azoethane radical anion did not react with oxygen and/or small amounts of water to give new spectra. We are thus forced to the conclusion that the spectrum originally assigned to the semidiazoxide is due to the azo radical anion and that the electrolytic reduction of CF_3NO gives hexafluoroazomethane radical anion as the only esr detectable radical.[19] The magnitude of the nitrogen coupling[4,17] is also more in line with azo radical anions[11–13] than with the (probably larger) coupling expected from a semidiazoxide.

As can be seen from a comparison of the data reported (Table I), the β-fluorine coupling appears to go through a minimum as the dihedral angle is varied from 30 to 90° (if the conformational assignments are correct). Such a possibility was suggested in an earlier paper based on the comparison of the β-fluorine coupling in perfluoroalkylketyls[5] and nitroxides.[20] Both theoretical calculations[21–23] and experimental data indicate that β-fluorine coupling increases when the dihedral angle decreases from 45°. However, experimental results disagree on the extent of β-fluorine coupling when the dihedral angle is 90°. In triptycene semiquinone[24] the bridgehead fluorine coupling is approximately one-third of the value found for the freely rotating trifluoromethyl group, whereas in perfluoroisopropyl *t*-butyl nitroxide[22,25] the β-fluorine coupling is small (2.77 G at 25°) and decreases with decrease in temperature (0.76 G at − 90°). In the perfluoroazoalkanes as shown in this work an unusually large β-fluorine coupling is observed when the dihedral angle is 90°. Clearly there is a need for data on systems where the dihedral angle *and* the spin density on the contiguous atom are known explicitly. Studies on perfluorobicycloazoalkane radical anions are planned.

It is of interest to note that no radicals were detected when hexafluoroazomethane (or hexafluoracetone[3]) was reduced under ion-pairing conditions, *e.g.*, sodium or potassium in tetrahydrofuran.

---

of equal intensity, consisting of two quintets, 8.51 and 21.89 G. Assignment to two equivalent nitrogens (2 N) and four equivalent fluorines (4 F) was not obvious from the intensities because of substantial overlap with peaks from the other spectrum. If the smaller coupling is assigned to 2 N and the larger to 4 F the structure could be assigned to cyclic tetrafluoroazoethylene radical anion (or some other azo radical anion with four fluorine atoms) obtained from impurities in the azomethane. Conversely if the smaller splitting is assigned to 4 F and the larger to 2 N we have considered the possibility of an azine radical anion structure produced from probable impurities. This possibility will be investigated.

$$\bar{C}F_2N{=}N\dot{C}F_2 \longleftrightarrow \bar{C}F_2\dot{N}N{=}CF_2 \longleftrightarrow \text{etc.}$$

(19) Studies with ^{17}O are planned to resolve this question.

(20) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966); see, however, E. T. Strom and A. L. Bluhm, *J. Phys. Chem.*, in press; E. G. Janzen, B. R. Knauer, J. L. Gerlock, and K. J. Klabunde, *ibid.*, in press.

(21) K. Morokuma, *J. Amer. Chem. Soc.*, **91**, 5412 (1969).

(22) G. R. Underwood, V. L. Vogel, and I. Krefting, unpublished; we acknowledge with appreciation the receipt of a preprint of this work.

(23) J. L. Meyer and E. G. Janzen, submitted for publication.

(24) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **92**, 409 (1970).

(25) K. J. Klabunde, *ibid.*, in press.

John L. Gerlock, Edward G. Janzen, John K. Ruff
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

Received November 1, 1969

Linkage Isomerization in Nitrogen-Labeled $[Ru(NH_3)_5N_2]Br_2$

Sir:

In other work, it was shown[1] that Cr(II) reacts readily and quantitatively with N_2O in the presence of $[Ru(NH_3)_5OH_2]^{2+}$ to form $[Ru(NH_3)_5N_2]^{2+}$. Since N_2O can be prepared[2] with the *exo* (or *endo*) nitrogen isotopically labeled, the possibility of preparing $[Ru(NH_3)_5N_2]^{2+}$ with the *endo* (or *exo*) nitrogen labeled suggests itself. The results to be presented show that the reaction does in fact take the indicated course, though there is some rearrangement of the specifically labeled complex during the time required to produce the salt of the complex. Approximate values for the rate of isomerization have been obtained, and these are of some use in assessing the stability of the π-bonded state.

Nitrogen-15-labeled N_2O was prepared by a modification of the method of Friedman and Bigeleisen.[2] Under the conditions described by them, we found ammonium nitrate to sublime virtually without decomposition. But by maintaining approximately 2 ml of degassed water open to the evacuated storage vessel and to the heated tube containing the ammonium nitrate, decomposition to N_2O did proceed smoothly. Water vapor was later removed by distilling the gaseous products through a glass wool trap kept at Dry Ice–acetone temperatures. Any NO formed as a side product was removed by pumping on the product gases condensed by liquid nitrogen. The conclusion[2] that $^{15}NH_4NO_3$ on decomposition leads to ^{15}NNO was confirmed by mass spectrometric analysis of the N_2O produced. Both NH_4^+- and NO_3^--labeled ammonium nitrate were used, each 95% enriched in ^{15}N; $^{15}NH_4NO_3$ was supplied by Bio-Rad and $NH_4{}^{15}NO_3$ by Mallinckrodt Nuclear.

The labeled $[Ru(NH_3)_5N_2]^{2+}$ was prepared by vacuum-line techniques.[3] $Ru(NH_3)_5Cl_3$ (50 mg) in 20 ml of a solution of 10^{-3} *M* in HCl was placed in a two-neck reaction flask. Air was removed by repetition of the freeze–pump–thaw cycle, and a fivefold excess of Cr^{2+} was then introduced into the reaction flask *via* a side arm. Approximately 3 mmol of the labeled N_2O was released into the reaction flask, and the reaction was allowed to proceed, with vigorous stirring, in the dark for 1 hr. To destroy residual Cr^{2+} and $[Ru(NH_3)_5OH_2]^{2+}$, oxygen was passed through the solution for a few minutes. Solid NaBr was added and the solid $[Ru(NH_3)_5N_2]Br_2$ which formed was separated, washed, and dried.

Nujol mulls of the solid were prepared and pressed between KBr disks, and the region[4] from 600 to 400 cm^{-1} was recorded on a Perkin-Elmer 421 grating ir spectrophotometer using the expanded wavelength scale.[5] All spectra were calibrated against water vapor, specifically at 502.3 cm^{-1} in the single-beam mode of

---

(1) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6874 (1969).

(2) L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, **18**, 1325 (1950).

(3) The authors wish to thank Mr. P. R. Jones for his assistance with the vacuum-line work.

(4) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967). These workers have concluded that the Ru–N stretching frequency appears at 499 cm^{-1}.

(5) The authors wish to thank Drs. L. Durham and M. Abe for their technical assistance with the ir phase of this work.

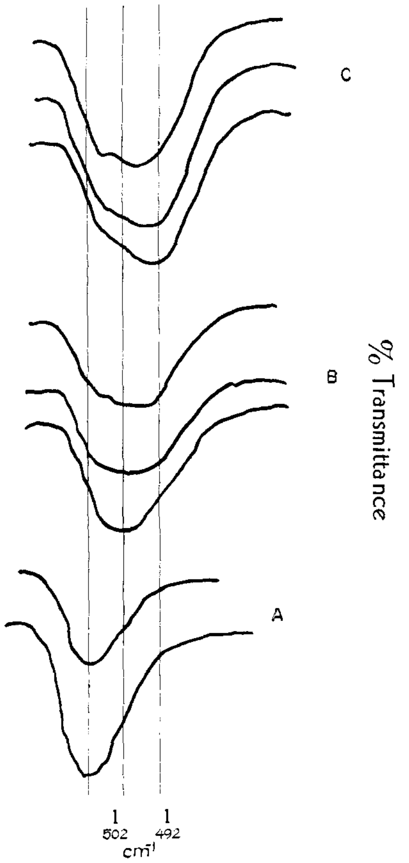


Figure 1. The Ru–N_2 stretching frequency using labeled and unlabeled N_2O in the reaction $Ru(NH_3)_5Cl_3$ + N_2O + excess Cr^{2+}. Reading from the bottom curve up: (A) NNO, 1 hr in solution, 7 days in the Nujol mull; (B) $N^{15}NO$, 1 hr in solution, 3 and 14 days in the Nujol mull; (C) ^{15}NNO, 1 hr in solution, 3 and 11 days in the Nujol mull.

operation.[6] The spectra obtained with the mulls kept for varying lengths of time are shown in Figure 1.

A significant shift of the band maximum for $[Ru(NH_3)_5{}^{15}NN]^{2+}$ (presumed[7] to be the product when ^{15}NNO is the reactant) compared to $[Ru(NH_3)_5N^{15}N]^{2+}$ is observed, and the latter complex in turn has a band maximum significantly shifted from that observed for $[Ru(NH_3)_5N_2]^{2+}$. As time progresses, the absorption bands for $[Ru(NH_3)_5{}^{15}NN]^{2+}$ and $[Ru(NH_3)_5N^{15}N]^{2+}$ reach a common condition, thus showing that linkage isomerization occurs. The fact, also demonstrated in Figure 1, that the band for $[Ru(NH_3)_5N_2]^{2+}$ is not shifted or broadened with time serves as a blank. The band does lose intensity; this feature is common to all the preparations and is ascribable to the slow decomposition of the complex.

To confirm the conclusion that the labeled material after more than 14 days really contains two species, a conclusion which is suggested by the fact that the band is broad and lies between the "zero-time" bands, we took advantage of the improved resolution to be expected at reduced temperature. The mull was placed in the hollow bore of a container which was cooled by liquid nitrogen. Dry N_2 was blown onto the faces of the disks and the spectrum was recorded. Figure 2 shows the low-temperature spectrum of the 14+-day sample derived from the series of experiments already described. Two maxima are clearly discernible, having a separation corresponding rather closely to those shown by the two zero-time samples of Figure 1.

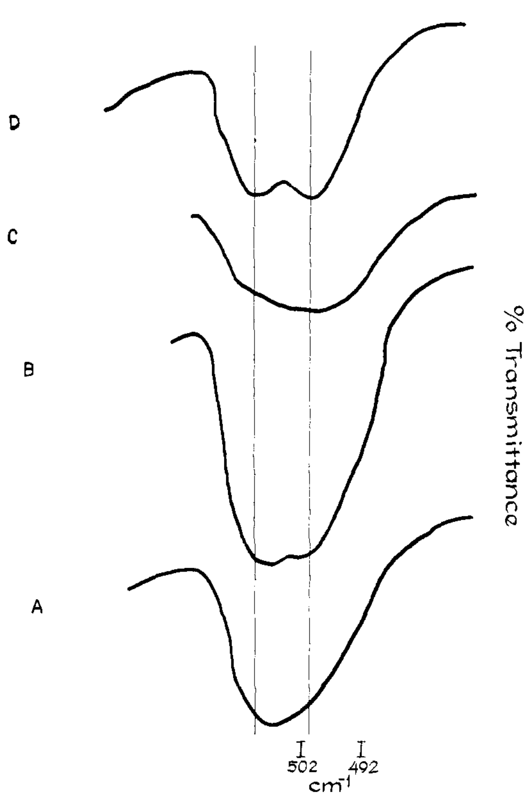


Figure 2. Cooled Nujol mulls of the bromide salt isolated from the product of the reaction $Ru(NH_3)_5Cl_3$ + $N^{15}NO$ + excess Cr^{2+}. Reading from the bottom curve up: (A) 1 hr in reaction solution, (B) 1 hr in reaction solution plus $^3/_4$ hr more in solution, (C) 1 hr in reaction solution plus 3 hr more in solution, (D) Nujol mull from Figure 1 cooled after 28 days.

It appears from Figure 1 that the half-time for isomerization of the bromide salt in Nujol is somewhat less than 3 days. In a second series of experiments, analyses were made at more frequent time intervals and the mull was stored in the dark in a desiccator between measurements. This series indicated the half-time for isomerization was 2 ± 1 day at about 22° in the dark.

The zero-time spectra of Figure 1 show that each of the samples is contaminated by the isomeric species. Since the zero-time samples have been in solution for an average time of approximately 0.75 hr, the contamination can reasonably be ascribed to significant isomerization having occurred in solution before the complex is precipitated. To get some idea of the rate of isomerization in solution, a series of experiments was done by redissolving the solid, prepared as above, in dilute HCl, and precipitating the complex from aliquots of the reaction solution at the time intervals noted. The results of those experiments are shown in Figure 2. Comparison of the spectra indicate that the half-time for isomerization in solution is of the order of 2 hr (at 25° in the dark).

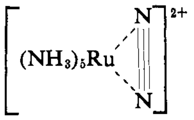
---

[6] L. R. Blaine, E. Plyler and W. Benedict, *J. Res. Nat. Bur. Stand., A*, **66**, 223 (1962).

[7] The isotopic substitution in the *endo* position of the coordinated nitrogen is expected to produce a greater shift in the Ru–N_2 frequency than substitution in the *exo* position. On this basis, we conclude that *exo* nitrogen of N_2O becomes attached to ruthenium.

The difference in the rate of isomerization in solution compared with that in the solid finds parallels in observations made with $[Co(NH_3)_5ONO]^{2+}$ (1.7×10^{-7} sec^{-1} in $[Co(NH_3)_5ONO]I_2$ compared with 1.7×10^{-5} sec^{-1} in solution, both at 20°)[8] and with $[Rh(NH_3)_5ONO]^{2+}$ (5.5×10^{-5} sec^{-1} as the Cl^- salt at 22° compared with 9.6×10^{-4} sec^{-1} in solution at 25°).[9] As is the case for the nitrito complexes, the isomerization in $Ru(NH_3)_5N_2{}^{2+}$ is intramolecular. This conclusion follows because the half-time for dissociation of N_2 from $[Ru(NH_3)_5N_2]^{2+}$ is 96 hr,[10] which is very much longer than the half-time for isomerization.

In undergoing isomerization, the complex[11] must pass through the state



and thus the energetics of the isomerization process should provide some clues to the stability of this configuration. If it is assumed that the entropy of activation for the isomerization of $[Co(NH_3)_5ONO]^{2+}$[9] is the same as that for $[Ru(NH_3)_5N_2]^{2+}$, the measured half-time of 2 hr for the isomerization of the latter in solution corresponds to an enthalpy of activation of 21 kcal/mol. Since the enthalpy of activation for the loss of N_2[10] is 28 kcal/mol, and the rate comparisons[1] indicate that the activation process for formation of the nitrogen complex involves largely bond breaking, the N_2 in the activated complex for isomerization approaches an unbound state.

Another argument suggests that the energy profile for the isomerization of $[Ru(NH_3)_5N_2]^{2+}$ is much like that of $[Co(NH_3)_5ONO]^{2+}$. Since $HONO_2$ is a somewhat stronger acid than CH_3CO_2H, the rate of aquation of $[Co(NH_3)_5ONO]^{2+}$ by Co–O bond breaking can be taken as being somewhat faster than that of $[Co(NH_3)_5O_2CCH_3]^{2+}$ (1.2×10^{-7} sec^{-1} at 25°).[12] Thus linkage isomerization for $[Co(NH_3)_5ONO]^{2+}$, k for which[13] is 3.2×10^{-5} sec^{-1} at 25°, is perhaps a factor of 50–100 faster than aquation. For $[Ru(NH_3)_5N_2]^{2+}$ the corresponding factor is approximately 45. Thus we are led to conclude that N_2 bound to Ru(II) in an intermediate position is no more stable relative to the starting complex than is the intermediate state for the isomerization of ONO on Co(III) relative to $[Co(NH_3)_5ONO]^{2+}$. This in turn suggests that the π-bound state is not unusually stable for the ruthenium–nitrogen complex.

Acknowledgment. Financial support for this research by the National Institutes of Health, both for Grant No. GM 13797 and predoctoral fellowships for J. N. A., 1967–present, is gratefully acknowledged.

John N. Armor, Henry Taube
Department of Chemistry, Stanford University
Stanford, California 94305
Received January 29, 1970

---

[8] B. Adell, *Z. Anorg. Allg. Chem.*, 271, 49 (1952).

[9] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1, 1 (1962).

[10] J. N. Armor and H. Taube, manuscript in preparation.

[11] Bimolecular mechanisms for the exchange are rejected on the basis of the following. (a) The exchange of $[Ru(NH_3)_5N^{15}N]^{2+}$ with N_2 in solution has been measured. It is very slow and fully accounted for by the aquation of the nitrogen complex and the reentry of nitrogen. (b) The ratio of the rate of isomerization of the nitrogen complex in solution compared with that of the solid is much the same as it is for the pentaamminecobalt(III) nitrito complexes (*vide infra*). The latter are known to be intramolecular processes.

[12] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 1241 (1962).

[13] R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Amer. Chem. Soc.*, 76, 5920 (1954).

Friedel–Crafts Chemistry. VI.[1] Alkylation of Heteroorganic Compounds with Dialkylhalonium Fluoroantimonates. A New General Preparation of Onium Ion Salts

Sir:

The reaction of excess primary and secondary alkyl halides with SbF_5–SO_2 solution has recently been shown to yield quantitatively dialkylhalonium fluoroantimonate salts.[1,2] The same dialkylhalonium ions can also be prepared from excess alkyl halides with anhydrous silver hexafluoroantimonate or related complex fluoro silver salts. The properties of dialkylhalonium ions should be reflected by their chemical reactions, and the suggested[2] possibility that they play a role in Friedel–Crafts alkylation reactions stimulated our interest in their general alkylating ability.

Presently we wish to report the alkylation of a variety of heteroorganic compound with dialkylhalonium ions **1** and **2** as an indication of the general nature of alkylation with this new class of alkylating agent. Table I shows the onium cations **3–38** obtained from alkylation of ethers, alcohols (water), ketones, aldehydes, carboxylic acids and nitro, sulfur, and amino compounds with halonium ions **1–2**. Only alkylation reactions of dimethyl- and diethylhalonium ions are reported. Other dialkylhalonium ions such as diisopropylbromonium and -chloronium ions[2] react in a similar fashion. In general, reactions were performed by addition of an aliquot portion of halonium ion in SO_2 at *ca.* −60° to a calculated amount of the heteroorganic n-base substrate at −78°. At least two runs with each system, one with alkylating agent in excess and one with n-base substrate in excess, were carried out. Alkylation of n-donor bases by dialkylchloronium and dialkylbromonium ions **1a,b** and **2a,b** appears to be indiscriminative but mild. Dialkyliodonium ions **1c** and **2c** do not react with n-donor bases in SO_2 or SO_2ClF solution at temperatures varied from −78 to 0°.

$$\underset{SbF_6^- \text{ or } Sb_2F_{11}}{RXR^+} + (R')_n\text{–}Y\!: \longrightarrow \underset{SbF_6^- \text{ or } Sb_2F_{11}^-}{(R')_n\text{–}Y\text{–}R^+} + R\text{–}X$$

1, R = Me
a, X = Cl
b, X = Br
c, X = I

2, R = Et
a, X = Cl
b, X = Br
c, X = I

R' = alkyl or aryl; $Y = \text{–}\ddot{\underset{\cdot\cdot}{O}}\text{–}, \text{–}\ddot{\underset{\cdot\cdot}{S}}\text{–}, \text{–}\ddot{N}\text{–}$; $n = 1, 2, 3$

Pmr spectra obtained for solutions prepared by addition of ions **1a,b** and **2a,b** in SO_2 to alcohols (water) and ethers are identical with spectra reported for the protonation of the corresponding ethers[3] (methanol[4])

---

[1] Part V: G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

[2] G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969).

[3] G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

[4] G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).