Lawrence Berkeley National Laboratory
Recent Work

Title

THE HYPERFINE COUPLING CONSTANTS AND RATES OF EXCHANGE FOR C13N- WITH THE AXIAL AND EQUITORIAL POSITIONS IN Cr(CN)5NO-3

Permalink

https://escholarship.org/uc/item/90s397zb

Authors

Spencer, J. Brock
Myers, Rollie J.

Publication Date

1964

eScholarship.org Powered by the California Digital Library
University of California

UCRL-11153

University of California

Ernest O. Lawrence Radiation Laboratory

THE HYPERFINE COUPLING CONSTANTS AND RATES OF EXCHANGE FOR $C^{13}N^-$ WITH THE AXIAL AND EQUITORIAL POSITIONS IN $Cr(CN)_5NO^{-3}$

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Rept. submitted for pub. in the Journal of American Chemical Society.

UCRL-11153

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE HYPERFINE COUPLING CONSTANTS AND RATES OF EXCHANGE FOR $C^{13}N^-$ WITH THE AXIAL AND EQUITORIAL POSITIONS IN $Cr(CN)_5NO^{-3}$

J. Brock Spencer and Rollie J. Myers

January 1964

The Hyperfine Coupling Constants and Rates of Exchange for $C^{13}N^-$ with the Axial and Equitorial Positions in $Cr(CN)_5NO^{-3}$

J. Brock Spencer and Rollie J. Myers

Inorganic Materials Research Division
Lawrence Radiation Laboratory,
and Department of Chemistry
University of California, Berkeley, California

January 1964

It has been recently reported[1,2] that the magnetic hyperfine interaction of C^{13} was observable in paramagnetic resonance spectrum of aqueous solutions of $Cr(CN)_5NO^{-3}$. It seemed probable that this interaction was only due to the equitorial CN^- but the possible axial coupling remained unknown. In a preliminary report[3] of the exchange with $C^{13}N^-$ we were also unable to differentiate between the axial and equitorial positions. We have now been able to prepare the complex by exchange with C^{13} substituted primarily in the axial position and by synthesis with every cynide substituted by $C^{13}N^-$. Both the hyperfine interaction and the rates of exchange of the axial and equitorial positions have now been clearly resolved.

Samples of $K_3Cr(CN)_5NO$ were synthesized[4] utilizing NaCN enriched to 55% in C^{13} isotope. The largest hyperfine splitting in the paramagnetic resonance spectrum of $Cr(CN)_5NO^{-3}$ should arise from the species containing[5] Cr^{53}, N^{14} and five C^{13}. In the X-band spectrum of the enriched sample clearly resolved lines occur 62.4 gauss above and below the center of the spectrum. Since these lines must be due to a combination of axial and equitorial C^{13}

hyperfine interaction, this splitting can be combined with the previously assigned[1,2] C^{53}, N^{14} and C^{13} equitorial splittings to yield a value of 8.55±0.4 gauss for the axial C^{13} coupling constant.

A prominent hyperfine line can also be observed between the C^{12} and the expected equitorial C^{13} lines when the complex is exchanged in solutions containing nearly equal amounts of C^{13} enriched CN^- and HCN. Direct measurement of this line gives 8.93±0.2 gauss for the axial C^{13} coupling constant. Our values can be compared to the 8.43±0.2 gauss reported by Kuska and Rogers[6] from a resolution of the complex pattern observed for both axial and equitorial C^{13} substitution. A summary of our coupling constants is given in Table I.

In the temperature range 60-100°C the exchange with $C^{13}N^-$ can be observed without decomposition of the complex. We have followed the decrease in the signal due to unsubstituted complex and the increase in the signal resulting from equitorial C^{13} substitution while the samples were held at constant temperature in the microwave cavity of a paramagnetic resonance spectrometer. In solutions ranging from 0.015 -0.035 f in complex and 0.1-0.2 f in NaCN (55% in C^{13} isotope) we followed the adjacent lines for unsubstituted and C^{13} equitorial-substituted complex for the Cr^{53} species until approximately 50% of the complex was substituted with one $C^{13}N^-$. These experiments were conducted in the nearly complete darkness of the cavity. In separate experiments no pronounced light catalysis, as reported for other cyanide complexes,[7] was observed.

These exchange data were fit by rate laws assuming first order in unsubstituted complex and zero order in total CN^- concentration. An integrated rate law was used which took into account the possible substitution

of the axial and one of the four possible equitorial CN^-. The total rate constant ka+4ke can be directly obtained from the decrease in the unsubstituted complex and the equitorial rate constant ke can be evaluated by successive approximation from the growth of the equitorial C^{13} signal. At 75°C we obtain ka = 1 x 10^{-4} sec^{-1} and ke = 7 x 10^{-6} sec^{-1}. Over the range of temperatures we get $\Delta H_a^{\ddagger}$ = 33.5 ± 4 Kcal/mole, $\Delta S_a^{\ddagger}$ = 18 ± 8 e.u., $\Delta H_e^{\ddagger}$ = 30.5 ± 4 Kcal/mole and $\Delta S_e^{\ddagger}$ = 5 ± 8 e.u. In the solutions prepared by adding NaCN to neutral solutions of the complex the ratio ka/4ke = 4 ± 2 over the full range of temperature.

The apparent large positive value for $\Delta S_a^{\ddagger}$ indicates[8] that the activated complex for axial exchange is a protonated species. The formation of $HCr(CN)_5NO^{-2}$ by the removal of the proton from HCN could contribute about 40 e.u. to the apparent entropy of activation. When exchange experiments were conducted in acidified solutions so that both CN^- and HCN have nearly equal concentrations the axial rate is accelerated. In this case, as previously mentioned, a line due to axial substitution becomes prominent before the equitorial line is clearly observable. It seems probable that the formal charge of +1 on the NO group makes the axial CN^- more likely for protonation than the more adjacent equitorial CN^-. It is possible from our data, however, that the equitorial exchange is also partly acid catalyzed.

The similar values for the N^{14} and both C^{13} coupling constants do not give any clear contradiction or support to the bonding scheme proposed[9] for these complexes. The axial CN^- is more liable to exchange in aqueous solution primarily because of greater protonation at this position, and the enthalpies of activation are equally large for both positions. The theory for the isotropic hyperfine interaction in these compounds is necessarily complex, and both the signs of the coupling constants and the anisotropic terms

should be determined before a serious effort is made to explain the axial and equitorial coupling constants in terms of bonding.

Acknowledgment- This work was supported by a grant from the United States Atomic Energy Commission.

Table I

Hyperfine Coupling Constants

$A(Cr^{53})$	18.39±0.05 gauss
$A(N^{14})$	5.27±0.05
$A(C_e^{13})$	12.64±0.2
$A(C_a^{13})$	8.80±0.3

References and Footnotes

1. R. G. Hayes, J. Chem. Phys. 38, 2580 (1963).

2. I. Bernal and S. E. Harrison, J. Chem. Phys. 38, 2581 (1963).

3. J. B. Spencer and R. J. Myers, presented before the Inorganic Division of the American Chemical Society 144th. National Meeting, Los Angeles, April 1963.

4. W. P. Griffith, J. Lewis and G. Wilkinson, J. Chem. Soc., 1959, 872.

5. There is no observable hyperfine interaction from the N^{14} in the CN^-, Cr^{53} is 9.5% abundant.

6. H. A. Kuska and M. T. Rogers; we would like to thank Professor Rogers for sending us a pre-publication copy of their work.

7. A. G. MacDiarmid and N. F. Hall, J. Am. Chem. Soc. 76, 4222 (1954).

8. We would like to thank Professor R. E. Connick for suggesting this possibility to us.

9. H. B. Gray, I. Bernal and E. Billig, J. Am. Chem. Soc. 84, 3404 (1962).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.