[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Interaction of Manganic Ion and Oxalate. Rates, Equilibria and Mechanism

BY HENRY TAUBE

Recent observations[1] on the manganic ion catalysed reaction of chlorine and oxalic acid were shown to be consistent with a mechanism in which the slow step is the oxidation of oxalic acid by manganic ion. Accepting this assumption, the rate data fixed the rate law for this reaction and its specific rate in solutions at high hydrogen ion concentration. In the present work, the interpretation of the catalytic data has been checked by direct measurements of the rate of the manganic ion–oxalic acid reaction

$$2\mathrm{Mn(III)} + \mathrm{H_2C_2O_4} = 2\mathrm{Mn(II)} + 2\mathrm{H^+} + 2\mathrm{CO_2}$$

Measurements of the rate of this reaction in solutions at low hydrogen ion concentration have been reported.[2,3,4] However, since there are important differences in the conclusions reached by some of the observers,[2,3] and since in no case did the conditions sufficiently approach those obtaining in the catalytic work, unambiguous comparisons of rate could not be made. While the present measurements do not extend to solutions as acidic as those employed in the catalytic work—the rate of reduction of manganic ion at high hydrogen ion concentration being so rapid as to make direct measurement difficult—a comparison is still possible since the rate law established in the catalytic work predicts the variation of reaction rate with hydrogen ion concentration for conditions under which the assumed mechanism operates. The measurements reported here have been extended also to solutions at low hydrogen ion, and conclusions about the mechanisms operative over the whole hydrogen ion concentration range are offered.

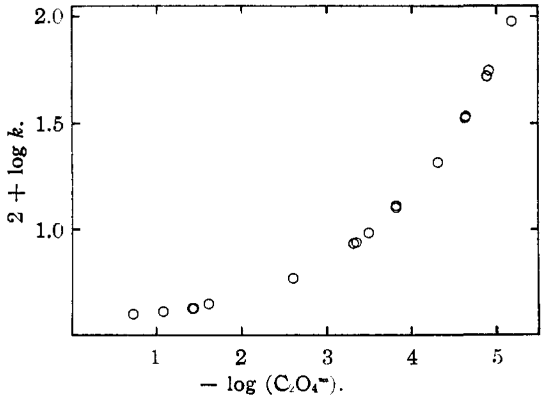

Fig. 1.—The variation of specific rate with oxalate ion concentration. Data are from Table I, experiments 1 to 17.

Method

To the solution containing oxalate, hydrochloric acid and manganous ion, a small volume of a solution of potassium permanganate was added. After sufficient time (*ca.* 1 min.) had elapsed to ensure complete reduction by the excess manganous ion of permanganate ion to Mn(III), a sample was withdrawn and quenched by discharging it into a solution of potassium iodide. Other samples were withdrawn at measured intervals of time and quenched in like manner, and the Mn(III) content determined by titrating the liberated iodine. The initial concentration of Mn(III) was of the order of 3.0×10^{-3} *M* in most cases, much less than the concentration of added oxalate, and, during the course of the run, the concentration fell to one-third to one-sixth of the original value. The first order specific rates calculated from the several samples, usually four, measured at intervals agreed within 1 to 2% of the mean, and in no case showed a significant drift. Over the concentration range covered, 3.0×10^{-3} *M* down to about 0.5×10^{-3} *M*, the reaction is strictly first order with respect to the concentration of Mn(III).

To remove oxygen, carbon dioxide was swept through the more acidic solutions, and nitrogen, from which residual oxygen had been scrubbed, through those in the range of low acid concentration. Except where otherwise noted, the reactions were carried out at 25.2°. The ionic strength was maintained at 2 in the majority of experiments by the addition of potassium chloride.

Results and Discussion

The Rate Determining Steps.—In Table I are recorded the results of a series of experiments, 1–17, in which the concentration of total oxalate and of acid have been varied, the ionic strength and temperature being constant. Each specific rate tabulated in column 6 is the mean of the several which were obtained during a single run. The specific rate is defined by the equation

$$k = \frac{2.303}{t} \log \frac{(\mathrm{Mn(III)})_0}{(\mathrm{Mn(III)})_t}$$

The time being expressed in minutes. The data show that at high acid concentration (low oxalate ion concentration) the specific rate increases rapidly as the acid concentration is raised, approaching variation with the second power, and that the specific rate at high oxalate ion concentration reaches a limiting value, which is independent of the oxalate ion or acid concentration. The important features are more strikingly portrayed in Fig. 1, in which log *k* for experiments 1–17 is plotted against $\log 1/(\mathrm{C_2O_4^=})$. The specific rate is observed to be fixed by the oxalate ion concentration, and does not depend directly on the hydrogen ion, oxalic acid or binoxalate ion concentrations.

These observations can be interpreted quantitatively by the simple mechanism in which each of the ions $\mathrm{MnC_2O_4^+}$, $\mathrm{Mn(C_2O_4)_2^-}$, $\mathrm{Mn(C_2O_4)_3^≡}$ known to be in rapid equilibrium,[1,5] undergoes

---

[1] THIS JOURNAL, **69**, 1418 (1947).

[2] Launer, *ibid.*, **54**, 2597 (1932).

[3] Lidwell and Bell, *J. Chem. Soc.*, 1303 (1935).

[4] Bradley and van Praagh, *ibid.*, 1624 (1938).

[5] Cartledge and Ericks, THIS JOURNAL, **58**, 2065 (1936).

TABLE I

KINETICS OF THE REACTION AT 25.2°

Columns 2, 3 and 4 express the compositions of the solutions in terms of the reagents initially added; column 5 presents the equilibrium concentration of oxalate ion at the time of withdrawing the first sample. All concentrations are expressed in moles per liter. $[MnCl_2]$ was 0.01 *M* except in experiment 18, $[KMnO_4]$ *ca.* 7×10^{-4} *M*, $(Mn(III))_0$ from 2×10^{-3} to 3×10^{-3} *M*. The ionic strength was 2 (maintained by KCl) except in experiment 19. The content of columns 7, 8, 9 and 10 is described in the text.

No.	$[HCl]_0$	$[H_2C_2O_4]$	$[K_2C_2O_4]$	$(C_2O_4^{=})_0$	k	Fraction[c] of Mn(III) as $Mn(C_2O_4)_3^{\equiv}$	Contribution to k by $MnC_2O_4^+$ path	Contribution to k by $Mn(C_2O_4)_2^-$ path	k calcd.
1	0.436	0.150		6.42×10^{-6}	0.95	0.004	0.877	0.088	0.965
2	.292	.150		1.22×10^{-5}	.558	.009	.466	.089	.555
3	.194	.150		2.27×10^{-5}	.342	.016	.252	.0895	.342
4	.194	.150		2.27×10^{-5}	.335	.016	.252	.0895	.342
5	.194	.0795		1.27×10^{-5}	.525	.009	.449	.089	.538
6	.0971	.150		4.85×10^{-5}	.208	.033	.116	.088	.205
7		.150		1.50×10^{-4}	.130	.0965	.0353	.083	.122
8		.150		1.50×10^{-4}	.128	.0965	.0353	.083	.122
9		.100	0.0200	3.20×10^{-4}	.0970	.186	.0147	.0748	.0966
10		.0900	.0284	4.52×10^{-4}	.0870	.244	.0097	.0693	.0890
11		.0743	.0249	4.67×10^{-4}	.0867	.250	.094	.0688	.0884
12		.0776	.0583	2.50×10^{-3}	.0596	.640	.0008	.0330	.0600
13		.0485	.0728	2.47×10^{-2}	.0448	.947		.0049	.0437
14		.0440	.0824	3.73×10^{-2}	.0429	.964		.0033	.0428
15		.0097	.0533	3.88×10^{-2}	.0429	.966		.0031	.0427
16		.0194	.1065	8.40×10^{-2}	.0416	.984		.0015	.0418
17		.0194	.214	1.92×10^{-1}	.0410	.994		.0007	.0413
18[a]		.0194	.214	1.92×10^{-1}	.0432				
19[b]		.0194	.214	1.92×10^{-1}	.0361				

[a] $[MnCl_2] = 0.05$ *M*. [b] No added KCl; ionic strength = 0.65. [c] Solutions in experiments 1–6 are a deep straw color; a reddish tint appears in experiments 7 and 8; at high oxalate ion concentration, the solutions are a wine red color.

decomposition. Thus to cover the whole oxalate ion concentration range, the three independent paths below are assumed

$$MnC_2O_4^+ \xrightarrow{k_1'}$$

$$Mn(C_2O_4)_2^- \xrightarrow{k_1''}$$

$$Mn(C_2O_4)_3^{\equiv} \xrightarrow{k_1'''}$$

The contribution by each path depends on the concentration of the ion in question and on its specific rate of decomposition.

$$-\mathrm{d}\,Mn(III)/\mathrm{d}t = k(Mn(III)) = 2k_1(MnC_2O_4^+) + 2k_1'(Mn(C_2O_4)_2^-) + 2k_1''(Mn(C_2O_4)_3^{\equiv})$$

The factor 2 is introduced into the equation above since it may reasonably be supposed, as in fact the comparison of the results at high acid with those of the catalytic experiments show, that the reducing intermediate formed in the rate determining step rapidly reacts with a second manganic ion, as for example

$$C_2O_4^- + Mn(III) = 2CO_2 + Mn(II)$$

This mechanism has been tested by assigning values to the specific rates k_1, k_1' and k_1'' and to the equilibrium quotients governing the distribution of Mn (III) among the three manganic species, and from these parameters, knowing the compositions of the solutions, calculating the values of k for each of the experiments 1–17 of Table I. The values of the above mentioned parameters which give close agreement between the experimental and calculated values for k were chosen as follows: k_1 has been measured[6] in the catalytic work as 11.8 min.$^{-1}$; k_1' has been selected as 0.046 min.$^{-1}$ to fit the present data; k_1'' is fixed by the present data at high oxalate ion concentration as 0.0205 min.$^{-1}$; K_b, the quotient governing the equilibrium

$$MnC_2O_4^+ + H_2C_2O_4 = Mn(C_2O_4)_2^- + 2H^+$$

was determined in the catalytic work as 42; $1/K_c$, governing the equilibrium

$$Mn(C_2O_4)_3^{\equiv} = Mn(C_2O_4)_2^- + C_2O_4^=$$

has been selected[7] to fit the present data as 1.4×10^{-3}. Values for the first and second dissociation constants of oxalic acid (K_1 and K_2) are also required, these in order to calculate the equilibrium concentrations of $H_2C_2O_4$, $HC_2O_4^-$, $C_2O_4^=$ and H^+ in each experiment; these constants are reported by Dawson[8] as 6.3×10^{-2} and 1.66×10^{-4} for a medium 2*M* in potassium chloride.

In making the calculations, allowance has been made for the changes produced in oxalate and acid by the net reduction of MnO_4^- to Mn (II)

---

(6) The data on the catalysis of the oxalic acid–chlorine reaction gave for k_1 and K_b values of 11.4 min.$^{-1}$ and 44, respectively; more recent data on bromine and oxalic acid catalyzed by manganic ion give for k_1 and K_b values of 11.9 min.$^{-1}$ and 41. Weighted means were chosen for the comparisons with the present results. Results obtained in the bromine–oxalic acid work furthermore show that there is no interference by chloride ion in the Mn(III)–oxalic acid reaction, if the oxalate ion concentration is as high as that used in the present work.

(7) The value of Cartledge and Ericks for 0° and lower ionic strength is 3.8×10^{-3}.

(8) Dawson, *J. Chem. Soc.*, 1889 and 2534 (1929).

and to the mangani–oxalate complexes. No corrections were applied for the oxalate consumed by association with Mn (II) since the pertinent equilibrium constants are not known; in any case, the effects due to this cause are small since the concentration of manganous ion is low in comparison to the total oxalate.

Data for a typical experiment are present below, and the calculation of the equilibrium oxalate ion concentration and of the specific rate outline to illustrate the factors which have been considered.

Experiment 9, Table I.—Square brackets denote stoichiometric, round brackets equilibrium concentrations.

$$[H_2C_2O_4] = 0.100\ M$$
$$[K_2C_2O_4] = 0.02\ M$$
$$[KMnO_4] = 6.9 \times 10^{-4}\ M$$

Since the concentration of oxalate ion in the solution will be low, it is convenient to express the concentrations in terms of $H_2C_2O_4$ and KHC_2O_4; thus: $[H_2C_2O_4] = 0.080\ M$ and $[KHC_2O_4] = 0.040\ M$

Time in minutes	0.00	3.33	7.00	11.12	15.38
$(\mathrm{Mn(III)}) \times 10^3$	2.350	1.710	1.195	0.800	0.525
k		0.0963	0.0968	0.970	0.974

The concentrations of oxalic acid and potassium oxalate are altered by the oxidation of Mn^{++} to Mn(III), and of oxalic acid to carbon dioxide (from one-quarter to one-half of the added total oxidizing power is lost by the time of the first sampling). Allowing for these changes, $[H_2C_2O_4]_{t=0}$ and $[KHC_2O_4]_{t=0}$ become 0.0797 M and 0.0352 M, respectively; allowing then for the dissociation of oxalic acid, the stoichiometry and equilibrium constants are satisfied by: $(H^+) = 0.0374\ M$, $(H_2C_2O_4) = 0.0426\ M$, $(HC_2O_4^-) = 0.0720\ M$ and $(C_2O_4^{=}) = 3.20 \times 10^{-4}\ M$.

The specific rate is calculated making use of the equation

$$k_{\text{calcd.}} = 2k_1 \frac{1}{1+b+c} + 2k_1' \frac{b}{1+b+c} + 2k_1'' \frac{c}{1+b+c} \qquad \text{I}$$

where

$$b = \frac{K_b}{K_1K_2}(C_2O_4^{=}) = 4.02 \times 10^6(C_2O_4^{=})$$

and

$$c = \frac{K_bK_c}{K_1^2K_2^2}(C_2O_4^{=})^2 = 2.87 \times 10^9(C_2O_4^{=})^2$$

In deriving the equation, the principal manganic ion species are considered to be the complexes with oxalate ion; even for the solution at lowest oxalate ion concentrations used in the present study, it is a sufficiently close approximation to neglect the species $\mathrm{Mn}_{\mathrm{Cl}}{}^{+++}$. The quotients in the three terms on the right-hand side of the equation I represent the fractions of the total manganic ion present as $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$ and $Mn(C_2O_4)_3^{\equiv}$, respectively. The fraction present as $MnC_2O_4^+$ is in every case small, being 0.04 in the maximum case of experiment 1. The fraction present as $Mn(C_2O_4)_3^{\equiv}$ has been entered in column 7 of Table I. The three terms of equation I give the contributions to the total specific rate by the decompositions of $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$ and $Mn(C_2O_4)_3^{\equiv}$, respectively, and were calculated by substituting the value of $(C_2O_4^{=})$ appropriate for each experiment into the terms of equation 1. The values of the first and second terms are recorded in columns 8 and 9 of Table I, and the sum of the three terms, representing the calculated values k to be compared to the experimental values, in the final column.

Some features of the data may require special emphasis. In the more acidic solutions, most of the reaction proceeds by decomposition of $MnC_2O_4^+$, which was the only path exposed by the catalytic data in the highly acid solutions there studied. Since the calculated values of k in experiments 1–5 are not very sensitive to the values assumed for k_1', k_1'' and K_c the quantitative agreement of the experimental and calculated values of specific rate in these experiments confirms the earlier cited conclusions about the character of the rate determining step in the catalytic work. The results also show definitely that at high oxalate ion concentration the rate becomes independent of this variable. This conclusion agrees with that reached by Lidwell and Bell,[3] but is at variance with that reached by Launer.[2] Not much emphasis can be placed on the agreement of the experimental and calculated values of k for intermediate ranges of oxalate ion concentration since both k_1' and K_c are adjustable parameters, and the limits of error on these constants are judged to be about 10 and 30%, respectively.

An additional feature of the manganic ion-oxalic acid reaction which was exposed by the catalytic work[1,6] has been checked by observations (qualitative only) on the direct reaction. Where the principal manganic species in solution is $Mn(C_2O_4)_2^-$, the rate of reaction is expected, and is observed, to rise rapidly as the oxalate ion concentration is reduced. If, however, the oxalate ion is reduced to such low values, that the dissociation of $MnC_2O_4^+$ to Mn^{+++} and $H_2C_2O_4$ takes place, the rate of reaction will *diminish* as the concentration of oxalate ion (proportional to oxalic acid) is decreased, and in the limit will be first order with respect to oxalic acid. These effects were observed in the manganic catalyzed chlorine–oxalic and bromine–oxalic reactions. In the present work it was shown that in a solution about $10^{-3}\ M$ in oxalic acid and 7 M in perchloric acid, the half-life of manganic ion is about fifteen seconds; if all the manganic ion were present as $MnC_2O_4^+$, a half-life of about three seconds would be expected. Furthermore, the half-life of manganic ion was observed to increase as the concentration of oxalic acid diminished.

Experiment 18 in comparison with 17 shows that a moderate change in Mn (II) concentration has only a minor effect on the rate of decomposition of $Mn(C_2O_4)_3^{\equiv}$; the slight increase observed when the prevailing manganous concentration is increased about eight-fold may however be real. A 20% reduction in rate of $Mn(C_2O_4)_3^{\equiv}$ decomposition is produced by changing the ionic strength from 2 to 0.65. The limiting Brönsted equation predicts no variation of specific rate with ionic strength for a reaction of this type. Since however the act of decomposition involves a separation of charged particles, it would not be surprising if the activity coefficients of the original ion and the activated, deformed ion are differently affected by media of high ionic strength.

Calculations of the type made above were applied also to the data of Lidwell and Bell[3] and of Bradley and van Praagh.[4] The calculated values of specific rate in typical cases, experiment 7, reference 3, and experiment 105, reference 4, for example, exceed by a factor of about 3 those observed by Lidwell and Bell. Part of the difference may be due to the differences in ionic strength and part to differences in temperature. No mention of removal of oxygen was made in the papers mentioned, and if this precaution was not taken, part of the difference may also be attributed to this cause.[9]

Temperature Coefficients of the Mangani-oxalate Decomposition.—The temperature coefficient of the rate of decomposition of $MnC_2O_4^+$ has already been measured[1]; in the present work new data for $Mn(C_2O_4)_3^{\equiv}$ are presented. These are recorded in Table II.

TABLE II

VARIATION OF THE RATE OF DECOMPOSITION OF $Mn(C_2O_4)_3^{\equiv}$ WITH TEMPERATURE

Initial Mn(II) = 0.01 *M*; E_3 is defined by $k_1'' = ae^{-E_3/RT}$

No.	$(C_2O_4^{=})$	Temp., °C.	$2k_1''$	E_3
1	0.120	17.9	0.0163	
2	.192	25.2	.0410	21,900
3	.180	35.6	.1455	22,200
4	.095	36.3	.156	22,500
			Mean	22,200 ± 500

Only the decomposition of $Mn(C_2O_4)_3^{\equiv}$ contributes appreciably to the reaction at the concentrations of oxalate ion used in the experiments above, and the activation energy measured may therefore be ascribed to this reaction.

The data on the specific rates, activation energies and frequency factors (*a* in the equation above Table II) for the mangani–oxalate decompositions are presented below.

	$MnC_2O_4^+$	$Mn(C_2O_4)_2^-$	$Mn(C_2O_4)_3^{\equiv}$
k_1 at 25.2°, min.$^{-1}$	11.8 ± 0.5	0.046 ± 0.005	0.0205 ± 0.001
E	18,300 ± 500		22,200 ± 500
a	2×10^{14}		3×10^{14}

An interpretation of the decrease in the rate of decomposition of the complexes as the number of associated oxalate ions increases, has been advanced elsewhere.[1] This interpretation attributes the decrease primarily to an effect on the activation energies and thus is supported by the data recorded in the table above. It may be noted that the interpretation is also consistent with the observation that a greater decrease in specific rate occurs for the first stage of the stepwise addition of oxalate ion than for the second.

The Products Formed in the Rate Determining Step.—It was observed in the catalytic work[1,10] that the reducing intermediate formed on decomposition of $MnC_2O_4^+$ reacts with Mn(III), Fe(III), Cl_2 and Br_2. Launer[9] has shown that the reducing intermediate reacts also with oxygen, and that it thereby induces the reaction

$$H_2C_2O_4 + O_2 = H_2O_2 + 2CO_2$$

This observation has been checked in the present work for more acidic solutions; in a solution 0.15 *M* in oxalic acid and 0.45 *M* in hydrochloric acid, with initial manganic ion sufficiently low, as many as twenty equivalents of hydrogen peroxide are produced for each equivalent of manganic ion consumed when oxygen is present. None of these observations, however, distinguish between the alternatives[1]

$$MnC_2O_4^+ = Mn^{++} + C_2O_4^- \text{ (or } CO_2 + CO_2^-\text{)} \quad (1)$$

$$MnC_2O_4^+ = Mn^+ + 2CO_2 \quad (2)$$

Evidence is offered below that part at least of the reaction must proceed to produce an organic radical, step 1, but some participation also by step 2 is not excluded by the new results.

It has been found that hydrogen peroxide is produced even in the absence of oxygen for solutions over a limited range of acidity (*ca.* 0.4 *M*–1 *M* hydrochloric acid). This was shown by experiments in which oxygen was removed by a current of carbon dioxide, and more rigorously by experiments in which the solutions were degassed by repeated freezing and evacuation, the solutions being mixed to initiate reaction after the system was sealed off. The amounts of hydrogen peroxide which appear, while not great, are great enough to make precise[11] determination of the rate of the mangani-oxalate decomposition difficult in the critical acid range. In the optimum case observed, a solution 0.45 *M* in hydrochloric acid with the initial manganic ion 1.2×10^{-3} *M*, about one-eighth of the oxidizing capacity appeared as hydrogen peroxide after the complex ion had decomposed. The residual oxidizing agent was identified as hydrogen peroxide by comparing its specific rate of reaction with iodide ion with that observed for hydrogen peroxide when this was added to the same iodide solution.

---

(9) Launer, THIS JOURNAL, **55**, 865 (1933).

(10) Publication of the data on Br_2—$H_2C_2O_4$ reaction catalyzed by manganic ion will be forthcoming.

(11) In experiment (1), Table I, the samples were quenched by using a solution low in iodide concentration cooled to 0°. The oxidation of iodide by the peroxide within the time of titration was small. Residual peroxide was determined and a correction applied for the fact that not each molecule of reducing intermediate accounted for a second molecule of mangani-oxalate ion.

There appears to be no chemically reasonable way of explaining the appearance of hydrogen peroxide if only Mn^+ is formed as the reducing intermediate. With the first alternative however, the observation can readily be understood. Two radicals $C_2O_4^-(HC_2O_4)$ or $CO_2^-(HCO_2)$ may be expected to form a peroxide on association. In the acid solutions the perdioxalic acid or perdiformic acid would hydrolyze to form hydrogen peroxide and regenerate the organic acid. Hydrogen peroxide is not produced in very acidic solutions presumably because the reducing intermediate reacts rapidly with $MnC_2O_4^+$, and the concentration of this ion increases with increasing acid concentration. At low acid, where the rate of decomposition of the mangani–oxalate complexes is low, the stationary concentration of the organic radicals will be similarly low, and the reaction of the radicals with Mn(III), being first order with respect to the radical concentration, will be favored over the association of the radicals. The decrease in peroxide production as the acidity is decreased however seems too sharp to be completely explained in this way, and it seems possible that effects due to an equilibrium

$$HC_2O_4 = H^+ + C_2O_4^-$$

become important when the hydrogen ion concentration is about 0.5 *M*. This would attribute to HC_2O_4 a dissociation constant about 0.5, and this value seems not unreasonable in comparison with 1.7×10^{-4} for $HC_2O_4^-$.

Summary

Kinetic data on the oxidation of oxalate by manganic ion over the range 6×10^{-6} *M* oxalate ion to 0.19 *M* oxalate ion are presented. These data are interpreted if it is assumed that the first order decomposition of each of the ions $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, $Mn(C_2O_4)_3^{=}$ contributes to the reaction. Values for the specific rates of decomposition of these ions, for the activation energy of the decomposition of $MnC_2O_4^+$ and $Mn(C_2O_4)_3^{=}$, and for the equilibrium quotients relating the complexes, are presented.

The rate of decomposition of $MnC_2O_4^+$ deduced from experiments on catalysis by manganic ion agrees quantitatively with that directly observed in the present work.

When the oxalate ion concentration is sufficiently great, *ca.* 0.1 *M*, the rate of reaction is independent of this variable.

Hydrogen peroxide is produced in the oxidation of oxalic acid by manganic ion within a limited acid concentration range, and conclusions about the detailed mechanism of reaction based on this observation are offered.

RECEIVED MAY 12, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phenyl Silicon Isothiocyanates

BY HERBERT H. ANDERSON

Five monoisothiocyanates remain the sole stable members of the corresponding ternary series. They are: $(CH_3O)_3Si(NCS)$,[1] $SiCl_3(NCS)$,[1] $PCl_2(NCS)$,[1] $POCl_2(NCS)$[1] and $PF_2(NCS)$.[1]

Introduction of the small, neutral methyl group allowed isolation of the first complete ternary series—$(CH_3)_3Si(NCS)$, $(CH_3)_2Si(NCS)_2$ and $(CH_3)Si(NCS)_3$.[2] Apparently the normal boiling point of the compound was not an important factor in determining stabilities; the "acidity" of the other group seemed to be the criterion.

To test this further, the author has now synthesized a complete series of phenyl silicon isothiocyanates, in which the phenyl groups are definitely more acidic than the neutral methyl groups of the only previously known complete series, and less acidic than methoxyl and the halogens. Moreover, phenyl is a group of rather large molar volume, approximately double that of isothiocyanate.

Steric effects may be encountered in proposed future syntheses of isopropyl and tertiarybutyl silicon isothiocyanates; the planar phenyl ring was no steric hindrance to introduction of isothiocyanate groups.

Preparation of New Compounds.—Dr. E. G. Rochow of the General Electric Company, Schenectady, N. Y., kindly furnished samples of phenyltrichlorosilane and diphenyldichlorosilane, which were used after distillation at 200–202.5° and 301–303°, respectively. Triphenylchlorosilane, prepared from the diphenyl analog, was distilled at 189° under 3 mm. pressure.

Silver isothiocyanate in 30% excess converted each of the three phenylchlorosilanes, in benzene solution, into the corresponding isothiocyanate; after an hour at 80–90°,[3] the suspended silver salts were filtered and washed with benzene. After distillation of benzene at atmospheric pressure, each compound was distilled at 3 mm. pressure through a plain column 4 mm. i. d. and 300 mm. long. Middle fractions used in physical measurements and analyses were collected at the following temperatures: phenyl silicon triisothiocyanate, 153.5–154.5°; diphenyl silicon diisothiocyanate, 173–174°; triphenyl silicon isothiocyanate, 188.5–189.5°. Yields varied from 72 to 90%.

Analyses.—A weighed sample of each compound was decomposed in methanol; after addition of water, thiocyanate was determined by titration with silver nitrate solution in the presence of ferric iron. The slow rate of solution of triphenyl silicon isothiocyanate in methanol

---

[1] Anderson, THIS JOURNAL, **67**, 223, 2176 (1945); **69**, 2495 (1947).

[2] Anderson, *ibid.*, **69**, 3049 (1947).

[3] Forbes and Anderson, *ibid.*, **62**, 761 (1940).