

Short communication

THE HETEROGENEOUS RATE CONSTANT FOR THE $\text{Ru}(\text{bpy})_3^{3+/2+}$
COUPLE AT A GLASSY CARBON ELECTRODE IN AQUEOUS SOLUTION

CHARLES R. MARTIN *, ISRAEL RUBINSTEIN and ALLEN J. BARD **

Department of Chemistry, University of Texas, Austin, TX 78712 (U.S.A.)

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INTRODUCTION

We report here the determination of the heterogeneous rate constant for the reaction



where bpy = 2,2'-bipyridine, at a glassy carbon electrode in aqueous 0.1 M H_2SO_4 . Our interest in this reaction is based on the widespread use of $\text{Ru}(\text{bpy})_3^{2+}$ in luminescence and photochemical studies [1-4], as well as previous investigations involving this species in chemiluminescent reactions in both nonaqueous and aqueous media [4,5]. Primarily we were interested in how the media affects the rate of this reaction. Although the heterogeneous rate constant, k^0 , has been determined in *N,N*-dimethylformamide (DMF) at a Pt electrode [6] as 0.24 cm s^{-1} , to our knowledge a k^0 value for aqueous solutions has not been reported. Our laboratory [7] and others [8] have also recently investigated the behavior of this couple in different polymers on electrode surfaces. An additional motivation for this study is the desire to establish certain reference redox couples whose standard potentials and kinetic parameters have been determined precisely in a number of solvents [9]. The high stability and solubility of both forms of the $\text{Ru}(\text{bpy})_3^{3+/2+}$ couple and the minimal structural change on electron transfer suggest that this couple might be useful as such a reference system. The k^0 of this couple was determined by both cyclic voltammetry and potential step chronoamperometry [10,11].

EXPERIMENTAL

A glassy carbon rod (Atomergic Chemical Co., Plainview, NY), sealed in a heat shrinkable Teflon tube, was used as the working electrode (geometric area = 0.079

* Present address: Department of Chemistry, Texas A&M University, College Station, TX 77843, U.S.A.

** To whom correspondence should be addressed.

cm²). Before use, the electrodes were sanded with 400- and then 600-grit silicon carbide paper and then polished with aqueous slurries of 1.0, 0.3, and 0.05 μm alumina powder on felt. The electrodes were then buffed on wet felt and stirred in ethanol for about 30 min. Immediately before use, the electrode was cycled ten times through the $\text{Ru}(\text{bpy})_3^{2+}$ wave. A conventional three-electrode cell with a parallel Pt foil auxiliary electrode and a saturated mercurous sulfate reference electrode (SMSE) was used. $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ was prepared from the chloride [5a]. The cell solution used throughout these studies was 1.0 mM $\text{Ru}(\text{bpy})_3^{2+}$ and 0.1 M H_2SO_4 and was deaerated with prepurified N_2 prior to use; all solutions were prepared in triply distilled water. Electrochemical measurements were performed with a Princeton Applied Research (PAR, Princeton, NJ) Model 173 potentiostat, Model 175 programmer and Model 179 digital coulometer. Current-potential curves were recorded on a Houston Instruments (Austin, TX) Model 2000 X-Y recorder or a Norland Model 3001 digital oscilloscope. Current-time transients were recorded on the Norland oscilloscope. Positive feedback was used to compensate for solution resistance. The extent of compensation was adjusted by applying a square wave (initial potential = 0.100 V, upper potential = 0.300 V, final potential = 0.100 V) of 20 ms duration to the cell and monitoring the resulting current transient on the Norland scope; only background currents (i.e., capacitive and residual faradaic) are observed over this potential range. The amount of compensation was increased until oscillations were observed in the current transient. The compensation value where oscillation was first observed was applied during the determinations of k^0 .

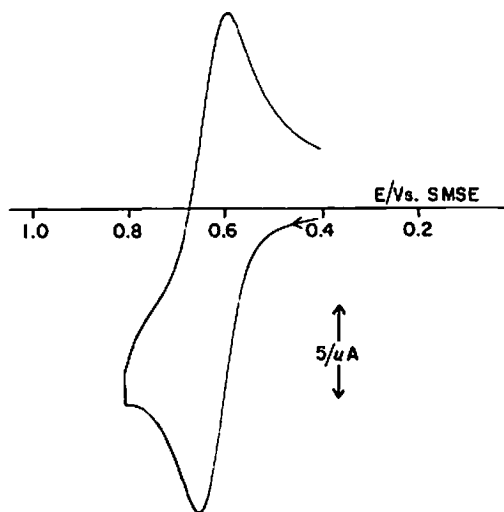


Fig. 1. Cyclic voltammogram for 10^{-3} M $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ in 0.1 M H_2SO_4 . Scan rate = 100 mV s^{-1} .

RESULTS

Cyclic voltammetry

A cyclic voltammogram (CV) for the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ is shown in Fig. 1. The oxidation of water at the glassy carbon commences at about 0.75 V vs. SMSE; this causes the flattening at the anodic current immediately following the anodic peak. A formal potential, E^0 , of 0.624 V vs. SMSE (corresponding to 1.27 V vs. NHE) was determined from CVs at slow scan rates, v (50–200 mV s^{-1}), where Nernstian behavior is observed. The diffusion coefficients obtained for the 2+ (D_R) and 3+ (D_O) forms from CV peak current vs. $v^{1/2}$ plots or from potential steps to values where Cottrell behavior [12] is observed are $D_R = 6.13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_O = 5.16 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. At higher scan rates the peak potentials are functions of v , and k^0 can be obtained from the variation of the difference between anodic and cathodic peaks, ΔE_p , with v [11], via the equation

$$k^0 = \psi [D_R \pi v (nF/RT)]^{1/2} / (D_R/D_O)^{(1-\alpha)/2} \quad (2)$$

where the ψ values are from the table given by Nicholson [11] and an α value of 0.4 (obtained from the potential step measurements discussed below) were used. Typical results are given in Table 1; an average k^0 value of 0.069 cm s^{-1} is obtained.

Potential step experiments.

Potential steps from a potential well negative of the foot of the CV wave, +0.4 V vs. SMSE, to potentials between 0.60 and 0.68 V yielded the $i-t$ transients (for times between 0.5 and 5 ms) shown in Fig. 2. These were fit to the equation [10]

$$i(t) = nFAk_a c^* \exp(H^2 t) \text{erfc}(Ht^{1/2}) \quad (3)$$

where

$$H = k_c/D_O^{1/2} + k_a/D_R^{1/2} \quad (4)$$

$$k_c = k^0 \exp[-\alpha nF(E - E^0)/RT] \quad (5)$$

TABLE 1

Kinetic data from cyclic voltammetric experiments

$v/\text{V s}^{-1}$	$\Delta E_p/\text{mV}^a$	ψ^b	$k^0/\text{cm s}^{-1c}$
100	134.8 ± 6.8	0.27	0.070
50	116.2 ± 3.7	0.38	0.070
20	9.7 ± 3.2	0.62	0.072
10	88.9 ± 2.0	0.82	0.068
5	81.0 ± 2.0	1.14	0.066

^a Error limits are \pm one standard deviation.

^b See ref. 11.

^c Assuming $\alpha = 0.4$ and D_R and D_O values presented in text.

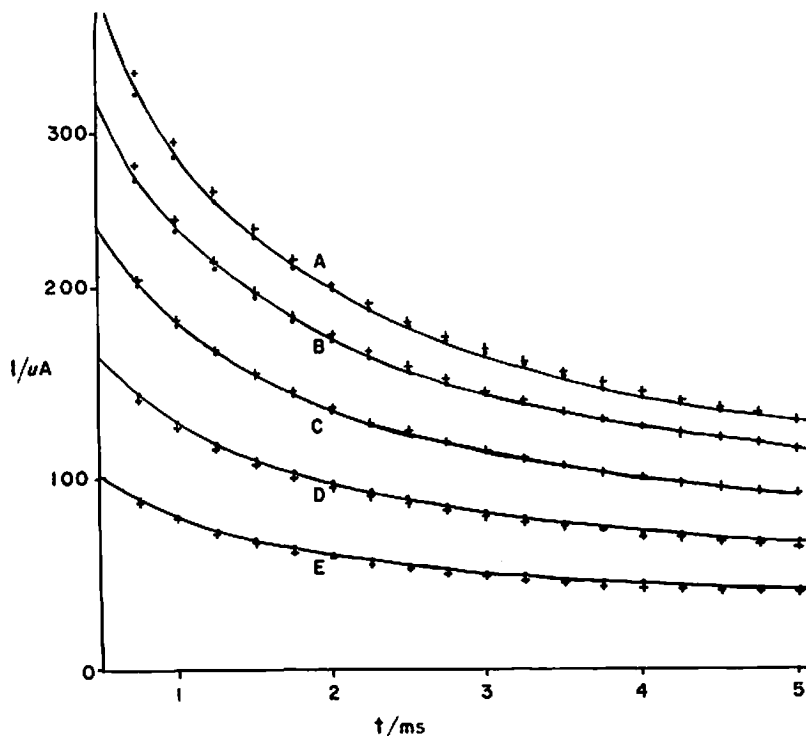


Fig. 2. Comparison of experimental (—) and simulated (+,●) current-time transients for steps from 0.400 V to (A) 0.680 V; (B) 0.660 V; (C) 0.640 V; (D) 0.620 V; and (E) 0.600 V vs. SMSE. (+) $\alpha = 0.5$; (●) $\alpha = 0.4$.

$$k_a = k^0 \exp\left[\frac{(1 - \alpha)nF(E - E^0)}{RT}\right] \quad (6)$$

with k_0 and α as adjustable parameters, C^* the bulk concentration of $\text{Ru}(\text{bpy})_3^{2+}$ and the E^0 , D_O and D_R values used in the CV experiments. The theoretical curves fit the experimental data with $k^0 = 0.06 \text{ cm s}^{-1}$ and $\alpha = 0.4$ (Fig. 2). An α value of 0.5 produces a somewhat poorer fit, although still probably acceptable within the experimental uncertainties of the measurement.

DISCUSSION

The k^0 found here in aqueous solutions, $0.065 (\pm 0.05) \text{ cm s}^{-1}$, is somewhat smaller than that reported in DMF at Pt, 0.24 cm s^{-1} [6]. This trend is generally what is expected for an outer sphere electron transfer with a greater solvation energy in water [13]. The reported homogeneous electron transfer for $\text{Ru}(\text{bpy})_3^{3+/2+}$ in aqueous solution, ca. $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [14], however, is larger than that in CD_3CN , $8.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [15]. An intercomparison of the aqueous heterogeneous and homogeneous rate constants, e.g., via the Marcus or Hush relations [13,16], is

difficult, because the double layer contributions at the carbon electrode are difficult to evaluate.

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