flux through the alloy core. The 4500-turn solenoids are alternately energized with direct current by means of a Microswitch operating off an adjustable speed cam. The check valves are constructed of 6 mm × 2 mm quartz discs hand-polished to the end of lengths of 6-mm capillary tubing. This simple valve provides an amazing seal, the total leakage for the four valves being less than 3% of the pump output at 100 Torr pressure differential.

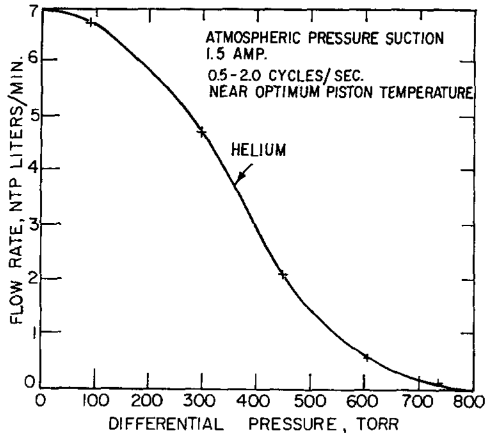

FIG. 2. Pump characteristic curve.

The pump characteristic curves, Fig. 2, indicate that the pump delivers more than ample pressure differential. A pump constructed from this design has been used for kinetic studies and has provided maintenance-free operation, except for several Microswitch changes, over more than 500 hr of operation without loss of capacity. Not only is the pump maintenance-free, but it is also quite versatile. It is capable of operating under pressure or vacuum conditions and, with adjustment of piston rings, can be operated up to the degradation temperature of Teflon.

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REFERENCES

1. TEMKIN, M. I., *Kinetika i Kataliz* **3**, 509 (1962).
2. TEMKIN, M. I., KIPERMAN, S. L., AND LUKYANOVA, L. I., *Doklady Akad. Nauk. SSSR* **74**, 763 (1950).
3. FUNNEL, W. S., AND HOOVER, G. I., *J. Phys. Chem.* **31**, 1099 (1927).
4. BENNETT, W. R., *Rev. Sci. Instr.* **28**, 1092 (1957).
5. STERNER, C. J., *Rev. Sci. Instr.* **31**, 1159 (1960).
6. SCALA, L. C., HICKAM, W. M., AND LANGER, A., *Rev. Sci. Instr.* **29**, 988 (1958).
7. ARTYUKH, YU. N., AND NIKOLENKO, A. F., *Kinetika i Kataliz* **1**, 620 (1960).

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Oxidation of Mn^{II} Acetate by Alkylperoxy Radicals

The catalytic effect of heavy metal ions such as those of Mn and Co often depends on their efficiency in generating free radical species from hydroperoxides, both in the lower and in the higher valency stage. The present communication deals with a case where both stages are relatively inert towards hydroperoxide. It is shown that Mn^{II} acetate is readily oxidized directly by alkylperoxy radicals to form Mn^{III} acetate. This direct oxidation has been postulated [e.g., ref. (*1*)] but not, to our knowledge, unequivocally demonstrated.

Cyanoisopropyl radicals (R·) were generated by thermolysis of azoisobutyronitrile (AIBN) in glacial acetic acid solution. In the presence of oxygen, R· rapidly adds on oxygen to form the corresponding alkylperoxy fragments ROO· (*2*). Oxidation of Mn^{II} acetate by these fragments probably occurs as follows:

$$ROO\cdot + Mn^{II} \rightarrow Mn^{III} + ROO^- \qquad (1)$$

Runs were carried out at temperatures ranging from 60° to 90°C, using 5–30 mmoles of Mn^{II} acetate and 5–15 mmoles of AIBN per liter. Oxygen was introduced with rapid stirring. The characteristic red-brown color of Mn^{III} acetate developed immediately; formation of Mn^{III} was followed spectrophotometrically, using the absorption band at 462 mμ. In the absence of oxygen, no manganic acetate was formed.

Rates appeared to be first order with respect to AIBN and independent of the Mn^{II} acetate concentrations as long as this was present in excess. Iodometric titrations at various intervals revealed that in addition in Mn^{III}, *two* further oxidimetric equivalents were simultaneously formed. Since *tert*-butylhydroperoxide was found to be stable under our reaction conditions, whereas hydrogen peroxide was rapidly decomposed, the two additional oxidimetric equivalents were assumed to be due to formation of a hydroperoxide as in (1). Deviations from the above simple behavior began to arise, however, after about 5 mmoles of hydroperoxide had been formed in the system.

Rate constants for Mn^{III} formation (Table 1) were close to those calculated on the basis of formation of 1.2 *free* radicals per molecule of AIBN, using the efficiency factor of 0.6 observed by Blanchard (*3*) for free radical formation from AIBN in glacial acetic acid at 60°C. The same factor was used by us at temperatures of 70–90°C, since the cage effect should not be strongly temperature-dependent.

The agreement between the rate constants given in the last two columns is so close as to warrant the conclusion that the oxidation of Mn^{II} is a highly efficient process, i.e., that Mn^{II} acetate is a very effective scavenger. Since no Mn^{III} is formed in the absence of oxygen, Reaction (1) would seem to be the most plausible interpretation of the present data. It may be noted that this reaction constitutes the *reverse* of the oxidation of hydroperoxide anions by Mn^{III}. Secondary reactions between hydroperoxide and Mn^{II} or Mn^{III} should lead to deviations from the stoichiometry observed, according to which *one* free radical R· corresponds to *one* Mn^{III} and *two* additional oxidimetric equivalents.

TABLE 1

RATE CONSTANTS (10^6 SEC^{-1}) FOR FORMATION OF Mn^{III} COMPARED WITH THOSE FOR DECOMPOSITION OF AIBN(k_d)

Temperature (°C)	$k_{Mn^{III}}$ (obs.)	$k_{Mn^{III}}{}^a$ (corr.)	$k_d{}^b$
60°	10.6	8.8	9.15
70°	40	33.3	41.6
80°	177	148	153
90°	612	510	500

[a] Corrected values for $k_{Mn^{III}}$ were obtained by dividing by 1.2 (2 × 0.6).

[b] Rates of decomposition in xylene (*4*). The rate at 80° and 82° has been shown to be the same in acetic acid and in xylene (*5, 6*); temperature dependencies are practically independent of solvent.

The fact that, under certain conditions, alkylperoxy radicals can be much more effective oxidizing agents than hydroperoxides is believed to be of general significance in metal-catalyzed autoxidation reactions. Experiments with other metal compounds are in hand in this Laboratory.

REFERENCES

1. VAN HELDEN, R., AND KOOYMAN, E. C., *Rec. Trav. Chim.* **80**, 57 (1961).
2. HAMMOND, G. S., BOOZER, C. E., AND SEN, J. N., *J. Am. Chem. Soc.* **77**, 3233 (1955).
3. BLANCHARD, H. S., *J. Am. Chem. Soc.* **82**, 2014 (1960).
4. VAN HOOK, J. P., AND TOBOLSKY, A. V., *J. Am. Chem. Soc.* **80**, 779 (1958).
5. LEWIS, F. M., AND MATHESON, M. S., *J. Am. Chem. Soc.* **71**, 747 (1949).
6. ARNETT, L. M., *J. Am. Chem. Soc.* **74**, 2027 (1952).

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