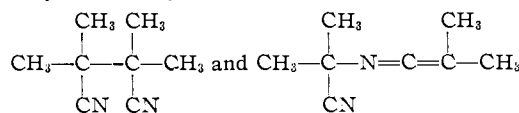tively mild brominating agent and is used to replace hydrogen atoms of the allylic type. The displacement takes place mainly on the carbon α to the cyano group, as expected from resonance considerations.
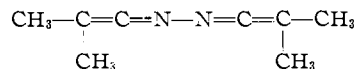
Experimental evidence has been obtained for the existence of a hybrid form for the cyanoisopropyl radical. In addition to the work of Talât-Erben and co-workers[12] mentioned above, Smith, et al.,[17] have recently identified two individual dimers of this radical as products in the thermal

(17) P. Smith and A. M. Rosenberg, J. Am. Chem. Soc., **81**, 2037 (1959); P. Smith and S. Carbone, ibid., **81**, 6174 (1959).

and photochemical decomposition of AIBN. The two dimers are tetramethyl succinonitrile and dimethyl-N-(2 cyano-2 propyl)-keteneimine

$$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \text{ and } CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=C=\overset{\overset{CH_3}{|}}{C}-CH_3$$

The third possible dimer, a diimine, was not observed, presumably because of thermal instability.

$$CH_3-\overset{\overset{}{}}{C}=C=N-N=C=\overset{\overset{}{}}{C}-CH_3$$
$$\qquad | \qquad\qquad\qquad |$$
$$\qquad CH_3 \qquad\qquad\qquad CH_3$$

The Kinetics of the Manganate–Permanganate Exchange by N.m.r.

BY ORLO E. MYERS AND JOHN C. SHEPPARD

The kinetics of the manganate–permanganate exchange reaction have been measured by the n.m.r. line broadening technique developed by McConnell and Weaver. The results indicate that in $1f$ potassium and sodium ion the reaction is first order with respect to each reactant. An activation energy of 8.3 kcal./mole was found in potassium ion system. These data are consistent with the results found from the tracer study of Sheppard and Wahl.

The kinetics of the manganate–permanganate exchange reaction have been studied extensively by tracer techniques[1] and found to be first order with respect to both manganate and permanganate ion concentrations. The rate was found to depend upon the nature (perhaps size) of the base cation present but was unaffected by the addition of other anions. Most of the work was done near 0° and at small reactant concentrations because of the speed of the reaction. Exchange half-times in the range 0.24–12.0 sec. were observed. McConnell and Weaver[2] developed the n.m.r. line broadening technique for the measurement of very rapid reactions and studied the rate of electron transfer between copper(I) and copper(II) ions in concentrated hydrochloric acid. A specific rate constant of $5 \times 10^7 f^{-1}\mathrm{sec.}^{-1}$ was observed. Giuliano and McConnell[3] studied the vanadium(IV)-vanadium(V) reaction in hydrochloric–perchloric acid mixtures by the same technique and found the specific rate constant for this reaction to be $1.5 \times 10^6 f^{-2}\mathrm{sec}^{-1}$. Both reactions are too rapid to be measured by even the most sophisticated tracer technique available at present.[4] It would be desirable to study a reaction where it would be possible to compare the n.m.r. method with the tracer technique. The manganate–permanganate exchange reaction appears to be the experimentally accessible reaction because it is rapid. In addition, manganese-55 possesses the desirable quality, for the purpose of measuring this reaction,

(1) J. C. Sheppard and A. C. Wahl, J. Am. Chem. Soc., **79**, 1020 (1957).
(2) H. M. McConnell and H. E. Weaver, J. Chem. Phys., **25**, 307 (1956).
(3) C. R. Giuliano and H. M. McConnell, J. Inorg. and Nuclear Chem., **9**, 171 (1959).
(4) B. M. Gordon and A. C. Wahl, J. Am. Chem. Soc., **80**, 273 (1958)

of high n.m.r. sensitivity as well as pure isotopic abundance.

The present investigation was undertaken to study the manganate-permanganate system using n.m.r. techniques for the purpose of comparison with and extension of the results of tracer studies as well as to verify the application of the n.m.r. method to chemical kinetic problems.

The observed width of the Mn-55 line of permanganate ion in sodium or potassium hydroxide solutions is about 20 millioersted (derivative peak-to-peak, corrected for modulation amplitude, modulation frequency, saturation and estimated field inhomogeneities in the Varian V-4012A 12-in. electromagnet[5,6]) and corresponds to a "natural" transverse relaxation time of $T_2 \approx 8$ milliseconds according to the equation

$$1/T_2 = 0.866\gamma\Delta H \qquad (1)$$

The paramagnetic manganate ion yields no observable nuclear resonance. The interaction between the nucleus and the unpaired electron of manganate ion shortens T_2 to such an extent that the line width must be many thousands of oersteds. The "electron-transfer" process

$$\overset{*}{Mn}O_4^- + MnO_4^{=} = \overset{*}{Mn}O_4^{=} + MnO_4^-$$
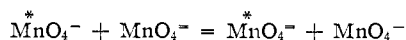
will, therefore, introduce an additional mechanism to the "natural" transverse relaxation. Using the approximation that the life expectancy of a magnetic state after an exchange event is zero, McConnell's treatment[2,7] reduces to

$$\frac{1}{t_2} = \frac{1}{T_2} + \frac{1}{\tau} \qquad (2)$$

(5) O. E. Myers and E. J. Putzer, J. Applied Phys., **30**, 1987 (1959).
(6) O. E. Myers, Bull. Am. Phys. Soc., **5**, 242 (1960).
(7) H. M. McConnell, J. Chem. Phys., **28**, 430 (1958).

t_2 = observed transverse relaxation time in the presence of MnO_4^-

T_2 = transverse relaxation time at zero MnO_4^- concentration

τ = average lifetime of MnO_4^- between exchange events

The natural lifetime of permanganate ion is relatively long and chemical lifetimes as long as 50 mseconds should be observable in the presence of "natural" relaxation because the permanganate ion nucleus is well insulated from quadrupolar interactions with the solvent by its tetrahedrally arranged oxygens.
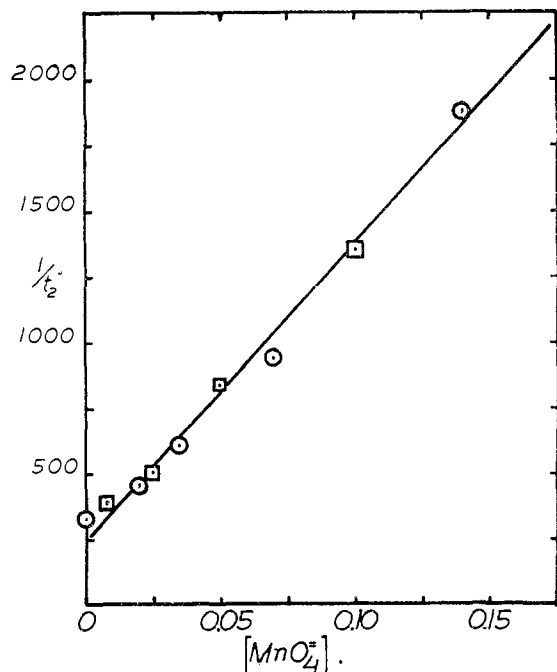

Fig. 1.—A plot of $1/T_2$ against manganate ion concentration at a total potassium ion concentration of 1.0 f and at 30°: $\square$ and $\odot$ indicate permanganate concentrations of 0.34 and 0.15f, respectively. The slope of these lines gives a specific rate constant of 1.43 $\times$ $10^4 f^{-1}$ sec.$^{-1}$.

The exchange rate R is the number of exchange events per unit time, so that if the reaction is bimolecular the following expression would be applicable

$$R = \frac{\pm\, d[MnO_4^-]}{dt} = k[MnO_4^-][[MnO_4^=] \quad (3)$$

The brackets denote formal concentrations and k is a formal specific rate constant at a given temperature. The average lifetime τ of MnO_4^- ion, then is given by

$$\tau = [MnO_4^-]/\frac{d[MnO_4^-]}{dt} \quad (4)$$

and it follows that

$$1/\tau = k[MnO_4^=] \quad (5)$$

equation 2 now has the form

$$\frac{1}{\tau_2} = \frac{1}{T_2} + k[MnO_4^=] \quad (6)$$

A graph of $1/t_2$ as ordinate and $[MnO_4^=]$ as abscissa should be a straight line with a slope corresponding to the specific rate constant k and intercept $1/T_2$. The data reported in this research were analyzed accordingly.
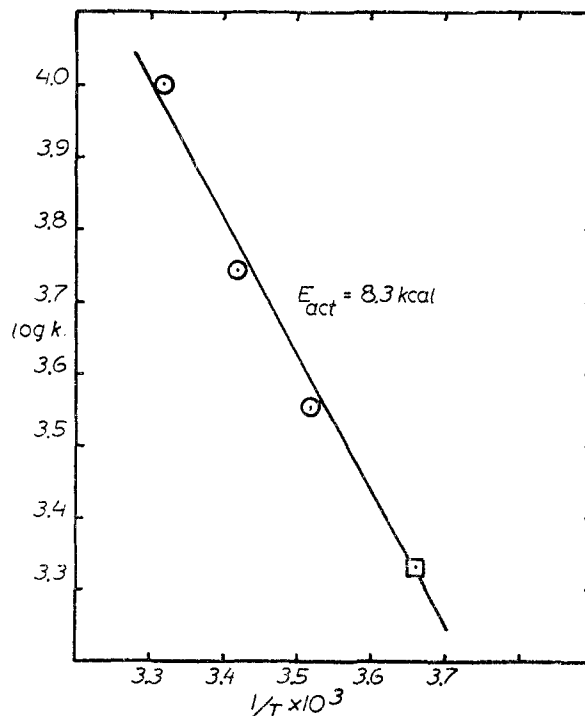

Fig. 2.—An Arrhenius plot of log k against the reciprocal of the absolute temperature, yielding an activation energy of 8.3 kcal./formula: $\odot$, n.m.r. points obtained from this research and $\square$, a point taken from the tracer study of Sheppard and Wahl.

Experimental

Preparation of Solutions and Analytical Method.—Insofar as practicable, the reagents were prepared in the same way as had been done for the tracer work.[1]   Reaction mixtures were prepared by addition of standardized manganate ion in 1.00f sodium or potassium hydroxide to standardized sodium or potassium permanganage solutions, followed by addition of standardized sodium or potassium hydroxide solution to adjust the positive ion concentration to the desired value.   The fact that the n.m.r. results were the same for solutions prepared at 0° or at room temperature was taken as evidence for stability of the manganate and permanganate ion in these experiments.   At room temperature the resonance did become noticeably broader over a period of several days but not rapidly enough to affect results from the freshly prepared solutions used.

Manganate and permanganate concentrations were determined by pipetting an aliquot of either of these ions into a known volume of standardized arsenous acid.   The excess arsenous was then titrated with standard ceric sulfate with osmium tetroxide (catalyst) and ferrous phenanthroline indicator.   As a further check of potassium manganate purity, it was analyzed spectrophotometrically and was found to contain 92% manganate and 8% permanganate.

Experimental, N.m.r. The solutions were stoppered, or sealed in 5 ml. test tubes, immersed in the thermostat assembly and then placed in the 4–8 mc. probe of the Varian V-4200B spectrometer.   All observations were made at 8.0 mc. and checked at 4.0 mc.   The frequency was monitored by a Hewlett–Packard 524B electronic counter.   Drift during a given run was uniformly less than 5 c.p.s. per minute.   A gyromagnetic ratio value of γ = 6319.6/sec. oersted for manganese-55 was used and obtained by comparison with sodium-23 whose gyromagnetic ratio was taken as 7076.1/sec. oersted.

The trace for each sample was recorded at least three times with both up and down field scanning to minimize errors from magnet and oscillator drift.   Corrections were then applied for broadening caused by finite sweep amplitude and frequency and for finite ratio frequency power level. Sweep amplitude was calibrated by vacuum tube voltmeter

TABLE I

Cation concn., f K^+	[MnO$_4$$^-$], f	[MnO$_4$$^-$], f	Temp., °C.	$\frac{10^{-3} k,}{f^{-1} \text{sec.}^{-1}}$
1.00	0.34	0.007–0.14	30 ± 0.6	14.3 ± 0.7
1.00	.15	.007– .14	30 ± .6	14.3 ± .7
0.57	.15	.012– .10	30 ± .3	10.2 ± .4
.57	.15	.020– .20	29.6 ± .6	9.8 ± .4
.57	.15	.020– .20	20.0 ± .5	5.6 ± .6
.57	.15	.020– .20	12.1 ± .4	3.6 ± .5
Na$^+$				
1.13	.31	.150– .35	30.7 ± .6	9.9 ± 1.0
1.13	.31	.150– .35	6.3 ± .4	3.0 ± 0.5

measurement, as corrected by a conversion factor obtained through use of a frequency counter. The H_i field was measured by probe current which was calibrated by fitting it to a normalized and corrected derivative saturation curve. Uncertainties indicated in the graphs are based on the average of the several determinations.

Results and Discussion

At each positive ion concentration, graphs of $1/t_2$ against the manganate ion concentration are straight lines within experimental error. Rate constants calculated from slopes of these lines are listed in Table I. Figure 1 is a plot of $1/t_2$ against the manganate ion concentration for two different permanganate ion concentrations in $1f$ total potassium ion solutions showing that the two curves are superimposed, so the present observations agree with the rate dependence on the reactants found by the tracer technique for the sodium hydroxide system. They are consistent with the assumption that the reaction is first order with respect to the manganate and permanganate ion concentrations, respectively. An activation energy of the reaction in $0.6f$ potassium hydroxide is 8.3 kcal./mole. This was calculated from an Arrhenius plot (Fig. 2). The 30, 20 and 12° points represent n.m.r. experiments while the 0° point is from the tracer data. These data are consistent also with salt effects found by Sheppard and Wahl.[1] Using the tracer data the extrapolated rate constant in $1f$ potassium hydroxide at 0°, assuming the linear salt effect, is $3550f^{-1}$ sec.$^{-1}$. Assuming an activation energy of 8.3 kcal./formula and using the n.m.r. data at 30°, the calculated rate constant is $3100f^{-1}$sec.$^{-1}$ at 0°. Using the 10.5 kcal./mole activation energy found in the tracer experiments and the n.m.r. data at 30°, the calculated rate constant for this reaction at 0° in $1f$ sodium ion concentration is $1500f^{-1}$sec.$^{-1}$ compared to $1700f^{-1}$sec.$^{-1}$ found in the tracer experiments. The two methods are in good agreement, and the observed discrepancies may be attributed to differences in sodium or potassium manganate purity or the method of analysis used.

[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

The Catalytic Effect of Chloride Ions on the Isotopic Oxygen Exchange of Nitric and Bromic Acids with Water

BY M. ANBAR AND S. GUTTMANN

The kinetics of the isotopic exchange of oxygen between nitric acid and water were investigated in the concentration range 1 to 7 M HNO$_3$, in the presence of chloride ions, at 60 and 100°. The rate of exchange was found to obey the rate law $R = [HNO_3]_f[H_3O^+](k_1 + k_2[Cl^-])$ where $[HNO_3]_f$ is the concentration of undissociated nitric acid; $k_1 = 4.8 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$, $k_2 = 3.2 \times 10^{-1}$ l.^{2} mole^{-2} min.$^{-1}$ at 100°. The energies of activation of the two processes are comparable, 22.1 and 21.8 kcal./mole, respectively. The isotopic exchange of oxygen between bromate ions and water in acid solutions which was investigated between $pH = 1.0$ to 2.25, in the temperature range 0–60°, showed a similar behavior $R = [BrO_3^-][H_3O^+]^2(k_1 + k_2[Cl^-])$; $k_1 = 5.6 \times 10^{-1}$ l.^{2} mole^{-2} min.$^{-1}$; $k_2 = 3.6 \times 10^{11}$ l.^{3} mole^{-3} min.$^{-1}$ at 30°; $E_1 = 14.6$ kcal./mole, $E_2 = 13.9$ kcal./mole. A bimolecular nucleophilic attack of chloride ions and of water molecules on the conjugate acids H$_2$NO$_3$$^+$ and H$_2$BrO$_3$$^+$ is suggested.

The isotopic exchange of oxygen between nitric acid and water has been investigated extensively in concentrated nitric acid solutions[1] at 0°. It was suggested that the rate determining step of the exchange reaction is the rate of dehydration of H$_2$NO$_3$$^+$ and the formation of the NO$_2$$^+$ ions.[2] The kinetic study of the exchange reactions of bromate[3] and chlorate[4] ions showed a second order dependence on hydronium ion concentration and an increased rate of exchange in D$_2$O solutions; these results

implied the participation of H$_2$BrO$_3$$^+$ and H$_2$ClO$_3$$^+$ as intermediates. Hoering suggests that the rate-determining step in the bromate and chlorate reactions is a nucleophilic attack of a water molecule on the conjugate acids. This assumption is based on the analogy with reactions of the halic acids with halide ions as demonstrated by the empirical equations proposed by Edwards.[5] There is however, no experimental proof that the rate determining step in the oxygen exchange reaction is really a bimolecular nucleophilic attack (Sn2) and not a monomolecular process. The same ambiguity was previously encountered in similar isotopic exchange reactions such as the exchange of nitrite ions with water[6] or the uncatalyzed path in the

(1) C. A. Bunton, E. H. Halevi and D. R. Llewellyn, *J. Chem. Soc.,* 4913 (1952).

(2) C. A. Bunton and E. A. Halevi, *ibid.,* 4917 (1952).

(3) T. C. Hoering, R. C. Butler and H. O. McDonald, *J. Am. Chem. Soc.,* **78,** 4829 (1956).

(4) T. C. Hoering, F. T. Ishimore and H. O. McDonald, *ibid.,* **80,** 3876 (1958).

(5) J. O. Edwards, *ibid.,* **76,** 1540 (1954).