

Fig. 4.

Summary

Ozonolysis followed by oxidative cleavage of a copolymer of butadiene and *o*-chlorostyrene has given a 73% yield of acidic products. Succinic acid was isolated in more than the expected amount and 1,2,4-butanetricarboxylic acid in less than the expected amount. This may indicate

some overoxidation of the latter acid to yield succinic acid. β -(*o*-Chlorophenyl)-adipic acid was obtained in 69.6% yield which indicates a random distribution of the styrene units along the polymer chain. Some unidentified acids were also isolated and are under further study.

URBANA, ILLINOIS

RECEIVED JANUARY 30, 1950

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Inhibition of Friedel-Crafts Polymerization¹. I. The Mechanism of Inhibition

BY J. GEORGE, H. WECHSLER AND H. MARK

The polymerization of olefins by such catalysts as aluminum chloride, tin tetrachloride and boron trifluoride,²⁻⁴ is a chain reaction, in the course of which the molecular weight of the polymer remains essentially constant, a high molecular weight material being obtained right at the start.⁵ An indication of the chain character is its sensitivity to inhibitors. Hydrogen halides, hydrogen sulfide and paraffin hydrocarbons lower the molecular weight of polyisobutylene formed in the presence of boron trifluoride⁶; hy-

drogen chloride inhibits the polymerization of styrene by tin tetrachloride,⁵ ethers and alcohols inhibit that of isobutylene⁴ and butyl vinyl ether⁷ and the passage of a stream of trimethylamine completely stops the absorption of acetylene by aluminum chloride.⁸ Since electron deficient molecules are involved in Friedel-Crafts polymerizations, it is not surprising to find that electron pair donors such as amines and oxygen compounds act as inhibitors. In the present work the proportion of inhibitor never exceeded 10% on the catalyst; the marked effect observed notwithstanding indicates that the inhibitor does not merely neutralize the catalyst but somehow interferes with the reaction itself.

Polymerization of styrene and α -methylstyrene was carried out with tin tetrachloride as catalyst and mono-, di-, tri-*n*-butylamine and dimethylaniline as inhibitors. Mixtures of nitrobenzene

(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) (a) H. M. Hulburt, R. A. Harman, A. V. Tobolsky and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943); (b) C. C. Price, *ibid.*, **44**, 351 (1943).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

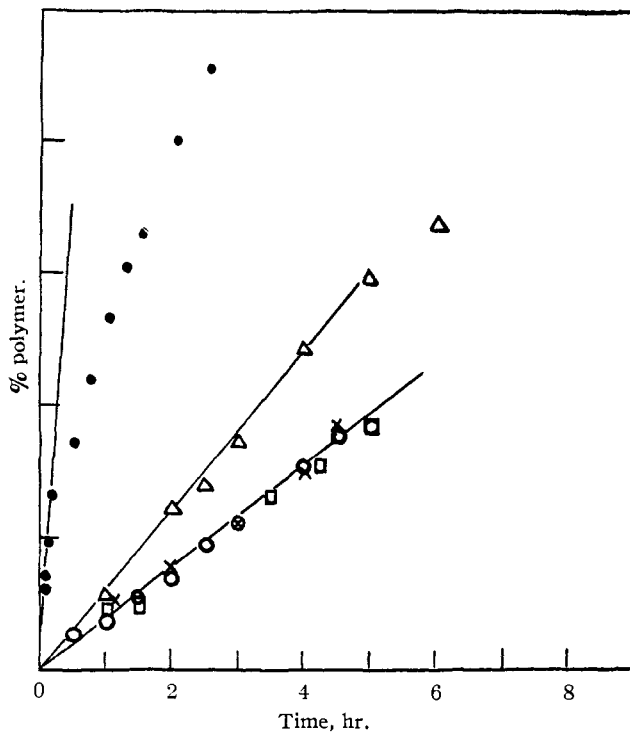
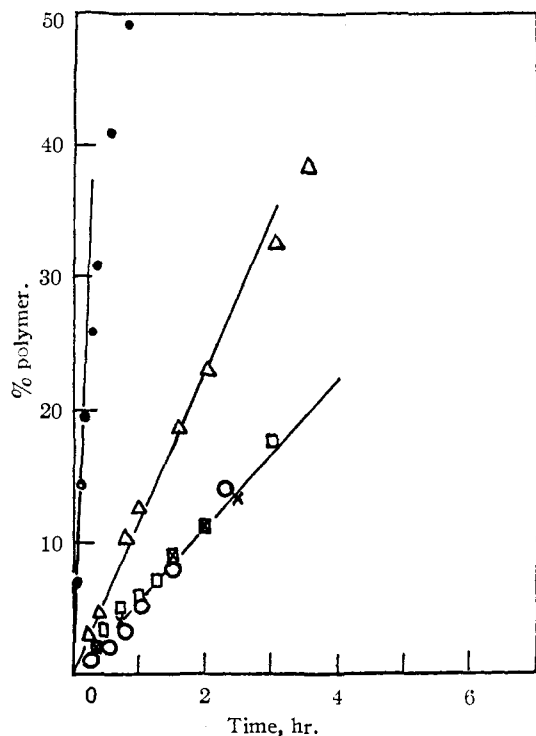
(4) P. H. Plesch, M. Polanyi and H. A. Skinner, *J. Chem. Soc.*, 257 (1947).

(5) G. Williams, *ibid.*, 246 (1938); 1046 (1938); 775 (1940).

(6) R. M. Thomas, W. T. Sparks, P. K. Frolich, H. Otto and M. J. Mueller-Cunardi, *THIS JOURNAL*, **62**, 276 (1940).

(7) D. D. Eley and D. C. Pepper, *Trans. Faraday Soc.*, **43**, 112 (1947).

(8) Hunter and Yohe, *THIS JOURNAL*, **55**, 1248 (1933).



Styrene, 0.8642 *M*; stannic chloride, 1.236×10^{-2} *M*; amine, 1.236×10^{-3} *M*; solvent 40 mole % nitrobenzene and 60 mole % carbon tetrachloride.

Styrene, 0.080 *M*; stannic chloride, 1.545×10^{-2} *M*; amine, 1.404×10^{-3} *M*; solvent 40 mole % nitrobenzene and 60 mole % carbon tetrachloride.

Figs. 1a and 1b.—Polymerization of styrene in the presence of amines: ●, no amine; △, BuNH₂; □, (Bu)₂NH; ×, (Bu)₃N; ⊗, dimethylaniline.

and carbon tetrachloride served as solvents. They have the following advantages: (a) they allow the reaction to proceed in a homogeneous phase; (b) a wide range of reaction rates can be obtained for the same monomer and catalyst concentrations; and (c) the effect of a change in the dielectric constant of the medium can easily be studied.

All experiments were carried out at 27.6°. Samples were withdrawn at various times and the extent of the reaction was followed by bromine addition to the unreacted monomer. When comparing rates with and without inhibitor, the uninhibited reaction was carried out in the presence of as much catalyst as was "free" in the inhibited case (approximately 90% of total tin tetrachloride).

Amines as Inhibitors.—Preliminary experiments showed that the polymerization of styrene by sulfuric acid and tin tetrachloride is considerably retarded by aliphatic and aromatic amines such as *n*-propylamine, mono-, di- and tri-*n*-butylamines, dimethyl- and diethylaniline and pyridine. Figures 1a and 1b represent curves obtained with four amines in a solution of dielectric constant 11.4, at two different monomer and catalyst concentrations. In both figures, the primary amine is the weakest inhibitor, whereas the other three amines are about equally effective.

Some initial rates of polymerization are given in Table I.

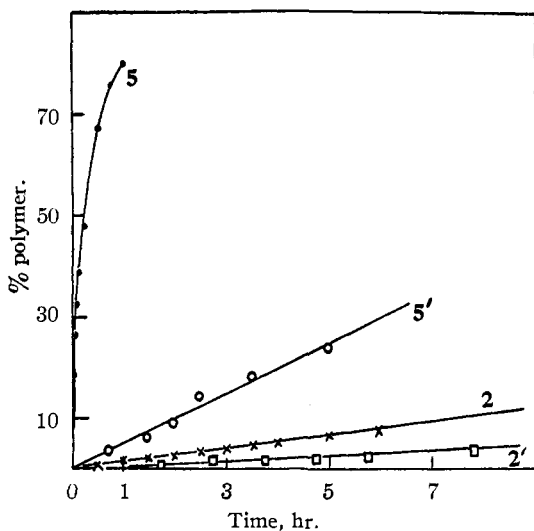
TABLE I
INITIAL POLYMERIZATION RATES OF STYRENE IN THE PRESENCE OF AMINES

Amine	Rate, moles/l./hr.	
	a	b
None	0.478	1.349
BuNH ₂	.054	0.125
(Bu) ₂ NH	.030	0.059

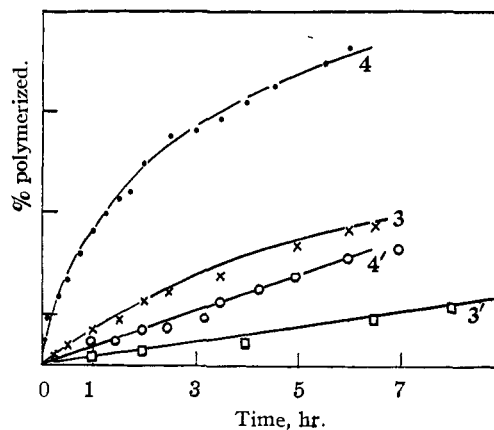
In these reactions approximately zero-order rates are obtained up to about 30% conversion. This differs from what Eley and Pepper⁷ observed for the inhibition of the polymerization of vinyl butyl ether, because their conversion curves exhibit a point of inflection corresponding to the end of an induction period and the molecular weights of the products increase during the induction period. Similar results were obtained in the present work as soon as the nitrobenzene or the tin tetrachloride were not rigorously purified.⁹ It is probable that this inhibition is due to ionized compounds in solution. Thus, as in the free radical polymerization of vinyl acetate,¹⁰ impurities temporarily inhibit the polymerization of styrene with tin tetrachloride.

(9) J. George and H. Wechsler, unpublished results.

(10) K. Nozaki and P. D. Bartlett, *THIS JOURNAL*, **68**, 2377 (1946).



Styrene, 0.8652 M; catalyst, 1.236×10^{-2} M;
(Bu)₂NH, 1.236×10^{-3} M.



Styrene, 0.8652 M; catalyst, 1.236×10^{-2} M;
(Bu)₂NH, 1.236×10^{-3} M.

Figs. 2a and 2b.—Effect of dielectric constant on inhibition: curve 5, 14.0; 4, 11.4; 3, 8.9; 2, 6.5.

On the basis of this mechanism, the termination rate in the absence of an inhibitor is given by $k_3 c_0^+ \cdot X^-$. Since negative particles in solution are always formed simultaneously with carbonium ions, the condition of electrical neutrality requires that $c^+ = X^-$ which leads to

$$-dc_0^+/dt = k_3 c_0^{+2}$$

for the termination rate. With an inhibitor added, the termination rate is given by

$$-dc_0^+/dt = k_3 c_0^+ X^- + k_1 c_1^+ n \quad (9)$$

where n = inhibitor concentration and k_1 = rate constant for the conversion of the carbonium into an ammonium ion.¹⁵ If it is assumed that, at the prevailing amine concentrations, the rate of the regular termination is negligible as compared to the termination by the amine, equation (9) becomes

$$-dc_0^+/dt = k_1 c_1^+ n \quad (10)$$

Denoting the rate of initiation by A , one obtains in the steady state $A = k_1 c_1^+ n$ and by rearrangement, $c_0^+ = (A/k_3)^{1/2} c_1^+ = A/k_1 n$. Therefore

$$r = \frac{c_0^+}{c_1^+} = \frac{k_1 n}{(k_3 A)^{1/2}} \quad (11)$$

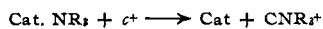
For experiments in which the monomer and catalyst concentration have been kept constant, one can write (10) in the form

$$r = \text{const. } k_1 n / (k_3 k_1)^{1/2} \quad (12)$$

where k_1 = rate constant of initiation.

The linear dependence of r on n provides a test for the suggested mechanism. The concentration of the amine, however, is not simply equal to the

(15) We are very much obliged to the referee for suggesting to us the possibility of the inhibition reaction



which takes place in addition to amine addition to the carbonium ion.

original concentration of the amine as added because of the various equilibria in which the latter can take part.^{15a} To test the above equation one must therefore have recourse to an indirect method which is provided by studying the effect of the dielectric constant on inhibition.

Effect of Dielectric Constant on Inhibition.—

If n is kept constant while the dielectric constant of the medium is varied, the rate ratio, r , should be affected because of the effect of the medium on k_1 , k_2 and k_3 . Qualitatively, one can assume the following: k_1 expresses the perpetuation of a positive ion and will be but slightly affected by a change of the dielectric constant; k_2 and k_3 , on the other hand, will be affected, the latter more strongly. Hence, an increase of the dielectric constant should cause a decrease of k_3 and thus an increase of r . Moreover, at constant monomer and catalyst concentration, the over-all rate of the inhibited polymerization is given by

$$(\text{Rate})_i = \text{const. } \frac{k_2 k_1}{k_3} \frac{1}{n} \quad (13)$$

If the dielectric constant is varied, k_2 and k_3 will be affected to about the same extent and will cancel each other's influence since they represent the same type of reaction and the carbonium ion is a common reactant to both; k_1 on the other hand, will be increased by an increase of the dielectric constant. Figures 2a and b summarize the data obtained with and without dibutylamine at four different dielectric constants, the primed numbers referring to the inhibited runs.

The initial rates of polymerization are given in Table IV.

(Rate)_i and the ratio r increase with the dielectric constant, the latter to a larger extent owing

(15a) Compare the following paper.

TABLE IV

EFFECT OF DIELECTRIC CONSTANT ON INHIBITION^a

Mole % nitrobenzene in solvent	Dielectric constant of soln.	Rate, moles/l./hr. (Rate) ₀	(Rate) _i	r
50	14.0	3.282	0.043	76.3
40	11.4	0.498	.030	16.6
30	8.9	.052	.013	3.9
20	6.5	.011	.004	2.5

^a All solutions contained: 0.8652 M monomer; 1.236 × 10⁻² M catalyst; 1.236 × 10⁻³ M dibutylamine.

to the increase of (Rate)₀. Using expressions derived by Glasstone, Laidler and Eyring,¹⁶ by Kirkwood,¹⁷ and by Laidler and Eyring,¹⁸ one arrives at the relation

$$\ln (\text{Rate})_i = \text{const.} + \text{const.}' \frac{D - 1}{2D - 1}$$

where D = dielectric constant. The linear plot in Fig. 3 lends support to this interpretation. The effect of the dielectric constant on r is given by

$$\ln \left(\frac{1}{r} \right) + K = \frac{K'}{D} + K'' \frac{D - 1}{2D + 1}$$

where K , K' and K'' are constants.

Theoretical curves for various values of K' and K'' are drawn in Fig. 4. The experimental points are represented by small circles. It is seen that no satisfactory agreement exists between theory and experiment. This discrepancy is not surprising in view of the many approximations involved: (a) It has been assumed throughout that the concentration of the inhibitor remains constant in spite of the changes of the dielectric constant. This is not strictly true because the amine and the catalyst form complexes of the formula $\text{SnCl}_4(\text{NR}_3)$.

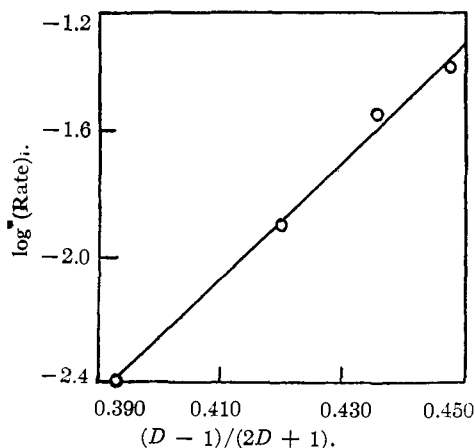


Fig. 3.—Effect of dielectric constant on the inhibited rate of polymerization.

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 419 ff.

(17) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(18) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

These complexes are more polar than either constituent and their formation should be favored by media of high dielectric constant. A reduction in the concentration of the free amine and thus of inhibiting power must therefore result at higher dielectric constants. This effect was not taken into account quantitatively because its magnitude could not be ascertained.

(b) There is some uncertainty as to the effective dielectric constant D to be used in the equations. The electric field between two reacting ions

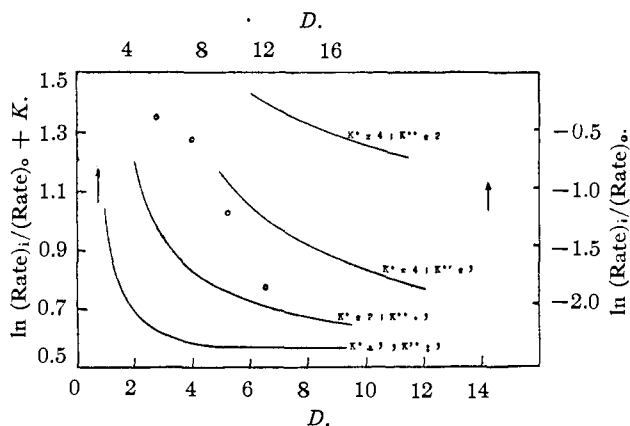


Fig. 4.—Theoretical curves for $\ln (\text{Rate})_i / (\text{Rate})_0 + K = K'/D + K''[(D - 1)/(2D + 1)]$; experimental results for $\ln (\text{Rate})_i / (\text{Rate})_0$ vs. D shown by upper abscissa and right-hand ordinate.

passes partly through the medium and partly through the molecules¹⁹ thus reducing the effective dielectric constant. On the other hand, in mixtures of such different solvents as carbon tetrachloride and nitrobenzene, a localized concentration of the latter around polar species may cause the local effective dielectric constant to be higher than the average value. These two conflicting tendencies may account for the fact that sometimes the effective dielectric constant appears lower,¹⁹ while sometimes it is higher than the average one²⁰; in several cases the measured dielectric constant seemed to be close enough to the effective one to make quantitative correlations possible.¹⁶

(c) Any attempt to separate composite polymerization reactions into elementary steps introduces uncertainties; they are magnified in the derivation of expressions such as that of r which contains the ratio of two dissimilar rate constants.

In view of these approximations no quantitative agreement can be expected for the dielectric constant dependence of such quantities as r ; the qualitative agreement however lends support to the assumed mechanism of inhibition. The quantitative agreement between theory and experiment for $\ln (\text{Rate})_i$ is probably the result of

(19) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

(20) See discussion of Menshutkin reaction in ref. 16.

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_D^{20} 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.

(21) Taylor and Kraus, *THIS JOURNAL*, **69**, 1731 (1947).

The amines (Sharples) were purified by fractional distillation: dimethylaniline, n_D^{20} 1.5584 ("Int. Crit. Tables" gives 1.5587); *n*-butylamine, n_D^{20} 1.4015 ("Int. Crit. Tables" gives 1.401), b. p. 78.0°; di-*n*-butylamine, n_D^{20} 1.4164; tri-*n*-butylamine, n_D^{20} 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 cooperation 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

[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 paper² 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 Friedel–Crafts polymerizations.

Inhibition by Tin Chloride–Amine Complexes

Inhibition was explained in the preceding article by the formation of a stable ammonium ion which

(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).

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 tetrachloride³; 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

$$-dn/dt = k_k(n)(\text{SnCl}_4) + k_i(c^+)(n) \quad (1)$$

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

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