TABLE IV

Compd.	Yield, %	B.p., °C. (mm.)	Formula	Calcd., % C	H	N	Found, % C	H	N	Picrate[a] m.p., °C.
Va	91	58–58.5[b]	$C_{14}H_{14}ClN$	72.57	6.09	6.04	72.44	6.12	6.09	
Vb	92	133–134 (0.15)	$C_{16}H_{16}ClN$	74.56	6.26	5.43	74.63	6.29	5.38	94.5
Vc	90	127–128 (0.15)	$C_{17}H_{18}ClN$	75.13	6.67	5.15	75.21	6.69	5.00	144–145
VIa	71,[c] 85[d]	105–106 (0.15)	$C_{14}H_{17}N$	84.37	8.60	7.03	84.49	8.68	7.01	181–182
VIb	70,[c] 90[d]	136–137 (0.2)	$C_{16}H_{21}N$	84.53	9.31	6.16	84.59	9.50	6.08	146–147
VIc	63,[c] 85[d]	126–127 (0.15)	$C_{17}H_{23}N$	84.59	9.61	5.80	84.62	9.68	5.83	150–151

[a] All of the picrates were crystallized from ethanol and had elemental analyses in agreement with theory. [b] Melting point (crystallized from dilute ethanol). [c] Yield in method A. [d] Yield in method B.

benzene-soluble portion on alumina gave a few per cent yield of the cyclization product (IVa, IVb, or IVc). The N-allyl compound (IIIa, IIIb, or IIIc) was not detected.

Attempted Equilibration of the N-Allyl Compounds (IIIa–c).—A 500-mg. sample of each of the N-allyl compounds was heated without solvent at 200° for 30 min. Chromatography of the reaction mixture on alumina resulted in the recovery of an almost quantitative amount of the unaltered compound. Column and thin layer chromatographies showed that the C-allyl compounds and the cyclization compounds were absent in the reaction mixture.

Acknowledgment.—The author is grateful to Professor E. Ochiai, Dr. K. Takeda, and Dr. H. Kano, for their encouragement.

Species in the Polymerization of Ethylenimine and N-Methylethylenimine

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The polymerization of ethylenimine was studied by the use of N,N-diethylethylenimmonium chloride as a model electrophilic reagent and various amines and imines as models for the nucleophiles involved. A high level of branching is indicated. N-Methylethylenimine was used as a model for the active end group. The polymerization of N-methylethylenimine in water is very rapid but stops short of completion because of a pseudo-first-order termination reaction. In aqueous ethanol polymerization is faster but termination earlier. There is a positive salt effect.

The polymerization of ethylenimine has three known kinetic main features. The rate slows markedly with increasing conversion, the polymerization goes eventually to completion, and there is a delicate balance in concentrated solution between explosive and sedate polymerization.[1] Kern and Brenneisen[2] showed that benzoylation of polyethylenimine is incomplete and deduced the presence of 20 to 30% tertiary nitrogen in the polymer. Konnecke[3] relied on Van Slyke analyses to prove branching. Barb[4] applied to ethylenimine the Flory condensation treatment which predicts the formation of dimer as a major intermediate and proposed a head-to-head reaction of dimer as a branching mechanism which would form quaternary ethylenimmonium ions. Similar ions were detected in the hydrolysis of nitrogen mustards by Golumbic, Fruton, and Bergmann.[5] Bartlett, Ross, and Swain[6] showed that diethyl-β-chloroethylamine cyclized completely before undergoing further reaction (at a concentration of 1 *N*). Methylbis-β-chloroethylamine was used by Gurin, Crandall, and Delluva[7] to rate the reactivity of various amines. Earley, *et al.*,[8] found protonated ethylenimine to be nearly twice as reactive to strong nucleophiles as protonated N-butylethylenimine but by no means so reactive as Bartlett, Ross, and Swain[6] had found N,N-diethylethylenimmonium ion to be.

The purpose of the present investigation was to simulate the kinetics of polymerization of ethylenimine and N-methylethylenimine. The intent was to confirm the degree of branching, to show the relative importance of several branching mechanisms, and to discover, if possible, a means of control of branching. Experiments with model compounds were done to obtain the desired individual rate constants.

The representation of the polymerization of ethylenimine is complicated by the probable participation of three electrophilic and five nucleophilic species. Those involved in acid-catalyzed polymerization are given below. If an alkylating agent is used to initiate polymerization, further species are added. The quaternary immonium species III would result from the attack of V on any of the electrophiles, a reaction which may be described as "head-to-head" polymerization. A branched polymer (VIII) would result either from a reaction of III or from the attack of a mid-chain nitrogen (VII) upon any of the electrophiles. The quaternary IX is that branched polymer which results from reactions of VIII. There are therefore two distinct causes of branching: the head-to-head reaction and reactions of VII and VIII.

The data to be simulated is not the over-all conversion rate which is insensitive to the individual simultaneous reactions. Rather, it is the analytically determined degree of branching and the general kinetic

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[1] G. D. Jones, A. N. Langsjoen, M. M. C. Neuman, and J. L. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).

[2] W. Kern and E. Brenneisen, *J. prakt. Chem.*, **159**, 193 (1941).

[3] H. G. Konnecke and M. Heise, *ibid.*, **9**, 232 (1959); E. Leibnitz, H. G. Konnecke, and G. Gawalek, *ibid.*, **6**, 289 (1958).

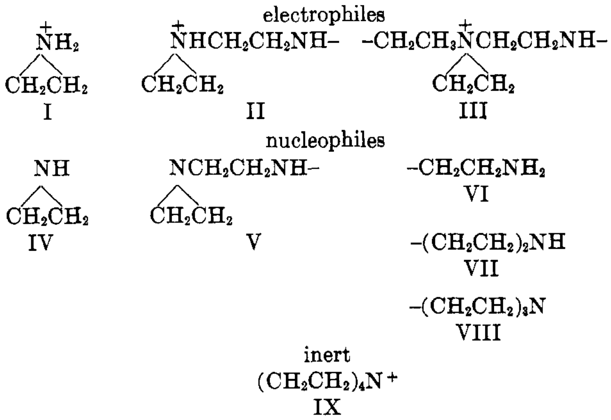
[4] W. G. Barb, *J. Chem. Soc.*, 2564, 2577 (1955).

[5] C. Golumbic, J. S. Fruton, and M. Bergmann, *J. Org. Chem.*, **11**, 518 (1946).

[6] P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947); **71**, 1415 (1949).

[7] S. Gurin, D. I. Crandall, and A. M. Delluva, *J. Org. Chem.*, **12**, 612 (1947).

[8] J. E. Earley, C. E. O'Rourke, L. B. Clapp, J. O. Edwards, and B. C. Lawes, *J. Am. Chem. Soc.*, **80**, 3458 (1958).



$$\begin{array}{lll}
1.\ \mathrm{IV} + & \left[\begin{array}{c} \\ \mathrm{I} \xrightarrow{a} \mathrm{VI} \\ \\ \mathrm{II} \xrightarrow{b} \mathrm{VII} \\ \\ \mathrm{III} \xrightarrow{c} \mathrm{VIII} \end{array}\right] & + \mathrm{V} + \mathrm{H}^+ \\
2.\ \mathrm{V} + & & + \mathrm{III} \\
3\ \ \mathrm{VI} + & & + \mathrm{VII} + \mathrm{H}^+ \\
4.\ \mathrm{VII} + & & + \mathrm{VIII} + \mathrm{H}^+ \\
5.\ \mathrm{VIII} + & & + \mathrm{IX}
\end{array}$$

features known previously. The relative importance of the different branching reactions is made visible in the simulation and rests on the model compound data. In the case of N-methylethylenimine a rapid termination reaction, which is also a branching reaction, occurs. The data which is simulated in this case is that of final conversion as a function of initial ratio of catalyst to imine. Such a reaction must also occur in the polymerization of ethylenimine because of the participation of V.

Experiments with model nucleophiles were done using N,N-diethylethylenimmonium chloride (X) as the electrophile (Table I). The electrophile solution was free of diethyl-β-chloroethylamine and stable for days under the conditions used. As models for species VI, VII, and VIII, mono-, di-, and triethylamines were used, correction being made for the inductive effect of nitrogen in the β-position in species VI, VII, and VIII (Table II). That this correction amounts to a twofold factor/β-nitrogen is indicated by the fact that the rate constant/nitrogen in the case of ethylenediamine was nearly one-half that of ethylamine; likewise that of tetramethylethylenediamine was half that of ethyldimethylamine. N-2-Hydroxyethylethylenimine was used as a model for V. In this case the concentration and ratio of reactants was selected to permit the estimation of the rate of the first step of a polymerization process (*cf.* Figure 1). A similar experiment with N-methylethylenimine is shown as Figure 2. There was a positive salt effect; the rate constant chosen was that in 0.2 *M* chloride ion concentration.

The experiment with model compounds gave additional information. A comparison of the rate constants of tetramethylethylenediamine (per nitrogen) and of

Table I

Summary of Rate Constants.
N,N-Diethylethylenimmonium Substrate (30°, 0.3 *M* Cl^-)

Nucleophile	pK_b	k, l. mole^{-1} sec.$^{-1}$ (× 10^2)	σ_{av}	No. of expt.
H_2O		0.00000100	0.00000002	3
OH^-		0.102	0.001_3	3
$S_2O_3^{-2}$		10.8		2
Et_3N	3.24	0.25	0.01	2
$EtNMe_2$		3.67		
Me_3N	4.26	12.0	0.13	3
Et_2NH	3.02	0.862 1.09[a]	0.004	3
Et_2NMe		1.14 1.25[a]		
Me_2NH	3.28	4.4		
$EtNH_2$	3.25	0.75		
$HOCH_2CH_2NH_2$		0.44		
$Me_2NCH_2CH_2NMe_2$	3.29	1.75[b]	0.07	2
$Me_2NCH_2CH_2NMeH$		1.08[b,c]		
$H_2NCH_2CH_2NH_2$	4.07	0.34[b]	0.013	3
$Me_2NCH_2CH_2NMe_3{}^+Cl^-$	8.0	0.26		
$HNCH_2CH_2$	6.0	0.16		
$MeNCH_2CH_2$	6.0	0.73[d] 1.63[e]	0.02	2
$HOCH_2CH_2NCH_2CH_2$		0.22[d] 0.36[a]		

[a] In 2.0 *M* Cl^-. [b] 1 equiv.$^{-1}$ sec.$^{-1}$. [c] Average value/N for the two kinds of N. [d] From initial rate in 0.2 *M* Cl^-. [e] From initial rates in 0.5 *M* Cl^-.

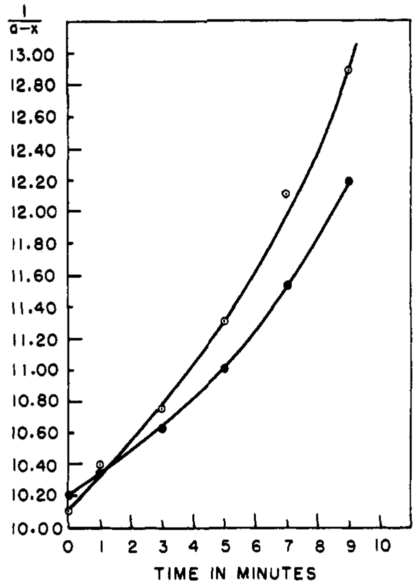


Figure 1.—Initial reaction of tertiary imines with X; N-(2-hydroxyethyl)ethylenimine (0.1 *M*) and X (0.1 *M*) treated in presence of sodium chloride: ⊙, 0.4 *M*; ●, 0.2 *M*.

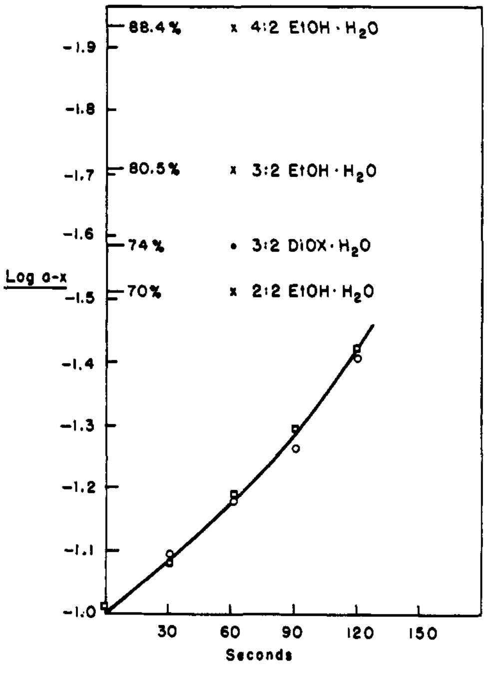


Figure 2.—Initial reaction of tertiary imines with X; N-methylethylenimine (0.1 *M*) and X (0.4 *M*) in presence of 0.2 *M* sodium chloride in water (curve) and mixed solvents (single points).

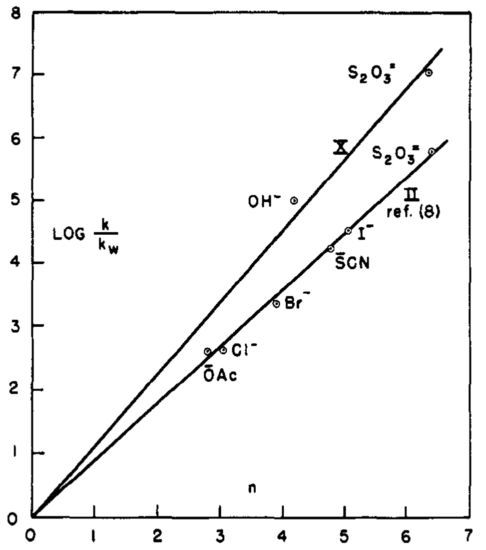


Figure 3.—Electrophilicity comparison of X and II with various nucleophiles.

Table II

Predicted Reactivities of Nucleophiles

Species	Model compd.	Inductive factor	Predicted 10^2k	Ratio
IV	C_2H_4NH		0.16	1
V	$HOC_2H_4NC_2H_4$		0.22	1.4
VI	$C_2H_5NH_2$	$^1/_2$	0.35	2.2
VII	$(C_2H_5)_2NH$	$^1/_4$	0.21	1.3
VIII	$(C_2H_5)_3N$	$^1/_8$	0.031	0.19

pentamethylethylenediammonium ion shows that the inductive factor is increased from 2 to 7 by placing a positive charge on a nitrogen in the β-position. Furthermore a rate constant could be estimated for the reactivity of the product obtained from triethylamine, namely pentaethylethylenediammonium ion. This rate constant was $^1/_{25}$ that of triethylamine, whereas a value $^1/_7$ as great would have been expected from inductive effect alone. The significance of a steric effect indicated in this case is raised again in connection with the reactivity of species VIII.

One must take into account differences in the reactivity of the electrophiles. The relevance of the data of Table I to reaction with electrophiles I and II depends upon the assumption of comparable discrimination of nucleophiles. The s value of Swain and Scott[9] is 0.89 for both ethylenimine and N-ethylethylenimine according to the data of Earley, *et al.*[8] The s value for N,N-diethylethylenimmonium ion is 1.1 based on reaction rate with thiosulfate (Figure 3). The hydroxide reaction seems normal, being first order in each reactant and somewhat slower than the reaction with amines, but has an n value of 4.5 instead of 4.2. The reactivity of III would be slightly higher because of an inductive effect of nitrogen (small relative to that of chlorine shown by Bartlett, Ross, and Swain[6]). The reactivity of III is thus an order of magnitude higher than that of the protonated imines.

The preparation of the benzamide of polyethylenimine was reinvestigated and the results were essentially the same as those of Kern and Brenneisen.[2]

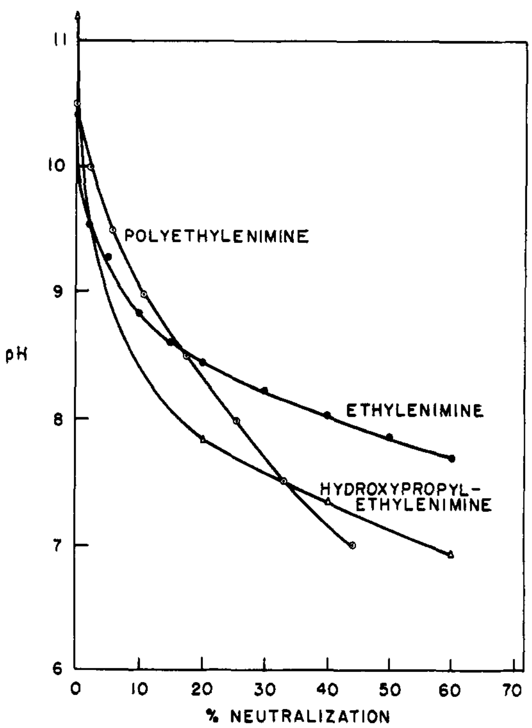
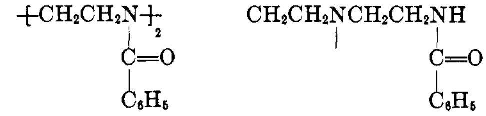


Figure 4.—Titration of polyethylenimine and imine monomers.

Benzoylation of polyethylenimine by the Schotten–Bauman method results in the precipitation of a gummy product containing free benzoic acid. In previous work chloroform was added during benzoylation to dissolve the product; however, the use of chloroform was found to give a product containing excess chlorine and was omitted. The gummy product was purified by refluxing with aqueous sodium carbonate and was unchanged by repeated benzoylation. Treatment with alcoholic sodium hydroxide produced hydrolysis and indication of prior dibenzamide content. The elemental composition, infrared absorption, and content of titratable base agreed roughly with a molar composition made up of two tertiary amides, one primary amide, and one tertiary amino group. For estimation of primary amide content the absorption at 6.6 μ due to in-plane H deformation had to be corrected for the absorption at 6.7 μ due to asymmetric methylene bending in the tertiary amide structure.



$$\left[\!\!\begin{array}{c}CH_2CH_2N\\ |\\ C{=}O\\ |\\ C_6H_5\end{array}\!\!\right]_2 \qquad \begin{array}{c}CH_2CH_2NCH_2CH_2NH\\ \qquad\qquad\qquad |\\ \qquad\qquad\qquad C{=}O\\ \qquad\qquad\qquad |\\ \qquad\qquad\qquad C_6H_5\end{array}$$

A further piece of structural evidence was obtained by passing the polyethylenimine through a Dowex 1 (OH) column and titrating for any quaternary base. Less than 1%, if any, of the nitrogen was in this form, despite the fact that for this test the polymer was made with a large (10 mole %) amount of catalyst in order to increase the yield of species IX.

Simulation.—The regeneration of species I and II by proton exchange was handled as shown for simulation. The titration curves for monomer and polymer are shown in Figure 4. The basicity of V is reduced nearly fourfold from that of IV by the inductive effect. At very low conversion the effective K_a of polymer is larger than the value used below, but the effect on prod-

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(9) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

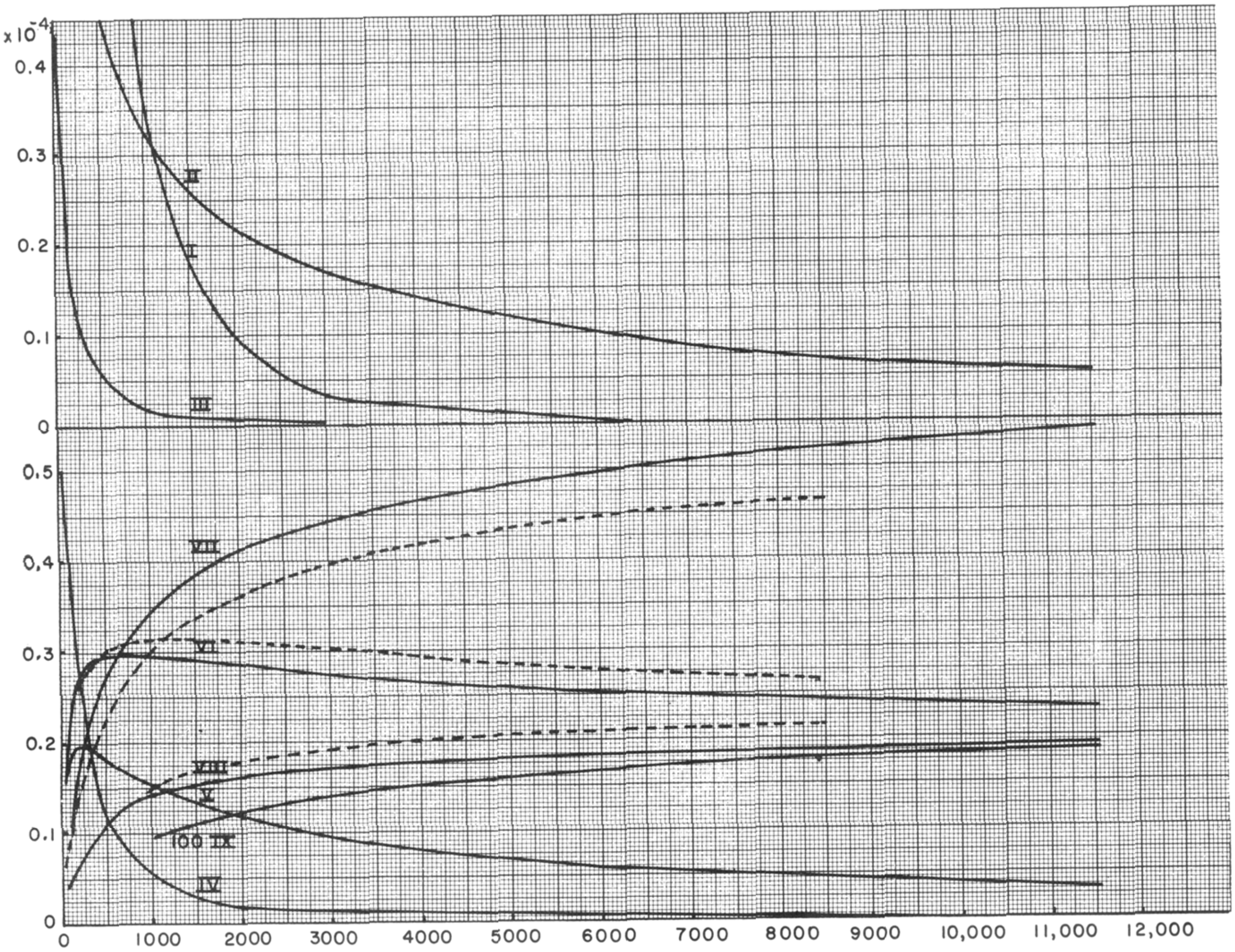


Figure 5.—Simulation of ethylenimine polymerization with $[IV]_0 = 0.995$, $[I]_0 = 0.005$, using Burrough B-5000 digital computer: solid lines from constants of Table III, trial C; dotted lines from constants of Table III, trial A.

uct ratio is negligible. For an initial catalyst concentration of 0.5 mole % the effective K_a of polymer is 4.5×10^{-9} at 2% conversion and 1.8×10^{-9} at 5%.

$$[H^+]_0 = [H^+] + [I] + [II] + [III] + [PH] + [IX]$$

$$P \equiv \text{polymer} = VI + VII + VIII$$

$$PH \equiv \text{protonated polymer}$$

$$K_{PH} \equiv K_A \text{ of slightly protonated polymer}$$

$$[H^+] = \frac{[H^+]_0 - [III] - [IX]}{\frac{[IV]}{K_I} + \frac{[V]}{K_{II}} + \frac{[P]}{K_{PH}} + 1} \qquad \begin{aligned} K_I &= 1 \times 10^{-8} \\ K_{II} &= 3.8 \times 10^{-8} \\ K_{PH} &= 1.4 \times 10^{-9} \end{aligned}$$

$$[I] = \frac{[IV][H^+]}{K_I}; \ [II] = \frac{[V][H^+]}{K_{II}}$$

It was found necessary to reduce the reactivity of VIII in order for the simulated polymerization to go to completion; otherwise the catalyst was converted to IX before the monomer was consumed. There is evidently a considerable steric effect in the reactivity of VIII.

The Burroughs B-5000 digital computer was used for the simulations reported in Table III and Figure 5 because previous simulation on the PACE electronic differential analyzer gave final product totals which exceeded 1.0. This was evidently due to noise and fluctuations in the signals of the electrophiles. It was necessary with the digital computer to integrate every 0.1 sec. initially and carry the simulated reaction times to 5000–6000 sec. The product ratios obtained with the analog computer were nearly the same. In Figure 6 there is plotted, in addition to the relative product concentrations, a dotted line which is the integrator signal for reaction 1a. This is the integrated rate of formation of dimer. It is apparent that the conversion to dimer never exceeds 20% when

Table III

Simulation Using Burroughs B-5000 Digital Computer

Trial	Rate constants tried[a] k_{IV}	k_V	k_{VI}	k_{VII}	k_{VIII}	Branching ratio of [VIII]/[VII]
A	1	1	2.15	0.675	0.025	0.46
B	1	1	2.15	0.675	0.050	0.46
C	1	1	2.15	0.337	0.025	0.36
D	1	2	2.15	0.675	0.025	0.64
G	1	1	1.075	0.250	0.025	0.55
H	1	0.5	1.075	0.337	0.025	0.41
I	1	0.5	1.075	0.250	0.025	0.37
J	1	0.5	2.15	0.337	0.025	0.26
K	1	0.5	2.15	0.169	0.025	0.20
L	1	0.75	2.15	0.253	0.025	0.28
M	1	1	2.15	0.253	0.025	0.33

[a] The relative reactivities of the electrophiles were assumed to be I:II:III = 2:1:10. A decrease in the reactivity of III from 10 to 5 did not change the product ratios.

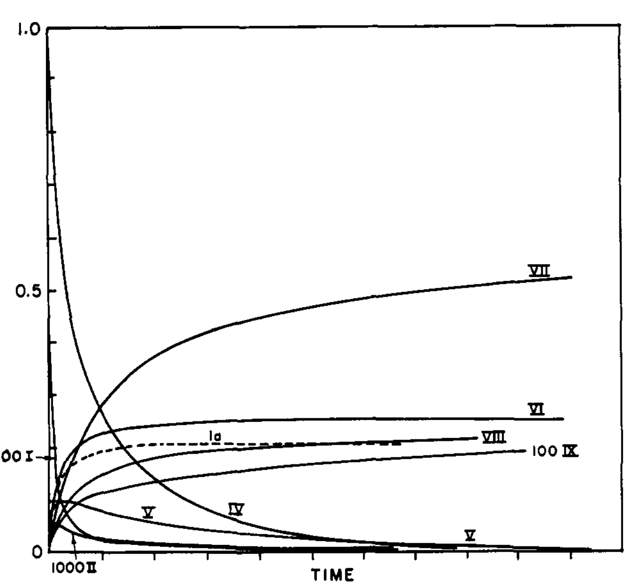


Figure 6.—Simulation of ethylenimine polymerization with $[IV]_0 = 0.995$, $[I]_0 = 0.005$, using PACE analog computer, of Table III, trial A.

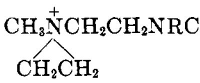
the catalyst concentration is 0.5% as is assumed in the simulation.

The results of several simulations are shown in Table III. Stoichiometry requires that, inasmuch as [IX] is small, the final values of [IV] and [VIII] be equal. As conversion approaches completion the ratio of IV/VII drops rapidly and some variation in analytically determined values of this ratio is understandable in terms of incomplete conversion. An increase in the degree of branching, shown by the ratio of VIII/VII of Table III, can be simulated by various changes. The effect of increasing the head-to-head assumed reactivity is shown in comparisons of trials D and B, G with I, and M with L. The lesser effect of increasing the assumed reactivity of mid-chain amino groups is shown by comparisons A with C and J with K. By inspection of Figure 6 it is clear that the former reaction is the major cause of branching initially and the latter becomes the major cause at high conversion. A decrease in the assumed reactivity of the primary amino group increases branching because it amounts to a relative increase in the reactivity of the other nucleophiles, as shown in comparison H with J.

N-Methylethylenimine.—The polymerization of N-methylethylenimine can, in principle, involve most of the complications of the polymerization of ethylenimine except that a living chain is conceivable. The species in the case of N-methylethylenimine are written below.

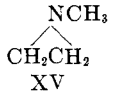
electrophiles

XIII
(XII, R = H)



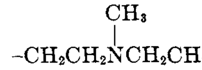
XIV

nucleophiles



XV

$-CH_2CH_2NRCH_3$
XVI (XVII, R = H)



$-CH_2CH_2N(CH_3)CH_2CH_2-$
XVIII

Unlike the case of ethylenimine it makes a difference whether the initiator is an acid or an alkylating agent. If an acid, then a head-to-tail reaction of a species such as XVII could regenerate a proton and transfer it to monomer as in the case of ethylenimine. This process would cease, however, with the disappearance of secondary amino groups, unlike the case of ethylenimine. As with ethylenimine there would be a tendency of the acid-catalyzed polymerization to slow with increasing conversion because of binding of protons by polymer. When, however, an alkylating agent is used as the initiator, species XII and XVII are absent, and, if R is bulky, one might expect a chain reaction of monomer with terminal quaternary. Such is the case with N,N-diethylethylenimmonium ion as the catalyst.

In the polymerization of N-methylethylenimine, and similarly N-2-hydroxypropylethylenimine, with various types of acids and alkylating agents, there was observed a very rapid polymerization and a termination reaction, so rapid that the conversion was essentially unchanged at reaction times longer than a few minutes. A number of alkylating agents were studied: N,N-diethylethylenimmonium chloride, ethyl sulfate, methyl and ethyl *p*-toluenesulfonate, and methyl perchlorate. Among the acids studied were perchloric, fluoboric, and numerous Lewis acids. In all cases the result was the same. Polymerization came to an end within a few minutes.

The relationship between conversion and initial catalyst concentration was investigated and it was found that the results could be represented as second-order propagation and first-order termination. There was an anomaly in regard to the apparent first-order termination. The plot of conversion *vs.* catalyst concentration based on a first-order termination did not pass through the origin. A kinetic treatment was then derived which took into account the consumption of available nucleophilic groups in the polymer as it participated in second-order termination.

A ≡ monomer; [A] = concentration of monomer A
$[B]_0$ ≡ initial concentration of catalyst relative to monomer
[B] ≡ concentration of active centers including catalyst N,N-diethylethylenimmonium chloride (assumed equal in reactivity to growing chain)
N ≡ tertiary amino groups in polymer (which are nucleophilic); [N] = concentration of tertiary amino groups
k_2 ≡ propagation rate constant
k_3 ≡ first-order termination rate constant
k_4 ≡ second-order termination rate constant
K_1 ≡ number of tertiary amino groups in polymer deactivated per termination by the inductive effect of ammonium nitrogen
L ≡ number of nitrogen deactivated by immonium nitrogen

$$\frac{d[N]}{dt} = k_2[A][B] - L\frac{d[B]}{dt} - K[B](k_3 + k_4[N])$$

$$\frac{d[A]}{dt} = k_2[B][A] \qquad -\frac{d[B]}{dt} = k_3[B] + k_4[B][N]$$

By the use of the analog computer d[A]/d*t* was integrated to the complete disappearance of B for increasing values of $[B]_0$. As shown in Figure 7 a good fit of the experimental data is obtained with assumed relative values of $k_2 = 1$, $k_3 = 0$, $k_4 = 0.15$, $K = 1.5$. Nearly as good a fit can be obtained with $K = 3$ and $k_4 = 0.18$. A trial solution with $k_3 = 0.02$ gives a slight deviation and, if k_3 is raised to 0.074 as in curve 2, Figure 7, the deviation is serious. Increasing k_3 and

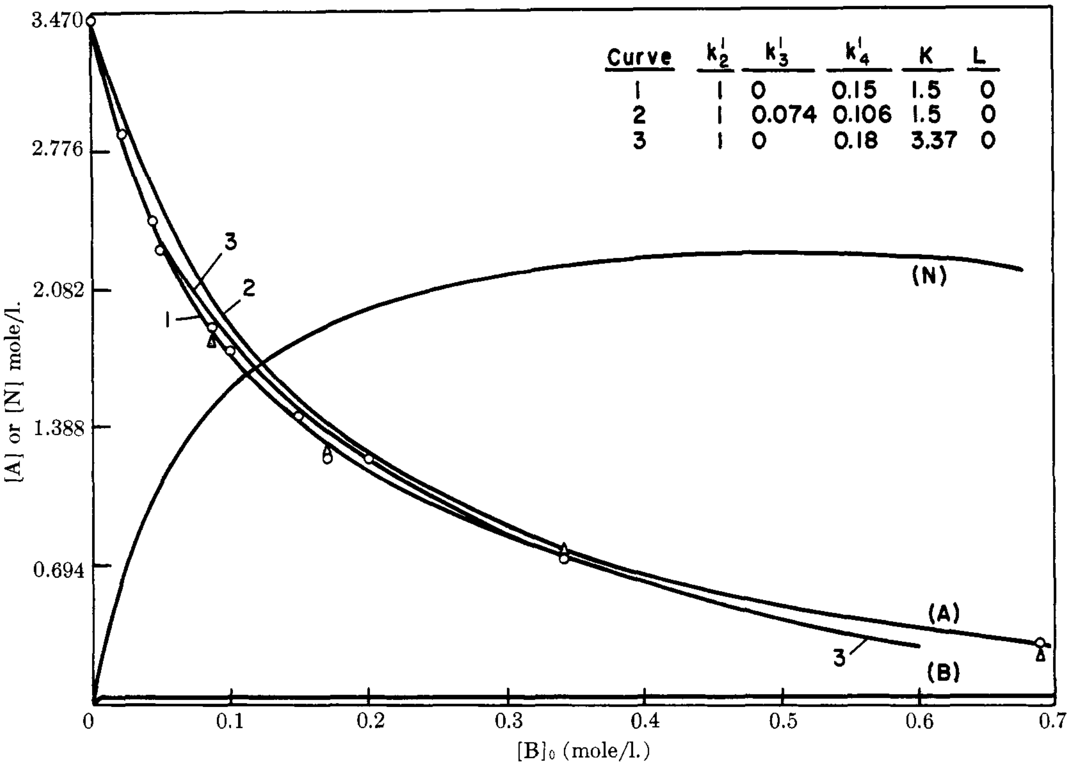


Figure 7.—Analog simulation of final conversion ($[A]_0 - [A]$) of N-methylethylenimine *vs.* initial catalyst concentration $[B]_0$, showing [N], the concentration of nucleophilic tertiary nitrogens in polymer.

decreasing k_4 causes the early part of the curve to fall too low and the latter part too high. Increasing K and k_4 flattens the curve. The value 0.18 for k_4 is in excellent agreement with the value 0.17 obtained from the model compound data ($^1/_4$ of the ratio of rate constants of methyldiethylamine and N-methylethylenimine where $^1/_4$ is an inductive factor correction). Figure 7 shows the significant fact that owing to progressive branching and the consequent inductive effect of quaternary ammonium nitrogens the concentration of nucleophilic nitrogens in the form of polymer levels off despite the increasing conversion. Thus termination becomes pseudo first order at higher conversion.

As a confirmation of the role of polymer in termination a sample of poly(N-methylethylenimine) was prepared at 46% conversion with 5 mole % of X as catalyst. The polymerization was then repeated in the presence of 46 mole % of this polymer and the conversion was 29%.

The addition of a strong nucleophile such as bromide ion or methyldiethylamine caused the polymerization to stop at lower conversion (*cf.* Table IV). Methyldiethylamine was about twice as effective as the above polymer sample per nitrogen. A commercially available sample of poly(N-methylethylenimine) was ineffective as a terminator.

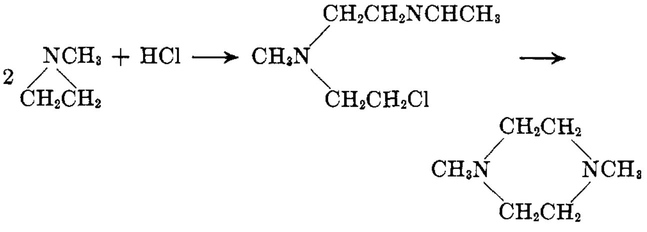
Table IV

Conversions in Polymerization of N-Methylethylenimine.[a] Effect of Adding Model Compound as Terminator

$(C_2H_4)_2NCH_3$, mole %	0	5	20.3	25
Conversion	49	46	32	22

[a] An equal volume mixture of N-methylethylenimine and water catalyzed with N,N-diethylethylenimmonium chloride and containing sodium chloride (both 5 mole % relative to monomer).

Prior to arrival at the above explanation for pseudo-first-order termination it was considered that termination might involve the formation of a substituted piperazinium ring at the end of the chain. It is possible to isolate N,N'-dimethylpiperazine from the reaction of acids with N-methylethylenimine as reported by Knorr[10]; however, the usual reaction involves, as shown below, a prior ring opening executed by the anion of the acid. This mechanism is inapplicable when the anion is perchlorate or even chloride ion at a concentration of 1.0 M or less; additions of such weak nucleophiles did not lower the conversion in the polymerization of N-methylethylenimine with methyl perchlorate as catalyst. A 10% yield (approximate) of dimethylpiperazine could be isolated when a large amount (67 mole %) of perchloric acid was added to N-methylethylenimine in 1 M solution and the mixture was allowed to stand for 18 hr. It is evidently possible but difficult for the neighboring nitrogen to cleave the ring directly. Backside attack is sterically hindered and the penultimate nitrogen is rendered less nucleo-



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[10] L. Knorr, *Ber.*, **37**, 3507 (1904).

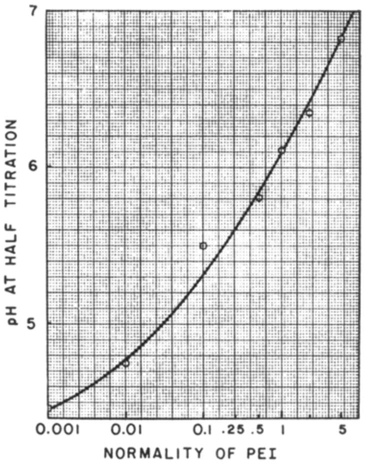


Figure 8.—Effect of concentration on pH at half titration of polyethylenimine (PEI).

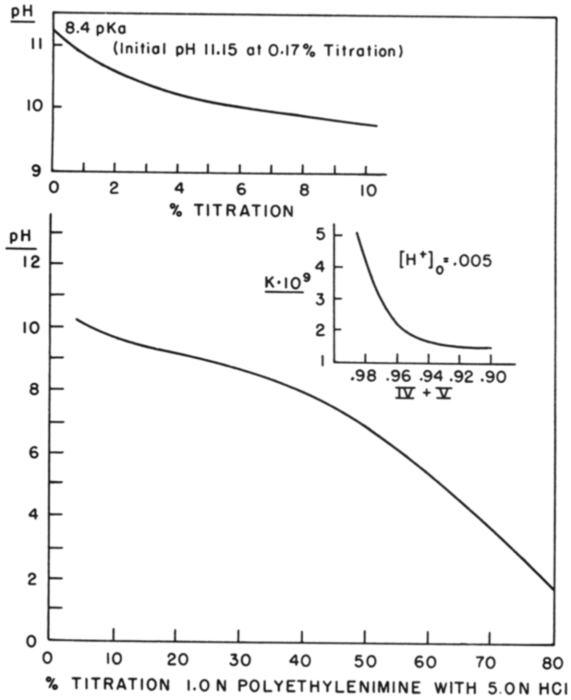


Figure 9.—Effect of initial conversion on apparent pK_A of polyethylenimine made with 0.5 mole % acid catalyst.

philic because of the positive charge on the terminal immonium nitrogen.

The assumption was made that the growing chain and the initiator are of similar electrophilic reactivity. To check this point the reactivity of N,N-dimethylethylenimmonium ion was compared with that of the diethyl derivative. The growing chain was expected to have an intermediate reactivity. N,N-Dimethylethylenimmonium ion was generated in 0.10 *M* solution in 42% yield. Inasmuch as chloride formation paralleled the disappearance of amine, it is indicated that the formation of N,N,N′N′-tetramethylpiperazinium salt was fast relative to cleavage of N,N-dimethylethylenimmonium ion by N,N-dimethyl-2-chloroethylamine. An immonium ion formation rate of 6×10^{-4} sec.$^{-1}$ was estimated from the initial data. By analog simulation the rate constants for cyclization and cleavage by N,N-dimethyl-2-chloroethylamine could be distinguished and the values obtained were 4.8×10^{-4} sec.$^{-1}$ (±0.3) and 8.0×10^{-3} l. mole^{-1} sec.$^{-1}$, respectively. No evidence for the presence of the intermediate cleavage product, N-2-chloroethyl-N,N,N′,N′-tetramethylethylenediammonium chloride, (estimated pK_a 6) was observed in the titration of the N,N-dimethyl-2-chloroethylamine (pK_a 8.3).

An electrophilicity evaluation was made using the N,N-dimethylethylenimmonium solution containing N,N,N′,N′-tetramethylpiperazinium ion and free of N,N-dimethyl-2-chloroethylamine. The rate of hydrolysis in neutral solution was four times that of N,N-diethylethylenimmonium ion and the rate of hydrolysis by hydroxide ion was 2.5 times greater. Polymerization with N,N-dimethylethylenimmonium chloride as the catalyst gave exactly the same shape of conversion curve as Figure 7 except that the yield relative to initiator was only one-third as great. The effect was ascribed to an increased rate of termination (by dimethylamino end group).

Higher conversion values are reached at 60° than at room temperature. One expects the imine, being less basic, to require a larger activation energy for reaction than an amine; therefore, propagation should be favored by raising the temperature.

Acid-catalyzed polymerization of N-methylethylenimine would be expected to become slightly faster than that catalyzed by alkylating agents because a head-to-tail reaction should become appreciable as the monomer concentration drops to a level comparable with that of the terminal secondary amine group. This is a condensation and transfer reaction because a proton is produced. Actually only slightly higher conversions are obtained with perchloric acid or fluoboric acid as catalysts and the dependence on $[B]_0$ is similar to that of Figure 7.

Water Effect.—A suggestion of means of altering the probability of the two branching mechanisms was provided by the water effect. Whether the initiator was an acid or an alkylating agent, the polymerization went to higher conversion in the presence of water; *cf.* Table V.

TABLE V

EFFECT OF WATER RATIO ON CONVERSION OF N-METHYLETHYLENIMINE

Water ratio	Conversion	Water ratio	Conversion	Water ratio	Conversion
A. With Alkylating Agent as Catalyst[a]					
0	2.3	0.17	8.3	1	49[b]
0.017	3.9	0.33	15.0	10	74[b]
0.033	2.9	0.67	22.3	32	59[b]
0.067	4.4	1.0	22.8		
B. With Acid Catalyst[c]					
0	42	2.0	75		
0.5	70	3.0	72		
1.0	71	5.0	66		
1.5	77				

[a] Ratio in v./v. of imine; conversion in %; temperature, 60°; catalyst, a N,N-dialkylethylenimmonium perchlorate, 0.5 mole %. [b] 5 mole % catalyst (N,N-diethylethylenimmonium chloride) at 30°. [c] 0.062 ml. of 48% HBF_4/ml. of imine; temperature, 37°.

It was possible by means of a rapid mixing device to obtain conversion results prior to complete termination. By the use of a fourfold ratio of initiator to imine the propagation reaction was restricted and the data of Figure 2 obtained. Extrapolation to zero time gave the rate constant cited in Table I. A reineckate could be precipitated from the solution shortstopped at 1 min. If, as estimated above, the growing chain is somewhat more reactive than initiator, one would expect some dimer even after 1 min., and the presence of the dimer would explain the formation of a reineckate.

The same rapid mixing technique was used for the experiments of Table VI. It was found that the initial rate was higher in aqueous ethanol than in water alone. In contrast, the data of Table VII shows that the final conversion is reduced by addition of alcohol or dioxane. The rate of attack of amines (and by inference the termination rate) is increased less by the addition of alcohol (Table VIII) than that of imine. Because the polymerization is a chain reaction, the small increase in termination rate causes, nevertheless, a reduction in final conversion (Table VII). The positive salt effect (Table I) suggests that proximity of chloride ion aids in the charge transfer and does so more effectively with decrease in dielectric constant and with imine than with the more basic and presumably more hydrated amine.

TABLE VI

EFFECT OF SOLVENT ON CONVERSION RATE OF N-METHYLETHYLENIMINE (EXCESS INITIATOR)[a]

Solvent	Ratio, v./v.	Conversion, %, in 1 min.
Water		31.6, 31.8
Ethanol–water	2:2	69.1, 70.3
Ethanol–water	3:2	79.8, 81.2
Ethanol–water	4:2	88.6, 88.1
Dioxane–water	3:2	71.8, 76.1
2,2-Dihydroxymethylbutanol–water	3:2	65.7, 69.5

[a] 0.4 *M* X; 0.1 *M* imine; 0.05 *M* NaOH; 30°.

TABLE VII

EFFECT OF ADDED WATER ON FINAL CONVERSION OF N-METHYLETHYLENIMINE WITH LOW CONCENTRATION OF INITIATOR (ETHYL SULFATE)

Monomer, % by vol.	Solvent	Ratio, v./v.	Initiator, mole %	Conversion,[a] %
50	Ethanol	. . .	1	12.8
50	Ethanol–water	2:1	1	21.8
50	Ethanol–water	1:1	1	24.7
50	Ethanol–water	0.5:1	1	27.3
50	Water		1	35.6
50	Water		1	41.5[b]
10	Dioxane		5	19.3
10	Dioxane–water	35:1	5	23.5
10	Dioxane–water	3.5:1	5	36.7

[a] Temperature, 35°; time, 1 hr. [b] Temperature, 57°; time, 1 hr.

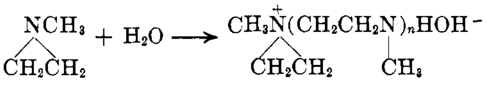
TABLE VIII

EFFECT OF ETHANOL ON CONVERSION IN REACTION OF N,N-DIETHYLETHYLENIMMONIUM ION WITH AMINES

Ethanol, ml.[a]	Conversion, %[b]	
	$(C_2H_5)_2NCH_3$[c]	$(C_2H_5)_2NH$[d]
5	52.4	90.8
10	56.1	93.0
15	61.1	96.0
20		90.8

[a] Total volume, 26.29 ml.; remainder water. [b] Amine, 0.48 *M;* X, 0.48 *M*. [c] Time, 2 min.; temperature, 30°. [d] Time, 15 min.; temperature, 30°.

A small amount of polymerization occurs when aqueous N-methylethylenimine is held in the absence of stronger base. Thus, when N-methylethylenimine is heated in water, the pH rises to 12.5 and then polymerization stops. This reaction is prevented in 0.1 *N* sodium hydroxide but occurs to a slight extent in 0.01 *N* sodium hydroxide. As soon as dimer has formed, the polymerization continues as a chain reaction, unlike the result with ethylenimine which is not



polymerized by water. Hydration of N-methylethylenimine gives a downfield n.m.r. shift of both CH_2 and CH_3 as would be expected for electrophilic substitution on nitrogen (Table IX).

TABLE IX

DOWNFIELD SHIFT PRODUCED BY WATER IN N.M.R. OF N-METHYLETHYLENIMINE[a]

	CH_2	CH_3
Neat	−0.87, −1.59	−2.15
In water (1:1)	−1.16, −1.68	−2.22

[a] Parts per million relative to tetramethylsilane; 60 Mc.

A further difference between ethylenimine and N-methylethylenimine is the hydrogen-bonding capability of the former. Presumably this is the reason that N-methylethylenimine is not polymerized by 99% sulfuric acid in the absence of water or alcohol, whereas ethylenimine is polymerized. Neither is polymerized by dry perchloric acid (added as a dioxane solution). Both are polymerized by dry hydrogen chloride.

Experimental

Assay of Imine and Substituted Immonium Compound.—Titration with thiosulfate[8] was used for determination of imine and substituted immonium compounds. The reaction conditions were a 2–3-fold ratio of thiosulfate to initial monomer concentration; room temperature; time, 15 min.; a nominal pH of 4.7 (acetate buffer); and concentration of thiosulfate reagent, 0.5 *M*. The excess of thiosulfate was never less than 1.7 times the initial amount of X and usually double this value. If polymeric amines were present, dimethylformamide was added to prevent precipitation of triiodide ion during titration of excess thiosulfate.

In a test of the reaction of N,N-diethyl-2-chloroethylamine and N,N-diethyl-2-bromoethylamine with thiosulfate in acid solution (pH 4.7) there was found 0 to 7% reaction, respectively, under the conditions used for imine determination.

Generation of N,N-Diethylethylenimmonium Ion.—N,N-Diethylethylenimmonium bromide was made by the method of Knorr.[10] Cyclization of N,N-diethyl-2-bromoethylamine was complete in 8 min. as shown by bromide ion liberation. Cyclization of N,N-diethyl-2-chloroethylamine was complete in 10 min. The reaction was carried out by the addition of an equimolar amount of sodium hydroxide to the amine hydrochloride in 0.3 to 1.0 *M* aqueous solution. The reaction was quantitative.

Generation of N,N-Dimethylethylenimmonium Ion.—N,N-Dimethyl-2-chloroethylamine hydrochloride (3.601 g.) was dissolved in approximately 200 ml. of water. Sodium hydroxide (25 ml., 1.0 *N*) was added and the volume was adjusted to 250 ml. Samples (10 ml.) were withdrawn and titrated with hydrochloric acid, others with silver nitrate, and others with sodium thiosulfate. The data for disappearance of amine and appearance of chloride showed identical rates but with deviation from first to lower order. The half-life was 20 min. at room temperature. The amine titration showed no evidence of the presence of a base weaker than N,N-dimethyl-2-chloroethylamine. The thiosulfate data is reliable only at the end of the reaction; apparently there is some direct displacement of chlorine from the amines. The yield of XI was 42% based on the final thiosulfate data.

Evaporation of the reaction mixture gave a residue which had infrared spectrum and elemental composition consistent with tetramethylpiperazinium dichloride.

Anal. Calcd. from $C_8H_{20}Cl_2N_2 \cdot 2NaCl$: C, 28.94; H, 6.07; Cl, 42.71. Found: C, 29.90; H, 6.13; Cl, 42.7.

Method of Conducting Model Compound Kinetic Experiments.—Aqueous diethylethylenimmonium chloride (X) and amine solutions (containing sodium hydroxide, if necessary) were prepared at twice the desired concentration, 0.05–0.15 *M* of X and 0.1–0.5 *M* amine. The solutions were mixed in 250-ml. stoppered flasks thermostated at 30°, run for the desired time, and short-stopped by adding the acid thiosulfate reagent.

There were several complications in the experiments. In the cases in which a proton is a by-product of the reaction it was necessary to add hydroxide ion; alternatively, one could correct for the amount of amine neutralized by taking into account relative basicity of reactant and product. With the weaker nucleophiles the addition of hydroxide ion necessitated a substantial correction for hydrolysis. In the reaction with trimethylamine in the absence of added hydroxide there was no hydrolysis product; presumably, therefore, no carbene intermediate.[11]

Method of Conducting Methylethylenimine Kinetic Experiments.—For the data of Figure 1 a two-chambered vessel was used. A 10-ml. cup of 3.5-cm. diameter was sealed in the bottom of a 100-ml. bottle of 4.5-cm. diameter fitted with a serum cap. The N,N-diethylethylenimmonium chloride solution was placed in the outer chamber and the monomer in the inner chamber. Nearly instantaneous mixing was obtained with a flick of the wrist. The reaction was short-stopped with acid thiosulfate solution which was injected into the now empty cup and the mixing action was repeated. The bottle was held at 30°. The concentrations of reactants after mixing were 0.1 *M* with respect to monomer and 0.4 *M* with respect to catalyst.

The data of Figure 7 was obtained using sealed ampoules at 35 instead of 30° but since the computer curves are all relative to the unit value assumed for propagation it was immaterial. The initial concentrations were monomer, 3.47 *M*, and catalyst X or XI, 0.2–0.7 *M* in different experiments. Water and immonium catalyst were mixed and frozen to −80°. Monomer was added and the reaction ampoule was flame sealed. The mixture was thawed in a water bath (usually at 35°) with agitation. After the required reaction time the ampoules were refrozen, broken open, and placed complete in the appropriate amount of thiosulfate reagent. After complete reaction the mixture was back-titrated.

For experiments on the role of water, glass vessels (diameter 0.75 in.) with Swagelok fittings were used. The reactions were started by injecting catalyst into the thermostated vessel (30°) and stopped by chilling or injecting cold water and emptying into acid thiosulfate solution.

Method of Calculation of Rate Constants.—Rate data for attack of water on X were plotted as a first-order process, and the resulting rate constant was divided by 55.5 to yield a second-order constant. Data for the hydroxide ion and amines were treated as second-order processes. The slopes of the second-order rate plots were generally constant. In those cases where deviations occurred owing to competition by sodium hydroxide (*e.g.*, the cases of less nucleophilic amines such as ethylamine or ethylenediamine) or to products entering the reaction the appropriate corrections were applied to the slope of the rate plot at zero time by linear interpolation. In severe cases (*i.e.*, corrections greater than 1.5 *k*) analog simulation was employed. The dilute solution data for methylethylenimine and X were extrapolated back to zero time. For Figure 7 conversion was plotted *vs.* catalyst concentration, all experiments having gone to completion. In order to simulate the polymerization of N-methylethylenimine (a) the integration of $d[A]/dt$ to disappearance of catalyst (b) was carried out by the analog computer for increasing values of $[B]_0$ each increment being 0.03% of $[A]_0$. The range of $[B]_0$ was 0–20 mole %. The form of Figure 7 is a plot of the end point with respect to [A] of each integration *vs.* $[B]_0$.

The concentration of nucleophilic nitrogen [N] in polymer was calculated for various assumed values of first- and second-order termination rate constants.

In the case of trimethylethylenediamine the rate constant of Table I is expressed in terms of normality inasmuch as both amino groups participate. The average rate constant is lower than that of tetramethylethylenediamine; therefore, the tertiary amino group participates more than the secondary. For this reason the rate follows second-order kinetics approximately. To the extent that reaction occurs at the secondary amino group a product of comparable reactivity is formed.

The objective of the model compound study was to assign tentative rate constants for analog simulation of the polymerization. There was some difficulty in arriving at a rate-constant prediction for species V. It was found that there is a pronounced salt effect. As shown in Figure 1 and Table VI a fourfold excess of X was used to differentiate the reaction of N-methylethylenimine with X and subsequent polymerization steps. This raised the chloride ion concentration from the value of 0.2 *M* used for the rest of the data of Table I to 0.5 *M*. When the reaction was conducted with $[X]_0 = 0.1\ M$ the initial rate was 7.3×10^{-3} l. mole^{-1} sec.$^{-1}$ (half that with $[Cl] = 0.5\ M$); when 0.3 *M* sodium chloride was added the initial rate could not be differentiated. N-2-Hydroxyethylethylenimine was considered a better model than N-methylethylenimine. The rate constants of ethanolamine and ethylenediamine were not greatly different; evidently the oxygen and nitrogen inductive effects are similar in magnitude. It was decided therefore to use the constant of 2-hydroxyethylethylenimine in 0.2 *M* $[Cl^-]$ as the predicted constant of species V for the purpose of Table II. The predicted values for VI, VII, and VIII were obtained from the constants of ethylamine, diethylamine, and triethylamine divided by 2, 4, and 8, respectively, as inductive effect corrections.

Amine Titration Data.—The pK_a of species II was estimated to be 3.8 times that of species I. For this purpose the pK_a of N-(2-hydroxyethyl)ethylenimine, found to be 7.17, was compared with that of ethylenimine. The base-weakening effect of nitrogen has been estimated[12] to be three-quarters of that of oxygen; the estimated base-weakening effect of the neighboring nitrogen in species II was adjusted accordingly.

The apparent initial pK_a of polyethylenimine was found to be 8.9 in dilute and 9.5 in concentrated solution. A 12.3-g. sample of freshly distilled ethylenimine was polymerized by refluxing with hydrochloric acid and the pH of a 34% aqueous solution was found to be 11.6 on a pH meter calibrated with freshly opened tetraethylammonium hydroxide. Potentiometric chloride titration showed the polymer to be 0.80% neutralized. The pH dropped to 11.35 on dilution to 22%. Another sample of polymer was prepared with 0.17% neutralization and the pH of a 1.0 *N* (4.3%) solution was found to be 11.15 (*cf.* Figures 8 and 9). A sample of polyethylenimine prepared similarly was passed through a column of Dowex 1 (OH^-) to convert any species IX to quaternary hydroxide. In 3.2% solution the titration began at pH 11.3.

Polyethylenimine was prepared by dropwise addition of 5 mole % hydrochloric acid to a 10% aqueous solution of ethylenimine. Conversion reached 97% in 8 days. A sample was passed through a column of Dowex 1 (OH) and the effluent was titrated. The initial pH was 11.5 at a polymer concentration of 0.36 *N*.

A sample of benzamide of polyethylenimine containing 20 mequiv. of nitrogen was dissolved in 1:5 aqueous alcohol and titrated from pH 7.8 to 3.0 with 5 mequiv. of 1.0 *N* hydrochloric acid. N,N-Dimethylbenzamide was found to have negligible acid consumption in this pH range.

Preparation of Benzamide of Polyethylenimine.—In prior work[1] the benzoylation was conducted with excess benzoyl chloride and aqueous caustic and with addition of chloroform to dissolve the product which otherwise quickly precipitated. The product was precipitated subsequently in excess paraffinic solvent, washed with caustic, and air dried to a tan powder. In the current work it was found that this procedure did not remove all of the benzoic acid contamination. An infrared absorption band due to benzoic acid (5.8 μ) was removed by agitation with hot aqueous sodium carbonate which softened the product. This treatment did not appear to hydrolyze the amide structure as did alcoholic sodium hydroxide.

The benzamide of polyethylenimine is not soluble in carbon tetrachloride, and it was necessary to resort to measuring the spectrum of a 1% solution in chloroform *vs.* solvent in matched 0.1-mm. cells.

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[11] W. K. Musker, *J. Am. Chem. Soc.*, **86**, 960 (1964).

[12] J. Clark and D. D. Perrin, *Quart. Rev.*, **18**, 295 (1964).

A.—A polymerization of 10% aqueous ethylenimine was conducted at room temperature with 5 mole % hydrochloric acid. After 3 days, conversion had reached 90%. The solution was evaporated, and the polymer was treated with excess benzoyl chloride and 10% sodium hydroxide. The polymer was refluxed with 10% sodium carbonate solution for 2 hr. to extract residual acids. It was dried and titrated in aqueous ethanol solution with hydrochloric acid. There was required 0.223 equiv./base mole (C_9H_9NO) to reduce the pH from 8.42 to 3.0. The ratio of secondary to tertiary amide by infrared measurement was 0.33.

Anal. Calcd. for $C_{29}H_{32}N_4O_3$, $C_6H_5CONHCH_2CH_2NCH_2CH_2N[C(O)C_6H_5]CH_2CH_2N[C(O)C_6H_5]CH_2CH_2$–: C, 71.9; H, 6.61; N, 11.57. Found: C, 69.30; H, 6.38; Cl, 1.21; N, 10.75.

B.—PEI benzamide sample B was prepared as C except that chloroform was present during benzoylation. The ratio of secondary to tertiary amide by infrared measurement was 0.51.

Anal. Found: C, 66.52; H, 6.41; Cl, 5.22; N, 8.93.

C.—Polyethylenimine was prepared by refluxing undiluted monomer and adding 0.5 mole % of 1.0 *N* hydrochloric acid. Polymerization was essentially complete in 2 hr. The acid was added slowly in dropwise fashion to prevent local overheating and runaway polymerization. A sample of the polyethylenimine was treated with excess benzoyl chloride and 10% sodium hydroxide solution with cooling to keep the temperature from rising above room temperature. The polymer was dissolved in chloroform, precipitated in pentane, and dried. A greater than 100% yield of tan powder was obtained. The polymer was heated as a melt with 10% sodium carbonate solution for several hours to extract residual benzoic and hydrochloric acid. On cooling and drying it could be again powdered.

Anal. Found: C, 70.9; H, 6.59; N, 11.89 (corrected for presence of 0.84% chloride).

The ratio of secondary to tertiary amide by infrared measurement was 0.43. An aqueous ethanol solution required 0.25 equiv./base mole (C_9H_9NO) of hydrochloric acid to reduce the pH from 7.85 to 3.0. (An additional 0.035 equiv. of base is presumed to have been present combined with HCl.) The polymer was then heated in alcoholic sodium hydroxide to hydrolyze any benzamide and after recovery the ratio of secondary to tertiary amide found to be 0.51.

Molecular Weight Measurements of Polyethylenimine.—Diffusion and sedimentation velocity constants were measured in a Spinco ultracentrifuge in ethanol solution at 30°, the former at low speed (Table X).

TABLE X

MOLECULAR WEIGHT AND VISCOSITY OF POLYETHYLENIMINE

$$M = \frac{RT}{1 - \bar{\nu}\rho}\frac{S_0}{D_0} = 9.202 \times 10^{10}\frac{S_0}{D_0}$$

$R = 8.316 \times 10^7$ $T = 303.2$

$\rho = 0.7809$ g./cc. $\bar{\nu} = 0.930$ cc./g.

ρ = density of solvent; $\bar{\nu}$ = specific volume of polymer in solution

Sample	$D_0 \times 10^7$ cm.^{2} sec.$^{-1}$	$S_0 \times 10^{13}$ svedbergs	$\overline{M}$	Viscosity,[a] c.p.s.
b	6.0	2.24	30,000	1.14
c	8.4	1.05	11,500	1.12

[a] Measured in 1% solution at pH 11. [b] A commercial polymer. [c] A laboratory sample made by refluxing 10 ml. of monomer, adding 1 ml. of 1 *N* HCl, and warming overnight on steam bath.

Acknowledgment.—The ultracentrifuge molecular weight measurements were made by Dr. H. W. McCormick, the analog and digital programming of the ethylenimine case was done by Dr. T. Chiu, kinetic treatment of the N-methylethylenimine case was due to Dr. J. Huff, and analog programming was due to C. E. Fahlgren (all of The Dow Chemical Company).

Reactions of *p*-Tolylsulfonylmethylmagnesium Bromide with α,β-Unsaturated Aldehydes and Ketones

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p-Tolylsulfonylmethylmagnesium bromide (II) reacted with crotonaldehyde, cinnamaldehyde, *trans*-4-phenyl-3-buten-2-one, benzalacetophenone, and 1,5-diphenyl-2,4-pentadienone, to give the 1,2-addition products in good to excellent yields. In this respect, the sulfonyl Grignard reagent behaved differently from conventional organomagnesium compounds which normally give large amounts of 1,4 products with α,β-unsaturated ketones. The presence of cuprous chloride did not affect the course of the reaction between II and benzalacetophenone. Alcohol products could be dehydrated to afford multiply unsaturated substances. The tertiary alcohols prepared from α,β-unsaturated ketones were extremely nonlabile toward derivative formation.

Grignard reagents of sulfones, typified by *p*-tolylsulfonylmethylmagnesium bromide (II), have been

p-$C_7H_7SO_2CH_2MgBr$
II

extensively studied by Field and co-workers.[2–8] Such reagents were found to behave in a manner resembling that of other Grignard reagents in their reactions with carbonyl compounds, nitriles, esters, isocyanates, and in alkylation reactions. Earlier workers had shown that α-halomagnesium derivatives of sulfones undergo acylation,[9–11] carbonation,[9,12] alkylation,[10] halogenolysis,[9,13] and hydrolysis.[9,13]

Our interest in the reactions of Grignard reagents of sulfones with α,β-unsaturated aldehydes and ketones was prompted by two considerations. The reactions were predicted to give rise to unsaturated alcohols and/or saturated ketones which are difficultly obtainable by other conceivable reactions. If indeed the hydroxy sulfones were obtained, they could presumably be converted to butadienes and other conjugate systems. Baliah and Shanmuganathan[14] have shown that methylsulfonylmethylmagnesium bromide and cinnamaldehyde react to give an unsaturated

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[1] This work was supported in part by National Science Foundation Grant GE 4064 (Undergraduate Research Participation).

[2] L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952).

[3] L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

[4] L. Field, *ibid.*, **78**, 92 (1956).

[5] L. Field, J. E. Lawson, and J. W. McFarland, *ibid.*, **78**, 4389 (1956).

[6] L. Field and R. D. Clark, *J. Org. Chem.*, **22**, 1129 (1957).

[7] L. Field, J. R. Holsten, and R. D. Clark, *J. Am. Chem. Soc.*, **81**, 2572 (1959).

[8] L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961).

[9] E. P. Kohler and H. A. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935).

[10] E. P. Kohler and M. Tishler, *ibid.*, **57**, 217 (1935).

[11] E. P. Kohler and H. A. Potter, *ibid.*, **58**, 2166 (1936).

[12] H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).

[13] W. M. Ziegler and R. Connor, *ibid.*, **62**, 2596 (1940).

[14] V. Baliah and S. Shanmuganathan, *J. Org. Chem.*, **23**, 1233 (1958).