Literature Cited

Amerine, M. A.; Ough, C. S. "Wine and Must Analysis"; Wiley: New York, 1974; p 33.
A.O.A.C. "Official Methods of Analysis", 13th ed.; Association of Official Analytical Chemists: Washington, D.C., 1980; p 15.
A.P.H.A. "Standard Methods for the Examination of Dairy Products"; Marth, E. H., Ed.; 14th ed.; Washington, D.C., 1978; p 159.
Burgess, K. J.; Kelly, J. *Ir. J. Food Sci. Technol.* **1979**, *3*, 1.
Davis, J. C. *Chem. Eng.* **1972**, *79*, 114.
De Boer, R.; De Wit, J. N.; Hiddink, J. *J. Soc. Dairy Technol.* **1977**, *30*, 112.
Delaney, R. A. M. *Fm Food Res.* **1972**, *3*, 112.
Demott, B. J. *Food Prod. Dev.* **1972**, *24*, 86.
Douglas, H. C.; Pelroy, G. *Biochem. Biophys. Acta* **1963**, *68*, 155.
Engel, E. R. British Patent 669 894, 1952.
EPA. "Analysis of Operations and Maintenance Costs for Municipal Waste Water Treatment Systems"; U.S. Environmental Protection Agency: Washington, D.C., 1978; No. 430/9-77-105, 34.
Forsum, E.; Hambraeus, L. *J. Dairy Sci.* **1977**, *60*, 370.
Gaden, E. L., Jr. *Chem. Ind.* **1955**, 154.
Gawel, J.; Kosikowski, F. V. *J. Food Sci.* **1978**, *43*, 1417.
Gillies, M. T. "Whey Processing and Utilization—Economic and Technical Aspects"; Noyce Data Corpn.: 1974; 42.
Goudedranche, H.; Maubois, J. L.; Van Opstal, C.; Plot, M. *Rev. Lait. Fr.* **1976**, *No.345*, 521.
Hiddink, J.; DeBoer, R.; Nooy, P. F. C. *Zuivelzicht*. **1976**, *68*, 1126.
Humphreys, M. Proc. 50th Jubilee Conference, N.Z. Soc. Dairy Sci. and Technol., Palmerston North, New Zealand, 1977.
Kosikowski, F. V.; Wzorek, W. *J. Dairy Sci.* **1977**, *60*, 1982.
Mahmoud, M. M. Ph.D Thesis, Cornell University, Ithaca, NY, 1980.
Mallette, M. F. "Methods in Microbiology"; Norris, J. R., Ribbons, D. W., Ed.; Academic Press: London and New York, 1969; Vol. 1, p 521.

Mann, F. M. Proc. 50th Jubilee Conference, N.Z. Soc. Dairy Sci. Technol., Palmerston North, New Zealand, 1977.
Morr, C. V. *Food Technol*. **1976**, *30*, 18.
Moulin, G.; Guillaume, M.; Galzy, P. *Biotech. Bioeng*. **1980**, *22*, 1277.
Muller, L. L. *N.Z. J. Dairy Sci. Technol*. **1979**, *14*, 121.
Peters, M. S.; Timmerhaus, K. D. "Plant Design and Economics for Chemical Engineers"; McGraw-Hill: New York, 1968; pp 109, 572.
Stanier, R.; Adelberg, E. A.; Ingraham, J. "The Microbial World", 4th ed.; Prentice-Hall, Inc.: Englewood Cliffs, N.J., 1976; p 256.
Switzenbaum, M. S. Clarkson College of Technology, Potsdam, NY, 1981; private communication.
Vilbrandt, F. C.; Dryden, C. E. "Chemical Engineering Plant Design"; McGraw-Hill: New York, 1959; pp 194–248.
Walker, Y. Proceedings, 18th International Dairy Congress, 1970, 1E, 327.
Wingerd, W. H. *J. Dairy Sci*. **1971**, *52*, 1234.
Wingerd, W. H.; Saperstein, S.; Lutwak, L. *Food Technol*. **1972**, *24*, 758.
Yang, H. Y.; Bodyfelt, F. W.; Berggren, K. E.; Larson, P. K. Proceedings, 6th National Symposium on Food Process Wastes, U.S. Environmental Protection Agency: Washington, D.C., 1975; p 180.
Yoo, B. W.; Mattick, J. F. *J. Dairy Sci*. **1969**, *52*, 900.

Kinetic Equation for the Chloromethylation of Benzene with Trioxane and Hydrogen Chloride Using Zinc Chloride as a Catalyst

L. Gutiérrez Jodra, A. Romero Salvador, and V. Muñoz Andrés*

Dpto. de Físico-Química de los Procesos Industriales, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid-3, Spain

A reaction mechanism is proposed for the chloromethylation reaction of benzene with trioxane and hydrogen chloride using $ZnCl_2$ as a catalyst. The experimental data fit the following kinetic equation based on the proposed mechanism: $dC_P/dt = k_P C_C [1 - (C_A/C_{AMP})]$, where C_P is the concentration of benzyl chloride at time t, k_P is the specific rate constant for formation of benzyl chloride, C_C is the concentration of catalyst, zinc chloride, C_A is the concentration of water, and C_{AMP} is the maximum concentration of water permitting the catalytic formation of benzyl chloride.

Chloromethylation reactions can be carried out by use of formaldehyde (formalin) and its polymers (trioxane, paraformaldehyde) or chloromethylated compounds (mono- and dichloromethyl ethers). In most cases, it is assumed that molecules of two or more carbon atoms split to give a fragment containing a single carbon atom which reacts with the aromatic nucleus, introducing a chloromethyl group.

Formalin in an acid medium (Tepnetsina et al., 1967) and paraformaldehyde in an aqueous medium (Budniv et al., 1971; Shein et al., 1967; Farverov, 1968) have been used with a protonated acid as catalyst. In these conditions, the disappearance of formaldehyde is proportional to the reagent concentration (Llushim et at., 1971) and to the proton concentration (Mironov et al., 1970, 1971). The proposed reaction mechanism (Brown and Kelson, 1953; Mironov et al., 1966; Ogata and Okano, 1956) is based on the attack of the aromatic nucleus by the hydroxymethyl cation. The compound formed is the corresponding al-

cohol, which reacts in hydrochloric acid to give the chloromethyl derivative.

Studies carried out with metal halides as catalysts (Llushim et al., 1970) were based on results obtained with protonating acids. The hydroxymethyl cation or a protonated chloromethyl alcohol (Olah and Yu, 1975) have been proposed as intermediates.

On the other hand, formaldehyde derivatives may be also converted into dichloromethyl ethers. Thus, dichloromethyl ether has been obtained from paraformaldehyde, trioxane, or formalin using an acid catalyst (Buc, 1956, Matejiceek and Furacka, 1966; Kaska and Matejiceek, 1965; Frantisech et al., 1969; Alvarez and Rosen, 1976), dichloromethoxymethane from formaldehyde also using an acid catalyst (Head, 1963), and a mixture of both products on treating paraformaldehyde with hydrogen chloride (Stapp, 1969, 1970). These reactions have not been studied sufficiently and the intermediate compounds formed are unknown.

Due to the lack of data on the transformation of polymeric compounds of formaldehyde into chloromethyl ethers and on the mechanism of the formation of chloromethyl derivatives, it was decided that a study on a reaction system that produces the chloromethylation would be useful. In the kinetic study, we used benzene to avoid position isomers and a trioxane–hydrogen chloride mixture because it is soluble in the medium and does not give off water. $ZnCl_2$ was chosen as the catalyst because of its activity (Belenskii et al., 1971; Markridin et al., 1970).

Experimental Section

Equipment. The experiments were carried out in a thermostated semicontinuous stirred reaction, 20 cm high and 10 cm in diameter. The mixture of benzene, trioxane, and $ZnCl_2$ was placed in the reactor and HCl was continuously fed into it. The HCl gas was dried over $CaCl_2$ and $ZnCl_2$. A rotameter was used to measure the rate of flow of HCl gas.

Procedure. The reagents, benzene and trioxane, were charged to the reactor and HCl was introduced to saturate them. The gaseous feed was 0.3 mol/min. After a certain time, the catalyst was added, the gaseous feed reduced to 0.05 mol/min, and the run initiated.

The samples were analyzed in a Perkin-Elmer F 7 G.L. chromatograph equipped with a 15% phenylsilicone DC550 on Celite 545 column. The column was maintained at 70 °C for 8 min and then at 150 °C for the rest, with a nitrogen carrier gas flow rate of 24 cm³/min.

Results and Discussion

The results obtained in preliminary experiments were used to establish the following conditions for the remaining experiments: reagent volume, 500 cm³; stirrer speed, 2000 rpm; initial trioxane concentration, 0.25–1.5 mol/L; catalyst concentration, 14–40 g/L; temperature, 30–50·°C; HCl feed, 0.3 mol/min. Under these conditions, the gas supply did not affect the conversion to benzyl chloride if the reagents were previously saturated with HCl. The gas absorption decreased considerably 6 to 20 min after starting the experiments and the feed was reduced to 0.05 mol/min.

Influence of the Catalyst and Trioxane Concentration. Series of experiments were carried out at different temperatures varying the catalyst concentration in each series or the trioxane concentration. Some of these runs are described in Table I, indicating its experimental conditions and results obtained.

These results show the existence of an induction period in which dichloromethyl ether and water are produced, but not benzyl chloride. This period increases with decreasing catalyst concentration and increasing trioxane concentration.

After the induction period the yield of benzyl chloride decreases with increasing reagent concentration. On the contrary, the yield of dichloromethyl ether increases.

The concentration of dichloromethoxymethane is very low and constant in each experiment. Neither diphenylmethane nor bis-chloromethylbenzene were detected in significant amounts (≤0.002 mol/L).

Influence of Water. Since the water formed dissolves the catalyst, experiments have been carried out with the addition of different quantities of water at the start to demonstrate their influence on the process. The experimental conditions and the results obtained are given in Table II.

The results obtained show that the greater the quantity of water added, the greater is the decrease in formation rate, the yield of benzyl chloride, and the length of the induction period. In all the experiments the concentration

Table I. Dichloromethyl Ether, C_D, and Benzyl Chloride, C_P, Concentrations for Different Reaction Times

$T = 40°C$; $C_C = 24 g/L$

t, min	C_D, mol/L	C_P, mol/L	conditions
25	0.10	0.24	$t_0 = 5 min$; $C_{A_0} = 0 cm^3/L$; $C_{T_0} = 0.25 mol/L$
50	0.12	0.42	
75	0.08	0.51	
100	0.04	0.60	
150	—	0.68	
25	0.08	0.35	$t_0 = 5 min$; $C_{T_0} = 0.33 mol/L$
50	0.09	0.50	
75	0.10	0.60	
100	0.08	0.68	
150	0.05	0.74	
200	0.03	0.78	
25	0.23	0.15	$t_0 = 5 min$; $C_{T_0} = 0.50 mol/L$
50	0.32	0.26	
75	0.37	0.35	
100	0.40	0.41	
150	0.35	0.49	
200	0.32	0.56	
50	0.32	0.15	$t_0 = 5 min$; $C_{T_0} = 0.66 mol/L$
100	0.43	0.22	
150	0.56	0.27	
200	0.54	0.31	

$T = 40°C$; $C_C = 32 g/L$

t, min	C_D, mol/L	C_P, mol/L	conditions
25	0.08	0.45	$t_0 = 5 min$; $C_{A_0} = 0 cm^3/L$; $C_{T_0} = 0.33 mol/L$
50	0.05	0.70	
100	0.05	0.90	
150	0.02	0.96	
50	0.20	0.50	$t_0 = 5 min$; $C_{T_0} = 0.50 mol/L$
100	0.20	0.70	
150	0.20	0.85	
200	0.18	0.94	
250	0.15	0.99	
300	0.28	1.04	
25	0.39	0.18	$t_0 = 5 min$; $C_{T_0} = 0.66 mol/L$
50	0.45	0.36	
100	0.47	0.56	
150	0.47	0.68	
200	0.44	0.76	
250		0.83	

$T = 40°C$; $C_C = 40 g/L$; $C_{T_0} = 0.50 mol/L$

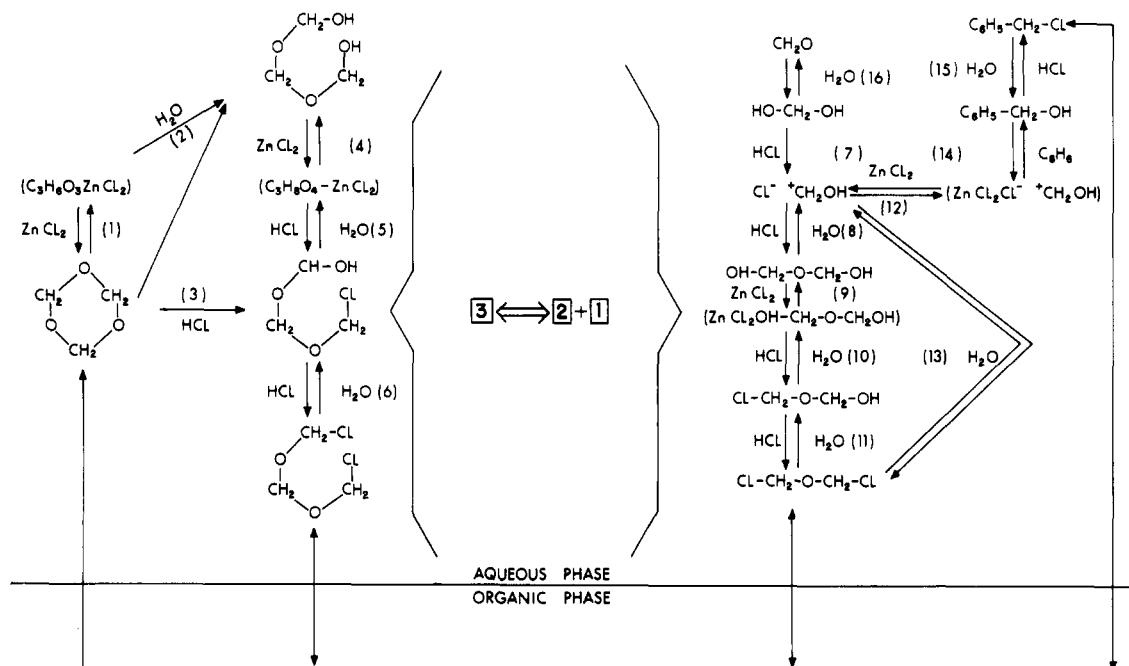| t, min	C_D, mol/L	C_P, mol/L	conditions
25	0.24	0.36	$t_0 = 2 min$; $C_{A_0} = 0 cm^3/L$
50	0.24	0.68	
100	0.24	1.02	
150	0.15	1.20	
250	0.08	1.35	
25	0.19	0.22	$t_0 = 5 min$; $C_{A_0} = 10 cm^3/L$
50	0.25	0.45	
100	0.36	0.66	
150	0.29	0.80	
200	0.24	0.90	
250	0.20	1.05	
25	0.22	0.10	$t_0 = 15 min$; $C_{A_0} = 14 cm^3/L$
50	0.31	0.24	
100	0.45	0.38	
150	0.42	0.44	
200	0.41	0.47	
300	0.37	0.55	
25	0.22	—	$t_0 = 50 min$; $C_{A_0} = 20 cm^3/L$
50	0.39	—	
100	0.54	0.06	
200	0.52	0.09	
250	0.51	0.11	

Figure 1. Reactions of the chloromethylation process: 3, compound of 3 carbon atoms; 2, compound of 2 carbon atoms; 1, compound of 1 carbon atom.

Table II. Maximum Water Concentration Permitting Catalysis of Benzyl Chloride Formation

temp, °C	C_C, g/L	C_{AMP}, g-mol H_2O/L
30	24	0.7
	32	1.1
	42	1.55
40	24	0.9
	32	1.3
	40	1.8
50	24	1.0
	32	1.7
	40	1.9

of dichloromethoxymethane is constant and has a practically negligible value.

It may also be observed that in the presence of a certain water concentration, benzyl chloride formation is prevented and this concentration depends on the catalyst concentration. This was confirmed by two experimental methods.

(a) Experiments were carried out over a sufficiently long period of time for the benzyl chloride concentration to remain constant. The amount of water produced in the reaction was obtained by comparison of the volume of the aqueous phase with the volume of catalyst solutions in hydrochloric acid of compositions similar to those in the experiment.

(b) Repeated experiments were carried out, with the addition of different volumes of water at the beginning of the experiment, until the measurement of the aqueous phase obtained in each experiment gave the minimum amount of water (added and produced in the reaction) preventing the formation of benzyl chloride.

The results obtained show the existence of a linear relationship between the amount of catalyst and the amount of water which inactivates the catalyst, C_{AMP}, the proportionality constant being 4.8, 5.0, and 6.7 mol of H_2O/mol of $ZnCl_2$ at temperatures of 30, 40, and 50 °C, respectively.

Nature of the Intermediate Compounds in the Different Synthesis. In order to ascertain the nature of the intermediate compounds in the different syntheses

the reaction of dichloromethoxymethane and dichloromethyl ether in concentrated hydrochloric acid with gaseous hydrogen chloride, in the presence or absence of $ZnCl_2$, was carried out. Dichloromethoxymethane and dichloromethyl ether are formed. These products were extracted with carbon tetrachloride. In the same way, trioxane and formaldehyde react to yield dichloromethoxymethane. When the reaction is prolonged for more than 20 min, dichloromethyl ether is also formed.

Taking into account the need of water for the conversion of dichloromethyl ether into benzyl chloride, it seems logical that it react similarly through the action of the water and hydrogen chloride and be transformed into a compound containing a single carbon atom, $^+CH_2OH$, $^+CH_2Cl$, and CH_2O are the possible structures.

The most characteristic bands of formaldehyde or methylene chloride do not appear in any spectra of the samples taken. Chloromethyl cation and chloride ion would form methylene chloride. Neither compound was obtained on treating methylene chloride with a catalyst in a benzene–water medium. Nevertheless, benzyl alcohol reacted with hydrochloric acid at high rates and without the need of a catalyst. It seems probable therefore that the carbon fragment is $^+CH_2OH$.

This has been confirmed by the addition of sodium hydroxide to the products obtained by treatment of the various reagent with hydrogen chloride in which paraformaldehyde is formed. These results could be explained by the following reaction.

$$n(^+CH_2OH) + n(OH^-) \rightarrow n(CH_2O-) + nH_2O$$
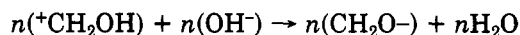
Hypothesis of the Reaction Mechanism

Based upon the experimental results and the empirical kinetic equations found (Jodra et al., 1977, 1978) for the formation of dichloromethyl ether and benzyl chloride, the mechanistic hypothesis shown in Figure 1 is proposed.

The trioxane is dissolved into the aqueous phase, forms a complex with the catalyst, and is converted into dihydroxymethoxymethane and hydroxymethoxy–chloromethoxymethane, respectively, by the action of the water, reaction 2, or of HCl, reaction 3, the ratio between them depending on the concentration of the catalyst.
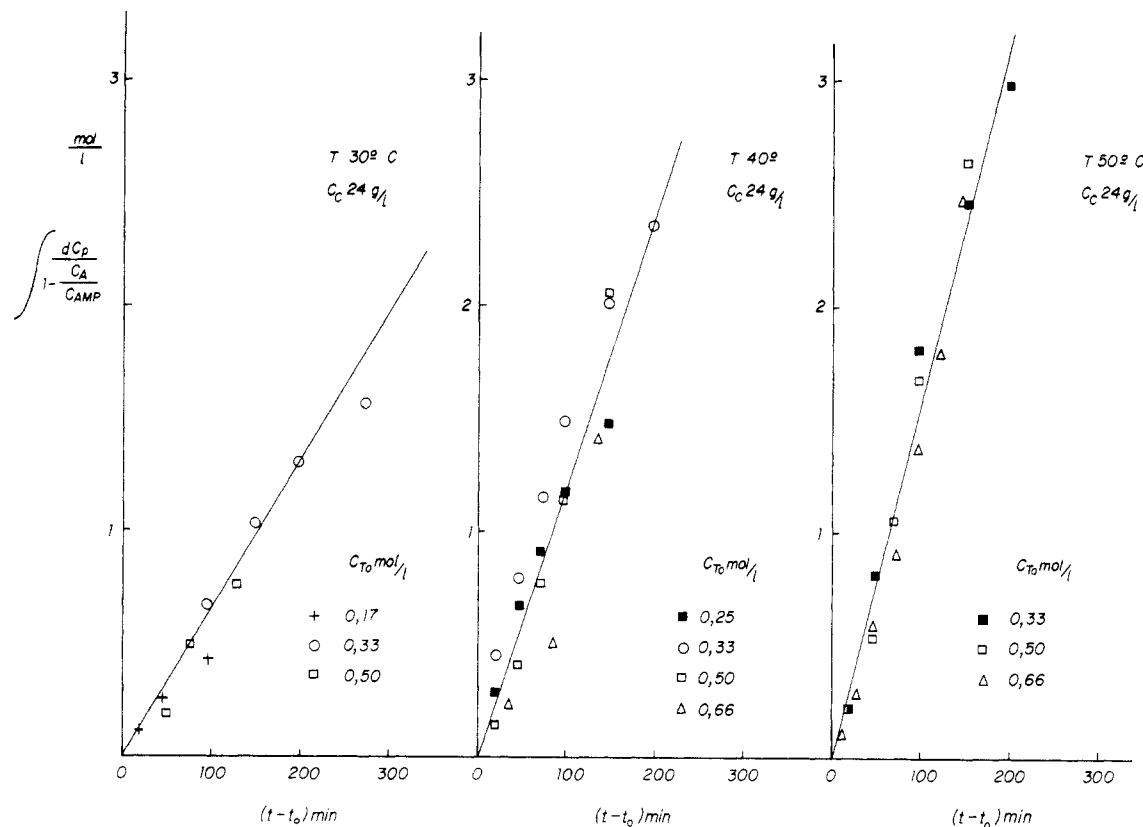
Figure 2. Plots of $k_r C_c$ values.

It has been experimentally observed (Jodra et al., 1978) that the concentration of dichloromethoxymethane remains constant during each experiment and is always low, increasing when the catalyst concentration decreases and the initial trioxane concentration and the amount of water added increase. This is justified by the existence of a catalyzed and an uncatalyzed reaction, both in the aqueous phase, in the reaction scheme.

The compound containing three carbon atoms, which only differ in their chloride content, may react with water or with HCl forming a single carbon and a two carbon atom fragments, whose possible structures are given in Figure 1. Dichloromethyl ether is obtained by successive reversible changes of the fragments and passes reversibly into the benzene phase, and the combination of $^+CH_2OH$ with benzene produces benzyl alcohol which reacts immediately with HCl to give benzyl chloride.

The transformation of $^+CH_2OH$ into benzyl alcohol and into dichloromethyl ether depends on the presence of the catalyst in these reactions, as at least the first reaction does not take place in its absence. From the fact that the final yield of dichloromethyl ether and benzyl chloride is greatly modified by the catalyst concentration, it may be deduced that the effects of the water in these reactions consists in the decrease of the catalyst–substrate complex concentration.

The induction period existing in the dichloromethyl ether formation (Jodra et al., 1978), increases with an increasing trioxane concentration or with the amount of water added at the beginning of the experiment and with a decreasing catalyst concentration. This compound is produced mainly from the $^+CH_2OH$ cation by reactions 8 to 11. Dihidroximethyl ether is produced in the first of these reactions and has remained undetected in all the experiments described. It could evolve according to reactions 8 and 9, as well as according the reversible reactions corresponding to the formation of the three carbon atom compound. If reaction 8 proceeds more quickly than re-

action 9, the $(ZnCl_2-HOCH_2-O-CH_2OH)$ complex will not be formed until an equilibrium (8) is reached, and thus dichloromethyl ether will not be formed.

As the final yield of dichloromethyl ether depends on the quantity of added or formed water and on the catalyst concentration, it may be deduced that both substances modify the "equilibrium". These results may be explained by consideration of the fact that reaction 8 is practically irreversible once the hydroxymethyl cation is stabilized with water. As the catalyst is water soluble, the $^+CH_2OH$ and the catalyst compete for it; thus, the higher the catalyst concentration, the lower the $^+CH_2OH$ concentration, the greater the yield of dichloromethyl ether and the shorter the induction period.

Once the maximum $^+CH_2OH$ concentration is reached, in absence of the catalyst, trioxane continues to disappear, the cation is converted into dichloromethyl ether by reaction 13, and into dichloromethoxymethane by the reactions shown in Figure 1, provided there is an excess of hydrogen chloride. If there is a deficit of hydrogen chloride, paraformaldehyde separates out, as it has been confirmed experimentally. The slow dissolution of dichloromethyl ether and dichloromethoxymethane in an acid medium without $ZnCl_2$ may be explained similarly.

For the above-mentioned reasons, the induction period of benzyl chloride should at least be the same as that of dichloromethyl ether. From the point at which the hydroxymethyl cation "equilibrium" concentrations are reached, the 1 and 2 carbon atom fragments formed from trioxane compete for the catalyst. It has been experimentally confirmed that the rate of benzyl chloride formation is lower than that of dichloromethyl ether, which indicates that reaction 9 is faster than reaction 12.

As dichloromethyl ether is formed from dihydroxymethyl ether, the water produced will retain the hydroxymethyl cation or the catalyst. Thus, when the catalyst:water ratio is large enough for the catalyst to accept part of the water formed, the difference between the in-
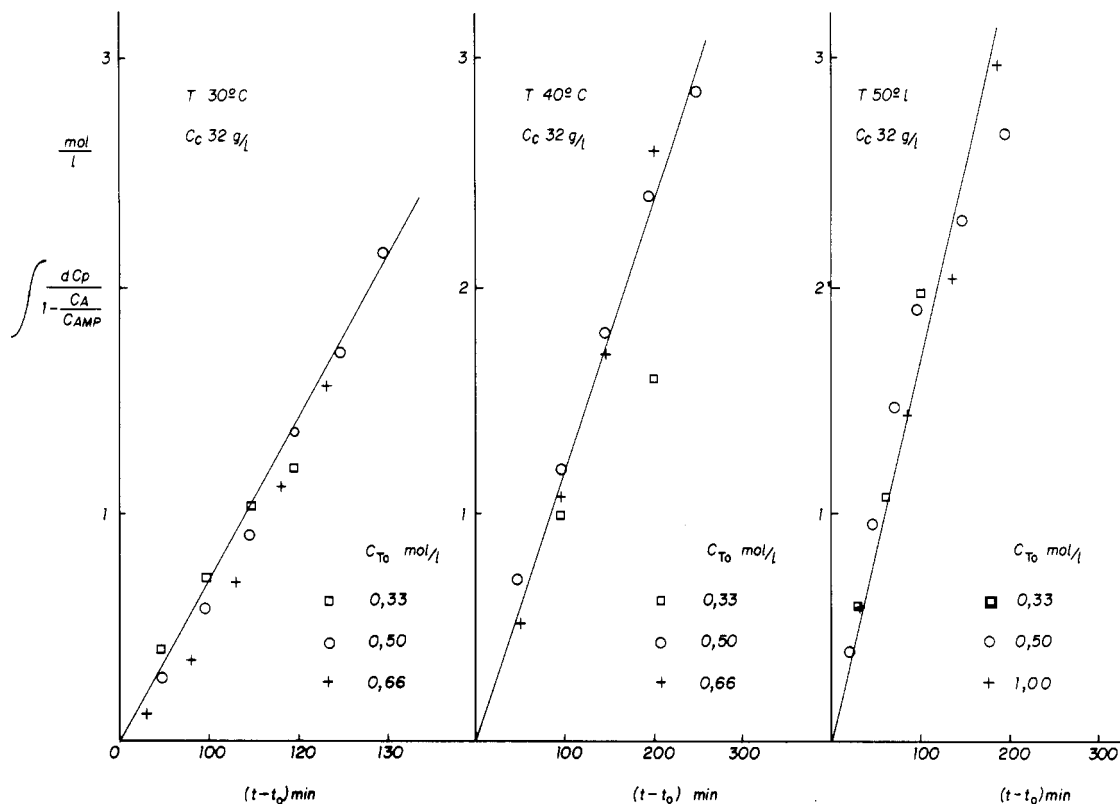
Figure 3. Plots of $k_r C_c$ values.

duction periods will be small. On the contrary, if the ratio is low, the amount of $^+CH_2OH$ which can form the ($ZnCl_2Cl^-$ $^+CH_2OH$) complex will be very low and the benzyl chloride induction period may be much longer than that of dichloromethyl ether.

When formalin is used without a catalyst, dichloromethoxymethane is first extracted with CCl_4 and if the reaction is prolonged, dichloromethyl ether is obtained. For that the formaldehyde must probably be transformed according to the reactions 16 and 7 to give the hydroxymethyl cation which then gives dihydroxymethyl ether, which then reacts to give dichloromethoxymethane. If hydrogen chloride has been bubbled through long enough, the equilibria are shifted toward the formation of dichloromethyl ether and this compound is extracted.

Benzyl Chloride Formation. According to the proposed scheme, the rate of benzyl chloride formation will be proportional to the rate of formation of the complex, i.e., to the $^+CH_2OH$ concentration not stabilized by water.

The hydroxymethyl cation is stabilized in water, forms a complex with the catalyst, or proceeds to form one of the reaction compounds, as paraformaldehyde was not formed in any of the experiments. Thus, once the induction period has elapsed, and if the C_C/C_{T_0} ratio is not too high, the concentration of hydroxymethyl cation not stabilized by water will be equal to the concentration of free active centres. Thus

$$\frac{dC_P}{dt} = k_1 C_1 C_C \tag{1}$$

$$C_1 = \text{no. of free active centers/g of catalyst} \tag{2}$$

$$C_0 = \text{g of catalyst}/V \tag{3}$$

The concentration of free active centers will be equal to the total number of active centers less the number of occupied active centers.

$$C_1 = C_L - C_0 \tag{4}$$

and the concentration of occupied centers will be proportional to the concentration of water not retained by the hydroxymethyl cation.

$$C_0 = k_2(C_A - k_3 C_H) \tag{5}$$

$$C_H = k_4 C_A \tag{6}$$

$$C_0 = k_5 C_A \tag{7}$$

substituting

$$dC_P/dt = k_1 C_C (C_L - k_5 C_A) \tag{8}$$

When the rate of formation of benzyl chloride is zero

$$C_L/k_5 = C_{AMP} \tag{9}$$

Then

$$\frac{dC_P}{dt} = k_1 C_C C_L (1 - C_A/C_{AMP}) \tag{10}$$

In each experiment

$$C_A = C_{A_0} + C_D + C_R + C_P \tag{11}$$

Thus

$$\frac{dC_P}{dt} = k_r C_C \left[1 - \frac{C_{A_0} + C_D + C_R + C_P}{C_{AMP}} \right] \tag{12}$$

and therefore

$$\int_0^{C_P} dC_P / \left[1 - \frac{C_{A_0} + C_D + C_R + C_P}{C_{AMP}} \right] = k_r C_C (t - t_0) \tag{13}$$

t_0 is the induction time for benzyl chloride.

The first part of the integral in eq 13 was repeatedly calculated using data which corresponded to experiments carried out at the same temperature and catalyst concentration, with the initial trioxane concentration and the quantity of added water as variables. the values of the integral and the reduced times corresponding to first-order
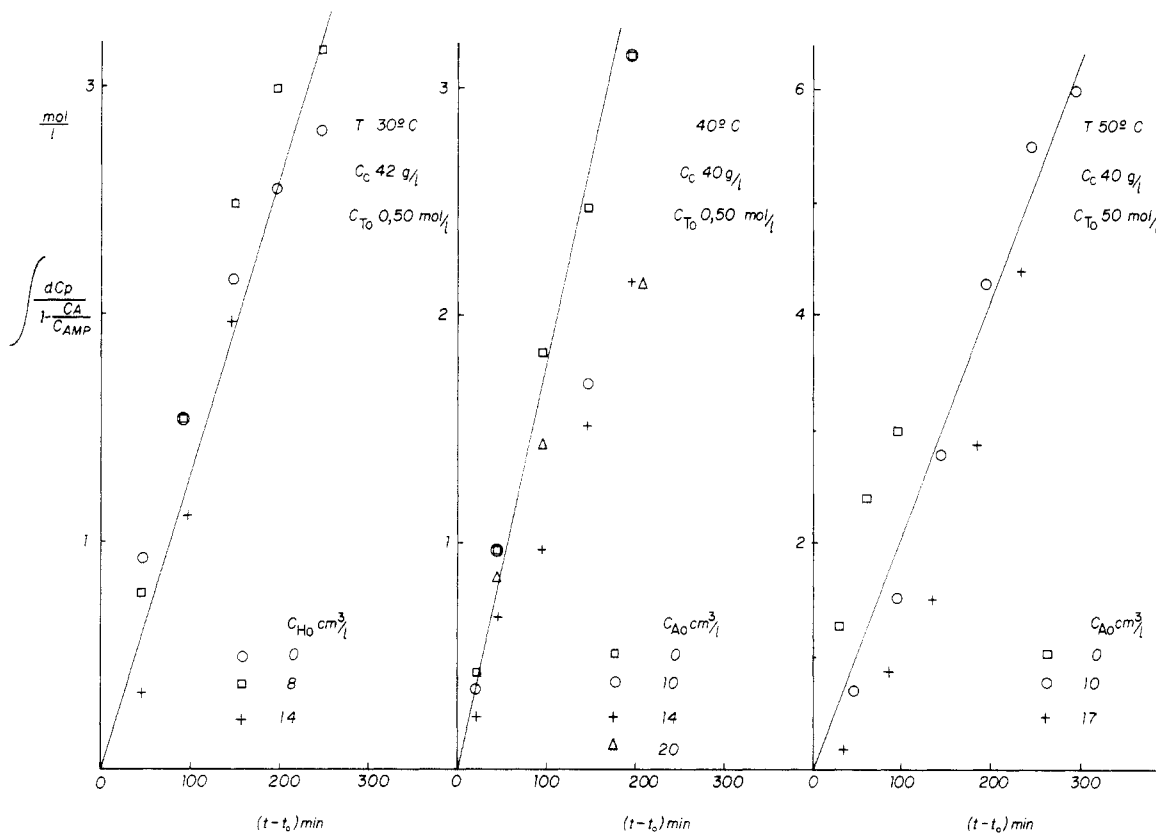
Figure 4. Plots of $k_r C_c$ values.
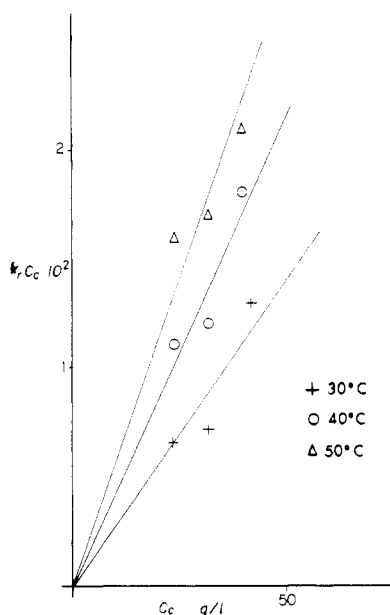
Figure 5. Plots of k_r values.

equations passing through the origin of the coordinates were adjusted (Figures 2, 3, and 4). The values of the specific rate constant at 30, 40, and 50 °C, shown in Table III, were obtained by adjusting the values of the slopes and the corresponding catalyst concentration to first-order equations (Figure 5).

By applying the Arrhenius equation, the specific rate constants permit the calculation of the apparent activation energy and the preexponential factor: $E = 6.6$ kcal/mol and $k_0 = 16$ mol/g of cat. min. Thus, the equation for the rate of formation of benzyl chloride is

$$\frac{dC_P}{dt} = 16 C_C \frac{C_{AMP} - C_A}{C_{AMP}} \exp(-6.6/RT)$$

Table III. Specific Rate Constants

temp, °C	$k_r \times 10^3$, (g-mol)(g of cat.)$^{-1}$(min)$^{-1}$
30	0.28
40	0.43
50	0.55

Nomenclature

C_i = concentration of compound i, mol of reagent/L
C_{i_0} = concentration of compound i at zero time, mol of reagent/L
C_{AMP} = maximum concentration of water permitting catalyst action for benzyl chloride formation, cm^3/L
t = time, min
t_0 = induction time for benzyl chloride formation, min
V = total reagent volume

Subscripts

A = water
B = benzene
C = catalyst
DOH = dihydroximethyl ether
D = dichloromethyl ether
H = hydroxymethyl cation
L = total number of active centers of catalyst
1 = free active centers of catalyst
O = occupied active centers of catalyst
P = benzyl chloride
R = dichloromethoxy methane
T = trioxane

Literature Cited

Alvarez, M.; Rosen, R. T. *Int. J. Environ. Anal. Chem.* **1976**, *4*, 241–5.
Belenskii, L. I.; Karmanova, I. B.; Kenshtein, Y. B. *Izv. Akad. Nauk. S.S.S.R. Ser. Khim.* **1971**, *5*, 956–63.
Brown, H. C.; Kelson, J. W. *J. Am. Chem. Soc.* **1953**, *75*, 6292–99.
Buc, S. R. "Organic Synthesis"; Vol. 36, Leonard, N. J., Ed.; Wiley: New York, 1956; p 1.
Budniv, I. V.; Mironov, G. S.; Farverov, N. I.; Zhukova, A. I. *Uch. Zap. Yarosl. Tekhnol. Inst.* **1971**, *27*, 70–7.
Farverov, M. I. URRS Patent 216693, 1968.
Frantiseck, J.; Metejiceek, A.; Kaska, J. Czech Patent 133269, 1969.

Head, F. M. *J. Chem. Soc.* **1963**, 2972–76.
Jodra, L. G.; Romero, A.; Muñoz, V. *An. R. Soc. Esp. Fis. Quin.* **1977**, *73*, 1485–92.
Jodra, L. G.; Romero, A.; Muñoz, V. *An. R. Soc. Esp. Fis. Quim.* **1978**, *74*, 121.
Kaska, J.; Matejiceek, A. Czech Patent 114 453, 1965.
Liushim, M. M.; Mekhtiev, S. D.; Guseiniva, S. M. *Zh. Org. Khim.* **1970**, *6*, 1432–34.
Liushim, M. M.; Makhtiev, S. D.; Guseinova, S. A. *Neftekhimiya* **1971**, *11*, 92–94.
Markridin, V. P.; Esipov, G. Z.; Filipov, N. D.; Landoya, V. V. *Sb. Nauch Tr. Zuzbas. Politechk. Inst.* **1970**, *26*, 206–7.
Matejiceek, A.; Furacka, F. Czech Patent 117 267, 1966.
Mironov, G. S.; Farverov, M. I.; Stein, S. D.; Bespalova, I. I. *Zh. Org. Khim.* **1966**, *2*, 1639–44.
Mironov, G. S.; Budnii, I. V.; Farverov, M. I.; Stein, V. D. *Zh. Org. Khim.* **1970**, *6*, 1224–26.

Mironov, G. S.; Farverov, M. I.; Budnii, I. V. Stein, V. D. *Uch. Zap. Yarosl. Tecknol. Inst.* **1971**, *26*, 21–7.
Mironov, G. S.; Stein, V. D.; Farverov, M. Y. *Uch. Zap. Yarosl. Technol. Inst.* **1971**, *22*, 115.
Ogata, O.; Okano, M. *J. Am. Chem. Soc.* **1956**, *78*, 5423–25.
Olah, G. A.; Yu, S. M. *J. Am. Chem. Soc.* **1975**, *97*, 2293–95.
Shein, D. V.; Mironov, G. S.; Farverov, M. I. *Zh. Prikl. Khim.* **1967**, *40*, 2006–14.
Stapp, R. P. *J. Org. Chem.* **1969**, *34*, 1143–43.
Stapp, R. P. U.S. Patent 3 488 393, 1970.
Tepnetsina, F. P.; Farverov, M. I.; Ivanovskii, A. P. *Zh. Prikl. Khim.* **1967**, *40*, 2540–6.

Organic Fillers by Anionic Dispersion Polymerization

James G. Murray* and Frederick C. Schwab

Mobil Chemical Company, Research & Development Laboratory, Edison, New Jersey 08817

Styrene–divinylbenzene mixtures were anionically polymerized in the presence of block polymeric dispersing agents in aliphatic hydrocarbons. Cross-linked fine particles with sizes as small as several hundred angstroms could be readily prepared by this technique. By suitable control of reaction variables, either isolated particles or structured agglomerates were formed. The latter agglomerates were efficient thickeners for hydrocarbon liquids and appeared to maintain their integrity even under high shear conditions. The living nature of the anionic polymerization permitted the introduction of various functional groups on the polymer chain ends in the particle. This functionality was useful in modifying the properties of the particles. For example, colored pigments, water dispersible materials, and highly reinforcing fillers for SBR rubber were produced by the appropriate choice of functionality.

Introduction

Anionic dispersion polymerization in hydrocarbons is a simple and versatile procedure (Barrett, 1975; Schwab, 1973). The present studies were stimulated by previous work in this laboratory in which a thermally and shear stable grease was formed by the anionic polymerization of styrene–divinylbenzene mixtures in motor oil containing a block copolymer dispersant (Heilweil and Schwab, 1974). This formation of a thermally and shear stable grease structure suggested that stable agglomerates of very fine cross-linked particles were formed in this polymerization and that by a similar polymerization in low boiling hydrocarbons, organic filler materials with unique properties could be isolated.

In this work it was found that under suitable polymerization conditions highly cross-linked (and therefore nonfusing and nonmelting) particles are readily formed using AB block polymers as dispersants (Figure 1). The reactions are simple to carry out (when air and moisture are excluded), and yields can be made quantitative; particles as small as a few hundred angstroms can be prepared. Furthermore, the terminal groups in the polymerization are "living" polymer anions. The reaction products are therefore ideally suited to modification of the chemical and physical character of the particle by a secondary reaction at these living polymer sites. It was also observed that the polymerization reaction can be controlled to produce largely isolated particles or to produce "structured" agglomerates of many particles. These structured agglomerates maintained their integrity under severe conditions

of temperature and shear. The utility of this chemistry in the formation of a variety of types of filler materials has been investigated and its application in a few specific situations has been studied.

Experimental Section. Typical Preparative Examples

A. Preparation of a High Structure Fine Particle Product. In a 3-L flask was placed 2 L of hexane and 6 g of 80:20 isoprene–styrene dispersant of 100 000 molecular weight and the mixture was stirred until dissolved. A small amount of styrene was added and *sec*-butyllithium was added dropwise until the orange color of the styryl anion persisted. An additional 125.6 mL of styrene and 13 mL of 55% divinylbenzene was then added together with 6 g of 10 000 mol wt polyisoprenyllithium dissolved in hexane. The reaction was initiated by the addition of 6.3 mL of 1.2 N *sec*-butyllithium. The mixture was stirred for 2.25 h and the temperature was increased from 32 to 54 °C with some warming at the end of the reaction.

The thick reaction mixture was treated by the addition of 0.5 mL of methanol followed by 1 mL of acetic acid. The product (129 g) consisted of structured agglomerates having individual particles generally less than 500 Å in size.

B. Preparation of a Low Structure Fine Particle Product. In a 12-L reaction flask maintained under an anhydrous nitrogen atmosphere was placed 8.8 L of hexane, 52.8 g of 80:20 wt % *tert*-butylstyrene–styrene dispersant of 100 000 molecular weight and 52.8 g of paraffin wax (to aid in redispersion), and the mixture was stirred until dissolved.