UCRL-10725

University of California

Ernest O. Lawrence Radiation Laboratory

THE EXCHANGE OF CN^- WITH $Cr(NO)(CN)_5^{-3}$ AS FOLLOWED BY ELECTRON SPIN RESONANCE

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.

UCRL-10725

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

THE EXCHANGE OF CN^- WITH $Cr(NO)(CN)_5^{-3}$ AS FOLLOWED BY ELECTRON SPIN RESONANCE

J. Brock Spencer and Rollie J. Myers

March 31, 1963

The Exchange of CN^- with $Cr(NO)(CN)_5^{-3}$ as Followed by Electron Spin Resonance

J. Brock Spencer and Rollie J. Myers

Department of Chemistry and Inorganic Materials Research Division
of the Lawrence Radiation Laboratory, University of California
Berkeley 4, California

ABSTRACT

The electron spin resonance of $Cr(NO)(CN)_5^{-3}$ has been reported by Bernal and Harrison[1]. From a variety of evidence it is concluded that the NO is essentially NO^+ and therefore it is a Cr^{+1} surrounded by six isoelectric ligands. The electron spin resonance lines in this complex are only a few gauss wide and the hyperfine interaction of $N^{14}O^+$ and Cr^{53} (9.5%) are clearly resolved.

Hayes[2] has shown that C^{13} in natural abundance can also be detected in the hyperfine splitting in the electron spin. We have followed the formation of $Cr(NO)(CN)_5^{-3}$ containing $C^{13}N^-$ by exchange in solution utilizing NaCN enriched in C^{13}. This exchange has been quantitatively followed in aqueous solutions containing CN^- enriched to 50% in C^{13}. The measurements were made by directly following the formation of $Cr(NO)C^{13}N(CN)_4^{-3}$ while the samples were heated directly in glass tubes in the electron spin resonance spectrometer. In Figure 1 a typical exchanged spectrum is shown. Below 100°C no net decomposition of the complex could be observed but it was detected above this temperature.

The reaction was assumed to be over-all second order and both the initial rate and the integrated rate were used to determine the rate for exchange. Some representative rate constants are given in Table I.

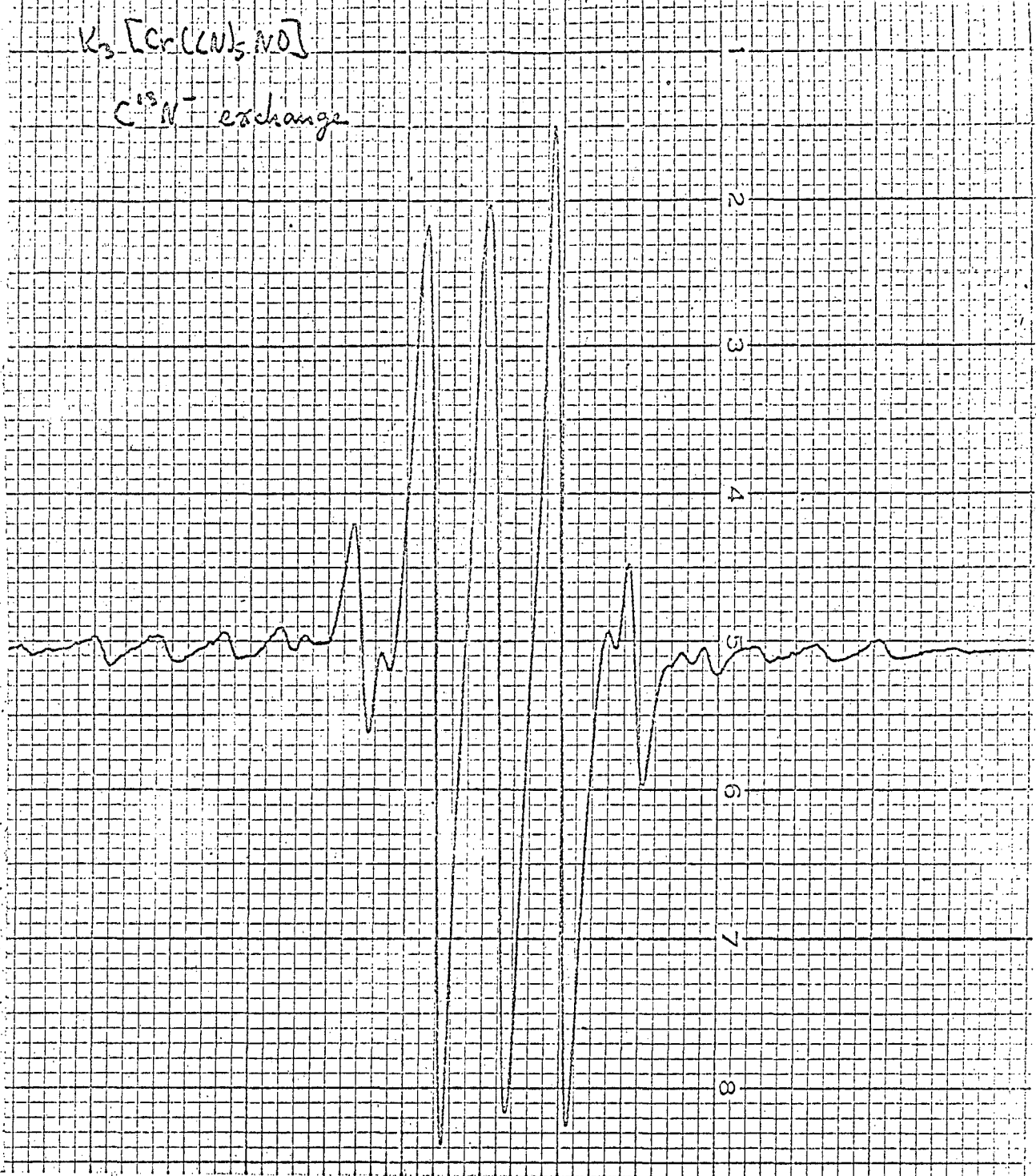

Figure 1. The center triplet is due to $N^{14}O^+$, the single line on either side is due to partially exchanged $C^{13}N^-$ and the weak lines are mainly Cr^{53}.

Table I.

$Cr(NO)(CN)_5^{-3}$ Exchange With $C^{13}N^-$

$[Cr^+]$	[CN]	t^oC	$k(hr^{-1}M^{-1})$
0.03	0.1	66	0.38
0.027	0.13	64	0.20
0.027	0.13	85	1.8
0.027	0.13	90	3.1
0.027	0.13	98	6.4

Ea = 22 to 25 Kcal/mole.

During the exchange it was observed that hyperfine interaction was produced which corresponded to two and more equivalent $C^{13}N^-$ in the complex. Since $Cr(NO)(CN)_5^{-3}$ has most certainly C_{4v} symmetry the observation of two magnetically equivalent CN^- must mean that the observed rate of exchange is not simply the rate of the axial CN^-. From intensities measurements with C^{13} in natural abundance Hayes[2] has concluded that the observed hyperfine coupling either corresponds to four or five magnetically equivalent CN^- sites. Since we have been unable to observe a unique set of hyperfine lines which can be ascribed to the axial CN^- there are several possible situations.

If all five of the CN^- are magnetically equivalent they may have very similar rates of chemical exchange. In this case we would be unable to differentiate between the axial and equatorial CN^-. If only the four equatorial CN^- are magnetically equivalent either the axial CN^- has a much slower rate of exchange, so that we have not been able to enrich this position, or its hyperfine interaction is particularly small so that we have not been able to detect it.

Since the NO^+ and CN^- are isoelectronic one might expect a similar unpaired spin density on the N^{14} and C^{13}, and the observed hyperfine interaction constants are in agreement with this. It is thus quite possible that all five CN^- are magnetically equivalent and the axial and equatorial CN^- may also exchange at the same rate. Further experiments are being done to check this point.

It would be of considerable interest to extend these exchange studies to further complex ions. This will not be possible in many cases since the large electron spin resonance line widths observed for most complex ions preclude the observation of hyperfine interactions.

References

1. I. Bernal and S. E. Harrison, J. Chem. Phys. 34, 102 (1961)
2. R. G. Hayes, Lawrence Radiation Laboratory Report UCRL-9873; also submitted for publication.

Figure Caption

Figure 1. The center triplet is due to $N^{14}O^{+}$, the single line on either side is due to partially exchanged $C^{13}N^{-}$ and the weak lines are mainly Cr^{53}.