discharge current i at an applied potential V is studied in bromine vapor over the temperature range 5 to 75°. A large-size Siemens type ozonizer energized by 1 to 8 kilovolts of 50 cycles frequency was used. At a given temperature, the net effect Δi increases with V; the corresponding relative effect $\%\Delta i$, however, decreases rapidly. At large V, Δi also decreases with V. Within limits, increase of pressure and reduction of temperature increase $\% \Delta i$. When excited at a low temperature and near the "threshold potential," the discharge current became negligible when exposed to ordinary light. The results are in agreement with Joshi's theory, which regards that an activated, adsorption-like, wall layer formed with ions and molecules of the gas is the chief seat of the effect Δi; light releases photo-electrons from this layer which owing to the electron affinity of the excited atoms, are captured by them to form slow moving negative ions and cause the decrease Δi as a space charge effect.

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

Catalysis by Manganic Ion of the Reaction of Bromine and Oxalic Acid. Stability of Manganic Ion Complexes

BY HENRY TAUBE

Earlier work[1a] on the reduction of manganic ion by oxalate demonstrated the important role played in the kinetics of the process by the formation of complexes between manganic ion and oxalate ion. The existence of such complexes also in media at very low oxalate ion concentration and their significance in the electron transfer process was demonstrated in an investigation of the manganic ion catalyzed reaction between chlorine and oxalic acid.[2]

A result of especial interest exposed in the catalytic work was that the initial rate of the catalyzed chlorine–oxalic reaction is independent of the concentration of chlorine. It depends only on the rate of interaction of manganic ion and oxalate, and the observed kinetics pointed to the decomposition of the complex ion $MnC_2O_4^+$ as the principal rate-determining step. The conclusion that the interaction of manganic ion and oxalate alone determines the initial rate of the catalyzed reaction was confirmed by the quantitative agreement observed for the rates of the direct and catalyzed reactions.[1b] It seemed of interest to extend the catalytic work, investigating the catalytic effect of manganic ion on the reaction with oxalic acid of oxidizing agents other than chlorine, particularly since quantitative agreement of initial rates with those observed in the catalyzed chlorine–oxalic acid reaction would further substantiate certain of the conclusions about mechanism. In the present paper the results obtained in a study of the reaction of bromine and oxalic acid

$$H_2C_2O_4 + Br_2 = 2H^+ + 2Br^- + 2CO_2$$

catalyzed by manganic ion are presented and discussed.

For the purpose of direct comparison with the earlier work, in some of the experiments the reaction medium was a solution 2 M in hydrochloric acid. Most of the results, however, were obtained using perchloric acid as the strong mineral acid. These results are of particular importance because the difficulty due to the unknown extent of complex ion formation between manganic ion and the halide ion is avoided in the experiments with perchloric acid. The chlorine–oxalic acid system required a reaction medium high in hydrochloric acid to reduce the rate of the spontaneous reaction sufficiently, but in the present system, at high hydrogen ion concentration, the rate of the spontaneous reaction remains small even when the concentration of bromide ion is as low as 0.001 M.

In most respects, the effects observed in the system under present study are similar to those noted in the chlorine–oxalic work. Thus, the kinetic behavior considering initial rates for the catalyzed reaction of bromine and oxalic acid in 2 M hydrochloric acid is the same as for the reaction between chlorine and oxalic acid under the same conditions, and, in fact, the specific rates for the two systems are identical within the limits of experimental error. When the reaction medium is 2 M perchloric acid, the form of the rate law with respect to the dependence of initial rate on the concentration of bromine, oxalic acid and manganic ion is unchanged, and the specific rates at moderate and high values of oxalic acid agree fairly closely with those obtained in 2 M hydrochloric acid.

The data obtained with perchloric acid as the reaction medium have yielded some new conclusions. From the results of the experiments for low concentrations of oxalic acid a value for the constant governing the association of oxalate and the uncomplexed (except by water or OH^-) manganic ion has been calculated. Further experiments, with chloride ion and other complexing anions added, have yielded information about the association also of these anions with manganic ion.

Over wide ranges of the concentrations of the

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(1) (a) Launer, THIS JOURNAL, **54**, 2597 (1932); Duke, *ibid.*, **69**, 2885 (1947); (b) Taube, *ibid.*, **70**, 1216 (1948).

(2) Taube, *ibid.*, **69**, 1418 (1947).

pertinent substances, the kinetics of the catalyst destruction process for the present system are similar to those observed for the chlorine oxalic reaction, and in fact, the rates of the catalyst destruction processes are nearly the same in both systems. At high bromide ion concentration and/or low values of the product of the manganous ion and oxalic acid concentrations, an effect unobserved in the chlorine–oxalic work appears, however. Under these conditions, the catalyst is destroyed more rapidly than it is under the usual conditions. The kinetics observed in the extreme concentration region indicate that the reaction leading to regeneration of the catalyst is[3]

$$Br_2^- + Mn^{++} + H_2C_2O_4 = MnC_2O_4^+ + 2H^+ + 2Br^-$$

and that it is measurably (and rapidly) reversible. As a consequence of the existence of this equilibrium, at high values of $(Br^-)^2/(H_2C_2O_4)(Mn^{++})$ the concentration of Br_2^- becomes so high that reactions involving it, as well as the usual type of process, lead to destruction of the catalyst. Since atomic chlorine is a much more powerful oxidizing agent than atomic bromine, a similar reversibility is not expected for the analogous reaction in the chlorine–oxalic system, nor was any evidence for it encountered there.

It has been found that under the conditions employed for the bromine–oxalic work, the reactions of the oxidizing agents iodine and persulfate ion with oxalic acid are not noticeably catalyzed by manganic ion. In view of the results obtained in the experiments with bromine, the failure to observe an effect with iodine is not surprising, and may be attributed to the fact that atomic iodine is not powerful enough appreciably to oxidize manganous ion to manganic ion. No definite conclusion can be drawn from the observation made with persulfate ion, since by analogy with the mechanism proposed for the halogen reactions (see below), two steps succeeding the decomposition of the manganioxalate complex are necessary to complete the catalytic cycle. Of these two steps, however, it seems likely that the one involving the reaction of SO_4^- (or $S_2O_8^{=}$) with Mn^{++} would be rapid, and the failure to observe a catalytic effect may be attributed to the slowness with which the reducing intermediate[2] (presumed to be $C_2O_4^-$ or HC_2O_4) reacts with $S_2O_8^{=}$.

Method, Conditions, Definitions

The experimental procedure was similar to that followed in the chlorine–oxalic acid study.[2] In the present work, however, the manganic ion was in most cases generated in the solution (after oxalic acid, perchloric acid, manganous ion and bromine were added) by adding ceric ion. Earlier experiments, and others conducted in the course of the present work, showed that under the usual conditions, the specific rates agree quantitatively with those obtained by adding manganic ion directly. It was found, however, that when fluoride or sulfate is present at high concentration, the ceric ion is not as rapidly reduced and in these experiments manganic ion (as the sulfate complex) was added directly.

Throughout the work, the temperature was 25.2°, the ionic strength 2 and the concentration of hydrogen ion very nearly 2 *M*. Time throughout is expressed in minutes and the concentration in moles per liter.

The data have been treated in the same manner as in the earlier work. A specific rate *k*, not necessarily a constant, defined by the relation $-d(Br_2)/dt = k(Mn(III))_0$, is calculated for each experiment using the corresponding integrated form

$$k = \Delta/(Mn(III))_0t \qquad (I)$$

In these equations, Δ represents the decrease in the concentration of bromine during an experiment (and is very nearly equal to the decrease in oxalic acid concentration) and $(Mn(III))_0$ represents the total trivalent manganese initially present. Values of k_0, the specific rate at zero time, were established by plotting *k* for each series at constant (oxalic acid) and (bromine) against the product $(Mn(III))_0t$ and extrapolating to zero values of the product.[2]

For convenience, the general features of the mechanism found to be consistent with the present and earlier work, are outlined here.

The manganic ion is distributed among various complexes: with oxalate ion ($MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, $Mn(C_2O_4)_3^{\equiv}$), with other ions if added to the system, and with water or hydroxide ion,[4] and equilibrium among the various species is established rapidly. For the highly acid solutions employed, $Mn(C_2O_4)_3^{\equiv}$ comprises only a negligible fraction of the total manganic ion; the concentration of the hydrated[4] (or hydrolyzed) ion, Mn^{+++} is also low except when the concentration of oxalate or other complex forming anion is very low.

The principal path[1b] for the electron transfer interaction of manganic ion and oxalate in the solutions investigated here has as the slow step the first order reaction

$$MnC_2O_4^+ \xrightarrow{k_1} Mn^{++} + C_2O_4^- \qquad (1)$$

The following rapid reactions, which result in catalysis of the reaction of bromine and oxalic acid, may be represented as

$$C_2O_4^- + Br_2 \xrightarrow{k_3} 2CO_2 + Br_2^- \qquad (3)$$

$$Br_2^- + Mn^{++} \xrightarrow{k_6} Mn(III) + 2Br^- \qquad (6)$$

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[3] The data require for their interpretation an equation of the form represented above. The fact that bromide ion enters as the square in the corresponding equilibrium quotient is strong evidence that atomic bromine associates with Br^- to form the complex Br_2^-. This conclusion was arrived at also by Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 386 (1933).

[4] In all the equations, it has been assumed that manganic ion is not appreciably hydrolyzed in 2 *M* H^+. Since the concentration of hydrogen ion has been kept constant, the form of the equations with respect to hydrogen ion has not been proven, but is assumed. An exception is the reaction for the addition of the second (and third) oxalate to the manganic ion.

These reactions do not explain the decrease in k (or in the concentration of the catalyst) with time. These effects under the usual conditions are explained by the reaction of various forms of manganic ion with the reducing intermediate

$$\mathrm{Mn(III)} + \mathrm{C_2O_4^-} \longrightarrow \mathrm{Mn^{++}} + 2\mathrm{CO_2}$$

It is evident from this formulation of mechanism that the rate of reaction of bromine and oxalic acid for any conditions under which the path outlined remains the principal one will be proportional to the concentration of $\mathrm{MnC_2O_4^+}$

$$-d(\mathrm{Br_2})/dt = k_1(\mathrm{MnC_2O_4^+}) \qquad \text{(II)}$$

The initial rate, defined as $k_0(\mathrm{Mn(III)})_0$, is thus equal to $k_1(\mathrm{MnC_2O_4^+})_0$, and from this it follows that $k_0 = k_1F$, where F is the fraction of the total manganic ion present as the labile complex $\mathrm{MnC_2O_4^+}$. This fraction, and thus the initial rate will depend on the concentration of oxalic acid and on that of any other complex forming substance.

Results and Discussion

Initial Rates in 2 *M* Hydrochloric Acid

Comparison of Initial Rates with Those Obtained in the Chlorine–Oxalic Acid Reaction.—In Table I are reported the values of k_0 observed for various values of $(\mathrm{Br_2})_0$, $(\mathrm{Mn(III)})_0$ and $(\mathrm{H_2C_2O_4})_0$.

TABLE I

KINETICS IN 2 *M* HYDROCHLORIC ACID

Temp. 25.2°; $\mu = 2$. $(\mathrm{MnCl_2}) = 5 \times 10^{-3}$ except in one experiment of series 1 for which an increase to 15×10^{-3} showed no effect on rate. See text for manner of calculating figures in the final column.

Series[a]	$(\mathrm{H_2C_2O_4})_0 \times 10^2$	$(\mathrm{Br_2})_0 \times 10^3$	$(\mathrm{Mn(III)_0}) \times 10^5$	k_0	k_0 calcd.
1	0.0512	2.05	1.59	4.8	4.8
2	.100	2.05	1.59	6.8	6.75
3	.980	4.50	4.94	9.9	10.05
4	.961	2.20	2.41	10.1	10.05
5	.990	9.85	5.00	10.1	10.05
6	3.10	2.30	1.55	8.9	8.85
7	7.25	2.33	1.55	6.7	6.75
8	18.70	1.98	1.55	4.1	4.05

[a] Each value of k_0 was obtained from a series of experiments, usually three or four, in which the reaction was allowed to proceed for different periods of time.

As in the reaction of chlorine and oxalic acid catalyzed by manganic ion, the initial specific rate depends only on the concentration of oxalic acid, and in the present system also, is maximum for an intermediate range of oxalic acid concentration.

The equilibria assumed in the previous work

$$\mathrm{MnCl^{++}} + \mathrm{H_2C_2O_4} = \mathrm{MnC_2O_4^+} + 2\mathrm{H^+} \quad \text{Quotient} = K_a$$
$$\mathrm{MnC_2O_4^+} + \mathrm{H_2C_2O_4} = \mathrm{Mn(C_2O_4)_2^-} + 2\mathrm{H^+} \quad \text{Quotient} = K_b$$

suffice to interpret the variation of k_0 with oxalic acid observed and reported above. From these equilibria it follows that

$$F = \frac{1}{\dfrac{(\mathrm{H^+})^2}{K_a\,(\mathrm{H_2C_2O_4})} + 1 + \dfrac{(\mathrm{H_2C_2O_4})K_b}{(\mathrm{H^+})^2}}$$

and k_0 may thus be calculated for any set of values of k_1, K_a and K_b by using the relation: $k_0 = k_1F$. A satisfactory agreement of experimental and calculated values of k_0 (compare data in columns 5 and 6 of Table I) was obtained by using for the three parameters 11.8 min.$^{-1}$, 5.3×10^3 and 41, respectively. The corresponding values for these parameters derived from the previous work[2] were 11.4 min.$^{-1}$, 5.1×10^3 and 44. These parameters agree within the limits of experimental error. Thus the observed initial rates are the same for the oxidizing agents chlorine and bromine, and it may be concluded that the same slow step operates in both systems, and that it is independent of the nature of the halogen.

Initial Rates in 2 *M* Perchloric Acid

Comparison with the Initial Rates in 2 *M* Hydrochloric Acid.—The results of this series of experiments are presented in Table II.

TABLE II

KINETICS IN 2 *M* PERCHLORIC ACID

Temp. 25.2°; $\mu = 2$; $\mathrm{Mn(ClO_4)_2} = 5 \times 10^{-3}$ *M*. For manner of calculating figures in the final column, see text.

Series	$(\mathrm{H_2C_2O_4})_0 \times 10^2$	$(\mathrm{Br_2})_0 \times 10^3$	$(\mathrm{Mn(III)_0}) \times 10^5$	k_0	k_0 calcd.
1	0.030	2.1	0.80	10.6	10.6
2	.0495	1.95	1.59	11.1	11.1
3	.100	2.1	1.59	11.5	11.5
4	.301	2.0	1.64	11.8	11.7
5	1.00	3.9	3.20	11.0	10.8
6	3.09	2.1	1.55	8.7	8.85
7	7.60	2.1	1.53	6.2	6.40
8	19.0	2.1	1.53	3.9	3.80

With 2 *M* perchloric acid as the reaction medium, k_0 also reaches a maximum at intermediate concentrations of oxalic acid. The decrease in k_0 at high oxalic acid takes place in the same concentration range as with hydrochloric acid, but the high values of k_0 continue to much lower concentrations of oxalic acid. The data can be fitted with an equation of the same form as was used above. Substituting for k_1, K_a and K_b in this equation the values 12.0 min.$^{-1}$, 1×10^5 and 46 the figures recorded in the final column of Table II are obtained.

Since k_1 in 2 *M* hydrochloric acid and 2 *M* perchloric acid agrees almost exactly (11.8 *vs.* 12.0 min.$^{-1}$), it seems safe to conclude that the complex undergoing decomposition in the two media is identical, and that $\mathrm{MnC_2O_4^+}$ does not associate appreciably with $\mathrm{Cl^-}$ to form mixed complexes These conclusions are supported also by the rather close agreement for the equilibrium quotients K_b in the two environments (41 as compared to 46). The difference is not greater than might be expected for solutions of such different ionic compositions.

If it is assumed that hydrolysis of manganic ion at high hydrogen ion and complex formation with perchlorate ion are relatively unimportant, the principal equilibrium in solutions low in oxalic acid may be formulated simply as

$$Mn^{+++} + H_2C_2O_4 = MnC_2O_4^{+} + 2H^{+}$$

The value of the quotient governing this equilibrium is given by the value of K_a chosen above, namely, 1×10^5. While this value cannot be considered as very accurate—the decrease in k_0 becomes appreciable only at oxalic acid concentrations so low as to make precise measurements in this range difficult—and may be in error by as much as 30%, it nevertheless seems of interest to apply this value in comparing the quotients governing the association of manganic ion with oxalate ion for each of the three stages. The value for the second stage is derivable from K_b, and for the third state was estimated (approximately) in earlier work.[1b] For the dissociation constants of oxalic acid the values of 6.3×10^{-2} and 1.66×10^{-4} measured by Dawson[5] for solutions 2 M in potassium chloride have been used in making the calculations. The three manganic–oxalate ion equilibria and corresponding quotients are

$$Mn^{+++} + C_2O_4^{=} = MnC_2O_4^{+} \qquad K = 9.5 \times 10^9$$
$$MnC_2O_4^{+} + C_2O_4^{=} = Mn(C_2O_4)_2^{-} \qquad K = 3.9 \times 10^6$$
$$Mn(C_2O_4)_2^{-} + C_2O_4^{=} = Mn(C_2O_4)_3^{\equiv} \qquad K = 7.1 \times 10^2$$

The regular decrease in the tendency to associate as the number of negative ions increases has been observed in other cases in which no rearrangement of *d* electrons takes place during the stepwise addition of the associating group.

The Complex of Chloride Ion and Manganic Ion.—Comparison of the parameters K_a for the hydrochloric acid and perchloric acid solutions shows that in the former medium some species, presumably chloride ion, competes with oxalate for the manganic ion. To learn the order of the effect of chloride ion on this equilibrium, a series of experiments was carried out in which the concentration of this substance was varied, the concentration of hydrogen ion being maintained at 2 M. These data are reported in Table III.

TABLE III

VARIATION OF RATE WITH CHLORIDE ION CONCENTRATION

Total mineral acid maintained at $2M$ with $HClO_4$. $\mu = 2$ $Mn(ClO_4)_2 = 5 \times 10^{-3}M$. For the definition of K'_a and method of calculation of the figures in the final column, see text.

Series	$(H_2C_2O_4)_0 \times 10^2$	(Cl^-)	k_0	$K'_a \times 10^{-3}$
1	0.0511	0.406	8.7	11.0
2	.0511	.865	7.0	10.9
3	.0300	1.00	5.2	11.5
4[a]	Various	2.00	Various	11.2

[a] Calculated from $K_a = 5.3 \times 10^3$.

The values of K'_a were calculated assuming that the principal manganic–chloride species is $MnCl^{++}$; the competition between chloride and oxalate corresponding to this is expressed by the equation

$$MnCl^{++} + H_2C_2O_4 = MnC_2O_4^{+} + Cl^{-} + 2H^{+}$$
$$\text{Equil. quotient } K'_a$$

A value of K_a was calculated for each series of experiments reported in Table III making use of the equation

$$K'_a = k_0 \frac{(Cl^-)(H^+)^2}{(H_2C_2O_4)_0\left[k_1 - k_0\left(1 + \frac{(H^+)^2}{1 \times 10^5\,(H_2C_2O_4)_0}\right)\right]}$$

This equation is derived on the assumptions that the principal manganic ion species are Mn^{+++}, $MnCl^{++}$ and $MnC_2O_4^{+}$, and that the rate of the reaction is proportional to the concentration of $MnC_2O_4^{+}$. In making the calculations from the data, the value of $k_1 = 11.9$ min.$^{-1}$ was used in the equation.

The values of K'_a are constant over the five fold range of chloride ion studied; it can thus be concluded that $MnCl^{++}$ is the principal Mn^{+++}—Cl^{-} species in the system. This formula for the mangani-chloride complex was tentatively suggested in an earlier paper from considerations based on data of a different type.

On combining the value of K'_a with that of the equilibrium quotient for the dissociation of $MnC_2O_4^{+}$, the equilibrium quotient for the reaction

$$Mn^{+++} + Cl^{-} = MnCl^{++} \text{ at } 25° \text{ and } \mu = 2$$

is estimated as 9 ± 3. It is of interest to note that the quotient for the corresponding equilibrium with ferric ion under the same conditions has nearly the same value, namely, 5.5.[6] However, with ferric ion appreciable concentrations of complexes higher than the 1:1 are formed already in 2 M Cl^-, but higher complexes appear to be less important with manganic ion at the same concentration of chloride ion.

Complexes with Fluoride Ion.—Some experiments were also performed with hydrogen fluoride added to the reaction medium. The results of these experiments are reported in Table IV.

TABLE IV

KINETICS IN THE PRESENCE OF HYDROGEN FLUORIDE

Total $(H^+) = 2M$; $\mu = 2$; temp. = 25.2. For definition of R, K_F and K'_F, see text.

Exp. No.	$(H_2C_2O_4) \times 10^3$	$(HF) \times 10^2$	R	K_F	K'_F
1	0.382	1.54	1.465	172	
2	.82	.77	1.184	104	
3	.84	1.54	1.334	109	335
4	.87	3.08	1.820	88	
5	1.81	1.54	1.250	68	295

In these experiments k_0 for each of the various sets of conditions was not determined. Instead, the value of Δ observed during a small fixed interval of time for an experiment without hydrogen fluoride added was compared with that observed when this complexing agent was present. The ra-

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

(6) Rabinowitch and Stockmayer, THIS JOURNAL, **64**, 332 (1942).

tios of these changes in bromine concentration for a fixed time interval are compared under the heading R in Table IV. Except for the slight error introduced by comparing the changes in bromine concentration, rather than the values of k_0, R is equal to the ratio of the concentration of $MnC_2O_4^+$ in the experiments compared.

For each experiment the quotient

$$K_F = \frac{1}{R - 1} \frac{(HF)(H^+)}{(H_2C_2O_4)}$$

was calculated (column 5, Table IV). If the manganic species in solution were principally MnF^{++} and $MnC_2O_4^+$, K_F would be constant, and would be, very nearly, the quotient for the equilibrium: $MnF^{++} + H_2C_2O_4 = MnC_2O_4^+ + HF + H^+$. Any trends in K_F as the concentration of hydrofluoric acid or of oxalic acid is changed, must presumably be interpreted as resulting from the presence in appreciable concentration of other manganic ions.

Experiments 2, 3 and 4 test the dependence of K_F on the concentration of hydrogen fluoride. The low value for K_F in experiment 4 as compared to those in experiments 2 and 3 is real, and means that as the hydrogen fluoride concentration increases, complexes higher in fluoride than the 1:1 complex are being formed. The data do indicate, however, that in the lower range of hydrogen fluoride concentrations studied substantially only the 1:1 complex is present.

The trend of K_F with increase in oxalic acid concentration at constant hydrogen fluoride concentration (experiments 1, 3 and 5) is very marked. A simple reasonable explanation for this trend is that mixed complexes, containing both fluoride and oxalate are formed, thus

$$Mn(C_2O_4)F + H^+ = MnC_2O_4^+ + HF$$

The data have been treated from this point of view to obtain estimates of the quotients for the two equilibria. It may be shown that if the principal manganic ions are $MnC_2O_4^+$, MnF^{++} and MnC_2O_4F, the following relation will hold

$$R = 1 + \frac{(H^+)(HF)}{K_F' (H_2C_2O_4)} + \frac{(HF)}{K_M(H^+)}$$

In this expression, K_F' and K_M are the quotients for the MnF^{++}–$MnC_2O_4^+$ and the $Mn(C_2O_4)F$ – $MnC_2O_4^+$ equilibria, respectively. The expression cannot hold exactly for experiments 1, 3 and 5 since the species Mn^{+++} and MnF_2^+ are also present. However, the concentration of Mn^{+++} does not exceed 15%, and in any case is partially corrected for in the equation by using R in place of k_1/k_0; also, experiments 2, 3 and 4 indicate that at 1.54×10^{-2} M hydrofluoric acid, the fraction of the manganic ion present as MnF_2^+ is not very great. Applying the equation to the data, and solving the simultaneous equations for experiment 1 compared with 3, and 1 compared with 5, the values of K_F' in the final column of Table IV are obtained. The mean of these values, used in conjunction with the value given above for the Mn^{+++}–$MnC_2O_4^+$ equilibrium yields 320 as the quotient for the equilibrium.

$$Mn^{+++} + HF = MnF^{++} + H^+$$

at $\mu = 2$ and 25.2°. Dodgen and Rollefson[7] have measured the quotient for the corresponding equilibrium with ferric ion at $\mu = 0.5$, and report 190 as its value. Work is now in progress in this Laboratory studying the manganic ion–fluoride ion equilibria, by observing the effect of hydrofluoric acid on the MnO_2, Mn^{++}–Mn^{+++} equilibrium. Preliminary data indicate conclusions in substantial agreement with those reported above.

The average value of K_M calculated from the data of Table IV is 3.7×10^{-3}. The reciprocal of this, 270, may be compared with 320 obtained for the equilibrium directly above, and shows that the affinity of fluoride for $MnC_2O_4^+$ is almost as great as it is for Mn^{+++}.

A few experiments were carried out with pyrophosphate added to the solutions. Complex equilibria are encountered here also, and the data were too incomplete to lead to quantitative conclusions. However, some qualitative conclusions did appear from the results: an effect of pyrophosphate is observed at concentrations equal to that of the oxalic acid, thus indicating an affinity of pyrophosphate for manganic ion of the same order of magnitude as that of oxalate; at low pyrophosphate, 0.5×10^{-3} M to 4×10^{-3} M, the ratio of manganic ion to pyrophosphate in the complex is 1:1; mixed complexes appear to be formed also in this system. A further study of the pyrophosphate complexes, of the mixed complexes and a study of the manganic–orthophosphate equilibria is planned.

Kinetics of the Catalyst Disappearance Reaction

As in the case of the catalyzed chlorine–oxalic reaction, there is a net consumption of the catalyst in the course of the reaction and as a result of this, the specific rates k decrease as time increases. For a series of experiments at constant oxalic acid and bromine concentration, k is a function of the product $Mn(III)_0 \times t$. In Table V typical results

TABLE V

KINETICS OF THE CATALYST DISAPPEARANCE REACTION

Temp. = 25.2°; μ = 2.0. For explanation of the content of columns 5 and 6, see text.

Series	$(H_2C_2O_4)_0 \times 10^2$	$(Br_2) \times 10^3$	k_0	Slope $\times 10^{-4}$	k_7'/k_8
		In 2 M $HClO_4$			
Table II, 5	1.00	3.2	11.0	0.73	0.19
Table II, 4	0.301	1.8	11.8	1.8	.23
Table II, 3	.100	1.6	11.5	3.0	.36
		In 2 M HCl			
Table I, 4	.961	1.8	9.9	1.3	.23
Table I, 3	.980	3.5	10.1	.7	.24
Table I, 5	.990	8.5	10.1	.2	*ca.* .2
Table I, 1	.050	1.9	4.8	.6	.5

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(7) Private communication from Dr. Harold Dodgen.

covering this phase of the investigation are presented.

The data have been treated in the same manner as those of the chlorine–oxalic acid work. In column 5 are recorded the slopes of the lines obtained on plotting k against $(\mathrm{Mn(III)})_0 \times t$. These slopes are equal to[2] $k_0{}^2k_7'/k_3(\mathrm{Br_2})$, where k_7' is the specific rate of reaction of the mangani complexes with the reducing intermediate

$$\mathrm{Mn(III)} + \mathrm{C_2O_4^-} \xrightarrow{k_7'} \mathrm{Mn(II)} + 2\mathrm{CO_2} \qquad (7')$$

In column 6, values of k_7'/k_3 are compared; they are observed to be independent of the concentration of the halogen, but to vary with the concentration of oxalic acid. The latter variation was previously observed,[2] and interpreted as due to a different rate of reaction of each of the various mangani complexes with the reducing intermediate.

The values of k_7'/k_3 for three different kinds of halogen are compared below at a constant value of oxalic acid concentration (0.01 M) such that the principal manganic species is $\mathrm{MnC_2O_4^+}$. For the series therefore, k_7' is essentially constant, and any significant differences may be attributed to variations in k_3.

	$\mathrm{Cl_2}$ in 2M $\mathrm{Cl^-}$	$\mathrm{Br_2}$ in 2M $\mathrm{ClO_4^-}$	$\mathrm{Br_2}$ in 2M $\mathrm{Cl^-}$
k_7'/k_3	0.3	0.19	0.23

The close agreement of the values of k_7'/k_3 is somewhat surprising. If the difference between the numbers for chlorine and bromine is significant, it implies that the specific rate of reaction of chlorine with the reducing intermediate is less than is the specific rate for the corresponding reaction of bromine.

Evidence for an Equilibrium Involving an Atomic Bromine Species.—The data bearing on this point are presented in Table VI. In experiment 1, the quotient Q defined in the heading of Table VI is extremely small, and in this experiment, a normal value for k is observed. In the remainder of the experiments, the concentrations were adjusted so as to increase Q, and, in all these experiments, k is much less than would be the case if some new effect were not decreasing the rate.

The possibility that the low rates are due to complexing of manganic ion by bromide ion can be rejected on the basis of several arguments. The most cogent of these is that this assumption does not explain the observed kinetics (for instance this assumption would offer no explanation for the effect of manganous ion). A further argument can be based on the fact that ferric ion is not appreciably complexed by bromide ion[6] at concentrations such as were employed in the experiments described in Table VI and it seems unlikely that the complex of manganic ion and bromide ion would be much more stable than the ferric–bromide complex.

The assumption that at high values of Q the lifetime of the catalyst is greatly reduced does, however, lead to a satisfactory interpretation of the observations. The manner of treating the data from this point of view is outlined below.

It may be shown that, whatever the particular paths involving mutual second order interactions of the substances: Mn(III), $\mathrm{Br_2^-}$ or the reducing intermediate and resulting in net disappearance of the catalyst, the rate of catalyst disappearance will be second order with respect to the concentration of manganic ion, *i. e.*

$$-\,\mathrm{d\,Mn(III)}/\mathrm{d}t = k_\mathrm{d}(\mathrm{MnC_2O_4^+})^2 = k_\mathrm{d}\,(\mathrm{Mn(III)})^2F^2 \qquad \text{(III)}$$

The specific rate k_d is not a constant, but is a function of the concentrations of $\mathrm{Br_2}$, $\mathrm{H_2C_2O_4}$, $\mathrm{Mn^{+++}}$, $\mathrm{Br^-}$ and $\mathrm{H^+}$. The particular form of the dependence differs for the different catalyst destruction paths. Equation III, after integration, together with the equation $-\mathrm{d(Br_2)}/\mathrm{d}t = k_1\,(\mathrm{Mn(III)})\,F$ leads to the result

$$\Delta = (2.3k_1/k_\mathrm{d}F)\log\,(1 - \mathrm{Mn(III)}_0tk_\mathrm{d}F^2)$$

This equation has been applied to the data of Table VI. By trial, for each experiment that value of k_d was found which would best reproduce the observed value of Δ. From each of these values of k_d was subtracted the part which results from the operation of the normal catalyst destruction process (reaction 7′). The resulting values, denoted by k_d', are tabulated in column 10 of Table VI.

Values of k_d'/Q are plotted against Q in Fig. 1. The figure shows that k_d' is a function of Q only, and that the functional relationship is of the type

$$k_\mathrm{d}' = aQ + bQ^2$$

Marked deviations from this relationship occur only in the region where k_d' is small. In this region, the correction for the normal catalyst destruction process is relatively great and the deviations are probably due to the associated uncertainties.

The observations described above may be understood in the following way. It is assumed that the reaction

$$\mathrm{Br_2^-} + \mathrm{Mn^{++}} + \mathrm{H_2C_2O_4} = 2\mathrm{Br^-} + 2\mathrm{H^+} + \mathrm{MnC_2O_4^+}$$

(equilibrium quotient K_d) is maintained as a rapid equilibrium. Therefore, when the concentrations of bromide ion and hydrogen ion are high and those of manganous ion and oxalic acid low, it may be expected that the concentration of $\mathrm{Br_2^-}$ becomes great enough so that catalyst destruction processes involving this species become operative. If these processes are assumed to be

$$\mathrm{Br_2^-} + \mathrm{MnC_2O_4^+} \xrightarrow{k_9} 2\mathrm{Br^-} + \mathrm{Mn^{++}} + 2\mathrm{CO_2}$$
$$\text{or}\quad \mathrm{Br_2} + \mathrm{Mn^{++}} + \mathrm{C_2O_4^{=}}$$

and

$$\mathrm{Br_2^-} + \mathrm{Br_2^-} \xrightarrow{k_5} \mathrm{Br^-} + \mathrm{Br_3^-}$$

the resulting mechanism requires the dependence of k_d' on Q

$$k_\mathrm{d}' = \frac{2k_9}{K_\mathrm{d}}Q + \frac{2k_5}{K_\mathrm{d}{}^2}Q^2$$

This is the variation of k_d' with Q which is observed experimentally.

TABLE VI

KINETICS AT RELATIVELY HIGH VALUES OF $Q = (H^+)^2(Br^-)^2/(Mn^{++})(H_2C_2O_4)$

$(HClO_4) = 2\ M$; μ varies from 2 to 2.15; $Mn(III)_0$ about $1.5 \times 10^{-5}\ M$ except in exp. 13. Temp., 25.2°. The initial values of (Br_2) and $(H_2C_2O_4)$ are recorded in the table; the values recorded for the equilibrium concentrations of Br^- have been corrected for the $Br^- + Br_2 = Br_3^-$ equilibrium. For definition of contents of columns 9 and 10 see text.

No.	$(Br_2)_0 \times 10^3$	$(H_2C_2O_4)_0 \times 10^2$	$(Mn^{++}) \times 10^3$	$Br^- \times 10^2$	$Mn(III)_0 \times t \times 10^5$	$\Delta \times 10^4$	k	$Q \times 10^{-2}$	$k_d' \times 10^{-4}$
1	1.90	1.015	6.25	...	5.12	5.06	9.9	...	...
2	2.02	1.015	6.25	3.06	5.13	4.56	8.9	0.60	0.67
3	1.94	1.015	6.25	3.06	5.30	4.65	8.8	.60	.72
4	1.77	1.015	25.0	6.17	5.16	4.54	8.8	.61	.65
5	1.76	1.015	56.4	9.28	5.10	4.48	8.8	.62	.69
6	1.84	1.050	12.9	6.17	5.45	4.26	7.8	1.16	1.47
7	2.62	1.030	6.35	6.22	5.28	3.60	6.8	2.40	2.88
8	1.89	1.030	6.35	6.27	5.28	3.41	6.5	2.45	3.24
9	1.77	1.030	6.35	6.27	5.35	3.42	6.4	2.45	3.21
10	1.21	1.030	6.35	6.30	5.25	3.40	6.5	2.47	2.93
11	1.97	1.030	6.35	6.26	1.82	1.55	8.5	2.42	3.44
12	1.70	1.030	6.35	6.27	9.80	5.15	5.3	2.45	2.87
13	1.89	1.030	6.35	6.27	8.50[a]	4.80	5.7	2.45	2.84
14	1.74	1.015	6.25	9.28	5.10	1.89	3.7	5.55	12.4
15	1.72	1.015	6.25	12.4	5.48	.95	1.8	9.75	34
16	1.84	2.06	6.35	9.43	5.43	3.26	6.0	2.75	3.70
17	1.84	0.516	6.35	6.27	5.50	2.25	4.1	4.91	10.2
18	1.72	.206	31.7	3.22	5.28	4.58	8.7	.71	.88
19	1.74	.206	6.35	3.22	5.28	2.95	5.6	3.40	4.96
20	1.91	.206	6.35	6.25	5.12	.85	1.65	12.1	46
21	1.86	.102	6.25	3.06	5.28	1.63	3.1	6.42	16.5

[a] $(Mn(III)_0) = 6.08 \times 10^{-5}\ M$.

It should perhaps be emphasized that the observation which requires the assumption of Br_2^- rather than Br as the principal atomic bromine species is that the factor $(Br^-)^2$ rather than (Br^-) appears in the expression for Q. The data above on the participation of Br_2^- in a chemical equilibrium therefore support the conclusion reached by Griffith, McKeown and Winn[8] and based on data of a different type, that Br forms a complex with Br^-

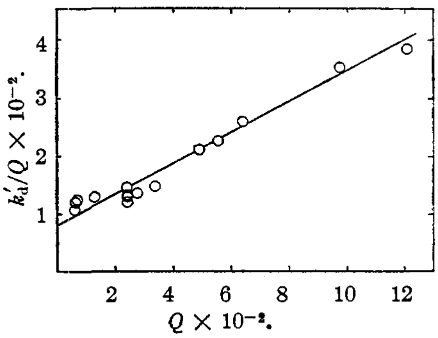

Fig. 1.—Kinetics of the catalyst disappearance at high values of $Q = (Br^-)^2(H^+)^2/(Mn^{++})(H_2C_2O_4)$.

The slope of the line in Fig. 1 gives for the ratio $2\ k_5/K_d^2$ the value of 0.27. It seems likely that the specific rate $2k_5$ is close to the collision frequency 10^{13}. K_d would then become 1.8×10^6, and taken with the value of the quotient for the Mn^{++}–$MnC_2O_4^+$ equilibrium, the quotient: $(Mn^{+++})(Br)^2/(Br_2^-)(Mn^{++})$ is calculated as 16. From this it appears that the Br^-–Br_2^- couple is slightly stronger oxidizing than is the Mn^{++}–Mn^{+++} couple. As yet E^0 for the Mn^{++}–Mn^{+++} couple is not precisely known. Latimer[9] records a value of −1.51 volts but experiments under way in this Laboratory on the MnO_2, Mn^{++}–Mn^{+++} equilibrium show that this value is probably too high and $E^0 = -1.6$ volt seems a somewhat better choice. The latter value would fix E^0 for the Br^-–Br_2^- couple at about −1.7 volt. This is substantially higher than the value of −1.95 volt that may be estimated for the Br^-–Br couple (this estimate assumes that ΔF^0 for Br aq. is about the same as for Br gas, and is therefore probably an upper limit). Comparison of E^0 for the Br^-–Br_2 and the Br^-–Br couples leads to a value of about 10^4 for the quotient governing the equilibrium $Br + Br^- = Br_2^-$. It is of interest that the value reported for the corresponding equilibria with I_2^-[9] and Cl_2^-[10] are of the same order of magnitude.

The intercept at $Q = 0$ in Fig. 1, and the value assumed for k_5 fixes the specific rate of the reaction of Br_2^- and $MnC_2O_4^+$ at about 10^8.

Summary

It has been shown that the reaction of bromine and oxalic acid at high concentration of hydrogen

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[8] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 386 (1933).

[9] Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

[10] Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

ion is catalyzed by manganic ion. The reactions of the oxidizing agents iodine and persulfate under the same conditions are not appreciably catalyzed.

The rate of the catalyzed bromine–oxalic acid reaction has been studied over a wide range of the concentration of the substances (except H^+) which affect the rate.

The initial rates in 2 *M* hydrochloric acid agree closely with those observed in the corresponding reaction of chlorine and oxalic acid; this agreement substantiates important conclusions about the mechanism of the changes.

Data obtained for a medium 2 *M* in perchloric acid have led to conclusions about the affinity of manganic ion and oxalate. By adding various complex forming substances—Cl^-, hydrofluoric acid and pyrophosphate—to the medium, it has been possible to reach conclusions also about the affinity of the corresponding anions and manganic ion.

Under certain conditions the kinetics of the catalyst disappearance reaction are identical, and even the rates nearly the same as in the catalyzed chlorine–oxalic acid reaction. At high values of the ratio $(Br^-)^2(H^+)^2/(Mn^{++})(H_2C_2O_4)$, however, the rate of catalyst disappearance is greatly enhanced. Analysis of the data for this concentration region has led to some conclusions about equilibria involving Br_2.

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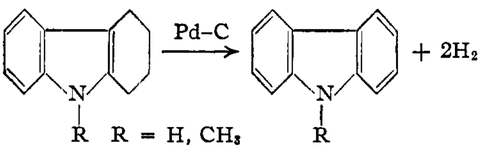
Aromatization Studies. VII. Alkylcarbazoles

BY E. C. HORNING, M. G. HORNING AND G. N. WALKER[1]

Carbazoles are generally prepared by the Graebe–Ullmann method,[2] or by the distillation of tetrahydrocarbazoles over heated lead oxide according to the procedure of Borsche.[3] The thermal decomposition of phenylbenzotriazoles gives good yields of carbazoles in a few cases,[2] but neither method is particularly satisfactory from a preparative point of view. It has now been found that a variety of alkylcarbazoles can be obtained easily by a method involving the aromatization of 1,2,3,4-tetrahydrocarbazoles with a palladium–carbon catalyst. The dehydrogenation reaction is best carried out in a solvent (trimethylbenzene), and the yields are usually nearly quantitative. The necessary 1,2,3,4-tetrahydrocarbazoles were prepared according to the recently published method of Rogers and Corson.[4] This one-step modified indole-type of synthesis provides an excellent way of obtaining alkyl (including N-alkyl) substituted tetrahydrocarbazoles in good yield. The usefulness of this procedure is apparently limited chiefly by the availability of the substituted cyclohexanones and phenylhydrazines which are combined to provide tetrahydrocarbazoles.



Although there is a considerable difference in the ease of hydrogenation of carbazoles and N-alkylcarbazoles, both 1,2,3,4-tetrahydrocarbazole and N-methyl-1,2,3,4-tetrahydrocarbazole undergo dehydrogenation with comparative ease. For all of the compounds investigated here, dehydrogenation occurred readily and there was no evident disproportionation. There was no need to consider the employment of a hydrogen acceptor, and, although no rate studies were made, it is evident that the aromatization required only a comparatively short time for completion. A previous study[5] described the dehydrogenation of several tetrahydrocarbazoles in molten cinnamic acid with a palladium catalyst, but the use of cinnamic acid as a solvent as well as a hydrogen acceptor has not found wide use in aromatization work.

In one case, that of 2,4-dimethyl-3-carboxy-1,2,3,4-tetrahydrocarbazole, the aromatization was accompanied by decarboxylation to give 2,4-dimethylcarbazole as the product. This carbazole was also obtained directly by the aromatization of 2,4-dimethyl-1,2,3,4-tetrahydrocarbazole.

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Experimental

All melting points are corrected.

Catalyst.—A 5% palladium–carbon catalyst was prepared according to Hartung's method.[6]

Dehydrogenation Procedure.—The general procedure is illustrated by the following example. To 5.00 g. of 1,2,3,4-tetrahydrocarbazole in 15 ml. of trimethylbenzene (Eastman Kodak Co. technical grade, redistilled, b. p. 168–172°) was added 1.5 g. of 5% palladium–carbon cata-

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(1) Research Corporation Research Assistant.

(2) Graebe and Ullmann, *Ann.*, **291**, 16 (1896).

(3) Borsche, *Ann.*, **359**, 74 (1908).

(4) Rogers and Corson, THIS JOURNAL, **69**, 2910 (1947).

(5) Hoshino and Takiura, *Bull. Chem. Soc. Japan*, **11**, 218 (1936).

(6) "Organic Syntheses," **26**, 77 (1946).