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The kinetics of the alkaline rearrangement of O,O-dimethyl-(2,2,2-trichloro-1-hydroxyethyl)phosphonate, (trichlorfon, 1), the active insecticidal component in such formulations as Dylox, was followed at 25±0.5°C by high pressure liquid chromatography (UV-vis detector, 210 nm). The rearrangement product, O,O-dimethyl-O-(2,2-dichloroethenyl)phosphate (dichlorvos, 2), which is a more potent biocide than trichlorfon, undergoes further reaction, and the kinetics, consequently, cannot be treated by a standard pseudo-first-order plot. A two-point van’t Hoff (initial rates) method was used to obtain pseudo-first-order rate constants (kψ) at 25, 35 and 45°C: 2.6×10⁻⁶, 7.4×10⁻⁶ and 2.5×10⁻⁵ s⁻¹, respectively. Arrhenius treatment of this data gave an activation energy (Ea) of 88 kJ⋅mol⁻¹ with a pre-exponential factor (A) of 5.5×10⁹ s⁻¹. Kinetic trials at pH 8.0 using phosphate and tris buffer systems show no buffer catalysis in this reaction and indicate that the rearrangement is subject to specific base catalysis. Estimates are reported for pseudo-first-order half-lives for trichlorfon at pH 8.0 for environmental conditions in aqueous systems in the Corner Brook region of western Newfoundland, part of the site of a recent trichlorfon aerial spray program.

Key words: trichlorfon, dichlorvos, phosphonate-phosphate rearrangement, kinetics

Introduction

Trichlorfon or O,O-dimethyl-(2,2,2-trichloro-1-hydroxyethyl)phosphonate, 1, (the bioactive agent in formulations such as Dylox®) is an organophosphorus insecticide that has been used in the protection of field and fruit crops (Matolcsy et al. 1988). Its relatively low mammalian toxicity (e.g., oral LD50 of 450-469 mg·kg⁻¹ in rats and dermal LD50 of 2000 mg·kg⁻¹ in rabbits [Verschuuren 1996a]) and effectiveness against a wide range of insects, worms and flukes has made it not only a broad spectrum insecticide but also an anthelmintic in the veterinary and medical pharmacopoeia (Walton et al. 1986). Although trichlorfon has been shown to be toxic to salmonid fish (Neubert 1986) and to a lesser extent to cyprinid fish...
(Anton and Ariz 1994), it has been used as an antiparasitic agent in aquaculture (Kozlovskaya et al. 1984). In 1980, global consumption of trichlorfon, which is also known as chlorofos, DEP, Dipterex and DETF and is marketed in a variety of formulations such as Metrifonate®, Agroforotox® and Dylox®, exceeded 3000 tonnes per year, but by 1987 usage had declined to about 850 tonnes per annum (Health and Safety Guide No. 66, 1991).

Trichlorfon has also been sprayed to control various forest pests; for example, the trichlorfon formulation Dylox® was used in an aerial spray program from late July to early August 1998 to control an incipient balsam fir sawfly (Neodiprion abietis) infestation in portions of the boreal forest of western Newfoundland. A post-spray surveillance report was undertaken by Environment Canada (Julien et al. 1999), using two treatment plots located east of Stephenville, Newfoundland (Block 213: 48°36’58” N, 58°01’02” W and Block 215: 48°34’58” N, 58°02’57” W). The focus of the report was on the aquatic fate and toxicological impact of 1 on ponds and streams situated in the test plots. The ponds examined by Environment Canada in Block 213 of this study had a mean temperature 17°C and a pH of 6.8, while the pond and stream of Block 215 had the same temperature, but a pH of 5.9. The report suggested that the buffer zones beside water bodies (200 m) in the treated zone at the application rate of 750 g a.i./ha were ineffective in preventing risk to aquatic organisms, particularly aquatic invertebrates; the risks to fish were less readily assessed, although the toxicological impact of trichlorfon on the invertebrates, the food source for the fish, was expected to place stress on the fish. These results, as well as public interest in the Corner Brook area, prompted us to reinvestigate the kinetics of abiotic decomposition of trichlorfon, particularly under conditions relevant to sites close to Corner Brook, Newfoundland, i.e., August aquatic temperatures in streams of approximately 18°C and at a pond near Corner Brook of about 12°C with pH values of close to 8 (Campbell 2000).

Abiotic decomposition of 1 is not a straightforward hydrolysis and the nature of this decomposition is an important consideration in any environmental risk assessment arising from its application. Unlike other organophosphorus pesticides which are, typically, organophosphate or organophosphorothioate esters that undergo hydrolysis via attack either at phosphorus or at a carbon center or both depending on reaction conditions (Faust and Gomaa 1972; Wolfe 1980; Balakrishnan et al., 2001), trichlorfon is an α-hydroxy organophosphonate ester and in aqueous media (pH 8–6) it is known to undergo a rearrangement (Janzen and Smyrl 1972; Janzen and Vaidya 1973) to another, and generally more toxic, organophosphate insecticide, dichlorvos (i.e., 2,Vapona® etc.) as shown in equation 1 (Barthel et al. 1955; Lorenz et al. 1955; Faust and Gomaa 1972; Chapman and Cole 1982). Table 1 provides a comparison of toxicities of trichlorfon and dichlorvos for a selected group of (mostly) aquatic organisms. As can be seen, generally, 2 displays a higher acute toxicity than its environmental precursor, 1.
Previous investigations into the kinetics of the rearrangement of 1 have either been conducted under conditions significantly different from those typical of the environment (i.e., in ethanol at 70°C; Faust and Gomaa 1972) or, at least, conducted at a temperature that differs (25 ± 3°C, 1% ethanol in water; Chapman and Cole 1982) from that found in summer in the aquatic systems near Corner Brook, Newfoundland, that were subjected to the recent trichlorfon aerial spray program. Clearly, the aquatic fate of 1 and, therefore, the assessment of risk associated with the application of trichlorfon is dependent on the rate of rearrangement of 1 to the more toxic 2 (equation 1). These, in turn, are dependent on reaction temperature as well as pH. In the current study, we report the pseudo-first-order rate constants (kₚ) for the aqueous alkaline (pH 8.0) rearrangement of trichlorfon to dichlorvos at 25, 35 and 45°C and the activation parameters for this reaction that permit the calculation of the half-life of 1 under aquatic environmental conditions commonly found in summer in the Corner Brook region of Newfoundland. The importance of knowing the activation parameters in the decomposition of organophosphorus pesticides so as to estimate the environmental fate of these contaminants has been noted by a number of authors (Faust and Gomaa 1972; Lartiges and Garrigues 1995).

### Materials and Methods

**Chemicals**

Trichlorfon (99+%) was purchased from Sigma (Oakville, ON; lot #19H0730). The 400 MHz proton NMR spectrum (CDCl₃, δ (in ppm from
TMS standard), J [in Hz]), measured using a Bruker Avance-400 spectrometer at Queen’s University, contained the following signals for trichlorfon and was free from extraneous peaks: δ 4.50 (d, J₆-H = 6.0, P(O)-CH), 3.93 (d, J₆-H = 6.0, P(O)-OCH₃) 3.90 (d, J₆-H = 6.0, P(O)-OCH₃), 3.51 (br s, OH). This trichlorfon was used without further purification in the kinetic studies. Dichlorvos (≥ 99.1%) was obtained from Chem Service (West Chester, Penn.). Its NMR spectrum (CDCl₃) was similarly clean: δ 6.96 (d, J₆-H = 2.6, P(O)-CH=CCl₂) and 3.84 (d, J₆-H = 5.8, P(O)-OCH₃) and the dichlorvos was used as purchased. Similarly, potassium dihydrogen phosphate and sodium hydrogen phosphate heptahydrate were obtained from VWR (Mississauga, ON) and used without further purification to prepare the phosphate pH 8.0 buffer, according to the recipe of Christian and Purdy (1962). Tris(hydroxymethyl)aminomethane pH 8.0 buffer solution was prepared from tris (VWR) and 0.10 M hydrochloric acid (VWR) as given in the CRC Handbook of Chemistry and Physics (1991). Distilled deionized water was used in the preparation of all aqueous solutions and buffers. High performance liquid chromatographic (HPLC) grade dichloromethane (for preliminary gas-liquid chromatography experiments) and acetonitrile (for HPLC kinetics) were purchased from Caledon (Georgetown, ON) in the highest purity available.

Instruments

Preliminary GLC analysis was carried out on a Hewlett-Packard 5980 Series II gas chromatograph, thermal conductivity detector (TCD), using an HP-5 (5% PhMe silicone) 10 m × 0.53 mm × 2.65 µm column. Ultraviolet-visible (UV-vis) spectra were recorded using wavelength scan with a Beckman DU-7400 diode-array spectrophotometer. Analysis by HPLC was carried out using the Varian Star 9012 solvent delivery system, the Varian Star 9050 variable wavelength UV-vis detector. A Varian C-18 reverse-phase 90Å 150 × 4.60 mm × 5 µm column was used in all analytical separations and for the kinetic determinations.

Preliminary GLC Analysis of Trichlorfon

A trichlorfon stock solution was prepared from a weighed quantity of 1 (0.2526 g; 98.12 mmol) in dichloromethane (100 mL) in a volumetric flask. Serial dilution with dichloromethane gave a solution with a final concentration of 9.812 × 10⁻⁴ M. Injection of samples of this solution (2 µL) failed to give reproducible chromatograms using the following parameters: injector temperature 220°C; oven temperature 40°C, ramped at 2°·min⁻¹ to a final temperature of 200°C; He flow rate 2.1 mL·min⁻¹; attenuation of the integrator 2. Nor could reproducible analyses be obtained under a range of analytical conditions that included varying the He carrier-gas flow rate and changing the ramp speed for the oven.

HPLC Kinetic Determinations

Analytical conditions

UV-vis spectrophotometric scans of stock solutions of 1 and 2 in water or 50:50 acetonitrile water gave spectra having wavelengths of max-
imum absorbance at 223 nm for 1 (ε = 16 M⁻¹ · cm⁻¹) and at 264 nm for 2 (ε = 4990 M⁻¹·cm⁻¹); both insecticides absorbed at 210 nm, though the greater intensity of the dichlorvos signal at this wavelength, combined with the difficulty in separating 1 from the phosphate buffer initially used, meant that kinetic runs were based on the appearance of 2 with respect to time. Analyses were conducted with the detector set at 210 nm (as previously used by Chapman and Cole 1982); flow rate of 1.0 mL·min⁻¹, using 50:50 acetonitrile:water; injection loop 10 µL. Retention times of 1 (ca. 1.6 min) and 2 (ca. 2.9 min) were determined separately using authentic samples of the insecticides. The same peaks were positively identified in a separate kinetic run by spiking the sample with 1 and 2.

**Standard kinetic treatment: phosphate and tris buffers, pH 8.0**

Samples of a stock solution of trichlorfon (1.00 × 10⁻³ M aqueous) were added to eight volumetric flasks (100 mL) in a water bath (25°C). The solutions were allowed to equilibrate before being made up to the mark with either phosphate buffer or tris buffer (both at pH 8.0) to give final concentrations of 1 of 1.00 × 10⁻⁵ M; four flasks were prepared with each buffer. Aliquots were removed from these flasks via syringe at time zero and at 2-h intervals with a final HPLC analysis at 18 h. Kinetic data for the four replicates in each buffer were initially analyzed by plotting the natural logarithm of the chromatographic peak area for 2 (ln[peak area]) versus time, but this did not give the expected linear plot for a first-order process (Connors 1990). Attempts to plot the data according to integrated zeroth-order (i.e., peak area versus time) or second-order (i.e., reciprocal of the peak area versus time) kinetic rate laws also failed to give expected straight lines (Connors 1990). The early data from these runs were later recalculated to give initial rates and then analyzed according to the rate law determined by the van’t Hoff method. This analysis showed that there was no significant difference in initial rate for the same initial concentration of trichlorfon whether phosphate or tris buffer was used and, consequently, no significant difference in the derived pseudo-first-order rate constants.

Small extraneous peaks were also noted in the HPLC chromatograms of kinetic experiments. These did not appear to change significantly over time and did not affect kinetic results from run to run.

**Van’t Hoff kinetic treatment: activation parameters**

In the two-point van’t Hoff treatment four volumetric flasks (100 mL) per temperature containing approximately 90 mL of tris buffer were thermostatted in a water-bath (25.0 ± 0.5°C; 35.0 ± 0.5°C and 45.4 ± 0.5°C). Once the flasks had achieved equilibrium temperature, aqueous trichlorfon stock solution (1.39 × 10⁻² M) was added by pipette and the flasks brought up to the mark with buffer. Concentrations were adjusted so that the second two flasks of each set contained double the initial concentration of the first two flasks of each set. In the case of the runs at ca. 25°C, aliquots were collected from each flask and analyzed by HPLC at time zero and every successive 5 min, over a 1-h period. For the samples at higher temperatures, aliquots were removed via syringe and analyzed at one min and for every successive five min over a 30–35 min period.
Data from these runs was plotted (peak area versus time) and gave good straight lines ($r^2 \geq 0.9965$ in each case; e.g., Fig. 1) the slopes of which represent the initial rates (i.e., with a duplicate run for each temperature).

![Fig. 1. Plot of dichlorvos peak areas versus time (35°C), an example of the determination of the initial rate. The slope is the initial rate in units of peak area(s$^{-1}$). These are converted to concentrations of dichlorvos (M) per second using the manufacturer’s reported cell pathlength and the measured molar absorptivity of dichlorvos. Equation of the line: Peak area = 94.087(time) + 11257; $r^2 = 0.9965$. Note that dichlorvos is present even at time = zero.](image-url)
Two-point plots of ln(initial rate) versus ln [trichlorfon]₀ at each temperature gave slopes representing the partial order of reaction with respect to trichlorfon. From this derived rate law (rate = -d[1]/dt = d[2]/dt = k_ψ[1], where the [OH⁻] is fixed by the buffer and is subsumed in the rate constant) and initial rate for formation of 2, as well as the concentration of 1 initial (determined by correcting the initial concentration of trichlorfon by subtraction of that which had converted at time zero (t = 0) to dichlorvos, using the manufacturer’s stated cell path length for the HPLC, the measured molar absorptivity for 2 and the maximum absorbance of the initial peak for 2 from the HPLC chromatogram, i.e., [trichlorfon]_{corrected} = [trichlorfon]_{initial} – [dichlorvos]₀), the pseudo-first-order rate constant for the process 1 — > 2 (equation 1), k_ψ, was calculated for each temperature. The duplicate runs for each temperature were in reasonable agreement and so an average k_ψ value for each temperature was calculated.

An Arrhenius plot of ln[k_ψ], using the average k_ψ values versus 1/T (T in °K) gave a good straight line (r² = 0.9974; Fig. 2) from whose slope the activation energy (E_a) and from whose intercept the Arrhenius pre-exponential factor (A) could be calculated.

Results

Preliminary Studies into the Decomposition of Trichlorfon:

GLC Results

Initially, it was intended to follow the kinetics of decomposition of trichlorfon by GLC. Attempts to analyze trichlorfon itself were unsuccessful. Extraneous peaks were apparent even when a freshly prepared trichlorfon solution (in dichloromethane) was injected. Although a direct injection GLC analytical method has been reported, using a cold on-column injector (Slahck 1988), even this method has been shown to give non-reproducible analytical results. Thermal decomposition of trichlorfon to dichlorvos, as well as 2,2,2-trichloroethanal (chloral) and dimethyl phosphate, apparently occurs even under conditions milder (Slahck 1988) than the GLC analytical protocols used in the current study. Consequently, all subsequent kinetic and analytical procedures utilized HPLC.

HPLC Kinetic Studies of the Rearrangement of Trichlorfon, 1, to Dichlorvos, 2

The reaction of 1 in pH 8.0 buffer, whether phosphate or tris buffer, was followed by HPLC (reverse-phase column, acetonitrile:water 1:1 v/v), using a UV-vis detector set at 210 nm. In the phosphate buffer, the small peak for trichlorfon was obscured, whereas in the tris buffer it was well separated from the peak for buffer. The kinetics of the reaction were obtained by following the formation of dichlorvos, 2, for a short period of time (1 h in the case of 25°C, and 30 to 35 min at 35 and 45°C) at a given initial concentration of trichlorfon. Generally, a peak for 2 was present in each chromatographic trace, even for the first aliquot analyzed (i.e., time = 0 point). Plots of the dichlorvos peak area (related directly to
the concentration of dichlorvos) versus time yielded good straight lines \(( r^2 \geq 0.9965 \text{ in each case; e.g., Fig. 1})\), the slopes of which gave the initial rate for conversion of 1 to 2. Generally, two determinations were made at each temperature. This process was repeated at each temperature for a doubled initial concentration of 1 and initial rates were again obtained.

![Arrhenius plot](image)

**Fig. 2.** Arrhenius plot of the natural log of the pseudo-first-order rate constants, \( k_p \), against the reciprocal temperatures (\(T\) in K). The slope is \(-E_a/R\). The equation of the line is given in the text (equation 3); \( r^2 = 0.9974 \).
Two-point van’t Hoff plots (Laidler 1987) of the natural logarithm of the initial rates versus the natural logarithm of the initial concentration of 1 (corrected for the dichlorvos present in the initial chromatographic trace) gave slopes representing the partial order with respect to the concentration of trichlorfon. While the slopes contained significant error the average slope was unity.

No difference was found in initial rate when tris buffer was used instead of phosphate buffer. In one experiment, a 10-fold dilution of the tris buffer was used and again the initial rate was found to be invariant with that measured using the standard tris buffer. Therefore, there was no dependence on the nature of the buffer or the absolute concentration of any component of the buffer.

From the derived rate law:

\[- \frac{d[1]}{dt} = \frac{d[2]}{dt} = k_\psi [1]\] (2)

and the corrected initial concentration of 1 the pseudo-first-order rate constant, \(k_\psi\), could be calculated at each temperature for the two determinations of \(k_\psi\) at each temperature. These values were averaged to give the quantities tabulated in Table 2.

An Arrhenius plot of the natural logarithm of these average \(k_\psi\) values versus the reciprocal of the Kelvin temperature \((1/T)\) produced a good straight-line \((r^2 = 0.9974)\) and this is shown in Fig. 2. The equation of the line is

\[y = \ln \left( k_\psi \right) = -10533(1/T) + 22.436 \] (3)

The slope is equal to \(-E_a/R\), where \(E_a\) is the Arrhenius activation energy. Standard conversion gives \(E_a\) a value of 88 kJ·mol\(^{-1}\). The intercept is equivalent to \(\ln A\), where \(A\) is the Arrhenius pre-exponential factor and has the value \(5.5 \times 10^9\) s\(^{-1}\) (and \(\log A\) is 9.74).

### Table 2. Kinetic parameters for the rearrangement of 1 to 2 at pH 8.0

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(k_\psi), s(^{-1})</th>
<th>(t_{1/2}), s (d)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0(^1)</td>
<td>2.6 \times 10^{-6}</td>
<td>2.7 \times 10^{5} (3.1)</td>
<td>This work(^2)</td>
</tr>
<tr>
<td>25(^3)</td>
<td>8.8 \times 10^{-6}</td>
<td>7.9 \times 10^{4} (0.91)</td>
<td>Chapman and Cole 1982</td>
</tr>
<tr>
<td>35.0(^1)</td>
<td>7.4 \times 10^{-6}</td>
<td>9.4 \times 10^{4} (1.1)</td>
<td>This work(^2)</td>
</tr>
<tr>
<td>45.4(^1)</td>
<td>2.5 \times 10^{-5}</td>
<td>2.8 \times 10^{4} (0.32)</td>
<td>This work(^2)</td>
</tr>
</tbody>
</table>

\(^1\)Temperatures were controlled to ± 0.5°C with a thermostatted, circulating water bath.

\(^2\)Rate constants are believed to be accurate to within 12%.

\(^3\)Temperature reported as 25 ± 3°C.
Discussion

Form of the Kinetic Rate Law

The van’t Hoff treatment of the kinetic data led to the formulation of the rate law for the rearrangement of trichlorfon to dichlorvos as given in equation 2. This is a pseudo-first-order rate law in which the rate has a first-order dependence on the concentration of trichlorfon. The pseudo-first-order rate constant subsumes the constant hydroxide ion concentration. As will be considered below other quantities are also likely embedded in this rate constant.

Significantly, no dependence was found on the absolute buffer concentration as shown by the finding that the initial rate was not affected by dilution of the tris buffer by a factor of 10. Nor was the initial rate affected by changing the buffer from phosphate to tris(hydroxymethyl)aminomethane. Therefore, we can conclude that this rearrangement is specific base catalyzed, i.e., only the concentration of the strongest base in the medium is significant. In water, hydroxide is the strongest base and, consequently, it is the only base that is significant; other bases that may be present — in this case, arising from the buffer — do not contribute to the rate, except to the extent that they influence the equilibrium concentration of hydroxide ion. This an important finding since in the aquatic environment there are many basic species, ranging notably from carbonate and hydrogen carbonate ions in calcareous fresh waters to the weaker carboxylate and aryloxide moieties of dissolved organic matter. If buffer catalysis had been found, it would be reasonable to presume that the conversion of 1 to 2 would also be catalyzed by dissolved organic matter, for example, and the reaction would be considered to be catalyzed by general bases.

On the other hand, it must be acknowledged that dissolved organic matter or particulates in aquatic systems could significantly influence the rate of rearrangement of 1 to 2 by sequestering the trichlorfon. Adsorption of organophosphorus pesticides to aquatic particulates has been shown previously to influence the rates of degradation of these compounds (Lartiges and Garrigues 1995; Omakor et al. 1995).

Regardless, the pseudo-first-order rate constants, \( k_{\psi} \), have been calculated as outlined in the Results section and are listed in Table 2. Comparison can be made of the \( k_{\psi} \) value determined in the current study to that previously reported (Chapman and Cole 1982); the earlier determination is over three-fold larger than that found in this study. This difference is also beyond the estimated error in the rate constants measured here (12%). However, it should be noted that temperature was more rigorously controlled in the present study and this difference in rate constants may partly reflect the effect of temperature on the rate constant, i.e., the previously determined rate constant contains greater inherent error than that reported here.

The question arises: If the form of the rate law is first-order with respect to trichlorfon, then why did the kinetic data fail to follow the linear form of a first-order integrated rate law, i.e., why did \( \ln(\text{peak area}) \)
versus time fail to give a good straight-line plot? There are several reasons for an analysis based on initial rates (i.e., the differential form of the rate law [Laidler 1987]) to disagree with that based on the presumed integrated form of the rate law. Notably, if the product of the process being monitored subsequently also reacts to give further products then the two approaches will disagree. In the van’t Hoff approach initial rates are considered, where the absolute concentration of dichlorvos would be relatively low. A subsequent kinetic decomposition, such as hydrolysis by attack at the phosphorus center of 2, would be expected to be dependent on the concentration of dichlorvos present. In the early portion of the reaction, then, the low concentration of 2 present would translate into a negligible rate of decomposition of 2. Therefore, only the conversion of 1 to 2 would be monitored by following the appearance of 2. But at later times 2 would react further and the kinetic trace would be complex, consisting both of the formation of dichlorvos and its disappearance; this overall complex process would not fit a first-order integrated rate law.

**Half-life of trichlorfon at pH 8.0**

The half-life (t1/2) for trichlorfon (pH 8.0) may be calculated readily from the pseudo-first-order rate constant, kψ (i.e., t1/2 = ln 2/kψ). The half-lives at the various temperatures are listed in Table 2. It is well recognized that first-order half-lives are particularly useful in categorizing and comparing the fates of anthropogenic chemicals in the environment, since such half-lives are independent of the initial concentration of the contaminant. Again, note that the half-life at 25°C determined in the present study is significantly shorter than that reported earlier (Chapman and Cole 1982).

**Activation Parameters at pH 8.0**

An Arrhenius treatment of the temperature dependence of the pseudo-first-order rate constants yielded an activation energy of 88 kJ·mol⁻¹ and a pre-exponential factor of 5.5 × 10⁹ s⁻¹ (log A = 9.74). There are no activation parameters in the literature for the rearrangement of 1 to 2, nor to the best of the authors’ knowledge are there reported activation parameters for comparable phosphonate-phosphate rearrangements under environmental conditions (i.e., typical pH values of 5 to 8 in aqueous media). However, Table 3 contains activation parameters for a selected set of hydrolysis reactions of some organophosphate and organophosphorothioate pesticides under environmental conditions (Faust and Gomaa 1972) and for the rearrangement of a set of O,O-dialkyl 2-hydroxy-1,1,1,3,3,3-hexafluoroisopropylphosphonates [O,O-dialkyl PO-C(OH)(CF₃)₂] to the corresponding O,O-dialkyl phosphates, as catalyzed by a variety of amines (e.g., aniline, N,N-dimethylaniline) in dichloromethane solvent (Janzen and Smyrl 1972). What emerges from the comparison is that phosphonate-phosphate rearrangements can have energy requirements similar to those of phosphate/phosphorothioate hydrolysis reactions. This suggests a similar rate-determining step in both mechanisms. It also accounts for the competition found in the current study between the
rearrangement of 1 to 2 and the (likely) hydrolysis of 2 that intervenes in the later portion of the reaction.

In the case of phosphate/phosphorothioate hydrolyses the slow step in the mechanism, at least under alkaline conditions, has generally been taken to be attack of hydroxide (sometimes competitively with water depending on pH) on the phosphorus site (Faust and Gomaa 1972; Wolfe 1980; Bunton 1968). Whether this step leads to immediate displacement (the SN$_2$(P) mechanism) or to a transient pentaco-ordinate intermediate (in the case of organophosphates, for example) that expels the leaving group in a second step (addition-elimination mechanism) is still the source of controversy (Bunton 1968; Bunton et al. 1997; Cox and Ramsey 1964) and, in any case, beyond the scope of the present study.

It is almost certainly fortuitous that the activation energy and pre-exponential factor (log A) for the phosphonate-phosphate rearrangement of O,O-diethyl 2-hydroxy-1,1,1,3,3,3-isopropylphosphonate to its phosphate isomer are so similar to those found in the rearrangement of trichlorfon, especially given the different reaction conditions. However, it emphasizes that the trichlorfon rearrangement likely occurs by a similar mechanism. Note also that this similarly suggests that the rate-determining step does not involve elimination, since overall elimination of HCl occurs

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Compound} & \text{E}_a \text{, kJ mol}^{-1} & \text{Log A} & \text{pH} & \text{Reference} \\
\hline
\text{Paraoxon} & 100 & \text{Not reported} & 1-5 & \text{Faust and Gomaa 1972} \\
& 68.6 & \text{Not reported} & 3.1 & \text{Faust and Gomaa 1972} \\
& 50.2 & \text{Not reported} & 9.0 & \text{Faust and Gomaa 1972} \\
\text{Parathion} & 110 & \text{Not reported} & 1-5 & \text{Faust and Gomaa 1972} \\
& 68.2 & \text{Not reported} & 3.1 & \text{Faust and Gomaa 1972} \\
& 60.7 & \text{Not reported} & 9.0 & \text{Faust and Gomaa 1972} \\
\text{O,O-dimethyl PO-C(OH)(CF}_3\text{)}_2 & 61.1 & 6.87 & \text{—} & \text{Janzen and Smyrl 1972} \\
\text{O,O-diethyl PO-C(OH)(CF}_3\text{)}_2 & 82.8 & 9.75 & \text{—} & \text{Janzen and Smyrl 1972} \\
\text{Trichlorfon} & 88 & 9.74 & 8.0 & \text{This work} \\
\hline
\end{array}
\]

$^1$Data found in the references are generally given in kcal/mol and have been recalculated.
in the rearrangement of 1 to 2, but elimination is not possible and does not occur with the substrates studied by Janzen and Smyrl (1972).

**Mechanism of trichlorfon rearrangement**

Our study suggests that trichlorfon rearranges to dichlorvos in which the rate-determining step is an attack of a “hydroxide-like moiety” on the phosphorus center in a mechanism similar to that proposed previously for phosphonate-phosphate rearrangements (Janzen and Smyrl 1972). This mechanism is shown in scheme 1.

An initial equilibrium ($K_{eq}$) between trichlorfon, 1, and hydroxide gives the trichlorfon alkoxide. The alkoxide moiety of this intermediate then attacks the phosphorus center in the slow step ($k_{slow}$), as suggested by the activation parameters found in the current study, to give a three-membered ring intermediate. A similar intermediate structure has been proposed by Janzen and Smyrl (1972) for related phosphonate-phosphate rearrangements. In agreement with the idea that this step should be rate limiting, it would be expected that the three-member ring would be strained and the transition state leading to its formation would also share in this strain. Consequently, this step would be anticipated to be slow.

The elimination of chloride ion to give dichlorvos, 2, may occur after ring opening to give a carbanion intermediate, as suggested for the systems studied by Janzen and Smyrl (1972) (where, however, elimination does not occur) or the elimination may occur in tandem with ring opening. Regardless, the ring opening and elimination process(es) are expected to be fast relative to the step involving internal attack of the alkoxide moiety of the trichlorfon alkoxide on the phosphorus center. Again, the similarity in activation parameters supports the view that elimination occurs after the rate-limiting step.
The rate law given in equation 4 follows from scheme 1:

\[ \text{Rate} = k_{\text{slow}} [\text{trichlorfon alkoxide}] \]  

(4)

and the concentration of the trichlorfon alkoxide is governed by the equilibrium constant, \( K_{\text{eq}} \):

\[ \text{Rate} = \frac{k_{\text{slow}} K_{\text{eq}} [\text{OH}^-]}{[\text{H}_2\text{O}]} \]  

(5)

Since the concentration of hydroxide is fixed in this study because the system is buffered and the concentration of water is, of course, effectively constant, these quantities may all be combined with the rate and equilibrium constants to define a new constant, \( k_\psi \). Thus, equation 5 transforms into the rate law given by equation 2.

The mechanism detailed in scheme 1 is, therefore, consistent with the current kinetic study. Furthermore, the scheme and equation (5) suggest that if an estimate can be made for the value of \( K_{\text{eq}} \) then \( k_{\text{slow}} \) can be determined and the pseudo-first-order rate constant for the rearrangement of trichlorfon could be calculated for any alkaline pH.

Estimates of the half-life of trichlorfon under environmental conditions

One aim of the present study was the estimation of the half-life of trichlorfon under the environmental conditions pertaining to the area near Corner Brook, Newfoundland, in summer and, more specifically, the conditions that existed during a recent Dylox spray program. Using equation (3) and the temperatures of a stream (18°C) and a pond (12°C) near Corner Brook, determined in August 1998 (Campbell 2000), the half-lives of trichlorfon were estimated to be 1.3 weeks at 18°C and 2.7 weeks at 12°C, at pH 8.0. These half-lives are significantly longer than those that might be naively expected based on the previously reported value at 25 ± 3°C (Chapman and Cole 1982) and emphasize again the importance of determining activation parameters for pesticide degradation (Faust and Gomaa 1972; Lartiges and Garrigues 1995).

However, it must also be noted that the effect of trichlorfon and its more toxic rearrangement product, dichlorvos, will also depend on the rate of disappearance of dichlorvos. We have shown that this rate is competitive with the rearrangement itself. A full assessment of the environmental fate of trichlorfon will require an analysis of the same activation parameters and kinetics for 2 under environmental conditions.

Conclusions

Trichlorfon, 1, has been shown to rearrange to 2 at pH 8.0 with a pseudo-first-order rate constant of \( 2.6 \times 10^{-6} \text{ s}^{-1} \), as determined by the method of initial rates; standard integrated rate law approaches to the kinetics failed as a result of the competitive decomposition of 2 that inter-
venes in the later portions of the reaction profile. The rearrangement was found to be subject to specific base catalysis as opposed to general base catalysis. This suggests that the nature of individual basic species in an aquatic system, e.g., basic sites of dissolved organic matter, will not significantly influence the kinetics of the rearrangement, except as these moderate the pH of the system. Activation parameters were determined for the alkaline rearrangement: $E_a = 88 \text{ kJ(mol}^{-1}\text{)}$ and log $A = 9.74$. Comparison and analysis of the activation parameters permitted the proposal of a mechanism that is consistent with the experimentally derived rate law and which suggests that rate constants and half-lives may be estimated for the rearrangement at any given alkaline pH. Finally, the Arrhenius equation was used to estimate the half-lives of trichlorfon under environmental conditions, relevant to Corner Brook, Newfoundland, part of the area involved in a recent Dylox (trichlorfon) aerial spray program.

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References


