1740, 1260 cm^{-1}. Glpc analysis (10 ft × 0.25 in. 10% SF-96, Chromosorb W, 140°) showed only one peak.

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Mechanisms of Chlorination by Hypochlorous Acid. The Last of Chlorinium Ion, Cl^+ [1]

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Abstract: Based on product formation, the chlorination of anisole, $CH_3OC_6H_5$ (AnH), by hypochlorous acid, HOCl, follows the rate law $d[AnCl]/dt = k'[HOCl]^2 + k''[H_3O^+][HOCl]^2 + k'''[AnH][H_3O^+][HOCl]$ in aqueous solutions containing perchloric acid ($H_3O^+ + ClO_4^-$), sodium perchlorate, and 0.01 M silver perchlorate. At 0.60 M ionic strength and 25° the rate constants are 0.124 M^{-1} sec^{-1}, 3.06 M^{-2} sec^{-1}, and 0.478 M^{-2} sec^{-1}, respectively. Terms second order in HOCl represent rate-determining formation of chlorine monoxide, Cl_2O, while the term first order in HOCl may result from a termolecular reaction or a reaction of AnH with hypochlorous acidium ion, H_2OCl^+, formed in a prior equilibrium step. An observed zero-order decomposition of HOCl explains the complex titrimetric rate based on HOCl. No term in the rate law is consistent with rate-determining formation of chlorinium ion, Cl^+. It is now extremely improbable that Cl^+ is significantly involved in any thermal reaction ever studied in solution.

The relatively unreactive hypochlorous acid,[2] HOCl, can be converted into more reactive chlorinating agents by catalytic anions, such as Cl_2 by Cl^- ion,[3] chlorine monoxide, Cl_2O, by ClO^- ion,[4] and ClOAc by acetate ion.[5] This mode of nucleophilic catalysis in the presence of acid is supported by the independently determined rate of Cl_2 formation,[6] and by formation constants for Cl_2O[7] and ClOAc[8] that allow for reasonable concentrations of these proposed intermediates. In the presence of sulfuric and perchloric acids, chlorination rates of benzene, toluene, and sodium α-toluenesulfonate are consistent with formation of the more reactive hypochlorous acidium ion, H_2OCl^+.[9]

The most reactive chlorinating agent should presumably be the chlorinium ion, Cl^+, a species that was proposed to explain the kinetics of chlorination of olefins and aromatic compounds by HOCl in aqueous solution at 25°.[10] Titrimetric rate expressions[10] included a contribution that was first order in HOCl, first order in H_3O^+, but independent of the concentration and nature of the organic substrate, and interpreted as rate-determining formation of Cl^+ from HOCl in a manner analogous to nitration *via* the nitronium ion NO_2^+ from HNO_3. Isotope effects in H_2O *vs.* D_2O solution are inconsistent with an alternative proposal of rate-determining formation of H_2OCl^+,[11] and in accord with this Cl^+ proposal. The Cl^+ mechanism has been publicized in many excellent textbooks.[12] However, thermodynamic arguments show that Cl^+ is highly unstable relative to coordinated species.[13] For dissociation of Cl_2 to Cl^+ and Cl^- in water at 25°, the estimated equilibrium constant is 10^{-40}, from which it can be calculated that $[Cl^+]$ is less than 10^{-40} M under conditions where the zero-order dependence on organic substrate was observed. From 1955 to 1967 this dilemma persisted as an outstanding challenge to physical organic chemistry; seemingly *no* mechanistic interpretation could be devised consistent with all of the facts.

The present work was undertaken to resolve this apparent conflict between kinetics, best explained by Cl^+ as an intermediate, and thermodynamics showing that the concentration of Cl^+ is too low to be kinetically significant.[14] We decided to study the chlorination, by HOCl in H_2O solution, of anisole, $CH_3OC_6H_5$, here-

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(1) Supported in part by research grants from the National Institutes of Health and the National Science Foundation and by a predoctoral NIH fellowship to D. R. C. For further experimental details, including computer programs, see DeLanson R. Crist, "Mechanism of Chlorinations by Hypochlorous Acid," Ph.D. Thesis, M.I.T., Jan 1967, 112 pp. Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14, 1967, Abstracts of Papers, S122.

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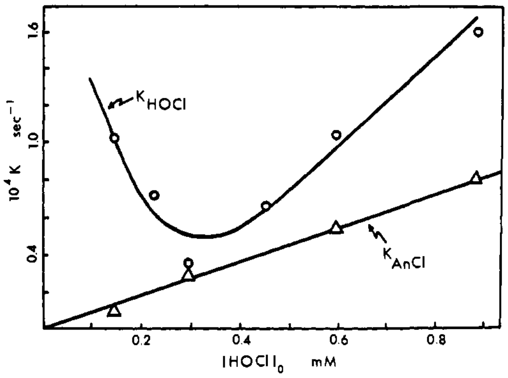

Figure 1. Dependence of initial first-order rate constants on concentration of HOCl, with 8.01 m*M* AnH, 0.46 m*M* H_3O^+, 0.01 *M* $AgClO_4$, and $NaClO_4$ for 0.10 *M* ionic strength.

after written as AnH, under those conditions for which a zero-order dependence on AnH had been reported,[10] *i.e.*, excess AnH in the presence of perchloric acid ($H_3O^+ + ClO_4^-$) to suppress hypochlorite catalysis (ClO^- less than 10^{-6} *M*) and $AgClO_4$ to suppress Cl^- catalysis (Ag^+ greater than 0.006 *M*, Cl^- less than 10^{-7} *M*).

Possible alternative explanations considered for kinetic terms first order in HOCl and zero order in AnH were (1) rate-determining formation of Cl_2[15] or $AgCl_2^+$[16,17] from trace amounts of AgCl, (2) extensive complexing between reactants that could allow for other molecules in the transition state not obvious from the rate law,[18,19] and (3) occurrence of parallel reactions of HOCl causing the titrimetric rate based on HOCl not to reflect accurately the rate of aromatic chlorination.

Results

State of Reactants. No evidence for extensive complexing between various pairs of reactants was found. For mixtures of HOCl and AnH the ultraviolet spectra are additive. The formation constant of the silver complex Ag^+–AnH is only 2.0 ± 0.2,[20] which shows that less than 3% of the AnH is complexed under kinetic conditions with 0.01 *M* $AgClO_4$. Ultraviolet spectral changes for HOCl in 10.0 *M* $HClO_4$ can be accounted for by trace amounts of ClO_2.

Kinetic Order in HOCl at Low Acidity. By measuring the rate of chloroanisole (AnCl) formation it was found that chlorination is second order in HOCl at 5×10^{-4} *M* H_3O^+. The reacting system is complicated by an apparent zero-order decomposition of HOCl which causes the overall rate of decrease of HOCl to change from zero to second order in HOCl over a sufficiently wide range.

The reaction mixtures at low acidity contained 0.46 m*M* H_3O^+, 0.01 *M* Ag^+, and $NaClO_4$ sufficient to provide an ionic strength of 0.10 *M*. Aliquots were analyzed for AnCl by spectroscopic analysis of a heptane extract and for residual HOCl by titration. Observed initial first-order rate constants for AnCl formation, k_{AnCl}, and for HOCl loss, k_{HOCl}, were determined from initial slopes of log ($[HOCl]_0 - [AnCl])/[HOCl]_0$ *vs.* time and log $[HOCl]/[HOCl]_0$ *vs.* time, respectively, and are recorded in Table I.

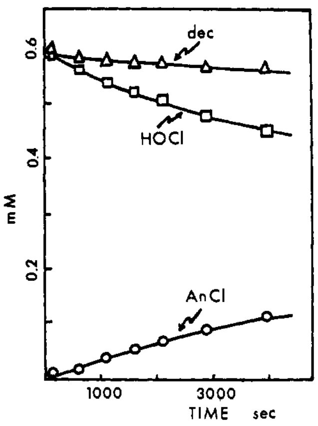

Figure 2. Reactant-product composition during chlorination of 8.01 m*M* AnH, with 0.46 m*M* H_3O^+, 0.01 *M* $AgClO_4$, and $NaClO_4$ for 0.10 *M* ionic strength.

Table I. Initial First-Order Rate Constants for Chlorination and HOCl Loss[a]

Initial $[HOCl]$, m*M*	$10^5 k_{AnCl}$, sec^{-1}	$10^4 k_{HOCl}$, sec^{-1}	$10^6 v_{dec}$,[b] m*M* sec^{-1}	AnCl, % yield
0.147	1.14	1.03	1.0	55
0.296	2.85	0.36	0.6	73
0.595	5.33	1.04	0.4	88
0.883	8.01	1.60	1.3	85
0.226		0.72		
0.453		0.66		

[a] In H_2O at 25.00 ± 0.06° with 0.46 m*M* $HClO_4$, 0.01 *M* $AgClO_4$, 8.01 m*M* AnH, and $NaClO_4$ for 0.10 *M* ionic strength. [b] Represents rate of decomposition of HOCl by paths not producing AnCl. See Figure 2.

The linear dependence of k_{AnCl} on $[HOCl]_0$ in Figure 1 shows that under these conditions chlorination is second order in HOCl with a rate given by eq 1 where k_2 is 0.0915 ± 0.0032 M^{-1} sec^{-1}.

In contrast to this well-defined chlorination reaction, the overall loss of HOCl is more complex (Figure 1), but understandable in terms of a side reaction competing with chlorination. Examination of the typical composition *vs.* time curve in Figure 2 shows a loss in material balance with time. The slope v_{dec} of the difference curve can be regarded as the velocity of a decomposition reaction. Data in Table I suggest that this decomposition is zero order in HOCl, since v_{dec} is reasonably constant (considering that all errors accumulate here in a small number) over a sixfold variation in $[HOCl]_0$. The overall rate of loss of HOCl, the sum of chlorination and decomposition reactions, is given by eq 2 with $k_0 = 0.7 \pm 0.4 \times 10^{-7}$ *M* sec^{-1} and $k_2 = 0.0915 \pm 0.0032$ M^{-1} sec^{-1}. Rewriting eq 2 as eq 3 for initial rates yields the dependence of k_{HOCl} on $[HOCl]_0$ given by eq 4.

$$d[AnCl]/dt = k_2[HOCl]^2 \qquad (1)$$

$$-d[HOCl]/dt = k_0 + k_2[HOCl]^2 \qquad (2)$$

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(15) G. V. Kupinskaya and E. A. Shilov, *Dokl. Akad. Nauk SSSR*, 131, 570 (1960); *Chem. Abstr.*, 57, 9711 (1962).

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(19) For a case in which bromination was zero order in the reactant in excess, see M. Christen and H. Zollinger, *Helv. Chim. Acta*, 45, 2057, 2066 (1962).

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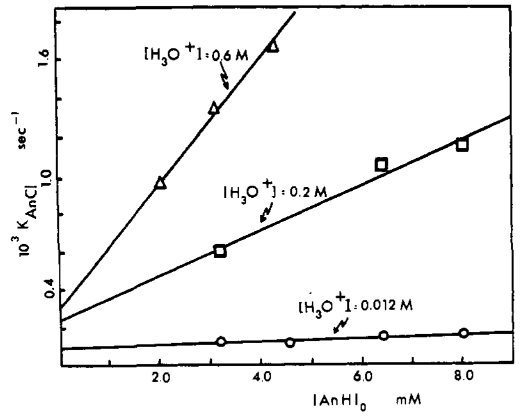

Figure 3. Dependence of chlorination rate constants on concentration of AnH, with various concentrations of H_3O^+ and 0.60 *M* ionic strength.

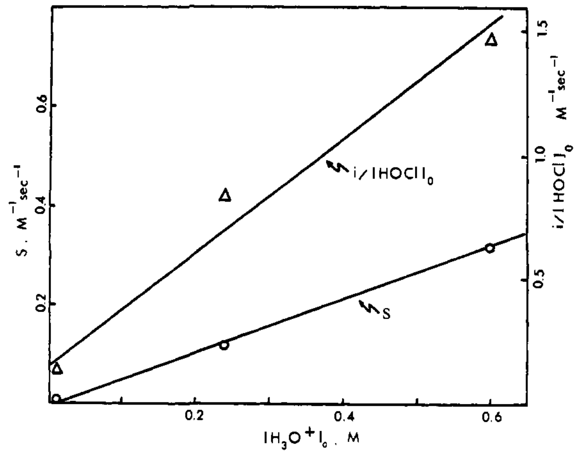

Figure 4. Dependence of intercept and slope values from Figure 3 on concentration of H_3O^+.

$$-d[\text{HOCl}]/dt = [(k_0/[\text{HOCl}]_0) + k_2[\text{HOCl}]_0][\text{HOCl}] \quad (3)$$

$$k_{\text{HOCl}} = (k_0/[\text{HOCl}]_0) + k_2[\text{HOCl}]_0 \quad (4)$$

Inspection of eq 4 shows that k_{HOCl} *vs.* $[\text{HOCl}]_0$ should have a minimum value at 0.28 m*M* HOCl with the above values for k_0 and k_2, in agreement with Figure 1. This minimum provides an alternative explanation for an apparent first-order decrease of HOCl.[10] In the restricted concentration range where second-order and zero-order terms are comparable, the overall rate can appear first order. At higher concentrations of HOCl the titrimetric rate is second order.[10] Additional evidence consistent with the unexpected zero-order decomposition is the decrease in yield of AnCl (Table I) as $[\text{HOCl}]_0$ decreases. This requires the competitive decomposition to be of lower order than chlorination.[21]

To investigate the possibility that these results depend specifically on Ag^+, chlorinations were also carried out using Hg^{2+} instead of Ag^+ to suppress Cl^-. Here [AnCl] was determined by continuous measurement of absorbance at 286 nm, and rate constants were calculated from initial slopes of $\log (A_\infty - A)/(A_\infty - A_0)$ *vs.* time. The first four runs in Table II show that k_{AnCl} increases tenfold for a tenfold increase in $[\text{HOCl}]_0$. Aromatic chlorination is second order in HOCl (eq 1), with a k_2 of 0.081 ± 0.010 M^{-1} sec^{-1}, the same within experimental error as that obtained in the presence of $AgClO_4$.

Table II. Chlorination with Hg^{2+} instead of Ag^+ [a]

$[Hg(ClO_4)_2]$, m*M*	[HOCl], m*M*	Added [KCl], m*M*	$10^5 k_{\text{AnCl}}$, sec^{-1}
0.108	0.085		0.61
0.108	0.170		2.27
0.108	0.424		4.3
0.108	0.848		7.13
0.001	0.429		37.0[b]
0.011	0.429		10.0[b]
0.043	0.424		7.3
0.108	0.424		4.3
0.431	0.424		5.3
1.13	0.429		7.2[b]
0.108	0.424	0.0084	4.8
0.108	0.424	0.0421	4.8

[a] In H_2O at 25.11 ± 0.04° with 0.05 m*M* $HClO_4$ and 5.53 m*M* AnH unless otherwise noted. [b] 5.68 m*M* AnH.

This determination of the kinetic order in HOCl was obtained at the concentration of Hg^{2+} where k_{AnCl} has its minimum value, as seen by the remaining data in Table II. At lower $[Hg^{2+}]$, reaction may be proceeding in part by Cl^- catalysis, while at higher $[Hg^{2+}]$ mercuration becomes important (see Experimental Section). Chlorination was not occurring *via* Cl_2 produced from either free or complexed Cl^-, since added Cl^- had no effect on the rate at 0.108 m*M* $Hg(ClO_4)_2$.

Acid Catalysis. The Complete Rate Law. The complete rate law, based on AnCl formation, was obtained by graphical analysis of data from runs of varying $[\text{AnH}]_0$ and $[H_3O^+]_0$. For each of three acidities, k_{AnCl} is linearly dependent on $[\text{AnH}]_0$ as shown in Figure 3. This result requires the expression for k_{AnCl} to take the form of eq 5. The $[H_3O^+]$ and [HOCl] dependence of *s* and *i* shown in Figure 4 are expressed by eq 6 and 7, and lead to eq 8 for the final form of k_{AnCl}. Substitution into eq 9 gives the complete rate law for aromatic chlorination, eq 10. Values of k', k'', and

$$k_{\text{AnCl}} = i + s[\text{AnH}] \quad (5)$$

$$s = k'''[H_3O^+] \quad (6)$$

$$i/[\text{HOCl}] = k' + k''[H_3O^+] \quad (7)$$

$$k_{\text{AnCl}} = k'[\text{HOCl}] + k''[H_3O^+][\text{HOCl}] + k'''[\text{AnH}][H_3O^+] \quad (8)$$

$$d[\text{AnCl}]/dt = k_{\text{AnCl}}[\text{HOCl}] \quad (9)$$

$$d[\text{AnCl}]/dt = k'[\text{HOCl}]^2 + k''[H_3O^+][\text{HOCl}]^2 + k'''[\text{AnH}][H_3O^+][\text{HOCl}] \quad (10)$$

k''' obtained by this method are 0.157 ± 0.074 M^{-1} sec^{-1}, 2.29 ± 0.23 M^{-2} sec^{-1}, and 0.538 ± 0.024 M^{-2} sec^{-1}.

For an established rate law, a more efficient method of evaluating rate constants is by least-squares analysis. In the present case, measured k_{AnCl} values can be regarded (eq 8) as a function of three parameters, k', k'', and k''', with the initial concentration factors as

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[21] Although no definite conclusions can be made on the nature of the decomposition, it is possible that peroxides are involved, as indicated by the work of E. Chirnoaga, *J. Chem. Soc.*, 1693 (1926), and P. Pierron, *C. R. Acad. Sci.*, 215, 354 (1942).

Table III. Comparison of Observed and Calculated Initial First-Order Rate Constants for Chlorination[a]

$[H_3O^+]$, mM	[AnH], mM	[HOCl], mM	Obsd 10^3k_{AnCl}, sec^{-1}	Calcd[b] 10^3k_{AnCl}, sec^{-1}
0.46	8.02	0.301	0.0394	0.0395
0.46	8.02	0.452	0.0518	0.0584
0.46	8.02	0.677	0.0842	0.0865
12.0	3.21	0.669	0.127	0.126
12.0	4.59	0.669	0.121	0.134
12.0	6.42	0.669	0.159	0.145
12.0	8.02	0.677	0.171	0.155
12.0	1.61	0.297	0.0623	0.0570
12.0	1.61	0.446	0.0855	0.0809
12.0	8.02	0.452	0.146	0.119
239	3.21	0.283	0.601	0.614
239	6.41	0.283	1.05	0.983
239	8.02	0.283	1.15	1.17
239	7.81	0.212	0.957	1.09
239	7.72	0.300	1.05	1.15
239	7.63	0.386	1.23	1.21
239	1.34	0.257	0.348	0.375
239	1.32	0.276	0.378	0.389
239	1.14	0.462	0.521	0.525
239	4.27	0.305	0.826	0.755
239	6.12	0.300	0.972	0.964
358	3.21	0.283	0.869	0.901
478	3.11	0.180	1.06	1.00
597	3.05	0.152	1.35	1.18
597	2.93	0.279	1.52	1.39
597	2.06	0.204	0.962	0.995
597	3.13	0.204	1.34	1.31
597	4.28	0.283	1.66	1.79

[a] In H_2O at 25.00 ± 0.06° with H_3O^+ from perchloric acid, 0.01 M Ag^+ from $AgClO_4$, and 0.60 M ionic strength from $NaClO_4$. Concentrations given are initial values for the concentration range in which k_{AnCl} was determined. Runs with 0.46–12.0 mM H_3O^+ were analyzed by the aliquot method; others were followed by the direct method. [b] Calculated from eq 8 with constants determined by multiple least squares and weighting factors proportional to $(1/k_{AnCl})^2$.

Table IV. Variation of First-Order Rate Constant within a Kinetic Run[a]

[HOCl], mM	[AnH],[b] mM	Obsd[c] 10^3k_{AnCl}, sec^{-1}	Calcd[d] 10^3k_{AnCl}, sec^{-1}
0.809	7.55	3.87	3.67
0.575	7.35	3.04	3.16
0.340	7.18	2.55	2.67
0.265	7.10	1.92	2.51
0.163	7.01	2.06	2.28

[a] In H_2O at 25.00 ± 0.06° with 0.582 M $HClO_4$. [b] Calculated from $[AnH]_0 - [AnCl]_t$ where $[AnCl]_t$ is the chloroanisole concentration at time t. [c] From $(\Delta AnCl/\Delta t)/[HOCl]_t$, not restricted as elsewhere to the value at zero time. [d] Calculated from eq 8 with concentrations given in columns 1 and 2.

known quantities. Standard least-squares procedure applied to data in Table III gave values for k', k'', and k''' of 0.124 ± 0.005 M^{-1} sec^{-1}, 3.06 ± 0.29 M^{-2} sec^{-1}, and 0.478 ± 0.023 M^{-2} sec^{-1}, respectively. These values, considered to be the more accurate ones, will be used in all further discussions. With these constants k_{AnCl} calculated from eq 8 agreed with actual values within an average error of 6.4%. This satisfactory agreement over a wide range of concentrations supports the rate law obtained graphically.

The expression for k_{AnCl} also predicts its variation within a single kinetic run as shown in Table IV. Initially terms second order in HOCl account for 42% of the rate. As the reaction proceeds and this contribution decreases, k_{AnCl} should decrease until it reaches the limiting value, $k'''[AnH][H_3O^+]$. Point by point rate constants, which agreed within experimental error with those calculated from eq 8, decreased to a constant value of 2.0×10^{-3} sec^{-1}. This value, divided by H_3O^+ and AnH concentrations, provides an estimate for k''' of 0.49 M^{-2} sec^{-1}, which is the same as that obtained by multiple least-squares analysis of all the data.

Product Distribution. The effect of acid and ionic strength on the product distribution was obtained from reaction mixtures containing 0.5 mM HOCl, 0.01 M AnH, and 0.01 M $AgClO_4$. Only *o*- and *p*-AnCl were formed, and as H_3O^+ concentration increased from 0.0005 to 1.0 M, the relative amount of *p*-AnCl decreased from 67.6 to 57.9%. At 5×10^{-4} M H_3O^+, this distribution was independent of added $NaClO_4$, but at 0.01 M H_3O^+, where the AnH-dependent term accounts for two-thirds of the initial rate, the effect of $NaClO_4$ parallels that of H_3O^+.[1] These changes in product distribution suggest a change to a less selective chlorinating agent at low [HOCl] but high $[H_3O^+]$.

Discussion

Terms Second Order in HOCl. The rate law for chlorination (eq 10) can be interpreted by parallel reactions leading to AnCl. Terms second order in HOCl probably represent rate-determining dehydrations

$$2HOCl \xrightarrow{k'} Cl_2O + H_2O \quad \text{(slow)} \quad (11)$$

$$2HOCl + H_3O^+ \xrightarrow{k''} Cl_2O + H_3O^+ + H_2O \quad \text{(slow)} \quad (12)$$

$$Cl_2O + AnH \longrightarrow AnCl + HOCl \quad \text{(fast)} \quad (13)$$

to Cl_2O, eq 11 and 12. These terms, zero order in substrate concentration, *cannot correspond to slow formation of Cl^+, $AgCl_2^+$, or Cl_2, since these processes would be first order in HOCl.* The value of k' for uncatalyzed dehydration agrees with that reported[5] for a similar term in the chlorination of allyl alcohol at 25° (0.14 M^{-1} sec^{-1}).

Acid-catalyzed dehydration (eq 12) is not surprising, since OH is converted to a better leaving group. The catalytic effect of acetic acid,[5] nitric acid,[22] and chloric acid[23] on Cl_2O formation has been reported. This is analogous to dehydration of carboxylic acids, which by microscopic reversibility is also acid catalyzed.[24] The earlier observation[11] that chlorination of *p*-methylanisole was faster in D_2O than H_2O (titrimetric rates) can now be interpreted as a solvent isotope effect on acid-catalyzed dehydration.

Kinetic Term First Order in HOCl. The third term in the rate law is consistent with two mechanisms, a termolecular reaction, eq 14, or formation of H_2OCl^+ in a fast prior equilibrium, eq 15 and 16. The route *via* eq 15 and 16 would be excluded if it could be proved

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(22) E. A. Shilov and S. N. Solodushenkov, *Dokl. Akad. Nauk SSSR*, 84, 1001 (1952); *Chem. Abstr.*, **46**, 9958 (1952).

(23) G. C. Israel, J. K. Martin, and F. G. Soper, *J. Chem. Soc.*, 1282 (1950).

(24) See V. Gold, *Trans. Faraday Soc.*, **44**, 506 (1948), for a review of acetic anhydride hydrolysis. See also S. C. J. Oliver and G. Berger, *Recl. Trav. Chim. Pays-Bas*, 46, 609 (1927), for the small catalytic effect of HCl on benzoic anhydride hydrolysis.

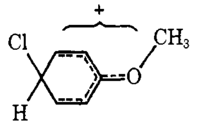
$$HOCl + H_3O^+ + AnH \xrightarrow{k'''} AnCl + H_3O^+ + H_2O \quad \text{(slow)} \quad (14)$$

$$HOCl + H_3O^+ \rightleftharpoons H_2OCl^+ + H_2O \quad \text{(fast)} \quad (15)$$

$$H_2OCl^+ + AnH \longrightarrow AnCl + H_3O^+ \quad \text{(slow)} \quad (16)$$

that formation of H_2OCl^+ is too slow, or its concentration too low, to account for the rate due to this term. Other methods have been used to exclude experimentally a similar pair of bimolecular mechanisms, leaving a termolecular mechanism (like eq 14), in several specially favorable systems.[25]

More detailed conclusions about a possible transition state structure can be made if one makes the reasonable assumption that this term corresponds to those of the same form reported[9] for chlorination of benzene and toluene. Partial rate factors for para chlorination in 1 M $HClO_4$ (relative to benzene, $k''' = 4.2 \times 10^{-4}$ M^{-2} sec^{-1}) can be calculated for toluene ($k''' = 0.027$ M^{-2} sec^{-1}, 23% para) and AnH ($k''' = 0.48$ M^{-2} sec^{-1}, 58% p-AnCl), yielding values of 1.0, 89, and 4000, respectively. A graph of log p_f^{R} *vs.* σ_p^{+}[26] gives a ρ value of -5.4, which indicates considerable interaction with the aromatic ring. The fact that the rates (titrimetric) for benzene and toluene follow H_0 at high acidities[9,27] suggests that H^+ has been completely transferred from H_3O^+ to the $HO^{\delta-}$ of HOCl at the transition state.[28] Finally it seems likely that the transition state is prior to the intermediate σ-complex **1**.[29] Although a primary hydrogen isotope effect was



1

reported for halogenation of AnH with ICl,[30] none was observed for brominations of AnH by Br_2[30] nor of benzene by $HOBr-H_3O^+$,[31] and the transition state should occur even earlier for chlorination than bromination.[32] These conclusions suggest a transition state about half-way between H_2OCl^+ + AnH and H_2O + **1** in structure.

A mechanism involving free Cl_2 generated from Cl^-, eq 17 and 18, is unlikely for the following reasons. The chlorination rate constant k_3 is probably greater than 4×10^4 M^{-1} sec^{-1} (the value for bromination of AnH in H_2O at 25°[33]), since chlorinations are generally

$$HOCl + H_3O^+ + Cl^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cl_2 + 2H_2O \qquad (17)$$

$$Cl_2 + AnH \xrightarrow{k_3} AnCl + HCl \qquad (18)$$

$$\frac{d[AnCl]}{dt} = \frac{k_1k_3[AnH][H_3O^+][Cl^-][HOCl]}{k_2 + k_3[AnH]} \qquad (19)$$

$$\frac{d[AnCl]}{dt} = k_1[H_3O^+][HOCl][Cl^-] \qquad (20)$$

faster than brominations.[34] For 6 mM AnH, it follows that the product k_3[AnH] is at least 20 times as large as k_2 (11 sec^{-1} at 20°).[6] Consequently at this and larger [AnH], Cl_2 reacts *faster* with AnH than with water, ruling out eq 17 as a fast prior equilibrium. These relative rates also preclude a steady-state concentration of Cl_2, which would predict a rate (eq 19) that reduces to an expression independent of AnH concentration (eq 20), contrary to what is observed.

Chlorination *via* Cl· is also unlikely, as judged from the product distribution. In this work p-AnCl was always less than 68% of the total AnCl product mixture. In contrast, free-radical chlorination of AnH (by SO_2Cl_2, benzoyl peroxide, and light) in H_2O at pH 2 gave a AnCl mixture containing 80% p-AnCl.[35]

Nature of Chlorinating Agents. On the basis of inadequate evidence in 1950 for Cl^+, chlorinations have been compared to nitrations, which proceed under certain conditions by a slow formation of NO_2^+.[36] Based on the present kinetic results, a more valid analogy between chlorinations by HOCl and nitrogen chemistry is that to N-nitrosation of amines. Kinetic terms such as $k[HONO]^2$,[37] $k'[H_3O^+][Br^-][HONO]$,[38] and $k'''[H_3O^+][amine][HONO]$[39] have been reported, and represent conversions of HO–NO to the more reactive nitrosating agents, NO_2–NO, Br–NO, and, possibly, H_2ONO^+. Kinetic terms in chlorination are directly analogous, with corresponding conversions of HO–Cl to the more reactive chlorinating agents, ClO–Cl, Cl–Cl, and, possibly, H_2OCl^+.

In retrospect, the most crucial of the previously cited studies following the stimulating work by de la Mare[10] was that by Bell,[13] who explained why Cl^+ is too unstable to be detectably involved. The most durable interpretation of the mechanism of chlorination by Cl_2-free HOCl was by Shilov,[4,22] who suggested Cl_2O as the probable chlorinating agent.

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(25) For example, J. M. W. Scott and J. G. Martin (*Can. J. Chem.*, **43**, 732 (1965)) found that the rate of RCOOH-catalyzed bromination of AnH by ArAcNBr compounds is proportional to [AnH][RCOOH][ArAcNBr], and the ratio of 2-bromo- to 4-bromoanisole depends on both R and Ar, inconsistent with AnH + RCOOBr but consistent with a termolecular process. The same kind of argument was used earlier (dependence of isomer ratio on methylating agent in Friedel–Crafts methylations, H. C. Brown and H. Jungk, *J. Amer. Chem. Soc.*, 77, 5584 (1955); E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 136), and numerous cyclic reactions are now recognized to involve making or breaking three or more bonds concertedly (R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969)). Unfortunately, present evidence does not distinguish conclusively between successive bimolecular *vs.* termolecular routes in analogous RCOOH-catalyzed chlorinations of AnH by ArAcNCl (J. M. W. Scott and J. G. Martin, *Can. J. Chem.*, **44**, 2901 (1966)), and our system is still less favorable for distinguishing between the two possibilities because the difference in elements involved is at most only the elements of a solvent water molecule.

(26) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1959); for σ_p^+ values used here, see C. G. Swain and E. C. Lupton, Jr., *ibid.*, 90, 4328 (1968).

(27) B. L. Murr, Jr., unpublished work in this laboratory.

(28) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(29) For the generally accepted theory of electrophilic substitution, see, for example, E. Berliner, *Progr. Phys. Org. Chem.*, 2, 253 (1964); H. Zollinger, *Advan. Phys. Org. Chem.*, 2, 163 (1964).

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(31) P. B. D. de la Mare, T. M. Dunn, and J. T. Harvey, *J. Chem. Soc.*, 923 (1957).

(32) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955); C. G. Swain and E. R. Thornton, *ibid.*, 84, 817 (1962); E. R. Thornton, *ibid.*, **89**, 2915 (1967).

(33) R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 63 (1961).

(34) Reference 2, p 108.

(35) F. S. Brown and L. P. Hager, *J. Amer. Chem. Soc.*, **89**, 719 (1967).

(36) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 292; 2nd ed, 1969, p 342; P. B. D. de la Mare and L. Main[17] apparently misread our 1967 disproof of Cl^-,[1] which they cite as evidence for Cl^+ or $AgCl_2^+$.

(37) E. D. Hughes, C. K. Ingold, and J. H. Ridd, *Nature* (*London*), **166**, 642 (1950).

(38) C. K. Ingold, *et al.*, *Bull. Soc. Chim. Fr.*, **19**, 667 (1952).

(39) H. Schmid, *Monatsh. Chem.*, **85**, 424 (1953).

Experimental Section[1,40]

Materials. Inorganic (reagent grade) and organic (Eastman pure) chemicals were used without purification unless otherwise noted. Water was redistilled from alkaline $KMnO_4$, and shown to be unchanged in absorbance at 400 nm after further distillation from 0.5 *M* H_3PO_4. Heptane, commercial 99% pure, was purified by treatment with fuming H_2SO_4, and then $ClSO_3H$, washing with 10% NaOH, drying over NaOH pellets, and distillation, bp 98.5–98.9°. AnH, washed with 1 *M* NaOH and dried over Na_2SO_4, was distilled through a 42-cm adiabatic column packed with glass helices. A fraction with bp 61.0–61.8° (22 Torr) contained *o*-$AnCH_3$ as an impurity identified by nmr and ir spectra.[41] A midcut was redistilled giving a fraction, bp 154.5–154.7° (760 Torr), with only 0.003% *o*-$AnCH_3$ present by glc. *p*-AnCl was distilled, bp 93–94° (27 Torr), and shown by glc to contain 0.05% *o*-AnCl. The *o*-AnCl, prepared[42] by a Sandmeyer reaction of *o*-anisidine, was purified by distillation, bp 196.0–197.0 (761 Torr) (lit.[43] 195–196° (760 Torr)), and shown to contain 0.02% *p*-AnCl (glc).

HOCl, prepared from HgO and Cl_2–H_2O,[10] was treated with a 5-g suspension of Ag_2SO_4 (Mallinckrodt analytical) for 30 min prior to final distillation.[44] Stock solutions were titrated amperometrically[45] by using a Sargent-Heyrovsky Polarograph XII to maintain 0.10 V between two stationary 5-mm long Pt electrodes (magnetic stirring). Thiosulfate titration of I_2 released from acidified KI showed that concentrations of the stock HOCl solution varied from 0.01 to 0.03 *M*, depending on the distillation time. These solutions, stored overnight at 0° when necessary, showed less than 2% decomposition over a 3-day period. Blank solutions 0.15–1.5 m*M* in HOCl and 0.01 *M* in $AgClO_4$ showed no decrease in titer during the interval of chlorination runs.

$NaClO_4$, G. Frederick Smith anhydrous reagent, was recrystallized from water and dehydrated to constant weight at 40° (50 Torr). Stock solutions of $AgClO_4$ or $Hg(ClO_4)_2$, 1–2 *M*, were made by adding 1 equiv of 71% $HClO_4$ to analytical grade Ag_2O or HgO purified by precipitation from hot $HClO_4$ solution. The filtered solution was diluted and analyzed by standard methods.[46]

Complexing of Reactants. The formation constant of the AnH–Ag^+ complex was measured[47] by the method of Andrews and Keefer,[20] but with a correction for the decreased solubility of free AnH due to the salt effect. Spectra of 1.9 m*M* HOCl in 1.68 and 10 *M* $HClO_4$ solutions were taken over 210–370 nm, but new bands at 355 and 235 nm indicated only the presence of ClO_2,[48] presumably formed by decomposition of HOCl *via* ClO_2^- ion in acid media.[49]

Kinetic Studies. Reaction was initiated by adding freshly prepared and standardized HOCl stock solution to a solution of the remaining reagents, both at 25°.

A. **Kinetics by Direct Method.** Runs with $HClO_4$ greater than 0.1 *M* or with $Hg(ClO_4)_2$ present were followed by direct measurements of absorbance on a Zeiss PM QII spectrophotometer at 286 nm, which is a maximum for *p*-AnCl. Product concentration was calculated from the *p*-AnCl/*o*-AnCl ratio, glc, and extinction coefficients (aqueous) for AnH, *p*-AnCl, *o*-AnCl, and HOCl of 20.3, 1150, 340, and 28, respectively.

The absorbance of a blank run containing only AnH and $Hg(ClO_4)_2$ increased with time, probably due to mercuration.[50] This reaction was slower than chlorination under the usual conditions, but was studied further to provide proper absorbance corrections. The k_{obsd} increased from 7.4×10^{-4} sec^{-1} for a run 5.7 m*M* in AnH and 1.1 m*M* in Hg^{2+} to 1.27×10^{-2} sec^{-1} for a run 0.51 m*M* in AnH and 0.124 *M* in Hg^{2+} (both at 0.5 m*M* $HClO_4$). Corresponding second-order rate constants[50] of 0.0013 and 0.0010 M^{-1} sec^{-1} were calculated by dividing by the reactant in excess. An increasing correction, $A_{b,t}$, was calculated from $A_{b,t} = A_{b,\infty} - (A_{b,\infty} - A_{b,0}) \exp(-k_2[\text{AnH}]t)$, where $A_{b,\infty}$ and $A_{b,0}$ refer to values from an AnH–Hg^{2+} reaction at the appropriate [AnH] (in large excess) and *t* refers to the time of an absorbance reading in a chlorination run. All rate constants in Table II are corrected for absorbance due to mercuration. These corrections, subtracted from observed readings, ranged from less than 1% of the total absorbance change for runs of the highest [HOCl] to 34% for the lowest.

B. **Kinetics by Aliquot Method.** Reaction aliquots were quenched by addition to enough NaI to produce a 25% solution by weight and acidified to pH 2 with H_2SO_4, and the liberated I_2 was titrated amperometrically with $Na_2S_2O_3$. Throughout the procedure for a given run, volumes and amounts of reagents were kept rigidly uniform to provide accurate blanks for spectrophotometric measurements and for $Na_2S_2O_3$ titer. After titration the aliquot was neutralized and extracted by shaking for 5 min with 5–25 ml of heptane. [AnCl] was determined as discussed below.

Product Analysis. The absorbance of heptane extracts of AnH and AnCl was measured at 247 (mostly AnH absorbance), 286, 287, 288, 289, and 290 (*p*-AnCl max) nm. Extinction coefficients, from triplicate determinations, were, for AnH, *p*-AnCl, and *o*-AnCl, respectively, as follows: (247 nm) 177, 101, and 120; (286 nm) 34.4, 1240, and 698; (287 nm) 20.7, 1250, and 406; (288 nm) 12.0, 1250, and 247; (289 nm) 6.86, 1540, and 150; (290 nm) 3.90, 1860, and 94.1. From these values the concentrations of the three species were calculated by multiple least-squares analysis. Each term in the sum of squares of deviations, $A_{i,\text{calcd}} - A_{i,\text{obsd}}$, was weighted by the reciprocal variance of $A_{i,\text{obsd}}$, which included errors of electrical drift, wavelength setting, and measurement of per cent transmission. The procedure was shown to give better than 2% agreement between actual and found values for total [AnCl] as determined from synthetic reaction mixtures containing 0.01 *M* $AgClO_4$, 4.93–9.86 m*M* AnH, and 0.5 m*M* AnCl (68–54% *p*-AnCl). To obtain satisfactory agreement at product concentrations below 0.1 m*M*, the procedure was modified by using the fraction of *p*-AnCl, *f*, obtained from glc data, and AnH concentration, obtained from the least-squares analysis of the spectrum. Total AnCl was calculated from the absorbance at 290 nm by the equation $[\text{AnCl}] = (A_{290} - \epsilon_{\text{AnH}}[\text{AnH}])/(f\epsilon_{p\text{-AnCl}} + (1 - f)\epsilon_{o\text{-AnCl}})$.

For kinetic runs the *p*-AnCl/*o*-AnCl ratio was measured on an Aerograph HY-FL 600 D gas chromatograph equipped with a flame ionization detector and a 3.4-m column of 15% cyanoethyl-type silicone fluid (G.E. XF1150) on Chromosorb P. With a carrier flow rate of 23 ml/min at 144°, retention times, in minutes, were as follows: AnH, 5.8; *o*-AnMe, 8.3; *m*-AnCl, 14.1; *p*-AnCl, 15.6; and *o*-AnCl, 19.1. Calibration showed that the actual ratio of para/ortho isomers is a factor of 1.03 greater than the observed ratio of areas (planimeter). For determining the effect of $HClO_4$ or $NaClO_4$ on the isomer ratio, an F and M 720 dual column gas chromatograph equipped with a thermal conductivity detector and electronic integrator was used, with a 1.06 calibration factor.

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[40] All boiling points are uncorrected. All solutions of HOCl and $AgClO_4$ were kept in black-coated flasks to minimize decomposition.

[41] National Research Council, Committee on Spectral Absorption Spectra, NRC–NBS, Washington, D. C., 1952 ff., Infrared Spectra, compound no. 1458.

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[45] For specific titration used here, see C. W. Foulk and A. T. Bawden, *J. Amer. Chem. Soc.*, 48, 2045 (1926); see also H. W. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis," 3rd ed, Van Nostrand, Princeton, N. J., 1958, p 555.

[46] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, MacMillan, New York, N. Y., 1952, pp 545, 547.

[47] Although it did not affect the value of the formation constant, it was found that the extinction coefficient for AnH in heptane was 55.4 at 237 nm, one-tenth that reported by Andrews and Keefer,[20] but comparable to other literature values of: 48, G. Scheibe, *Chem. Ber.*, **59**, 2625 (1926); 67, Ramart-Lucas and M. V. Vantu, *Bull. Soc. Chim. Fr.*, **3**, 1165 (1936); 51, Ramart-Lucas and M. Rabaté, *C. R. Acad. Sci.*, **196**, 1493 (1933); and 42, K. L. Wolf and W. Herold, *Z. Phys. Chem.*, *Abt. B*, **13**, 201 (1931).

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