the cancellation of uncertainties owing to the two similar reactions (k_2 and k_i) appearing in the quotient.

Experimental

Materials. **Carbon Tetrachloride** (Eimer and Amend) was purified by distillation through a 25-plate vacuum-jacketed column; only the fraction boiling in the range of 76.7–76.8° was used, n^{24}D 1.4579. The solvent was stored in a brown bottle over calcium chloride.

Nitrobenzene (Eimer and Amend) was fractionally frozen three times, about one-third of the total being poured off each time. It was washed with sulfuric acid (1:1) until the washings were colorless, then with a small quantity of sodium hydroxide and finally with distilled water. It was then dried over calcium chloride and distilled twice under reduced pressure. After letting the liquid stand over powdered barium oxide for twenty-four hours, it was finally distilled over activated alumina to remove any residual dissolved ions. This procedure follows closely that recommended by Taylor and Kraus.[21] The nitrobenzene so obtained had a dielectric constant of 34.05 at 27.6°. Its specific conductance was 4.77 × 10^{-9} when fresh but increased markedly on standing. "Aged" nitrobenzene depressed all polymerization rates considerably. So-called C. P. nitrobenzene varied considerably in color as well as effect on reaction rates and was used without purification only in preliminary experiments.

Styrene (Dow) was washed with 4% sodium hydroxide solution, and with water. It was dried over calcium chloride and distilled prior to use through an all-glass apparatus b. p. 31° (9 mm.).

Tin tetrachloride (C. P. Eimer and Amend) was refluxed over phosphorus pentoxide in an all-glass still for 1–2 hr. Without opening the system to the atmosphere the condenser was then inclined in position for distillation, the tin tetrachloride was cooled and suction was applied. (Cenco Pressovac pump.) As a distillate receiver, a soft-glass 10-cc. test-tube was used to which a side-arm had been applied and whose bottom was drawn into a thin capillary. After the correct amount of catalyst had been collected, the adapter stopcock was closed and the capillary was sealed off the rest of the tube by touching it several times with the tip of a non-luminous bunsen flame. Evacuation was continued for some time; the upper part of the receiver tube was then removed, washed with hydrochloric acid (to dissolve any hydrates of tin tetrachloride adhering to the walls) then with water and acetone. It was then weighed to obtain the amount of tin tetrachloride in the ampoule.

The amines (Sharples) were purified by fractional distillation: dimethylaniline, n^{20}D 1.5584 ("Int. Crit. Tables" gives 1.5587); *n*-butylamine, n^{20}D 1.4015 ("Int. Crit. Tables" gives 1.401), b. p. 78.0°; di-*n*-butylamine, n^{24}D 1.4164; tri-*n*-butylamine, n^{24}D 1.4290. The polymerizations were carried out in sealed glass tubes thermostatted at 27.6°, one tube being opened for each titration of the residual monomer by bromine/carbon tetrachloride solution. No attempt was made to exclude water rigorously as it was found that good reproducibility could be attained using the present technique. Addition of small amounts of water caused a decrease in the rate of polymerization.[9] Ampoules containing the catalyst were opened under the surface of the liquid to start the reaction. Viscosities (for mol. wt. determinations) were measured in Ostwald viscosimeters, with an efflux time of between 100 and 200 sec. for the solutions employed.

Acknowledgment.—The dielectric constant measurements were done in the Sterling Laboratories, Yale University, New Haven, Conn. The helpful coöperation of Prof. R. M. Fuoss and Mr. D. Edelson is gratefully acknowledged.

Summary

1. The retardation of the Friedel–Crafts polymerization of styrene by four amines has been studied.

2. Under two sets of conditions it was found that *n*-butylamine is the weakest inhibitor, with di-, tri-*n*-butylamine and dimethylaniline being about equally effective.

3. The ratio (degree of polymerization without inhibitor):(degree of polymerization with inhibitor) is found to be smaller than the corresponding ratio for over-all rates of reaction. This may be due to chain transfer.

4. The mechanism of inhibition is assumed to be the conversion of the carbonium into an ammonium ion. Kinetic expressions are derived for this mechanism.

5. Evidence for this inhibition mechanism is obtained from rate measurements in the presence and absence of the inhibitor in media of varying dielectric constant.

Brooklyn 2, N. Y. Received October 7, 1949

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[21] Taylor and Kraus, This Journal, **69**, 1731 (1947).

[Contribution from the Polytechnic Institute of Brooklyn]

Inhibition of Friedel–Crafts Polymerization.[1] II. Factors Affecting Inhibitor Power

By J. George, H. Mark and H. Wechsler

It was shown in the preceding paper[2] that different amines retard the polymerization of styrene by tin tetrachloride to a different degree. The present investigation intends to determine the factors responsible for the relative efficiency of inhibitors in Freidel–Crafts polymerizations.

Inhibition by Tin Chloride–Amine Complexes

Inhibition was explained in the preceding article by the formation of a stable ammonium ion which recalls the inhibition in free-radical polymerizations where an active radical is replaced by a sluggish one.[•] The similarity does not extend too far, however. Amines are known to form salt-like complexes with generalized acids such as tin tetrachloride[3]; this reaction, together with the ammonium ion formation, will tend to decrease the effective amine concentration. The rate of amine disappearance is given by the expression

$$-\mathrm{d}n/\mathrm{d}t = k_k(n)(\mathrm{SnCl_4}) + k_i(\mathrm{c}^+)(n) \qquad (1)$$

where n = inhibitor; c^+ = carbonium ion; k_k

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[1] This paper is part of the dissertation presented by Harry Wechsler to the Faculty of the Graduate School, Polytechnic Institute of Brooklyn, in partial fulfillment of the degree of Ph.D.

[2] George, *et al.*, This Journal, **72**, 3891 (1950).

[3] See for example H. Ulich, E. Hertel and W. Nespital, *Z. physik Chem.*, **B17**, 21 (1932).

and k_i = rate constants for complex formation and inhibition reactions, respectively. If the amine is a powerful chain terminator the effective termination rate is $k_i(c^+)(n)$; if the amine, however, is a weak chain terminator the termination reaction is

$$k_3(c^+)(X^-) = k_3(c^+)^2$$

(X^-) being the concentration of negative ions in solution. In the first case assumption of the steady state leads to

$$-dn/dt = k_k(n)(SnCl_4) + A = a(n) + A \quad (2)$$

where A = rate of initiation and $a = k_k(SnCl_4)$ = constant, the amount of tin tetrachloride consumed in complex formation being negligible as compared to total. Equation (2) leads to

$$n = Ce^{-at} - B$$

Where B and C are constants for certain experimental conditions. Alternatively, if the termination is $k_3(c^+)^2$ and $(c^+) = (A/k_3)^{1/2}$ equation (1) becomes

$$-dn/dt = k_k(n)(SnCl_4) + k_i(A/K_3)^{1/2}(n) = b(n)$$

where b = constant. This leads to

$$n = n_0e^{-bt}$$

In both cases, the amine concentration decreases rapidly as a function of time since the constants a and b which appear in the exponent, contain k_k, the rate constant for the rapid neutralization of tin tetrachloride by the amine. As a consequence, the inhibition should stop soon after the reaction has started. This, however, is not the case as Figs. 1a and b, ref. 2, show. The effect of the amine persists over a long period of time, the conversion curves being similar to those without amines. This indicates that essentially the same amine concentration is active throughout the reaction. We shall therefore assume[4] that the reaction

$$SnCl_4 + xNR_3 \rightleftarrows SnCl_4 + xNR_3 \quad (3)$$

is reversible and maintains an almost constant amine concentration. The gas-phase dissociation of acid–base complexes has recently been studied by Brown and collaborators.[5] Nevertheless the effect of complex decomposition could not be taken for granted in these experiments because of the possibility for ammonium ion formation which does not occur in the other cases where acid–base equilibria of type (3) have been studied. If the equilibrium (3) is established rapidly complexes could serve as inhibitors as well as the free amines.

Figure 1 represents the results obtained with dibutylamine and with dibutylamine–tin tetrachloride complex as inhibitors in a medium of dielectric constant 11.4. The same rate curve is seen to describe both experiments satisfactorily, which supports the existence of equilibrium (3) in solution.

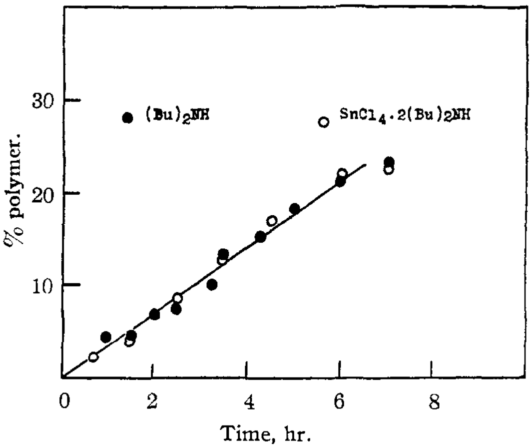


Fig. 1.—The complex $SnCl_4 \cdot 2(Bu)_2NH$ as inhibitor: styrene, 0.8642 *M*; stannic chloride, 1.236×10^{-2} *M*; $(Bu)_2NH$, 1.236×10^{-3} *M*.

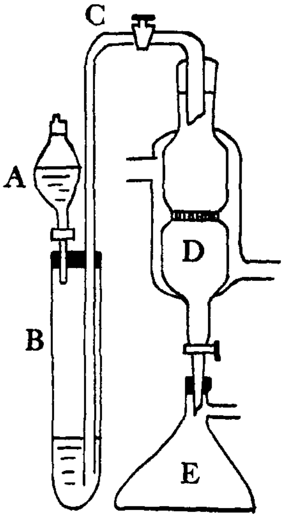


Fig. 2.—Apparatus for the preparation of $SnCl_4$·amine complexes.

The apparatus used to prepare the complexes is shown in Fig. 2. A is a separatory funnel half-filled with a solution of the amine in carbon tetrachloride; it can be evacuated through E. The amine solution together with several carbon tetrachloride washings is transferred to the test-tube B while maintaining the vacuum. Fresh carbon tetrachloride is then poured into A, this time filling it almost to the brim. An ampoule containing tin tetrachloride is broken under the surface of the liquid, the funnel is shaken and the solution quickly run into B. The complex forms in B where outside cooling can be applied to facilitate precipitation of the complex from carbon tetrachloride. D is a sintered glass filter to which a glass jacket has been sealed. By applying vacuum to E, the slurry can be drawn from B to D where filtration occurs. The precipitate is then washed *in vacuo* with fresh quantities of carbon tetrachloride. If cooling is needed to assist crystallization in B, ice-water is passed through the jacket of D during filtration and washing. To dry the precipitate, the ice-water is discontinued and warm water is passed through the jacket while continuing to apply the vacuum. Efficient drying is thereby obtained without having to transfer the precipitate and thus expose it. After the sample is dry, the two stopcocks leading

[4] Compare G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[5] Compare H. Brown and collaborators, *J. Chem. Phys.*, **14**, 114 (1946); THIS JOURNAL, **69**, 1137 (1947); *ibid.*, **69**, 1332 (1947).

TABLE I

Amine	Formula of complex	Mol. wt.	Nitrogen, % Calc.	Nitrogen, % Obsd.	M. p., °C.	Remarks
$C_4H_9NH_2$	$SnCl_4 \cdot 2NH_2(C_4H_9)$	406.8	6.89	6.24	255 (dec.)	White solid turns brown at 150°
$(C_4H_9)_2NH$	$SnCl_4 \cdot 2NH(C_4H_9)_2$	519.0	5.39	5.29	65 (sharp)	
$(C_4H_9)_3N$						Too unstable to be analyzed by conventional methods
Dimethylaniline	$SnCl_4 \cdot N(CH_3)_2C_6H_5$	381.5	3.67	4.0	165 (sharp)	White crystalline substance; melts to green liquid; solid turns green on standing in air

to D are closed and the sample is ready to use.[5a]

In preparing the four complexes, the same ratio of tin tetrachloride to amine was used as in the actual polymerization experiments, *i. e.*, 10:1. In the case of dibutylamine, the same complex $SnCl_4 \cdot 2NH(C_4H_9)_2$ was formed when a ratio $SnCl_4$: amine of 1:1 was used as when the ratio was 10:1. The results are summarized in Table I. The coördination number of stannic chloride is seen to vary between 1 and 2 in these compounds. From the appearance of the complexes it is obvious that $(C_4H_9)_3N$ is the weakest base since its complex is easily hydrolyzed by atmospheric moisture. It can be prepared as a white crystalline substance but on standing in air it deliquesces to a brown liquid. Because of its instability, results obtained with this complex are unreliable. A more refined method than the one used here must be devised for handling it. The complexes of dimethylaniline and of the primary amine, while not undergoing visible changes, could not be dissolved in nitrobenzene–carbon tetrachloride mixtures, even when kept dry immediately after their preparation. This happens in spite of the fact that no precipitate appears in the same solvents when the complex is formed *in situ*. Only the complex $SnCl_4 \cdot 2NH(C_4H_9)_2$ could therefore be tried as inhibitor and the results obtained with it were identical with those obtained with dibutylamine itself.

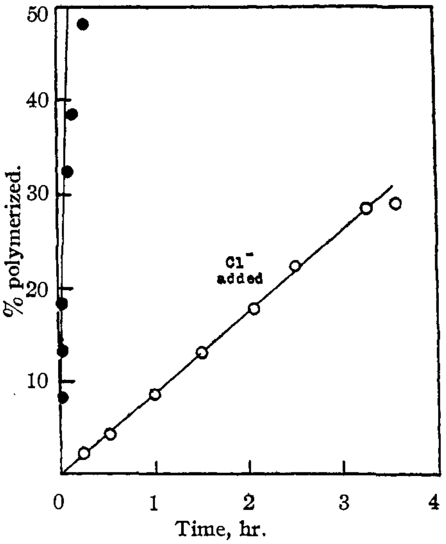


Fig. 3.—Effect of chloride ions on the polymerization of styrene: styrene, 0.864 mole/liter; $SnCl_4$, 1.237 × 10^{-2} mole/liter; $(C_2H_5)_4NCl$ 1.237 × 10^{-3} mole/liter.

Chloride Ions as Inhibitors.—The dissociation of the complex into the original components

$$SnCl_4 \cdot xNR_3 \rightleftharpoons SnCl_4 + xNR_3$$

is not the only reaction which the complex can undergo in solution. Instead of the coördinative N:Sn breaking, a different bond may break with the consequent formation of ions, especially in solvents which favor ionization.

Two types of complex ionizations are possible, depending on whether the base or the acid is dissociated. An example of the former is the increased ionization of alcohols observed when aluminum alcoholates are dissolved in them.[6]

$$Al(OR)_3 + ROH \rightleftharpoons H^+ + Al(OR)_4^-$$

Dissociation of the generalized acid appears to occur in such compounds as $Cl_3As \cdot NC_5H_5$ obtained by dissolving arsenic trichloride in pyridine.[7]

$$C_5H_5N + AsCl_3 \rightleftharpoons C_5H_5N \cdot AsCl_3 \rightleftharpoons (C_5H_5N \cdot AsCl_2)^+ + Cl^-$$

Applied to the complexes discussed here, the following two ionizations are conceivable.

(a) $SnCl_4 \cdot 2NHR_2 \rightleftharpoons (Cl_4Sn \cdot NHR_2NR_2)^- + H^+$

and

(b) $SnCl_4 \cdot 2NHR_2 \rightleftharpoons (Cl_3Sn \cdot 2NHR_2)^+ + Cl^-$[4]

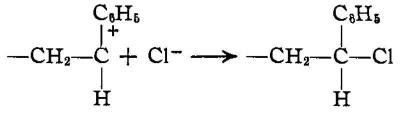
Case (a) is ruled out because it could not take place with tertiary amines which nonetheless are strong inhibitors. Case (b), however, had to be investigated. To this end chloride ions were added to a solution containing styrene and tin tetrachloride in a solvent of dielectric constant 14.0. Tetraethylammonium chloride was prepared (see experimental part), and a solution of it in nitrobenzene was added to a mixture of styrene, stannic chloride and solvent. The results obtained in a solution of dielectric constant 14.0 are shown in Fig. 3.

The inhibitory effect observed in the presence of chloride ions can apparently be ascribed to a reaction between the chloride ion and the growing polymer chain.

[5a] In the preparation of some complexes, control of temperature is rather important. The complex $SnCl_4 \cdot C_6H_5NO_2$, for example, is made by adding excess $SnCl_4$ to nitrobenzene while cooling. As the complex melts at 11°, and nitrobenzene at 5.6°, the separation must be done at an intermediate temperature, *i. e.*, where nitrobenzene is liquid while $SnCl_4 \cdot C_6H_5NO_2$ is solid. This can be done by controlling the temperature of the cooling water in the jacket of D.

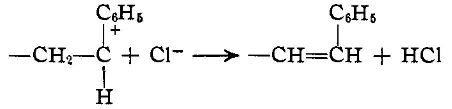
[6] H. Meerwein, *Ann.*, **455**, 227 (1927).

[7] W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley & Sons, New York, N. Y., 1946, p. 51.



$$-CH_2-\underset{H}{\overset{C_6H_5}{C^{+}}} + Cl^- \longrightarrow -CH_2-\underset{H}{\overset{C_6H_5}{C}}-Cl$$

or



$$-CH_2-\underset{H}{\overset{C_6H_5}{C^{+}}} + Cl^- \longrightarrow -CH{=}\overset{C_6H_5}{C}H + HCl$$

Such reactions are known to occur with carbonium ions.[8]

This influence of chloride ions on the polymerization represents another indication of the carbonium-ion character of the reaction. Interaction between the growing carbonium ion chain and a negatively charged particle has been assumed to constitute the termination in the mechanism postulated by Polanyi and co-workers[9] and have been confirmed by various authors.[10]

The observed effect cannot be attributed to the increased ionic strength of the medium. At the concentration of tetraethylammonium chloride used here, (1.237×10^{-3} mole/l.) the ionic strength $\mu = 2.474 \times 10^{-3}$. At such low μ's, the Debye–Hückel limiting law applies and the reaction rate constant is given by Brönsted's formula

$$\log k = \log k_0 + Z_aZ_b\,(\mu)^{1/2}$$

By this formula, making the same assumptions with respect to the mechanism of polymerization as in ref. 2, the initiation and propagation reactions will not be affected by μ. The termination rate, however, should decrease and the over-all rate increases as μ increases. This, is not observed, which indicates that the chloride ions must be involved in a specific inhibition reaction. Inhibition by chloride ions or the Cl end of the HCl dipole is probably also responsible for the inhibiting effect of hydrogen chloride on the polymerization of styrene catalyzed by tin tetrachloride.[11]

Hydrogen chloride may be looked upon as a combination of a catalyst and an inhibitor. In the presence of olefins a carbonium ion is formed by proton addition and the chain is very soon terminated by a chloride ion. Polymers, when obtained, are of a very low degree of polymerization, *e. g.*, dimers.[12] As a consequence, hydrogen chloride is a poor catalyst for Friedel–Crafts polymerizations.

Another role hydrogen chloride can assume in Friedel–Craft systems is that of a co-catalyst. Its presence has been shown to be essential in high temperature carbonium reactions such as polymerizations and alkylations.[13]

At low temperatures, probably because of a high over-all energy of activation, the co-catalytic effect of hydrogen chloride is not manifested. The prevailing action is therefore inhibitory, as observed in the polymerization of styrene and of isobutylene.

Although the above evidence shows that chloride ions *can* act as inhibitors, they do not seem to be responsible for the inhibition observed in our experiments. If the complex would ionize according to scheme (b) alone, one mole of any amine–tin chloride complex should never exceed the inhibiting power of one mole of chloride ions; indeed the two would be equally effective as inhibitors only if the complex would be 100% dissociated.[14]

Instead, at equal molar concentrations, inhibition by chloride ions is even less effective than that by primary amines. The over-all rates in mole/l./hr. of polymerization with various inhibitors obtained in a solution of dielectric constant 14.0 are: none, 3.28; butylamine, 0.059; dibutylamine, 0.043; chloride ions, 0.076.

Thus scheme (b) of dissociation of the complex is not the prevailing effect responsible for inhibition. This is further corroborated by the fact that the rate of polymerization in the presence of inhibitors, $(\text{Rate})_i$, increases with the dielectric constant. Ionization (b), however, should be greatly enhanced at higher dielectric constants and thus, if its effect were considerable, $(\text{Rate})_i$ should decrease as the dielectric constant increases.

Information on whether ionization (b) plays any role whatsoever in such systems as studied here, could be obtained by measuring the conductivity of the solution where the complexes would be prepared under vacuum. Such measurements were not carried out in the present work. It was found, however, that old nitrobenzene, having a high specific conductance, depressed all rates of polymerization. This is probably due to the presence of negatively charged ions.

Inhibition of α-Methylstyrene Polymerization.—Two factors determine the efficiency of an inhibitor: (a) its "free" concentration, as determined by equilibrium (3), and (b) the reaction between amine and carbonium ion. In order to test the importance of steric factors in the latter, a monomer other than styrene seemed interesting to investigate. It was reasonable to assume that weaker inhibition should occur when the substituents on the carbonium ion are bulkier. Accordingly, models were built of α-methylstyrene and the various amines. It was found that the steric requirements of the substituent groups were increasingly conflicting in the series $C_4H_9NH_2$, $(C_4H_9)_2NH$, $(C_4H_9)_3N$, $C_6H_5N(CH_3)_2$. The last

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[8] See for example the formation of α-chloro-β-bromoethane from ethylene, bromine water and sodium chloride, Francis, THIS JOURNAL, **47**, 2340 (1925).

[9] M. Polanyi and co-workers, *J. Chem. Soc.*, 252, 257 (1947), etc.

[10] See for example D. C. Pepper, *Nature*, **158**, 789 (1946); F. S. Dainton and G. B. B. M. Sutherland, *J. Polymer Sci.*, **4**, 37 (1949).

[11] G. Williams, *J. Chem. Soc.*, 1046 (1938).

[12] Risi and Gauvin, *Can. J. Research*, **B14**, 255 (1936).

[13] L. Schmerling, THIS JOURNAL, **66**, 1422 (1944); **67**, 1778 (1945), etc.

[14] Ionization of more than one of the four chlorine atoms is ruled out as highly improbable.

two amines formed which appeared to be rigid ammonium ions in some forced position of high strain.

The results for the polymerization of α-methylstyrene in the presence of amines are shown in Fig. 4.

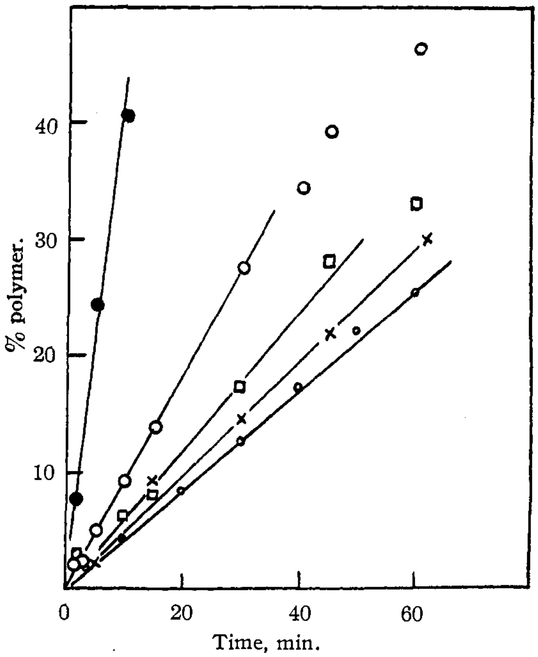


Fig. 4.—Polymerization of α-methylstyrene in presence of amines: ●, no amine; O, Bu-NH_2; O, $(Bu)_2NH$; ×, $(Bu)_3N$; □, dimethylaniline.

A lower over-all monomer concentration had to be used in these experiments as compared to styrene because of the faster rate of reaction. However, the ratio between monomer and catalyst as well as between catalyst and amine were the same as in the polymerization of styrene. From Fig. 4, the inhibiting power of the amines is seen to increase in the order $C_4H_9NH_2 < C_6H_5N(CH_3)_2 < (C_4H_9)_3N < (C_4H_9)_2NH$. The following over-all rates can be obtained from the conversion curves.

Inhibitor	Rate, moles/l./hr.
None	1.156
Butylamine	0.239
Dimethylaniline	.152
Tributylamine	.127
Dibutylamine	.110

These results are consistent with the occurrence of considerable strain in the formation of α-methylstyreneammonium ions. It will be noticed also that toward α-methylstyrene *all* inhibitors are weaker than in the polymerization of styrene; this too is consistent with the assumed manifestation of strain in the former case.

Denoting as before, $(Rate)_0$ = uninhibited rate of polymerization; $(Rate)_1$, $(Rate)_2$, $(Rate)_3$ and $(Rate)_{DMA}$ = polymerization rates in the presence of mono-, di-, tri-*n*-butylamines and dimethylaniline, one obtains

$$(Rate)_0/(Rate)_1 = 4.8\ (10.6);\quad (Rate)_0/(Rate)_{DMA} = 7.6\ (16.6)$$

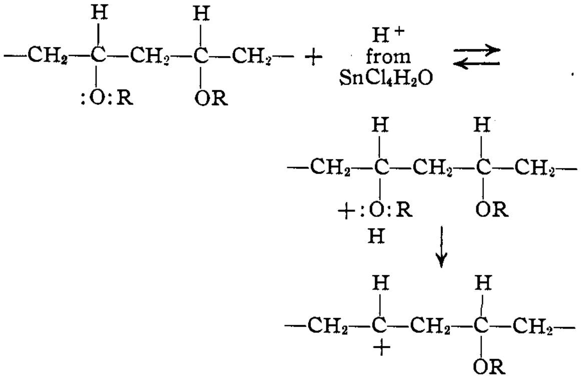
$$(Rate)_0/(Rate)_3 = 9.1\ (16.6);\quad (Rate)_0/(Rate)_2 = 10.4\ (16.6)$$

The figures in parentheses represent the corresponding ratios for the polymerization of styrene; they are seen to be consistently higher showing more efficient inhibition.

Depolymerization of Polyvinyl Alkyl Ethers.—The phenomena of Friedel–Crafts inhibition seem to be related to stabilization of certain polymers against aging. Polyvinyl alkyl ethers change over a period of weeks or months, at room temperature, from solid or rubbery materials into liquids. The breakdown is accelerated by heat, light or the addition of Friedel–Crafts catalysts, the product of degradation being low polymers, alcohols and aldehydes.

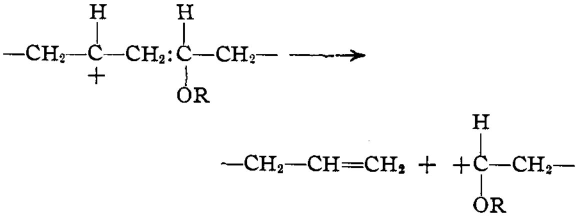
To prevent this degradation 0.5–1% generalized bases are added[15] as stabilizers. They exhibit varying degrees of efficiency; amines are better stabilizers than other compounds, secondary amines being more efficient than primary. This parallelism between stabilization of depolymerization and inhibition suggests that one of the possible mechanisms of depolymerization involves a carbonium ion chain mechanism. It is not unreasonable to assume that remnants of the acidic catalyst initiate a chain by attacking the basic oxygen of an alkoxy group and leads to the following steps.

Initiation



$$-CH_2-\overset{H}{\underset{:O:R}{C}}-CH_2-\overset{H}{\underset{OR}{C}}-CH_2- + \begin{matrix}H^+\\ \text{from}\\ SnCl_4H_2O\end{matrix} \rightleftarrows -CH_2-\overset{H}{\underset{+:\underset{H}{O}:R}{C}}-CH_2-\overset{H}{\underset{OR}{C}}-CH_2- \downarrow -CH_2-\overset{H}{\underset{+}{C}}-CH_2-\overset{H}{\underset{OR}{C}}-CH_2-$$

Propagation



$$-CH_2-\overset{H}{\underset{+}{C}}-CH_2:\overset{H}{\underset{OR}{C}}-CH_2- \longrightarrow -CH_2-CH=CH_2 + +\overset{H}{\underset{OR}{C}}-CH_2-$$

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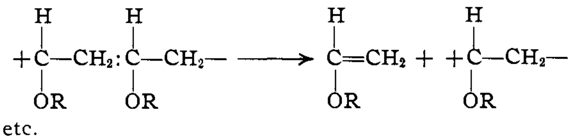
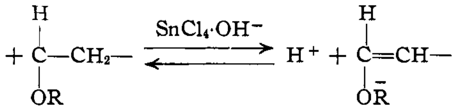
[15] C. E. Schildknecht, A. D. Foss and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).



$+\underset{OR}{\overset{H}{C}}-CH_2{:}\underset{OR}{\overset{H}{C}}-CH_2- \longrightarrow \underset{OR}{\overset{H}{C}}=CH_2 + +\underset{OR}{\overset{H}{C}}-CH_2-$

etc.

Cessation:



$+\underset{OR}{\overset{H}{C}}-CH_2- \overset{SnCl_4{\cdot}OH^-}{\rightleftarrows} H^+ + \underset{\overset{-}{OR}}{\overset{H}{C}}=CH-$

By this mechanism both monomer and low polymers are produced. The monomer which is known to be easily hydrolyzable can then split into alcohol and aldehyde. Thus, all products of degradation can be accounted for.

The stabilizer acts on the carbonium ion in exactly the same fashion as in the cessation of a polymerization chain. The alkyl ether carbonium ion should behave sterically in a similar fashion to styrene. It is not surprising, therefore, that secondary amines are better stabilizers than primary amines. Finally, since benzoyl peroxide and light catalyze the aging, it may be that a radical depolymerization occurs side by side with the carbonium ion chain.

Experimental

Nitrobenzene, carbon tetrachloride, styrene and the amines were purified as described in the preceding paper. α-Methylstyrene (Dow) was distilled under reduced pressure through an all-glass apparatus, b. p. 43° (2 mm.).

Polymerizations were carried out as described in the preceding paper, bromine addition being used to determine both residual styrene and α-methylstyrene.

Tetraethylammonium chloride was prepared as follows: Commercial triethylamine was purified by double distillation. It was refluxed in benzene with an equimolar amount of ethyl iodide for a period of thirty minutes. The mixture was then cooled and filtered. The solid was washed with benzene and ether, then dried in vacuum.

$N(C_2H_5)_4I$ was dissolved in water and shaken for one-half an hour with a slight excess of silver chloride. After filtering, the filtrate was distilled to dryness in vacuum. The solid residue was recrystallized twice from ethyl acetate to which a few drops of alcohol had been added, then filtered and dried in vacuum. The amount of chlorine was determined by dissolving part of the sample in water and titrating against standardized mercuric nitrate using *s*-diphenylcarbazone as an indicator; Cl found, 21.05; Cl calcd. 21.40.

The quaternary chloride does not melt but, rather, decomposes slowly on heating.

Summary

1. Tin tetrachloride dibutylamine complex inhibits Friedel–Crafts polymerization as much as the amine itself.

2. Chloride ion inhibits the polymerization of styrene, thus adding weight to the proposed mechanism of polymerization of Polanyi and coworkers. Chloride ions, however, are not responsible for inhibition by tin tetrachloride–amine complexes.

3. The inhibiting efficiency of amines toward α-methylstyrene has been found to differ from styrene and to follow the order $C_4H_9NH_2 < (CH_3)_2NC_6H_5 < (C_4H_9)_3N < (C_4H_9)_2NH$. This order is explained in accordance with the general mechanism of inhibition.

4. An explanation is offered for the relative efficiency of stabilizers in the aging of polyalkyl vinyl ethers by assuming a carbonium-ion mechanism of degradation.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Hydrolytic Behavior of Metal Ions. I. The Acid Constants of Uranium(IV) and Plutonium(IV)[1]

BY KURT A. KRAUS AND FREDERICK NELSON

In the course of a study of the hydrolytic behavior of metal ions the existence of the species U^{+4} was confirmed and the equilibrium constants (acid constants) for the reaction

$$M^{+4} + 2H_2O \rightleftarrows MOH^{+3} + H_3O^+ \qquad (1)$$

for uranium(IV) and plutonium(IV) were determined. In addition to reaction (1) which was found to be practically instantaneous, slow hydrolytic reactions were also observed. These are probably due to aggregation of hydrolysis products. The aggregates, which will be called "polymers," reach colloidal size, their composition approaches that of the hydroxide, and they greatly affect the chemistry of uranium(IV) and plutonium(IV) systems.[2,3,4] They will be considered in some detail in later papers. The oxygenated species MO^{++} ($M(OH)_2^{++}$) were not observed.

Experimental

Uranium(IV) stock solutions were prepared by reduction of uranium(VI) chloride or perchlorate solutions with known amounts of zinc or by electrolytic reduction. The uranium(IV) concentration and completeness of reduc-

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[1] This document is based on work performed under Contract No. W-7405 eng 26 for the Atomic Energy Commission at Oak Ridge National Laboratory. Part of this work has previously been published in the project reports CN-2289 (November, 1944), MonN-370 (September 1947), CNL-37 (April 1948) and AECD-1888 (April 1948). Part of the material was included in a paper presented at the meeting of the American Chemical Society on April 21, 1948.

[2] K. A. Kraus, F. Nelson and G. L. Johnson, THIS JOURNAL, **71**, 2510 (1949).

[3] K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949).

[4] For a summary of some observations on polymeric plutonium(IV) see K. A. Kraus, National Nuclear Energy Series (NNES) Division IV, Vol. 14B 3.16, McGraw-Hill Book Co., Inc., New York, 1949; (b) K. A. Kraus and F. Nelson, Report AECD-1888 (April, 1948).