Estimation of the pKa for various Brønsted acids in polar aprotic media using electrochemical measurements of chromium (III) with picolinic acid

Mildred I. Rodríguez Cordero [a,*], Vincent Piscitelli [b], Carlos Borras [a], José Daniel Martínez [b], Mary Lorena Araujo [b], Pedro Silva [c], Vito Lubes [a]

[a] Departamento de Química, Universidad Simón Bolívar, Sartenejas, Apartado 89000, Caracas 1080A, Venezuela
[b] Universidad Central de Venezuela, Facultad de Ciencias. Escuela de Química, Apartado 205. Los Chaguaramos, Caracas 1020A, Venezuela
[c] Carretera Panamericana, Km 11, Altos de Pipe, Centro de física, IVIC, Apartado 21827, Caracas 1020A, Venezuela

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ABSTRACT

The electrochemical reduction of Crpic and the effect of various proton-donors in DMF were investigated in this work. Measurements showed important electrochemical changes in the presence of proton-donors such as ascorbic acid, benzoic acid and acetic acid. Dissociation constants and acid strength are estimated using the Nernstian behavior of the chromium (III) complex and the proportional relation between ΔEp vs pKa are assistance to estimate the dissociation constants and the acid strength.

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1. Introduction

The understanding of the environmental factors that regulate the potential and reaction pathways involving different species linked to a proton redox couple in natural systems is an active area of research [1]. Proton coupled electron transfer (PCET) reactions are used to describe reactions in which both an electron and a proton are transferred, either in two separate steps or in a single step [2,3]. Reactions, in which electron and proton transfers between the same donor and acceptor, i.e., hydrogen atom transfer, are not considered here since the electrochemical PCET reactions, consider that the electrons are flowing into or from an electrode while protons are transferred between acid and base. These reactions are relevant because the proton coupled electron transfer (CPET) has an important role in a wide range of biological processes, including enzymatic reactions, photosynthesis and respiratory processes [1,2]. In particular, the quinones being fundamental for some biological functions are one of the most studied systems since they can promote interactions with the hydrogen bonds and/or proton transfer.

Cyclic voltammograms (CV) are known as a useful technique for nondestructive characterization of electron transfer and to understand the mechanisms of reactions involving electron transfers [4,5]. Previous modeling work [6,7] found to be advantageous to determine the acidic constant in systems that exhibit a reversible behavior in polar aprotic mediums is the case of the complex of Chromium (III) with picolinic acid.

The acidity of chemical species in aqueous media depends upon a variety of factors such as the properties of the solvent, the structure of the acid, and the location of the proton with the functional group [5]. The relative acidity in aprotic medium may be clearly different when compared to the results in aqueous medium [3,6]. Acetic acid (pKa = 4.8) is an example having a pKa more acidic than ammonium ion (pKa = 9.2) in water, while the behavior is reversed for DMSO with acetic acid pKa 10.5 and 12.6 of the ammonium ion. The effect is more significant in acetonitrile with pKa = 22.3 for acetic acid and pKa = 16.5 for the ammonium ion [5,6,8–10].

Abbreviations: BQ, benzoquinone; CPET, coupled electron transfer; Crpic, Chromium (III) picolinate, $(Cr^{III} (pic)_3)$; CV, cyclic voltammograms; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; ΔEp, ΔEp = Ep2 − Ep1; Ep1, is the peak potential of the original peak due to the first reduction of 1 mM Crpic; Ep2, is the peak potential of the new reduction peak of Crpic in the presence of 1 mM Brønsted acid; ΔE°, ≅ ΔEp; E°′$_{new}$, formal potential in the presence of acid; E°′$_{original}$ = $E_1^{0'}$, formal potential in the absence of acid; EPR, electron paramagnetic resonance; GC, glassy carbon; HA, Brønsted acid; Hpic, picolinic acid; IR, infrared resonance; Ka, acidic constante; PCET, proton coupled electron transfer; pKa, −log Ka.

* Corresponding author.

Brønsted acids are classified in general as weak, mild and strong according to their ability to donate a proton to the redox species. The CV curve will have a particular trend/response, and the donor ability will be affected by the environment [1]

The presence of hydrogen bonding agents with weak Brønsted acids such as ethanol upon the reaction of 2,5-dichloro-1,4-benzoquinone at 100 mV/s, tends to change the couple redox potential to more positive values [1–3,7]. These changes increase with the concentration of the agent, without change in the electrochemical reversibility. Potential changes are due to the fast equilibrium of the hydrogen bond and the mono and di-anion, where the constant of the hydrogen bond is negligible.

For benzoquinone (BQ) in the presence of an agent of mild strength, such as trifluoroethanol, there would be changes on the positive side of the potential, and an increase in the height of the first redox signal will occur with the irreversibility of the second redox couple. As in the previous case, the change in the behavior of the potential is related to the basicity of the BQ. The increase in the current is related to the disproportionate benzoquinone [2,3,7]

$$2BQ^{\cdot-} \underset{\leftarrow}{\rightarrow} BQ + BQ^{2-}. \qquad (1)$$

When a quinone has a strong basicity, a new shoulder appears before the first original redox couple, even at low concentrations of the binding agent and the formation of hydrogen bridges take place. The new signal is attributed to the reduction of the hydrogen bonded to the quinone, which is confirmed by a slight change in the UV–visible spectrum to the red on the quinine [3].

Chloranil is a weak basic quinine. In the presence of a strong acid such as trifluoroacetic acid, a cathodic peak is observed before the first redox couple. This peak grows in height at the expense of the original signal. This suggests the presence of two species in reducible equilibrium [3]. Protonation of the quinone is discarded and a hydrogen-bonded complex is favored.

1.1. Method to evaluate a new peak caused by Brønsted acid upon 1,4-benzoquinone

When ΔE_p is plotted versus pKa for the appropriate aprotic medium, a linear behavior is observed with a correlation coefficient in the range of 0.99 to 0.97 for DMSO and acetonitrile, assuming ΔE_p is less than 50 mV between two adjacent signals. Based on the ECE mechanism, the electrochemical and chemical processes can be represented by Scheme 1 such as [6]:

$$BQ \underset{\leftarrow}{\overset{E_1^0}{\rightarrow}} BQ^{\cdot-} \underset{\leftarrow}{\overset{H^+}{\rightarrow}} BQH^{\cdot} \underset{\leftarrow}{\overset{E_2^0}{\rightarrow}} BQH^{-} \qquad \text{Scheme1}$$

After combination of the Nernst equation the acid–base equilibrium expression is [6]:

$$\Delta E^{0'} = E_{new}^{0'} - E_{original}^{0'} = \frac{E_2^{0'} - E_1^{0'}}{2} + \frac{2.3RT\left(pK_a^Q - pKa\right)}{2F} \qquad (2)$$

assuming $\Delta E^{0'} \cong \Delta E_p$, where $\Delta E^{0'} = E_{new} - E_{original}$; considered $E_{original} = E_1^{0'}$ as the peak potential of BQ due to the first reduction, and $E_{New}^{0'} = \frac{E_2^{0'} + E_1^{0'}}{2} + \frac{2.3RT(pK_a^Q - pK_a)}{2F}$ as the peak potential of BQ in the presence of acid, when [BQ] = [BQH⁻]. The initial concentrations of HA and BQ are similar, discarding the transfer of a hydrogen atom [6].

2. Experimental part

2.1. Synthesis of the complex

The synthesis of Chromium (III) picolinate has been previously reported [11,12]; some modifications were made in this work to ensure efficient percentage yield. Chemical reagents used for experimental development are of analytical grade (Sigma-Aldrich). The metal salts (E. Merck), and all solvents were of spectroscopic or biological grade.

Crpic was synthesized by first dissolving 3.76 g CrCl3·6H2O in 25 mL warm (50 °C) ethanol. Thereafter, 4.79 g of picolinic acid in 25.0 mL ethanol was added, the resulting solution was mixed in a round-bottom three necked saturated Ar vessel, and maintained under continuous stirring for 24 h at room temperature. The mixture was then refluxed with stirring for 8 h at 60 °C until reddish crystals began to form. The solution was then left standing at 15 °C for 2 weeks and the supernatant was discarded, with t vacuum filtered removed excess of the unreacted ligand. The crystals were washed 5 times with 3 mL of cold ethanol, then washed 3 times with 3 mL of ether and dried under vacuum for 24 h. Analysis of the crystals indicated that the complex consisted of 3 mol picolinate per 1 mol Cr^{3+}. Analytical calculations for the $[Cr(pic)_3] \cdot H_2O$ Cr ($C_{18}H_{14}N_3O_7$) complex; correspond to C: 49.55%; H: 3.23%; and N: 9.63%, and the elemental analysis gave C: 49.78%, N: 9.57% and H: 2.36%. IR measurements were taken using a Thermo Scientific Nicolet IS10 model, DTGS detector with 32 scans and resolution of 2. For Crpic stretching (ν) of the COOH groups was observed, and the deformations in the plane (γ) and out of plane (δ) were absent, suggesting deprotonation of the ligand. The $\nu(C{=}O)$ and $\nu(CO)$ ligand bands became ν as (COO–) and νs (COO–) [13], which implies formation of the complex. The difference between the vibrational stretching ν as (COO–) and νs (COO–) is greater than the corresponding to the free ion $CH_3COO–(\sim 164 \text{ cm}^{-1})$ [13], the connection of the metal with the group carboxylate is monodentate, and deformation out of the plane although both are present in the complex are shifted to higher frequencies [13]. Other bands appearing in the IR spectrum of the complex include the Cr–O around 474 cm⁻¹ stretching. The UV–visible spectrum in $HClO_4/CH_3COOH$ 70% (Agilent 8453 diode array) showed two bands in the visible region, at 539 nm, and a third one in the UV region is occult, but it was calculated semi-empirically using equations reported by Lever for complex d^3, 250 nm [14]. Another experiment on the complex used was electron EPR (Bruker EMX spectrometer). A g = 1.98 value was measured, which is characteristic of chromium (III) complexes [14].

2.2. Electrochemical measurements

Cyclic voltammogram experiments were done using Autolab PGSTS 12 potenciostat/galvanostat controlled with a computer. The standard three electrode cell was used with a Pt counter electrode, a GC work electrode (area = 0.283 cm²) and Ag/AgCl (BAS, MF-2052) as reference electrode. The electrode was calibrated against the $[Fe(C_5H_5)_2]/[Fe(C_5H_5)_2]^+$ redox couple, +0.43 V vs Ag/AgCl. The CV of acetic acid [15], benzoic acid [16], and ascorbic acid [17] without complexes had been already published by other authors, founding, as this work also with picolinic acid, that no peaks were observed even in working potential range. The stretch of acid is important to study different electrochemical behaviors. The acetic acid had been used to study catalyst process by electroreduction of proton with complexes under anaerobic conditions [16,18–21]; benzoic acid [16,19,22–24] and ascorbic acid [5,17,25] had been assessed as strong acid in DMF medium.

For the experiments DMF (Sigma, biotech. grade), 0.1 M of tetrabutylammonium hexafluorophosphate and 1 mM of Crpic and Brønsted acid solutions were used. All measurements were recorded without oxygen by purging the solution with Ar.
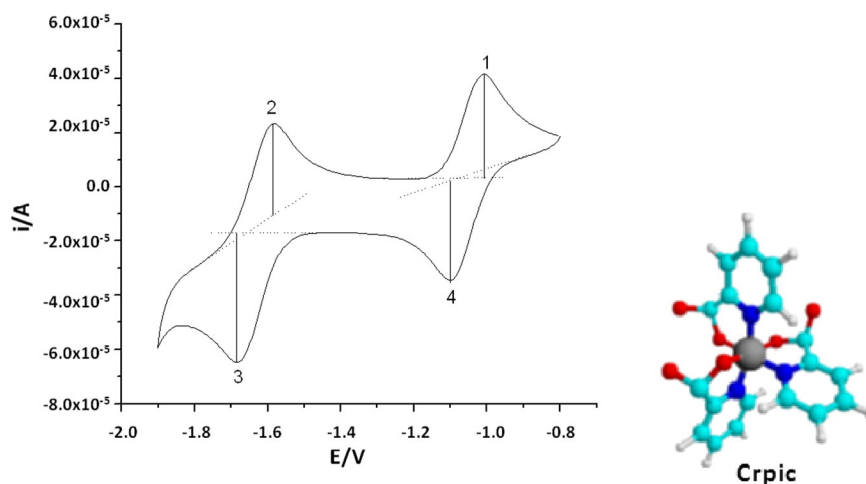
**Fig. 1.** Cyclic voltammograms of Crpic in DMF solution at 100 mV/s, 22 °C.

3. Results and discussion

The redox behavior of the Crpic complex was investigated using CV as shown on Fig. 1 The CV of 1 mM solutions of the compounds in DMF were recorded at 22 °C at scan rates of 100 mV/s. The complex evinces only redox process in the range of potential from −0.750 V to −2.00 V. Two reversible couple redox, the first peaks (1 and 4) correspond to the response to the metal center and the second peaks (2 and 3) are relevant to ligands.

It is expected that in the presence of the ligand a shift of the potential signal takes place. If it is not related to the redox couple, it will remain unchanged. In general this situation is shown in all the graphs with Brønsted acids, Figs. 2 to 5. The observed wave formation around −1.33 V, corresponding to the acidic proton electrochemical response accompanies each ligand. A slight difference in the potential signal of the first redox couple is present in the Crpic solution with Hpic. This could be attributed to some uncompensated solution resistance.

Using the mathematical approach referred to in the introduction and changing the parameters related to benzoquinone, for those corresponding to Crpic a linear relationship was established between pKa and both Nernst equations. The complex pKa is obtained, assuming

that $[Cr^{II}(pic)_2pic] = [A^-] = [Cr^{III}(pic)_3]$ which in this case represents the ʟ-ascorbic acid, pKa = 9.6 [5], as seen on Scheme 2 and Fig. 2

$$[Cr^{III}(pic)_3] + e \underset{\leftarrow}{\rightarrow} [Cr^{II}(pic)_3]^- + H^+ + e \underset{\leftarrow}{\rightarrow} [Cr^{II}(pic)_2picH]$$
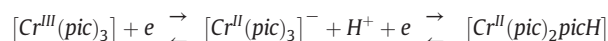
Scheme 2

represent the ECE behavior of complex with Brønsted acid.

In the presence of picolinic acid, a new signal appears as intermediate between the two redox couple, Fig. 3. At the beginning, while still the proton did not react with the complex an intermediate shoulder is observed, but when the cycle advances, it is consumed until the shoulder disappears, the original potential is displacement towards slightly positive values.

The reduction of makes the tris(chelate) structure unstable (Cr(III)/ Cr(II)), then a picolinate ligand probably becomes monodentate or could also be lost, opening a coordination site(s). Probably the first case is possible, because if the complex lost a ligand the CV of will be losing its reversible behavior, Fig. 3.

Considering the reaction scheme suggested by Speetjeen [26,27], which proposes that before the redox reaction, the protonation of the
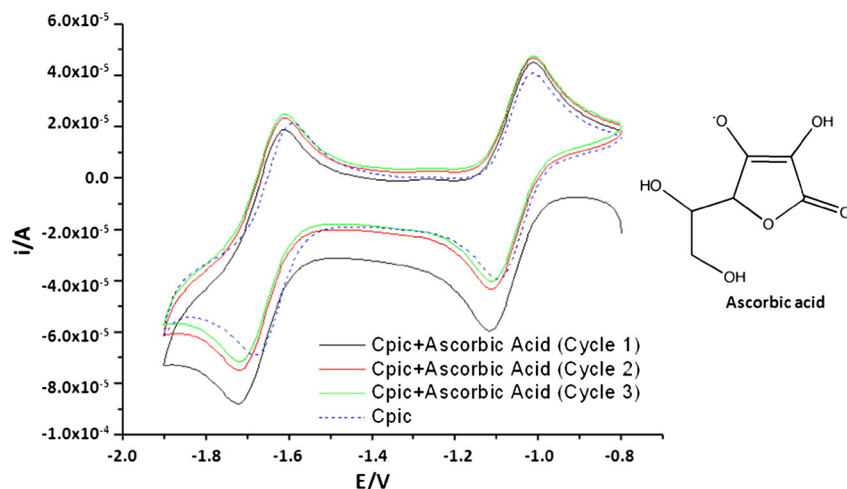

Fig. 2. Cyclic voltammograms of 1 mM Crpic (———); and 1 mM of Crpic + 1 mM ascorbic acid to several cycles in DMF solution at 100 mV/s, 22 °C.
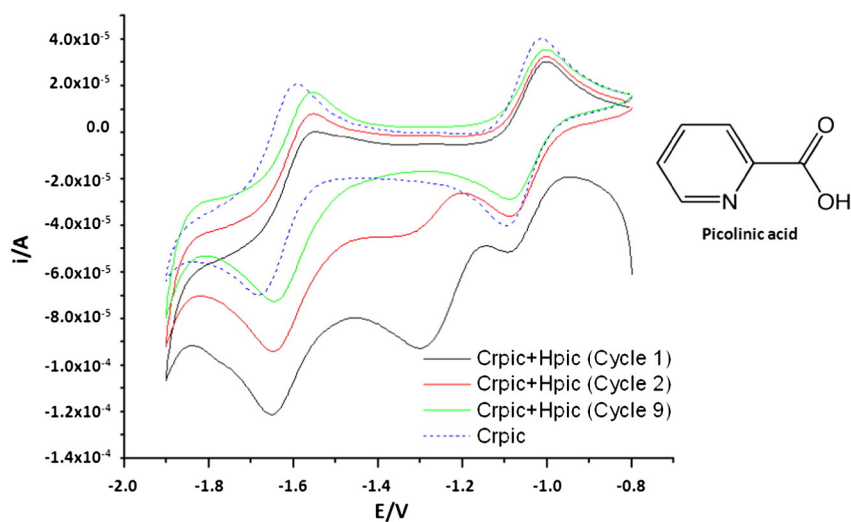
Fig. 3. Cyclic voltammograms of 1 mM Crpic (———); and 1 mM of Crpic + 1 mM picolinic acid to several cycles in DMF solution at 100 mV/s, 22 °C.
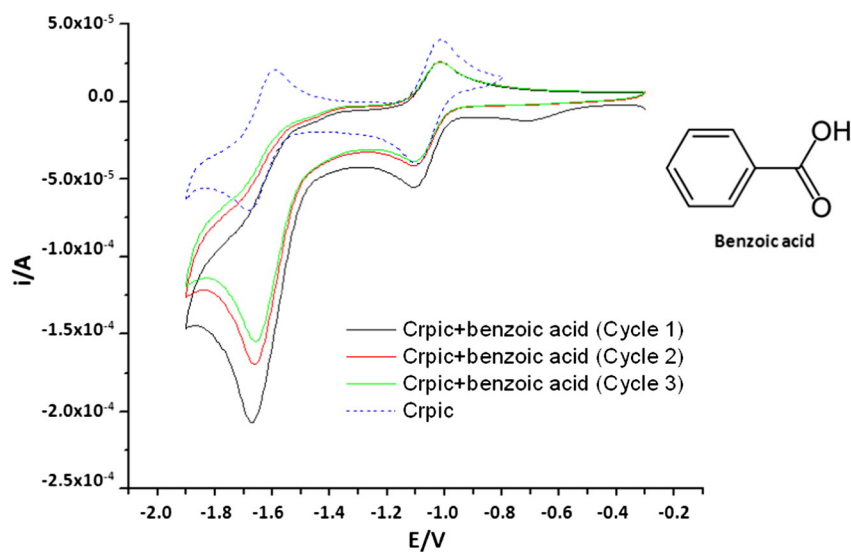

Fig. 4. Cyclic voltammograms of 1 mM Crpic (———); and 1 mM of Crpic + 1 mM benzoic acid to several cycles in DMF solution at 100 mV/s, 22 °C.
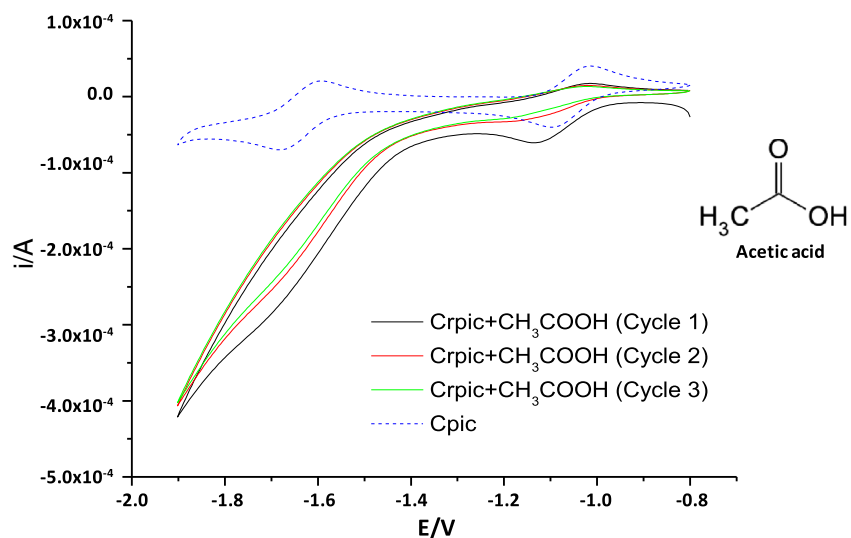

Fig. 5. Cyclic voltammograms of 1 mM Crpic (———); and 1 mM of Crpic + 1 mM acetic acid to several cycles in DMF solution at 100 mV/s, 22 °C.

Table 1
pKa of Crpic and Brønsted acids.

Brønsted acids	pKa ± 0.2 (DMF)[a]	pKa ± 0.2 (DMF)[b]	pKa (reported)
Chromium (III) picolinate, Crpic	8.9[a]	8.9[b]	---
Picolinic acid, Hpic	5.7[a]	13.0[c]	---
Benzoic acid	10.2[a]	12.1[b]	10.2 [9], 11.5 [5], 12,3 [32], 12.39 [33], 12.27 [34], 12.20 [35]: 12.28 [36], 12.27 [37]
Acetic acid	9.7[a]	13.5[b]	11.1 [9], 12.4 [5], 13.5 [32], 13.5 [34], 13.95 [38]

[a] $\Delta Ep = Ep2-Ep1$, where $Ep1$ is the peak potential of the original peak due to the first reduction of 1 mM Crpic and $Ep2$ is the peak potential of the new reduction peak of Crpic in the presence of 1 mM Brønsted acid.
[b] Considering irreversible electrochemical process in the presence of Brønsted acid.
[c] Considering Kim's model and before that chemical reaction finish.

complex occurs while a site is released in the complex. This vacant site could be occupied as the ligand a molecule of the solvent (DMF) [28] as the ligand picolinate, which would explain the presence of a second signal. This behavior is not observed with benzoic acid or with acetic acid, because none of them has a good coordinating capacity.

The appearance of a signal at more positive potential values, even before the first redox couple is characteristic of a strong strength acid, as benzoic acid, Fig. 4. The more positive potential signal may be related to hydrogen bond formation.

This irreversible behavior in the second redox couple can be attributed to an association with the complex and benzoate ion, similar to that reported by Astudillo [29,7,30].

Finally, Fig. 5 shows the complex electrochemical response of Crpic in the absence and presence of acetic acid. This system shows a behavior more difficult to understand, since both reversible redox couples are lost, and no signal was observed at higher potential values; therefore it does not behave as a weak acid either as a mild acid. However, according to the pKa value it is described as mild type. This measurement is affected by the presence of water in the solution.

In general, the ΔEp of the functional groups follow the following protonation order in DMF medium: amine > phenols > carboxylic acids [31]. The Brønsted acids studied in the presence of Crpic also follow the same tendency, as shown in Table 1.

The picolinic acid in the presence of Crpic has a pKa = 13.0 during the chemical reaction and pKa = 5.7 after the chemical reaction, then Kim's model must be established to set the time to determine it. This behavior is probably due to the presence of more than one functional group able of protonated, unlike other acids.

4. Conclusions

The linear mathematical model proposed by Kim [6] to determine the pKa of acids ΔEp based Brønsted was found to be applicable for complex chromium (III) with picolinic acid, because it involves two reversible redox couples in DMF at 22 °C, using GC as working electrode. In addition, the shown data support the reversible behavior of Crpic. The model fits the approximations and assumptions.

The model works when reversibility is evaluated in the presence of Brønsted acids with a functional group able of deprotonated or protonated as acetic acid, ascorbic acid or benzoic acid, however with picolinic acid probably it is important to set the time to determine pKa.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2015.07.019.

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