lets will also freeze after being carried upward to the higher and colder region of the thundercloud. It is widely accepted that the charge generation and separation processes in a thundercloud are closely associated with the development of precipitation and the main charge centers that appear above the freezing level. It is natural to associate their generation with the ice phase. Previously attention has been given to the fragmentation of a freezing water drop (*1, 2*) in the forms of shattering, splintering, or bursting, which has occurred occasionally during the freezing period. The observation presented here suggests that the ejection of small droplets by the freezing of a supercooled water drop may be important in studies of thundercloud dynamics and in the generation of thunderstorm electricity.

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19 May 1969; revised 10 August 1970

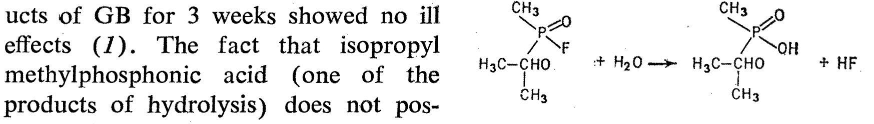
Rate of Decomposition of GB in Seawater

Abstract. *The hydrolysis rate of isopropyl methylphosphonofluoridate (GB) in seawater can be predicted from known or extrapolated rate constants for the reaction between GB and the hydroxo-metal complexes of magnesium and calcium and between GB and the hydroxide ion. At 25°C and* pH *7.9 (typical values of many surface waters) the half-life of GB is approximately 30 minutes.*

The introduction of the nerve gas isopropyl methylphosphonofluoridate (GB) into seawater raises many questions concerning the potential hazards to marine life and the ecology of the ocean environment. Included in the information required to assess the potential hazards are the rate of decomposition of GB in seawater and the toxicity of the hydrolysis products. Rats fed water containing as much as 200 parts per million (ppm) of the hydrolysis products of GB for 3 weeks showed no ill effects (*1*). The fact that isopropyl methylphosphonic acid (one of the products of hydrolysis) does not possess activity similar to that of GB is consistent with expectations based on our knowledge of the mechanism of the toxicity of GB (and other phosphorus esters).

The physiological effectiveness of GB is related to its ability to react rapidly with and inactivate the vital enzyme cholinesterase. (The bimolecular rate constant for the reaction between GB and red blood cell cholinesterase is approximately 10^7 liter mole^{-1} min^{-1}.) The reaction of GB with cholinesterase and with many nucleophiles in aqueous solution is rapid because GB possesses an electrophilic phosphorus atom and an easily displaced fluorine atom. Replacement of the fluorine in GB with less easily displaced groups produces anticholinesterases of lower reactivity and lesser physiological effectiveness. If, however, the fluoride is replaced with a hydroxyl group to produce the anion of isopropyl methylphosphonic acid, there is a complete loss of reactivity and toxicity, because, not only has the fluoride been replaced with a very much less easily displaced group, but also the anion resists nucleophilic attack by the enzyme as a result of charge repulsion.

The hydrolysis of GB in water occurs as follows:



$$CH_3P(=O)(F)OCH(CH_3)_2 + H_2O \rightarrow CH_3P(=O)(OH)OCH(CH_3)_2 + HF \qquad (1)$$

The rate of hydrolysis is *p*H-dependent; the *p*H profile of GB in distilled water at 25°C is shown in Fig. 1.

One can see the reason for the difficulty in predicting the rate of destruction of GB from an examination of the information given in Eq. 1 and Fig. 1. Since the hydrolysis of GB produces two acidic materials [the pK_a (negative logarithm of the acid constant) of the isopropyl methylphosphonic acid is 1.96; that of HF is 3.14], the rate of hydrolysis of GB in unbuffered or only slightly buffered dilute aqueous solutions of $p\text{H} \geqq 7$ changes with time as a result of the lowering of the *p*H of the water by the acidic hydrolysis products. If the concentration of GB is sufficiently low ($10^{-4}M$ to $10^{-5}M$) so that a goodly percentage must be hydrolyzed before the *p*H of the water is lowered only slightly, then the hydrolysis rate of GB also decreases slightly; as hydrolysis continues, the rate decreases further until a *p*H is attained such that there is no further change in the rate of hydrolysis. At this *p*H (6.5) the hydrolysis rate is at a minimum, and solutions of GB at this *p*H are relatively stable, the half-life at this *p*H being approximately 150 hours.

When the concentration of GB is high ($\geqq 0.01M$), relatively large quantities of acid are produced with only a small percentage of GB decomposing, thus producing low *p*H levels (< 4). Subsequent hydrolysis results in lower *p*H's and higher rates of GB decomposition. In this case there is an autocatalysis of hydrolysis and the rates can far exceed that predicted from the *p*H of the initial solution.

The *p*H dependency of the rate of GB hydrolysis in seawater is qualitatively similar to that in distilled water, and seawater has only small buffering capacity. The quantity of acid produced by the total hydrolysis of a $10^{-4}M$ GB solution (~ 15 ppm) is already sufficient to overwhelm the buffer content in the seawater. A constant *p*H (less than 0.1 unit *p*H change) is maintained if the solution is equal to or less than $10^{-5}M$ in GB. If the concentration is between $10^{-5}M$ and $10^{-4}M$, then the rate of hydrolysis will decrease with time. Such solutions will be relatively more stable than more dilute solutions. If, however, the initial concentration of GB is $\geqq 10^{-2}M$, then one observes an autocatalysis of hydrolysis. Figure 2 shows a plot of the percentage of the initial GB ($0.25M$) remaining in seawater as a function of time (*2*).

The plot in Fig. 1 represents the decomposition of GB as a result of attack by water molecules, hydrolysis catalyzed by acid, and attack by hydroxide ion. For distilled water or for waters of low solid content, or even for waters containing relatively large quantities of alkali metal salts of strong acids, the quantitative relationship shown in Fig. 1 will provide a reasonable estimate of the half-life of GB in low concentrations at 25°C. But studies of the catalytic effect of metal ions on the rate of hydrolysis have shown that relatively small concentrations of metal ions can markedly accelerate the rate of GB decomposition in water. From studies of *p*H dependency it has been shown that the observed kinetics of GB hydrolysis were consistent with the conclusion that the metal-hydroxo complex, formed by dissociation of the hy-

Table 1. Comparison of predicted with experimentally found half-lives.

Temperature (°C)	pH	$t_{1/2}$ Calculated	$t_{1/2}$ Experimental
25	7.6	61.2 min	58.1 ± 0.3 min*
	7.9	30.7 min	25 ± 3 min†
15	7.7	167 min	159 ± 2 min*
0.2	7.7	28.8 hr	15.9 ± 0.1 hr*

* Two determinations. † Four determinations.

drated metal ion, is the active attacking species (*3*). The bimolecular rate constants for the reaction between GB and the hydroxo-metal complex were higher than the rate constants of the GB-hydroxide reaction, so that in regions of neutral and slightly alkaline *p*H, attack by the metal-hydroxo species produced by even trace quantities of metal salts could be the primary course of GB decomposition. For example, the half-life of GB in water at *p*H 6.5 and 25°C is approximately 175 hours; the half-life of GB in water of the same *p*H and temperature, to which 1 ppm of Cu^{2+} has been added, is 2 hours.

The ions present in seawater that might be expected to contribute to the hydrolysis rate are metal-hydroxo ions, hydroxide ions, and bicarbonate and carbonate anions. However, from studies of the effects of various salts on the hydrolytic stability of GB, it is expected that the primary ions present in seawater that would affect the hydrolysis rate are calcium and magnesium (*3*). The activities (*4*) of these ions in seawater are: $A_{Mg^{2+}} = 0.0169$ and $A_{Ca^{2+}} = 0.00264$, respectively. Other metallic ions, although excellent catalysts for the hydrolysis of GB, are present in concentrations that are too low to be practically significant. Even the hydroxide ion contributes very little to the overall hydrolysis rate, and the contributions of the bicarbonate and carbonate anions may be neglected.

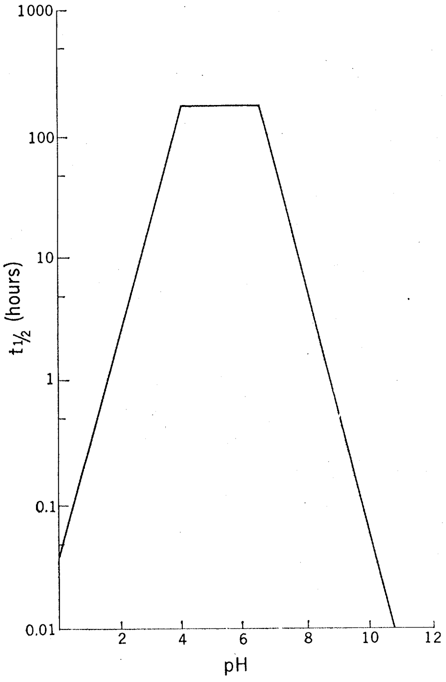


Fig. 1. The *p*H profile of GB in water at 25°C.

The first-order rate of decomposition of GB in seawater, if we assume constant *p*H, can be estimated from the equation:

$$k_{obs} = k_2 \cdot \frac{K_a \cdot C_0}{[H^+] + K_a} + k_2' \cdot \frac{K_a' \cdot C_0'}{[H^+] + K_a'} + k_2'' \cdot \frac{K_w}{[H^+]} \qquad (2)$$

where k_2 and k_2' are the bimolecular rate constants for the hydroxo complexes of magnesium and calcium, respectively, and k_2'' is the bimolecular rate constant for the reaction with the hydroxide ion (*5*); K_a and K_a' are the ionization constants (*6*) for the two hydrated alkaline-earth ions at 25°C (pK_a of $Mg^{2+} = 11.4$ and pK_a of $Ca^{2+} = 12.7$), and C_0 and C_0' are their activities in seawater ($Mg^{2+} = 0.0169$ and $Ca^{2+} = 0.00264$). The values of k_2 and k_2' at 25°C, at unit activities, are 3.9×10^3 and 3.4×10^3 liter $mole^{-1}$ min^{-1}, respectively. For values of k_2, k_2', K_a, and K_a' at lower temperatures, it was assumed that the temperature dependence of k_2 and k_2' (not available) is the same as that of k_2'' (*5*) and that of K_a and K_a' is the same as that of K_w, the water constant.

A comparison of the predicted values with the experimentally determined (*2*) values is shown in Table 1. The agreement between the calculated and experimental values at 15° and 25°C is very good; at 0.2°C the predicted value is too high by a factor of approximately 2, a result that is not too surprising in view of the assumptions and the long extrapolation.

At a constant *p*H of 7.7, the half-life $t_{1/2}$ of GB at any temperature T between 0° and 25°C can be calculated from the equation:

$$\log t_{1/2} = \frac{4325}{T} - 12.84 \qquad (3)$$

Had the assumption been made that the Arrhenius activation energy is 1.0 to 1.5 kcal less for the reaction of the metal-hydroxo complex than for the hydroxide ion reaction, the predicted value at 0.2°C would have been ex-

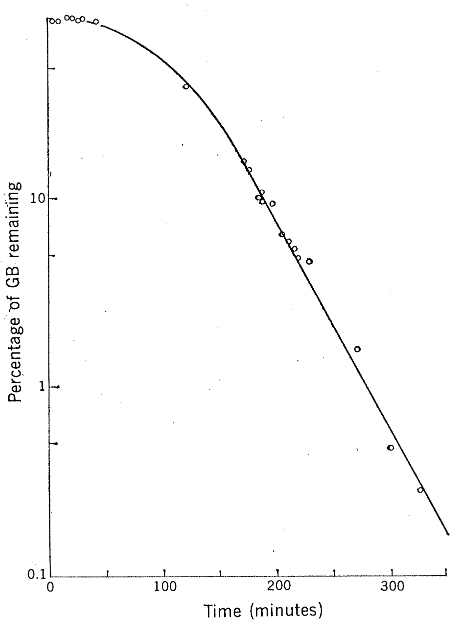


Fig. 2. Decomposition of GB in seawater at 25°C. Initial GB concentration, 0.25*M*.

tremely close to the observed one; however, at 15°C the predicted value would be about 1.5 times that of the observed value.

Because of the effect of the salts of the alkaline-earth metals, the *p*H profile of GB in seawater at 25°C is thought to be as shown in Fig. 3. Attack by water molecules, which in distilled water is the dominant reaction pathway in the *p*H range from 4 to 6.5, occurs in seawater over the narrower range of 4 to 5.5.

The foregoing discussion applies to

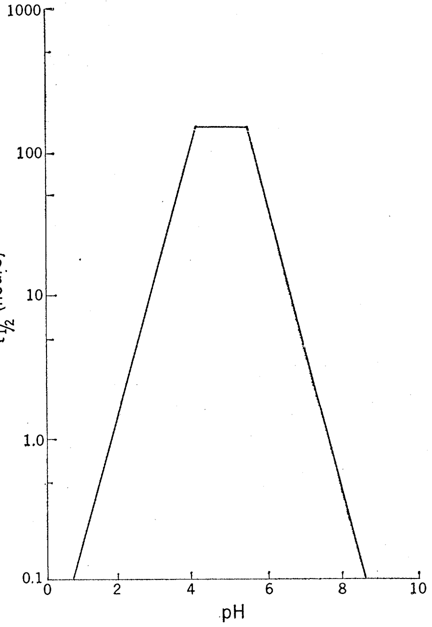


Fig. 3. The *p*H profile of GB in seawater at 25°C (postulated).

the situation in which GB is placed in a definite volume of seawater and the concentration of GB is uniform in that volume. If GB were introduced into a small portion of the total volume of seawater, the GB concentration–time profile (needed to assess the potential hazard) would be greatly influenced by diffusional and current velocities.

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28 August 1970

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Auroral-Particle Precipitation and Trapping Caused by Electrostatic Double Layers in the Ionosphere

Abstract. *Interpretation of high-resolution angular distribution measurements of the primary auroral electron flux detected by a rocket probe launched into a visible aurora from Fort Churchill in the fall of 1966 leads to the following conclusions. The auroral electron flux is nearly monoenergetic and has a quasi-trapped as well as a precipitating component. The quasi-trapped flux appears to be limited to a region defined by magnetic-mirror points and multiple electrostatic double layers in the ionosphere. The electrostatic field of the double-layer distribution enhances the aurora by lowering the magnetic-mirror points and supplying energy to the primary auroral electrons.*

It was suggested by Alfvén as long ago as 1958 (*1*) that auroral particles could be accelerated by double-layer electrostatic fields that had components parallel to the earth's magnetic lines of force. He hypothesized that these fields arise from charge separation in the upper ionosphere caused by the connection by electric currents of plasma regions of different density and temperature. He also suggested that such parallel electrostatic fields play an important role in the generation of aurorae. His hypothesis is supported by the data summarized in this report, which were obtained in 1966 auroral-sounding experiments.

The existence of field-aligned electric currents was postulated by Birkeland in 1908 (*2*) and has since been observed in the ionosphere (*3*) as well as in artificially produced laboratory plasmas (*4*). Many theoretical interpretations of the experimental data have been advanced (*5*). It has been postulated (*6*) that parallel electric fields similar to the fields involved in solar flare theory (*7*) may be responsible for auroral-particle acceleration.

The evidence presented here indicates that parallel components of electrostatic fields (electrostatic double layers) do exist in the earth's ionosphere and that such double layers played a role in the production of a visible aurora observed during the fall of 1966. Data obtained from a rocket experiment suggest that the following physical processes occur in visible aurorae:

1) Mirror points of auroral-zone electrons are lowered by the presence of electrostatic double layers in the ionosphere thereby causing additional electron precipitation and contributing to the subsequent formation of a visible aurora.

2) Precipitating electrons are scattered by the atmosphere, which creates transient populations of electrons trapped between their magnetic-mirror points and the region of ionospheric electrostatic double layers.

The present experiment is not sufficiently definitive to determine how much of the approximately 10-kev electron energy (above a lower limit of 5 percent) was supplied by the parallel electrostatic field. However, it strongly suggests that electrostatic double layers contributed to the generation of a visible aurora by causing electron mirror points to be lowered into the atmosphere. We cannot rule out the possibility that a significant contribution to the electron energy was supplied by a process of longitudinal drift through a perpendicular electric field component (*8*) or that an acceleration mechanism in the neutral sheet exists (*9*).

The electron energy spectra that were measured by this experiment during a Nike-Tomahawk rocket flight launched from Fort Churchill on 16 September 1966 have been discussed previously (*10*). The inherent high angular resolution ($\approx 1/2°$) of the measurements was fully utilized in obtaining the present results.

Figure 1 shows the angular distributions obtained for the first five electron data sets. Rocket apogee (~ 250 km) occurred between the third and fourth electron data set. Of special interest is the deep trough at about 80°. This feature disappears at an altitude of about 200 km during the downleg of the rocket flight. (The large dip in the angular distribution that occurred near 90° is an instrumental effect caused by the shadow of the rocket. However, close observation of the orientation of the rocket spin axis throughout the flight precludes ascribing any other observed structure in the angular distribution data to shadowing effects.)

The trough observed at 80° appears to represent the dividing line between precipitating electron flux at smaller angles and a transient population of electrons trapped at larger angles extending up to 90°. Straightforward calculations indicate that the flux observed at less than 80° precipitates into the atmosphere, whereas the flux observed at larger angles mirrors at an altitude that is high enough to survive several reflections with moderate atmospheric scattering. The rapid falloff of electron flux that occurs near 100° is a result of atmospheric scattering losses.

Arguments for the above interpretation of the data are more clearly presented with the aid of Fig. 2 and a few mathematical relations derived below. Let us first consider the precipitating electrons. Assume that electrons of energy E_1 are spiraling along a magnetic line of force of strength B_1 at a pitch angle of α_1, when an electrostatic double layer with an accelerating voltage V_L in the direction of the magnetic field is encountered. We assume that the magnetic moment of the electron μ is not affected by the presence of the electric field. We then obtain the following relations, where α_0 and E_0 refer to the pitch angle and energy of the electron when these quantities are observed by the detector at some altitude (with field strength B_0) below the double layer:

$$\mu = E_{\perp}/B = \text{constant}$$

$$\frac{E_1 \sin^2 \alpha_1}{B_1} = \frac{E_0 \sin^2 \alpha_0}{B_0}$$

$$E_0 = E_1 + V_L$$