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Alkyl Halide Induced Solvolysis of $Cr(CN)_5NO^{3-}$ in DMSO

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$Cr(CN)_5NO^{3-}$ in DMSO solution reacts with alkyl halides such as methyl iodide or tertiary butyl chloride to yield, ultimately, $Cr(DMSO)_5NO^{2+}$. Cyanide ligands are removed in five consecutive steps and replaced by DMSO to form a series of intermediates with the general formula $Cr(CN)_{5-n}(DMSO)_nNO^{n-3}$, but other intermediates are also present. Extensive ESR data are presented and used to identify the intermediate species. Kinetic evidence suggests a nucleophilic substitution reaction followed by loss of coordinated isocyanide.

Introduction

Reactions of transition metal cyano-complexes with alkyl halides or alkyl sulfates have been known for nearly one hundred years.[1] The products are, in most cases, stable alkyl isocyanide coordination complexes. Typical examples[1] include the reaction of solid $Ag_4Fe(CN)_5$ with methyl iodide or of solid $K_4Fe(CN)_6$ with dimethyl sulfate to yield salts of $Fe(CNCH_3)_6^{2+}$. Some other reactions however,[1] such as those with $Cr(CN)_6^{3-}$, lead to poorly characterized products. Such studies have usually been conducted using two phase reaction conditions, but I have found that reactions also proceed smoothly in dimethyl sulfoxide (DMSO) solution. Alkyl halides and alkyl sulfates react with $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Cr(CN)_6^{3-}$, $Cr(CN)_5N_2^{4-}$, and $Cr(CN)_5NO^{3-}$ in DMSO. This paper is an attempt to identify some of the products of the reaction of alkyl halides with pentacyanonitrosylchromate(I), $Cr(CN)_5NO^{3-}$ in DMSO. In addition, a mechanism for the reactions will be proposed.

DMSO is one of the better solvents for nucleophilic substitution reactions;[2] S_N2 reactions tend to be orders of magnitude faster in DMSO than in water.[3] For instance, the reaction of sodium or potassium cyanide with primary or secondary alkyl halides in DMSO produces alkyl nitriles in good yield,[4] but tertiary halides exhibit great reluctance to pursue normal S_N1 pathways. Under the same conditions, t-butyl chloride yields no nitrile but only 2-methyl propene.[4] Evidently the t-butyl cation is strongly acidic in DMSO.

Transition metal cyano-complexes, with their large negative charges and accessible nitrogen atoms are likely to be potent nucleophiles. It would be no surprise if they formed alkyl isocyanides following an S_N2 reaction with alkyl halides. We might expect protonation and loss of unstable hydrogen isocyanide in reactions with tertiary alkyl halides.

The acid catalyzed hydrolysis of $Cr(CN)_5NO^{3-}$ has been studied by Burgess, Goodman, and Raynor,[5] who found that addition of an excess of strong acid to aqueous solutions of $Cr(CN)_5NO^{3-}$ generates four consecutive intermediate species before ultimately producting $Cr(H_2O)_5NO^{2+}$. By use of electron spin resonance (ESR) and kinetic measurements they deduce the formation of $Cr(H_2O)_n(CN)_{5-n}NO^{n-3}$ intermediate species where n = 1, 2, 3, or 4. Each species in the sequence is formed after addition of one equivalent of acid to the preceding species, and the first intermediate results from removal of the axial cyanide ligand of $Cr(CN)_5NO^{3-}$. These observations are in accord with those of Spencer and Myers[6] who studied the acid catalyzed exchange of ^{13}C-labelled cyanide on $Cr(CN)_5NO^{3-}$ in aqueous solution and found that the axial cyanide exchanges much more rapidly than does the equatorial.

Experimental Section

$K_3Cr(CN)_5NO$ was prepared by a standard procedure[7] and purified by slow recrystallization from an aqueous solution containing a slight excess of KCN. Large green crystals are formed which may easily be separated from the KCN matrix. Labelled material was prepared by treating a solution of $K_3Cr(CN)_5NO$ with perchloric acid, followed, an hour later, by addition of excess $K^{13}CN$, filtration and then recrystallization.

DMSO solutions were prepared from weighed amounts of pure compounds, using reagent grade alkyl halides and DMSO. $K_3Cr(CN)_5NO$ dissolves very slowly; even finely ground material may require a week in contact with DMSO and with occasional shaking to reach 0.02 m (m = moles of solute per Kg. of DMSO). For each experiment, a DMSO stock solution of $K_3Cr(CN)_5NO$ was mixed with alkyl halide

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(1) « Isocyanide Complexes of Metals » by L. Malatesta and F. Bonati, Wiley-Interscience, New York, 1969.

(2) A.J. Parker in « Advances in Organic Chemistry. Methods and Results », Vol. 5, R.A. Raphael, E.C. Taylor and H. Wynbert, Eds., Interscience, New York, 1965.

(3) A.J. Parker, *J. Chem. Soc.* (1961), 1328.

(4) L. Friedman and H. Schelechter, *J. Org. Chem.*, *25*, 877 (1960).

(5) J. Burgess, B.A. Goodman, and J.B. Raynor, *J. Chem. Soc.* (A), 501 (1968).

(6) J.B. Spencer and R.J. Myers, *J. Am. Chem. Soc.*, *86*, 522 (1964).

(7) W.P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

Table I. Isotropic ESR Data for the Six Chromium Complexes Detected in this Study [a].

Complex	<g>	<A>(^{14}N)	<A>(^{53}Cr)	<A>(^{13}C) [b]	<A>(^{13}C') [b]	ΔH [c]
I	1.9934	5.64±0.1	18.82±0.1	13.0 ±0.4(4)	8.6±0.2(1)	1.0
II	1.9924	6.3 ±0.2	18.6 ±0.3	12.7 ±0.3(4)	—	1.0
III	1.9870	6.4 ±0.2	20.6 ±0.3	12.9 ±0.5(2)	12.2±0.5(1)	1.5
IV	1.9826	6.45±0.1	21.52±0.1	13.57±0.1(2)	—	2.5
V	1.9743	6.8 ±0.2	23.4 ±0.3	13.1 ±0.5(1)	—	3.0
VI	1.9694	6.65±0.1	25.1 ±0.2	—	—	4.3

[a] For complexes in DMSO solution at 21°C. Absolute values of coupling constants are given in Gauss units. [b] Numbers in parentheses refer to the number of magnetically equivalent carbon atoms in cach ion which contribute to the coupling constant. These numbers have been approximately determined by intensity studies with ^{13}C substitution. [c] ΔH is the width, in Gauss units, of the central hyperfine line.

and flame sealed into a pyrex glass « melting point » capillary which serves as the ESR sample tube. The ESR spectrometer was set to sweep repeatedly through the spectrum and changes were noted as a function of time.

Absolute concentrations of paramagnetic species are notoriously difficult to measure by ESR methods, however for this work the initial concentration is known and only relative concentrations need be measured. Other factors being constant, the concentration of any species with a Lorentzian line shape is proportional to the maximum ESR derivative peak height times the square of the derivative peak-to-peak width. During the course of the reaction, no changes were made in critical ESR instrument settings, thus simplifying the calculation of relative concentration.

Table II. Anisotropic ESR Data for Three Chromium Complexes [a].

	I	IV	VI
g_x	2.0042	2.008	1.9944
g_y	2.0042	2.006	1.9944
g_z	1.9718	1.932	1.9194
a_z(^{53}Cr)	31.9±1	—	39.4±1
a_x(^{14}N)	6.6±1	—	8.0±1
a_y(^{14}N)	6.6±1	7±2	8.0±1

[a] For complexes in DMSO glass at 100°K. Absolute values of coupling constants are given in Gauss units.

Results and Discussion

DMSO solutions of $K_3Cr(CN)_5NO$ are very stable; after two years in the dark in a sealed container at 20 °C, one sample showed no sign of decomposition. The solution was clear and both visible and ESR spectra were unchanged over that period. The ESR spectrum of $K_3Cr(CN)_5NO$ in DMSO is very similar to that of $Cr(CN)_5NO^{3-}$ (Complex I) in other chemical systems,[6,8] and is seen to result from hyperfine interactions with one ^{14}N nucleus (I = 1, ~100% abundant), one ^{53}Cr (I = 3/2, 9.5%) as well as four magnetically equivalent equatorial and one axial ^{13}C (I = ½, 1.1%). Tables I and II present the data for DMSO. Coupling constants and g-values differ only slightly from values measured in aqueous solution.[6,8] The visible spectrum of Complex I in DMSO (Table III) is also very similar to the data from aqueous solution.[9]

Alkyl halides react with I to produce, consecutively, five additional species labelled, for convenience, II, III, IV, V, and VI. Each of the six species exhibits a distinctive ESR spectrum with parameters listed in Tables I and II. The ESR data show that chromium and nitrogen are present in every species in what is roughly a constant chemical environment, so that one can confidently describe each species as a chromium(I) nitrosyl complex. The unpaired electron in these low spin d_5 complexes resides in a d_{xy} orbital[9,10] and so one expects the equatorial ligands to have a large influence on the g-value and on the chromium hyperfine coupling while the axial ligand will have only a small effect. This suggests that an axial substitution on species I produces II since in the two species both ⟨ g ⟩ and the chromium hyperfine coupling are almost identical. Only the nitrogen hyperfine coupling shows a large relative change as would be expected from the « *trans* effect » of an axial substituent.

Labelling experiments with ^{13}C demonstrate that complex I loses an axial cyanide in order to form II, since the axial carbon coupling disappears. It is, of course, possible that the cyanide ligand is modified in some way and that the axial carbon is not seen in II because its coupling constant is too small, *i.e.* less than about 1G. Additional ^{13}C data show that complex II loses an equatorial cyanide to form III which is left with two cyanides trans to each other and one opposite the new ligand. Two possible isomers might be expected from species IV but evidently only one is formed. Complex V contains only one cyanide and VI, the final product, is left with no ^{13}C label.

Figure 1 graphically compares the ⟨ g ⟩ and ⟨ A ⟩ values from Table I with data from a similar set of chromium complexes observed by Burgess, Goodman and Raynor[5] in the acid hydrolysis of $Cr(CN)_5NO^{3-}$. It may be seen that the parallel comparison is rather close; the complexes formed in DMSO must be very similar to $Cr(CN)_{5-n}(H_2O)_nNO^{3-n}$. In addition, the visible spectrum of VI is practically identical to that[9] of $Cr(H_2O)_5NO^{2+}$ and very similar to that of $Cr(NH_3)_5NO^{2+}$ but distinctively different from the spectrum of $Cr(CN)_5NO^{3-}$.

By analogy with the alkylation reactions of most transition metal cyanides,[1] the products of these reactions should be alkyl isocyanide complexes. But we

(8) B.A. Goodman, J.B. Raynor, and M.C.R. Symons, *J. Chem. Soc.* (A), 994 (1966).

(9) B.A. Goodman, J.B. Raynor, and M.C.R. Symons, *J. Chem. Soc.*, (A), 1973 (1968).

(10) P.T. Manoharan, and H.B. Gray, *Inorg. Chem.*, 5, 823 (1966).

Table III. Optical Data for Three Complexes in DMSO Solution.

Transition [a]	I [b]	IV [c]	IV
$6e \to 2b_2$	14,600 cm^{-1}	15,250 cm^{-1}	17,500 cm^{-1}
$6e \to 7e$	21,600 cm^{-1}	22,500 cm^{-1}(sh)	22,500 cm^{-1}(sh)
$2b_2 \to 38_1$	27,800 cm^{-1}	30,300 cm^{-1}	—
$5e \to 2b_2$	—		25,600 cm^{-1}(sh)

[a] Transitions are assigned by analogy with the ions studied by B.A. Goodman, J.B. Raynor, and M.C.R. Symons, *J. Chem. Soc.* (A), 1973 (1968). [b] Data for complex I are from D.C. McCain, *Inorg. Nucl. Chem. Letters,* 5, 873 (1969). [c] The spectrum of complex IV is from an impure solution. See the text for details.

can rule these out because the carbons are lost. That all five product species should have near zero carbon coupling constants for isocyanide ligands in every coordination site is highly unlikely. Isocyanide ligands, with their potential for backbonding, would not be expected to be so similar spectroscopically to water ligands. The only other likely ligand in this system is DMSO itself which would be expected to resemble water, both in bonding strength and type of interaction if coordination links an oxygen atom with the chromium. Thus, the only reasonable formula for complexes I through VI is $Cr(CN)_{5-n}(DMSO)_nNO^{n-3}$ where $0 \leqslant n \leqslant 5$. It would seem that Cr^I nitrosyls more closely resemble Cr^{II}, to which DMSO bonds with oxygen,[11] than Cr^0 which bonds to the sulfur[12] in DMSO ligands.

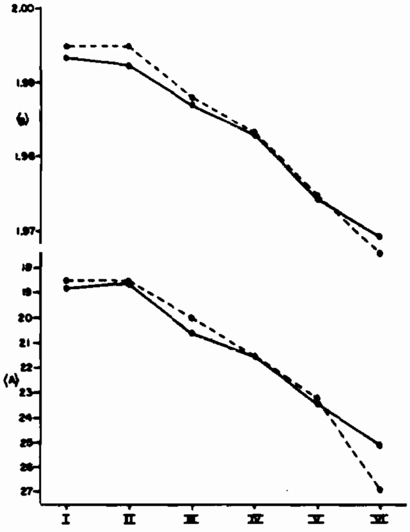

Figure 1. A graphical comparison of <g> and <A> (^{53}Cr) the six consecutive species produced by solvolysis of $Cr(CN)_5$-NO^{3-} in DMSO (solid line) and H_2O (dashed line). H_2O data are from J. Burgess, B.A. Goodman and J.B. Raynor, *J. Chem. Soc.* (A), 501 (1968).

When t-butyl chloride (2-methyl-2-chloro propane) is added to a DMSO solution of complex I, slow changes occur, some of which may be seen in Figure 2. The ESR signal of I decays at a rate described by the first order expression $-d[I]/dt = k_I[\text{t-butyl Cl}]$ where $k_I = 2 \times 10^{-8}$ sec^{-1} at 21 ± 1°C. Species II is formed simultaneously with the decay of I, to be followed in turn by III, IV, V, and VI. II and III decay with rate constants about equal to k_I, but the rate constant for decay of IV is $k_{IV} = 1 \times 10^{-9}$ sec^{-1}. The reaction is more than a simple five step process, however, because the total intensity of II at its maximum concentration in the t-butyl chloride solutions represents only about 10% of the concentration expected if all molecules of I were converted to II, and only 5% of the total chromium appears in IV. In spite of this, VI, when finally formed, continues to grow long after all lines of V have disappeared until finally VI includes 100% of the initial chromium. Figures 2(b) and (c) show a wide unresolved background signal under the spectrum of the narrow line species. This background varies in width and apparent g-value as the reaction proceeds. Evidently more than one wide line species is present. Total integrated intensities show that the wide lines contain all of the chromium missing from the narrow lined spectra.

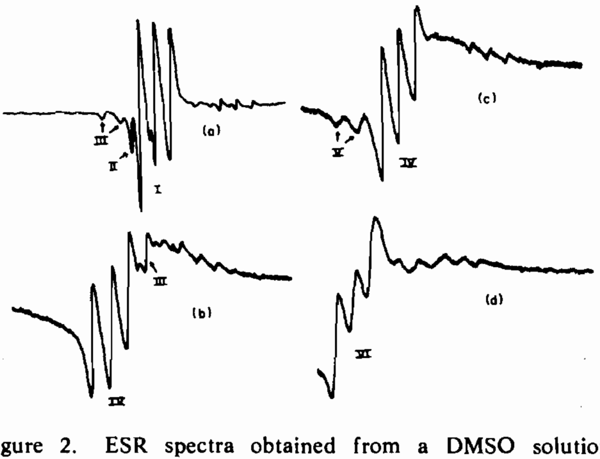

Figure 2. ESR spectra obtained from a DMSO solution initially containing 0.02 m $K_3Cr(CN)_5NO$ and 1.70 m t-butyl chloride. Temperature was held at 21 ± 1°C. Magnetic field increases to the left. Each sweep is centered on 3400 G. and is 100 G. wide. Gain settings vary from sweep to sweep. *Sweep* (*a*) shows the spectrum after 5 days. The three main lines of species 1, due to interaction with ^{14}N ($I = 1$) have decayed somewhat to be replaced by the nearly superimposed lines of II and the fairly well shifted spectrum of III. Narrow ^{53}Cr ($I = 3/2$, 9.5% abun.) hyperfine lines are seen on the low field (right hand) side. High field ^{53}Cr lines are much wider due to incomplete averaging of anisotropies and they are not seen at this gain setting. In *sweep* (*b*) after 10 days species IV dominates. One line of the spectrum of complex III is well resolved. I and II are nearly gone. *Sweep* (*c*) after 14 days shows species IV, its ^{53}Cr lines at low field and a small amount of V. In *sweep* (*d*) after 21 days, species VI is dominant.

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(11) D. G. Holah and J. P. Fackler, *Inorg. Chem.*, *4*, 1721 (1965).
(12) W. Strohmeier, G. Popp, and J.F. Guttenberger, *Chem. Ber.*, 99, 165 (1966).

Table III includes some results from the visible absorption spectrum of t-butyl chloride mixtures. The data listed under complex IV were taken at a time when IV was the only important narrow line species, although most of the chromium in that solution was present in some other form. The spectrum is very similar to that[9] of $Cr(H_2O)_3(CN)_2NO$. One could tentatively conclude from this similarity either that the wide line species have a visible spectrum about like that expected for $Cr(DMSO)_3(CN)_2NO$, or that their visible absorption spectrum is weak compared to the spectrum of IV.

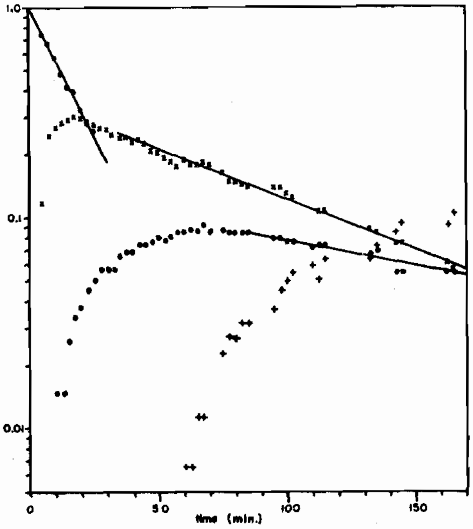

Figure 3. A plot of chromium complex concentration *vs* time for a DMSO solution at 21±1°C initially containing 0.02 m $K_3Cr(CN)_5NO$ and 0.244 m CH_3I. Species I is represented by open circles, species II by X, III by filled circles and IV by +. Straight lines are drawn to indicate the approximate regions of exponential decay.

Methyl iodide also reacts with DMSO solutions of complex I. Figure 3 shows the logarithm of the relative concentrations of the four narrow line species as a function of time and represents an example of the kinetic data obtained. These narrow line species produced by CH_3I were found to have ESR parameters identical with those obtained in t-butyl chloride solutions. But, in contrast to the previous case, the rate expression for decay of chromium species is second order overall and $-d[I]/dt = k_I[I][CH_3I]$ where $k_I = 4.1\times10^{-3}$ sec^{-1} m^{-1}, $k_{II} = 8.6\times10^{-4}$ sec^{-1} m^{-1}, $k_{III} = 4\times10^{-4}$ sec^{-1} m^{-1} and $k_{IV} = 3.6\times10^{-6}$ sec^{-1} m^{-1} at 21±1°C. These rates were checked for a number of initial concentrations of CH_3I and $K_3Cr(CN)_5NO$ with consistent results. For instance, from the data shown in Figure 3 taken with a solution containing 0.020 m $K_3Cr(CN)_5NO$ and 0.244 in CH_3I, it is apparent that species I decays exponentially in a reaction which can be followed over a period of about two half lives. These pseudo-first order kinetics are consistent with a second order rate law and a rate constant $k_I = 4.09\pm0.17\times10^{-3}$ sec^{-1} m^{-1} derived from the measured half life of 11.5±0.5 min. Keeping the concentration of $K_3Cr(CN)_5NO$ at 0.020 m but changing CH_3I to 0.175 m produces a 16.0±0.5 min half life and $k_I = 4.12\pm0.13\times10^{-3}$ sec^{-1} m^{1-}; with 0.010 m $K_3Cr(CN)_5NO$ and the same CH_3I concentration, the half life remains at 16.0±0.5 min. With 0.010 m $K_3Cr(CN)_5NO$ and 0.090 m CH_3I, the measured half life is 30±1 min and $k_I = 4.24\pm0.14\times10^{-3}$ sec^{-1} m^{-1}. Additional data from runs including higher CH_3I concentrations were used in a similar manner to determine k_{II}, k_{III}, and k_{IV}. No value for k_V is reported here; species V is too difficult to follow.

Less of the wide lined species is produced by CH_3I than by t-butyl chloride. Complex II accounts for about 35% of the chromium from I and IV represents 20%. However with CH_3I, as with t-butyl chloride, when the reaction is complete VI includes 100% of the original chromium. During the course of the reaction the solution darkens as molecular iodine is formed. This may be due to a side reaction between DMSO and iodide ion.[13] I_2 slightly catalyzes the reaction of IV and V but does not affect k_I, k_{II}, or k_{III}. Methyl iodide slowly reacts even with pure DMSO to produce I_2 but this side reaction is slower than the other reactions considered here. The presence of I_2 does preclude visible spectroscopy in CH_3I solutions. Added potassium iodide has no large effect on any of the rates. Toward the end of the reactions, the strong, very distinctive odor of methyl isocyanide, CH_3NC, can be detected if the sample seal is broken. This « aroma » is so characteristic that its detection has been considered[1] a reliable qualitative analysis for the presence of organic isocyanide compounds. Little or no such odor is detected over t-butyl chloride reaction mixtures. As an additional check, a colorimetric, Cu^{II}-benzidene method[14] gave a positive test for isonitriles in the vapor over the CH_3I reaction mixture.

Perdeutero methyl iodide was used to study the kinetic isotope effect. Solutions of CD_3I were compared directly with others containing approximately the same concentrations of CH_3I. Both sets of solution were mixed simultaneously and run alternately on the ESR to follow the relative rates of each step. CD_3I is definitely faster than CH_3I. Measured isotope effects are $k_H/k_D = 0.78$ for the first step, 0.76 for k_{II}, 0.79 for k_{III}, 0.85 for k_{IV} and 0.87 for k_V with an estimated uncertainty in k_H/k_D of about ±0.05 for all but k_{IV}. The first three reactions are quite fast but the fourth is slower, making more precision possible. Five determinations of k_H/k_D for k_{IV} gave 0.875, 0.842, 0.849, 0.856, and 0.822. This result is quite close to the value expected for an S_N2 reaction on methyl iodide. Llewellyn, Robertson and Scott[15] measured $k_H/k_D = 0.87$ for the hydrolysis of methyl iodide and after an extensive theoretical discussion, concluded that the kinetic isotope effect depends on the size of the entering nucleophile, on its proximity to the carbon at the transition point, and also on the nature of the leaving group. Perhaps a suitable model compound is triethyl amine which, like the tran-

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(13) J.H. Krueger, *Inorg. Chem.*, 5, 132 (1966).

(14) E.V. Crabtree, E.J. Poziomek, and D.J. Hoy, *Talanta*, *14*, 857 (1967).

(15) J.A. Llewellyn, R.E. Robertson and J.M.W. Scott, *Can. J. Chem.*, *38*, 222 (1960).

sition metal cyano-complexes, presents a reactive nitrogen. When triethyl amine reacts with methyl iodide,[16] $k_H/k_D = 0.877 \pm 0.004$. Many other S_N2 reactions of CH_3I are known for which $k_H/k_D \approx 0.9$. In no case is $k_H/k_D > 1.0$. It seems safe to say that $k_H/k_D = 0.85$ (found for k_{IV}) is a reasonable value which points to an S_N2 mechanism.

Kinetic data from two other alkyl halides have been obtained. For 1,3 dibromopropane, $k_I = 8 \times 10^{-5}$ sec^{-1} m^{-1}. For benzyl chloride, the first step is predominantly second order with $k_I = 2 \times 10^{-5}$ sec^{-1} m^{-1} while the fourth step is mostly first order with $k_{IV} = 1 \times 10^{-9}$ sec^{-1}; steps two and three are intermediate between first and second order.

Conclusions

The narrow line species have been identified as $Cr(DMSO)_n(CN)_{5-n}NO^{n-3}$ using indirect evidence from both ESR and visible spectra and from ^{13}C isotopic labeling experiments. The axial cyanide is the first to go, a conclusion consistent with two previous studies in aqueous solution.[5,6] No suggestions concerning the identity of the wide line species are offered here; too many possibilities remain.

Second order rate expressions are found with rate constants for the first steps in the order methyl iodide > 1,3 dibromopropane > benzyl chloride. These data as well as the kinetic isotope effect for methyl iodide are consistent with a normal S_N2 reaction mechanism. The initial product formed by an S_N2 reaction should be an alkyl isocyanide coordinated to the chromium, but this isocyanide could be removed by a rapid solvolysis reaction to yield the observed products. Free methyl isocyanide was detected in methyl iodide reaction mixtures.

An S_N1 mechanism is suggested by the first order rate expression for t-butyl chloride and for the last steps of the benzyl chloride reaction. Normally,[2] t-butyl chloride prefers an S_N1 mechanism and benzyl chloride is known to switch from S_N2 to S_N1 as the nucleophilicity of the attacking group is reduced. The apparent absence of alkyl isocyanide in t-butyl chloride reaction mixtures can be explained by a rate determining S_N1 step producing t-butyl cation which rapidly protonates the chromium species to yield coordinated HNC and 2-methyl propene. Similar HNC coordination complexes are known in other systems.[1] Following solvolysis, free HNC should rearrange to HCN.

These reaction mechanisms are only suggested. They can by no means be considered proved. Much work remains to be done with other alkyl halides and different solvent systems. It is possible, however, that transition metal cyano-complexes may provide a useful model system for the study of nucleophilic substitution reactions because nucleophilicity will vary with total ion charge while the chemical environment of each reactive site remains otherwise relatively unchanged.

(16) K.T. Leffek and J.W. MacLean, *Can. J. Chem.*, *43*, 40 (1965).