

KINETICS AND MECHANISM OF OXIDATION OF V(II) IONS WITH TRICHLOROACETIC ACID

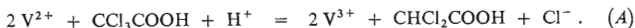
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The kinetics and mechanism of the redox reaction of V(II) ions with trichloroacetic acid were studied in the medium of 0.04–2.0M-HClO₄. The results of kinetic measurements were compared with the analogous oxidation of U(III) ions with trichloroacetic acid, and the exchange rate constant for the reaction $U^{3+} + *U^{4+} \rightarrow U^{4+} + *U^{3+}$ was calculated. The influence of binary mixtures on the kinetic parameters of the reaction and the application of the Marcus' equation show that the oxidation of V²⁺ ions with trichloroacetic acid proceeds by an outer-sphere mechanism.

The subject of the present work is a kinetic study of oxidation of V(II) ions with trichloroacetic acid in the medium of perchloric acid and its comparison with the analogous oxidation of U(III) ions in the same medium¹. The oxidation agent was in excess and the reaction products correspond to the stoichiometric equation



EXPERIMENTAL

Chemicals. Solutions of V²⁺ ions were prepared from reagent grade NaVO₃ (Merck) in 1M-HClO₄ by means of zinc amalgam, with which they were in contact during use. During reduction, the solution turned light blue (formation of V(IV)), then green (V(III)), and finally violet (V(II)). To prevent oxidation of V²⁺ ions with air, they were kept in an atmosphere of pure nitrogen which was freed from traces of oxygen by means of a solution of Cr²⁺ ions. Nitrogen was led through a three-way stopcock and polyethylene tubings; water siphons prevented back diffusion of oxygen into the polarographic cell. The concentration of V²⁺ ions was determined polarographically. Trichloroacetic acid (Reanal, Budapest) was of reagent grade as other chemicals. Solutions were prepared from redistilled water. The supporting electrolyte was HClO₄ and the ionic strength was adjusted with NaClO₄.

Kinetics. The time dependence of the limiting polarographic diffusion current of V²⁺ ions was recorded at +0.1 V (s.c.e.), until the reaction proceeded to at least 80%. The polarograph was of the type OH-102 (Radelkis, Hungary), the Kalousek polarographic cell was tempered by means of a U-10 thermostat (Prüfgerätewerk, Medingen, GDR).

Identification of reaction products. The rate constants were also determined by spectrophotometry at 400 nm, whereby the V³⁺ ions were detected. After the reaction had been finished,

only these ions were found as reaction products. The extinction coefficients for V^{2+} , V^{3+} , and VO^{2+} are in accord with the published ones². Dichloroacetic acid was detected by capillary isotachoforesis; the diameter of the capillary was 0.3 mm and the conductivity detector $I = 50 \mu A$. The leading electrolyte was 0.01M histamine chloride + 0.01M histamine (pH 6), the terminating electrolyte was $5 \cdot 10^{-3} M$ capronic acid. Chloroacetic acids were identified by comparing the conductivities of the corresponding zones with standards.

RESULTS

The rate constants were evaluated from the decrease of the limiting diffusion current of V^{2+} ions by using the integrated form of the first-order kinetic equation; the concentration of CCl_3COOH was in excess against V^{2+} ions (0.02–1.0M- CCl_3COOH and 0.001M- V^{2+}). The order with respect to the oxidant was found from the dependence of the first-order rate constant on the concentration of CCl_3COOH , which is linear in the whole range under study. Its slope gave $k = 2.8 \cdot 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in 0.4M- $HClO_4$ at 40°C. At constant pH, the rate equation has the form

$$-d[V^{2+}]/dt = k[V^{2+}][CCl_3COOH]. \quad (1)$$

The value of k decreases with increasing concentration of H_3O^+ ions at constant ionic strength; this dependence was measured at 30, 40, and 45°C (Table I) and is linear in the coordinates $1/k$ against $[H_3O^+]$. At constant pH, the value of k decreased by 11% when the ionic strength increased from 0.08 to 2.0 mol/dm³.

The stoichiometry of the studied reaction was determined by polarometric titration; two V^{2+} ions react with one CCl_3COOH molecule. The reaction products

TABLE I
Dependence of Rate Constant on Concentration of Hydrogen Ions at Various Temperatures
 $I = 2.0 \text{ mol/dm}^3$.

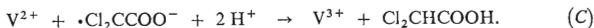
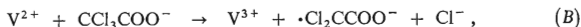
H_3O^+ mol/dm ³	$k_{exp}, 30^\circ C$ mol ⁻¹ s ⁻¹ dm ³	$k_{exp}, 40^\circ C$ mol ⁻¹ s ⁻¹ dm ³	$k_{exp}, 45^\circ C$ mol ⁻¹ s ⁻¹ dm ³
0.04	$1.48 \cdot 10^{-2}$	$4.13 \cdot 10^{-2}$	$8.3 \cdot 10^{-2}$
0.08	$1.49 \cdot 10^{-2}$	$4.09 \cdot 10^{-2}$	$8.3 \cdot 10^{-2}$
0.1	$1.48 \cdot 10^{-2}$	$4.06 \cdot 10^{-2}$	$8.3 \cdot 10^{-2}$
0.4	$1.42 \cdot 10^{-2}$	$3.86 \cdot 10^{-2}$	$7.6 \cdot 10^{-2}$
0.8	$1.32 \cdot 10^{-2}$	$3.56 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$
1.0	$1.27 \cdot 10^{-2}$	$3.46 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$
1.4			$5.8 \cdot 10^{-2}$
1.6	$1.2 \cdot 10^{-2}$	$3.14 \cdot 10^{-2}$	$5.3 \cdot 10^{-2}$
2.0	$1.11 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	

correspond to the stoichiometric equation (A): V^{3+} ions were detected by spectrophotometry, CCl_2HCOOH by isotachoforesis, and Cl^- ions by potentiometric titration with a silver electrode.

Mixtures of water with isopropanol and tert-butanol were used to study the solvent effect. The plot of $\log k$ against molar fraction of alcohol shows a minimum and a maximum (Fig. 1). The activation parameters were determined from the dependence of k on the temperature and the Eyring equation as $\Delta H^\ddagger = 81.8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -12 \text{ J K}^{-1} \text{ mol}^{-1}$.

DISCUSSION

The rate equation involves a bimolecular interaction between V^{2+} ions and trichloroacetic acid, which proceeds similarly to the oxidation of U^{3+} ions by this acid in two steps as follows:



This is supported by the same character of the dependence of the rate constant on the concentration of hydrogen ions. The explanation is that V^{2+} ions react with CCl_3COO^- anions; the rate equation is derived as in ref.¹ and the measured rate constant is given as

$$1/k_{exp} = 1/k + [H^+]/kK, \quad (2)$$

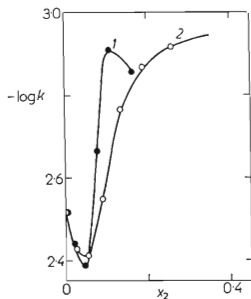


FIG. 1
Dependence of Logarithm of Rate Constant
on Mole Fraction of Alcohols
1 $1 \cdot 10^{-3} M$ - V^{2+} , $0.1 M$ - CCl_3COOH , $0.4 M$ - $HClO_4$; $40^\circ C$. 2 tert-butanol, 3 isopropanol.

where k is the rate constant of the elementary reaction step and K is the dissociation constant of CCl_3COOH . This equation fits well the experimental results. The value of K was determined as $5.4 \text{ dm}^3 \text{ mol}^{-1}$ at 40°C , which is in good agreement with the value in ref.¹ and lies in the interval of values found by other authors³. The quantities corresponding to the elementary reaction step are given in Table II.

The dependence of $\log k_{\text{exp}}$ on the mole fraction of isopropanol and tert-butanol (Fig. 1) can be qualitatively discussed as in ref.¹. We assume that the solvent structure changes markedly at a mole fraction x_2^* (0.04 for tert-butanol at 40°C , 0.05 for isopropanol at 40°C), which is manifested on the kinetics mainly of redox reactions with an outer-sphere mechanism⁴. Therefore, it is apparent that the oxidation of V^{2+} ions with CCl_3COOH proceeds by an outer-sphere redox mechanism.

Of the outer-sphere electron transfer theories, the Marcus theory seems to be preferable. Under certain reaction conditions (at least one reactant is uncharged, or the ionic strength is high), a simplified form of the equation for the rate constant of the reaction with an outer-sphere electron transfer applies:

$$k_{\text{AB}} = (k_{\text{AA}}k_{\text{BB}}K_{\text{AB}})^{1/2}, \quad (3)$$

where k_{AA} and k_{BB} are rate constants of exchange reactions of the reactants A and B, K_{AB} is the equilibrium constant.

When two different reductants reduce the same oxidant, the ratio of rate constants of these reactions will be given as

$$k_{\text{AB}}/k_{\text{AC}} = (k_{\text{BB}}/k_{\text{CC}}) K. \quad (4)$$

The quantity K expresses the difference between the reducing powers of reductants B and C. Eq. (4) can be used to calculate the rate constant $k(\text{U}^{4+}/\text{U}^{3+})$ of the exchange

TABLE II
Activation Parameters of Elementary Redox Reaction
 $I = 2.0 \text{ mol/dm}^3$.

$T, \text{ K}$	k $\text{mol}^{-1} \text{ s}^{-1}$ dm^3	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{JK}^{-1} \text{ mol}^{-1}$
303.15	0.015	80.6	-14.7
313.15	0.041		
318.15	0.086		

reaction $*U^{3+} + U^{4+} \rightarrow *U^{4+} + U^{3+}$. (Only two values of this constant were published^{5,6}, differing appreciably from each other.) Reductant B is in our case U^{3+} , C is V^{2+} . Then $K = [U^{4+}][V^{2+}]/[U^{3+}][V^{3+}] = 2.76 \cdot 10^6$; the standard potential of the reaction $U^{4+} + e \rightarrow U^{3+}$ is $E^0 = -0.63$ V and that of the reaction $V^{3+} + e \rightarrow V^{2+}$ is $E^0 = -0.255$ V (ref.⁷).

The rate constant for the reaction of U^{3+} ions with CCl_3COOH with $[H^+] = 1.0$ mol/dm³, $I = 2.0$ mol/dm³ is $k_{AB} = 3.7$ mol⁻¹ dm³ s⁻¹ at 25°C; and for the reaction of V^{2+} ions with this acid we have under the same conditions $k_{AC} = 7.3 \cdot 10^{-3}$ mol⁻¹ dm³ s⁻¹. The exchange rate constant⁸ $k_{CC} = k(V^{3+}/V^{2+}) = 0.01$ mol⁻¹ dm³ s⁻¹ at 25°C, $I = 2.0$ mol/dm³. We calculated $k(U^{4+}/U^{3+}) = 9.3 \cdot 10^{-4}$ mol⁻¹ dm³ s⁻¹ at 25°C, $I = 2.0$ mol/dm³, which is close to the value of 10^{-4} mol⁻¹ dm³ s⁻¹ given by Lavallee and coworkers⁶. These values are also comparable with the rate constants of the exchange reactions $k(Np^{4+}/Np^{3+}) = 4.6 \cdot 10^{-4}$ mol⁻¹ dm³ s⁻¹ (ref.¹²) and $k(Eu^{3+}/Eu^{2+}) = 10^{-4}$ mol⁻¹ dm³ s⁻¹ (ref.⁹).

The most important factor determining the entropy of the activated complex is its charge¹⁰. The formal entropy of the activated complex for the reaction of U^{3+} with CCl_3COOH is given as

$$S_1^* = \Delta S_1^\ddagger + S^0(U^{3+}) + S^0(CCl_3COO^-)$$

and for the reaction of V^{2+} with CCl_3COOH

$$S_2^* = \Delta S_2^\ddagger + S^0(V^{2+}) + S^0(CCl_3COO^-).$$

Activation entropies are denoted as ΔS_1^\ddagger and ΔS_2^\ddagger ; S^0 denotes standard entropy of reactants participating in the formation of the activated complex. Since the latter value for CCl_3COO^- is not known, we cannot calculate the formal entropies of the activated complexes, but only their difference $S_1^* - S_2^* = -30$ J K⁻¹ mol⁻¹, which suggests that the formal charges of these activated complexes differ by one unit^{11,12}.

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REFERENCES

1. Adamčíková L., Treindl L.: *This Journal* 45, 26 (1980).
2. Gordon G., Tewari P. H.: *J. Phys. Chem.* 70, 200 (1966).
3. Palm V. A.: *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions*. Vol. I. VINITI, Moscow 1975.
4. Treindl L., Adamčíková L.: *This Journal*, in press.
5. Adegite A., Egboh H., Ojo J. F., Olieh R.: *J. Chem. Soc., Dalton Trans.* 1977, 834.
6. Lavallee C., Lavallee D. K., Deutsch E. A.: *Inorg. Chem.* 17, 2217 (1978).

7. Latimer W. M.: *Oxidation States of the Elements and their Potentials in Aqueous Solutions*. Prentice-Hall, New Jersey 1952.
8. Krishnamurty K. V., Wahl A. C.: *J. Amer. Chem. Soc.* **80**, 5921 (1958).
9. Choi M., Creutz C., Sutin N.: *J. Amer. Chem. Soc.* **99**, 5615 (1977).
10. Newton T. W., Rabideau S. W.: *J. Phys. Chem.* **63**, 365 (1959).
11. Linck R. G.: in the book: *Transition Metals in Homogeneous Catalysis* (G. N. Schrauzer, Ed.), Chapter 7. Dekker, New York 1971.
12. Lavallee C., Lavallee D. K.: *Inorg. Chem.* **16**, 2601 (1977).

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