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Rate of the Manganate-Permanganate Exchange by Pulsed Nuclear Magnetic Resonance^{1a}

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The electron-exchange between MnO_4^{2-} and MnO_4^- is investigated by measurements of relaxation times T_1 and T_2 , using spin-echo techniques. The results are in agreement with the results of isotopic-tracer techniques as to the value of the rate constant k and the kinetic order of the exchange.

The electron-exchange between MnO_4^{2-} and MnO_4^- has been measured by Sheppard and Wahl with the isotopic-tracer technique.² The reaction was found to follow second order kinetics and to be first order with respect to either MnO_4^{2-} or MnO_4^- . The rate was found to increase with increasing electrolyte concentration and to depend on the specific cations present.

Electron-exchange reactions may be studied also by the techniques of nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.). The e.s.r. spectrum of MnO_4^{2-} has been investigated but was found to be unresolvable in liquid solution.³ The continuous-wave n.m.r. spectrum of MnO_4^- shows a singlet absorption peak. Since one singlet absorption peak is observed, the system is suitable for study by pulsed n.m.r. as well as continuous-wave (c.w.) n.m.r. The measurement of relaxation times by pulsed n.m.r. has certain experimental advantages over the line-broadening technique of c.w. n.m.r. No corrections for radio frequency power saturation and over-modulation are necessary, as the r.f. oscillator is not in operation during the period of measurement. Magnetic field inhomogeneities, which may broaden absorption peaks by the c.w. n.m.r. method, have no effect on the pulsed n.m.r. measurements (in the absence of appreciable diffusion). Lastly, the pulsed n.m.r. technique measures T_1 far more accurately and conveniently than does the c.w. n.m.r. technique.

T_1 and T_2 were measured by the pulsed n.m.r. technique for a series of MnO_4^{2-} and MnO_4^- mixtures of accurately known composition. Relationships between relaxation time and composition enabled the evaluation of the rate constant k . Independent variation of either the MnO_4^- concentration or the MnO_4^{2-} concentration afforded information as to the kinetics of the exchange.

Experimental

Materials.—Concentrated solutions of NaMnO_4 were prepared by dissolving C.P. $\text{NaMnO}_4 \cdot 3\text{H}_2\text{O}$ and filtering through asbestos mats. Concentrated solutions of Na_2MnO_4 were prepared by boiling solutions of concentrated NaMnO_4 in 5*f* NaOH until a complete conversion of MnO_4^{2-}

(pink) to MnO_4^- (green) was observed and filtration of the resulting suspension through asbestos mats. Solutions of Na_2MnO_4 tagged with Mn^{54} were prepared by air oxidation of tagged MnO_2 in a molten NaOH flux, dissolution of the cooled melt in water and removal of the excess MnO_2 by filtration through asbestos mats. Concentrations of either NaMnO_4 or Na_2MnO_4 were determined by reaction with excess $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and titration of the excess with standardized KMnO_4 . All other reagents were commercial chemicals of analytical grade.

Procedure.—Solutions for pulsed n.m.r. studies were prepared at 0° in the dark by accurate dilution of aliquots of concentrated stock solutions. Immediately prior to the pulsed n.m.r. measurements, the solutions were either ultracentrifuged at 20,000 r.p.m. for one hour or filtered through 450 μ millipore filters.

Aliquots of the solutions were diluted accurately and the concentrations in the resulting solutions spectrophotometrically determined by their absorption at 564 and 615 μ . Concentrations were obtained from formulas derived from the respective extinction coefficients, under the assumption of additive optical densities.

$$D_{564} = 1.37 \times 10^3 [\text{MnO}_4^-] + 1.15 \times 10^3 [\text{MnO}_4^{2-}] \quad (1)$$

$$D_{615} = 2.0 \times 10^2 [\text{MnO}_4^-] + 1.50 \times 10^3 [\text{MnO}_4^{2-}] \quad (2)$$

$$[\text{MnO}_4^-] = \frac{D_{564} - 0.767 D_{615}}{1.21 \times 10^3} \quad (3)$$

$$[\text{MnO}_4^{2-}] = \frac{D_{615} - 0.145 D_{564}}{1.33 \times 10^3} \quad (4)$$

D_λ = measured optical density at wave length λ

Spectrophotometrically determined concentrations were compared with the total oxidizing capacity of many solutions. Measured and calculated total oxidizing capacities agreed to ± 2 to 3%, on the average, for more than 50 solutions; the maximum discrepancy was 6%.

T_2 was evaluated by a sequence of one 90° pulse, followed by a series of 180° pulses. T_1 was evaluated by a 180-90° pulse sequence. The two techniques have been described.⁴

Results and Discussion

The results of the experiment are listed in Table I. The rate constant k was evaluated graphically

TABLE I
Temperature = 0°, $\mu = 1.06$ (except the neutral solution)

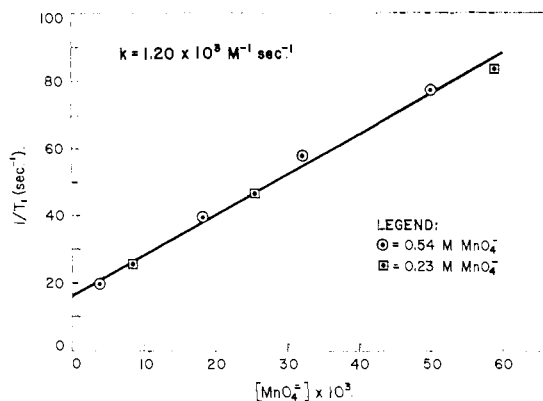
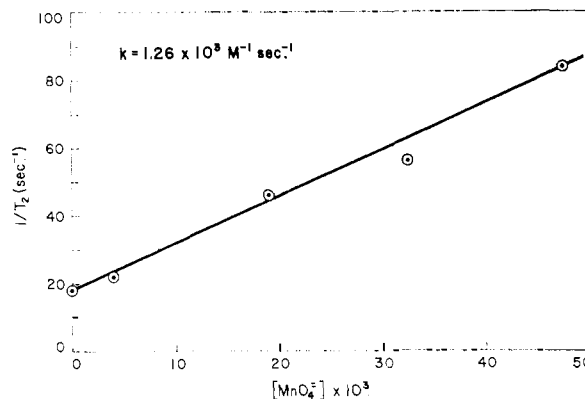
MnO_4^-	Concentration in gram ions/liter			Na^+	Characteristic time in msec.		
	MnO_4^{2-}	OH^-	SO_4^{2-}		T_1	T_2	
0.554	0	10^{-7}	0.577	0	..	56	
.547	4.3×10^{-3}	0.30	1.00	0.063	46	47	
.531	1.86×10^{-2}	.30	1.00	.047	25	22	
.549	3.30×10^{-2}	.30	1.00	.033	17	17	
.543	4.88×10^{-2}	.30	1.00	.017	13	12	
.228	8.3×10^{-3}	.68	1.00	.063	39	..	
.234	2.46×10^{-2}	.68	1.00	.047	22	..	
.226	5.82×10^{-2}	.68	1.00	.017	12	..	

(4) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(1) (a) Taken in part from a thesis submitted by A. D. Britt in partial fulfillment of the requirements for the degree of Master of Arts at Washington University, June 1961. This work was supported by research grants from the National Science Foundation and the Office of Scientific Research, United States Air Force. (b) Ohio Oil Fellow 1959-1960.

(2) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).

(3) S. I. Weissman, private communication. The e.s.r. spectrum of MnO_4^{2-} in mixed crystals has been obtained by A. Carrington, D. J. E. Ingram, K. A. K. Lott, D. S. Schonland and M. C. R. Symons, *Proc. Roy. Soc. (London)*, **A254**, 101 (1960).

Fig. 1.— T_1 data.Fig. 2.— T_2 data.

(Figs. 1 and 2) by the relationships

$$\left(\frac{1}{T_2}\right)_m = \left(\frac{1}{T_2}\right)_1 + k [\text{MnO}_4^{2-}] \quad (5)$$

$$(T_2)_m = (T_1)_m \text{ (experimentally)}$$

$$\left(\frac{1}{T_1}\right)_m = \text{constant} + k [\text{MnO}_4^{2-}] \quad (6)$$

$(T_2)_m$ = measured T_2 value in the presence of electron-exchange

$(T_1)_m$ = measured T_1 value in the presence of electron-exchange

$(T_2)_1$ = measured T_2 value at zero MnO_4^{2-} concentration

$[\text{MnO}_4^{2-}]$ = concentration of MnO_4^{2-} in g. ions/liter

k = rate constant of the $\text{MnO}_4^{2-} - \text{MnO}_4^-$ electron-exchange

Sheppard and Wahl obtained a value of $k = 1.70 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ for a similar system using the isotopic-tracer technique.² A repetition of their experiment was performed at MnO_4^- concentrations higher by a factor of 50 and MnO_4^{2-} concentrations higher by a factor of 10. The value of $k = 1.70 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ was obtained at these higher concentrations, confirming the applicability of the second order rate equation ($R = k [\text{MnO}_4^{2-}][\text{MnO}_4^-]$) over a large range of MnO_4^{2-} and MnO_4^- concentrations.

On the basis of an approximate calculation of the errors involved in the pulsed n.m.r. measurements, the standard deviation of the rate constant k is $\pm 20\%$. An error calculation for the isotopic-tracer experiments gives a standard deviation of the rate constant k of $\pm 13\%$.

$$k_{\text{n.m.r.}} = (1.23 \pm 0.25) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$$

$$k_{\text{i-t}} = (1.70 \pm 0.22) \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$$

Conclusion.—It was not possible to make measurements on a system both by the n.m.r. technique and by the isotopic-tracer method. Solutions which were dilute enough to be studied by isotopic-exchange gave undetectable resonance signals. However, it was possible to compare similar systems in which the temperature, type and concentration of positive ion and the ionic strength were the same, although the MnO_4^- concentration differed by a factor of 200–500 and the MnO_4^{2-} concentration by a factor of 20–50. The comparison of the results obtained by the two techniques then involves the assumption that the second-order rate law applies over the large variation in reactant concentrations.

The experimental results tend to validate this assumption in two ways. First, an increase by a factor of 50 in total reactant concentration ($\text{MnO}_4^- + \text{MnO}_4^{2-}$) in the low concentration range caused no change in the rate constant k as measured by isotopic-exchange. Secondly, in the high concentration range, the first-order dependence of the reciprocal of T_1 or T_2 on the MnO_4^{2-} concentration, together with lack of dependence on the MnO_4^- concentration, offers strong indication that the rate is first-order with respect to MnO_4^{2-} and to MnO_4^- .

The values of the rate constant k obtained by the two methods are different by about 30%, which is about the experimental uncertainty. Therefore, the conclusion is drawn that, within the experimental uncertainty of $\sim 30\%$, the specific rates measured by the n.m.r. and isotopic-tracer method are the same.

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