U(Cup)$_4$, the extent to which the A and B waves have been made more positive (easier reduction) showing qualitatively the high stability of the complexed reduction product. Quantitatively, however, it can only be said of the E wave that its true half-wave potential is more positive than +0.1 v., the point at which the anodic dissolution of mercury in this medium permits the wave to appear. The H wave apparently represents reduction of the free excess cupferron.

The G wave must represent the counterpart of the (IV) to (III) C wave. Since it now results from a process which involves reduction beyond the complexed (IV) state, its $E_{1/2}$ should be more negative than that of the C wave if the (III) product were in a simple state. Its more positive position argues that U(III) must also form a cupferrate, whose stability is as great or greater than that of U(Cup)$_4$. In 16 mM cupferron solution the G wave is still more positive, with $E_{1/2}$ being about −0.15 v.

Studies on the current efficiencies of milligram-level electrolytic reductions of the uranyl ion in the presence of cupferron confirm the existence of a U(III) complex. It is also evident from these studies that U(III) cupferrate is readily soluble in ether.

This positive evidence for a U(III)-cupferron complex is interesting in view of the recent statement that, "Little is known about possible complex ions of U^{+3} in aqueous solution, although the general impression is that little complex-ion formation is to be anticipated."(6)

(6) G. T. Seaborg and J. J. Katz, ed., "The Actinide Elements," McGraw-Hill Book Co., New York, N. Y., 1954, p. 162.

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The Stability of Potassium Permanganate in Alkaline Solutions Containing Telluric Acid

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The decomposition of potassium permanganate in alkaline medium and its bearing on the oxidation with that reagent was discussed by Stamm,[1] Duke,[2] Drummond and Waters[3] and Symons.[4] Decomposition in strong alkaline solutions (>3 N NaOH) is enhanced in presence of manganese dioxide and is largely inhibited in presence of telluric acid.[5] The stabilizing action of telluric acid is evidently brought about by its complexing power on quadrivalent manganese preventing the precipitation of MnO$_2$.[6] Whether or not the same stabilizing effect will be manifested by telluric acid on alkaline permanganate solutions is the aim of this investigation.

Experimental

Potassium permanganate solutions (~0.1 N) were prepared by the procedure recommended by Stamm[1] by dissolving the appropriate amount of the solid in 200 ml. of water twice distilled from alkaline permanganate in an all glass apparatus. The solution is boiled and then left to stand for 24 hrs., after which period it was filtered twice through 1 G4 sintered glass funnel and diluted to the appropriate volume. They were stored in brown colored bottles and checked with A.R. sodium oxalate. From these concentrated (~0.1 N) KMnO$_4$ solutions, 20–4 mmolar solutions were prepared for the kinetic study by accurate dilution.

Sodium hydroxide solutions (5–16 N) were prepared from the "Analar" B.D.H. product. The solutions were kept in a thermostat adjusted at 25° and mixed only after 0.5 hr. to ensure thermal equilibrium. 0.1 gram of telluric acid dissolved in little alkali was added to the proper volume of KMnO$_4$ in a brown bottle followed by the requisite volume of alkali solution and the mixture which is made up to 100 ml. with water is thoroughly agitated. At intervals of one hour (along a period of five hours) 10-ml. portions of KMnO$_4$ were titrated potentiometrically with monovalent thallium at 1.5–2 N NaOH, after checking the decomposition by dilution with the appropriate volume of water.

Monovalent thallium was found to be a very suitable reagent for the rapid potentiometric titration of KMnO$_4$, the errors amounting only to ±0.1–0.2%. It was prepared from the B.D.H. product by dissolving in twice distilled water and standardized by titration with permanganate.[7]

Results

The stability of potassium permanganate of concentrations varying from 4–20 mmolar, in 2–10 N NaOH was studied in presence of telluric acid.

TABLE I

NaOH concn.,(b) N KMnO$_4$ = 4.5×10^{-3} M	Initial rate × 10^3 0–2 hr.	Final rate × 10^3 3–5 hr.	Av. rate, $r \times 10^3$
4	0.100	0.117	0.110
5	.225	.273	.254
7	.240	.340	.300
8	.370	.390	.386
10	.455	.490	.476
KMnO$_4$ concn. (c), M NaOH = 4 N			
16.85×10^{-3}	0.035	0.04	0.038
14.79×10^{-3}	.033	.05	.045
11.16×10^{-3}	.047	.067	.057
7.50×10^{-3}	.075	.117	.100
3.50×10^{-3}	.235	.250	.245

The results obtained are listed in Table I and shown graphically in Figs. 1 and 2.

From these results it is apparent that the rate of decomposition is greatly inhibited by the introduction of telluric acid. A solution 0.02 M with respect to KMnO$_4$ is quite stable in 4 N NaOH for a period of 4 hours, whereas it undergoes considerable decomposition in absence of telluric acid. However, despite the lower rate of decomposition observed, the behavior is much the same in absence of telluric acid. The rate of decomposition increases with rise of alkalinity and with decrement of permanganate concentration.

These results can be made use of in determining the order of the reaction. Thus by plotting the logarithm of the average rate of decomposition r against the logarithm of the reciprocal of the permanganate concentration c at three different alkalinities, *viz.*, 4, 5 and 7 N NaOH, curves A, B and C,

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(1) H. Stamm, "Newer Methods of Volumetric Analysis," Trans. by Oesper, D. Van Nostrand Co., New York, N. Y., 1938, p. 55.

(2) F. R. Duke, THIS JOURNAL, **70**, 3975 (1948).

(3) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

(4) M. C. R. Symons, *ibid.*, 3956 (1953); 3676 (1954).

(5) I. M. Issa, *et al.*, *Anal. Chim. Acta*, **11**, 198 (1954); **11**, 518 (1954).

(6) O. Tomicek, O. Procke and V. Pavelka, *Collection Czech. Chem. Commun.*, **11**, 449 (1939).

(7) I. M. Issa and R. M. Issa, *The Analyst*, **79**, 771 (1954); *Anal. Chim. Acta*, in press.

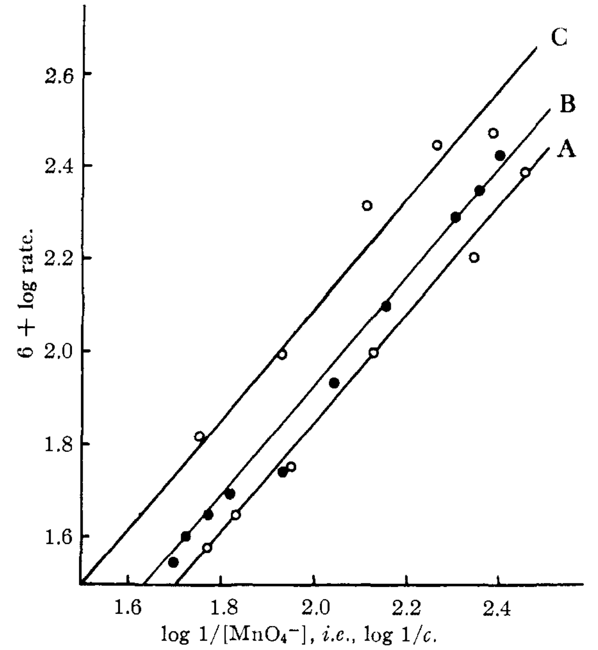

Fig. 1.—A, 4 *N* NaOH; B, 5 *N* NaOH; C, 7 *N* NaOH.

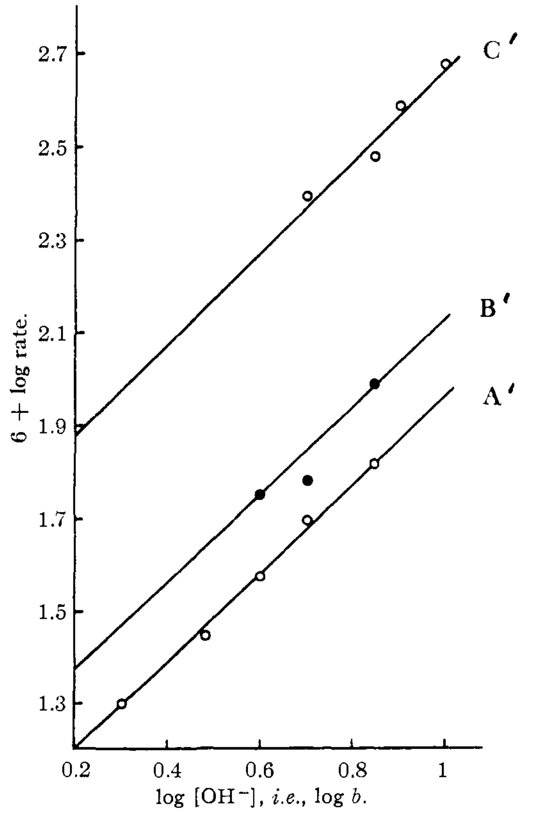

Fig. 2.—A′, 19 × 10^{-3} *M;* B′ = 11.3 × 10^{-3} *M;* C′ = 4.5 × 10^{-3} *M.*

Fig. 1 are obtained. The curves are linear with slopes amounting to 1.10, 1.15 and 1.10, respectively, indicating that the rate of decomposition depends on the permanganate concentration raised to a power of −1. Also by plotting log *r* against the logarithm of alkali concentrations *b* (for three different permanganate concentrations) curves A′, B′ and C′, of Fig. 2 are obtained. These curves also are linear, with the respective slopes of 0.95, 0.95 and 1 indicating a first-order reaction with respect to OH^- ions.

The role played by telluric acid is not very clear. Save for the fact that it dissolves the freshly precipitated manganese dioxide, nothing is known about its compounds with the higher oxidation states of manganese. In the reactions under hand, however, owing to the high alkalinity of the solutions, reduction of permanganate does not proceed below the manganate state (*cf.* ref. 4).

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Chelate Compounds of 7-(α-Anilinobenzyl)-8-quinolinol

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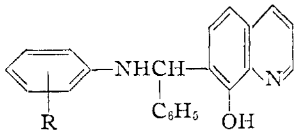
7-(α-Anilinobenzyl)-8-quinolinol (I, R = H) and derivatives in which the presence of the large 7-substituent might conceivably furnish an additional donor group for chelation as well as exert steric hindrance[1,2] form compounds with metal ions the compositions of which were determined in this investigation. The derivative (I, R = *o*-COOH) containing the chelating centers of both anthranilic acid and 8-quinolinol in one molecule is of particular interest because both the parent compounds are chelating agents of closely similar properties, and unusual behavior toward metals might be anticipated from the combination.[3] For comparative purposes two new compounds (I, R = *o*-$COOC_2H_5$, and R = *p*-COOH) were also prepared.



I

In general the chelate compounds of 7-(α-anilinobenzyl)-8-quinolinol were observed to have approximately the same colors (and sometimes fluorescence) as the corresponding 8-quinolinol compounds as well as the same ratio of metal to reagent (Table I), showing that the new reagent is apparently only bidentate in spite of the presence of the side chain nitrogen. However, some differences in the behavior of the new reagent as compared to 8-quinolinol were also noted. As expected from its higher molecular weight 7-(α-anilinobenzyl)-8-quinolinol gave precipitates with smaller amounts of metals in sensitivity tests with representative ions. Although the scandium compound of 8-quinolinol contains a molecule of added 8-quinolinol,[4,5] no such added reagent was observed with the new compound, possibly because of different experimental conditions (precipitation from a cold

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(1) H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2910 (1954).

(2) R. Belcher, A. Sykes and J. C. Tatlow, *ibid.*, 376 (1955).

(3) J. F. Flagg, "Organic Reagents," Interscience Publishers, Inc., New York, N. Y., 1948, p. 76.

(4) T. Moeller and M. V. Ramaniah, THIS JOURNAL, **76**, 6030 (1954).

(5) L. Pokras and P. M. Bernays, *ibid.*, **73**, 7 (1951).