189. Photon-Triggered Complex Formation: Radical Complexes of *o*-Benzosemiquinone, Dopa, Dopamine and Adrenaline Formed by Electron-Transfer Reaction from Excited Tris(2,2′-bipyridyl)ruthenium(II)

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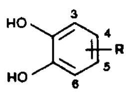
Summary

The pyrocatechol derivatives, dopamine (**2**), adrenaline (**3**) and L-dopa (**4**) form in their semiquinoid oxidation states complexes with several closed-shell metal ions like Zn^{2+}, Cd^{2+} and Y^{3+}. This complex formation can be triggered by visible light *via* a one-electron transfer reaction from the pyrocatechol derivative to $(^3CT)Ru(bpy)_3^{2+}$, which is thereby reduced (*Schemes 1* and *2*). The quenching of the triplet charge-transfer state, $(^3CT)Ru(bpy)_3^{2+}$ cannot be measured by conventional methods (*Stern-Volmer* plot), because the bimolecular electron-transfer rate is too slow ($k_q < 10^{-7} M^{-1} s^{-1}$). ESR. spectroscopy shows, however, clearly the paramagnetic reaction products. The concentration of these paramagnetic species is strongly enhanced by complex formation.

The hindered rotation of the side chain in L-dopa and in its Y^{3+}-complex is described within a two-jump model, which gives best agreement between calculated and measured spectra assuming an energy of 37 $kJmol^{-1}$ for the rotational barrier.

Introduction. – Metal complexes of free radicals have been prepared by various methods, such as generation by alkali-metal reduction [1] or using electrochemical techniques [2]. Oxidation by molecular oxygen has been used for the formation of *o*-semiquinone from pyrocatechol in basic solutions, in which complexes with various metal ions can be formed [3]. Semiquinones are very versatile ligands in radical complexes [4]. Recently, the generation of semiquinone radicals and their metal complexes by photolysis with UV. light has been described [5] [6]. Photolytic generation of the radicals takes place in these reactions through absorption of light in the hydroquinone (**1**) moiety H_2Q.



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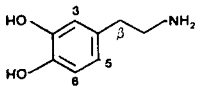

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1) Part of the dissertation to be submitted to the University of Fribourg.

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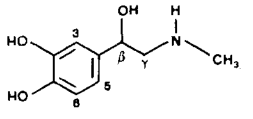
In this communication we report on the formation of radical complexes of *o*-semiquinone and its derivatives, particularly dopamine (**2**), adrenaline (**3**) and dopa (**4**).



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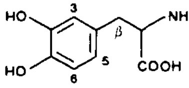

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The radicals and their complexes are generated by an electron-transfer reaction from the excited state of Ru(bpy)$_3^{2+}$ (= tris(2,2′-bipyridyl)ruthenium(II)). This new method of generating radical complexes can also be applied to several other ligands [7]. Contrary to the direct photolytic generation, it can be carried out with visible light. The basic mechanism can be formulated as given in *Equations 1–3*.

$$\mathrm{Ru(bpy)_3^{2+}} \xrightarrow[452\ \mathrm{nm}]{h\nu} \mathrm{(^3CT)Ru(bpy)_3^{2+}} \tag{1}$$

$$\mathrm{(^3CT)Ru(bpy)_3^{2+} + H_2Q \rightarrow Ru(bpy)_3^{+} + 2\,H^+ + Q^{\dot{-}}} \tag{2}$$

$$\mathrm{M^{n+} + Q^{\dot{-}} \rightarrow M(Q^{\dot{-}})^{(n-1)+}} \tag{3}$$

The ^{3}CT excited state of Ru(bpy)$_3^{2+}$ is sufficiently long-lived to undergo a bimolecular electron-transfer process with the hydroquinone according to *Reaction 2* [8]. The yield of *Reaction 2* depends strongly on the pH of the solution, which is primarily due to the cage-escape process [7]. The reactions are carried out in a flow system using aqueous solutions. Generation of the radicals and their complexes is accomplished by direct irradiation into the ESR. cavity. The fate of the reaction products is not known. Probably the back reaction to Ru(bpy)$_3^{2+}$ and H_2Q is the most important process; other products are formed slowly, however.

All the complexes formed with the semiquinone radicals have a 1:1 chelate structure where both O-substituents of the 'aromatic' ring are deprotonated. As in other radical complexes, the unpaired electron remains largely confined to the ligands.

Experimental. – *Materials. Pyrocatechol,* L-*3-(3,4-dihydroxyphenyl)alanine* (L-*dopa), 2-(3,4-dihydroxyphenyl)ethylammonium chloride (dopamine hydrochloride), 4-[1-hydroxy-2-(methylamino)ethyl]-pyrocatechol* (L-*adrenaline,* L-*epinephrine)* of the best commercial grade available *(puriss, Fluka)* were used without further purification.

Ru(bpy)$_3$Cl$_2$ · 6H$_2$O was kindly supplied by Dr. *P. Belser* of this laboratory.

Metal salts solutions were prepared with ZnCl$_2$ *(p.a., Merck)*, CdCl$_2$ · H$_2$O *(purum, Merck)*, Y$_2$O$_3$ *(puriss, Fluka)*. All other chemicals were of the best commercial grade available. Deionized water or D$_2$O was used to prepare the solutions.

Apparatus. The paramagnetic resonance spectra were recorded with a *Varian E9*-ESR.-spectrometer (X-Band: 9.6 GHz; *Varian E-101* microwave bridge) using a *Varian E-272B* field-frequency lock accessory, and a *Varian E-102* double cavity. The solution was pumped with a *Perpex JU/VAR II* peristaltic pump through a *Wilmad WG-814* ESR. flat cell (60 mm long × 10 mm wide × 0.25 mm internal depth) (see *Fig. 1*).

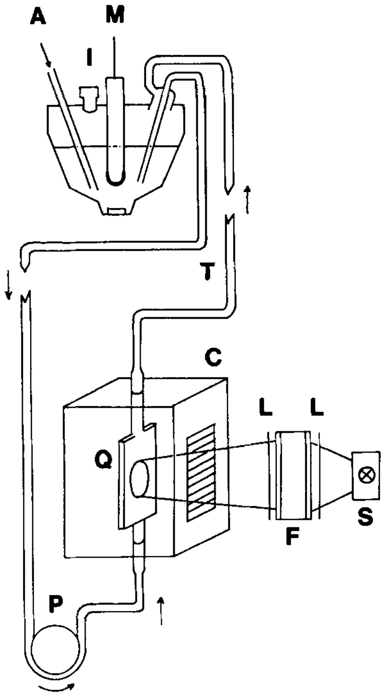


Fig. 1. *Schematic representation of the apparatus* (A: Ar-inlet, C: ESR.-X-band cavity, F: filter system, I: inlet, L: lenses, M: pH-meter, P: peristaltic pump, Q: ESR.-quartz flat cell, S: light source, T: silicone tubing)

Irradiation was performed with an *Oriel* model *6141* lamp-housing using a *Hanovia LS 179-000* 1000 Watt Xe high-pressure arc lamp and an *Oriel* model *8540* power supply. A modified liquid filter (10 cm length) containing a 10^{-2} molar aqueous solution of $Cu(edta)^{2-}$ was used. The transmittance of this filter and of a $Ru(bpy)_3^{2+}$-solution is given in *Figure 2*.

The pH of the solution was measured with a *Metrohm E-510* or *E-632* pH-meter and a *Metrohm EA 120* combined glass electrode.

Procedure. All experiments were carried out on freshly prepared solutions. The $Ru(bpy)_3^{2+}$ concentration was 10^{-3} M. The concentration of the pyrocatechol derivatives was in the range of 10^{-2} to 10^{-3} M. The solutions were buffered with acetic acid/sodium acetate (pH = 4.5–5.0) or sodium salt of 5,5-diethylbarbituric acid (*Veronal;* pH = 7.0–7.5). The pH-dependence was obtained by addition of 1 M NaOH to the reagents dissolved in 1 M HCl (pH = 0–2) or in a mixture of H_2SO_4, CH_3COOH and *Veronal* (pH = 1.6 to 9).

The metal salts were dissolved in acetic acid/sodium acetate buffer (0.05 M); their concentrations were 0.95 M (Zn^{2+}, Cd^{2+}) and 0.19 M (Y^{3+}); known amounts of these solutions were added during the experiments. The volume of the solution, before addition of metal ions or NaOH, was 50 ml (25 ml in D_2O). In all experiments Ar was continuously bubbling through the solution.

Unless otherwise stated, the flux of the solution was maintained at about 0.08 ml s^{-1} giving an average of speed of *ca.* 3 cm · s^{-1} in the flat cell.

Concentration measurement were carried out using *4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl* ($2 \cdot 10^{-4}$ M) as a reference sample in the double cavity. Second integrals were calculated using a *Varian 620 L* on-line computer.

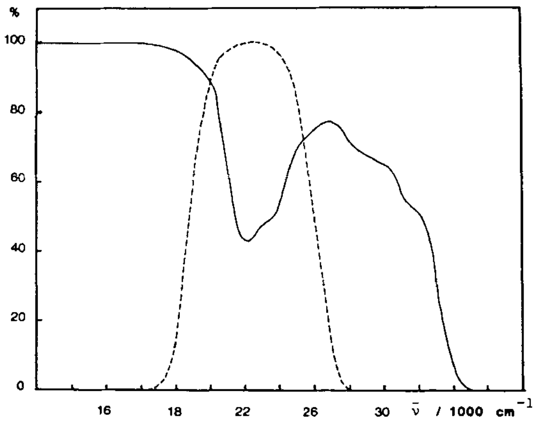


Fig. 2. *Transmittance of the solution of Ru(bpy)$_3^{2+}$ in the flat cell* (10^{-3} M; l = 0.025 cm) (full curve), *and of the filter solution* (Cu(edta)$^{2-}$; 10^{-2} M; l = 10 cm) (dashed curve)

Results and discussion. – Upon irradiation of a solution containing Ru(bpy)$_3^{2+}$, pyrocatechol or a substituted pyrocatechol, like dopamine or adrenaline at pH = 4.6 (acetate buffer), weak ESR. signals are observable. The wavelength of the radiation is chosen so that the Ru(bpy)$_3^{2+}$-complex is the only absorbing species among the starting materials. Indeed, no ESR. signal is observed in solutions with the same compositions, except that no Ru(bpy)$_3^{2+}$ is added. The pH-dependences of the strengths and the line shapes of the signals were determined for pyrocatechol and also for *p*-hydroquinone/*p*-quinone and pyrogallol. These findings will be reported elsewhere [7]. The acetate buffer has turned out to be the best compromise con-

Table 1. *Coupling constants (µT) of the semiquinone ligands and their metal complexes*

Ligand	M	pH	Coupling constants in µT						Ref.
			$a_{H(3)}$	$a_{H(5)}$	$a_{H(6)}$	$a_{H(\beta)}$		a_{other}	
Dopamine (**2**)	–	8.5	45	365	95	300			This work
	–	7	46	358	94	298			[9]
	Zn^{2+}	6.3	18	389	68	338			This work
	Zn^{2+}	5.5	16	388	67	336			[9]
	Cd^{2+}	7.6	22	380	71	326		$a(^{111}Cd) = 670$; $a(^{113}Cd) = 701$	This work
	Cd^{2+}	6	–	383	63	330		$a(^{111}Cd) = 688$; $a(^{113}Cd) = 658$	[9]
	Y^{3+}	7.0	16	393	63	344		$a(^{89}Y) = 65$	This work
Adrenaline[a] (**3**)	Zn^{2+}	4.7		383		330			This work
Dopa[b] (**4**)	–	7.8	51	358	93	187	336		This work and [5]
	Zn^{2+}	5.5	25	383	67	265	311	$a(^{67}Zn) = 140$	[5]
	Cd^{2+}	5.5	29	374	69	246	314	$a(^{111}Cd) = 681$; $a(^{113}Cd) = 713$	[5]
	Y^{3+}	6.1	20	393	64	290	300	$a(^{89}Y) = 65$	This work

[a] The ESR. spectrum of the free ligand is very weak and poorly resolved. A definite assignment was not possible. [b] See text for the simulation of the spectra.

cerning stability of the solutions and interference of complex formation with protonation and hydrolysis of the metal ions. The weak ESR. spectra can be attributed to the *deprotonated* semiquinoid form Q^{-} of pyrocatechol and its derivatives which are mainly present. The coupling constants which give the best fit between simulated and observed spectra are given in *Table 1.*

Addition of metal salts to the solutions increases strongly the concentration of the radical species in most cases and modifies at the same time the ESR.-hyperfine pattern. *Figures 3–6* show spectra of some radical species detected in irradiated solutions. All spectra can be attributed to the semiquinoid forms of pyrocatechol and its derivatives. Some spectra show metal hyperfine splittings, which are the ultimate proof of complex formation. The coupling constants are given in *Table 1.*

Mechanism of formation of the radical complexes. The formation of the semiquinones upon irradiation at the wavelength where $Ru(bpy)_3^{2+}$ absorbs is due to *Reaction 2.* Quenching of the excited state of $Ru(bpy)_3^{2+}$ by *p*-hydroquinone has been found earlier using flash photolysis [8] and emission measurements. The rate constant for the quenching of $(^3CT)Ru(bpy)_3^{2+}$ with pyrocatechol cannot be determined by luminescence measurements using the *Stern-Volmer* equation, because

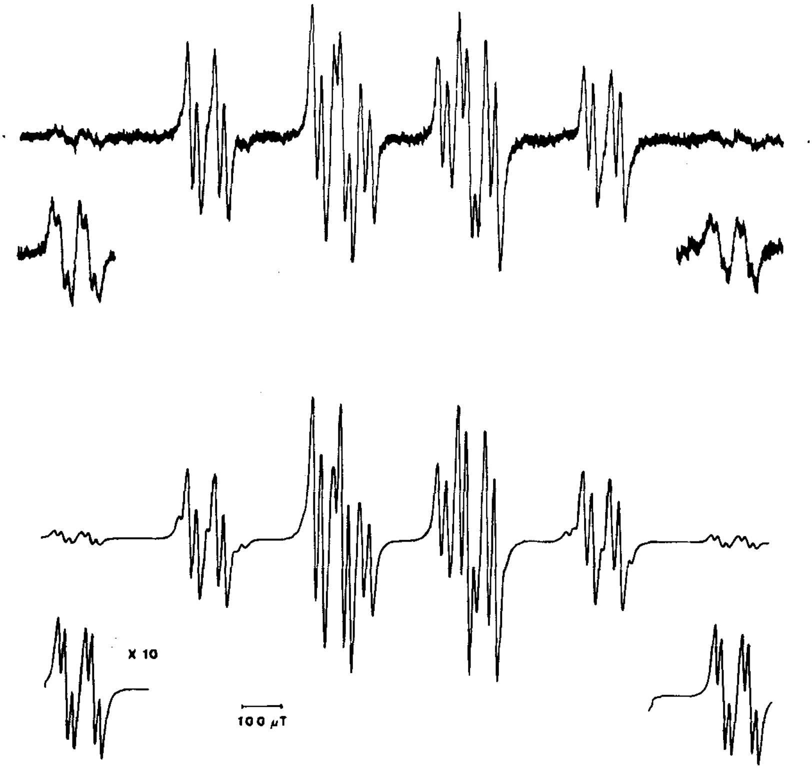


Fig. 3. *Measured and simulated spectra of the Cd^{2+}-dopamine-radical complex* (Satellites are due to the two isotopes ^{111}Cd and ^{113}Cd)

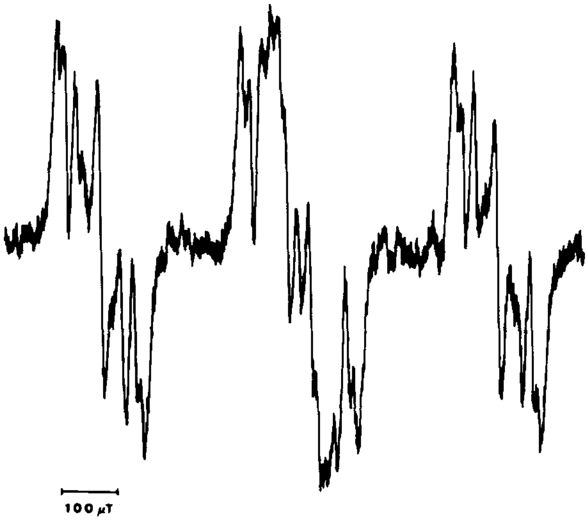


Fig. 4. *Experimental spectrum of the* Zn^{2+}*-adrenaline radical complex in* D_2O

k_q is too small ($k_q < 10^7\ \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$, which is in agreement with the value found for k_q of hydroquinone [8]). If it is assumed that pyrocatechol and hydroquinone follow the same order in the photochemical reaction as in the thermal oxidation with $Fe(phen)_3^{3+}$ (= tris(1,10-phenanthroline)iron(III) [10] the former should be 10 to 100 times slower.

The quenching of $(^3CT)Ru(bpy)_3^{2+}$ is probably only due to the uncomplexed H_2Q because Zn^{2+} is complexed by Q^{2-} to a very small extent only at pH = 5. According to the findings of *Darwent & Kalyanasundaram* [8], the probability of escape for the semiquinone from the cage $[Ru(bpy)_3^+ \text{ - - - } H_2Q^+]$, which exists immediately after electron transfer *(Scheme 1, step 3)* is quite high *(Scheme 1, step 4)*. The relative rates of *steps 3* and *4, i.e.* back reaction in the cage *vs.* cage escape has been shown to be relatively favorable for hydroquinone [8] so that $Ru(bpy)_3^+$ could easily be detected by flash photolysis. This escape is accompanied by a double deprotonation of the strong acid H_2Q^+ [11], yielding the semiquinone anion.

ESR. spectroscopy allows for the detection of the semiquinone radical, whereas from the species $Ru(bpy)_3^+$ no signal is obtained presumably because of very large line-widths of the ESR.-solution spectra and/or a very small stationary concentration under the present conditions. The most probable route for the back reaction is the reaction *step 5, i.e.* the reoxydation of $Ru(bpy)_3^+$ by Q^{-}, followed by a very fast protonation of the strong base Q^{2-}. Another possibility would be an intermediate disproportionation of the semiquinone anion to quinone and hydroquinone, which can be fast too. There are much slower reactions, which could change the composition of the solution irreversibly, like *e.g.* the evolution of H_2 from $Ru(bpy)_3^+$ and H_2O. This step is, however, not very efficient unless it is catalyzed.

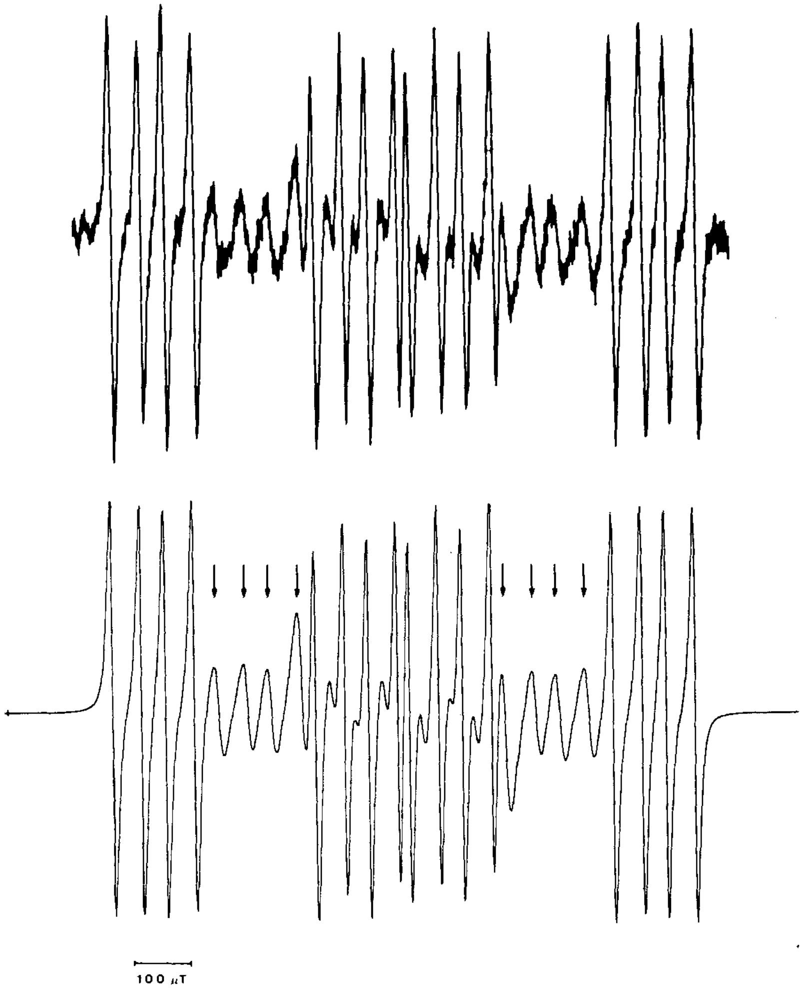


Fig. 5. *Measured and simulated spectra of the* L-*dopa radical* (Clearly visible selectively broadened lines are indicated by arrows)

Steps 1, 2 and *3* are not influenced by the addition of a metal ion, whereas *step 5* is slowed down considerably, if M^{2+} forms a stable complex with Q^{-} (see *Scheme 2*). The route *via the steps 6* and *7* is then a much slower back reaction than *step 5*, partly, because two cations react together and partly because of the change of the red/ox potential of Q^{-} upon complex formation.

The present discussion of the reaction mechanism is only qualitative, yet. Preliminary kinetic measurements using effect-modulated ESR. have given indications, however, that the reaction *Schemes 1* and *2* represent the essential features of the system. More detailed measurements are in preparation.

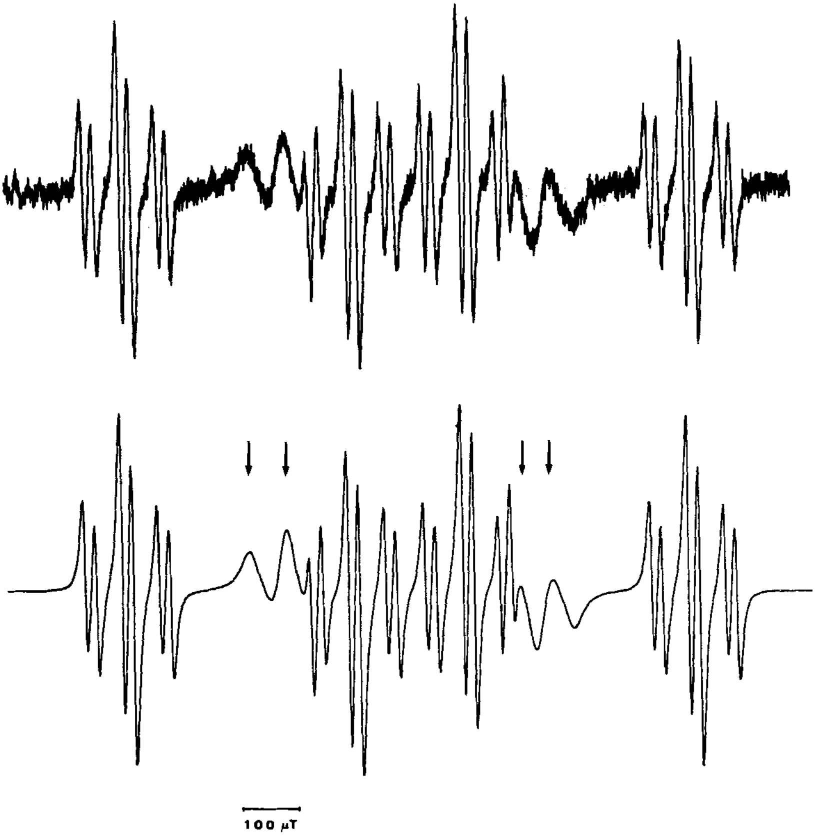
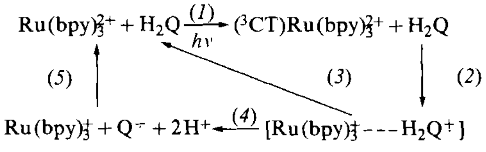


Fig. 6. *Measured and simulated spectra of the Y^{3+}-(L-dopa)-radical complex* (Clearly visible selectively broadened lines are indicated by arrows)

Electronic structure of the radical complexes. Coupling constants can be accurately measured for a series of complexes, since the formation of the radical complexes increases the photostationary concentration of the radical species considerably. *Table 1* gives all constants derived from interpretations using simulations of the isotropic spectra. The various ligands behave in the following way.

o-*Benzosemiquinone.* The coupling constants observed are all in excellent agreement with the values found earlier in radical complexes generated in a dif-

Scheme 1



Scheme 2

$$\begin{tikzcd}
\mathrm{Ru(bpy)_3^{2+}} + \mathrm{H_2Q} + \mathrm{M^{2+}} & & \mathrm{Ru(bpy)_3^{+}} + \mathrm{Q^{\cdot-}} + 2\mathrm{H^+} + \mathrm{M^{2+}} \arrow[ll, "(5)"'] \arrow[dl, "(6)"] \\
& \mathrm{Ru(bpy)_3^{+}} + \mathrm{M(Q^{\cdot-})^+} + 2\mathrm{H^+} \arrow[ul, "(7)"] &
\end{tikzcd}$$

ferent way. There can be no doubt, that the assignment given in *Table 1*, which corresponds to the one used earlier, is correct. It corresponds to the interpretation given by *Eaton* [3], *Kuwata et al.* [12] and more recently by *Felix & Sealy* [6], and it confirms some recent results of quantum chemical calculations [13]. We have shown earlier, that the coupling constants in coordinated *o*-benzosemiquinone are always of the same order of magnitude, even in substituted *o*-semiquinones [14].

L-*Dopa-semiquinone.* The observed coupling constants for the free ligand are in good agreement with the values reported by *Felix & Sealy* [5]. The values for the Y^{3+}-complex are reported for the first time. The near identity of the coupling constants of the metal nuclei in the complexes of L-dopa-semiquinones as compared to *o*-benzosemiquinone indicate that the spin densities on the ligand O-atoms is equal in both ligands, since it has been shown that the isotropic metal hyperfine coupling is almost exclusively due to a spin polarization effect from ligand atoms and not to a delocalization onto the metal. These findings can be generalized to the other ligands discussed below. It seems therefore that the side chain in position 4 has no effect on the spin density at the ligand O-atoms. All spectra clearly show the effect of the hindered rotation of the side chain described by *Felix & Sealy* [5]. The magnetic inequality of the two β-protons can be taken into consideration in a simulation program for a two-jump process. *Figures 5* and *6* show the experimental and the simulated spectra of the free ligand and its Y^{3+}-complex, respectively. The simulation is based on the assumption of an energy minimum for the conformation of the side chain corresponding to the one found in the crystalline solid [15]. The angles of the two $C(\beta)$,H-bonds with respect to a line which is perpendicular to the plane of the 6-membered rings are 81.3° and 39.6°, respectively *(Fig. 7)*. Using the relation $a_H = 9.64 \cdot \cos^2\theta$, [5] coupling constants of 22 and 572 μT are obtained. If it is further assumed that the coupling constants in the limit of fast rotation is given by an average *(Eqn. 4)* of the coupling constants between the crystal conformation (A) and another one (B) with similar energy, then the calculation can be performed.

$$a_{\text{fast}} = 1/2\,(a_A + a_B) \tag{4}$$

a_A and a_B are the coupling constants corresponding to these two conformations. Their values are reported in *Table 2.*

The following scheme obtained for the four lines due to the two protons is shown in *Figure 8.*

Since $\delta H(1) < \delta H(2)$, the modulation due to the hindered rotation is much more effective for the $(+,-)$ and $(-,+)$ combinations than for $(+,+)$ and

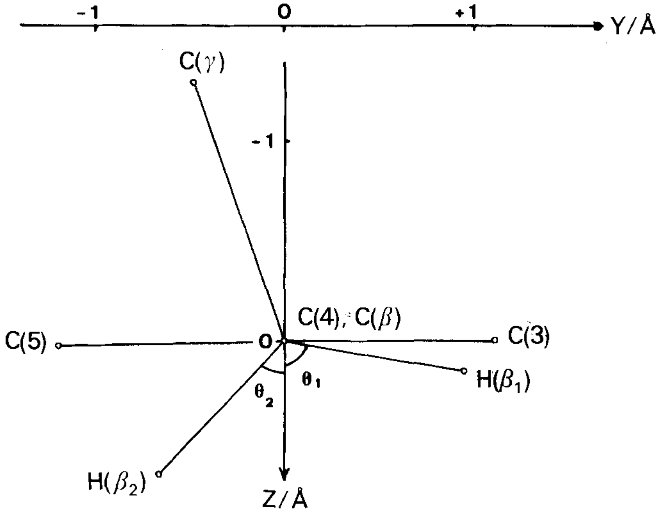


Fig. 7. *Projection in the* yz-*plane of a part of dopa, according to the X-ray analysis* (The origin is fixed at the C(4). The 0x-axis is defined by the C(4),C(β)-bond. The *yz*-plane is defined by the atoms C(3), C(4) and C(β))

Table 2. *Coupling constant* (μT), *exchange rates* (22°) *and conformational parameters for the β-protons in* L-*dopa radical and its* Y^{3+}-*complex*

Radical	Configuration	a_H	a_H	θ_1	θ_2	$\log(k_{ex}/s^{-1})$
L-Dopa	A	22	572	81.3°	39.6°	
	B	352	100	52.8°	71.2°	
	[a]	187	336			7.82
Y^{3+} (L-Dopa)	A	22	572	81.3°	39.6°	
	B	558	28	45°	89.1°	
	[a]	290	300			7.95

[a] Fast exchange.

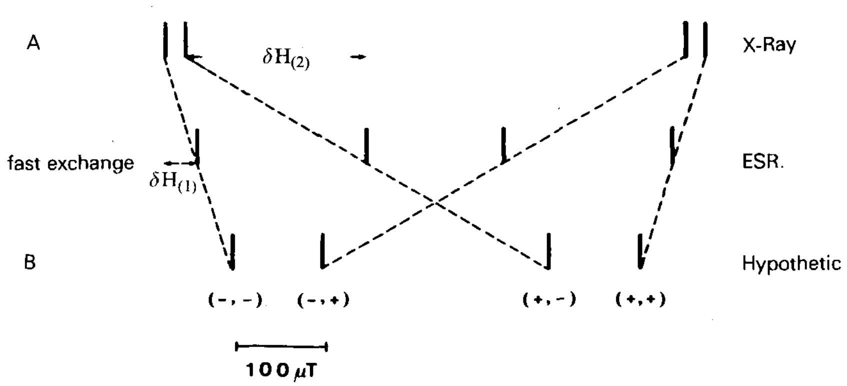


Fig. 8. *Stick diagram of ESR. spectra corresponding to the conformations used for the simulation of the spectrum of dopa-semiquinone*

(–, –), respectively. The data for the dynamical process obtained by the simulation is given in *Table 3*. The activation energy for the two-jump process thus determined is 37 kJmol^{-1}. This is in good agreement with theoretical results obtained for similar systems [16]. In the case of the Y^{3+}-complex of the L-dopa radical similar phenomena of selective line-broadening can be observed as in the free ligand. Because no structural data on a metal complex of the ligand are known, the assumption of values for the coupling constants in the limiting cases of rigid conformations becomes even less certain than in the free ligand. Nevertheless the spectra can be simulated using the model of a two-jump process *(Fig. 5)*. The data set used for this simulation is given in *Table 2*.

Table 3. *Temperature-dependence of the exchange parameters in* L*-dopa radical* (I_b/I_n is the ratio of the signal amplitudes of the broadened and the narrow lines; k_{ex} is the exchange rate constant between the two conformations A and B)

T/°C	$\log(k_{ex}/s^{-1})$	I_b/I_n calc.	I_b/I_n obs.	Ref.
20	7.69	0.14	0.14	[5]
22	7.82	0.21	0.21	This work
28	7.94	0.29	0.29	[5]
55	8.44	0.63	0.62	[5]

Dopamine-semiquinone. This radical and its metal complexes are reported. The coupling constants indicate a similar spin distribution as in the other semiquinone complexes. The effect of 'pushing away' spin density from the atoms close to the metal is also clearly seen in these complexes. The radical concentrations are of the same order of magnitude as in the case of pyrocatechol. The stabilization of the radical by complex formation is particularly high with this ligand. *Figure 3* shows the measured and the simulated spectra of the Cd^{2+}-complex.

L-*Adrenaline-semiquinone.* To our knowledge this radical and its metal complexes have not been observed in aqueous solution. The photostationary concentration of the free ligand is exceedingly low, *i.e.* near the detection limit of the instrument. The enhancement due to metal ions is, as in the other cases, quite strong and those signals are therefore more easily observable. *Figure 4* shows the spectrum of the Zn^{2+}-complex in D_2O as solvent. Essentially the same spectrum is observed in H_2O, but the line-width is somewhat larger in the latter solvent. The resolution of the hyperfine lines is, even in D_2O, not quite sufficient to allow for a complete assignment of the coupling constants. The set of constants given in *Table 1* is therefore incomplete. *Stegmann et al.* [17] recently published a radical complex obtained by autoxidation of adrenaline in the presence of organothallium compounds in organic solvents. These authors attribute the smallest observed splitting constant of 25 μT to a coupling with a second Tl-atom bound to the OH-group in the side chain. Since we observe an identical coupling in the Zn-complex, we attribute it to a proton hyperfine splitting. This cannot be the OH-proton in the side chain, because the splitting is also observed in D_2O. The most probable explanation is a coupling due to one of the γ-protons, which are magnetically nonequivalent due to the position adjacent to an asymmetric C-atom. Whether the side chain has a rigid conformation, as claimed by *Stegmann et al.* [17], cannot be decided on grounds of the ESR. spectra of these complexes.

These solutions show other signals with different *g*-values after prolonged irradiation. At least two other, as yet unidentified radical species are formed upon irradiation in slow secondary reactions.

As a conclusion, it can be stated that the Ru(bpy)$_3^{2+}$-sensitized photolysis of hydroquinones is a clean method for the production of semiquinone radicals. Subsequent formation of metal complexes can stabilize the radical species to a large extent suppressing thereby the back reaction. The study of the ESR. spectra can yield substantial information about the mechanism of the formation of such complexes and their electronic structure.

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