Equilibrium and Kinetic Parameters of the Oxygenation Reaction of Oxygen Carriers. Conformational Effects in Cobalt(II) Schiff-base Chelates derived from Salicylaldehyde and Substituted Ethylenediamines

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Steric and conformational effects on the reversible oxygenation reaction in pyridine solutions of cobalt(II) chelates with Schiff bases obtained from salicylaldehyde and 1,2-disubstituted ethylenediamines have been studied. The equilibrium and reaction rate constants have been determined by polarographic methods. The results suggest that the oxygenation reaction is hindered by folding of the chelate induced by the steric requirements of the substituents of the ethylenediamines.

INVESTIGATIONS of inorganic models of the active sites of metallo-enzymes and -proteins are of current interest for the identification of factors influencing the mechanisms of enzymatic reactions. As the knowledge of the three-dimensional molecular structures of naturally occurring molecules gives more information about the functional groups involved in such reactions and about the structure surrounding the reactive site, it becomes necessary to design and investigate more sophisticated models in order to test more subtle influences on the reactivity.

A number of transition-metal chelates which can be considered as models of biological oxygen carriers has been studied.[1] The cobalt(II) chelates are particularly suitable as reversible oxygen carriers, while the corresponding iron(II) chelates generally undergo irreversible oxidation. The electronic factors influencing the 1 : 1 adduct formation by cobalt chelates have been determined from the correlation between the equilibrium constant for reversible oxygenation and the nature of the axial ligand *trans* to the dioxygen bonding site.[2]

A substantial step toward understanding of oxygenation in haemoglobin and myoglobin resulted from work on some peculiar model iron chelates: the behaviour of these 'picket-fence' porphyrins[3] and capped porphyrins[4] showed how bulky substituents on the macrocycle can prevent the formation of a 2 : 1 adduct and hinder irreversible oxidation. On the other hand, conformational changes are likely to be responsible for even more important effects in allosteric phenomena.[5]

Ugo and co-workers[6] have investigated a series of diastereoisomeric chelates (L) of cobalt(II) with quadridentate ligands obtained from salicylaldehyde and 1,2-disubstituted ethylenediamine (Figure 1 and Table 1). The crystal and molecular structures of some of these complexes, $[Co^{II}L]$, and of their monopyridine derivatives, $[Co^{II}L(py)]$ was subsequently determined.[7-9] The equilibrium constant of the reaction (1) in pyridine solution was also reported. The K_{O_2} values were obtained by spectroscopic and manometric measurements, but in some cases the absorption of dioxygen was found to be greater than required by the stoicheiometry,[1] suggesting irreversible oxidation.[10] It was thus necessary to try some other approach to the determination of the reaction parameters.

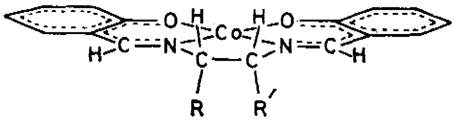
$$[Co^{II}L(py)] + O_2 \xrightleftharpoons{K_{O_2}} [Co^{II}L(py)(O_2)] \quad (1)$$

In the present paper we report the equilibrium and rate constants for reaction (1) as calculated from the characteristics of polarographic waves due to the oxidation process $Co^{II} \longrightarrow Co^{III}$ in the presence of dissolved molecular oxygen, where the electron transfer is preceded by the dioxygenation reaction, and to the reduction process $Co^{III} \longrightarrow Co^{II}$, where it is followed by the oxygenation reaction as in (2). The cobalt chelates investigated are specified in Table 1.

$$\begin{tikzcd}
{[Co^{III}L(py)]^+} \arrow[d, shift left, "+e"] & \\
{[Co^{II}L(py)] + O_2} \arrow[u, shift left, "-e"] \arrow[r, shift left, "k_1"] & {[Co^{II}L(py)(O_2)]} \arrow[l, shift left, "k_{-1}"] & (2)
\end{tikzcd}$$

TABLE 1

Complexes studied, $[Co^{II}L]$



$[Co^{II}L]$

L	R	R′
NN′-Ethylenebis(salicylideneiminate), salen	H	H
NN′-Propane-1,2-diylbis(salicylideneiminate), sal(+)pn	H	CH_3
NN′-1-Phenylethylenebis(salicylideneiminate), sal(−)pen	H	C_6H_5
NN′-Butane-2,3-diylbis(salicylideneiminate), sal(+)bn or sal(*m*)bn	CH_3	CH_3
NN′-1,2-Diphenylethylenebis(salicylideneiminate), sal(+)dpen or sal(*m*)dpen	C_6H_5	C_6H_5
NN′-1,2-Cyclohexylenebis(salicylideneiminate), sal(+)chxn or sal(*m*)chxn	$-(CH_2)_4-$	

RESULTS

Polarography of [Co^{II}L] *Complexes in Oxygenated Pyridine Solution at* 0 °C.—The polarographic behaviour of [Co^{II}L] complexes has been reported previously.[11] In oxygenated pyridine solution (where it is assumed that one molecule of pyridine is co-ordinated to cobalt) characteristic changes are observed due to the formation of the 1 : 1 oxygen adduct. In addition to the *anodic* wave in the range −0.1 to −0.4 V *vs.* the saturated colomel electrode (s.c.e.) due to the process (3), a new *cathodic* wave appears in the range

$$[\mathrm{Co^{II}L(py)}] \xrightarrow{-e} [\mathrm{Co^{III}L(py)}]^+ \qquad (3)$$

−0.6 to −0.7 V *vs.* s.c.e. (Table 2) which is attributed to the reduction of the oxygen adduct [12] [equation (4)]. The

$$[\mathrm{Co^{II}L(py)(O_2)}] \xrightarrow{+e} [\mathrm{Co^{II}L(py)(O_2)}]^- \qquad (4)$$

dependence of the height of the reduction wave on P_{O_2} for a given [Co^{II}L] concentration allows a Hill plot to be drawn and the equilibrium constant for reaction (1) to be obtained, as reported for [Co^{II}(salen)].[13] This method was found to be convenient when the oxygenation equilibrium is rapidly established and there are no side reactions.

TABLE 2

Polarographic half-wave potential ($E_{\frac{1}{2}}$/V) for [Co^{II}L] complexes and their oxygen adducts in py–[NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}) at 0 °C [a]

[Co^{II}L]	$E_{\frac{1}{2}}$ Co^{II} ⟶ Co^{III}	Co^{II} ⟶ Co^{I}	[Co^{II}L(O$_2$)] ⟶ [Co^{II}L(O$_2$)]$^-$
O$_2$ ⟶ O$_2^-$			−0.860
[Co(salen)]	−0.395	−1.382	−0.705
[Co{sal(±)pn}]	−0.357	−1.320	−0.650
[Co{sal(±)pen}]	−0.361 [b]	−1.305	−0.642
[Co{sal(±)bn}]	−0.364	−1.324	−0.700
[Co{sal(*m*)bn}]	−0.285	−1.375	−0.710
[Co{sal(±)dpen}]	−0.351 [b]	−1.261	−0.664
[Co{sal(*m*)dpen}]	−0.163 [b]	−1.290	−0.595
[Co{sal(±)chxn}]	−0.360	−1.420	−0.651
[Co{sal(*m*)chxn}]	−0.253	−1.370	−0.604

[a] Determined for all chelates under the same experimental conditions. Values are estimated to be accurate to within 3 mV and represent a correction of values reported earlier.[11] [b] Quasi-reversible.

In the oxygenated solution the only *anodic* wave observed at the potential of Co^{II} ⟶ Co^{III} oxidation is displaced toward more positive values by increasing P_{O_2} but logarithmic analysis of the wave still indicates a reversible one-electron transfer. The limiting current decreases and acquires a kinetic character (Figure 1). The slope of the log i against log t plot was found to be 0.22 for $P_{O_2} = 0$ (diffusion-controlled current) and 0.36—0.46, depending on the complex, for $P_{O_2} = 760$ Torr * (kinetic process). As the anodic wave in oxygenated solution is due to the process (3) the [Co^{II}L(py)] species electroactive in this potential range can only be generated by dissociation of the 1 : 1 O$_2$ adduct, *i.e.* by a chemical reaction preceding the electron transfer.

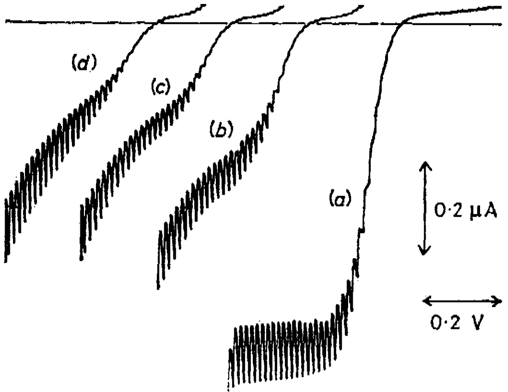


FIGURE 1 Dependence of the anodic wave on P_{O_2} for [Co{sal(±)pn}] (1.76 × 10^{-3} mol dm^{-3}) in py–[NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}) at 0 °C; each curve starts from 0.0 V *versus* s.c.e.: (*a*) deoxygenated solution; (*b*) $P_{O_2} = 310$; (*c*) $P_{O_2} = 480$; (*d*) $P_{O_2} = 760$ Torr

This diffusional problem was solved by Koutecky.[14] The calculation is carried out using the relation (5) where ρ =

$$\frac{i_k}{i_d - i_k} = 0.886\sqrt{\frac{\rho t_1}{\sigma}} \qquad (5)$$

k_{-1} is the rate constant for the formation of the electroactive species, σ is the ratio of the concentrations of the electroinactive and electroactive forms, i_d is the mean

$$\sigma = [\mathrm{Co^{II}L(py)(O_2)}]/[\mathrm{Co^{II}L(py)}] = K_{O_2}P_{O_2} \qquad (6)$$

diffusion current, i_k is the mean kinetic current controlled by the rate of the preceding chemical reaction, and t_1 is the drop time of the dropping mercury electrode (d.m.e.). Introducing the equilibrium constant K_{O_2}, equation (5) may be rewritten as (8). As required by this equation, a plot of

$$K_{O_2} = [\mathrm{Co^{II}L(py)(O_2)}]/[\mathrm{Co^{II}L(py)}][\mathrm{O_2}] = k_1/k_{-1} \qquad (7)$$

$$\frac{i_k}{i_d - i_k} = \frac{0.886}{K_{O_2}}\sqrt{\frac{k_1 t_1}{P_{O_2}}} \qquad (8)$$

log $[i_k/(i_d - i_k)]$ against log P_{O_2} (at constant t_1) was found to be a straight line, with slope −0.5 (Figure 2).

The K_{O_2} values (Table 4) were obtained from the experimental data for i_d, i_k, and t_1, and from the k_1 values obtained from the shift of the half-wave potential of the cathodic waves in oxygenated solution, as described below.

Polarography of Cobalt(III) *Complexes in Oxygenated Pyridine Solution at* 0 °C ($P_{O_2} = 760$ Torr).—In oxygenated solution the cathodic wave due to the Co^{III} ⟶ Co^{II} reduction is still reversible, diffusion controlled, and practically unchanged in height relative to the deoxygenated solution. On the other hand, the half-wave potential is displaced toward more positive values by an extent depending on the actual complex examined. This can be interpreted as a consequence of the inactivation of reduced

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

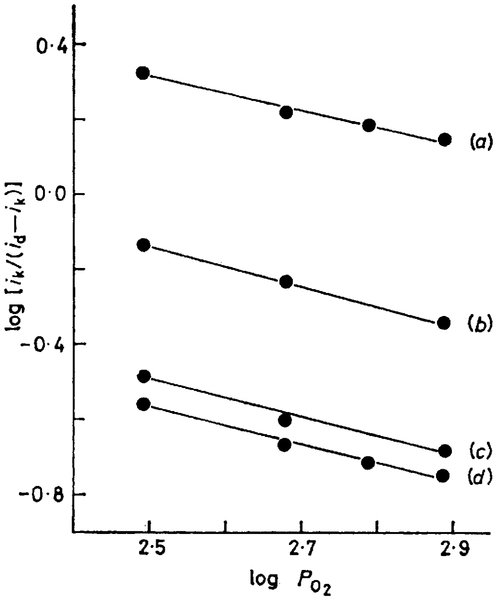

FIGURE 2 log–log dependence of $i_k/(i_d - i_k)$ on P_{O_2}: (*a*) [Co(salen)] (1.06×10^{-3}); (*b*) [Co{sal(+)pn}] (1.13×10^{-3}); (*c*) [Co{sal(*m*)bn}] (1.03×10^{-3}); and (*d*) [Co{sal(+)bn}] (0.62×10^{-3} mol dm^{-3}) in py–[NEt_4][ClO_4] (0.1 mol dm^{-3}) at 0 °C

species, by the oxygenation reaction following the electron transfer, as shown in equation (2). From the solution of the diffusional problem,[15] the final expression for the half-wave potential is (9), where $E_{\frac{1}{2}}$ is the half-wave potential of

$$E_{\frac{1}{2}} = E^{\ominus} + (RT/nF)\log 0.886\sqrt{\rho\sigma t} \qquad (9)$$

the $Co^{III} \longrightarrow Co^{II}$ reduction measured in the presence of the inactivation reaction, $E^{\ominus}$ is the standard potential of the redox couple Co^{III}–Co^{II}, and ρ and σ have the same meaning as above. In our case at 0 °C the equation (9)

$$E_{\frac{1}{2}} - E^{\ominus} = (0.054/2)\log k_1P_{O_2} + (0.054/2)\log t_1 + 0.054\log 0.886 \quad (10)$$

becomes (10) which allows the calculation of k_1 from $E_{\frac{1}{2}}$.

To achieve pseudo-first-order conditions, the maximum obtainable oxygen concentrations were maintained (saturation at P_{O_2} = 760 Torr). Moreover, the concentration of Co^{III} was kept between 0.2×10^{-3} and 0.4×10^{-3} mol dm^{-3}. The measured $E_{\frac{1}{2}} - E^{\ominus}$ value was found to be independent of the concentration of [$Co^{III}L(py)$]$^+$ species as required by equation (4). Owing to the difficulty of realizing experimental pseudo-first-order conditions using higher P_{O_2} values, the dependence of $E_{\frac{1}{2}}$ on P_{O_2} was not controlled. On the other hand, the slope of $E_{\frac{1}{2}}$ *vs.* log *t* at constant P_{O_2} was found to be 54/2 mV as required by equation (10) (Table 3).*

The sensitivity of the polarographic half-wave potentials and currents to the rate of the coupled chemical reaction and the reproducibility of the experimental measurements allow the calculation of rate constants to within *ca.* 100 dm^3 mol^{-1} s^{-1}. The rate of oxygenation of [Co{sal(*m*)chxn}] is apparently below this limit. The diastereoisomers [Co{sal(+)dpen}] and [Co{sal(*m*)dpen}] exhibit a slightly irreversible redox process which prevents reliable use of the method.

TABLE 3

Shifts (in mV) of the half-wave potential of the cathodic wave of cobalt(III) complexes in py–[NEt_4][ClO_4] (0.1 mol dm^{-3}) at P_{O_2} = 760 Torr and *t* = 3 s, and dependence (in mV) on drop time

Complex	$E_{\frac{1}{2}} - E^{\ominus}$	$d\,E_{\frac{1}{2}}/d\log t$
[Co(salen)]$^+$	79	12
[Co{sal(±)pn}]$^+$	50	24
[Co{sal(+)bn}]$^+$	14	27
[Co{sal(*m*)bn}]$^+$	22	23
[Co{sal(−)chxn}]$^+$	48	27

DISCUSSION

Both the equilibrium and kinetic data have been examined with reference to the known or most likely molecular structure of the chelates in the complexes [$Co^{II}L(py)$] and [$Co^{II}L(py)(O_2)$]. The stereochemistry relevant to the oxygenation process is that of the five-co-ordinate complex, as present in pyridine solution.[7-9]

TABLE 4

Equilibrium and kinetic data for the reaction of [$Co^{II}L(py)$] with O_2 in py–[NEt_4][ClO_4] (0.1 mol dm^{-3}) at 0 °C. Standard state: [O_2] = 1 mol dm^{-3}

Complex	$\frac{K_{O_2}}{\text{dm}^3\,\text{mol}^{-1}}$	$\frac{k_1}{\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$
[Co(salen)]	$(1.6 \pm 0.07) \times 10^{4}$ [a]	$(5.7 \pm 0.5) \times 10^{5}$ [a]
[Co{sal(±)pn}]	$(4.2 \pm 0.1) \times 10^{3}$	$(7.0 \pm 0.5) \times 10^{3}$
[Co{sal(+)bn}]	$(2.4 \pm 0.2) \times 10^{3}$	$(3.2 \pm 0.6) \times 10^{2}$
[Co{sal(*m*)bn}]	$(3.2 \pm 0.2) \times 10^{3}$	$(7.6 \pm 0.8) \times 10^{2}$
[Co{sal(−)chxn}]	2.3×10^{2} [b]	$(6.2 \pm 0.8) \times 10^{3}$
[Co{sal(*m*)chxn}]	95 [b]	$< 10^{2}$
[Co{sal(−)dpen}]	25 [b]	
[Co{sal(*m*)dpen}]	10^{3} [b]	

[a] From ref. 13. [b] From ref. 10.

In the complexes containing salen derivatives the actual geometry appears to be sensitive to the steric requirements of the substituents in the *NN'*-ethylene bridge. The crystal structure of [Co{sal(+)bn}(py)] shows that two crystallographically independent molecules are present,[7] one of which may be described as a distorted square pyramid while the other is intermediate between a square pyramid and a trigonal bipyramid. Two crystallographically independent molecules are present also in crystals of complexes of Co^{II} and Fe^{II} with *NN'*-[2-(2'-pyridyl)ethyl]ethylenebis(salicylideneiminate).[16] Both of them are distorted towards a trigonal-bipyramidal geometry.

This indicates that the chelate is fairly flexible and that it can easily be distorted in the crystal packing. The distortions of [Co{sal(+)bn}(py)] from square-pyramidal geometry (Figure 3) are determined mainly by two kinds of interactions: those between the hydrogens of the CH(CH_3) groups of the *NN'*-ethylene bridge and the hydrogens of the azomethine groups, and those between the pyridine molecule and the *NN'*-ethylene bridge. The former are best alleviated by the bis axial conformation of the CH_3 groups and by a suitable torsion angle around the C(8)–C(10) bond. The latter lead to a decrease of the N(1)-Co-O(2) and N(2)-Co-O(1)

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* For [Co(salen)] the slope is smaller than expected and k_1 calculated from equation (10) is *ca.* 10^4 dm^3 mol^{-1} s^{-1}, which is not in agreement with the value obtained from this equation using K_{O_2} as determined from the Hill plot. This is probably due to the higher rate of oxygenation under which pseudo-first-order conditions break down.

angles giving a 'reversed-umbrella' shape to the five co-ordination bonds. The torsion angle around C(8)–C(10) and the displacements of the set of donor atoms N(1),N(2),O(1),O(2) of the Schiff base from the equatorial plane are connected through the trigonal nature of the nitrogen atoms. Thus the dihedral angle between the N(1)–C(8)–C(10) and N(2)–C(10)–C(8) planes is related to the dihedral angle between the planes N(1)–Co–O(1) and N(2)–Co–O(2), which determines the distortion of the molecule from square-pyramidal towards trigonal-bipyramidal geometry with the five-membered *NN'*-ethylene chelate ring in an envelope conformation.

The structure of [Co{sal(±)pn}(py)] is not known but the CH_3 substituent in the *NN'*-ethylene ring is likely to be situated in an axial position, on the side opposite to the pyridine ligand. The situation is again such as to result in a reversed-umbrella shape for the molecule. In this structure the CH_3 group partially shields the sixth co-ordination position, thus hindering approach of a dioxygen molecule.

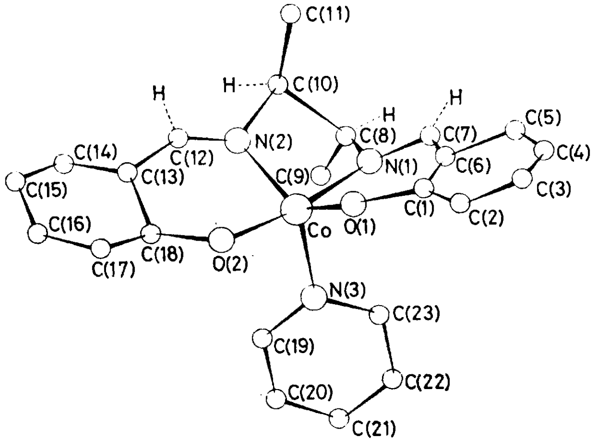

FIGURE 3 Perspective of [Co{sal(+)bn}(py)] molecule

The formation of the 1 : 1 adduct of a trigonal bipyramidal complex with molecular oxygen requires flattening of the quadridentate chelate ring in the equatorial plane of an octahedral geometry. This was demonstrated in the case of {*NN'*-[2-(2'-pyridyl)ethyl]-ethylenebis(salicylideneiminato)}cobalt(II) and its 1 : 1 oxygen adduct.[16] The ease of this structural rearrangement clearly depends on the presence of substituents in the ethylene bridge. It is determined by the possibility of opening the N(1)–Co–O(2) and N(2)–Co–O(1) angles and of rotation about the C(8)–C(10) bond in the presence of interactions of CH_3 and CH–N hydrogens.

With these considerations in mind we can explain the strong decrease which was found both in the rate of oxygenation and in the equilibrium constant of the substituted derivatives relative to the parent chelate. The presence of one CH_3 group in the *NN'*-ethylene bridge is apparently sufficient to increase the energy involved in the rearrangement from the folded towards a square-pyramidal geometry. A second CH_3 group as in [Co{sal(+)bn}(py)] and [Co{sal(*m*)bn}(py)] leads to a further increase of this energy, the extent being apparently higher in the former, where the second CH_3 group is axial, than in the latter where it is equatorial in the *NN'*-ethylene bridge.

The complex [Co{sal(+)chxn}(py)], where both the CH_2 groups of the cyclohexylene ring are in pseudo-equatorial conformation, undergoes more ready oxygenation than [Co{sal(*m*)chxn}(py)] where one CH_2 group of the cyclohexylene ring is pseudo-axial, the other pseudo-equatorial, because of the greater folding in the latter.

Finally, the greater difference in the oxygenation rate between the two [Co{salchxn}(py)] as compared with the two [Co{salbn}(py)] diastereoisomers may be due to the higher rigidity of the former.

EXPERIMENTAL

Materials.—The cobalt chelates were a gift from Professor Ugo and his co-workers. Pyridine (py) (Fluka 82702) was dried with 4-Å molecular sieves. The compound [NEt$_4$]-[ClO$_4$] (Carlo Erba) was crystallized twice and dried *in vacuo* at 40 °C. Extra pure, dry nitrogen was used as the purge gas, and as diluent for oxygen in the oxygenation experiments.

Apparatus and Methods.—Polarograms and controlled-potential electrolyses were carried out with an Amel 471 multipolarograph equipped with a model 460 stand. A model 694 universal cell was used in the polarographic experiments. The characteristics of the dropping mercury electrode (d.m.e.), made from a 45° bent glass capillary, in py–[NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}) at 0 °C were: flow rate, 0.72 mg s^{-1}; height of mercury level, 85.5 cm. A Metrohm saturated calomel electrode (s.c.e.) filled with a saturated aqueous solution of NaCl was used as the reference electrode, separated by a salt bridge containing the same electrolyte in pyridine as the examined solution. A platinum wire was used as counter electrode. Controlled-potential electrolyses were carried out with the same reference electrode. All experiments were carried out in solutions of complexes in anhydrous pyridine and 0.1 mol dm^{-3} [NEt$_4$][ClO$_4$] at 0 °C.

The kinetic currents (i_k) were measured from the polarographic anodic waves (Figure 1) of a pyridine solution of [Co^{II}L] (giving the monopyridine complex) equilibrated by bubbling with N_2–O_2 mixtures at P_{O_2} = 310, 480, 620, or 760 Torr for *ca.* 30 min. The instantaneous current plot (log i − log t) was drawn using a d.m.e. with drop time t = 7 s.

The solubility of dioxygen in the electrolyte solution required for calculations using equations (8) and (10) was taken as 4.15×10^{-3} mol dm^{-3} (in pyridine at 18 °C) [17] assuming that the temperature effect on the Bunsen coefficient is negligible.

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