Thermal Decomposition of Poly(vinyl chloride): Kinetics of Generation and Decay of Hydrogen Chloride in Large and Small Systems and the Effect of Humidity

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ABSTRACT

Experiments in which PVC wire insulation was decomposed by an electrical overload in a plenum or in a 200 ℓ PMMA box showed that the highest concentration of HCl in the atmosphere was always less than 40% of the theoretical amount of chlorine in the original sample. Furthermore, this concentration quickly decays to a level that is dependent on humidity, but never more than 4% of the theoretical maximum. A mathematical model was used to determine a number of parameters that describe the system. The same model applies to both large and small scale tests. This treatment showed that less than 48% of the chlorine in the wire reached the atmosphere. It also showed that the rate of decay was primarily dependent on the rate of transport in the system, producing a half life of 5-6 min without external agitation. Furthermore, the final HCl concentration was found to be dependent on relative humidity, and on surface composition (painted gypsum or PMMA).

INTRODUCTION

Large scale experiments have recently been conducted[1] in order to confirm earlier observations from small scale work[2-7] that hydrogen chloride (HCl) is not indefinitely stable in the atmosphere, but rather that it "decays." With the objective in mind of developing a mathematical model of the airborne HCl concentrations observed, which can be used for a variety of scenarios, smaller scale experiments were designed to facilitate quantification of the effects of relative humidity (RH) and air recirculation on the transport and decay of HCl.

EXPERIMENTAL

The large scale experiments consisted of the decomposition of 30 ft of commercially available, PVC-insulated wire typical of that used to carry electric power in a home or office[1]. The decomposition was performed in an 8 ft x 12 ft x 12 ft enclosure divided into an 8 ft high room and a 4 ft plenum. Decomposition was afforded by current overload of 180 or 250 A.

In addition, the apparatus included a rudimentary air recirculation system which withdrew air from the plenum in the center of the 4 ft x 8 ft wall, filtered it and returned it through a duct which extended from the center of the 4 ft x 12 ft plenum wall to the center of the ceiling and down into the room. This was run at eight room-air-changes per hour in Experiment 3 and not used in

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the others. In some of the experiments (2 and 3) an 8 in by 24 in grating was placed in the ceiling centered along and within a foot of the 12 ft wall. This grating became a part of the air recirculation system in Experiment 3, serving as the return air vent.

The apparatus was instrumented with continuous analyzers for CO, CO_2 and hydrocarbons. HCl was analyzed by drawing the atmosphere for a prescribed period of time through 3 mm tubes packed with 20-30 mesh soda lime. Hereafter, these are called soda lime tubes or SLTs. Additional detail on the apparatus and methods of analysis is documented elsewhere.[1]

Four variations were conducted in the large scale apparatus. The first three tests were designed to investigate flow conditions, with similar sample configuration and decomposition, at 180 A. For the first test the recirculation system was off and the ceiling was solid (no grate). For the second experiment, the grate was in place. For the third experiment, both the recirculation system and the grate were utilized. The fourth experiment used a large decomposition current, 250 A, but was configured as in the first. Heating ceased in this experiment after 5 minutes when the conductor fused open.

For mathematical treatment of the large scale experiments, plenum HCl values were averaged, and are presented in Table I. For Experiments 1, 2 and 4, this is an average of three sites. For Experiment 3 (where the recirculation system is utilized) the SLT site over the grate was not included as the final HCl concentrations recorded at this site were significantly different from the others. They are noted separately in Table I as is the room site with the highest readings. Note that forced recirculation (Test 3) causes a significant amount of HCl to be transferred to the room. Also, in Test 2 there is a large difference in HCl concentration between the sites directly above and below the grate which are separated by only 2 ft.

TABLE I. HCl Concentrations for Large Tests (ppm in Atmosphere).

	Test 1		Test 2		Test 3			Test 4		
Time, min	Plnm Avgs	Room Ste 7	Plnm Avgs	Room Ste 7	Plenum Ste 1&2	Ste 3	Room Ste 7	Time, min	Plnm Avgs	Room Ste 7
3-7	326	10	370	<10	280	220	<10	0-2	97	<10
7-11	2553	<10	2593	<10	1635	1680	100	2-4	2103	<10
11-15	2260	<10	2163	<10	935	1310	200	4-7	2897	10
15-20	1463	<10	1410	<10	370	440	150	7-11	1767	10
20-25	950	<10	877	10	150	210	60	11-15	1110	10
25-30	603	10	640	<10	65	210	40	15-20	663	10
30-37	436	<10	430	<10	30	410	10	20-25	400	10
37-45	250	<10	277	10	20	290	10	25-30	243	10

After the first large scale test, a sample of ceiling tile was analyzed for chlorine. Extrapolation of excess chlorine recovered from this sample to the entire ceiling surface area accounted for 17 per cent of the chlorine originally present in the insulation. A crude estimate of total chlorine deposition can be obtained by further extrapolation to the entire plenum wall and ceiling surface. This would account for 62 per cent of the chlorine originally present.

The small scale experiments were conducted in a 47.25 in x 16.5 in x 14.125 in poly(methyl methacrylate) (PMMA) box, similar to the chamber used in the NBS toxicity protocol.[8] This is a direct scale down of the larger tests based on mass PVC per plenum unit volume. Mixing was accomplished by a small fan fitted at one end of the box.

The wire samples consisted of 6 in of PVC insulation left in the center of a 2 ft section of conductor, laid on a small Marinite® board, elevated two inches by placement on an inverted Pyrex dish. Decomposition was accomplished by 180 A current overload. Instrumentation for sampling the same gases as in the large scale experiments was incorporated into the box.

Three HCl sampling devices were situated at different heights to test vertical stratification. In addition to three thermocouples situated vertically through the box at the wire sample end, one thermocouple was attached directly to the wire with a standard potting ceramic. Wall deposition of HCl was measured in these tests by analysis of evenly spaced 3 in x 3 in PMMA coupons placed on the floor of the box. Also, after each experiment the atmosphere was pumped through a large soda lime tube. This was combined with a similar "filter" on the continuous sampler throughout the experiment and analyzed in the same manner as the other SLTs.

Ten small scale tests (numbered 11 through 20) were conducted, all at 180 A. The recirculation fan was on for 6 of the these 10 tests although the recirculation rate could not be set totally reliably. The relative humidity (RH) levels used were 80, 50 and 5%. The order of experimentation was obviously influenced somewhat by the weather.

Data for the small scale tests are presented in Tables II and III. HCl concentrations represent averages of all the sampling sites. For some of the Fan On experiments, however, only the top two sets of SLTs were analyzed (Tests 11, 14, 17 and 18), when it was determined that the fan truly produced a homogeneous atmosphere. Final HCl concentrations are very low--<300 ppm in any event--representing less than 4% of the chlorine in the original sample. Chlorine analyses for the char, filters and coupons (assuming the coupons represent a uniform coating on the interior surfaces of the test chamber) are also included.

SLTs provide HCl values averaged over the time the sample was taken; however, for the mathematical treatment, distinct time/concentration pairs are necessary. To accomplish this the time intervals presented in Tables I and II were represented by the median value. The shape of these curves, shown in Figure I, suggest exponential phenomena for both production and decay of the HCl concentrations. In addition, a term must be included to account for the final, non-zero, HCl concentrations. While this seems at first to be a complex problem, equations of this form have been used to explain the kinetics of various chemical systems. A general set of equations that describes a group of species, the concentrations of which are interrelated by first-order phenomena, has been described by Moore and Pearson.[9]

Use of these mathematical techniques is by no means limited to chemistry. A scheme that represents the physical system in a manner consistent with this approach is shown in Figure II, along with equations adapted to the model. In addition to the three constants, k_{12}, k_{23} and k_{32}, an induction period, t_0, and the total amount of HCl released, A_0, must also be estimated.

TABLE II. HCl Concentrations for Small Scale Tests.[1]

Time, min	Test 11	Test 12	Test 13	Test 14	Test 15	Test 16	Test 17	Test 18	Test 19	Test 20
0-2	0	53	87	30	60	0	40	0	0	0
2-4	0	83	170	40	123	87	65	70	120	113
4-6	130	490	413	310	495	1270	545	440	1407	1147
6-8	255	547	503	1115[2]	867	1743	1060	920	2283	1850
8-10	265	447	330	430[3]	545	1513	730	805	2020	1500
10-14	185	273	213	245	260	1000	335	500	1340	1017
14-19	155	203	137	170	117	617	125	255	733	503
19-25	115	177	137	115	73	430	95	150	400	257
25-30	95	133	110	100	47	207	55	70	207	143
30-35	80	127	83	100	47	143	50	40	117	90
35-40	60	110	80	95	37	107	40	40	83	57
40-45	50	97	80	60	37	80	35	30	57	47

[1] Parts per million in atmosphere
[2] Time for this sample is 6-7 min
[3] Time for this sample is 8.33-10 min

FIGURE I. Full Scale Test 1, Average Plenum Concentrations.

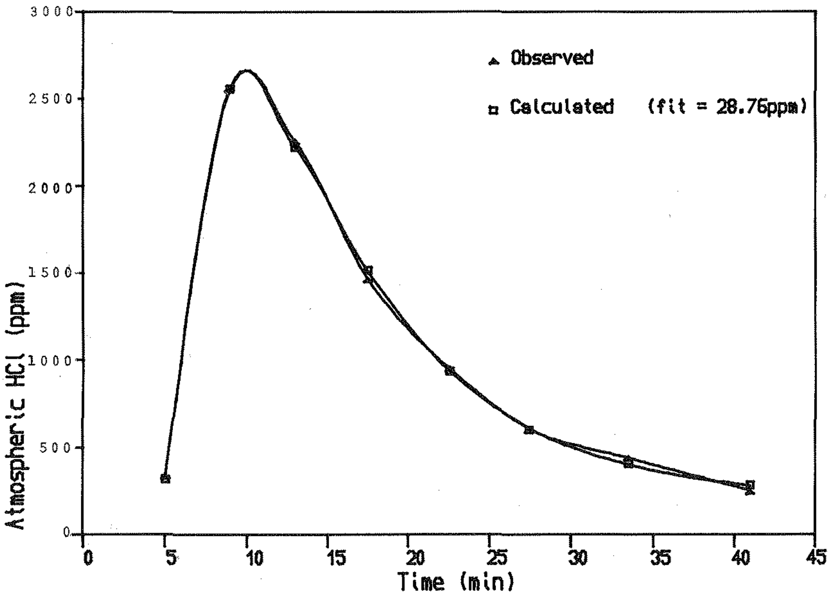


TABLE III. Wet Analyses for Chlorine.[1]

	Test 11	Test 12	Test 13	Test 14	Test 15	Test 16	Test 17	Test 18	Test 19	Test 20
Char	31.5	40.7	30.3	42.1	55.6	39.1	46.4	32.7	21.5	45.5
Surface[2]	4.2	6.5	4.1	4.2	4.0	8.9	3.1	2.6	5.8	4.6
Filters	1.4	5.9	1.5	1.4	1.0	8.6	2.7	2.7	8.9	9.0

[1] Per cent of total theoretical (2.08 g Cl/sample)
[2] Extrapolated from coupons

The simplex method[10] was chosen as the mathematical optimization protocol. This system investigates a local area of the goodness-of-fit response surface and uses the slope of this portion to estimate a direction and magnitude for the adjustment of the parameters. Graphically, this results in a dimension for each of the parameters to be optimized plus one for the goodness-of-fit, thus producing a six-dimensional problem. Two computer programs were independently developed for the IBM Personal Computer to incorporate the methods outlined by Deming and Morgan and each gave essentially the same results. Goodness-of-fit was found using a simple standard deviation with n-1 weighting.

FIGURE II. Proposed Deposition Process and Mathematical Treatment.

$$\underset{[A]}{\begin{array}{c}\text{Potential}\\ \text{HCl}\end{array}} \xrightarrow{k_{12}} \underset{[B]}{\begin{array}{c}\text{Atmospheric}\\ \text{HCl}\end{array}} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \underset{[C]}{\begin{array}{c}\text{Deposited}\\ \text{HCl}\end{array}}$$

$$[B] = A_0\left[\frac{k_{12}k_{32}}{l_2 l_3} + \frac{k_{12}(k_{32}-l_2)}{l_3(l_2-l_3)}\, e^{-l_2 t} + \frac{k_{12}(l_3-k_{32})}{l_3(l_2-l_3)}\, e^{-l_3 t}\right]$$

where

$$l_2 = \frac{(p + q)}{2} \qquad l_3 = \frac{(p + q)}{2}$$

and

$$p=(k_{12} + k_{23} + k_{32}) \qquad q=[p^2-4(k_{12}k_{23} + k_{12}k_{32})]^{1/2}$$

A three-dimensional presentation of the goodness-of-fit response surface is presented in Figure III. For the three dimensions not shown, the induction period t_0 was fixed at 4.8 min, k_{32} was fixed at 0.0087 min^{-1}, and k_{23} was described empirically as a function of k_{12} and A_0 by the equations:

$$k_{23} = k_{12} - 0.5231 + 0.7319x - 1.332x^2 + 0.6696x^3$$

with $x = (A_0-4000)/7000$.

The simplex program was modified so as to hold one of the parameters constant while optimizing the others and, after all the points of the simplex produced similar goodness-of-fit (in this case +/- 0.01), to step the first parameter to a new point in order to investigate better the area at the bottom of the response surface "valley". This approach details the bottom of the valley, and the result is presented in Figure IV, together with the production and decay rate-constants corresponding to these points. This graph clearly shows the same general form noted for the valley in Figure III and further reveals a distinct minimum at low values of A_0. The exact minimum was found using a fully optimized simplex routine and the optimum values for the parameters were confirmed by reproduction from a different starting point.

RESULTS AND DISCUSSION

The results of the modeling calculations for the large scale tests are presented in Table IV. All tests produced similar values for the total amount of HCl released, A_0, representing 53% of the theoretical maximum, based on the chlorine in the PVC (the somewhat smaller value for Test 3 could be due to less

TABLE IV. Summarized Large Scale Test Results - Fully Optimized Constants

	Starting Points (A_0) ppm HCl	A_0, ppm HCl	t_0, min	k_{12}, min^{-1}	k_{23}, min^{-1}	k_{32}, min^{-1}	Goodness of Fit, ppm HCl
Test 1	4000	4551.8	4.78	0.338	0.120	0.0059	28.76
	5000	4569.3	4.78	0.336	0.121	0.0059	28.79
Test 2	3500	4294.0	4.77	0.401	0.116	0.0070	23.42
	5000	4258.5	4.77	0.406	0.114	0.0067	23.32
Test 3	2500	3687.7	4.80	0.402	0.244	0.0017	7.51
Test 4	3500	4002.7	2.61	2.010	0.138	0.0053	43.68
	4500	3996.8	2.67	2.350	0.137	0.0052	43.30
Average		4194.4[1]	4.78[2]	0.377[2]	0.124[3]	0.0060[3]	
Std Dev		296.4	0.01	0.032	0.008	0.0006	
Percent Variation		7.1	0.2	8.6	6.5	10.7	

1) All tests
2) Tests 1, 2 & 3 only
3) Tests 1, 2 & 4 only

FIGURE III. Response Surface Analysis, Large Scale Test 1.

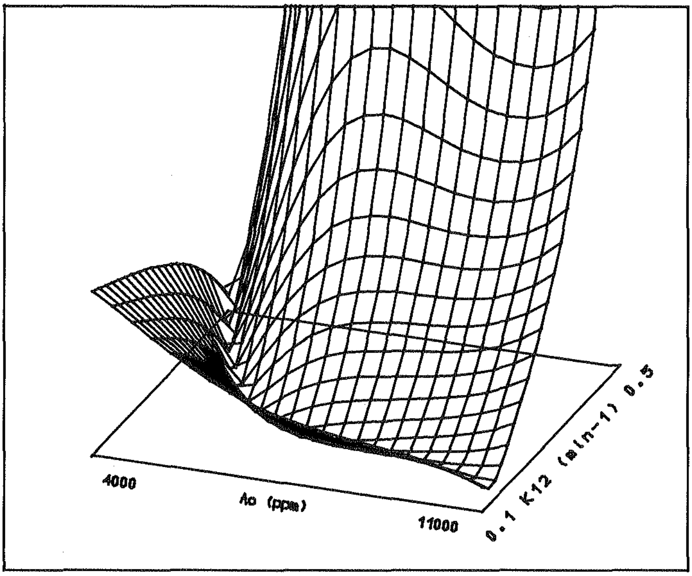
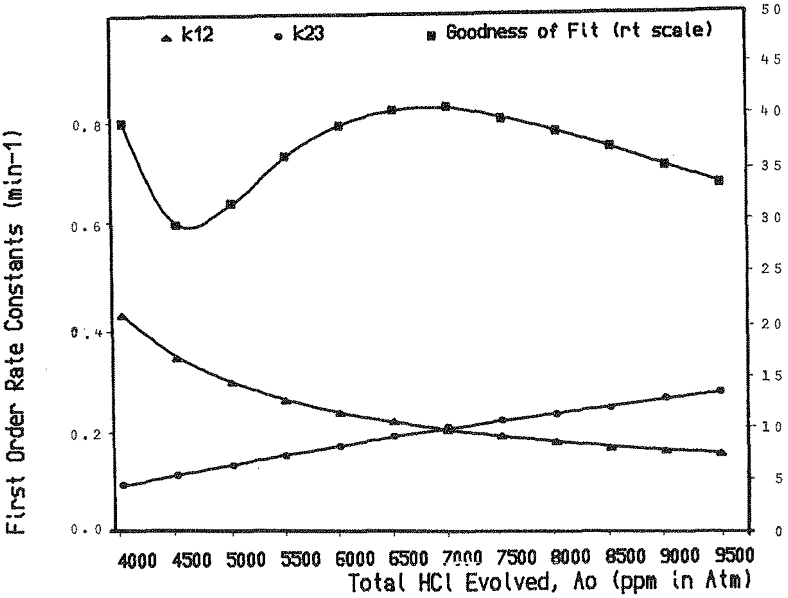


FIGURE IV. Response Surface Cross-Section, Large Scale Test 1.



complete decomposition). In Tests 1, 2 and 3, the values of the k_{12} and t_0 are the same while in Tests 1, 2 and 4 the values of k_{23} are the same. This shows that k_{12} and t_0 are related to production of HCl as caused by the use of current and are not affected by the recirculation fan. The fan, however, affects the rate of transport of HCl to the sampling site, shown by the higher value of k_{23} in Test 3. Two further points of interest are that the presence of the grate does not affect rates (compare Tests 1 and 2) and that k_{23} in Test 3 is virtually identical to the recirculation rate (0.26 min^{-1}), confirming that k_{23} closely tracks the rate of transport. In all static tests, k_{23} assumes similar values but is much smaller in the dynamic test.

No relationship was found in the small scale tests between chlorine in the char and RH. Recirculation decreased the HCl found on the coupons and on the filters. Although this result seems initially surprising, it is conceivable that the assumption of homogeneous HCl deposition is poor, and that greater decomposition occurs on the ceiling than the floor in "Fan Off" experiments. HCl concentration on filters and surfaces increased slightly with RH.

Since the total recovery of HCl from char, filters and extrapolated surfaces was significantly less than 100%, experiments were performed to determine other possible deposition sites. These experiments were carried out in a similar PMMA box and they showed that no less than 48% of the theoretical chlorine ultimately becomes attached to the Maranite® on the floor of the box. Significantly more may reside in the Maranite® used to support the sample. HCl also condenses on metallic surfaces. Additionally, sorptive surfaces other than Maranite exhibited similar behavior when tested (e.g. painted drywall, ceiling tile and cement block). The rate of HCl decay and maximum HCl concentration were lower in the presence of these sorptive surfaces.[11]

TABLE V. Summarized Small Scale Tests - Fully Optimized Constants

Expt	RH, %	Wt Lost, gm	A_0, ppm	t_0, min	k_{12}, min^{-1}	k_{23}, min^{-1}	k_{32}, min^{-1}	Std Dev, ppm	Cl, Moles[1]	Pct Theo
						FAN ON				
13	80	3.67	1250	2.49	0.315	0.293	0.0217	40.79	0.0087	14.8%
14	80	3.30	1882	4.89	1.620	0.425	0.0254	30.16	0.0131	22.3%
15	50	2.51	1363	4.75	1.800	0.257	0.0086	41.79	0.0095	16.2%
17	50	2.64	1930	4.57	0.838	0.303	0.0082	25.61	0.0134	22.8%
18	5	3.76	1457	4.48	0.729	0.178	0.0048	25.32	0.0101	17.2%
						FAN OFF				
12	80	2.17	1158	2.85	0.645	0.182	0.0232	27.85	0.0080	13.7%
16	50	3.50	2321	4.20	1.077	0.118	0.0036	40.13	0.0161	27.4%
19	5	4.04	3337	4.25	0.786	0.141	0.0022	40.06	0.0232	39.6%
20	5	3.25	2550	4.40	1.067	0.143	0.0020	35.14	0.0177	30.2%
				Fan Off Avg.		0.146			Avg.	22.7%

(1) Based on 6.94E-6 moles/ppm

The results of applying the mathematical model to the small scale tests (except Test 11) are presented in Table V; they show graphical patterns similar to those of Figure III. The total HCl released (A_0) and the production rate constant (k_{12}) do not seem to be affected by RH. The induction periods for all experiments were similar except 12 and 13. No other data (wire temperature, hydrocarbon production, etc.) suggest a different effective starting time for these tests; however, the SLT sample times were recorded on a clock separate from that used for the other data. The decay rate constant, k_{23}, shows a slight positive relationship with humidity for the Fan On experiments but little or no effect without forced circulation. Comparing k_{23} for the small-scale and large-scale Fan Off tests reveals that within the accuracy of these calculations all values are the same. This again supports the hypothesis that k_{23} is related to the rate of transport.

The final parameter, k_{32}, increases strongly with RH. The values vary over a full order of magnitude (0.02 to 0.002), are very constant from test to test and are not dependent on circulation. Curiously, they also vary directly with residual airborne HCl, suggesting that k_{32} may be a measure of "non-decayable" HCl, perhaps present as an aerosol. Therefore, if in two identical experiments the chamber volume were to be changed, the values of k_{32} would change in the same way. In fact, in the large scale tests, k_{32} decreased by a factor of three when the recirculation system was on. This factor corresponds to the ratio of the volume of the entire apparatus to that of the plenum. Assuming the room is not involved in the experiments <u>without</u> recirculation, while the entire volume of the apparatus is involved <u>with</u> recirculation, the change in k_{32} could be viewed simply as a dilution factor, and as another indication that the constant in some way tracks residual HCl.

CONCLUSIONS

Clearly this work confirms earlier observations that HCl, generated during the thermal decomposition of PVC, decays. The peak concentrations of HCl were less than 45 of the maximum theoretical concentration and quickly decreased from this level. Decay continued until after about thirty minutes the concentration of HCl reached 300 ppm for the large scale and 30-100 ppm for the small scale tests.

A mathematical model facilitated calculation of a number of parameters that describe the atmospheric HCl concentration observed and lead to an understanding of the system. Decay rates found suggest half-lives for HCl of 5-6 min without external agitation. This rate is primarily dependent upon the rate of transport in the system, but also varies with the type of surface.

There are no indications that the concentration of HCl rises above 50% of the theoretical concentration based upon total release of chlorine. Even though decomposition approaches 100%, about 25% of the chlorine remains bound in the char as inorganic salts. The observation of low A_0 values may indicate that 20 to 30% of the HCl is deposited very quickly and never gets further than a few inches from the decomposition site. This may not, however, be valid for every possible experimental design. An additional parameter, used to account for the final HCl concentration, suggests that these values are humidity dependent; however, a complete understanding of the significance of the parameters awaits further study.

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