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IONIC STRENGTH AND BUFFER EFFECTS IN THE ELIMINATION REACTION OF 1,1,2,2-TETRACHLOROETHANE

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Abstract—The rate constant for the abiotic reaction of 1,1,2,2-tetrachloroethane in aqueous solution has been studied as a function of ionic strength, buffer composition, temperature, and pH. The rate of reaction is found to be independent of ionic strength and buffer composition, with the parent compound quantitatively converted into trichloroethene by a base mediated elimination reaction for values of pH > 3.5. The Arrhenius parameters for the elimination reaction are $\log_{10} A = 16.32 \pm 0.40$; $E_a = 95.0 \pm 2.5$ kJ/mol. No evidence for a neutral hydrolysis reaction was found, indicating that the rate constant for such a reaction is $< 2 \times 10^{-7}\ \mathrm{s}^{-1}$ at 90°C.

Key words—1,1,2,2 tetrachloroethane, chloroalkanes, abiotic reaction, elimination reaction, dehydrohalogenation reaction

INTRODUCTION

Halogenated organic compounds represent a significant contaminant in both surface and groundwater. In the subsurface environment, halogenated alkanes are believed to be relatively stable. However, such compounds can undergo biologically mediated changes. They can also be transformed by abiotic reactions, or adsorbed onto particles. Heterogeneous catalysis can also act to transform halogenated organic compounds by both thermal and photochemical processes (Zepp and Wolfe, 1987). All of the above processes, along with others such as photolysis and volatilization, determine the fate of halogenated alkanes in the aqueous environment.

In a previous publication (Cooper *et al.*, 1987), the results of a detailed study of the elimination reaction of 1,1,2,2-tetrachloroethane (TeCA) were presented. The reaction was studied at 11 temperatures in the range 30–95°C, and at values of pH in the range 5–9, in 0.100 M phosphate buffered solution. Gas chromatography was used to monitor both the concentration of starting material and that of the product of the reaction, trichloroethene (TCE). For the experimental conditions used in the study, TeCA was quantitatively converted to TCE by a base-mediated bimolecular reaction. Based on the experimental results, the Arrhenius parameters for the reaction rate constant were determined, and found to be in good agreement with those found in previous studies.

The present work gives the results of further investigation of the abiotic reaction of TeCA. Three additional features of the reaction have been studied. First, the effect of changes in ionic strength on the rate constant for the elimination reaction has been investigated. Second, the reaction has been studied in a variety of different buffer systems to determine whether or not the elimination reaction is catalyzed by specific buffer ions. Third, experiments have been carried out at lower values of pH than used in the previous study to find out if an additional neutral hydrolysis reaction of TeCA occurs, as has been previously reported (Mabey *et al.*, 1983; Haag *et al.*, 1986; Jeffers *et al.*, 1989).

MATERIALS AND METHODS

Buffer solutions were prepared as follows. Borate buffer, pH 9.0, was prepared as a solution of sodium tetraborate. Carbonate buffer, pH 9.0, was prepared as a 10:1 (v/v) mixture of equimolar solutions of sodium hydrogen carbonate and sodium carbonate. Phosphate buffer, pH 5.0, was prepared as an 80:1 (v/v) mixture of equimolar solutions of potassium dihydrogen phosphate and potassium hydrogen phosphate. Phosphate buffer, pH 7.0, was prepared as a 1:1 (v/v) mixture of equimolar solutions of potassium dihydrogen phosphate and potassium hydrogen phosphate. Phosphate buffer, pH 9.0, was prepared as a solution of potassium hydrogen phosphate. Tartrate buffer, pH 3.5, was prepared as a saturated solution of potassium hydrogen tartrate. In every case reagent grade chemicals were used (Mallinckrodt), with buffer solutions prepared in deionized distilled water. In experiments where potassium perchlorate was added to the buffer solutions, the reagent grade chemical was used (Mallinckrodt). Buffer pH was determined

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using an Orion 811 pH meter with an accuracy of ±0.03 pH units. Standard solutions of 1,1,2,2-tetrachloroethane (99%) and trichloroethene (99 + %) were prepared in methanol. Both methanol and pentane (used in sample extraction) were trihalomethane grade (Burdick and Jackson).

To determine the rate of the reaction, 200 μl of a stock solution of TeCA was added to 60 ml of buffer solution, giving a nominal TeCA concentration of 450 nmol/l. Ampules were sealed and placed in an ice-water bath to minimize reaction prior to the start of the experiment. During the experiment, ampules were incubated in a water bath at a constant temperature within ±0.1°C. After incubation, ampules were rapidly cooled in an ice-water bath to prevent further reaction. TeCA and TCE were then extracted with 5 ml pentane, and analyzed on a Hewlett-Packard Model 5890 gas chromatograph equipped with two ^{63}Ni electron capture detectors and two 3392A reporting integrators. Large-bore fused-silica capillary columns, 30 m in length and 0.53 mm i.d., coated with 1.5 μm of DB-5 were used. Concentrations of TeCA and TCE were found by comparison against a calibration curve obtained by measurements on standard solutions with known concentrations of the compounds.

Additional information concerning the methods used in the study and tests of the experimental protocol are as previously reported (Mehran *et al.*, 1984; Cooper *et al.*, 1987).

RESULTS

The results of a series of studies of the elimination reaction of TeCA in various concentrations of borate, carbonate, phosphate, and tartrate buffer are presented in Table 1. With the exception of the tartrate buffer measurements, experimental measurements were carried out for each buffer system and temperature at four different buffer concentrations ranging from 0.01 to 0.10 M. Each data set consists of 5–9 measurements of both the concentration of starting material, TeCA, and that of the product of the elimination reaction, TCE. The reaction was followed for a minimum of 70% decomposition of the initial TeCA concentration, and in some cases was followed to >95% decomposition of the starting material.

For an E2 reaction that is first order in the halogenated species and hydroxide ion, and under conditions of fixed hydroxide ion concentration, as occurs in the present experiments, the disappearance of TeCA and appearance of TCE are expected to follow pseudo-first order kinetics, with

$$[\mathrm{TeCA}]_t/[\mathrm{TeCA}]_0 = \exp(-k_{\mathrm{obsd}}t) \qquad (1)$$

and

$$[\mathrm{TCE}]_t/[\mathrm{TCE}]_\infty = 1 - \exp(-k_{\mathrm{obsd}}t) \qquad (2)$$

where in the absence of other reactions besides elimination $k_{\mathrm{obsd}} = k_e[\mathrm{OH}^-]$. Observed rate constants are obtained both from the rate of disappearance of TeCA and from the rate of appearance of TCE, using methods previously described (Cooper *et al.*, 1987). The agreement between the rate constants obtained from the disappearance of TeCA and those found from the rate of appearance of TCE is good. However, because the observed rate constants obtained

Table 1. Summary of experimental data for TeCA elimination reaction in borate, carbonate, phosphate, and tartrate buffer

Temp. (°C)	pH	[Buffer]*	No. of points	10^3k_{obsd}† (h^{-1})	k_e ($\mathrm{M}^{-1}\mathrm{s}^{-1}$)
40	9.08	0.01 M bor	8	505.0 (0.998)	3.41
40	9.10	0.02 M bor	8	530.0 (0.999)	3.22
40	9.28	0.05 M bor	8	584.0 (0.999)	2.14
40	9.36	0.10 M bor	8	681.0 (0.999)	1.91
40	9.26	0.01 M carb	8	595.0 (0.999)	2.83
40	9.16	0.02 M carb	7	461.0 (0.999)	2.66
40	9.11	0.05 M carb	6	411.0 (0.998)	2.49
40	9.11	0.10 M carb	8	407.0 (0.999)	2.30
90	5.37	0.01 M phos	5	192.0 (0.998)	544
90	4.75	0.02 M phos	6	54.8 (0.999)	619
90	5.09	0.02 M phos	8	146.0 (0.999)	756
90	5.07	0.05 M phos	7	122.0 (0.999)	609
90	5.26	0.05 M phos	6	145.0 (0.999)	469
90	4.59	0.10 M phos	6	41.2 (0.998)	580
70	7.02	0.01 M phos	6	500.0 (0.999)	73.1
70	6.97	0.02 M phos	7	445.0 (0.999)	69.0
70	6.87	0.05 M phos	7	403.0 (0.999)	71.9
70	6.82	0.10 M phos	7	359.0 (0.999)	66.1
50	7.00	0.01 M phos	6	24.4 (0.999)	10.8
50	6.97	0.02 M phos	7	21.8 (0.997)	9.87
50	6.89	0.05 M phos	6	19.7 (0.998)	9.86
50	6.85	0.10 M phos	8	17.3 (0.997)	8.76
40	9.14	0.01 M phos	9	611.0 (0.999)	3.60
40	9.31	0.02 M phos	8	693.0 (0.999)	2.61
40	9.36	0.05 M phos	7	935.0 (0.987)	2.86
40	9.37	0.10 M phos	8	799.0 (0.999)	2.20
30	9.20	0.01 M phos	6	112.0 (0.999)	1.14
30	9.32	0.02 M phos	6	149.0 (0.999)	1.09
30	9.36	0.05 M phos	7	166.0 (0.999)	1.00
30	9.34	0.10 M phos	6	152.0 (0.999)	0.887
90	3.62	Sat tar	8	3.8 (0.998)	562
90	3.56	Sat tar	5	4.0 (0.999)	674

*bor, borate buffer; carb, carbonate buffer; phos, phosphate buffer; sat tar, saturated tartrate buffer.
†Correlation coefficient is given in parentheses.

Table 2. Summary of experimental data for TeCA elimination reaction in 0.02 M phosphate buffer/sodium perchlorate solution

Temp. (°C)	pH	[NaClO$_4$]	No. of points	$10^3 k_{obsd}$* (h^{-1})	k_e (M^{-1}s^{-1})
40	9.16	0.02 M	8	430.0 (0.996)	2.22
40	9.26	0.04 M	7	442.0 (0.999)	1.77
40	9.07	0.06 M	8	437.0 (0.999)	2.66
40	9.10	0.08 M	8	414.0 (0.999)	2.31

*Correlation coefficient is given in parentheses.

from the rate of appearance of TCE exhibit a larger error and more scatter than those obtained from the rate of disappearance of TeCA (due to the sensitivity of the value of k_{obsd} obtained from the TCE data to the value of $[TCE]_\infty$ used in the calculation), the observed rate constants reported in Table 1 are those obtained from the measurement of TeCA concentrations. The correlation coefficient for each data set is also given in Table 1. In all but one case r, the linear correlation coefficient, is 0.997 or larger.

In addition to the experiments whose results are summarized in Table 1, a small number of additional experiments were carried out at 40°C in fixed concentration of phosphate buffer and various concentrations of sodium perchlorate, a non-nucleophilic salt. The results of these experiments are summarized in Table 2.

Elimination rate constants k_e for the data in Tables 1 and 2 are obtained from k_{obsd} from the relationship

$$k_e = k_{obsd}/[OH^-]. \tag{3}$$

To find the hydroxide ion concentration, the pH of the solution was measured at the temperature at which data were obtained. Since

$$pH = -\log_{10}(a_{H^+}) \tag{4}$$

and

$$pK_w = -\log_{10}(a_{H^+}a_{OH^-}) \tag{5}$$

the activity of the hydroxide ion is

$$a_{OH^-} = 10^{pH}K_w. \tag{6}$$

Using the experimental value for pH for the buffer solution and the ionization constant for water at the temperature at which data were obtained (Marshall and Franck, 1979), the activity for hydroxide ion can be found.

Under dilute solution conditions it is a good approximation to say that $a_{OH^-} = [OH^-]$ (i.e. to assume that γ_{OH^-}, the activity coefficient for hydroxide ion, is approximately equal to 1). However, for the buffers used in the present experiments, the above assumption is not valid. Instead, values for the activity coefficient for hydroxide ion are estimated using the Debye–Huckel equation (Debye and Huckel, 1923; Bates, 1964)

$$-\log_{10}\gamma_{OH^-} = AI^{1/2}(1 + B\mathring{a}I^{1/2})^{-1} \tag{7}$$

where I is the ionic strength of the buffer solution (defined as $I = \Sigma c_i z_i^2$, where c_i is the concentration and z_i the charge of the ith ion in the solution), $\mathring{a}$ is the ion size parameter (equal to 3.5 A for hydroxide ion), and A and B are constants whose value depends on temperature. Values for $\mathring{a}$, A, and B are given in Bates (1964) and summarized in Table 3. The hydroxide ion concentration can then be calculated from the relationship

$$[OH^-] = a_{OH^-}(\gamma_{OH^-})^{-1}. \tag{8}$$

Values for k_e reported in Tables 1 and 2 have been calculated using the above procedure for finding the hydroxide ion concentration. Values for γ_{OH^-} for the buffers used in the present study are in the range 0.65–0.90. The above procedure was also used to recalculate values for k_e from the previous study by Cooper *et al.* (1987). An Arrhenius plot of the data from the two studies is given in Fig. 1.

Using the data obtained in the present study combined with the recalculated values for k_e for the data previously reported by Cooper *et al.*, a revised set of Arrhenius parameters for the elimination reaction of TeCA can be found. The Arrhenius preexponential factor is $\log_{10} A = 16.32 \pm 0.40$, and the activation energy is $E_a = 95.0 \pm 2.5$ kJ/mol, where the uncertainties are given for 95% confidence limits (Bevington, 1969). These results are in good agreement with previously reported values, as seen in Table 4. Note that when possible, we have recalculated the error limits for previously reported data in the same manner as used in the present study, to account for the fact that there is some correlation between the values for the parameters in the Arrhenius equation. When error limits are calculated taking this into account, one obtains larger error limits for these data sets than have been reported in the past. These revised error limits better represent the actual uncertainty in the Arrhenius parameters.

An examination of the data presented in Table 1 and Table 2 also shows that the rate constant for the

Table 3. Summary of parameters used in hydroxide ion activity coefficient calculation*

Temp. (°C)	A	B	$-\log_{10} K_w$
30	0.5161	0.3291	13.836
40	0.5262	0.3323	13.541
50	0.5373	0.3346	13.275
70	0.5625	0.3397	12.813
90	0.5920	0.3456	12.431

*Values for A and B are taken from Bates (1964), and values for $\log_{10} K_w$ are caculated as discussed in Marshall and Franck (1979).

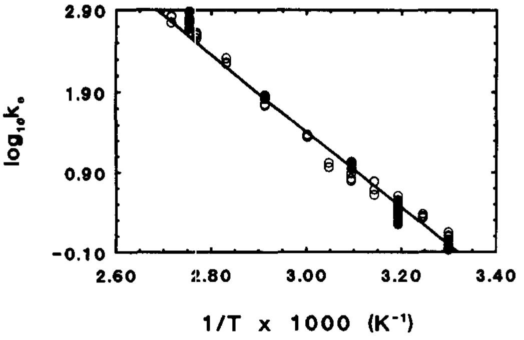

Fig. 1. Plot of $\log_{10}(k_e)$ vs $1/T$ for the elimination reaction of TeCA. ●, present results; ○, data from Cooper *et al.* (1987), recalculated as discussed in the text.

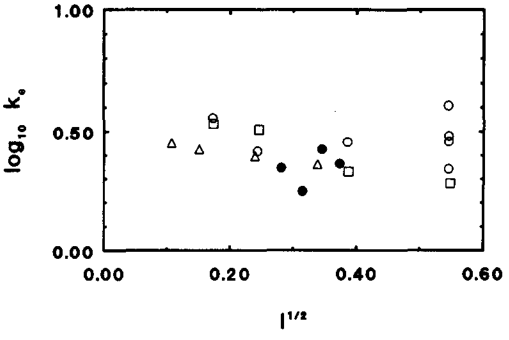

Fig. 2. Plot of $\log_{10}(k_e)$ vs $I^{1/2}$ for the elimination reaction of TeCA. I is the ionic strength of the solution. All data are at $T = 40$°C. □, borate buffer; △, carbonate buffer; ○, phosphate buffer; ●, phosphate buffer + sodium perchlorate.

elimination reaction is not significantly affected by changes in the ionic strength or buffer used in the experimental measurements. This may be seen more clearly in Fig. 2, where the logarithm of the rate constant for the elimination reaction is plotted against the square root of the ionic strength of the solution for experiments run at 40°C. In the limit of low ionic strength, such a plot is expected to have a slope equal to $2Az_Az_B$ (Hammett, 1970), where z_A and z_B are the charges on the species involved in the rate determining step of the reaction, and A is a constant dependent on temperature and the dielectric constant of the solvent. For water at 40°C, $A = 0.5262$ (Bates, 1964). A least squares analysis of the data in Fig. 2 gives a slope equal to zero within the precision of the measurements (-0.09 ± 0.15), and clearly different than ± 1.052, the value expected for the reaction of two singly charged ions. This suggests that one or both species involved in the rate determining step of the elimination reaction is neutral. This is consistent with an E_2 mechanism for the elimination reaction. Further, the value obtained for the rate constant is the same to within the precision of the experimental measurements for all of the buffers used in the present study, indicating the absence of catalysis by specific buffer ions. Such behavior has previously been observed in similar compounds, such as pentachloroethane (Roberts and Gschwend, 1991), that are believed to react by an E_2 mechanism.

Finally, a limited number of experiments were carried out at high temperature and low pH in tartrate buffer to determine whether a neutral substitution reaction of TeCA takes place in addition to the base mediated elimination reaction, as has previously been claimed (Mabey *et al.*, 1983; Haag *et al.*, 1986; Jeffers *et al.*, 1989). The agreement in the experimental value for the rate of disappearance of TeCA at low pH with results obtained at higher value of pH, where elimination is known to be the only reaction to occur, and the lack of systematic variation in the total concentration of TeCA and TCE in the reaction system with time both indicate that the maximum contribution the substitution reaction makes to the total rate of reaction for the disappearance of TeCA at 90°C and pH 3.6 is 20%. This gives an upper limit for k_{sub}, the rate constant for the substitution reaction, of $2 \times 10^{-7}\ s^{-1}$ at 90°C. This upper limit for k_{sub} is significantly smaller than the value $k_{sub} = 6 \times 10^{-6}\ s^{-1}$ calculated from the data of Mabey *et al.* (1983) and Haag *et al.* (1986), but is consistent with the value $k_{sub} = 1.3 \times 10^{-7}\ s^{-1}$ found using the Arrhenius parameters reported for the substitution reaction by Jeffers *et al.* (1989).

CONCLUSIONS

The rate constant for the elimination reaction for TeCA is independent of ionic strength and buffer composition, and depends only on temperature and pH. At pH 7 and 25°C, the half-life for TeCA is 172 days, based on the results of the present study, which are in good agreement with previous results. The substitution reaction of TeCA is not important except at low values of pH.

Table 4. Summary of data on rate of elimination reaction of 1,1,2,2-tetrachloroethane

Reference	$\log_{10} A$*	E_a (kJ/mol)	$t_{1/2}$ (25°C)† (days)
Walraevens *et al.* (1974)	16.4 ± 2.3‡	94 ± 13‡	94
Cooper *et al.* (1987)	15.87 ± 0.54	91.1 ± 3.4	99
Jeffers *et al.* (1989)	13.41 ± 0.05§	78.1 ± 1.0§	151
Present results	16.32 ± 0.40	95.0 ± 2.4	172

*The Arrhenius pre-exponential factor is in units of $M^{-1}\ s^{-1}$.

†Half-life for elimination reaction at pH = 7.0.

‡Error ranges recalculated from original data. Range reported in this table is at the 95% confidence limits.

§Error range as reported in Jeffers *et al.* (1989).

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