

Catalysis of the Reaction between Isocyanates and Protonic Substrates. I. Metal Salt–Amine Complexes as Catalysts in the Polyurea Foaming Process

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Synopsis

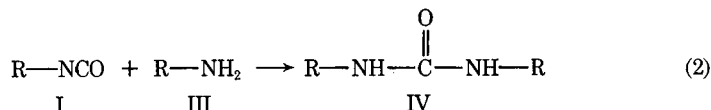
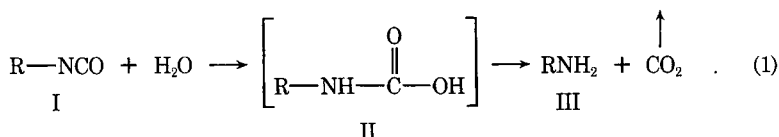
Tertiary amines and metal [Cu(II), Zn(II)] salts exhibit a synergistic effect in the catalysis of the isocyanate water reaction. The amino complexes of zinc and copper salts display a very large versatility in defining the most suitable formulations for the polyurea foam production. The foaming process is indeed controlled by the nature and the composition of these new catalytic combinations; kinetics of foaming and textural characteristics of final foams are easily modified in that way.

INTRODUCTION

Polyurethane and polyisocyanurate foams are very efficient thermal insulating materials with suitable mechanical properties; they are produced from crude 4,4'-diphenylmethane diisocyanate (MDI) and special polyols. Their insulating properties are improved beyond those of traditional products as a result of their high level of inert gas (Freon)-filled closed cells.

On the other hand, polyurea foams could be prepared by reaction of crude MDI with water and give rise to valuable industrial products. Expensive polyols are indeed replaced by water; the density of polyurea foams is four or five times lower than that of polyurethane foams; and, moreover, the foaming of polyureas occurs spontaneously as a result of the carbon dioxide evolving during the isocyanate–water reaction.

The reaction of isocyanate with water is often described by a very simplified reaction scheme:



In a first approximation, reaction (1) corresponds to the foaming step, whereas

reaction (2) is responsible for the polymerization process which yields a tridimensional network when isocyanate I is polyfunctional. Both reactions are sensitive to tertiary amine catalysts, but also to a large number of other catalysts.¹⁻⁷

However, the industrial production of polyurea foams depends on the accurate control of foaming and polymerization, which are consecutive and competing reactions. Up to now, collapse or shrinkage are generally observed in the reactions commonly catalyzed by tertiary amines.^{1,2}

It is noteworthy that carbamic intermediates other than carbamic acid II can be generated in the medium, i.e., carbamate salt $R-NH-\overset{O}{\parallel}C-O-M^+$ (V) and carbamic anhydride $R-NH-\overset{O}{\parallel}C-O-\overset{O}{\parallel}C-NH-R$ (VI). The counteraction in V can be either a metal cation, when inorganic bases are added, or the ammonium ion derived from an amine catalyst or from the intermediate aniline III. Compound VI is an addition product of the carbamic intermediates II or V to the isocyanate. The formation of intermediates V and VI was postulated by Shkapenko⁸ to explain a deficiency in the amount of carbon dioxide released during hydrolysis of *o*-tolyl isocyanate in dioxane solution. On the other hand, sodium carbamates V have been isolated and their decarboxylation rates measured as a function of pH and buffer concentration.⁹

Investigation of new catalyst combinations based on typical decarboxylating agents was considered attractive in an attempt to achieve improved control in polyurea foam production. Among the efficient decarboxylating agents claimed in the literature¹⁰⁻¹⁴ are copper(II) and zinc(II) salts as well as their amino-complexes. Certain zinc derivatives are known to be essential in the decarboxylation steps of biological cycles.¹⁵ This article reports the results obtained in the tertiary amine-metal salt complex catalysis of the polyurea foaming process.

EXPERIMENTAL

Materials

Crude MDI containing 30–32 wt % NCO (Shell Chemicals), tris(2-chloroethyl) phosphate or TCEP (Hoechst), 2-methylimidazole (2MI) (BASF), and *N,N*-dimethylaminoethanol or DMAE (Union Carbide) were used as received.

Copper chloride ($CuCl_2 \cdot 2H_2O$), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), and zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) were pure-grade UCB products. Zinc cyanide ($Zn(CN)_2$) was purchased from Merck.

Synthesis of 2MI-Copper Chloride Complexes

Dichlorobis- and tetra(2 methylimidazole)-copper complexes were prepared from acetone or ethanol solutions according to the method of Eilbeck et al.¹⁶

Synthesis and Analysis of 2 MI-Copper (or Zinc) Nitrate Complexes

By mixing at RT aqueous solutions containing 2MI and $\text{Cu}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$, respective precipitates were formed after a few minutes. After standing for 24 h, the precipitates were isolated by filtration. The precipitates were washed with water and dried under vacuum, whereas the washing liquors were added to the filtrates. The 2MI contents of the filtrates were determined by titration with 1N HCl in the presence of methyl yellow as an indicator. The 2MI contents of the precipitates were then calculated by difference. Copper (or zinc) was titrated in both filtrate and precipitate according to the Titriplex III (EDTA 0.1N) method of Merck.¹⁷

General Procedures

The experimental conditions were chosen to approach, as closely as possible, the conditions required by the industrial foam production (proportions and addition mode of reagents, stirring, absence of solvent). The standard formulation used was accordingly crude MDI (100 parts), TCEP (35–50 parts), water (25–35 parts), and catalyst. (TCEP is a well-known flame retardant.¹⁸)

The CO_2 evolution was monitored with a device which included a flat-bottom thick glass cylinder reactor with a four-necked cap. One of these is a Sovirel screw neck with a gas-tight padding which allows vigorous stirring (1000 rpm) with a powerful high-speed electric motor and a stainless steel mixing head. Two other necks were fitted with self-sealing joints, one for the introduction of a thermocouple and the other for the injection of water. The last opening was connected to the top of a 2-L graduated cylinder filled with ethylene glycol for the determination of the evolved gas volume. The liquid level was recorded every 10 s: the volumetric data obtained were corrected for atmospheric pressure (H , cm Hg), temperature (t , °C), and height of the liquid in the column (f):

$$V_{\text{cor}} = V_r \frac{1}{1 + t/273} \frac{H - f}{76} \quad (3)$$

V_{cor} is corrected volume at 0 °C and 76 cm Hg. V_r is read volume, and $f = [97.2 - (V_r \times 0.0486)] \times 0.0815$. The V_{cor} values were averaged over the number of experiments and reported in percentage of total volume calculated under standard conditions (i.e., 837.8 ml). The results of these calculations were plotted against time by an IBM computer using a FORTRAN-4 program.

For these experiments, the amounts of reagents used were adjusted to a constant weight of MDI (10 g), and a defoaming agent (Siloprene from Rhône-Poulenc) was added. The experiments were performed starting at RT according to the one-shot method (two or three components). In the first case (two components), a solution of the catalyst in water was added to the premix of isocyanate, TCEP, and defoamer. In the second case (three components), the amine (or metal salt) solution in TCEP was first added to the MDI and defoamer premix. The aqueous solution of metal salt (or amine) was then quickly poured into the mixture under very vigorous stirring. When complexes with a well-defined amine salt molar ratio were used, they were dissolved in TCEP and used in a three-component method, the aqueous phase then being pure water.

Foaming was tested on a reduced scale according to the one-shot technique, with sometimes two but usually three components. The metal salt was thus

generally added in TCEP and the amine, in water. The formulation was prepared by vigorous stirring of the components during 6 s with a heavy-duty drill motor equipped with a high-intensity mixing head at about 3000 rpm; it was then poured into cubic brown paper boxes (15 cm side) lined with a polyethylene foil. The parameters T_c (cream time), T_f (fiber time), and T_r (rise time) were recorded to characterize the foaming process.

RESULTS AND DISCUSSION

Carbon Dioxide Evolution Diagrams

Figures 1 to 9 report the carbon dioxide evolution vs. time for the systems involving copper(II) or zinc(II) salts and 2-methylimidazole (2MI). The amine-salt molar ratio (ASR), the addition mode of the catalytic components, and the nature of the metal salts are the main parameters that have been studied.

Influence of the Catalytic System: Composition and Preparation Route

It is obvious from Figures 1 to 5 that the addition of either Cu(II) or Zn(II) salts to 2MI significantly enhances the observed reaction rate compared to the amine alone at the same molar concentration. Exceptions are to be noted for the lower 2MI-copper salt molar ratios (Figs. 1, 3, and 4), and a more complex situation is observed for $Zn(NO_3)_2$ at the highest ASR values (Fig. 5). As far as metal nitrates are concerned, the Cu(II) salt is more active than the Zn(II) salt for the same addition mode of the catalytic components (Figs. 1 and 2).

Furthermore, the metal has an influence on the total amount of CO_2 evolved at the end of the reaction. In comparison with 2MI used alone at the same molar

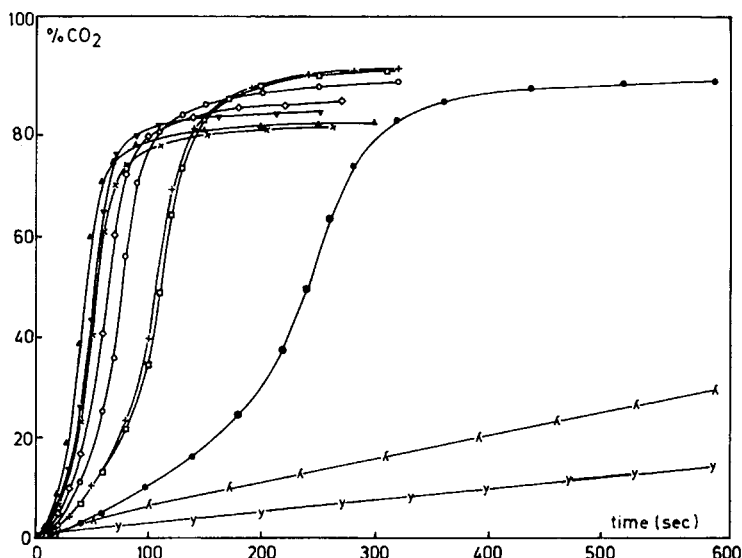


Fig. 1. Carbon dioxide evolution curves. Catalyst: 2MI/ $Cu(NO_3)_2 \cdot 3H_2O$ combinations at different molar ratios. 2MI (1.3×10^{-3} mol) previously dissolved in water, and copper salt in TCEP. ASR: 10/1 (+), 8/1 (\square), 6/1 (\circ), 5/1 (\diamond), 4/1 (∇), 3/1 (\triangle), 2/1 (\times), 1/1 (\wedge), 2MI alone (\otimes), $Cu(NO_3)_2 \cdot 3H_2O$ alone (1.3×10^{-3} mol) (γ).

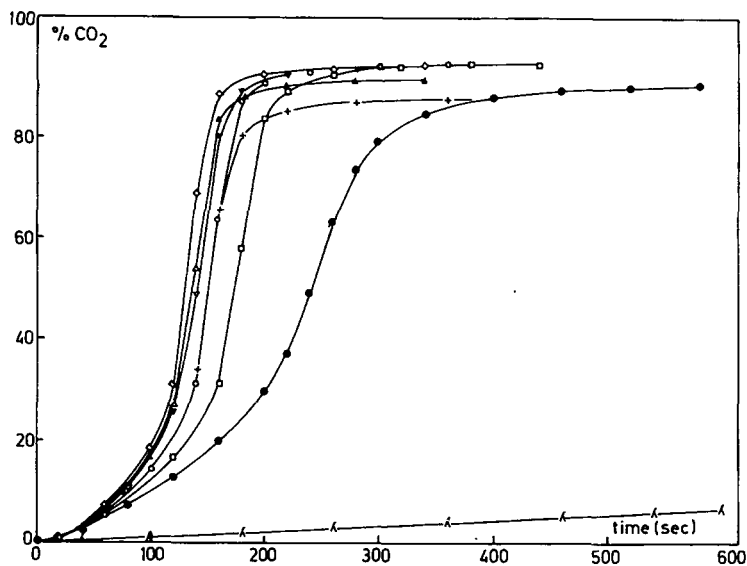


Fig. 2. Carbon dioxide evolution curves. Catalyst: 2MI/ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ combinations at different molar ratios. 2MI (1.3×10^{-3} mol) previously dissolved in water and zinc salt in TCEP. ASR: 20/1 (\square), 10/1 (\circ), 6/1 (\diamond), 4/1 (∇), 2/1 (Δ), 1/1 ($+$), 2MI alone (\otimes), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ alone (1.3×10^{-3} mol) (\wedge).

concentration, the amino complexes based on Zn(II) yield systematically higher amounts of CO_2 , whereas the amino Cu(II) complexes do the same only at ASR higher than 6/1. These observations indicate the important influence of the metal ion on the activation mechanism of the process and show a practically inverse correlation between the activity of the catalytic system (rate of CO_2 ev-

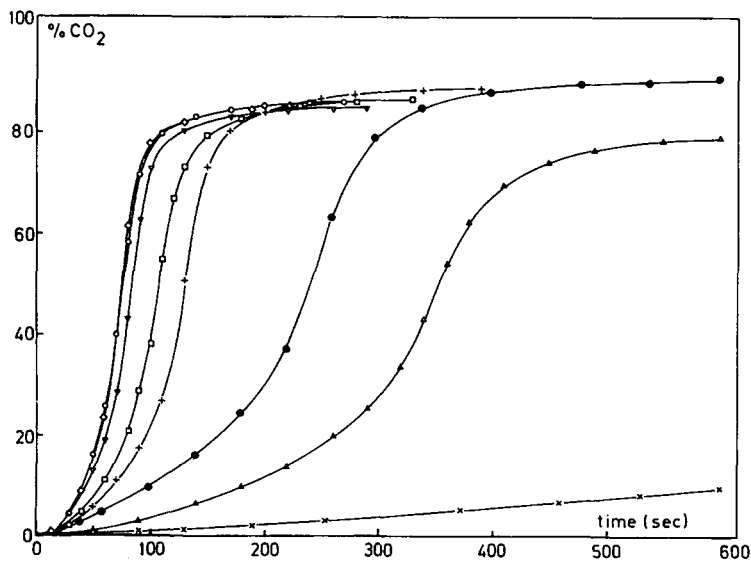


Fig. 3. Carbon dioxide evolution curves. Catalyst: 2MI/ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ combinations at different molar ratios. Both components added in water (2MI 1.3×10^{-3} mol). ASR: 8/1 ($+$), 6/1 (\square), 5/1 (\circ), 3,76/1 (this catalytic solution was previously filtered and titrated) (\diamond), 3/1 (∇), 2/1 (Δ), 2MI alone (\wedge), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ alone (1.3×10^{-3} mol) (\times).

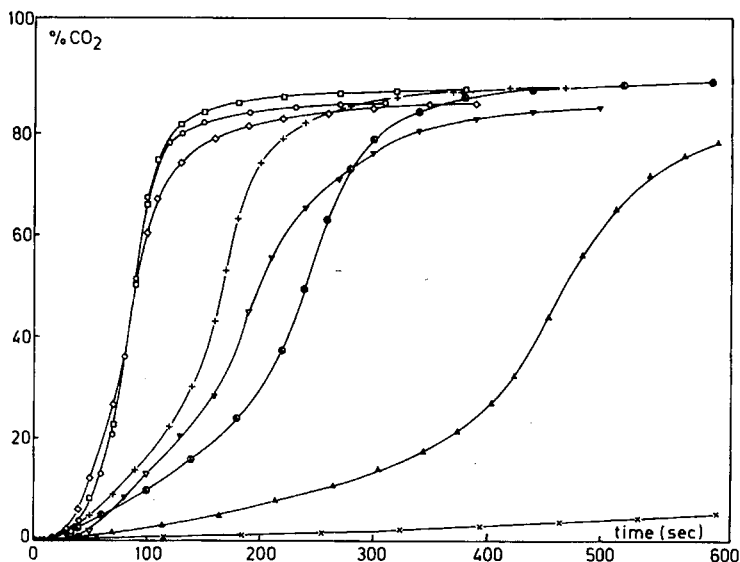


Fig. 4. Carbon dioxide evolution curves. Catalyst: 2MI/CuCl₂·2H₂O combinations at different molar ratios. Both components added in water (2MI 1.3×10^{-3} mol). ASR: 20/1 (+); 6/1 (□), 5/1 (○); 4/1 (◇), 3/1 (▽), 2/1 (Δ), 2MI alone (∧), CuCl₂·2H₂O alone (1.3×10^{-3} mol) (X).

olution) and its apparent ability to decarboxylate the carbamic intermediates (amount of CO₂ evolved).

The CO₂ evolution curves relative to a 4/1 ASR (Figs. 7 and 8) indicate also that the addition mode of the catalytic components is of prime importance on the CO₂ evolution rate. For both copper and zinc salts, the most efficient mode corresponds to the addition of the metal salt in TCEP and the amine in water, the less efficient one being the addition of both components in water.

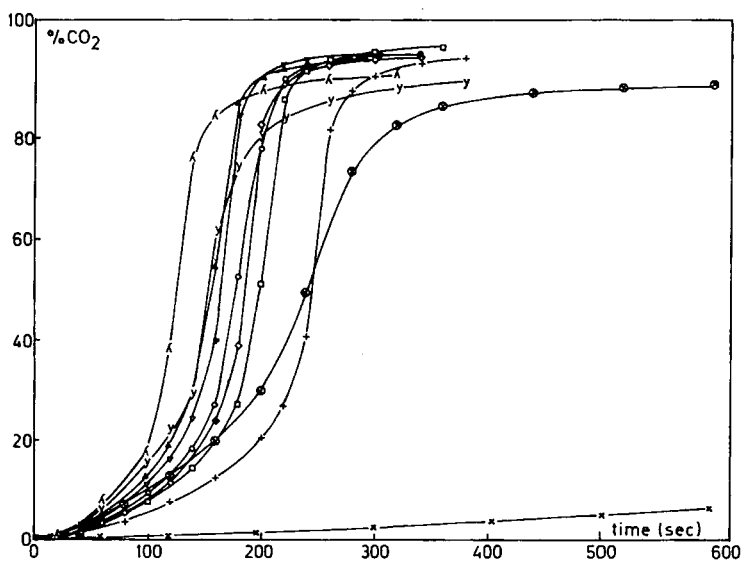


Fig. 5. Carbon dioxide evolution curves. Catalyst: 2MI/Zn(NO₃)₂·6H₂O combinations at different molar ratios. Both components added in water (2MI 1.3×10^{-3} mol). ASR: 10/1 (+), 8/1 (□), 6/1 (○), 5/1 (◇), 4/1 (▽), 3/1 (Δ), 2/1 (∧), 1/1 (∇), 2MI alone (⊗), Zn(NO₃)₂·6H₂O alone (1.3×10^{-3} mol) (X).

In the case of CuCl_2 , both 4/1 and 2/1 2MI/ CuCl_2 complexes have been previously prepared in ethanol.¹⁶ Figure 6 compares the behavior of the well-defined complexes dissolved in TCEP to the one of the corresponding systems directly formed in water. In this latter case, the activity is somewhat lower,

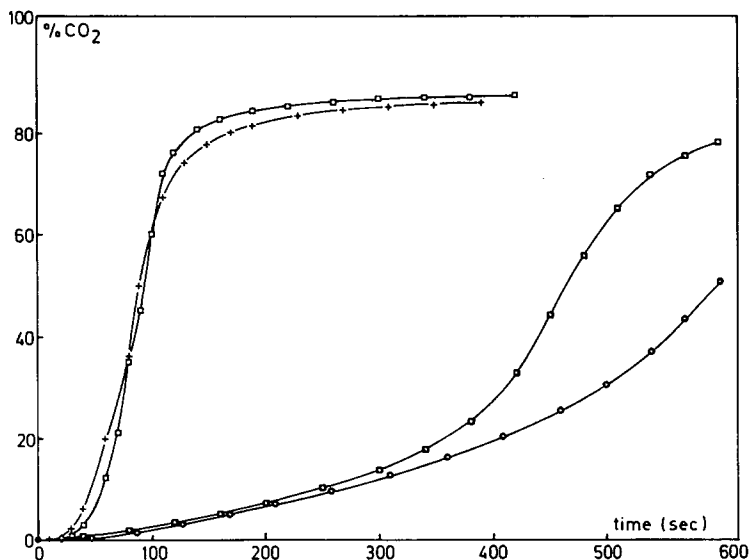


Fig. 6. Carbon dioxide evolution curves. Catalyst 2MI/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ combinations. Influence of the preparation route of the complex (2MI 1.3×10^{-3} mol): (+) 4/1 complex formed in aqueous solution and used as prepared; (□) 4/1 complex synthesized in dry acetone and used in TCEP solution; (○) 2/1 complex formed in aqueous solution and used as prepared; (◇) 2/1 complex synthesized in absolute ethanol and used in TCEP solution.

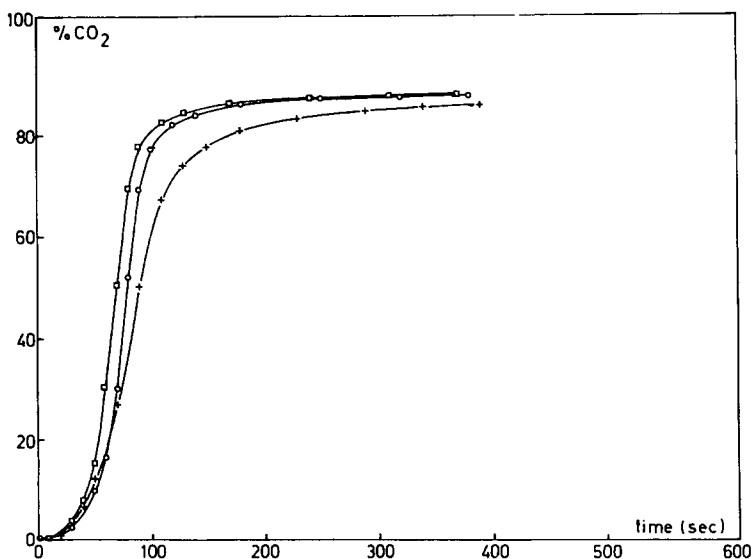


Fig. 7. Carbon dioxide evolution curves. Catalyst: 4/1 2MI/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ combinations. Influence of the addition mode of the components (2MI 1.3×10^{-3} mol): (+) 2MI and copper chloride both added in water; (□) 2MI added in water and copper chloride in TCEP; (○) 2MI added in TCEP and copper chloride in water.

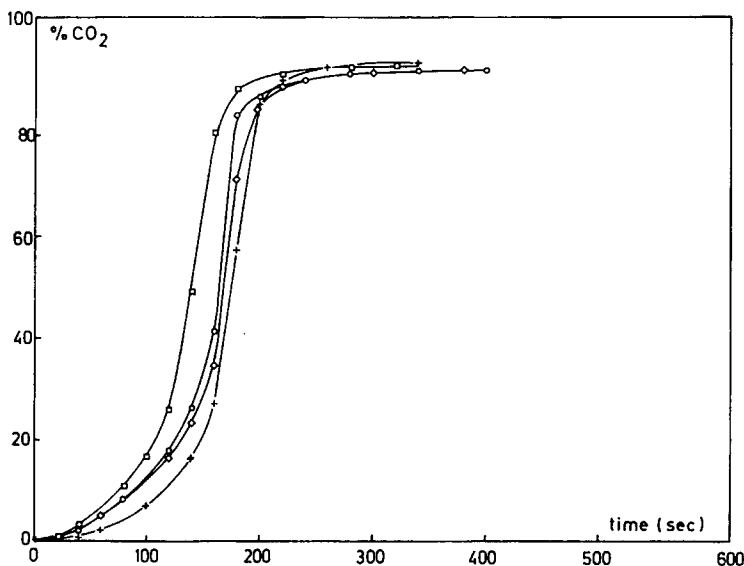


Fig. 8. Carbon dioxide evolution curves. Catalyst 4/1 2MI/ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ combinations. Influence of the addition mode of the components (2MI 1.3×10^{-3} mol): (+) 2MI and zinc nitrate both added in water; (\square) 2MI added in water and zinc nitrate in TCEP; (\circ) 2MI added in TCEP and zinc nitrate in water; (\diamond) 2MI and zinc nitrate both added in TCEP.

especially for the 2/1 combination. The slow precipitation of poorly soluble complexes noted when 2MI and metal salts are mixed together in water can be responsible for the lower activity recorded.

These observations, which are very significant for the practical production of foams, are apparently not easy to explain. The effect of ASR on the kinetics of the reaction is, however, more clearly observed by plotting $t_{\text{CO}_2/2}$, i.e., the time necessary to evolve half the theoretical amount of CO_2 [eq. (1)], vs. ASR (Fig. 10). Curves with a minimum are obtained; their general shape depends mainly on the nature of the metal, but also on the addition mode of salt and 2MI. These curves have only a qualitative kinetic meaning, as it is practically impossible to know the efficient concentration of the active species present in each phase at the reaction time.

The literature data indicate that 2MI always forms 4/1 coordination complexes with Zn(II) and Cu(II) salts.^{16,19-22} It is therefore expected that these 4/1 2MI-metal complexes are the main catalytic species active in the formulations used. In that respect, when aqueous solutions of constant 2MI amount and various metal salt amounts are mixed together, a precipitate is formed after a few minutes. The composition of both the insoluble part and the filtrate has been determined after the mixture has been allowed to stand for one day. The results presented in Table I show that the composition of the precipitate tends to a constant 4/1 2MI/metal ratio at initial ASR equal to or higher than 4/1 (CuCl_2) or 2/1 ($\text{Zn}(\text{NO}_3)_2$); at initial ASR lower than these latter values, the precipitate has a different composition, around 1.1/1 to 1.4/1.

Thus, it is possible to explain the occurrence of a minimum in the corresponding $t_{\text{CO}_2/2}$ vs. ASR curves (Fig. 10). At initial ASR higher than the critical 4/1 [Cu(II)] or 2/1 [Zn(II)] values, 2MI and Cu(II) or Zn(II) really form a poorly water-soluble 4/1 complex, the concentration of which increases in the reaction

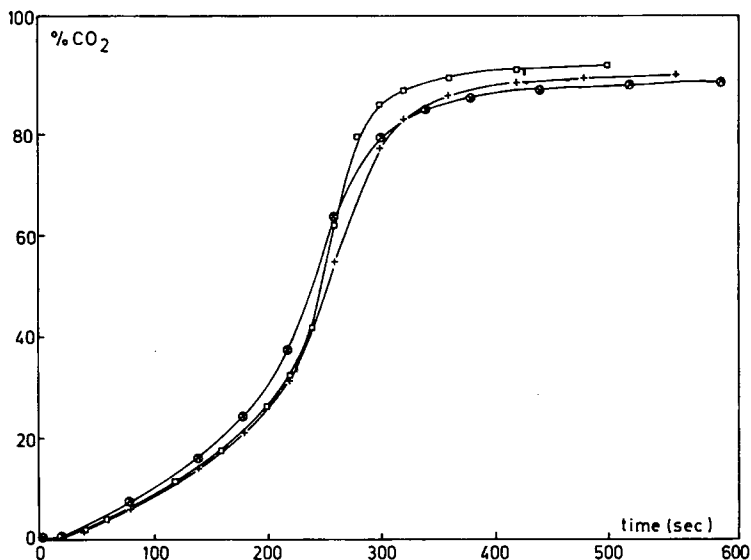


Fig. 9. Carbon dioxide evolution curves. Catalyst 2MI/Zn(CN)₂ combinations. Influence of the coordinating power of the anion. Both catalysts added in water (2MI 1.3 × 10⁻³ mol). ASR: 6/1 (□), 4/1 (○), 2MI alone (⊗).

medium as the initial ASR decreases (Table I). At the same time, the amount of the noncomplexed 2MI decreases whereas the catalytic activity increases (decreasing $t_{CO_2/2}$, Fig. 10). This means that the 4/1 2MI-metal complex is most probably an active species in the whole foaming process. Below the critical ASR values, a different but less active complex is formed, the concentration of which decreases as the initial ASR tends to 1/1 (Table I); $t_{CO_2/2}$ accordingly increases (Fig. 10).

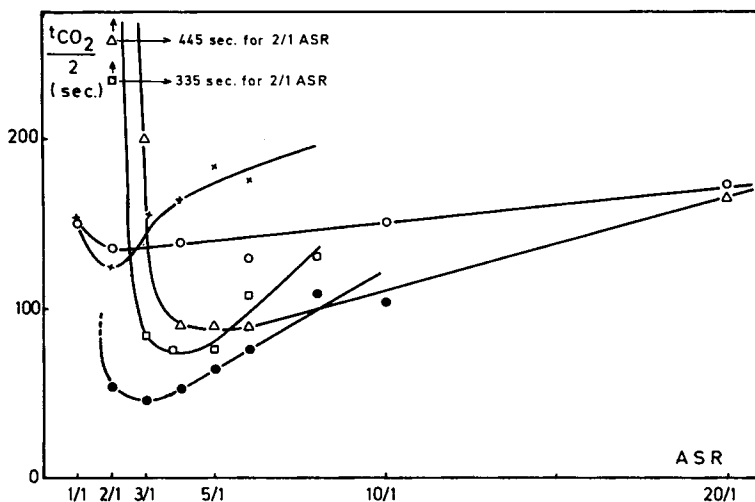


Fig. 10. Time necessary to evolve half the theoretical amount of CO₂ ($t_{CO_2/2}$) vs. amine/metal salt molar ratios (ASR). Catalyst: (●) 2MI previously dissolved in water and Cu(NO₃)₂ in TCEP; (□) 2MI and Cu(NO₃)₂ both added in water; (Δ) 2MI and CuCl₂ both added in water; (○) 2MI previously dissolved in water and Zn(NO₃)₂ in TCEP; (+) 2MI and Zn(NO₃)₂ both added in water.

TABLE I
Composition of Precipitate and Filtrate Separated from the 2MI/Metal Salt Mixtures in Water

Initial ASR ^a	Pre- cipitated metal, %	Pre- cipitated 2MI, %	ASR ^a in precipitate	ASR in the filtrate	Complex concentration in the filtrate,		Excess concentration		
					$\frac{\text{mL}^{-1} \times 10^{-3}}{4/1}$	$\frac{\text{mL}^{-1} \times 10^{-3}}{1.4/1}$	$\frac{\text{mL}^{-1} \times 10^{-3}}{\text{Salt}}$	$\frac{\text{mL}^{-1} \times 10^{-3}}{2\text{MI}}$	
Cu(NO ₃) ₂									
1/1	80	86	1.1/1	0.7/1	—	21	21	—	—
2/1	61	42	1.4/1	2.9/1	—	41	—	—	64.5
4/1	28	29	4.1/1	4.0/1	37.5	—	0	0	—
8/1	49	25	4.1/1	11.7/1	13.5	—	—	—	104
10/1	70	31	4.5/1	22.9/1	6.5	—	—	—	120
Zn(NO ₃) ₂									
1/1	25	35	1.4/1	0.85/1	—	97.5	60	—	—
2/1	26	55	4.3/1	1.3/1	23.5	—	54	—	—
8/1	88	43	3.9/1	126.3/1	3.0	—	—	—	107

^a ASR = Amine/metal salt molar ratio.

This effect is evident for Cu(II) salts because of the very low solubility of the corresponding complexes: 61 to 80% Cu(II) is precipitated compared to 25% for Zn(II) (Table I). The decrease of the amine-salt complex concentration, as ASR decreases below the critical value, could be explained by a salting-out effect. A large excess of salt is indeed noted for the 2MI/Cu(NO₃)₂ system in the 1/1 ASR (Table I). The lower activity of the complexes formed below the critical ASR is evidenced from the 2MI/Zn(NO₃)₂ system formed in water. The *t* CO₂/2 value is indeed similar at both 1/1 and 2/1 ASR (Fig. 10), whereas Table I shows that the assumed active 4/1 complex (ASR 2/1) is four times less abundantly formed than the 1.4/1 system (ASR 1/1).

If the catalytic components are now added separately into the reaction medium (metal salt in TCEP and 2MI in water), the *t* CO₂/2 vs. ASR curves are either shifted [Cu(II)] or modified [Zn(II)], so that a higher overall catalytic activity is observed. The coordination complexes are now formed *in situ* at a rate depending on the diffusion of each component in the heterophase reaction medium. The greater catalytic activity observed when 2MI and Cu(NO₃)₂ are separately added could be explained by the transient formation of the more active 4/1 complex at the starting of the foaming reaction, before the complexation has reached its equilibrium.

Influence of the Counteranion of the Metal Salt

The results obtained with Zn(NO₃)₂ and Zn(CN)₂ (Figs. 2 and 9) show the role played by the coordinating power of the anion; NO₃⁻ is a poor coordinating agent compared to CN⁻, which is quite strong.²³ The kinetics of the polyurea formation is significantly enhanced by the addition of Zn(NO₃)₂ to 2MI (Fig. 2), whereas the addition of Zn(CN)₂ has practically no effect (Fig. 9).

The same phenomenon is observed when Cu(NO₃)₂ (Fig. 3) and CuCl₂ (Fig. 4) are compared. The latter is somewhat less active than the former, according to the higher coordination power of the chloride anion. The sensitivity of the

catalysis to the coordinating character of the anion is therefore another parameter to keep in mind for consistent production of good-quality polyurea foams.

Results of Foaming Tests

The results of the foaming tests are summarized in Tables II, III, and IV. As before, the amount of 2MI is kept constant (3.0 parts), whereas the metal salt is added in different molar ratios; 2MI is used in water and the metal salt in TCEP. From these results, it can be concluded that both copper and zinc salts enhance the reaction rate; the rise time (T_r) effectively decreases as the metal salt amount increases (or ASR decreases). The cream time (T_c) is, however, unaffected by the addition of the metal salt, whereas the T_r/T_c ratio decreases with ASR. This means that the *in situ* formation of increasing amounts of the amino complex has no significant effect on the first stage of the process (T_c constant), in contrast to the rate of the whole process (T_r decreasing). The fiber time (T_f) can be considered related to the polymerization step, eq. (2), while T_r is related to the foaming, eq. (1), and secondarily to the polymerization step, eq. (2). The constancy of the T_f/T_r ratio is noteworthy. From these observations, it is difficult to correlate the general acceleration of the process to a specific action

TABLE II
Effect of the Addition of $\text{Cu}(\text{NO}_3)_2$ to 3.0 Parts 2MI on the Foaming Parameters

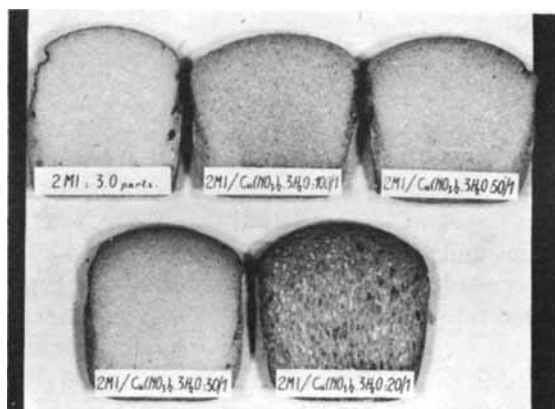
Foaming parameters	2MI 3.0 parts	2MI/ $\text{Cu}(\text{NO}_3)_2$ molar ratios			
		100/1	50/1	30/1	20/1
T_c , s	10	10	10	12	12
T_f , s	103	84	73	63	55
T_r , s	117	101	86	80	64
T_r/T_c	12	10	8.6	6.7	5.3
T_f/T_r	0.88	0.83	0.85	0.79	0.86

TABLE III
Effect of the Addition of CuCl_2 to 3.0 Parts 2MI on the Foaming Parameters

Foaming Parameters	2MI 3.0 parts	2MI/ CuCl_2 molar ratios			
		100/1	50/1	30/1	20/1
T_c , s	10	11	11	11	11
T_f , s	103	88	78	60	50
T_r , s	117	105	91	76	60
T_r/T_c	12	8.7	8.3	6.9	5.5
T_f/T_r	0.88	0.84	0.86	0.79	0.83

TABLE IV
Effect of the Addition of $\text{Zn}(\text{NO}_3)_2$ to 3.0 Parts 2MI on the Foaming Parameters

Foaming parameters	2MI 3.0 parts	2MI/ $\text{Zn}(\text{NO}_3)_2$ molar ratios					
		100/1	50/1	30/1	20/1	15/1	10/1
T_c , s	10	11	12	11	11	11	10
T_f , s	103	86	70	54	45	43	40
T_r , s	117	104	81	64	57	51	47
T_r/T_c	12	9.5	6.7	5.8	5.2	4.6	4.7
T_f/T_r	0.88	0.83	0.86	0.84	0.79	0.84	0.85



(a)



(b)

Fig. 11. (a) Influence of the 2MI/Cu(NO₃)₂·3H₂O molar ratio on the foam structure (3.0 parts 2MI for 100 parts MDI). (b) Influence of the 2MI/Zn(NO₃)₂·6H₂O molar ratio on the foam structure (3.0 parts 2MI for 100 parts MDI).

of the amino complex on one or the other elementary step of the foaming process, eqs. (1) and (2).

However, the ratio of the amine to the metal salt influences greatly the quality of the foam. Photographs (Fig. 11) illustrate the texture of the foams obtained which becomes coarser when the amount of copper nitrate in the catalyst is too high; the best ASR lies between 50/1 and 30/1. When zinc nitrate is used, the structure of the foam is bad for high ASR values, but it becomes finer and more regular as the relative amount of Zn(NO₃)₂ increases.

The foaming tests are also in agreement with the already mentioned effects due to the addition mode of the catalytic components on the reaction rates. The results reported in Table V indicate that significantly longer reaction times (*T_r*) are observed when amine and metal salts are used in aqueous solution. The lower *T_f*/*T_r* ratios obtained when the metal salt is added in TCEP, could indicate a preferential catalytic action on the polymerization process in this case. As already mentioned, the partial precipitation of the amino complex formed by mixing the catalytic components in water could also be responsible for the dif-

TABLE V
Effect of the Addition Mode of the Catalytic Components on the Foaming Parameters

Foaming parameters	2MI 3.0 parts	Zr(NO ₃) ₂ used in ^a		Cu(NO ₃) ₂ used in ^a	
		Water	TCEP	Water	TCEP
T_c , s	10	12	11	11	12
T_f , s	103	94	45	81	63
T_r , s	117	106	57	95	80
T_r/T_c	12	8.8	5.1	8.6	6.7
T_f/T_r	0.88	0.89	0.79	0.85	0.79

^a 2MI used in water and amounted to 3.0 parts; 2MI/Zn(NO₃)₂ = 20/1; 2MI/Cu(NO₃)₂ = 30/1.

ferences observed. It is to be noted that T_c is not obviously affected by the addition mode of 2MI and metal salt.

It is attractive to explore the possibility of reducing the amine concentration while keeping appropriate foam properties. Correct foaming cannot be obtained by reducing the 2MI amount from 3.0 to 2.0 parts. The addition of various amounts of Cu(NO₃)₂ to 2.0 parts 2MI does not yield better results. On the contrary, Zn(NO₃)₂ used in 10/1 to 6/1 ASR gives rise to good foams (Fig. 12). It is even possible to reduce the 2MI amount down to 1.5 part, provided the ASR is lower than 6/1.

Another interesting formulation is obtained by combining simultaneously copper and zinc nitrates (in TCEP) to 3.0 parts 2MI (in water). The usual foaming parameters are reported in Table VI. From these experiments, it is obvious that the reaction is more activated by a combination richer in zinc than

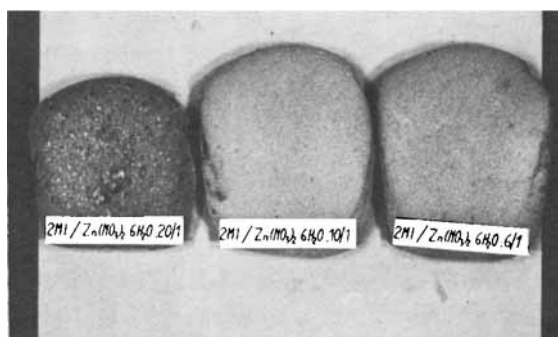


Fig. 12. Foams prepared from only 2.0 parts 2MI plus Zn(NO₃)₂·6H₂O in different molar ratios.

TABLE VI
Combinations of Both Cu(NO₃)₂ and Zn(NO₃)₂ with 2MI (3.0 Parts)

Foaming parameters, s	2MI/Cu(NO ₃) ₂ = 100/5	100/1	50/1
	2MI/Zn(NO ₃) ₂ = 100/1	100/5	50/5
T_c	11	11	10
T_f	53	40	34
T_r	66	50	44

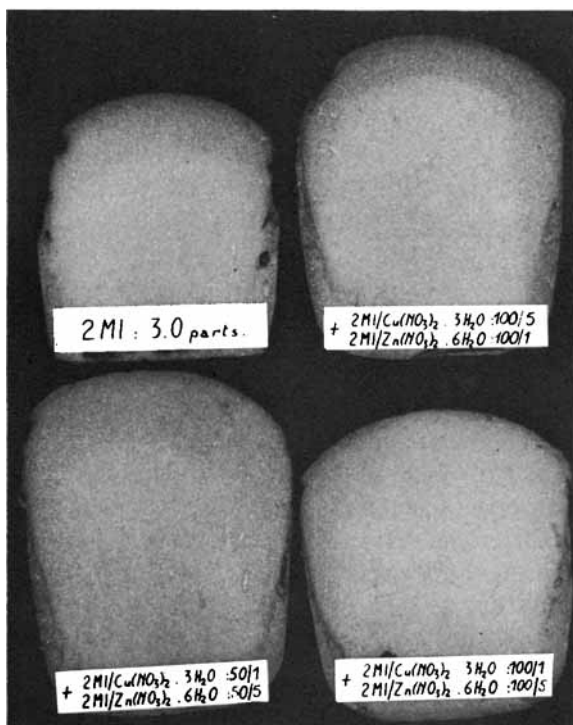


Fig. 13. Foams prepared from 3.0 parts 2MI and different combinations of both copper and zinc nitrates.

in copper nitrate; however, the combination based on (100/5) 2MI/Cu(NO₃)₂ and (100/1) 2MI/Zn(NO₃)₂ molar ratios seems to promote the best foam quality (Fig. 13). Table VII compares the results obtained with the latter formulation to those already mentioned for 2MI alone and combined successively to Cu(NO₃)₂ (100/5) and Zn(NO₃)₂ (100/1). Figure 14 shows the improvement of the foam texture when the two metal salts are combined together, although the role of Zn(NO₃)₂ is not evidenced by the kinetic results (columns A and A + B of Table VII).

Another parameter which can be modified in these catalytic systems is the type of amine. In particular, whereas it is impossible to obtain a satisfactory foam with 3.26 parts dimethylaminoethanol (DMAE), improvements are observed when some copper nitrate is added (Table VIII). Zinc nitrate, however, is less efficient in this case. Moreover, for a constant 30/1 DMAE/Cu(NO₃)₂ molar ratio, the amine and salt concentrations can be reduced down to 2.0 parts DMAE (Table IX).

TABLE VII
Effect of the Separate or Simultaneous Combination of Cu(NO₃)₂ and Zn(NO₃)₂ to 2MI

Foaming parameters, s	2MI	2MI/Cu(NO ₃) ₂ 100/5	2MI/Zn(NO ₃) ₂ = 100/1	A + B
	3.0 parts	A	B	
T_c	10	12	11	11
T_f	103	55	86	53
T_r	117	64	104	66

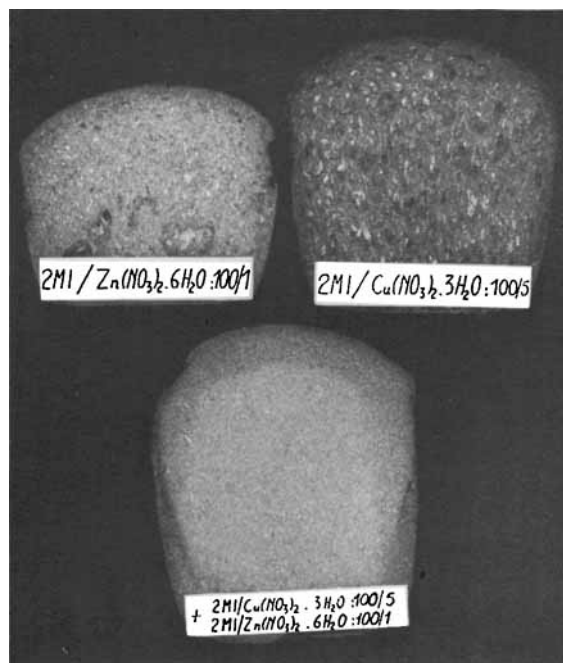


Fig. 14. Foams prepared from 3.0 parts 2MI added respectively with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ASR 100/1), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (ASR 100/5), and a combination of both copper and zinc nitrates in the same ASR.

CONCLUSION

Carbon dioxide evolution measurements as well as foaming tests have shown a synergistic effect between amines and metal salts in the catalysis of the isocyanate-water reaction. It is also evident that these new catalytic combinations offer a significant versatility in defining the most suitable formulations. A great number of parameters can be varied readily in order to bring about a broader control of the foaming process. Variation of the nature of the metal (Zn or Cu), of the anion (NO_3^- , Cl^- , and CN^- were tested), and of the amine (2MI, DMAE, or others) can be made in these formulations. The ratio between the amine and the metal salt exerts also a deep influence, whereas some combinations of both copper and zinc nitrates give very interesting textural improvements. It must be pointed out that the activity of a given metal salt is dependent on the amine

TABLE VIII
Effect of $\text{Cu}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$ Addition to 3.26 Parts Dimethylaminoethanol (DMAE)^a

Foaming parameters, s	DMAE 3.26 parts	DMAE/ $\text{Cu}(\text{NO}_3)_2$ 30/1 ^b	DMAE/ $\text{Zn}(\text{NO}_3)_2$ = 20/1 ^c
T_c	30	10	12
T_f	—	26	56
T_r	92 ^d	35	56 (d)

^a DMAE used in water and the metal salts in TCEP.

^b Very good foam, not at all friable.

^c Partial collapse and holes in the foam.

^d Poorly reliable value due to collapse.

TABLE IX
Reduction of DMAE and $\text{Cu}(\text{NO}_3)_2$ Concentrations at a Constant 30/1 DMAE/ $\text{Cu}(\text{NO}_3)_2$ Molar Ratio^a

Foaming parameters, s	DMAE 3.26 parts	DMAE 2.0 parts ^b	DMAE 1.5 parts
T_c	10	10	11
T_f	26	41	—
T_r	35	49	52 ^c

^a DMAE used in water and $\text{Cu}(\text{NO}_3)_2$ in TCEP.

^b Good and not friable foam.

^c Poorly reliable value due to collapse.

used, i.e., zinc salts give the best results when added to 2MI, whereas copper derivatives are the most active when combined to DMAE.

Of course, the formulations tested here are not exhaustive, our aim being only to show the effect of the amino complexes of zinc and copper salts in the production of polyurea foams. These new catalytic combinations are very attractive to accelerate the reaction while reducing the concentration of expensive amines and replacing a part of them by cheaper transition metal salts. In some cases, it seems even possible to reduce the total concentration of catalyst.

Further studies are in progress to elucidate the effect of metal salt-amine complexes upon the molecular mechanism of polyurea formation.

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