4 and 8. With all four compounds the half-wave potentials became approximately constant at a value of about −0.95 volt (*vs.* S.C.E.) over the *p*H range 9 to 12. The half-wave potentials lie so close together that it is impossible to determine one compound in the presence of the others.

TABLE IV

THE EFFECT OF *p*H ON THE HALF-WAVE POTENTIAL

	Half-wave potentials (volts *vs.* S. C. E.)			
*p*H	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
2.1	−0.60	−0.63	−0.56	−0.49
4.0	.67	.71	.65	.58
5.1	.81	.82	.76	.77
6.1	.86	.86	.82	.84
7.0	.88	.90	.86	.90
8.0	.91	.93	.89	.94
8.9	.92	.94	.93	.96
10.0	.93	.95	.94	.97
10.9	.94	.95	.95	.98
11.9	.96	.95	.96	.98

The reduction probably proceeds in acid solution according to the equation

$$R{-}NO_2 + 4H^+ + 4e^- \longrightarrow R{-}NHOH + H_2O$$

while in alkaline solution the equation for the reduction probably is

$$R{-}NO_2 + 3H_2O + 4e^- \longrightarrow R{-}NHOH + 4OH^-$$

The latter equation would account for the slight effect of the *p*H of the solution upon half-wave potential in the alkaline range since the irreversible reduction is not dependent upon the hydrogen ion concentration.

Summary

The rate of transformation in buffered solutions of four nitroparaffins into the corresponding aci-nitroparaffins has been followed polarographically. The rate constants for these reactions were determined and the reactions were found to be first order involving a simultaneous reverse reaction. The positions of the equilibria were found for each compound over the *p*H range 6 to 11. The rate of reaction decreased in the following order: nitromethane > nitroethane > 1-nitropropane > 2-nitropropane.

RECEIVED APRIL 16, 1948

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

Reactions Involving Like-Charged Ions. I. A Neutral Intermediate in Alkaline Permanganate Oxidations

BY FREDERICK R. DUKE[1]

The lattice energies of ionic crystals amount to one hundred or more kcal. per mole.[1a] When such a crystal dissolves in the form of unassociated ions the hydration energy is approximately the magnitude of the lattice energy. The energy of dissociation of hydrated oppositely charged ions is small.[2] We may, therefore, conclude that like-charged ions can readily collide on the periphery of their solvation spheres and that appreciably closer approach of the ions in solution is prohibited. The problem of the activation energy of reaction through the solvation layers is difficult to treat theoretically, but published experimental evidence, some of which is cited below, indicates that the energy requirements are often large.

In the general case of acid–base reaction involving like-charged ions, typified by $[Fe(OH)_2(H_2O)_4]^+ + H^+ \rightleftarrows [Fe(OH)(H_2O)_5]^{++}$, the obvious low energy path is provided by direct reaction of a neutral base[3] (followed, in some cases, by dissociation of ions)

$$[Fe(OH)_2(H_2O)_4]^+ + H_2O \rightleftarrows [Fe(OH)(H_2O)_5]^{++} + OH^-$$

Oxidation–reduction reactions of this type occasionally are clearly oppositely charged ionic reactions, such as the reaction of Fe^3 with Sn^2 in hydrochloric acid solution, where negative chloride complexes of iron have been shown to provide the reaction path.[4] Certain other electron-transfer reactions between like-charged ions proceed very slowly; for example, Sn^2 and Fe^3 react 10^{-5} to 10^{-6} as fast in perchloric as in hydrochloric acid.[3] Even in this case, a minute concentration of complex involving perchlorate as well as hydroxyl *may* provide the reaction path. $[Co(NH_3)_6]^{+3}$ does not exchange with Co^{++}.[5] Other examples might be cited to show that the energy involved in electron transfer through solvation spheres is high.[6]

It is interesting to calculate the magnitude of concentration of neutral or oppositely charged intermediate necessary to provide the reaction path, taking reasonable numbers for the equation $k = Ke^{-\Delta H/RT}$, where k is the specific rate constant, K a constant involving the frequency factor and the entropy of activation, and ΔH the experimental energy of activation. If the entropies for the processes involving like-charged ions on the one hand and a neutral or oppositely charged intermediate on the other, may be considered ap-

---

(1) Present address, Department of Chemistry, Iowa State College, Ames, Iowa.

(1a) Helmholz and Mayer, *J. Chem. Phys.*, **2**, 245 (1934).

(2) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

(3) Gorin, *ibid.*, **58**, 1794 (1936).

(4) Robertson and Law, *Trans. Faraday Soc.*, **31**, 899 (1935).

(5) McCallum and Hoshowsky, *J. Chem. Phys.*, **16**, 254 (1948).

(6) Harbottle and Dodson, THIS JOURNAL, **70**, 880 (1948); Prestwood and Wahl, *ibid.*, **70**, 880 (1948); Van Alten and Rice, *ibid.*, **70**, 883 (1948).

proximately the same, the ratio of the specific rate constants is: $2.3 \log (k_1/k_2) = (\Delta H_2 - \Delta H_1)/RT$, where subscripts $_1$ refer to the direct reaction and subscripts $_2$ to that involving the intermediates. If we take $RT = 600$ and $\Delta H_2 - \Delta H_1 = 10{,}000$ cal., $k_1/k_2 = 10^{-7}$ (10 kcal. seems a reasonable minimum on the basis of the evidence cited above).[7] If the rate of one reaction were 10^2 times the other, experimentally it is likely that only one reaction would be detected. Thus, the $K_{\text{equil.}}$ for the reaction as written: Ion $\rightleftarrows$ Neutral or oppositely charged Intermediate, may be less than 10^{-5}. It can be seen that the concentration of intermediate may be extremely small. We conclude that like-charged ions rarely react directly and that intermediates occur in rapid reactions involving such ions.

Among the most difficult to explain of the reactions between like-charged ions are the alkaline permanganate oxidations of such ions as sulfite, phosphite or formate, and the rapid exchange of manganate and permanganate ion.[8] There is no obvious neutral or positive intermediate in any of these oxidations. Since permanganate is the common ion in the reactions, it appears to be necessary for this ion to be in equilibrium with a neutral or positive particle which eventually reacts with the reducing agent, the permanganate reacting directly with a neutral or positive substance present in the solution. It can be arranged that the only positive ions present are alkali or alkaline earth ions, and the only neutral substance is water; higher oxidation states of these positive ions are extremely improbable leaving the most likely equilibrium

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^= + HO + H^+ \quad \text{(I)}$$

The hydroxyl radical has been found necessary to the explanation of data obtained in a study of the reaction between ozone and hydrogen peroxide[9] and, more recently, the reaction of ozone with cobaltous ion in aqueous solution.[10] Weiss[11] has made use of the hydroxyl radical in explaining the decomposition of hydrogen peroxide at metallic surfaces. No data have been obtained concerning the existence of the equilibrium in equation I, and this study of the decomposition of alkaline permanganate to manganate and oxygen was undertaken to test the theory. The stoichiometry $4MnO_4^- + 2H_2O \rightarrow 4MnO_4^= + O_2 + 4H^+$ is of such a nature that a stepwise reaction is a necessity. Probable steps are

I $MnO_4^- + H_2O \rightleftharpoons MnO_4^= + HO + H^+$
II $HO + HO \longrightarrow H_2O_2$
III $MnO_4^- + H_2O_2 \longrightarrow HO_2 + MnO_4^= + H^+$
IV $HO_2 + MnO_4^- \longrightarrow O_2 + MnO_4^= + H^+$[12]

The equilibrium of reaction I must be established rapidly if it provides the reaction path for the oxidation of ions such as sulfite. The slow reaction might be expected to be the combination of the hydroxyls (reaction II) due to the extremely low concentration of this species. Latimer[13] gives the potentials $H_2O \rightarrow HO + H^+ + e$ (−2.2 v.) and $MnO_4^= \rightarrow MnO_4^- + e$ (−0.54 v.); these values lead to the result that permanganate in solution with hydroxyl ion, activities 0.1 and 1.0, respectively, yields an equilibrium molar concentration of hydroxyls between 10^{-7} and 10^{-8}. Thus, measurements of the rate of decomposition of alkaline permanganate should provide data from which may be obtained relative concentrations of hydroxyl radical arising from reaction I with various concentrations of reactants and products present.

Experimental

Because the decomposition was found to be heterogeneous, the same Corning glass erlenmeyer flask was used for all measurements. The volume of the flask (500 ml.) was large compared with that of the reaction mixture, allowing the removal of small samples for analysis without appreciable change in surface area in contact with the solution.

C.P. reagents were used. In some experiments the barium hydroxide was "purified" by allowing permanganate to decompose completely in the solution to insoluble barium manganate. The use of solutions purified in this manner yielded data in agreement with solutions not so purified. The sodium manganate solution was prepared by igniting equal weights of manganese dioxide and sodium hydroxide in a nickel crucible. The cake was dissolved in freshly prepared 1 *M* sodium hydroxide, the unreacted manganese dioxide allowed to settle, and the resulting solution analyzed iodometrically.

The procedure used is as follows: The desired quantity of sodium or barium hydroxide solution, sodium nitrate or perchlorate solution to maintain constant ionic strength, and potassium permanganate solution (and in some experiments, sodium manganate solution) were placed in a 50-ml. volumetric flask. After dilution to the mark with water and thorough mixing, the mixture was transferred to a dry Corning glass flask (500 ml.) in a water-bath maintained to ±0.1°. At known times, 2-ml. samples were removed by pipet, and the permanganate present determined.

When barium ion was present in the reacting solution, the samples were carefully removed in such a manner that the precipitated barium manganate was not disturbed. These samples were quenched in an excess of perchloric acid solution and diluted to 10 ml. in a volumetric flask. The extinction of the resultant acid solution was measured at 530 mμ with a Cenco-Sheard Spectrophotelometer. The high permanganate concentrations were determined by the same procedure, after an additional twenty-five-fold dilution.

When no barium ion was present in the solution, 5-ml. samples of the reacting mixture were added to an excess of barium hydroxide solution which had been "purified" as described above, and diluted to 10 ml. with the same solution. After thorough mixing, samples were removed, centrifuged for one minute and 3 ml. of the resulting alkaline solution were treated identically as the samples with barium ion present. The time was recorded uniformly when the reacting solution was added to the barium hydroxide.

Oxygen and nitrogen atmospheres were used interchangeably, the nitrogen being purified by bubbling through alkaline pyrogallol and alkaline permanganate. The oxygen was passed through the alkaline permanganate

---

(7) Compare with the conclusions reached by Gorin, ref. 3.

(8) Libby, This Journal, **62**, 1936 (1940).

(9) Taube and Bray, *ibid.*, **62**, 3357 (1940).

(10) Hill, *ibid.*, **70**, 1306 (1948).

(11) Weiss, *Trans. Faraday Soc.*, **31**, 1547 (1934).

(12) Weiss (ref. 11), has found HO_2 necessary to the explanation of H_2O_2 decomposition; see Walsh, *J. Chem. Soc.*, 331 (1948).

(13) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 43.

only. The experiments were conducted in artificial light (tungsten lamp) and, in part, in complete darkness without effect.

Results

In order to demonstrate whether or not the concentration of products of the decomposition of permanganate affected the rate, the following points had to be studied:

1. Since the reaction was found to be heterogeneous, the surface of the vessel in which the decomposition was run had to be proved to remain constant. It was found that identical rates on identical solutions were obtained after discarding the first ten runs. The experiments were controlled by frequent checking of the surface at one set of concentrations of reactants and products.

2. The reaction, as is common to many similar heterogeneous reactions was found to be nearly zero order in permanganate. This indicated that wide changes in manganate and hydrogen ion concentrations would need to be tested in order to demonstrate the effect of these products on the decomposition rate. In the case of manganate, this could readily be accomplished by adding the latter to obtain a high concentration and by adding barium ion to obtain and maintain a low concentration. It was considered much more important to vary $[\mathrm{MnO_4^=}]$ than to vary $[\mathrm{H^+}]$, since the hydroxyl ion *might* be considered to be a reactant. The relative rates of decomposition of permanganate at constant temperature, ionic strength and hydroxyl ion concentration, and with the manganate ion concentration varying from run to run are shown in Fig. 1. In addition, the effects of variation of permanganate are shown, other substances constant; and effects of variation of hydroxyl ion, again other substances constant.

3. The anion used to maintain constant ionic strength had to be shown to have no direct effect on the rate of the reaction. This was done by interchanging nitrate and perchlorate ions without effect.[14]

4. It had to be demonstrated that oxygen, an end-product, has no effect on the reaction. Experiments run in nitrogen and oxygen atmospheres yielded identical results: 6.0×10^{-4} mole per liter of $\mathrm{MnO_4^-}$ converted to $\mathrm{MnO_4^=}$ in twelve hours, ($\mathrm{Ba(OH)_2} = 0.36\ M$ and $\mathrm{NaNO_3} = 0.42\ M$, original $[\mathrm{MnO_4}]^-$, 2.75×10^{-4} m./l., $T = 46°$).

5. It was necessary to show that manganate is essentially stable with respect to decomposition to manganese dioxide and permanganate for the duration of the experiment, and that manganate is not oxidized to permanganate by oxygen. A 0.72 M sodium hydroxide solution 0.0025 M in $\mathrm{MnO_4^=}$ was maintained at 46° for eighteen hours. At the end of this time, "purified" barium hydroxide solution in excess was added, and the $\mathrm{MnO_4^-}$ determined colorimetrically as described above. The permanganate found was approximately $0.4 \times 10^{-4}\ M$. The precipitated barium manganate was analyzed iodometrically and 0.0020 mole per liter was found.

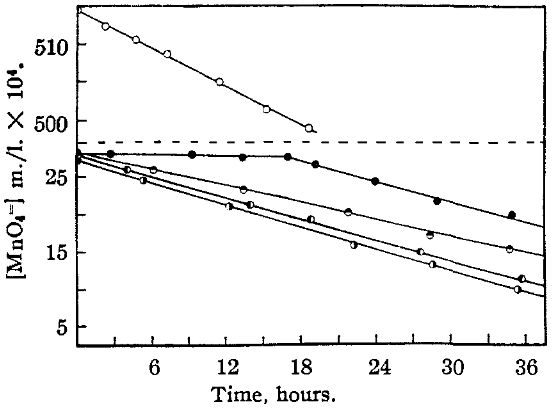

Fig. 1.—The decomposition of alkaline permanganate solutions at 46° ± 0.1°: ○, $[\mathrm{Ba(OH)_2}] = 0.36\ M$, $[\mathrm{NaNO_3}] = 0.42\ M$; ●, $[\mathrm{NaOH}] = 0.72\ M$, $[\mathrm{NaNO_3}] = 0.78\ M$, $[\mathrm{MnO_4^=}] = 0.0025\ M$, $[\mathrm{Ba(OH)_2}]$ equivalent to twice $[\mathrm{MnO_4^-}] + [\mathrm{MnO_4^=}]$ added at the break; ◓, $[\mathrm{Ba(OH)_2}] = 0.036\ M$, $[\mathrm{Ba(NO_3)_2}] = 0.32\ M$, $[\mathrm{NaNO_3}] = 0.42\ M$; ◐, $[\mathrm{Ba(OH)_2}] = 0.36\ M$, $[\mathrm{NaNO_3}] = 0.42\ M$; ◑, $[\mathrm{Ba(OH)_2}] = 0.36\ M$, $[\mathrm{NaClO_4}] = 0.42\ M$.

6. It was necessary to demonstrate whether or not precipitated barium manganate affects the rate of the reaction. A solution 0.42 M in sodium nitrate, 0.36 M in barium hydroxide, 2.8×10^{-3} M in $\mathrm{MnO_4^-}$ containing approximately 1 g. of freshly precipitated barium manganate decomposed at the same rate as the solutions to which no barium manganate had been added: 6.0×10^{-4} mole per liter of $\mathrm{MnO_4^-}$ was converted to $\mathrm{MnO_4^=}$ in twelve hours.

Discussion

The results shown graphically in Fig. 1 demonstrate clearly that the concentration of products of the decomposition of permanganate markedly affect the rate of the reaction. The only possible interpretation of the data is that a reversible reaction is involved in the process. The fact that oxygen has no effect on the rate eliminates one possible substance from the role of oxidant of the manganate; this leaves the hydroxyl radical as the most likely intermediate and points directly to the equilibrium expressed in equation I.

Another set of alternatives must be considered; the equilibrium may take place only at the surface on which the hydroxyl radicals are found to combine, or the hydroxyls may be formed in solution and combine on the surface with a much lower activation energy than the homogeneous reaction permits. There are no data in the present study to distinguish either of the alternatives. If, however, the hydrated permanganate ion can produce hydroxyl radicals on a surface, it is reasonable to

---

[14] Taube (ref. 9) has shown that nitrate and perchlorate ions have different effects on the rate of reaction of ozone with hydrogen peroxide. This was done in acid solution, under which condition hydroxyl radicals are much more reactive than they are in alkaline solution: $\mathrm{HO} + \mathrm{H^+} + e \rightarrow \mathrm{H_2O}$.

believe that the former can donate hydroxyl radicals to a reducing agent, and that alkaline permanganate solution reacts essentially as a very dilute solution of hydroxyl radicals; this view provides a simple explanation for the oxygenating action of the permanganate-to-manganate reaction, for example, sulfite to sulfate, as well as the rapid exchange of manganate and permanganate.[8] The investigation of these reactions is continuing.

Summary

The decomposition of alkaline permanganate to manganate has been shown to involve an equilibrium reaction in one of its steps

$$\text{I}\quad MnO_4^- + H_2O \rightleftarrows MnO_4^{=} + HO + H^+$$

The slow step in the decomposition is taken to be the combination of the hydroxyl radicals. The equilibrium nature of reaction I was proved by carefully controlled experiments which demonstrated that the presence of products of reaction I affected the rate of the decomposition.

The data do not allow a decision on whether equilibrium I is homogeneous or heterogeneous, but in either case it is likely that a reducing agent, particularly a negatively-charged one, is oxidized through the agency of the hydroxyl radical.

EAST LANSING, MICHIGAN RECEIVED JUNE 17, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

Solubility of Iodine in 1,2- and 1,1-Dichloroethanes, *cis*- and *trans*-Dichloroethylenes and Perfluoro-*n*-heptane

BY H. A. BENESI* AND J. H. HILDEBRAND

Solutions of iodine offer unusually valuable tests of the theory of solution of non-electrolytes by reason of the reliability of the analytical procedure used, the distinction between "chemical" and "physical" effects afforded by color, and the high London forces of iodine molecules, giving a wide spread in its solubilities in ordinary solvents. These solutions have been discussed by the senior author and collaborators in a series of papers.[1] The solubility curves, plotted as log x_2 *vs.* $1/T$, where x_2 is the mole fraction of iodine, fall into two types, corresponding to color, those of the violet solutions obviously belonging to a family. This suggested the now familiar designation of such solutions as "regular." The curves for the red, yellow and brown solutions, on the other hand, all have smaller and individual slopes and all the evidence points to varying degrees of solvent–solute interaction.

Solutions in ethylene bromide (1,2-dibromoethane) seemed to straddle the above distinctions; they are pure violet in color but, like the curve for the red solutions in benzene, the solubility curve has a slightly smaller slope than the one that was drawn through the adjacent experimental points for carbon disulfide. This investigation was undertaken, in part, in order to throw light upon the reason for the apparent discrepancy. It is now well known that the dipole moments of 1,2-dichloro- and dibromoethanes[2,3,4] vary with temperature and, when in solution, with the solvent used, due possibly to shifts in the relative amounts of *cis*- and *trans*-configurations, and it was thought that perhaps the interaction of the two forms with iodine might be different and hence cause an anomalous temperature coefficient of solubility. In order to magnify such a possible difference, chlorides were selected rather than bromides, and we decided to compare the solubility of iodine in (a) 1,2-dichloro- and 1,1-dichloroethanes, and (b) *cis*- and *trans*-1,2-dichloroethylenes. A preliminary report of the solubility of iodine in normal perfluoroheptane which was made for another purpose is included in this communication.

Materials and Purification

Reagent grade iodine by General Chemical Company was used without further treatment.

Ethylene chloride (1,2-dichloroethane) by Eastman Kodak Company showed a negative test for chloride ion and was carefully distilled through a 15-plate fractionating column. The first and last portions were discarded and the middle portion, boiling at 83.0–83.1° at 752 mm., was collected and stored in a dry, glass-stoppered flask. After all solubility measurements had been carried out, the remaining ethylene chloride still showed a negative test for chloride ion.

cis- and *trans*-1,2-dichloroethylene (acetylene dichlorides) were prepared by fractionally distilling 500 cc. of the commercially prepared mixture of the isomers through a 30-plate fractionating column at a reflux ratio of 30:1. The original mixture showed a negative test for chloride ion. Two fractions were obtained boiling at 60.0–60.2 and 47.7–48.0° at 755 mm. The low boiling *trans*-isomer decomposed and gave a positive test for chloride ion upon standing. This isomer was therefore shaken with sodium carbonate solution, washed with distilled water, dried over "Drierite" and redistilled just before using. After the solubility measurements were made, both the *cis*- and *trans*-isomers were recovered and redistilled. The boiling points had not changed; therefore no appreciable isomerization had occurred.

A sample of pure perfluoro-*n*-heptane which we had in the laboratory was distilled and boiled at 81.9–82.0°.

Ethylidene chloride (1,1-dichloroethane) from Eastman

---

* American Chemical Society Postdoctoral Fellow, 1947–1948.

(1) (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL **42**, 2180 (1920); (b) J. H. Hildebrand, *ibid.*, **51**, 66 (1929); (c) G. R. Negishi, L. H. Donally and J. H. Hildebrand, *ibid.*, **55**, 4793 (1933); (d) J. H. Hildebrand, *ibid.*, **57**, 866 (1935); (e) *ibid.*, **59**, 2083 (1937); (f) *Science*, **90**, 1 (1939); (g) J. H. Hildebrand, "Solubility of Non-Electrolytes," 2nd Ed., Reinhold, New York, N. Y., 1936, pp. 153–157.

(2) G. I. Bloom and L. E. Sutton, *J. Chem. Soc.*, 727 (1941).

(3) C. T. Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932).

(4) L. Onsager, **58**, 1486 (1936).