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Oxidation of D-Galacturonic Acid by Vanadium(V)

G. MICERA*

Istituto di Chimica Generale e Inorganica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

S. DEIANA, A. DESSÌ

Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, C.N.R., Via Vienna 2, 07100 Sassari, Italy

A. PUSINO

Istituto di Chimica Organica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

and C. GESSA

Istituto di Chimica Agraria, Università di Sassari, Via E. de Nicola 10, 07100 Sassari, Italy

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Abstract

The kinetics of the oxidation of D-galacturonic acid by vanadium(V) in acid solution have been studied. The reaction is of the first order with respect to both vanadium(V) and the organic substrate. Formic acid and oxovanadium(IV) are the final reaction products. The reaction rate is increased with increasing acidity, suggesting that variously protonated vanadium(V) species are active in the substrate oxidation.

Introduction

Vanadium(V) is active in the oxidation of several organic substrates, such as aliphatic and aromatic alcohols, hydroxycarboxylic acids and carbohydrates (see, e.g., refs. 1–4). This implies that a wide range of interactions may be responsible for the reduction of vanadium(V) and the biotransformations of the element.

In this respect, we have shown previously that the end-units of polygalacturonic acid, a polyuronic component of plant cell walls, are oxidized by metavanadate(V) to yield formic acid and oxovanadium(IV) ions coordinated to the polymeric matrix [5]. This reaction, according also to a recent report [6], may be relevant for the vanadium supply of plants, as it allows the uptake of vanadium in a cationic form and/or it prevents the accumulation of vanadium(V), which is responsible for inhibitory effects [7].

To complement this work and to compare the interaction mechanisms through which monomeric and polymeric uronic acids are oxidized by vanadium(V), we have now investigated the oxidation of D-galacturonic acid by vanadium(V) in aqueous solution.

Experimental

Materials

D-Galacturonic acid (Sigma) solutions were prepared in doubly distilled water. Oxidant solutions were prepared by dissolving $NaVO_3$ (Sigma) in HCl aqueous solutions of appropriate concentration.

Physical Measurements

Kinetic measurements were carried out on a Carlo Erba Spectra-comp 601 spectrophotometer with the cell compartment thermostated at 35.0 ± 0.1 °C. The changes of the absorbance at 770 nm, the wavelength corresponding to the d–d absorption maximum for aqueous VO^{2+}, were followed to estimate the amount of reduced vanadium after construction of the calibration curve in the $0–1 \times 10^{-2}$ M range. X-band ESR spectra were taken using a Varian E-9 spectrometer. Formic acid was determined by ion chromatography with conductometric detection, according to a method described earlier [8].

Results and Discussion

Stoichiometry of the Reaction

The oxidation of D-galacturonic acid by vanadium(V) yields formic acid and oxovanadium(IV), as

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*Author to whom correspondence should be addressed.

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substantiated by chromatographic detection of formic acid and spectroscopic (ESR and electronic absorption) analysis of oxovanadium(IV) in the reaction mixtures.

The quantitative yields of formic acid or oxovanadium(IV) ions were measured by employing large excesses of metavanadate(V) or D-galacturonic acid, respectively, and the following stoichiometry was established:

$$C_6H_{10}O_7 + 8VO_3^- + 24H^+ \longrightarrow 6HCOOH + 8VO^{2+} + 11H_2O$$

Whatever the extent of the reaction, no organic intermediate was detected by analytical (TLC and HPLC) methods. Particularly, the formation of formaldehyde was ruled out, also on the basis of the dimedone-test. The reaction involves a free-radical mechanism as proved by the positive test for the initiation of acrylonitrile polymerization.

Kinetics of the Reaction

The kinetics of the oxidation were studied under pseudo-first-order conditions by maintaining the organic substrate and hydrochloric acid concentrations in a large excess over that of vanadium(V). Linear plots of $\log\{[V]_0/[V]\}$ against time (Fig. 1) were observed and indicated a first-order dependence of the rate on the vanadium(V) concentration. The concentration of the organic substrate was then varied and the pseudo-first-order rate constant (k_1) was calculated from the integrated form of the rate equation (Fig. 1). Plots of k_1 against the initial substrate concentration at constant acidity proved to be linear with a zero intercept. The results (Table I) thus support that the reaction is of the first order with respect to the organic substrate and also rule out any kinetic evidence for the intermediate complex formation between vanadium(V) and the substrate.

Dependence on Acid Concentration

The effect of acidity on the reaction rate was studied at constant chloride concentration (2 M) maintained by addition of NaCl. The results indicate that the oxidation rate increases with the increase of acid concentration. However, as shown in Fig. 2, where the variation of the rate constant over the 0.05–2 N HCl concentration range is reported, a simple law is not observed. Besides, the reaction rate decreases further below this acidity range. Such a trend is usually observed when the reactants are involved in acid–base equilibria [9]. In particular,

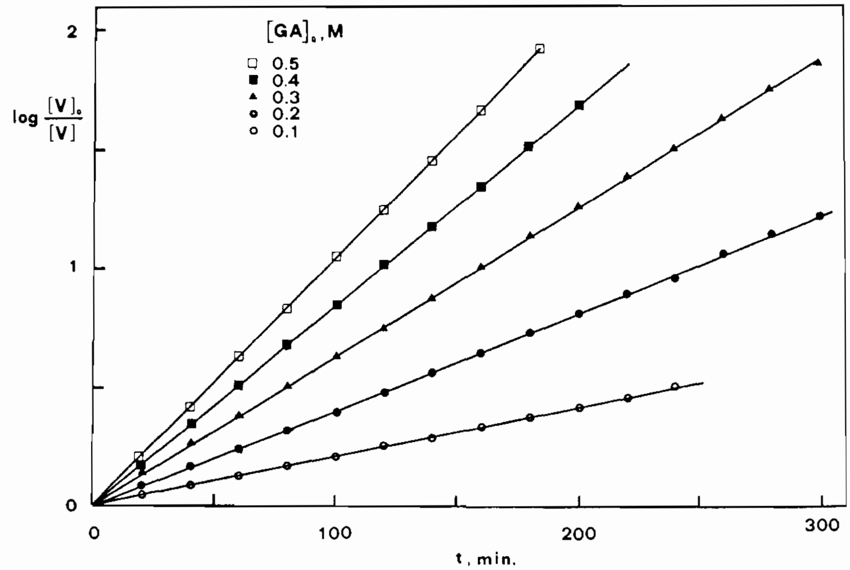

Fig. 1. First-order plots for the reaction of V(V) with D-galacturonic acid. $[V]_0 = 1 \times 10^{-2}$ M; $[H^+] = 0.5$ N.

TABLE I. Variation of the Pseudo-first-order Constants (k_1) as a Function of the D-Galacturonic Acid Initial Concentration ($[GA]_0$) in 0.5 N HCl at Vanadium(V) Initial Concentration 1×10^{-2} M

$[GA]_0$, M	0.1	0.2	0.3	0.4	0.5
$10^4\ k_1$, s^{-1}	0.360	0.683	1.055	1.419	1.744
$10^4\ k_1/[GA]_0$, M^{-1} s^{-1}	3.60	3.42	3.52	3.55	3.49
Average $10^4\ k_1/[GA]_0 = 3.51 \pm 0.07$ M^{-1} s^{-1}					

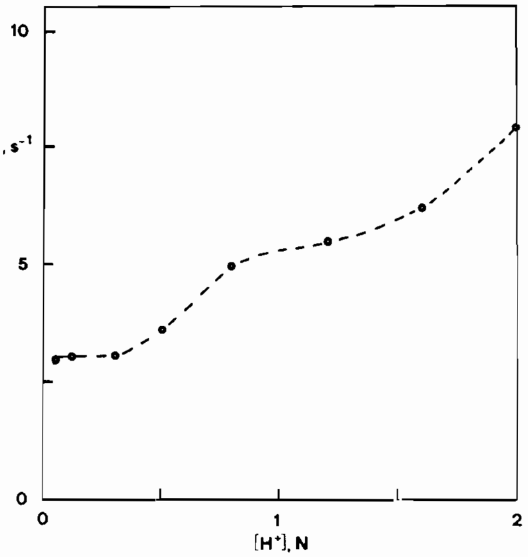

Fig. 2. Variation of the first-order constant with HCl concentration. $[GA]_0 = 1 \times 10^{-1}$ M; $[V]_0 = 1 \times 10^{-2}$ M.

the experimental behaviour indicates that several reactant species, related to each other by protonation equilibria, exist and all of them are active in the reaction. In this respect, it is well-known that anionic vanadium(V) protonates in acidic media to give VO_2^+ (single species at acidity high as 0.05 M). VO_2^+ may be further protonated to give HVO_2^{2+} and then $H_2VO_2^{3+}$ [1, 10]. Thus, the acid dependence of the reaction appears to reflect the stepwise transformation of vanadium(V) into VO^{2+}, HVO_2^{2+} and $H_2VO_2^{3+}$, which are increasingly more reactive towards the substrate.

Solvent Influence

Kinetic data for the reaction in acetic acid–water mixtures (Table II) show that the rate constant increases with increasing acetic acid content, that is, with decreasing dielectric constant.

TABLE II. Variation of Rate with Acetic Acid–Water Composition. $[GA]_0 = 0.1$ M, $[V]_0 = 0.01$ M and $[HCl] = 0.5$ N

Acetic acid (*v*/*v*%)	30	50	60	70
$10^4\ k_1, s^{-1}$	1.33	3.25	7.25	13.30

Such a behaviour is expected when the charge is more dispersed in the activated complex than in the reactants, as, for instance, in the case of a reaction between an ion and a neutral molecule [11]. Thus, the oxidation most likely involves, as the rate determining step, the reaction between a positively charged vanadium(V) species and a neutral substrate molecule.

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