Table II. Rate Constants for Some Reactions of Chromium(II) at 0°

| Reaction | $k_d$[a] $M^{-1}$ sec$^{-1}$ | $k_s$[b,h] $M^{-1}$ sec$^{-1}$ | $k_d/k_s$[h] | $\Delta H^*$, kcal mole$^{-1}$ | $\Delta S^*$, cal mole$^{-1}$ deg$^{-1}$ | Ref |
|---|---|---|---|---|---|---|
| *cis*-$Cr(N_3)_2^+ + Cr^{2+}$ | 60[c] | 1.9[d] | 31 | 8.1 | −27 | This work |
| $CrN_3^{2+} + Cr^{2+}$ | ... | 1.3 | ... | 9.6 | −22.8 | ...[e] |
| *cis*-$CrF_2^+ + Cr^{2+}$ | ... | $1.2 \times 10^{-3}$ | <0.01 | 13 | −24 | ...[f] |
| $CrF^{2+} + Cr^{2+}$ | ... | $3.2 \times 10^{-3}$[d] | ... | 13.7 | −20 | ...[f] |
| *cis*-$Co(NH_3)_4(N_3)_2^+$ | $>10^3$ | $>10^3$ | 0.6[g] | ... | ... | This work |
| *cis*-$Co(en)_2(N_3)_2^+$ | $>10^3$ | $>10^3$ | 0.2[g] | ... | ... | This work |

[a] Rate constant for reaction proceeding *via* a double-bridged activated complex. [b] Rate constant for reaction proceeding *via* a single-bridged activated complex. [c] Reference 3. [d] Extrapolated value. [e] Reference 11. [f] Reference 5. [g] From the ratio [*cis*-$Cr(N_3)_2^+$]/[$CrN_3^{2+}$] produced. [h] If the values of $k_s$ are corrected for the symmetry number factor, the values of $k_d/k_s$ must be multiplied by 2.

It was found that chromium(II) indeed catalyzes the aquation of *cis*-$Cr(N_3)_2^+$. Kinetic measurements were carried out by following the decrease in absorbance at 275 m$\mu$, and the results are summarized in Table I. Identical results (see Table I) were obtained when *cis*-$Cr(N_3)_2^+$ was prepared *in situ* by treating *cis*-$Co(NH_3)_4(N_3)_2^+$ with an excess of chromium(II): following the very rapid *cis*-$Co(NH_3)_4(N_3)_2^+$–$Cr^{2+}$ reaction ($k > 10^3$ $M^{-1}$ sec$^{-1}$ at 15°), the slower chromium(II)-catalyzed aquation of *cis*-$Cr(N_3)_2^+$ was observed.

In Table II we present a summary of rate constants for some related reactions of chromium(II). One feature of interest is the large variation in the relative importance of double- and single-bridged transition states. The complexes *cis*-$Cr(N_3)_2^+$ and *cis*-$CrF_2^+$ display extreme behaviors. In the former case, the path that features two azide bridges is by far the dominant one. In the latter case, the exchange reaction mediated by two fluoride bridges could not be detected in spite of a thorough search.[5] The complexes *cis*-$Co(NH_3)_4(N_3)_2^+$ and *cis*-$Co(en)_2(N_3)_2^+$ exhibit an intermediate behavior, and both single- and double-bridged paths provide substantial contributions to the over-all reaction. The decrease of $k_d/k_s$ upon substitution of ammonia by ethylenediamine suggests that fairly mild modifications in the structures of the reactants may affect the relative importance of single- and double-bridged transition states. However, no rationalization can be offered, at the present stage of development of the subject, for the observed effects, and we hope that further experimentation will uncover some of the factors conducive to favoring one mechanism over the other.

It was noted previously, in comparing the rates of exchange of $CrN_3^{2+}$ and $CrF^{2+}$ with $Cr^{2+}$, that the enthalpy of activation was primarily responsible for the difference in rates.[11] Similarly, the difference in the rates of the chromium(II)-catalyzed aquations of *cis*-$Cr(N_3)_2^+$ and *cis*-$CrF_2^+$ is predominantly an enthalpy effect.

Finally, we note that the rates of the reactions of chromium(II) with $CrN_3^{2+}$ and with *cis*-$Cr(N_3)_2^+$ (catalyzed aquation) are remarkably similar, suggesting that the nonbridging ligand effects of water and azide in *cis* positions are of comparable magnitude. Analogous results were obtained in previous work: the rate constants for the iron(II) reductions of *cis*-$Co(NH_3)_4(OH_2)N_3^{2+}$ and *cis*-$Co(NH_3)_4(N_3)_2^+$ differ by less than a factor of 2.[12,13]

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(10) We found the reaction of chromium(II) with *cis*-$Co(NH_3)_4(N_3)_2^+$, followed by ion-exchange separation, a convenient way of preparing *cis*-$Cr(N_3)_2^+$ solutions.

(11) R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

(12) A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963); **86**, 2352 (1964).

(13) On the basis of the present work, it may be necessary to revise the previous suggestion[12] regarding the double-bridged mechanism for the *cis*-$Co(NH_3)_4(N_3)_2^+$–$Fe^{2+}$ reaction. This suggestion was made by taking cognizance of the relatively large increase in rate observed upon substitution of *cis*-$NH_3$ by $N_3^-$ in $Co(NH_3)_5N_3^{2+}$. However, it may be more appropriate to consider the change in rate upon substitution of $H_2O$ by $N_3^-$ in *cis*-$Co(NH_3)_4(OH_2)N_3^{2+}$. The mild decrease in rate[12] coupled with the results of the present work would suggest that both *cis*-$Co(NH_3)_4(OH_2)N_3^{2+}$ and *cis*-$Co(NH_3)_4(N_3)_2^+$ make use, at least in part, of a single azide bridge.

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## Nuclear Magnetic Resonance Spectroscopy. III. Structure of Phenyldiazonium Ion from $^{15}N$–H Coupling Study[1]

*Sir:*

Nuclear spin–spin interaction between $^{15}N$ and $^1H$ makes nmr spectroscopy a method of great potential for elucidation of the structure of organic compounds containing two or more nitrogen atoms. In pmr spectra $^{15}N$ (spin = $^1/_2$) produces a sharp doublet for the proton directly bonded to the nitrogen; the corresponding signal for $^{14}N$–$H$ is usually a single broad peak because $^{14}N$ possesses quadrupole moment and spin = 1. The large coupling (~90 cps) between directly bonded $^{15}N$ and $^1H$ is of particular advantage in pmr spectra. The measurement of the area under the doublet due to $^{15}N$–$H$ and the singlet due to $^{14}N$–$H$ may be used for a quantitative estimation of the relative amounts of $^{15}N$ and $^{14}N$ in compounds under investigation.

We have used pmr spectroscopy of $^{15}N$-labeled compounds for studying the possibility of the isotope rearrangement (Ia $\rightleftarrows$ Ib) during the generation or reactions of phenyldiazonium ion (I).

$$\underset{\text{Ia}}{(C_6H_5{}^{15}N{\equiv}N)^+} \rightleftharpoons \underset{\text{Ib}}{(C_6H_5N{\equiv}{}^{15}N)^+}$$

Phenyldiazonium chloride was prepared from $^{15}N$-aniline by diazotization with unlabeled sodium nitrite and subjected to the reactions outlined in Scheme I. The pmr spectra of the resulting compounds II and III recorded on a Varian A-60A spectrometer

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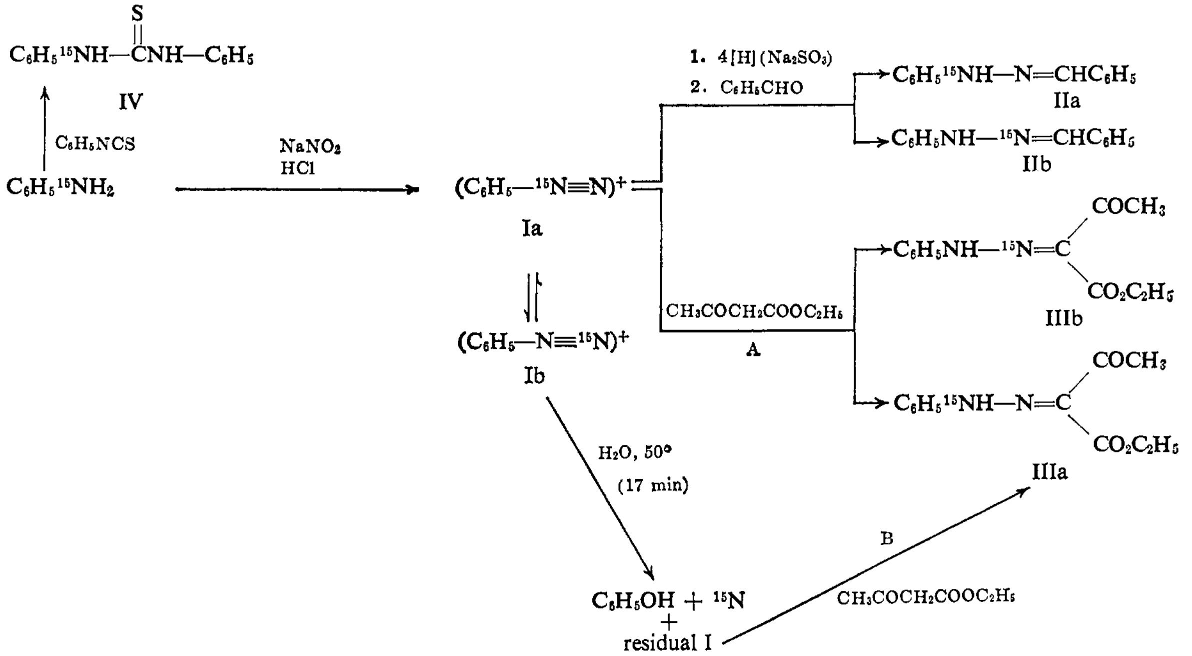
(1) Part II: A. K. Bose, M. S. Manhas, and E. R. Malinowski, *J. Am. Chem. Soc.*, **85**, 2795 (1963); Part I: E. R. Malinowski, M. S. Manhas, G. H. Müller, and A. K. Bose, *Tetrahedron Letters*, 1161 (1963).

Scheme I

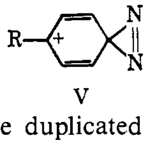


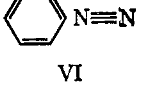
with about 80-mg samples in 0.25 ml of solvent were studied. In order to increase (where necessary) the signal to noise ratio and thus enhance the accuracy of measurements we have used a time-averaging computer (Varian C-1024 CAT) for recording pmr spectra.

A comparison of the area under the doublet corresponding to $^{15}$N-*H* signal and the singlet due to $^{14}$N-*H* in III (and II) indicated that 96.5 ± 0.3% of the nitrogen adjacent to the phenyl ring and directly bonded to a proton corresponded to $^{15}$N. The $^{15}$N content of the starting material was determined to be 96.6 ± 0.3% from the pmr spectrum of $^{15}$N-diphenylthiourea (IV) prepared from $^{15}$N-aniline.[2]

If the isotope rearrangement Ia → Ib had taken place, the species IIb and IIIb would have been generated along with IIa and IIIa. The fact that the $^{15}$N content of the nitrogen adjacent to the phenyl ring in hydrozones II and III was the same as that of the starting material indicated that no noticeable isotope randomization had taken place.

Recently Lewis and Insole[3] reported that when $^{15}$N-diazonium fluoroborate is subjected to hydrolysis at 50° until about 80% of the diazo compound is converted to phenol, the residual diazo compound is found to have undergone about 2.3% randomization. In order to explain the apparent rearrangement Ia → Ib accompanying the hydrolysis of diazonium salts, Lewis and Insole suggest the presence of the intermediate V along with the caged pair VI.


V


VI

We have duplicated the experimental conditions of Lewis and Insole. $^{15}$N-Labeled phenyldiazonium fluoroborate was subjected to decomposition in water for 17 min at 50°. The residual diazo compound was converted to the hydrazone III and its pmr spectrum (obtained by time averaging over 80 runs) was studied. From the measurement of areas, the $^{15}$N content of the N-H group was found to be 96.5 ± 0.2% in the samples of III obtained by route A as well as route B. The same $^{15}$N content for both of these samples was also found from their mass spectra.

To verify the accuracy of the pmr method for isotope level determination we diluted the above sample of hydrazone III with unlabeled III so that the resulting $^{15}$N content was 95.5%. Using the "CAT" with a sample size of 15 mg, the isotope level at the α-nitrogen in this sample was determined to be 95.7 ± 0.4%. This indicates that had the isotope rearrangement taken place to the extent of 2–3% as suggested by Lewis and Insole, our spectral measurements would have detected it.

Apparently the observations of Lewis and Insole were affected by large limits of error inherent in their method of analysis. Our findings are that the diazonium ion Ia does not undergo rearrangement to Ib during reduction, coupling, or hydrolysis.

The formation of the intermediate V during hydrolysis of phenyldiazonium ion is improbable in the light of our observations. Our conclusions are consistent with recently reported kinetic investigations of Brown and Drury.[4]

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[2] $^{15}$N-Aniline was purchased from Merck Sharp and Dohme of Canada. The isotopic purity was reported to be 97%.

[3] J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, 85, 122 (1963); 86, 32, 34 (1964).

[4] L. L. Brown and J. S. Drury, *J. Chem. Phys.*, 43, 1688 (1965).

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## The Optical Rotatory Properties of Poly-L-proline

*Sir:*

Despite considerable study by several groups of investigators,[1–6] the optical rotatory properties of poly-L-