Appendix C
Experimental Program Conducted to Support the Water Reactivity Analysis

To supply an empirical basis for the amount of toxic by inhalation (TIH) gas emitted upon the reaction of a substance with water, we carried out a series of small-scale experiments with representative materials. Experimental data were needed since quantitative data from observations of TIH gas evolving from hazardous chemicals added to water do not exist in the chemical literature. We examined a total of 21 substances, a few of which we were seeking to rule out as TIH by water reactivity (TIHWR) substances. We examined about a quarter of our TIHWR list, with an emphasis on the large class of hydrochloride (HCl) emitters.

C.1 Apparatus and Experimental Method

We tested water-reactive materials for their ability to generate gases by mixing small amounts (about 1 millimole [mmol]) of the material with water in a closed system. A diagram of the apparatus used is shown in Figure C.1. We followed the release of gas over time by observing the displacement of a manometric fluid. For example, when gaseous HCl was generated, HCl vapor (saturated) was evolved into a burette that contained HCl-saturated octane and was held at an angle of about 15 degrees from the horizontal. This arrangement allowed the volume of the closed system to increase substantially yet limited the increase in the pressure in the system to less than 10 to 15 cm of octane (less than 0.015 atm).

The apparatus was calibrated by reacting concentrated sulfuric acid with a known mass of potassium chloride; this reaction yielded the predicted volume of gaseous HCl. All reactions were carried out at room temperature (24°C). Although the reactions were all exothermic, the small volume of the reacting system led to efficient cooling; the temperature of the gas remained at 24°C.

Two experiments, using different methods, were carried out with each substance.

- **Method A:** Stoichiometric amounts of water and the water-reactive material were used. The reaction flask was purged with dry nitrogen, the water-reactive material was injected through a side arm sealed with a rubber cap, and the water was then injected over a period of about 10 s. The reaction mixture was magnetically stirred. As an example of a typical experiment, 0.121 mL (0.129 g = 1.00 mmol) of dimethyldichlorosilane $(CH_3)_2SiCl_2$ was reacted with 0.018 mL (1.00 mmol) of water to yield HCl and a polymeric siloxane. With this method, we sought to verify the possible evolution of the TIH material, to measure the fraction of the stoichiometric yield that actually resulted, and to estimate the primary rate constant for the reaction.
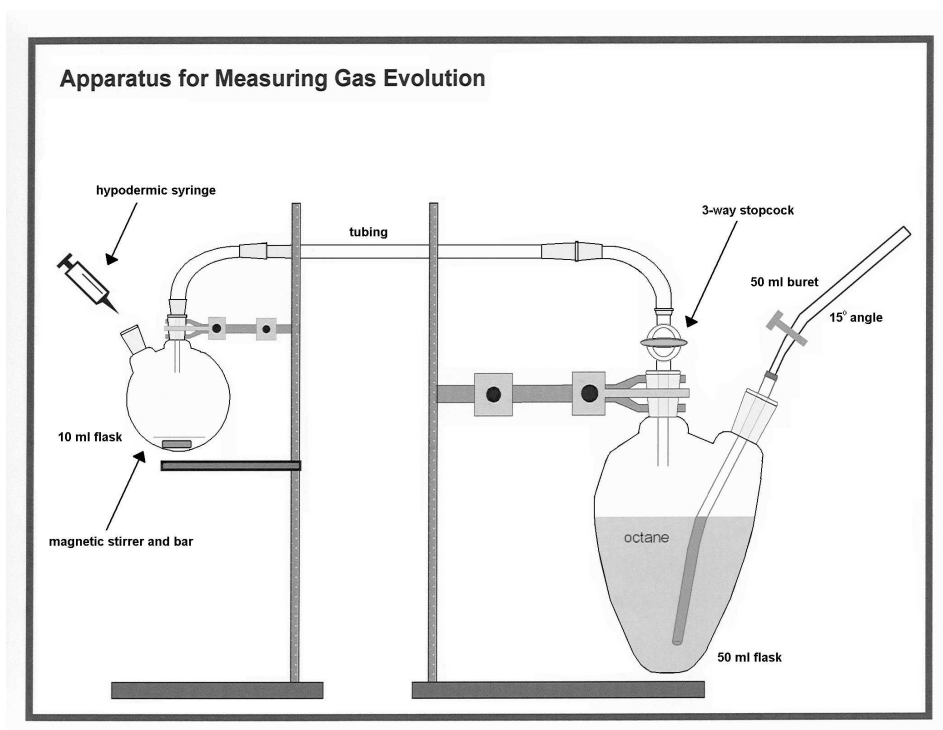
Figure C.1 Diagram of the Apparatus for Measuring the Rate and Amount of TIH Gases Released When a Material Reacts with Water

- **Method B:** The water-reactive material was added to the water, which was present in fivefold molar excess. Again, the reaction system was pre-purged with dry nitrogen. As an example, to study dimethyldichlorosilane, 0.090 mL (0.090 g = 5.00 mmol) of water was put in the reaction flask, and then 0.121 mL (0.129 g = 1.00 mmol) of $(CH_3)_2SiCl_2$ was injected through a side arm over a period of about 10 s. With this experimental method, we sought to reproduce a more likely scenario for an actual spill. We usually found differences between this method and Method A.

C.2 Experimental Results

The following subsections detail the experimental procedures, the observed results, and our interpretation of what was observed. All masses are given in grams.

C.2.1 Tetrachlorosilane (0.170 g = 1.00 mmol), $SiCl_4$

$$SiCl_4 + 2 H_2O \longrightarrow 4 HCl + SiO_2$$
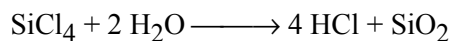
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.034	0.046
5	0.041	0.050
10	0.043	0.048
20	0.046	0.043

Comments: The balance equation predicts that the theoretical yield of HCl would be 0.146 g (4.00 mmol) from 0.170 g of tetrachlorosilane (silicon tetrachloride), $SiCl_4$. In the experiment, after 20 min, only about 30 to 33% of the theoretical amount of HCl had been generated. Both methods indicated that a considerable portion of the theoretical yield of HCl gas had not evolved. On contact with water, the tetrachlorosilane immediately formed a white, solid, polymeric silicon oxide. This product undoubtedly sequestered some water, preventing it from reacting promptly with the $SiCl_4$.

C.2.2 Trichloromethylsilane (0.299 g = 2.00 mmol), CH_3SiCl_3

$$2 CH_3SiCl_3 + 3 H_2O \longrightarrow 6 HCl + 2 \text{ --[--}CH_3Si\text{--}O_3\text{--]-- polymer}$$

Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.023	0.050
5	0.041	0.064
10	0.055	0.068
20	0.059	0.073

Comments: The balance equation predicts a theoretical yield of 0.219 g (6.00 mmol) of HCl. Only 27% and 33% of this amount was actually generated in Methods A and B, respectively. On contact with water, the trichloromethylsilane immediately formed a white, solid, polymeric siloxane, which undoubtedly sequestered a considerable portion of the water, preventing its reaction.

C.2.3 Dichlorodimethylsilane (0.129 g = 1.00 mmol), $(CH_3)_2SiCl_2$

$(CH_3)_2SiCl_2 + H_2O \longrightarrow 2\ HCl + \text{--[--}(CH_3)_2Si\text{--O--]-- polymer}$

Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.0113	0.0182
5	0.043	0.027
10	0.068	0.030
20	0.073	0.030

Comments: In Method A, the theoretical amount of HCl gas, 0.073 g based on the equation, was generated. In Method B, over half of the HCl apparently dissolved in the excess water. In the free atmosphere, advection of the gas that would be produced would tend to reduce dissolution, increasing the yield.

C.2.4 Chlorotrimethylsilane (0.109 g = 1.00 mmol), $(CH_3)_3SiCl$

$2\ (CH_3)_3SiCl + H_2O \longrightarrow 2\ HCl + (CH_3)_3SiOSi(CH_3)_3$
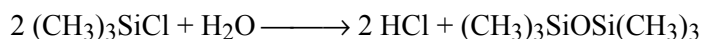
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.0046	0.0102
5	0.0102	0.0125
10	0.0114	0.0137
20	0.0125	0.0137

Comments: The balance equation predicts a theoretical yield of 0.0365 g (1.00 mmol) of HCl. However, only 34% and 38% was generated in Methods A and B, respectively. Apparently, the majority of the HCl that was produced was absorbed in solution to form hydrochloric acid.

C.2.5 Titanium Tetrachloride (0.190 g = 1.00 mmol), $TiCl_4$

$$TiCl_4 + 2\,H_2O \longrightarrow 4\,HCl + TiO_2$$
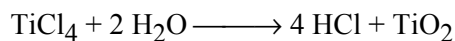
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.023	0.023
5	0.039	0.0114
10	0.039	0.0091
20	0.039	0.0091

Comments: $TiCl_4$ is explosively reactive. In Method A, the injected water was immediately covered with a white crust of titanium dioxide. This cover seemed to prevent the full reaction of water with the remaining $TiCl_4$. Only 27% of the predicted theoretical yield occurred. In Method B, it appeared that in addition, some HCl that initially escaped as a gas dissolved in the excess water. The yield peaked at 16% of maximum after 1 min and dropped to 6% within 10 min. In the free atmosphere, a smaller fraction of the HCl produced would dissolve in the excess water as a result of advection.

### C.2.6 Calcium Hypochlorite (0.143 g = 1.00 mmol), $Ca(OCl)_2$

$$Ca(OCl)_2 + H_2O \longrightarrow \text{no reaction}$$
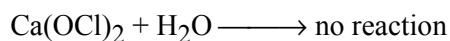
Time (min)	Mass of Cl_2 (g)	
	Method A	Method B
1	0	0
5	0	0
10	0	0
20	0	0

Comments: The experiment showed decisively that no Cl_2 release occurs when calcium hypochlorite is mixed with water under these conditions. No formation of any gaseous product was detected, but the dissolution of the material in water may have produced some heat, causing the slight volume change that was observed (on the order of 0.5 mL).

C.2.7 Oleum (fuming sulfuric acid, 0.122 g $\approx$ 1 mmol)

$$H_2SO_4*(SO_3)_n + n\ H_2O \longrightarrow H_2SO_4 + heat$$
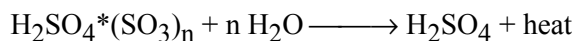
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0	0
5	0	0
10	0	0
20	0	0

Comments: Little formation of any gaseous product was detected. The dissolution in water produced a large amount of heat, which caused a slight observable volume change (on the order of 1 mL). Also, the formation of additional sulfuric acid from sulfur trioxide is highly exothermic. The TIH concern associated with this material is the production of an acidic mist. However, neither Method A nor Method B simulated conditions that might generate an acidic mist.

C.2.8 Aluminum Bromide (anhydrous, 0.267 g = 1.00 mmol), AlBr$_3$

$$AlBr_3 + x\ H_2O \longrightarrow AlBr_3*(x\ H_2O)\ (hydration)$$

Time (min)	Mass of HBr (g)	
	Method A	Method B
1	0	0
5	0	0
10	0	0
20	0	0

Comments: Gaseous product did not appear. The hydration reaction was rapid and quite exothermic. The observed small change in volume (on the order of 1 mL) was attributed to this heating. The production of an acidic mist by the intense heating of a restricted quantity of water should not be ruled out as the result of a natural spill of large quantities of aluminum bromide.

C.2.9 Aluminum Chloride (anhydrous, 0.133 g = 1.00 mmol), $AlCl_3$

$$AlCl_3 + x\ H_2O \longrightarrow AlCl_3 * (x\ H_2O)\ \text{(hydration)}$$

Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0	0
5	0	0
10	0	0
20	0	0

Comments: Gaseous product did not appear. The hydration reaction was rapid and quite exothermic. The observed small change in volume (on the order of 1 mL) was attributed to this heating. The production of an acidic mist by intense heating of a restricted quantity of water should not be ruled out as the result of a natural spill of large quantities of aluminum chloride.
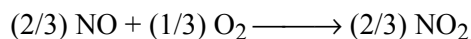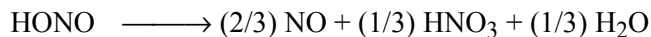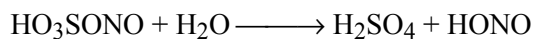
C.2.10 Tin Tetrachloride (0.260 g = 1.00 mmol), $SnCl_4$

$$SnCl_4 + 4\ H_2O \longrightarrow SnO_2 \cdot 2H_2 + 4\ HCl$$
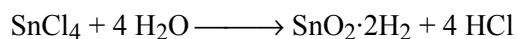
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.0023	0.0023
5	0.0023	0.0023
10	0.0023	0.0023
20	0.0023	0.0023

Comments: Less than 2% of the theoretical maximum gaseous HCl (0.146 g) was generated.

## C.2.11 Nitrosylsulfuric Acid (0.127 g = 1.00 mmol), HO_3SONO

$$HO_3SONO + H_2O \longrightarrow H_2SO_4 + HONO$$

$$HONO \longrightarrow (2/3) NO + (1/3) HNO_3 + (1/3) H_2O$$

$$(2/3) NO + (1/3) O_2 \longrightarrow (2/3) NO_2$$

Time (min)	Mass of NO_2 (g)	
	Method A	Method B
1	0.086	0.0316
5	0.0028	0.0302
10	0.0014	0.0273
20	0.0	0.0244

Comments: The theoretical yield of NO_2 according to the equations above would be 0.0307 g. The nitrogen purge was omitted because oxygen is required for the production of the TIH NO_2. The red NO_2 appeared immediately. Conversion of NO to NO_2 (as represented in the last of the three chemical equations above) was rapid and complete. One mole of oxygen was removed from the closed test system for every two moles of NO_2 that were generated. Therefore, the number of moles of NO_2 that were produced was 3/2 times larger than indicated by the volume changes. This factor was included in computing the masses in the table. In Method B, the mass of NO_2 produced after 1 min slightly exceeded (by about 3%) the theoretical maximum because reactions in addition to those represented above occurred. Dissolution of the gaseous NO_2 in the acidic water after the first minute accounted for the reduction in the amount of gaseous NO_2 in the system after the first minute.

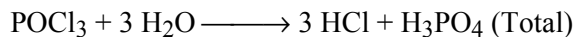### C.2.12 Thionyl Chloride (0.119 g = 1.00 mmol), $SOCl_2$

$$SOCl_2 + H_2O \longrightarrow 2\ HCl + SO_2$$
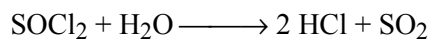
Time (min)	Method A		Method B	
	Mass HCl	Mass SO_2	Mass HCl	Mass SO_2
1	0.023	0.020	0.041	0.060
2	0.053	0.047	0.043	0.064
3	0.070	0.061	0.040	0.064
5	0.073	0.064	0.039	0.060
10	0.073	0.056	0.039	0.052
20	0.073	0.052	0.039	0.048

Comments: This case was unusual in that two TIH gases were emitted at the same time in a fixed ratio. The maximum theoretical yield of HCl according to this equation would be 0.0730 g of HCl and 0.064 g of SO_2. The two gases were generated concurrently. The experiment measured the total volume of evolved gas and not the separate volumes. In Method A, in which 1.00 mmol of water was mixed with $SOCl_2$, the theoretical amount of HCl and SO_2 (as shown in the "yield" column) appeared within 5 min as all the water was consumed. The assignment into masses of HCl and SO_2 assumed no dissolution of either gas in the unreacted water. The reduction in the amount of gases after 5 min was ascribed to the loss of SO_2, because SO_2 (but not HCl) can be absorbed by the manometric fluid (octane previously saturated with HCl). In Method B, the partition into mass of HCl and mass of SO_2 was estimated by assuming that the rate-course of the reaction was the same as that in Method A. It is clear that about 40% of the HCl dissolved in the excess water or was produced in solution as hydrochloric acid.

C.2.13 Phosphoryl Chloride (phosphorus oxychloride, 0.153 g = 1.00 mmol), $POCl_3$

$$POCl_3 + 3 H_2O \longrightarrow 3 HCl + H_3PO_4 \text{ (Total)}$$

$$POCl_3 + H_2O \longrightarrow HCl + POCl_2OH \text{ (First step)}$$

Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.016	0.0228
2	0.0171	0.0103
3	0.0182	0.0068
5	0.0194	0.0046
10	0.0205	0.0043
20	0.0228	0.0043
30	0.0251	-----
60	0.0274	-----
180	0.0297	-----

Comments: The maximum theoretical yield of HCl according to the first equation would be 0.1095 g of HCl. In Method A, the reaction was incomplete. Essentially just one chlorine atom was hydrolyzed, as indicated by the second equation. Over a period of several hours, the additional slow formation of HCl gas was observed. In Method B, most HCl gas was absorbed in the excess water to form a solution of hydrochloric acid. In the free atmosphere, advection would prevent much of the absorption, causing the release of a substantial amount of HCl gas.

### C.2.14 Fumaryl Chloride (0.153 g = 1.00 mmol), ClCOCH=CHCOCl

$$ClCOCH=CHCOCl + 2\ H_2O \longrightarrow 2\ HCl + HOOCCH=CHCOOH$$
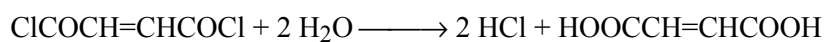
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0	0
2	0	0
5	0	0
10	0	0
20	0	0

Comments: Essentially no HCl gas formation was observed (<0.3 mL); the material was quite unreactive. Fumaryl chloride should be removed from the list of TIHWR compounds.

## C.2.15 Chloroacetyl Chloride (0.113 g = 1.00 mmol), $ClCH_2COCl$

$$ClCH_2COCl + H_2O \longrightarrow HCl + ClCH_2COOH$$
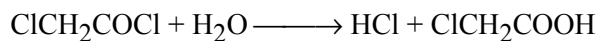
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.00046	0.00046
2	0.00068	0.00114
3	0.00114	0.00230
4	0.0014	0.00114
5	0.0018	0.00046
10	0.0062	0
20	0.014	0
30	0.023	-----
40	0.027	-----
50	0.030	-----
60	0.032	-----
90	0.035	-----
120	0.036	-----
150	0.036	-----

Comments: The maximum theoretical yield of HCl according to the equation would be 0.0364 g. In Method A, there was a slow initial period followed by a speed up, which suggested autocatalysis. Ultimately, the theoretical amount of gaseous HCl appeared. In Method B, most of the HCl was absorbed in the excess water to form a hydrochloric acid. However, in the free atmosphere, the several minutes of contact between HCl and water required would not be available, causing substantial emission.

C.2.16 Phosphorus Tribromide (0.271 g = 1.00 mmol), PBr$_3$

$$PBr_3 + 3\ H_2O \longrightarrow 3\ HBr + H_3PO_3$$
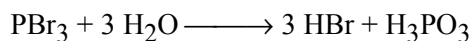
Time (min)	Mass of HBr (g)	
	Method A	Method B
1	0.0081	0
2	0.0202	0
3	0.0405	0
5	0.0809	0
10	0.162	0
20	0.217	0
25	0.228	0
30	0.233	0
60	0.238	0

Comments: The maximum theoretical yield of HBr according to the equation would be 0.243 g. This case is quite interesting. In Method A, the reaction slowly generated HBr and eventually released an amount of HBr close to the theoretical maximum. However, in Method B, in the presence of excess water, the solubility of HBr was sufficiently high that the gas dissolved before it could be released. Therefore, the material is not considered a TIHWR chemical, even though in the exothermic, violent conditions of a large spill, some HBr would probably be released as a gas.

### C.2.17 Phosphorus Pentabromide (0.430 g = 1.00 mmol), PBr_5

$$PBr_5 + 4\ H_2O \longrightarrow 5\ HBr + H_3PO_4$$
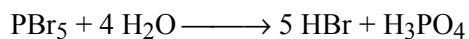
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.131	0.126
2	0.126	0.015
5	0.126	0
10	0.126	0

Comments: The maximum theoretical yield of HBr according to the equation would be 0.405 g. The high solubility of HBr was evidenced in this experiment also, but the reaction rate was much higher, leading to a different conclusion than that for the tribromide form. In Method A, the reaction was so violent that some water was spattered as droplets onto the walls of the container and out of contact with the PBr_5. In Method B, HBr gas formed rapidly (in much less time than 1 min) in a similarly violent fashion. All of the HBr then dissolved in the excess water within the first 2 min. In an actual spill, the HBr would be emitted into the atmosphere and advected away before it would have a chance to dissolve in the water. Therefore, phosphorus pentabromide is included as a TIHWR, and phosphorus tribromide is not, because of the different relationships between reaction rate and the rate at which HBr dissolves.

C.2.18 Calcium Phosphide (0.182 g = 1.00 mmol), Ca_3P_2

$$Ca_3P_2 + 6\ H_2O \longrightarrow 2\ PH_3 + 3\ Ca(OH)_2$$
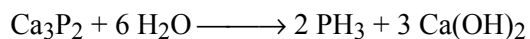
Time (min)	Mass of PH_3 (g)	
	Method A	Method B
1	0.00212	0.00425
2	0.00425	0.0106
5	0.00425	0.0170
10	0.00425	0.0191
20	0.00425	0.0191

Comments: This case is very interesting as a representative of the class of metallic phosphides, which can emit the very deadly phosphine gas upon reaction with water. The maximum theoretical yield of PH_3 according to the equation would be 0.0680 g. In both methods, the hydrolysis stopped short of completion. With a limited amount of water, the production reached nearly 7% of maximum; but with a fivefold excess water supply, it reached 28% of maximum. Samples of other metallic phosphides proved difficult to obtain, and the class clearly deserves careful further study. Some metallic phosphides among those listed in 2000ERG will not react, according to the literature; others, like calcium phosphide, will react substantially.

## C.2.19 Phosphorus Trichloride (0.137 g = 1.00 mmol), PCl_3

$$PCl_3 + 3\ H_2O \longrightarrow 3\ HCl + H_3PO_3$$
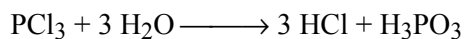
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.059	0.036
2	0.091	0.021
3	0.100	0.0114
5	0.107	0.0046
10	0.109	0.0023
20	0.109	0.0011

Comments: The maximum theoretical yield of HCl according to the equation would be 0.109 g. In Method A, the reaction generated the theoretical maximum amount of gaseous HCl. In Method B, a substantial portion of the HCl gas dissolved in the excess water. In the free atmosphere, probably close to one-third of the maximum yield of HCl would occur, because the gas would not remain in contact with the water for enough time (on the order of 1 min) to permit dissolution.

C.2.20 Sulfuryl Chloride (0.135 g = 1.00 mmol), SO_2Cl_2

$$SO_2Cl_2 + 2\,H_2O \longrightarrow 2\,HCl + H_2SO_4$$
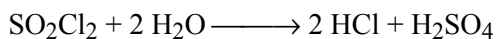
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0.0068	0.0091
2	0.0114	0.0114
3	0.015	0.0125
5	0.023	0.0137
10	0.041	0.0148
15	0.055	0.0125
20	0.059	0.0114
30	0.064	0.0114
60	0.068	-----
90	0.071	-----
120	0.071	-----

Comments: The maximum theoretical yield of HCl according to the equation would be 0.0729 g. In Method A, essentially the stoichiometric amount of gaseous HCl was generated, but slowly, requiring over 1 h for completion. In Method B, a substantial portion of the HCl dissolved in the excess water, but 16% of the maximum was generated. In an unenclosed spill, somewhat more than 16% would be released to the atmosphere, with at least one-third of the maximum amount probably appearing in the first 5 min.

C.2.21 Methanesulfonyl Chloride (0.114 g = 1.00 mmol), CH_3SO_2Cl

$$CH_3SO_2Cl + H_2O \longrightarrow HCl + CH_3SO_2OH$$
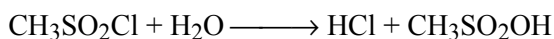
Time (min)	Mass of HCl (g)	
	Method A	Method B
1	0	0
5	0	0
10	0	0
20	0	0

Comments: No gases were generated from contact of methanesulfonyl chloride with water. The material is not a TIHWR chemical.