Lade 5404

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Oxygen-17 NMR Shifts Caused by Cr++ in Aqueous Solutions* MASTER

By

Jasper A. Jackson, Joe F. Lemons, and Henry Taube+

[University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico]

ABSTRACT

Cr++ in solution produces a paramagnetic shift in the NMR absorption of O^{17} in ClO_4^-, as well as the expected paramagnetic shift for O^{17} in H_2O. As the concentration of ClO_4^- increases, the shift in the H_2O^{17} absorption is diminished, and eventually changes sign. The effects are ascribed to preferential replacement by ClO_4^- of water molecules from the axial positions in the first coordination sphere about Cr++.

INTRODUCTION

We are reporting observations on the influence which Cr++ in aqueous solution exerts on the NMR absorption of H_2O^{17} contained in the solvent and on some anions present as part of the solute content. Two of the effects are quite striking. They are that Cr++ shifts the NMR absorption of the oxygen contained in ClO_4^-, and ClO_4^- exerts a profound effect on the shift which Cr++ produces in the absorption by oxygen contained in the solvent. The effects indicate strongly that there is substantial replacement by ClO_4^- of water from the first coordination sphere of Cr++.

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EXPERIMENTAL

The solution containing $CrCl_2$ was prepared by the action of amalgamanted Zn on a solution of $CrCl_3$ in dilute HCl. Oxygen-free argon was used as a blanketing gas during the manipulation and storage of the Cr^{++} solution.

The NMR shifts were measured at 8 Mc using a Varian wide-line spectrometer as described previously.[1,2] The samples were contained in a sealed 16 mm. O.D. test tube from which the air had been removed by the flow of argon gas introduced into the bottom of the test tube by means of a glass capillary. Sample temperature was approximately 18°C.

RESULTS

In Table I we summarize some of the data we have obtained for the shifts produced by Cr^{++} in the NMR absorption of various species present in solution.

Table I

Shifts in NMR Absorption of H_2O and of Some Anions Caused by Cr^{++} in Solution (Concentrations recorded as molalities; Zn^{++} present at 1/2 concentration of Cr^{++}; other cation H^+ or an alkali metal ion.)

Cr^{++} Conc.	Cl^- Conc.	Other Anion Type	Other Anion Conc.	Shift in H_2O,[a] parts in 10^4	Shift in other anion, parts in 10^4
0.40	1.3	None	--	-0.55 ± 0.05	--
0.45	1.6	ClO_4^-	2.0	-0.50 ± 0.03	-0.85 ± 0.1[b]
0.49	1.7	ClO_4^-	4.8	-0.18 ± 0.05	-0.95 ± 0.1[b]
0.57	1.9	ClO_4^-	8.5	$+0.33 \pm 0.05$	-1.20[b]
0.56	1.9	I^-	1.3	-0.48 ± 0.05	--[c]
0.56	1.9	I^-	2.7	-0.36 ± 0.05	--
0.56	1.9	I^-	5.3	-0.22 ± 0.1	--
0.47	9.3	None	--	-0.05 ± 0.05	-5.7[d]
0.56	1.9	SO_4^-	6.4	-0.14 ± 0.05	-1.2[e]

[a]Referred to pure water.

[b]Shift of O^{17} resonance in ClO_4^- from ClO_4^- in aqueous $HClO_4$.

[c]The shift for I^{127} in I^- by Cr^{++} is very large. In a solution 0.053 molal in Cr^{++}, 0.027 molal in Zn^{++}, 0.18 molal in Cl^- and 3.0 molal in KI, the shift for I^{127} is -3.9 (from I^- in aqueous KI).

[d]Cl^{35} shift from Cl^{35} resonance in saturated aqueous solution of NaCl.

[e]Shift of O^{17} resonance in SO_4^- from SO_4^- signal in aqueous $(NH_4)_2SO_4$.

At constant ClO_4^- concentration, the shift in ClO_4^- absorption is at least approximately proportional to Cr^{++} concentration. Thus, in a solution 0.90 $\underline{M}$ in Cr^{++}, ca. 4.0 $\underline{M}$ in ClO_4^- and 1 $\underline{M}$ in H^+ (Na^+ also was present), O^{17} in ClO_4^- is shifted -2.3 parts/10^4 from its resonance frequency in $NaClO_4$ as reference solute; when the solution is diluted 1:2 with water, but maintaining ClO_4^- constant, the shift is reduced to -1.2 parts/10^4. The shifts for the solvent are -1.1 $\pm$ 0.1 parts/10^4 and -0.65 $\pm$ 0.1 parts/10^4 respectively in the two experiments.

Not all solutes behave as do ClO_4^-, Cl^-, I^- and SO_4^-, each of which decreases the shift in H_2O^{17} absorption caused by Cr^{++}. Thus when enough ethylenediamine (en) was added to a solution 0.11 molal in $CrCl_2$, 0.055 molal in $ZnCl_2$ and 0.04 molal in HCl, to provide two moles of en for each mole of Cr^{++} and Zn^{++}, the shift in the NMR absorption of H_2O^{17} was observed to be -0.43. This corresponds to a molal shift of -4.0 as compared to -1.4 without adding en. The value recorded with en present is a lower limit, and the actual value may be much higher, since by the time the reading was made, most

of the Cr^{++} had been carried down in the precipitate which formed even at the rather low initial concentration of Cr^{++} which was used.

Cr^{++} is the only cation which we have found to produce a marked shift in the NMR absorption of O^{17} in ClO_4^-. Among the others that have been examined are Co^{++}, Ni^{++}, Fe^{++}, Fe^{+++}, Cu^{++}, Mn^{++} and the rare earth ions; for each of them the shift in ClO_4^- absorption brought about by the paramagnetic ion at concentrations of the order of 0.50 molal is less than 0.05 parts/10^4 which is approximately the limit of detection. The influence of ClO_4^- on the molal shift in H_2O^{17} caused by a paramagnetic ion deserves a detailed study, but this has been carried through, and then not exhaustively, only with the rare earth ion Dy^{+++}. The data bearing on this question appear in Table II, and they show that the molal shift for D_2O produced by Dy^{+++} is independent of ClO_4^- (and Dy^{+++}) concentration.

Table II

The Shift in NMR Absorption of O^{17} in D_2O as Function of the Concentration of $Dy(ClO_4)_3$

(Concentrations in molality.)

Dy^{+++}	ClO_4^-	H^+	Shift	Molal Shift[a]
0.495	1.75	0.27	+1.85	3.74
1.06	3.75	0.57	+4.15	3.92
2.46	9.70	1.32	+9.2 ± 0.1	3.74

[a]Shift divided by molality of Dy^{+++}. The shift is linear in the molality, but not molarity. On a molar basis the ratio of concentration of Dy^{+++} in the third solution as compared to the first is 4.02.

Cr^{++} is also the only paramagnetic ion studied which caused observable broadening of the O^{17} signal from ClO_4^-, the observed width for most of the experiments with Cr^{++} being 2 to 4 times the width in $HClO_4$. Precise measurements of the ClO_4^- line widths were not attempted because of the low signal to noise ratio available at the 0.04% natural O^{17} abundance level of the ClO_4^- used in these experiments.

The observed broadening of the H_2O signal in the presence of Cr^{++} is evidence that the lifetime of H_2O in the hydration sphere of Cr^{++} is not longer than about 10^4 sec. This is consistent with the previous observation of Plane and Taube[3] using the isotopic dilution method that the exchange is complete in 2 minutes.

DISCUSSION

The observation that Cr^{++} shifts the NMR absorption for O^{17} in ClO_4^- suggests that substantial net replacement of H_2O on $Cr(H_2O)_6^{++}$ by ClO_4^- takes place. Shifts of the magnitude of those reported are in general not observed unless the ligand which contains the absorbing nucleus makes a direct bond to the paramagnetic center. The observation cannot however be taken as proof of substantial Cr^{++}-ClO_4^- complex formation, because it is possible that the specific effect of Cr^{++} on ClO_4^- oxygen is exceptionally great, and that a small fractional conversion of ClO_4^- to the complex with Cr^{++} suffices to give the effect. The possibility of a very large specific effect must be taken into account particularly for a central ion such as Cr^{++} because the groups that

comprise the first coordination sphere about it are probably not equivalent. It is reasonable to suppose that Cr^{++} in solution, as in the solid,[+] demands a strong distortion of what would otherwise be an octahedral arrangement of groups in the first coordination sphere, with two groups at the axial positions being at a greater distance from Cr^{++} than are the other four. Thus when the shift in absorption for H_2O^{17} is considered, it must be regarded as the sum of the effects at the two positions, and the net effect may be small only because these have opposing signs. The analysis outlined in the following in fact suggests that just this situation is realized for Cr^{++} acting on H_2O.

When account is taken of the influence which ClO_4^- exerts on the $Cr^{++}-H_2O$ interaction, the conclusion that substantial replacement of H_2O by ClO_4^- on Cr^{++} takes place seems inescapable. As long as the probability of a water molecule being adjacent to the paramagnetic ion is unaffected by an increase in the number of ClO_4^- ions (at constant ratio of Cr^{++}/H_2O) the shift in the H_2O absorption brought about by paramagnetic ion should remain constant - -

this situation is apparently realized in perchlorate solutions of Dy^{+++} (see Table II). But increasing the ClO_4^- concentration is observed to exert a profound effect on the $Cr^{++}-H_2O$ interaction: increasing ClO_4^- concentration decreases the shift in NMR absorption of H_2O caused by Cr^{++}, and when the ClO_4^- concentration is increased sufficiently, a reversal in the sign of the shift caused by Cr^{++} is observed.

The reversal in sign is perhaps the most interesting of the results we are reporting. It finds a simple explanation by adapting suggestions made by Shulman[5] and Orgel[6] to the particular problem of Cr^{++}. Let us assume that σ interactions between Cr^{++} and the ligands surrounding it are dominant for the effects we observe in solution. Let us assume further that the single $d\gamma$ electron occupies the d_{z^2} orbital (which we take as oriented along the unique axis) so that the $d_{x^2-y^2}$ orbital is unoccupied. Now, when an electron transfers to Cr^{++} from an s or p orbital of an oxygen ligand lying along the z axis, the spin left on the oxygen will have the same direction as do those of the Cr^{++} electrons, so that a paramagnetic shift in the NMR absorption of the oxygen ligand will be observed. But when an electron transfers from an oxygen ligand in the x-y plane to the unoccupied $d_{x^2-y^2}$ orbital, the electron in the orbital will tend to have the same sign of spin as do the other Cr^{++} electrons, so that a spin of opposite sign remains on oxygen, and a diamagnetic shift will be developed in the oxygen ligand.

As pointed out by Lewis,[7] an additional contribution to the shift comes from the overlap of the d_{z^2} orbital with the oxygen 2s orbital. In the iron group fluorides[8] this contribution is larger than the electron transfer effect, but the relative magnitudes of these two terms in hydrated ions is not yet known and may be comparable. This shift will be paramagnetic for the oxygens on the z axis, but will vanish for those in the x-y plane where there is no overlap. Thus it does not oppose the above effect, but merely enhances the paramagnetic shift for oxygens on the z axis.

If we take the view then that ClO_4^- occupies axial positions preferentially, the reversal in sign of the effect which Cr^{++} exerts on water can be understood. The results show that other anions, e.g. I^-, Cl^-, SO_4^-, form complexes with Cr^{++}, and, as does ClO_4^-, enter the axial positions preferentially. The effect of ethylenediamine can also be readily understood. This "strong field" ligand preferentially enters the positions in the xy plane, and it enhances the effect of Cr^{++} on H_2O at least in part by cancelling the diamagnetic contribution to the total effect.

The description has been made in terms of either electron transfer or overlap as the mechanism for producing unpaired electron spin in the O^{17} coordinated to Cr^{++}. Another effect which should be considered is the electronic dipolar field of the Cr^{++}. For regular octahedral arrangement of H_2O molecules about Cr^{++}, this field will average to zero but a distorted arrangement of the hydrated ion will result in an anisotropic magnetic susceptibility of the Cr^{++} which will lead to a dipolar field at the oxygen positions. The direction of this field will depend upon the angle between the Cr-O bond in question and the distortion axis, as well as upon the sign of the susceptibility anisotropy. Since the sign of the anisotropy is not certain, the direction of the dipolar field is unknown.

For the susceptibility greatest along the distortion axis, the dipolar field at the oxygens on that axis will produce a paramagnetic shift and at the other oxygens, a diamagnetic shift. Fortunately, the anisotropy is likely to be relatively small in Cr^{++},[9] and it seems quite unlikely to be large enough to account for the shifts reported here.

For example, the D_2O^{17} molal shift for Cr^{++} when it is complexed by en is at least 4.6 parts/10^4. To produce a shift of this magnitude in the solvent through the agency of the two groups in axial positions requires that the shift for the molecules of D_2O in the coordination sphere be 55.5/2 x 4.6 parts/10^4 or 130 parts/10^4, whereas it is estimated that the dipolar field at the axial position has an upper limit of about 0.4 parts/10^4.

The question of complex formation of ClO_4^- in aqueous solution is of considerable interest to solution chemists because of the anions in common use, ClO_4^- seems to have the smallest tendency to associate with cations. It is frequently used to minimize complications arising from complex ion formation, and it is therefore important to know just how great the affinity of ClO_4^- for various cations is. Evidence for the formation of perchlorate complexes has been adduced, but the values of the association constants,[10] based as they are on measurements in which the law of mass action is applied to complex ions which are admittedly not very stable, can not be taken as being established.[11] We feel that our results do not seriously bring into question the utility of ClO_4^- as a non-complex forming anion. In the first place, Cr^{++} is a rather unusual cation, and even in this unusual case it is perhaps more nearly correct to stress that it exerts little discrimination between ligands in the axial position, at least when these have approximately the same local charge density, than it is to stress the affinity of Cr^{++} for ClO_4^-. At the large distances in question, the local charge densities are probably more important in determining the affinities than are changes

in charge density brought about by the cation acting in the ligand. The latter component becomes important when the distances of approach become smaller, and tends to increase the discrimination which the cation exerts. In the second place, rather large concentrations of ClO_4^-, well in excess of 1 $\underline{M}$ are required to bring about a substantial replacement of H_2O on Cr^{++} by ClO_4^-, and the complex even in this unusual case cannot be regarded as a particularly stable one. The affinity is so low that the dissociation constant cannot be measured by experiments which depend on an application of the law of mass action.[11] The effects on equilibrium behavior arising from the association of Cr^{++} and ClO_4^- are no greater than those that might be expected from a change in activity coefficients because of a change in solute composition. This point is illustrated by the results of experiments done on the effect which dipositive ions exert on the solubility of $KClO_4$ in water. Each solution was made up to contain 1.26 $\underline{M}$ Cl^-, 0.33 $\underline{M}$ K^+, 0.61 $\underline{M}$ H^+ and 0.16 $\underline{M}$ M^{++} (i.e. Cr^{++}, Mg^{++} or Ni^{++}). The solubility of $KClO_4$ in the solution containing Cr^{++} was found to be ca. 8% greater than in the solutions containing Mg^{++} or Ni^{++}, but it would be incautious indeed to ascribe this difference to the association of Cr^{++} with ClO_4^-.

ACKNOWLEDGMENT

We wish to express our appreciation to Dr. W. B. Lewis for his interest in this work, and for the benefit of many helpful discussions.

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*This work performed under the auspices of the U.S. Atomic Energy Commission.

+Present address: Department of Chemistry, Stanford University, Stanford, California.

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