

Kinetics of Chemical Oxidation of Dipyridylum Quaternary Salts

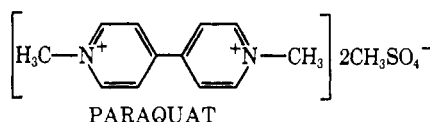
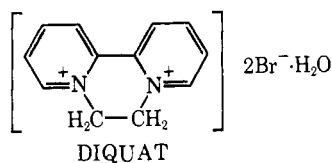
Hassan M. Gomaa and Samuel D. Faust

The oxidative capacities of ClO_2 , Cl_2 , and KMnO_4 were tested for the removal of residual diquat and paraquat from water. Chlorine dioxide appears to be the oxidant of choice for the removal of residual dipyridylum quaternary salts. A very fast rate of oxidation was obtained which was not measured by the experimental techniques employed in this study. The oxidative reaction was almost complete in less than 1 min from the start of the experiment. The oxidation of either diquat or paraquat by KMnO_4 or Cl_2 conform to a second-order rate

expression. With KMnO_4 , the reaction rate constant varies greatly with pH. KMnO_4 was found to be a better oxidant in an alkaline compared to acidic medium. Chlorine, on the other hand, has no effect on diquat or paraquat under acidic conditions. An increase in the pH value of the system will increase the velocity of the oxidation. In general, the rates determined for paraquat with KMnO_4 or Cl_2 were slower when compared to those obtained for diquat under the same experimental conditions.

Surface waters are transporting greater and greater quantities of organic contaminants. This is an exceedingly complex problem, as there are numerous species of compounds involved in the contamination. Consequently, production of potable waters for public consumption becomes feasible when the basic parameters which govern treatment processes are obtained.

In general, it is considered good practice to keep potable waters free from organic herbicides. Conversely, aquatic weed control may become necessary in water supply reservoirs. In recent years, several organic herbicides have been introduced for aquatic weed control. During an examination of a number of quaternary ammonium compounds at Jealott's Hill Research Station, Berkshire, England, one showed exceptional phototoxic activity. This was the salt obtained by reacting 2,2'-dipyridyl with ethylene dibromide (Brian *et al.*, 1958) to yield 1,1'-ethylene-2,2'-dipyridylum dibromide monohydrate (diquat). Later, a chemically related compound, paraquat, 1,1'-dimethyl-4,4'-dipyridylum dimethyl sulfate, was found also to have herbicidal properties.



These compounds show promise in aquatic situations, especially water supply reservoirs, where diquat and paraquat gave 85% or better control of submerged weeds at 1 mg per l. (Riemer, 1964). As diquat and paraquat resist biological degradation in aquatic environments, they may persist for considerable periods of time (Hemmett, 1968). Numerous studies have been made on methods of removal of trace organic compounds from aqueous solutions with chemical oxidants (Aly and Faust, 1965; Edgerly *et al.*, 1967). The objectives, therefore, of this research are to determine the feasi-

bility and the kinetics of chemical oxidation of the two dipyridylum salts by potassium permanganate, chlorine, and chlorine dioxide. These oxidants have found use in the production of potable waters.

EXPERIMENTAL TECHNIQUES

Reagents and standard solutions: Sodium thiosulfate solution, 0.1 *N*, standardize daily (Standard Methods, 1965). Potassium permanganate solution—standardize against the sodium thiosulfate, 0.1 *N* (Kolthoff and Sandell, 1952). Ammonium oxalate solution, 0.1 *N* standard.

Chlorine solution: stock solutions of aqueous chlorine approximately 0.05 *M* were prepared by bubbling chlorine gas into chlorine-demand free, double-distilled water. These solutions were stored in low actinic Pyrex vessels (Corning No. 51500) at 4° C. Fresh solutions were prepared weekly. These chlorine solutions were standardized by iodine-thiosulfate titration with starch as an indicator (Standard Methods, 1965).

Chlorine dioxide solution: Prepared by the reaction between sodium chlorite (10 g in 750-ml of distilled water) and sulfuric acid (20 ml of 10% H_2SO_4). Air is bubbled through the reaction flask for approximately one-half hour or until a deep yellow color is obtained. This solution should be stored in dark bottles away from light and prepared fresh weekly. A fresh standard solution was prepared before the start of each experiment by dilution of a suitable aliquot of the stock solution. The concentration of chlorine dioxide was determined by the thiosulfate titration.

Stock solutions of diquat and paraquat were prepared by direct weighing of the oven-dried (105° C) compounds (analytical reference grade) with dissolution in double-distilled water.

The pH of the reaction solution was maintained by addition of buffer salts. Orthophosphate solutions were used to cover the pH range 5 to 10 (Christian and Purdy, 1962).

PROCEDURE OF KINETIC STUDIES

Reactions were conducted in a thermostatically controlled chamber at $20 \pm 0.2^\circ \text{C}$ in diffused light. To a 1-l. volumetric flask was added the desired amount of oxidant and pH buffer. To another 1-l. flask, the calculated amount of KCl was added to fix the ionic strength at 0.02 *M* as well as the desired quantity of diquat or paraquat. Both flasks were allowed to reach temperature equilibrium, after which the contents of each flask were poured simultaneously into the reac-

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tion vessel. A blank solution of oxidant was used under the same conditions. A stop watch was started at the initial pouring. After desired time intervals, aliquots of the reaction and blank solutions were withdrawn (usually 100 ml) to determine the residual oxidant and herbicidal concentrations. Each experiment was repeated three times.

As diquat and paraquat absorb strongly in the ultraviolet region, this is the basis of a simple and accurate analytical technique for their quantitative determination at 306 and 256 $m\mu$, respectively (Faust and Hunter, 1965). Residual potassium permanganate was determined by the iodine-thio-sulfate titration using starch as an indicator near the end point. However, ammonium oxalate was used for the back titration of permanganate in the paraquat systems since thio-sulfate interferes in the ultraviolet spectrophotometric determination.

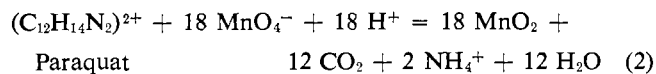
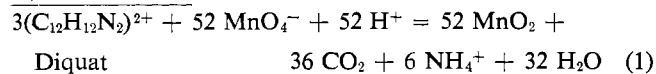
Residual chlorine was determined spectrophotometrically by the orthotoluidine method at a wavelength of 435 $m\mu$ (Standard Methods, 1965).

Residual chlorine dioxide was determined spectrophotometrically by using H-acid reagent (1-amino-8-naphthol-3,6-disulfonic acid). Color intensity was measured at a wavelength of 525 $m\mu$ (Post and Moore, 1959).

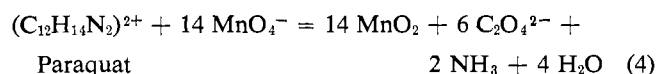
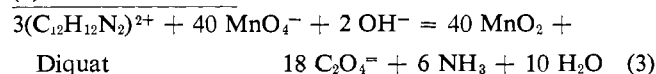
EXPERIMENTAL RESULTS

Potassium Permanganate Oxidations. Before proceeding to the kinetic studies, experiments were conducted to discover the fate of the two reactants. During the oxidation of either diquat or paraquat (whether under acidic or alkaline conditions), oxides of manganese are precipitated. Thus, the permanganate is reduced to MnO_2 and not to the Mn^{2+} state. To start the oxidation with a reasonable concentration of both reactants, an assumption is made that either diquat or paraquat is oxidized to CO_2 or $C_2O_4^{2-}$, H_2O , and NH_4^+ (Stewart, 1965) depending on the pH of the medium.

(a) Acid Medium



(b) Alkaline Medium



Thus, the application of $KMnO_4$ at a molar concentration of 25 times the herbicide's concentration should be sufficient to proceed to the complete oxidation. The above proposed redox reactions were verified experimentally using an excess of MnO_4^- . Good agreement was reached between the calculated and the experimentally determined stoichiometry (Gomaa and Faust, 1971). It would appear, therefore, that the reactions proceed from left to right in accord with the indicated molar ratios and to the products as written. In all probability, the oxidation of these organics, diquat and paraquat, proceeds through a series of intermediate and partially oxidized compounds. Thus, any rate constant would reflect several intermediate reactions. This would not affect, however, in-

Table I. Observed Rate Constants of Oxidation of Diquat and Paraquat by $KMnO_4^a$

Sampling time (min)	Residual $KMnO_4$ mole/l. $\times 10^{-5}$	Residual Herb. mole/l. $\times 10^{-5}$	K_{obsd} l. mole $^{-1}$ min $^{-1}$
(a) Diquat-Oxidation pH 5.12			
120	97.3	3.99	0.142
330	95.7	3.83	0.143
570	94.3	3.68	0.132
870	92.3	3.46	0.142
1200	90.5	3.30	0.132
		Mean	0.138
(b) Diquat-Oxidation pH 9.13			
15	82.3	2.76	10.68
30	77.6	2.11	10.63
45	73.5	1.60	10.73
60	71.2	1.27	10.58
120	68.1	0.52	10.61
		Mean	10.65
(c) Paraquat-Oxidation pH 5.12			
180	97.0	3.47	0.119
360	95.4	3.35	0.104
600	91.5	3.14	0.101
900	88.7	2.96	0.098
1440	87.0	2.71	0.107
		Mean	0.106
(d) Paraquat-Oxidation pH 9.13			
30	91.5	2.50	6.63
60	86.4	1.77	6.56
120	82.2	0.96	6.46
180	79.8	0.54	6.40
360	74.6	0.08	6.73
		Mean	6.56

^a Ionic strength of solution = 0.02 M. Temperature = 20° \pm 0.2° C.

terpretation of the overall kinetics of the oxidation of diquat and paraquat.

Determination of the order of the above reactions was accomplished by fitting the data (examples appear in Table I) into various kinetic equations. An integrated form of a second-order expression provided reasonably constant K_{obsd} values. The above reactions suggest also that the rate of the reactions would be pH dependent. This was observed but the $[H_3O^+]$ was kept constant by the phosphate buffer at the specified pH value. No changes in pH value were observed throughout the course of the reaction. Thus, the following equation may be used to represent the oxidation reaction kinetics (Benson, 1960).

$$\frac{2.303}{a C_{KMnO_4}^0 - b C_{Herb.}^0} \log \frac{C_{Herb.}^0 C_{KMnO_4}^0}{C_{KMnO_4}^0 C_{Herb.}^0} = K_{obsd} t \quad (5)$$

where t = time in minutes
 $C_{Herb.}^0$ = initial molar concentration of diquat or paraquat
 $C_{KMnO_4}^0$ = initial molar concentration of $KMnO_4$
 $C_{Herb.}$ = residual herbicide diquat or paraquat in solution at time t (mole/l.)
 C_{KMnO_4} = residual molar concentration of $KMnO_4$ at time t
 K_{obsd} = observed rate constant in l. mole $^{-1}$ min $^{-1}$
 a = number of herbicide moles given in the redox reaction
 b = number of oxidant moles given in the redox reaction.

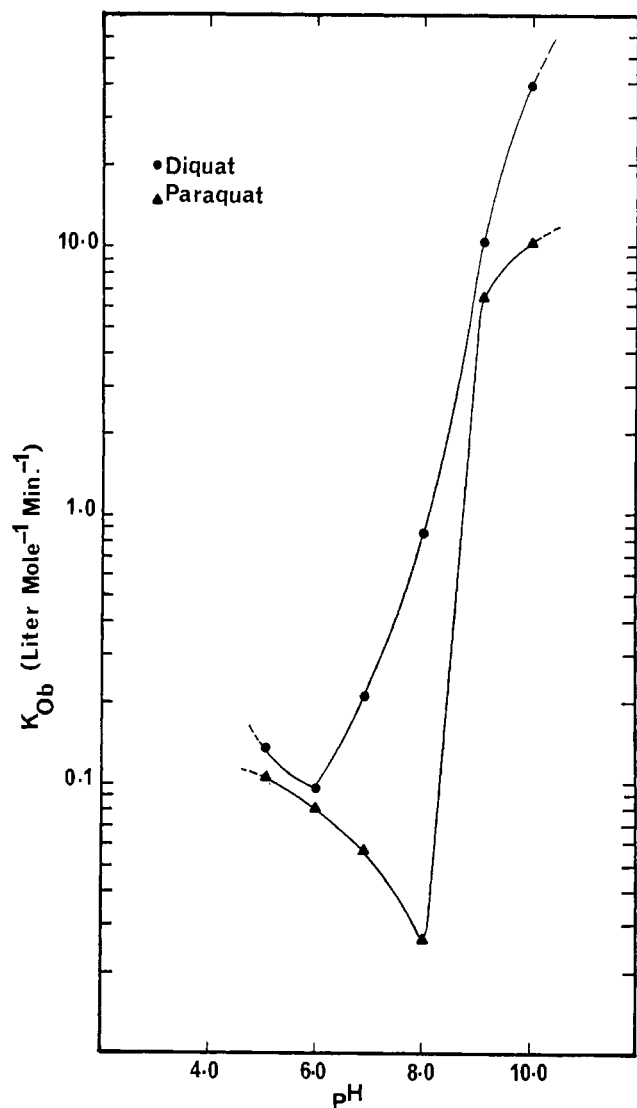


Figure 1. Potassium permanganate oxidation of diquat and paraquat

Table II. Verification of Order of the Permanganate Reactions^a

System	pH	Mean $K_{obsd}(\text{l. mole}^{-1} \text{min}^{-1})$		
		Initial	10-fold dilution	100-fold dilution
Diquat- KMnO ₄	5.12	0.138	0.140	0.132
	9.13	10.65	10.43	10.52
Paraquat- KMnO ₄	5.12	0.106	0.107	0.101
	9.13	6.56	6.42	6.31

^a Ionic strength = 0.02 M. Temperature = 20° ± 0.2° C. Average of three experimental runs at the indicated pH.

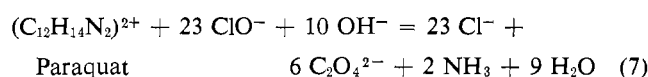
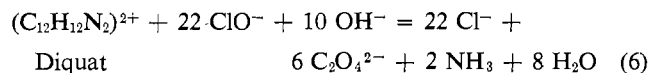
That the rates of KMnO₄ oxidation of diquat and paraquat conform to the above second-order rate expression is seen in Table I. The observed rate constant, K_{obsd} , was calculated at each sampling time by Equation 5. The rate constants in Table I were obtained with initial concentrations of KMnO₄ of 10⁻³ M, diquat of 4.16 × 10⁻⁵ M, and paraquat of 3.65 × 10⁻⁵ M. Confirmation was made of the second-order reaction at pH values of 5.15 and 9.13 using a 10-fold and 100-fold dilution of the above concentrations. The kinetics of these

diluted reactants still obey Equation 5, as shown by the constancy of K_{obsd} values in Table II.

That the rates of KMnO₄ oxidation of diquat and paraquat are pH dependent is seen in Figure 1 where the observed rate constants are plotted against pH.

Chlorine-Oxidations. From a preliminary experiment conducted to test for the feasibility of chlorine in the oxidation of diquat and paraquat, it was found that pH was a very important factor. Chlorine had no oxidative effect on diquat and paraquat under acidic conditions. On the other hand, as the pH value of the system was increased, the velocity of the oxidative reaction increased. Thus, it was concluded, tentatively, that the oxidation proceeded *via* a ClO⁻ mechanism rather than by Cl₂ or HOCl.

As in the case of KMnO₄ oxidation, the same assumption can be made about the end products of oxidation.



Only a molar ratio of 5:1 chlorine to herbicide concentration was used in this investigation because of the analytical convenience for the determination of residual Cl₂ and also for the simulation of dosages used in water treatment plants.

The reactions of diquat and paraquat with chlorine conform to the integrated form of the second-order kinetic equation also.

$$\frac{2.303}{a C_{\text{Cl}}^0 - b C_{\text{Herb}}^0} \log \frac{C_{\text{Herb}}^0 C_{\text{Cl}}}{C_{\text{Cl}} C_{\text{Herb}}^0} = K_{obsd} t \quad (8)$$

where, C_{Cl}^0 = initial molar concentration of chlorine

C_{Cl} = molar concentration of chlorine in an oxidation state of +1 at time t (or the molar sum of Cl₂, HOCl, and OCl⁻).

The reactions were studied in the pH range of 5 to 10. Table III shows an example of data obtained for the oxidation of diquat and paraquat at pH 8.14. As in the case of permanganate oxidation, the order of the oxidative reactions was confirmed, as shown in Table IV.

Chlorine had no oxidative effect on diquat at pH 5.06. An increase of the pH value of the system from 6.17 to 10.13 resulted in an increase of the velocity of the oxidation. Paraquat, in the pH range 5.06 to 7.12, was not oxidized within 24 hr. In the pH range 8.14 to 10.13, the rates of the paraquat reaction are pH dependent, as shown in Table V.

Since a dibromide salt of diquat was used in this investigation, it was necessary to investigate whether or not the consumption of chlorine was due to the oxidation of the bromide ion or due to the oxidation of the dipyridylum structure. As proof that chlorine was attacking the dipyridylum structure, the uv absorbancy was decreased with time when measured at the wavelength of maximum absorption of diquat. As for the question of whether or not the bromide anion is oxidized, a dichloride salt of diquat was prepared and was used at the same molar concentration (4.16 × 10⁻⁵ M). The experiment was repeated at pH 9.04 using 2.0 × 10⁻⁴ M chlorine. A K_{obsd} value of 3.55 l. mole⁻¹ min⁻¹ was obtained that compares favorably to the rate constant from the dibromide salt (3.41 l. mole⁻¹ min⁻¹). Therefore, when the bromide salt of diquat is used, part of the chlorine will be consumed in the oxidation of

Table III. Observed Rate Constants of Oxidation of Diquat and Paraquat by Chlorine^a

Sampling time (min)	Residual Cl ₂	Residual Herb.	<i>K</i> _{obsd} l. mole ⁻¹ min ⁻¹
	mole/l. × 10 ⁻⁵	mole/l. × 10 ⁻⁵	
(a) Diquat-Cl ₂			
120	12.9	2.47	1.14
180	12.2	2.26	1.00
360	9.6	1.58	1.03
720	4.7	0.62	1.42
		Mean	1.15
(b) Paraquat-Cl ₂			
360	19.2	3.50	6.77 × 10 ⁻³
600	18.4	3.35	5.42 × 10 ⁻³
900	17.5	3.19	5.41 × 10 ⁻³
1440	15.5	2.82	5.40 × 10 ⁻³
		Mean	5.75 × 10 ⁻³

^a Initial diquat concentration = 4.16 × 10⁻⁵ M. Initial paraquat concentration = 3.65 × 10⁻⁵ M. Initial Cl₂ concentration = 2.0 × 10⁻⁴ M.

Table IV. Verification of Order of Reaction Using Chlorine^a

System	pH	Mean <i>K</i> _{obsd} (l. mole ⁻¹ min ⁻¹)		
		Initial	10-fold dilution	100-fold dilution
Diquat-Cl ₂	8.14	1.14	1.15	1.13
Paraquat-Cl ₂	8.14	5.75 × 10 ⁻³	5.12 × 10 ⁻³	5.44 × 10 ⁻³

^a Ionic strength = 0.02 M. Temperature = 20° ± 0.2° C. Average of three experimental runs at the indicated pH.

Table V. Effect of pH Upon the Rate Constants of Oxidation of Diquat and Paraquat by Chlorine^a

pH	<i>K</i> _{obsd} (l. mole ⁻¹ min ⁻¹)	
	Diquat-Cl ₂	Paraquat-Cl ₂
5.06	No reaction	No reaction
6.17	2.03 × 10 ⁻²	No reaction
7.12	0.515	No reaction
8.14	1.14	5.75 × 10 ⁻³
9.04	3.41	1.70 × 10 ⁻²
10.13	7.43	3.02 × 10 ⁻²

^a Temperature = 20° ± 0.2° C. Ionic strength = 0.02 M. Average value of three experimental runs at the indicated pH.

the bromide anion in solution to bromine or the hypobromite form, depending upon the pH of the solution. However, the last two species might contribute also toward the oxidation of the diquat cation in solution. Similar reactions may occur in the permanganate system.

CHLORINE DIOXIDE OXIDATIONS

In the oxidation of diquat and paraquat with chlorine dioxide at pH values of 8.14, 9.04, and 10.15, the rates were extremely fast and could not be measured with the experimental techniques. These reactions were almost complete in less than 1 min. On the other hand, chlorine dioxide had no effect on diquat and paraquat at pH values of 5.06, 6.17, and 7.12. Table VI summarizes these oxidative reactions at 20° C. Lowering the temperature from 20° to 10° C had no effect on the oxidative kinetics.

ACTIVATION ENERGIES OF THE OXIDATION REACTIONS

Another portion of this study examined the effect of temperature on the rate constants which, in turn, led to the cal-

Table VI. Diquat and Paraquat—Chlorine Dioxide Oxidation^a

pH	Herbicide, mg/l.		Residual ClO ₂ , mg/l.	Reaction Time
	Initial	Residual		
Diquat-Chlorine Dioxide				
10.15	15.00	0.00	2.61	1 min
	30.00	8.93	0.00	1 min
9.04	15.00	0.00	2.60	1 min
	30.00	8.83	0.00	1 min
8.14	15.00	0.00	2.59	1 min
	30.00	8.83	0.00	1 min
7.12	15.00	15.00	6.74	1 min
	15.00	15.00	6.72	3 hr
	15.00	15.00	6.66	24 hr
6.17	15.00	15.00	6.74	1 min
	15.00	15.00	6.72	3 hr
	15.00	15.00	6.65	24 hr
5.06	15.00	15.00	6.73	1 min
	15.00	15.00	6.70	3 hr
	15.00	15.00	6.67	24 hr
Paraquat-Chlorine Dioxide				
10.15	15.00	0.00	2.84	1 min
	30.00	9.23	0.00	1 min
9.04	15.00	0.00	2.81	1 min
	30.00	9.23	0.00	1 min
8.14	15.00	0.00	2.85	1 min
	30.00	9.33	0.00	1 min
7.12	15.00	15.00	6.73	1 min
	15.00	15.00	6.72	3 hr
	15.00	15.00	6.72	24 hr
6.17	15.00	15.00	6.73	1 min
	15.00	15.00	6.73	3 hr
	15.00	15.00	6.72	24 hr
5.06	15.00	15.00	6.72	1 min
	15.00	15.00	6.71	3 hr
	15.00	15.00	6.70	24 hr

^a Initial chlorine dioxide concentration = 6.75 mg/l. Ionic strength of solution = 0.02 M. Temperature = 20° ± 0.2° C.

Table VII. Potassium Permanganate and Chlorine Oxidations—Effect of Temperature^a

Temp. °C	<i>K</i> _{obsd} (l. mole ⁻¹ min ⁻¹)			
	Diquat-KMnO ₄		Paraquat-KMnO ₄	
	pH 5.12	pH 9.13	pH 5.12	pH 9.13
10	0.059	4.814	0.038	3.135
20	0.141	10.431	0.105	6.393
30	0.308	16.831	0.219	11.928
40	0.561	29.624	0.402	22.283
Temp. °C	Diquat-Cl ₂ ^b		Paraquat-Cl ₂	
	pH 6.17	pH 9.04	pH 8.14	pH 9.04
	10	0.007	1.847	0.001
20	0.020	3.415	0.006	0.017
30	0.037	5.255	0.015	0.040
40	0.052	7.751	0.039	0.090

^a Average of three experimental runs. Ionic strength of solutions = 0.02 M.

ulation of the activation energies of the oxidations. The rate constant, *K*_{obsd}, was evaluated at 10°, 20°, 30°, and 40° C, from the slope of a plot of the left-hand side of Equations 5 and 8 as a function of time. That the rate constants of the reaction vary greatly with temperature is shown in Table VII. These values were obtained at the indicated pH value with an initial chlorine concentration of 20 × 10⁻⁵ M, KMnO₄ concentration of 10 × 10⁻⁴ M, diquat and paraquat concentrations of 4.16 × 10⁻⁵ M, and 3.65 × 10⁻⁵ M, respectively. The Arrhenius equation tested the effect of temperature.

$$K_{obsd} = A_{obsd} e^{-E_{obsd}/RT} \quad (9)$$

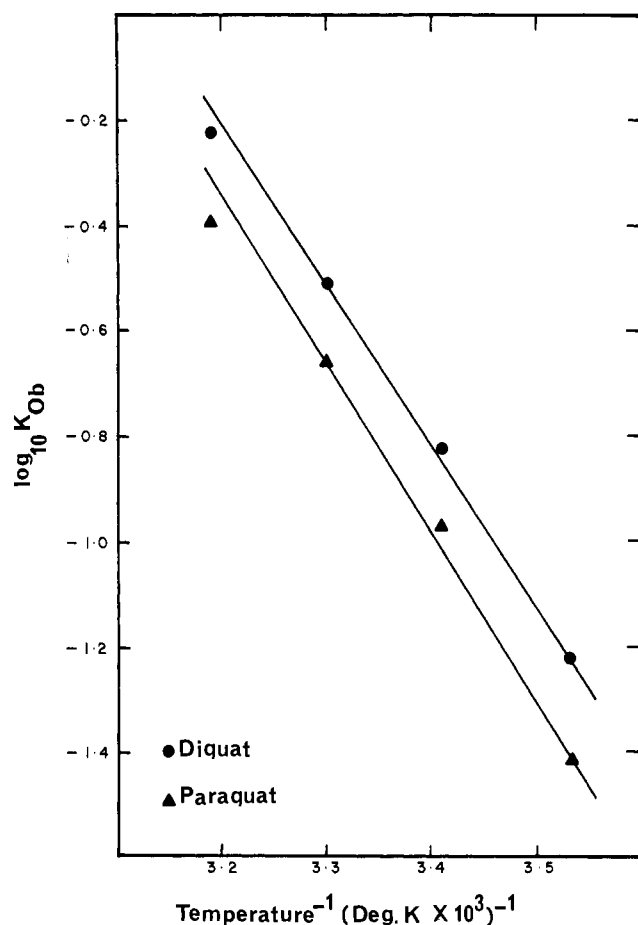


Figure 2. Effect of temperature on the potassium permanganate oxidation of diquat and paraquat

Table VIII. Activation Energies of the Oxidation Reactions

Reaction	pH	E_{obsd} (kcal mole ⁻¹)
Diquat-KMnO ₄	5.12	14.2 (7)
	9.13	10.8 (1)
Paraquat-KMnO ₄	5.12	15.1 (3)
	9.13	11.5 (4)
Diquat-Cl ₂	6.17	14.3 (8)
	9.04	9.0 (3)
Paraquat-Cl ₂	8.14	17.5 (4)
	9.04	13.9 (1)

where K_{obsd} = observed rate constant (l. mole⁻¹ min⁻¹)

A_{obsd} = constant known as the frequency factor

E_{obsd} = observed activation energy of the reaction (kcal mole⁻¹)

T = absolute temperature

R = constant equal to 1.986 cal mole⁻¹ deg⁻¹.

The logarithmic form of the Arrhenius equation is:

$$\log_{10} K_{\text{obsd}} = \log_{10} A_{\text{obsd}} - \frac{E_{\text{obsd}}}{2.303 RT} \quad (10)$$

It follows from Equation 10 that a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature would yield a straight line with a slope of $-E_{\text{obsd}}/4.574$. The observed activation energies, E_{obsd} , are given in Table VIII.

That the data conform to the Arrhenius equation is shown in Figure 2 for the KMnO₄ oxidations. The rate of the reac-

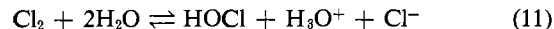
tion was approximately doubled for each 10° increase in temperature. Slight deviations appear at 30° and 40° C. The observed activation energy for the diquat-KMnO₄ reaction at pH 9.13 is approximately 0.7 kcal, smaller than that for paraquat-KMnO₄ oxidation under the same conditions. Activation energy was increased by about 3.5 kcal as a result of decreasing the pH from 9.13 to 5.12 for diquat. This was observed also for paraquat-KMnO₄ system. Chlorine oxidations are characterized, generally, by lower activation energies under alkaline conditions when compared with neutral or slightly acidic conditions.

DISCUSSION

Soluble organic contaminants, like diquat and paraquat, are extremely difficult to remove from water. At potable water treatment plants, the general approach to solve this problem is to employ adsorption or chemical oxidation reactions.

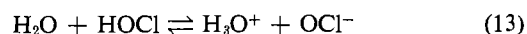
The rate of reaction of diquat-KMnO₄ at pH 9.13 is about 77 times faster than at pH 5.12, whereas the paraquat-KMnO₄ reaction is about 62 times faster at pH 9.13 than at 5.12 at 20° C. This means that potassium permanganate is a more effective oxidant of dipyrindylum cations in an alkaline medium than in an acid medium. This may be due to the fact that the activation energy of the oxidation is decreased as the pH increases and as a result the feasibility for the reaction to proceed increases.

The rates of reaction of aqueous chlorine with diquat and paraquat may vary with pH because of the effect of [H₃O⁺] on hydrolysis and protolysis of chlorine species in water. The relative concentrations of molecular chlorine, hypochlorous acid, and hypochlorite ion in aqueous solutions are controlled by two equilibria. When chlorine is dissolved in water it hydrolyzes.



$$K_h = \frac{[\text{HOCl}][\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{Cl}_2]} \quad (12)$$

The equilibrium constant of the above reaction has been determined as about 3.88×10^{-4} at 20° C (Connick and Chia, 1959). Hypochlorous acid, a weak acid, protolyzes in water.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} \quad (14)$$

The acidic, dissociation constant for HOCl was determined by Morris (1966) as 2.62×10^{-8} at 20° C.

Thus, any free chlorine in water will immediately distribute itself between HOCl and OCl⁻, with the molar ratio of the two species controlled entirely by pH in accord with Equation 12. At pH 5.0 or below, chlorine is present at molecular chlorine. When pH is between 5.0 and 6.0, chlorine exists almost entirely as HOCl acid. Above pH 6.0, hypochlorite ions are present and become predominant above 7.5 (Fair and Geyer, 1957).

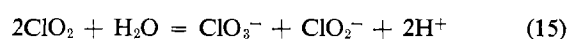
Apparently, diquat can be oxidized by hypochlorite ion, but not by hypochlorous acid. At pH 5.06, chlorine had no effect on diquat. But at pH 7.12, since chlorine is present as hypochlorite in approximately 25%, the oxidation proceeds appreciably (K_{obsd} of 0.515 l. mole⁻¹ min⁻¹). At pH 9.04, the percentage of hypochlorite ion in solution is 97.1. Consequently, the rate constant was increased to 3.41 l. mole⁻¹ min⁻¹. Likewise, paraquat, in the pH range 5.06 to 7.12, was not oxidized during a 24-hr period. Whereas, in the pH range

of 8.14 to 10.13, the rate constant was increased steadily. Concurrently, the activation energy of the oxidation reactions was decreased as the pH value was increased.

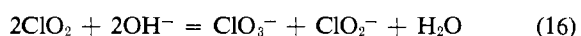
The redox potentials of diquat and paraquat were determined potentiometrically by Michaelis and Hill (1933). E_0 for the diquat cation was +0.349 V, while that for paraquat is +0.446 V. These redox potentials are independent of pH and the nature of the anion. Michaelis and Hill reported that the 1,1'-dipyridyl diquatery ammonium base will be ionized even in alkaline solution, and may be formulated both in acid and alkaline media as a bivalent cation.

In accord with the aforementioned redox potentials, paraquat would be expected to be more resistant to oxidation than diquat. This is confirmed partially with the activation energy for the diquat- Cl_2 reaction approximately 5 kcal lesser than that for the paraquat- Cl_2 system at pH 9.04.

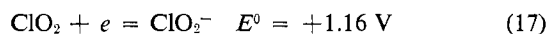
Chlorine dioxide does not appear to hydrolyze or to protolyze in aqueous solutions. Also, it does not dissociate or disproportionate under acid or neutral conditions, as suggested by the reaction (Dodgen and Taube, 1949):



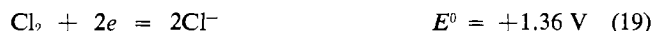
Disproportionation can be forced, however, to occur at pH values of 11 to 12.



Thus, pH is a factor in aqueous chlorine dioxide solutions only under high hydroxide ion concentrations. In the presence of reducing agents such as organic matter, chlorine dioxide does not have the tendency to be reduced completely to Cl^- , but prefers to remain at the chlorite (Cl^{+3}) oxidation state (Dodgen and Taube, 1949).



Although chlorine dioxide theoretically has $2\frac{1}{2}$ times more the oxidation capacity of chlorine,



is not all used, as the majority of reactions with reducing substances in water only causes reduction to chlorite.

Data obtained in this investigation revealed that chlorine dioxide acted as a strong oxidizing agent towards diquat and paraquat (in an alkaline medium between pH 8.14 and 10.15). Lowering the reaction temperature from 20° to 10° C had no effect on the oxidation kinetics that suggest a low activation energy. It seems that the disproportionation of chlorine dioxide (Equation 16) occurs to a certain extent at pH 8.14 and increases steadily as the pH value is increased. As a result, ClO_2^- and ClO_3^- will occur and may attract the positively charged divalent cation to explain the rapid rate of reaction.

Since the detention times of the water treatment plant reactors are in the order of 15 to 60 min, chemical reactions employed in the removal of any trace organic matter from water

must go to completion in a short period of time. If, on the other hand, the reaction kinetics are not favorable, compensation must be made, which is usually in the form of applying excess oxidants. Temperature is another reaction variable that must be considered. Since reaction kinetics are usually slower at lower temperatures, excess reactants can be employed again to force the reaction to completion.

Chlorine dioxide seems to be the oxidant of choice from the three for the removal of residual dipyridylum quaternary salts from water. Its use would require preadjustment of pH of water to slightly alkaline values (above pH 8.0). Temperature appeared to have little or no effect on velocity of reaction, which only will require a contact time of less than 1 min. Also, the required dosages of chlorine dioxide are within normal operation at a water treatment plant. Chlorine, the most commonly used oxidant, also requires adjustment of the pH value to slightly alkaline side, where it will be very active as an oxidant for the removal of residual dipyridylum herbicides, but not as efficient as chlorine dioxide. Potassium permanganate, on the other hand, would be the oxidant of choice under neutral or slightly acidic conditions.

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