min at 270 °C. Compounds were identified by comparison of retention data with standards.

1,3,5-Trimethylbiuret (2). A mixture of 1,3-dimethylurea (100 g, 1.14 mol) and 500 mL of methyl isocyanate was refluxed at 40 °C for 7 h. After reflux, the reaction mixture was cooled to 7 °C and filtered to give 139.5 g of white solid, which was purified by washing with hexane. Upon drying, 136.3 g of **2** was obtained: mp 122–124 °C (lit.[31] mp 125–126 °C); IR (KBr) 3400, 3280, 2940, 2910, 1700, 1650, 1520, 1460, 1430, 1410, 1315, 1260, 1220, 1180, 1155, 1085, 1045, 945, 850, 770, 760, 660 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.70 (d, J = 5 Hz, 6 H), 3.21 (s, 3 H), 8.20 (br s, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 26.7, 29.8, 156.6.

1,1,3-Trimethylurea (3). Treatment of dimethylcarbamoyl chloride (13.0 g, 0.12 mol) in 200 mL of ether with gaseous methylamine according to the procedure described by Snyder[32] afforded 5.1 g of **3** as a hygroscopic white solid, mp 72–73 °C (lit.[32] mp 73–74 °C): IR ($CHCl_3$) 3500, 3370, 3000, 2450, 1680, 1530, 1420, 1360, 1220, 1140, 1070, 970, 650 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.59 (d, J = 5 Hz, 3 H), 2.80 (s, 6 H), 6.24 (br s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 27.1, 35.7, 158.8.

1,1,3,5-Tetramethylbiuret (4).[33] A solution of **3** (5 g, 0.049 mol) in 45 mL of dichloromethane was kept at 0 °C while 44 mL of a toluene solution containing 12.5% of phosgene (0.055 mol) was added dropwise. The mixture was then warmed to 25 °C. Nitrogen was bubbled into the reaction mixture as it was heated to reflux for 30 min. After cooling to 25 °C, the solvent was evaporated under reduced pressure to produce a pale yellow solid,

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which was triturated with ether. The ether filtrate, after evaporation, gave 2.7 g of a pale yellow oil. The oil was redissolved in 150 mL of ether at room temperature and methylamine gas was bubbled in for 60 min. The reaction mixture was filtered; the filtrate was evaporated under reduced pressure to yield 2.7 g of a yellow oil identified as **4** by spectral analyses: IR ($CHCl_3$) 3380, 3000, 2950, 2450, 1685, 1640, 1535, 1490, 1450, 1420, 1380, 1290, 1220, 1130, 1055, 900, 655 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.65 (d, J = 5 Hz, 3 H), 2.88 (s, 6 H), 2.94 (s, 3 H), 7.00 (br s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 26.7, 33.0, 36.8, 156.0, 158.7 HRMS measured M^+ = 159.1007, calculated for $C_6H_{13}N_3O_2$ M^+ = 159.1008.

1,3,5-Trimethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (MIC Trimer) (5). Methyl isocyanate (100 g, 1.75 mol) was added dropwise to a stirred mixture containing 6 g of anhydrous ferric chloride in 200 mL of anhydrous ethyl acetate at 69 °C. The addition required about 3 h. After the addition, the reaction temperature was slowly raised to 83 °C over a 2-h period. After cooling to room temperature, the reaction mixture was evaporated to dryness under reduced pressure to produce 77 g of solid. The latter was dissolved in 350 mL of dichloromethane and was filtered through Hi-Flow filtering aid to remove the ferric chloride catalyst. The filtrate, upon evaporation to dryness under reduced pressure, gave 70 g (70%) of **5**: mp 175–178 °C (lit.[34] mp 175 °C); IR ($CHCl_3$) 1690, 1480, 1395, 1050 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.16 (s); ^{13}C NMR (Me_2SO-d_6) δ 28.8, 149.3.

1,3-Dimethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (6). Compound **6** (3.6 g) was prepared from a mixture of potassium cyanate (20 g, 0.25 mol) and methyl isocyanate (57 g, 1.0 mol) in 1 L of *N*,*N*-dimethylformamide according to the procedure described by Kolonko:[35] mp 218–220 °C (lit.[35] mp 221–222 °C); IR ($CHCl_3$) 3450, 1735, 1695, 1600, 1470, 1385 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.12 (s, 6 H), 11.5 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 28.0, 148.9, 150.4.

Dihydro-1,3,5-trimethyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione (7). The procedure was essentially the same as that described by Etienne.[17] **7** (0.9 g) was obtained from a mixture of **2** (4.0 g, 0.027 mol), 37% aqueous formaldehyde (2.4 g, 0.029 mol), and 6 mL of concentrated sulfuric acid: mp 87–92 °C (lit.[17] mp 95 °C); IR ($CHCl_3$) 3000, 2950, 2880, 2800, 1710, 1660, 1520, 1475, 1450, 1415, 1300, 1260, 1200, 1080, 1040, 960, 650 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.85 (s, 6 H), 2.95 (s, 3 H), 4.40 (s, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 27.8, 32.1, 60.6, 153.2.

2,4-Dimethylallophanyl Chloride (DMAC). A 1.6 M solution of phosgene in toluene (195 mL, 0.31 mol) was added slowly over a 15-min period to a stirred mixture of **1** (25 g, 0.28 mol) and 250 mL of 1,2-dichloroethane at 8 °C. After the addition, the reaction mixture was stirred at 8–25 °C for 60 min and then heated at reflux temperature for 30 min while a nitrogen stream swept through the reaction vessel. After cooling, the reaction solvent was removed on a rotary evaporator leaving a thick oily residue. The latter was washed several times with ether (200 mL each). The ether washings were combined and concentrated on a rotary evaporator to produce a pale yellow oil which solidifed on standing. The crude product was washed with cold hexane to leave 23.4 g (55%) of white solid identified as 2,4-dimethylallophanoyl chloride by spectral analyses: mp 31–33 °C (lit.[36] mp 36 °C); IR ($CHCl_3$) 3450, 3020, 1740, 1560, 1300, 1240, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.76 (d, J = 5 Hz, 3 H), 3.33 (s, 3 H), 7.80 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.7, 35.6, 153.1, 160.1.

1,3-Dimethyldiazetidinedione (Methyl Isocyanate Dimer). Treatment of a mixture of freshly sublimed 1,4-diazabicyclo[2.2.2]octane (4.55 g, 0.051 mol) and 100 mL of ether with 2,4-dimethylallophanyl chloride (7.00 g, 0.046 mol) according to the procedure described by White[37] provided 4.3 g of crude product, which, upon recrystallization from hexane, gave 1.6 g (30%) of the desired product as white plates: mp 97–99 °C (lit.[37] 96–98 °C); IR ($CHCl_3$) 1780, 1730, 1450, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.86 (s); ^{13}C NMR (Me_2SO-d_6) δ 25.6, 158.1.

Methyl Isocyanate Polymer. The polymeric compound (1.15 g) of methyl isocyanate was obtained by refluxing a mixture of freshly distilled methyl isocyanate (6 g, 0.11 mol) and 10 mg of hexamethylenetetramine according to the procedure described by Tarricone:[9] mp 209–216 °C (lit.[9] mp 221 °C); IR (KBr) 3400, 2980, 1700, 1450, 1300, 1060 cm^{-1}.

Methylcarbamoyl Chloride (MCC). Anhydrous hydrogen chloride (80.2 g, 2.2 mol) was sparged into a stirred solution of methyl isocyanate (114.1 g, 2.0 mol) in 500 mL of dichloromethane at 15–20 °C with external cooling over a 30-min period. After the addition was complete, the reaction mixture was stirred at 15 °C for 30 min longer and then chilled to −35 °C and filtered to remove 41.3 g of white solid. Concentration of the filtrate on a rotary evaporator under reduced pressure resulted in a second crop of product: total solid weighed 101.7 g (54.4%); mp 47–49 °C (lit.[38a] mp 40–41 °C; lit.[38b] mp 43–46 °C); IR (KBr) 3130, 3050, 3000, 2965, 1905, 1582, 1532, 1462, 1428, 1264, 1001, 957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.85 (d, J = 5 Hz, 3 H), 6.00 (br s, 1 H).

Acknowledgment. The contributions and expert assistance of E. J. Boros, S. Sridhar, K. M. Hurst, K. A. Mede, D. W. Peck, U. H. Gibson, G. B. Elder, S. Chippett, C. H. Apperson, W. L. Calhoun, F. A. Hunter, H. H. Hannah, C. A. Busacca, and E. C. Bailey are gratefully acknowledged. We particularly thank C. A. Smitley and D. C. Ketter for carrying out the reactions and S. J. Ferrell, M. L. Emerick, and D. J. Scarborough for gas chromatographic analysis. We also thank J. A. Durden, T. N. Wheeler, and P. A. Cain for helpful discussions.

Registry No. **1**, 96-31-1; **2**, 816-00-2; **3**, 632-14-4; **4**, 54070-65-4; **5**, 827-16-7; **6**, 6726-48-3; **7**, 41221-01-6; DMAC, 13188-08-4; MCC, 6452-47-7; $CH_3N{=}C{=}O$, 624-83-9; ($CH_3N{=}C{=}O$) (homopolymer), 30108-95-3; $CHCl_3$, 67-66-3; $^{13}CHCl_3$, 31717-44-9; dimethylcarbamoyl chloride, 79-44-7; methylamine, 74-89-5; phosgene, 75-44-5; potassium cyanate, 590-28-3; formaldehyde, 50-00-0; 1,3-dimethyldiazetidinedione, 36909-44-1; methylamine hydrochloride, 593-51-1; dimethylamine hydrochloride, 506-59-2; trimethylamine hydrochloride, 593-81-7; iron, 7439-89-6; chromium, 7440-47-3; nickel, 7440-02-0; tetramethylurea, 632-22-4.

Supplementary Material Available: Table IV (thermal stability studies of synthetic mixture), Table V (^{13}C NMR chemical shifts of dione **7**), Tables VI, VII, and VIII (mass spectral data), Figure 7 (NMR spectra of unenriched and ^{13}C-enriched chloroform), and Figures 8a, 8b, 8c, and 9a, 9b (mass spectra of dione **7** and dichloromethane) (6 pages). Ordering information is given on any current masthead page.

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