antibonding orbital, with the last having the largest overlap of the three. The overall effect is antibonding for π and bonding of course for σ plus π. Surprisingly, although the π overlap population is much larger in OF_2 than in O_3, in the former this bonding leads to virtually no charge redistribution in these orbitals, in contrast to O_3.

Our results therefore confirm the qualitative conclusion of the Xα calculation[1] that the high binding energy of the central oxygen 1s level is mainly due to charge migration into the bond; in particular, we have shown that π orbitals play a crucial role. The higher binding energy in ozone compared to oxygen difluoride appears to be due to ground-state effects, as reflected in the Koopmans' theorem energies. This is despite the fact that the calculated total charges are almost equal. Conflicts of this type have been observed previously and are usually resolved in favor of the Koopmans' theorem energies.[4] Comparison of our computed orbital energies with experimental binding energies for ozone suggests that the relaxation energy should be slightly greater for the central oxygen ionization; this conclusion, however, may have to be altered if it is shown that correlation energies contribute differently to the two binding energies. In this connection, it would be very interesting to carry out accurate configuration interaction calculations to determine the correlation energies for core ionization.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research under Grant No. AFOSR-77-3145 and in part by the National Science Foundation (Grant No. CHE-7918390). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Vanderbilt University Research Council for partial support of this research.

Optical Rotatory Dispersion Studies. 134.[1] Absolute Configuration and Circular Dichroism Spectrum of (R)-[2-$^2H_1$]Cyclopentanone. Demonstration of a Conformational Isotope Effect

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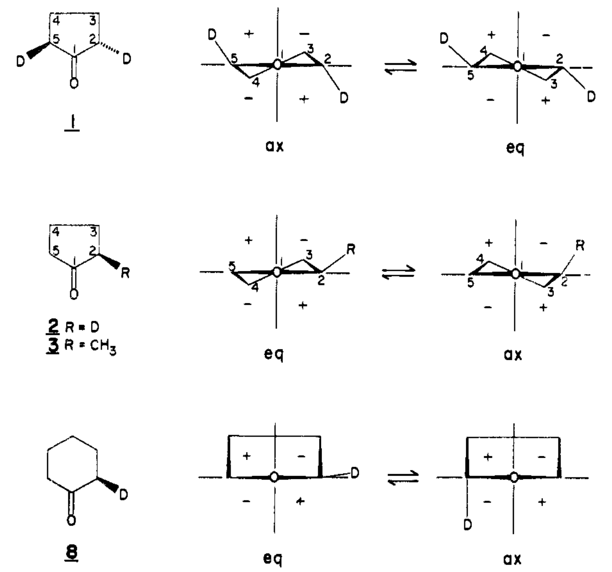
Abstract: The absolute configuration of (R)-[2-$^2H_1$]cyclopentanone is established through synthesis using as the key step chiral epoxidation with the Sharpless reagent. Its circular dichroism (CD) spectrum is unusual in that it exhibits a bisignate Cotton effect being negative at 310 and positive at 275 nm. From the interpretation on the variable-temperature CD measurements, the unexpected conclusion is reached that the twist conformation with the deuterium in the quasi-equatorial position is energetically preferred by ca. 10 ± 2 cal/mol. Evidently, even at room temperature, the contribution toward the spectrum resulting from the conformational isotope effect is of the same or larger amplitude but opposite sign compared to the difference between the partial octant contributions of an α-quasi-equatorial and α-quasi-axial deuterium substituent.

Introduction

Several recent publications[2] have been concerned with the determination of the octant contribution of a deuterium substituent toward the Cotton effect associated with the n → π^* transition of ketones. This work resulted in a consistent picture in cyclohexanones; i.e., deuterium was found to make a dissignate contribution in the α-axial and β-equatorial position and a much smaller consignate contribution in the α-equatorial and β-axial positions. Similar results were obtained for β-deuterium substitued cyclopentanones.[3] Therefore, it was surprising to note that α-deuterium substituted cyclopentanones apparently behave anomalously. Hine et al.[4] have reported that the chiral base-catalyzed α-deuterium exchange of [2,2,5,5-$^2H_4$]cyclopentanone yields optically active [2,5-$^2H_2$]cyclopentanone (**1**, Scheme I) which exhibits a positive Cotton effect. From considerations of the reaction mechanism the 2S, 5S configuration was assigned to this molecule. Dauphin et al.[5] obtained [2-$^2H_1$]cyclopentanone (**2**, Scheme I)

Scheme I



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[4] (a) Hine, J.; Li, W.-S. *J. Am. Chem. Soc.* **1975**, *97*, 3550-3551. (b) Hine, J.; Li, W.-S.; Zeigler, J. P. *Ibid.* **1980**, *102*, 4403-4409.

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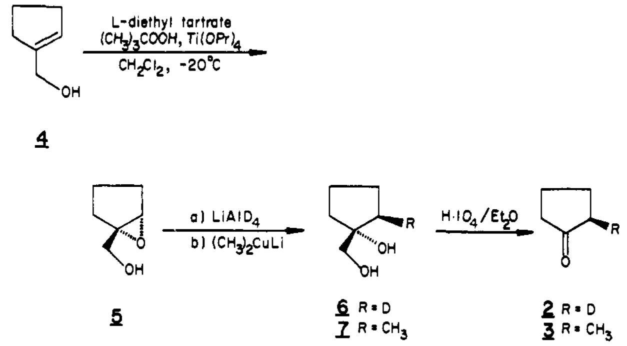
Scheme II



by enzymatic reduction of [2-$^2H_1$]-2-cyclopentenone and reported a negative Cotton effect for this compound. From analogous studies of the six-membered ring analog the *R* configuration was assigned to **2**. As pointed out by both authors, and explained in more detail below, these assignments are in disagreement with those one would have reached from the interpretation of the chiroptical data. Before searching for an explanation of this discrepancy, we considered it indispensable to establish the absolute configuration of **2** unambiguously through synthesis and to investigate its CD spectrum in more detail.

Synthesis

The method of asymmetric epoxidation of allylic alcohols, recently reported by Sharpless et al.,[6] provided a very convenient access to the desired [2-$^2H_1$]cyclopentanone (**2**) (Scheme II). Epoxidation of cyclopentene-1-methanol (**4**)[7] afforded optically active (−)-1,2-epoxycyclopentane-1-methanol (**5**) which was converted via ring opening with $LiAlD_4$[8] to the diol **6** and by subsequent cleavage with periodic acid in ether[9] to optically active **2**. The absolute configuration of **5** was established as 1*S*,2*S* through conversion to (*R*)-2-methylcyclopentanone (**3**) of known[10] absolute configuration by ring opening with $(CH_3)_2CuLi$[11] to the diol **7** followed by periodic acid cleavage. This assigment is in agreement with the observation made by Sharpless et al.[6] that, in the presence of L-diethyl tartrate, the epoxide invariably possesses the 1*S*,2*S* configuration. Since both the ring opening with $LiAlD_4$ and dimethylcopper lithium proceed via the same reaction mechanism (S_N2), it follows that **2** must possess the *R* configuration. The molar ellipticity ([θ]) of **3** was found to be ca. 20% larger than reported by Partridge et al.[10], who had assumed their product to be optically pure. Using the method of Mosher et al.,[12] the enantiomeric excess of **5** was shown to be >95%. Therefore, we conclude that the epoxidation proceeds with nearly complete enantioselectivity and that no racemization occurs during the reactions leading to **2** and **3**.

Result and Discussion

From the investigation of stereochemically rigid cyclohexanones[1,2c] it has been established that an α-equatorial deuterium substituent makes a small consignate ($\Delta[R] = 0.03$) and an α-axial deuterium a much larger dissignate ($\Delta[R] = 0.25$) contribution toward the Cotton effect of the C=O n → π^* transition. With these reference values the Cotton effect sign and amplitude of (*R*)-[2-$^2H_1$]cyclohexanone (**8**, Scheme I) could be predicted quite accurately[1] assuming that this molecule exists in a dynamic equilibrium between the two possible chair conformations (Scheme I). In order to apply a similar analysis to (*R*)-[2-$^2H_1$]cyclopentanone (**2**), two important differences between these molecules must be taken into consideration.

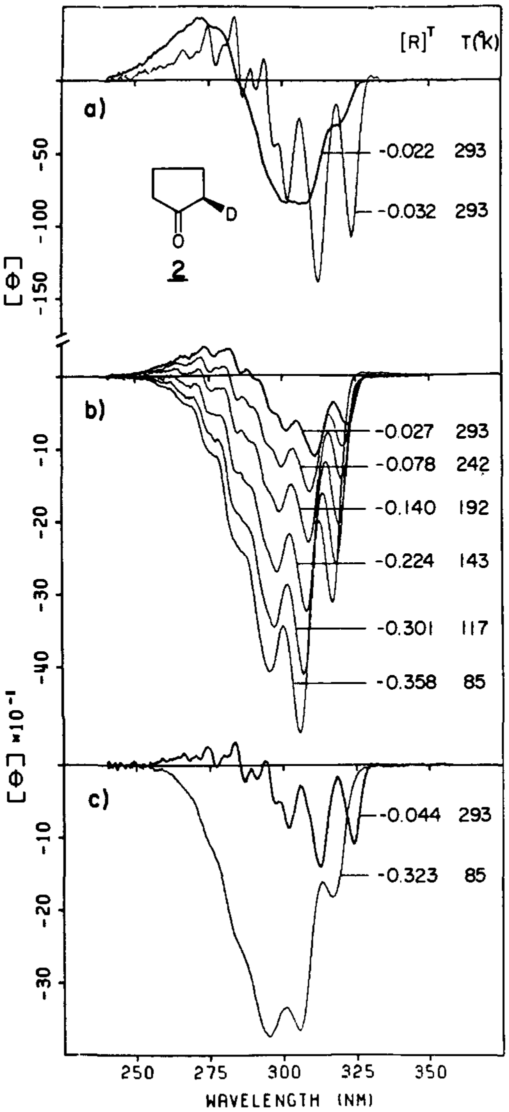


Figure 1. Circular dichroism spectra of (*R*)-[2-$^2H_1$]cyclopentanone (**2**) (a) in methanol (heavy line), *c* = 1.65 g/L, and isooctane (thin line), *c* = 2.42 g/L; (b) in EPA (ether–isopentane–ethanol 5:5:2), *c* = 2.39 g/L; and (c) in IPM (isopentane, methylcyclohexane 4:1), *c* = 1.04 g/L, at various temperatures between 293 and 85 K.

First, cyclopentanone is known[13] to exist in a conformational equilibrium between two twist conformations which, in contrast to cyclohexanone, possess large rotational strengths of opposite sign.[14] As a consequence, even a small conformational isotope effect, biasing the equilibrium toward one or the other side, could lead to an appreciable amplitude in the CD spectrum; we shall refer to this effect as a conformational contribution. Second, the partial octant contributions for an α-deuterium substituent are not identical in both ring systems as is obvious from a comparison of the angular relationships of the C–D bonds and the horizontal sector plane (see octant diagram representations for **2** and **8** in Scheme I). Nevertheless, it appears justified to assume that a

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Table I. Estimates for the Rotational Strength $[R]_{\mathrm{obsd}}$ of (R)-[2-$^2H_1$]Cyclopentanone (2)[a]

	experimental	from partial octant contributions[b]	CNDO/S[c]
$[R]_{\mathrm{ax}}$		$+[R]_{\mathrm{ring}} + 0.25$	$+7.35$[d]
$[R]_{\mathrm{eq}}$		$-[R]_{\mathrm{ring}} + 0.03$	-6.95
$[R]_{\mathrm{obsd}}$	-0.022 (methanol) -0.032 (isooctane)	$+0.14$	$+0.20$

[a] Estimates neglect any conformational contributions, i.e., $[R]_{\mathrm{obsd}} = 0.5\ ([R]_{\mathrm{ax}} + [R]_{\mathrm{eq}})$ where $[R]_{\mathrm{eq}}$ and $[R]_{\mathrm{ax}}$ are the rotational strengths of the conformers 2eq and 2ax respectively. [b] Values obtained from cyclohexanones (ref 2c). [c] The method of calculation is equivalent to the one employed by Lightner et al.[3c] The state wave functions were calculated by the QCPE 174 version of CNDO/S and the dipole-length formalism used for the calculation of the rotational strength. Atomic coordinates for cyclopentanone were taken from ref 13b and the C-D bond length foreshortened by 0.02 Å for the deuterium substituted conformers 2eq and 2ax. [d] For the twist conformation of cyclopentanone a rotational strength of ±7.08 was calculated as outlined in footnote c.

quasi-axial deuterium in cyclopentanone will give a larger and dissignate contribution as compared to its quasi-equatorial counterpart. This assumption receives support from CNDO/S calculations which have previously[3c] been shown to reproduce quite accurately the rotational strength of a variety of dueterium-substituted ketones. An α-quasi-axial deuterium substitution is calculated (Table I) to lead to a dissignate contribution of $\Delta[R] = 0.27$ vs. 0.13 for the α-quasi-equatorial position.

Neglecting then the presence of a conformational isotope effect, i.e., assuming a cancellation of the conformational contributions, a positive Cotton effect is predicted for **2** (Table I). By the same line of argument a negative effect would be predicted for **1** whose amplitude is expected to be twice that of **2**.

The CD spectra of **2** in methanol and isooctane are reproduced in Figure 1a. Two bands of opposite sign are observed in both solvents and the rotational strength (obtained through integration over both bands) is found to be negative. Although such bisignate CD spectra are not uncommon,[15] that is the first instance when such a behavior has been observed for a monoketone which owes its chirality solely to isotopic substitution. In view of the nearly unchanged intensity distribution in the polar and nonpolar sovlent, the presence of a solute–solvent equilibrium appears to be an unlikely explanation. Alternatively, since the observed spectrum results from the difference in the spectra of the participating conformers 2ax and 2eq (Scheme I) a difference in the intensity distribution among their vibrational components could lead to an unequal cancellation and thus to a bisignate CD spectrum. This interpretation is substantiated by the variable-temperature CD measurements whose results are shown in Figure 1b and 1c. In both the polar (EPA: ether–, isopentane–, ethanol) and nonpolar (IPM: isopentane–, methylcyclohexane) solvent systems, the rotational strength of the negative band increases with the concomitant disappearance of the positive one. This behavior, and in particular its similarity in both solvents,[16] is quite typical for the presence of a temperature-dependent conformational equilibrium. From an inspection of the octant diagram representations (Scheme I), we conclude that *the equilibrium is shifted toward the conformer of negative rotational strength* (*i.e.*, *2eq*) *on lowering the temperature.*

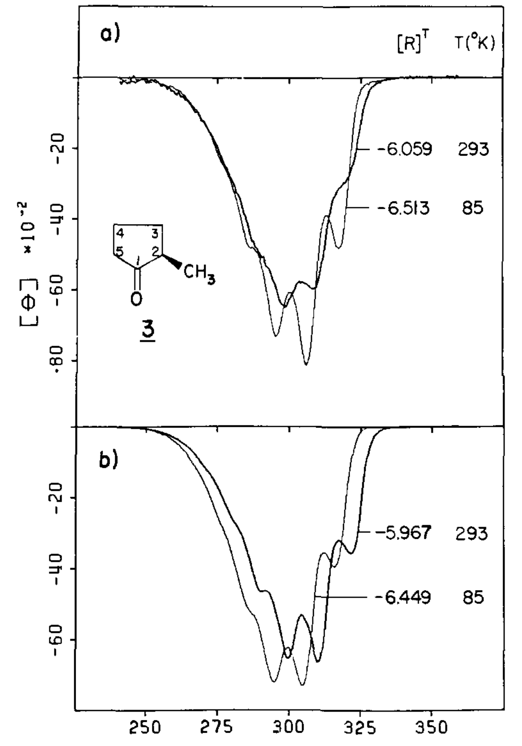

Figure 2. Circular dichroism spectra of (R)-2-methylcyclopentanone (**3**) (a) in EPA (ether–isopentane–ethanol 5:5:2) and (b) in IPM (isopentane–methylcyclohexane 4:1) at room temperature and 85 K.

This conclusion is surprising in light of our previous studies on conformational isotope effects in cyclic ketones where we have consistently observed that the conformation with the deuterium occupying the position of larger nonbond strain, i.e., axial in the β- and γ-substituted cyclohexanones[17] and quasi-axial in the β-substituted cyclopentanones,[3a,b] was of lower energy by ca. 2–7 cal/mol. That in cyclopentanone the α-quasi-equatorial position is of lower nonbond strain energy is demonstrated by the example of (R)-2-methylcyclopentanone (**3**) where already at room temperature the equilibrium 3eq ⇄ 3ax (see Scheme I) is shifted toward the conformation with the methyl group in the quasi-equatorial position (i.e., 3eq) as indicated by the relative small intensity change of the CD amplitude between 293 and 85 K in EPA and IPM (Figure 2a and 2b). We further point out that empirical force-field (EFF) calculations[3b,17] which assume smaller nonbonded interactions for deuterium compared to hydrogen predict 2ax to be of lower energy. Obviously the simple model of viewing deuterium to be of "smaller size" fails to provide an explanation for the energetic preference of 2eq. Although we do not wish to speculate about the physical origin of this unusual conformational isotope effect, it is nevertheless clear that the vicinal relationship between the C=O and C—D bonds must be a determining factor. Kirk[14b] has estimated the rotational strength of the twisted cyclopentanone to be $[R] = \pm 17$. Using this value and the $[R]^T$ values given in Figure 1b, the energy difference between 2ax and 2eq is calculated to be 10 ± 2 cal/mol.

Conclusion

The above outlined interpretation now offers an explanation for the previously cited difficulties in relating the Cotton effect sign of (R)-[2-$^2H_1$]-cyclopentanone (**2**) with its absolute configuration. In contrast to the equilibrium of (R)-[2-$^2H_1$]cyclohexanone (**8**),[1] the conformational contribution toward the CD spectrum of **2** cannot be neglected and, in fact, is opposite in sign and larger than the difference between the partial octant contributions of the quasi-axial and quasi-equatorial α-deuterium substituent, since, even at room temperature, the conformational

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(16) Although the change of rotational strength between 293 and 85 K is similar in both solvents (0.33 in EPA and 0.28 in IPM), a peculiar loss of vibrational fine structure associated with a rather large blue shift of 8 nm is observed in the nonpolar solvent mixture. A similar observation was made previously with the β-deuterium-substituted cyclopentanones (ref 3b), and we suggested that this unexpected behavior resulted from a solute–solute interaction.

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contribution $[R]_{\mathrm{conf}}$ is calculated to be −0.15 (corresponding to an equilibrium distribution of 50.43% **2**eq: 49.57% **2**ax). Our studies indicate that in situations where a molecule can assume conformations which possess large and oppositely signed rotational strengths, the presence of a conformational isotope effect can complicate the interpretation of the chiroptical data and lead to ambiguous conclusions with respect to the determination of absolute configurations.

Experimental Section

Circular dichroism spectra were recorded on a JASCO J-40 instrument using a previously described[18] cell for the low-temperature measurements. Absorption spectra were measured with a Hewlett-Packard HP 8450A UV–vis spectrophotometer. Optical rotations were determined on a Rudolf Autopol III polarimeter in a thermostated 10-cm cell using chloroform as solvent. Infrared (IR) spectra were recorded as neat liquid films between NaCl plates on a Perkin-Elmer 700A spectrometer. ^{1}H NMR spectra were obtained on a Varian T-60 spectrometer and given as δ values using deuteriochloroform as solvent and tetramethylsilane as internal standard. Mass spectra (MS) were obtained on a Varian MAT-44 spectrometer. High resolution mass spectra were determined by Ms. A. Wegmann on a Varian MAT-711 spectrometer; both instruments operated at 70 eV with a direct inlet system.

(1*S*,2*S*)-Epoxycyclopentane-1-methanol (5). Epoxidation of cyclopentene-1-methanol (**4**)[7] (9 g, 0.1 mol), using the modified procedure of Sharpless et al.,[6] gave after distillation 4 g (38% yield) of **5**: bp 52–53 °C (0.05 mm); $[\alpha]^{20}{}_{\mathrm{D}}$ −23.92° (0.054); IR 3175 cm^{-1}; ^{1}H NMR: 1.5–1.8 (m, 6 H), 3.46 (s, 1 H), 3.83 (d, 1 H, J = 14 Hz), 3.86 (d, 1 H, J = 14 Hz); MS m/z 114 (12, M$^+$), 97 (23), 96 (20), 86 (28), 83 (56), 71 (23), 70 (95), 67 (30), 57 (77), 55 (100); mol wt (calcd for $C_6H_{10}O_2$) 114.06807, found 114.0671.

(1*R*,2*R*)-[2-^{2}H$_1$]-1-Hydroxycyclopentane-1-methanol (6). Reduction of the epoxide **5** (2 g, 0.017 mol) with 2 g of $LiAlD_4$ in refluxing ether (12 h) gave 1.09 g (50% yield) of the diol **6**: IR 3175 cm^{-1}; ^{1}H NMR 1.63 (bs, 5 H), 3.36 (bs, 2 H), 3.56 (q, 2 H, J = 6 Hz); MS m/z 117 (28, M$^+$), 86 (100), 70 (53), 68 (50), 58 (30), 57 (30), 42 (48), 41 (40).

(1*R*,2*R*)-1-Hydroxy-2-methylcyclopentane-1-methanol (7). The epoxy alcohol **5** (1.16 g, 0.01 mol) was added to a solution of $(CH_3)_2CuLi$ (prepared from 7 g of cuprous bromide and 70 mL of 1.5 M methyllithium) in 150 mL of anhydrous ether. The reaction mixture was stirred at room temperature for 12 h. After workup and chromatography on silica gel using ether as eluting solvent, 0.5 g of **7** was obtained (37% yield); $[\alpha]^{20}{}_{\mathrm{D}}$ 26.6° (0.0225); IR 3175 cm^{-1}; ^{1}H NMR 0.9 (d, 3 H, J = 8 Hz), 1.4–2.3 (m, 7 H), 3.47 (d, 1 H, J = 14 Hz), 3.60 (d, 1 H, J = 14 Hz); MS m/z 130 (1, M$^+$), 99 (60, M − CH_2OH), 87 (15), 81 (40), 55 (40), 43 (100), 41 (40).

(*R*)-[2-^{2}H$_1$]Cyclopentanone (2). The diol **6** (234 mg, 2 mmol) in 0.5 mL of wet ether was added to a solution of 470 mg (2 mmol) of periodic acid in 10 mL of ether and the mixture stirred for 30 min at room temperature, then cooled to −20 °C and filtered over a small amount of silica gel. Evaporation of the ether followed by bulb to bulb distillation at 140 °C gave **2**: MS m/z 85 (55, M$^+$), 56 (50), 55 (82), 45 (42), 43 (40), 31 (100); isotopic purity 98%. Since the samples contained small amounts of ether, the concentrations for the CD measurements were determined from the absorption spectrum (ϵ_{278} 17.7 methanol, ϵ_{300} 17.2 isooctane): CD $[\theta]_{312}$, −139, $[\theta]_{285}$ 42 (isooctane); $[\theta]_{304}$ −84, $[\theta]_{272}$ 42 (methanol). Somewhat smaller values were reported by Dauphin et al.[5] for material prepared by enzymatic means: $[\theta]_{299}$ −55, $[\theta]_{274}$ 22 (ethanol).

(*R*)-2-Methylcyclopentanone (3). The periodide oxidation of **7** was performed as outlined for **2**. The concentrations for the CD measurements were determined from the absorption spectra (ϵ_{298} 17.9 isooctane, ϵ_{287} 19.3 methanol: CD $[\theta]_{297}$ −6040 (methanol), $[\theta]_{310}$ −6650 (isooctane). Other spectral properties (IR, ^{1}H, NMR) were identical with those of an authentic sample (Columbia Organic Chemicals Co., Inc., Columbia, Ohio) of racemic 2-methylcyclopentanone.

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Polymer Films on Electrodes. 5. Electrochemistry and Chemiluminescence at Nafion-Coated Electrodes

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Abstract: The electrochemical behavior of 10–15-μm thick films of the cation-exchange polymer Nafion on substrates of pyrolytic graphite, glassy carbon or platinum-containing $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) (or other cations) is described. The reaction of electrogenerated $Ru(bpy)_3^{3+}$ with oxalate dissolved in the solution leads to production of $Ru(bpy)_3^{2+*}$ and light emission. A model for the reaction scheme is proposed and digital simulation of the current–potential and current- and light emission–time curves allowed estimation of the rate constants for various processes and apparent diffusion coefficients of the species in the polymer film. The results provide information about the mechanism of excited-state production, with evidence for penetration of the polymer film by oxalate and also possible quenching of $Ru(bpy)_3^{2+*}$ by $Ru(bpy)_3^{3+}$.

In a recent communication[1] we described a new type of polymer-coated modified electrode, which consisted of pyrolytic graphite (PG) coated with a layer of Nafion ion-exchange polymer,[2] in which a large amount of $Ru(bpy)_3^{2+}$ (where bpy = 2,2′-bipyridine) was incorporated by electrostatic binding.[3] This modified electrode was shown to exhibit large oxidation–reduction waves for the attached $Ru(bpy)_3^{2+}$, to be exceptionally stable in aqueous solution, and to catalyze some oxidation reactions.

In aqueous solutions containing oxalate ions at pH ~6, switching the potential of this electrode to the $Ru(bpy)_3^{2+}$ oxidation

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