Scavengers for Hydrogen Chloride

EVALUATION AND KINETIC STUDIES

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ONE of the most serious problems arising from the use of chlorinated organic materials is their tendency to liberate hydrogen chloride under the influence of light, heat, or electric discharge. Not only does this lead to corrosion and deterioration of the associated parts of the system but, in some cases, the hydrogen chloride accelerates the further degradation of the chlorinated compound itself.

The work described in this paper was undertaken primarily to develop a method for evaluating various stabilizers that are used in conjunction with chlorinated aromatic hydrocarbon liquids. In particular, this work was concerned with stabilizers for a mixture of hexachlorodiphenyl (60%) and trichlorobenzene (40%), a noninflammable cooling medium for high voltage transformers, designated as transformer Askarel. When this material is decomposed by an arc in the transformer, hydrogen chloride gas is liberated and, unless it is soon removed, will cause extensive deterioration and corrosion. The name "scavenger" has been applied to substances which are capable of reacting with hydrogen chloride to produce innocuous products. A good scavenger must be stable under use conditions and its reaction with hydrogen chloride must be rapid and irreversible.

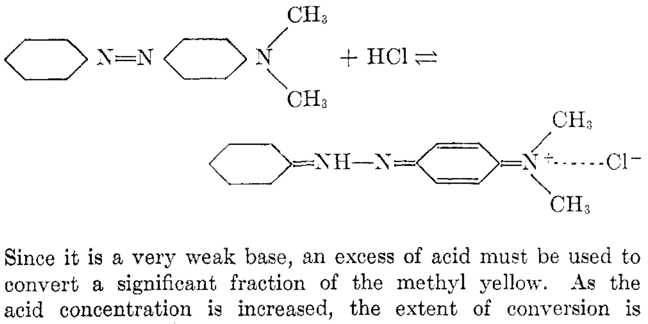
There are two classes of compounds which are very well suited to this application, organometallics, especially the aryl derivatives of lead, tin, and mercury (*1*), and ethylene oxide and its homologs (*2*, *3*).

Tetraphenyltin, $(C_6H_5)_4Sn$, and phenoxypropene oxide, C_6H_5-$OCH_2—CH—CH_2$, have been studied as representative members of these two classes.

$$C_6H_5OCH_2—\underset{\diagdown\;O\;\diagup}{CH—CH_2}$$

METHOD

Methyl yellow is converted by strong acids to an intensely colored red salt.



Since it is a very weak base, an excess of acid must be used to convert a significant fraction of the methyl yellow. As the acid concentration is increased, the extent of conversion is shifted to the right, and the color deepens. Consequently, the light absorption is a measure of the hydrogen chloride present. It is possible to select concentrations such that the amount of hydrogen chloride combined with the indicator is a negligibly small part of the total concentration. The effect of hydrogen chloride on the absorption spectrum of methyl yellow is shown in Figure 1. The negative logarithm of the transmittancy is plotted against wave length for a 2.50×10^{-5} M solution of transformer Askarel from measurements made in a Beckman quartz photoelectric spectrophotometer using a 1.002-cm. Corex cell. Because of the low solubility of hydrogen chloride in transformer Askarel (0.11 mole per liter at 1 atmosphere and 25° C.), it was necessary to take precautions against volatilization losses. In the scavenger studies, optical measurements were made with a Fisher electrophotometer using the green filter supplied with the instrument. Absorption cells were made by attaching 24/40 standard taper joints and stoppers to two 200-mm. borosilicate glass test tubes. One was filled with transformer Askarel and used as a standard for 100% transmittancy. The second was used for calibrating the method and studying the reaction kinetics. Its volume was determined by subtracting the weight when empty from the weight when filled with distilled water. The tube was then filled with the measured volume, less 0.5 ml., of a $1.25 \times 10^{-5}M$ solution of methyl yellow in transformer Askarel (hereafter referred to as indicator solution), thereby leaving a tiny air bubble in the tube when the stopper was inserted. Due to the high viscosity of this liquid, it was found expedient to employ a set of glass syringes fitted with stainless steel needles to deliver known volumes.

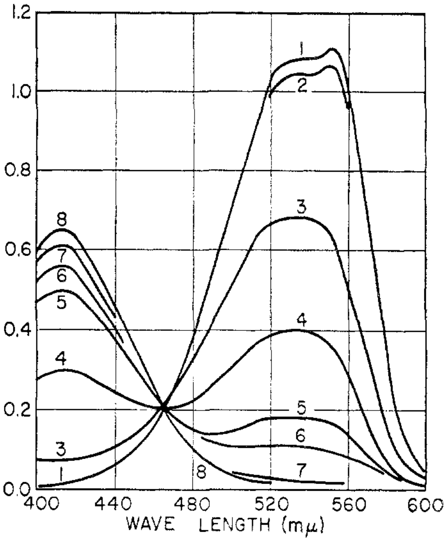


Figure 1. Effect of Hydrogen Chloride on Absorption Spectrum of $2.50 \times 10^{-5}M$ Methyl Yellow in Transformer Askarel

Concn. of added HCl, M

1.	6.6×10^{-2}	5.	1.2×10^{-4}
2.	1.3×10^{-2}	6.	6.0×10^{-5}
3.	1.5×10^{-3}	7.	2.4×10^{-5}
4.	3.0×10^{-4}	8.	0

Calibration. A saturated solution of hydrogen chloride in the indicator solution was prepared by allowing hydrogen chloride from a cylinder to flow through a train of three Nesbitt gas absorption bulbs (Fisher Scientific Co.). The first and third tubes were packed with anhydrous calcium chloride and the second tube was filled with indicator solution. The gas was allowed to flow through the solution for about 15 minutes at the rate of two bubbles per second. The absorption bulb containing the hydrogen chloride solution was then opened and a sample drawn into a 1-ml. Gilmont ultramicroburet (Emil Greiner Co.) with the tip held at least 2 inches below the liquid surface. The tip was then wiped clean, two or three drops expelled, and a known volume of hydrogen chloride solution introduced into the previously prepared optical absorption cell. The tip was held about 1/2 inch below the liquid surface. The tube was then stoppered and the contents were mixed by repeated inversion. The small air bubble greatly facilitated the mixing operation. A simple calculation showed that it absorbed a negligible amount of hydrogen chloride. Two or three aliquots were delivered from the buret into 5.00 ml. of 0.02*N* triphenylguanidine in benzene and back titrated with 0.02*N* *p*-toluenesulfonic acid in chloroform, using methyl yellow as indicator (*4*). In this way, the concentration of the hydrogen chloride in the saturated solution was determined, and the concentration in the optical cell could then be calculated. The calibration curve shown in Figure 2 was obtained in this manner.

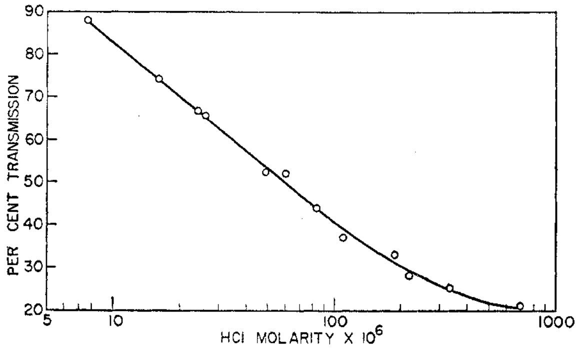


Figure 2. Calibration Curve

MEASUREMENT OF REACTION RATE. The optical absorption cell was filled as described above with an indicator solution containing a known concentration of scavenger. After the contents were mixed for 1 minute, the absorption cell was transferred to the electrophotometer and measured at 1-minute intervals. By the use of the calibration curve, it was thus possible to obtain the concentration as a function of the time. In all cases, an excess of scavenger was used in order to simplify the handling of the rate data. The initial concentrations of the experimental runs which were made are listed in Table I. All measurements were made at 26° ± 1° C.

TABLE I. INITIAL CONCENTRATIONS OF REACTANTS

Expt. No.	Initial HCl Concn., Mole/L.	Initial Scavenger Concn., Mole/L.
	Tetraphenyltin	
T-1	0.000174	0.004546
T-2	0.000281	0.004546
T-3	0.000720	0.004546
T-4	0.000300	0.002266
	Phenoxypropene Oxide	
P-1	0.000918	0.0240
P-2	0.000306	0.0240
P-3	0.000157	0.0240
P-4	0.000280	0.0485
P-5	0.000235	0.0112

RESULTS

In view of the large number of closely spaced experimental points obtained in each run, it was easy to evaluate the instantaneous rate as a function of instantaneous concentration. Logarithmic plots (Figures 3 and 4) clearly show that the rate is first order in hydrogen chloride for tetraphenyltin and 3/2 order in hydrogen chloride for phenoxypropene oxide. If A represents the instantaneous hydrogen chloride concentration, it follows that in the tetraphenyltin reaction, log A should be a linear function of the time, whereas with phenoxypropene oxide, $A^{-1/2}$ should be linear with time. Figures 5 and 6 show that this is indeed the case. In every case studied, the experimental points deviated from the linear relationship when, and only when, A fell below 20×10^{-6} mole per liter. This is the concentration below which an appreciable fraction of the hydrogen chloride present is in combination with the indicator.

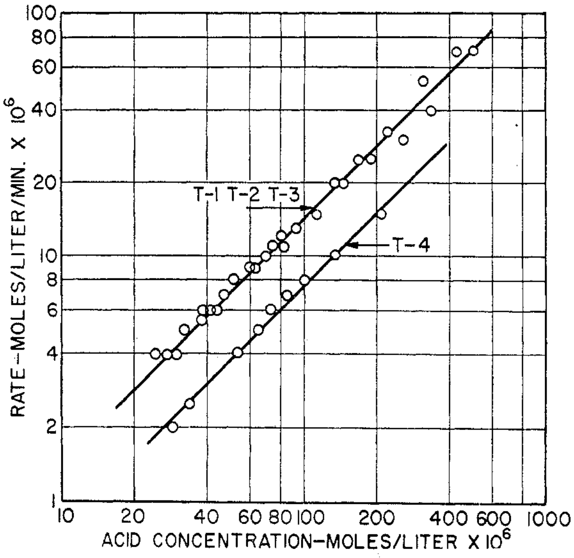


Figure 3. Dependence of Rate on Acid Concentration for Tetraphenyltin

DISCUSSION

The reaction of tetraphenyltin with hydrogen chloride conforms to the equation

$$-\frac{dA}{dt} = k_T\,SA \tag{1}$$

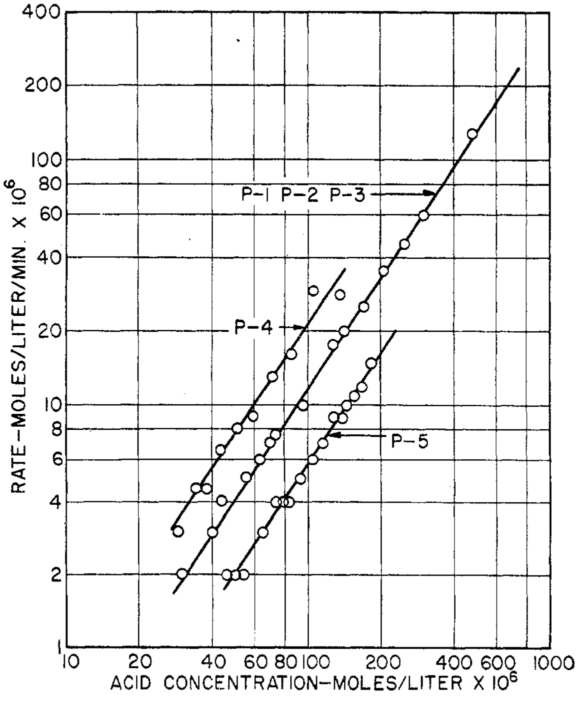


Figure 4. Dependence of Rate on Acid Concentration for Phenoxypropene Oxide

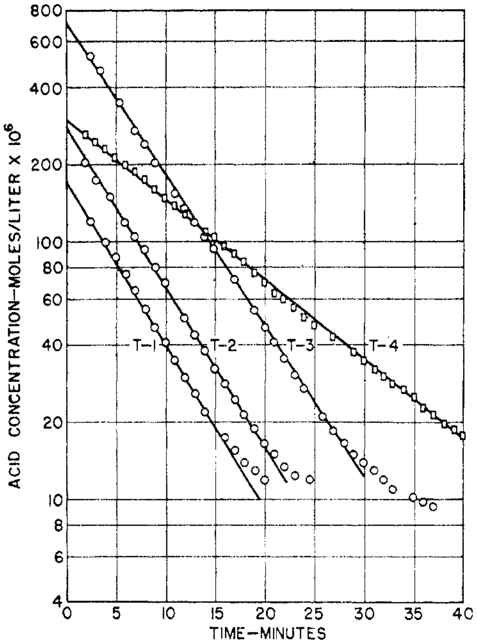


Figure 5. Reaction Rate Curves for Tetraphenyltin

where S is the scavenger concentration, and the rate constant, k_T, has the value 0.52 ± 0.01 mole^{-1} liter second^{-1}. It would seem that this reaction proceeds either by a simple bimolecular collision process or by the unimolecular decomposition of an addition compound. More succinctly,

$$(C_6H_5)_4Sn + HCl \rightarrow (C_6H_5)_3SnCl + C_6H_6$$

$$\text{or } (C_6H_5)_4Sn + HCl \rightleftharpoons (C_6H_5)_4SnHCl \rightarrow (C_6H_5)_3SnCl + C_6H_6$$

On the other hand, the reaction of phenoxypropene oxide with hydrogen chloride presents a more complicated picture. Here the kinetics is described by

$$-\frac{dA}{dt} = k_p S^{0.90} A^{3/2} \qquad (2)$$

with k_p = 5.49 ± 0.04 when concentrations are expressed in moles per liter and time in seconds. The 3/2 order in hydrogen chloride suggests that one of the reactants participating in the rate-determining step is an ion. The deviation from first-order dependence in scavenger may possibly be due to clustering of the phenoxypropene oxide molecules in the hydrophobic solvent. In any case, this deviation will be neglected in discussing the mechanism of the reaction. In view of the low dielectric constant of the solvent (approximately 4.5), it may be assumed that ionic dissociations proceed to a very small extent. Hence,

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$S + HCl \rightleftharpoons SHCl \rightleftharpoons SH^+ + Cl^-$$

where SH^+ and SHCl are the oxonium ion and oxonium salt associated with the ring oxygen atom. It will be assumed that the ionic equilibria are governed by:

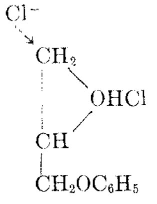
$$[H^+][Cl^-] = K_1A \qquad (3)$$

$$\frac{[SHCl]}{[S]} = K_2A \qquad (4)$$

$$\frac{[SH^+][Cl^-]}{[SHCl]} = K_3 \qquad (5)$$

It turns out that there are two possible rate-determining steps that will give the observed kinetics.

1.



$$Cl^- + SHCl \rightarrow CH_2ClCHOHCH_2OC_6H_5 + Cl^-$$

$$\text{Rate} = k_a[Cl^-][SHCl] = k_aK_2SA^{3/2}(K_1 + K_2K_3S)^{1/2} \qquad (6)$$

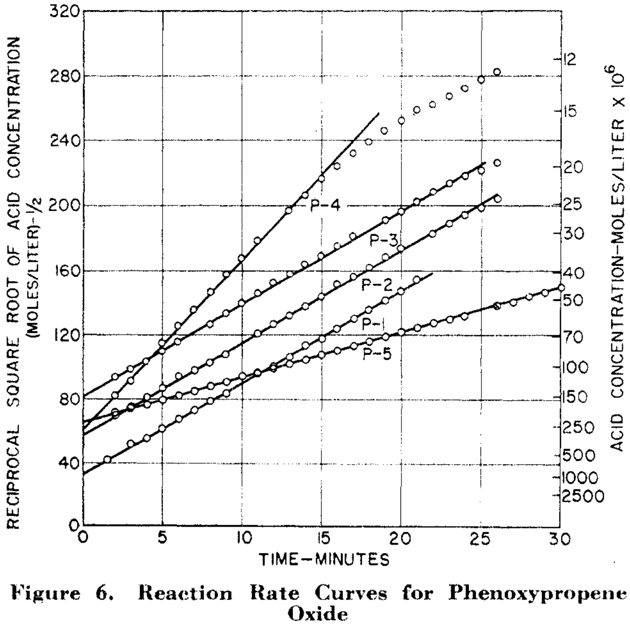


Figure 6. Reaction Rate Curves for Phenoxypropene Oxide

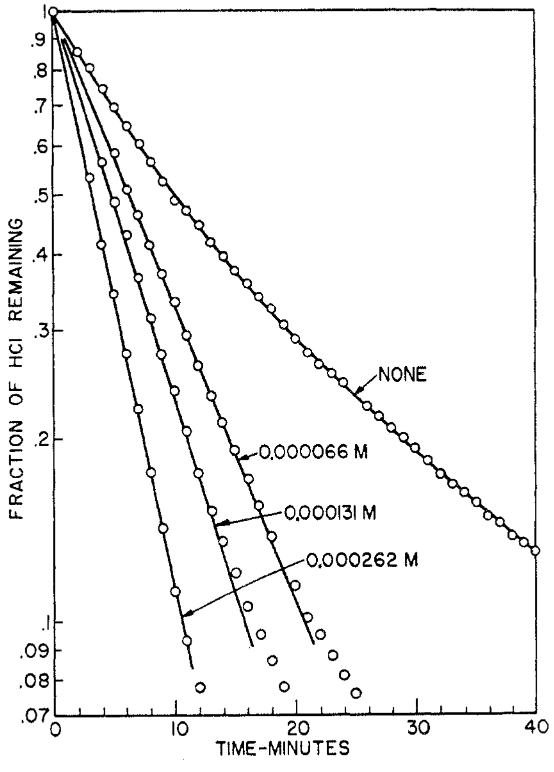
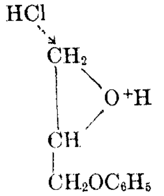


Figure 7. Reaction Rate Curves of Phenoxypropene Oxide with Hydrogen Chloride in Presence of Tribenzylamine Hydrochloride

2.



$$HCl + SH^+ \rightarrow CH_2ClCHOHCH_2OC_6H_5 + H^+$$

$$\text{Rate} = k_bA\ [SH^+] = k_bK_2K_3SA^{3/2}(K_1 + K_2K_3S)^{-1/2} \quad (7)$$

In either case, it is necessary to make the reasonable assumption that $K_1 >> K_2K_3S$ (the reviewer of this paper has pointed out that this is equivalent to the assumption that the oxonium ion, SH^+, is a moderately strong acid) so that,

1. $\text{Rate} = k_aK_2K_1^{1/2}\ SA^{3/2} \quad (8)$
2. $\text{Rate} = k_bK_2K_3K_1^{-1/2}\ SA^{3/2} \quad (9)$

Mechanism 1 predicts a strong acceleration of the reaction by the addition of neutral chlorides. Mechanism 2, however, requires a slight retardation due to the suppression of the ionic dissociation of the oxonium salt. In Figure 7 are shown the results of adding trace quantities of tribenzylamine hydrochloride to solutions initially containing 0.024M phenoxypropene oxide and 0.000235M hydrogen chloride. The striking increase in rate clearly indicates that mechanism 1 is the true mechanism. With higher concentrations of added salt, the reaction proceeded so rapidly that it could not be conveniently measured. It may be seen from the increasing linearity of the logarithmic plots that the reaction is approaching first order in hydrogen chloride. This behavior is readily understood in terms of the proposed mechanism. In the presence of a sufficient amount of added salt, the chloride ion concentration remains nearly constant during the reaction at a value determined by the salt concentration. Consequently, the rate varies only with the instantaneous concentration of phenoxypropene oxide hydrochloride. Application of Equation 4 to mechanism 1 under the above conditions gives

$$\text{Rate} = k_aK_2\ [Cl^-]\ SA \quad (10)$$

in agreement with the first-order dependence on hydrogen chloride observed experimentally. As might be expected, this catalytic effect is not limited to chlorides. Preliminary experiments with bromides and p-toluenesulfonates show similar accelerations in the rate of removal of free acid. However, salts of weak acids are unsuitable for kinetic studies of this kind, since they cannot coexist in solution with hydrogen chloride.

On the other hand, the addition of tribenzylamine hydrochloride to the tetraphenyltin reaction system produced no measurable alteration in the rate of reaction with hydrogen chloride. This emphasizes the difference in the mode of action of the two scavengers considered in this work.

ACKNOWLEDGMENT

The author is indebted to Thomas W. Dakin of the Westinghouse Research Laboratories for his many helpful suggestions during the course of this work.

LITERATURE CITED

(1) British Thomson-Houston Co., Brit. Patent 594,655 (Nov. 17, 1947).
(2) *Ibid.*, 601,359 (May 4, 1948).
(3) I. G. Farbenindustrie Aktiengesellschaft, Brit. Patent 418,230 (Oct. 22, 1934).
(4) Vorlander, D., *Ber.* **66**, 1789 (1933).

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Intrinsic Viscosities and Molecular Weights of Cellulose and Cellulose Derivatives—Correction

In the article on "Intrinsic Viscosities and Molecular Weights of Cellulose and Cellulose Derivatives" [IND. ENG. CHEM., **45**, 2500 (1953)] the following corrections should be made:

p. 2504. In line 2 following Equation 20b, insert an equal sign instead of a minus sign after $[\eta]$ and a comma after the word "constant."

p. 2504. Equation 21 should read

$$\overline{R^2} = \overline{R_0^2}\,\alpha^2$$

p. 2505. 3rd paragraph, line 4

$[\eta]$ *vs.* M should read
$[\eta]$ *vs.* N_m

p. 2505. In the second column, 3rd paragraph, 2nd last line, should read

$N/[\eta]$ *vs.* N_m instead of *vs.* $N^{1/2}$

p. 2505, Figure 4. Caption should read:

Relative Intrinsic Viscosity, $[\eta]_{rel} = [\eta]/[\eta]_m$ as a Function of the Number of Statistical Chain Elements, N_m, *(56)*

Add to subcaption: $[\eta]_m$ = intrinsic viscosity of a single bead

p. 2506, Figure 5. On the abscissa → log $N^{1/2}$ should read → log N_m.

Omit ξ ← from above the caption.

The caption should read: Logarithm of $N/[\eta]_{rel}$ *vs.* Log N_m for $a_0/b_0 = 0.3$ *(55)*.

+. Experimental data for cellulose acetate in acetone ($N_m = \overline{DP}/4.15$) *(1, 66)*.

p. 2507. In Table IV the headings of columns 5 and 6 should read:

R Calcd.^{c}, A., and Ratio $R/R_{ext.}$

At the bottom of the table:

$^c\ \sqrt{\overline{R^2}} = \alpha\sqrt{\overline{R_0^2}}$ (see Equation 21), where

$\sqrt{\overline{R_0^2}} = 10.5\,(\overline{DP})^{1/2}$ [Benoit, H., *J. Polymer Sci.*, **3**, 376 (1948)].

p. 2509. The last line of 1st paragraph, column 1, should read:

$$\overline{(R^2/\overline{DP})}^{1/2}$$

p. 2509. In line 7, 1st paragraph, second column, replace 40 by 26.

p. 2510. In the Nomenclature, second column, the thirteenth item from the end should read: $[\eta]_{rel} = [\eta]/[\eta]_m$ ($[\eta]_m$ = $[\eta]$ of a single bead).

E. H. IMMERGUT
F. R. EIRICH