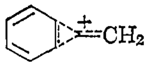
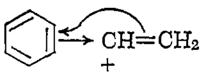
heptatriene. Rather, its presence has been inferred from the existence of reactions of cycloheptatriene which generate products logically derived from norcaradiene. In no previous case, however, have these reactions rationally *required* the prior formation of norcaradiene. In the present instance, by contrast, the kinetic results can only be explained by invoking in the transition state for ionization the full electron-donating capability associated with preformed cyclopropane rings.

The observed solvolysis rate constant for Ib actually underestimates the solvolytic reactivity of IV. From the observed free energy of activation for solvolysis of Ib must be subtracted the free energy difference between Ib and the less stable IV, in order to obtain the actual free energy of activation for solvolysis of IV. Since the nmr spectrum ($CDCl_3$) of Ib shows no trace of IV, this free energy difference must be at least 2.5 kcal/mole. It is more likely in the range 6–14 kcal/mole.[22] By assuming the *minimum* value of this range, one calculates that the true rate constant for solvolysis of IV (100°) is 2.6×10^{-2} sec^{-1}, a value more than two powers of ten greater than that for the most reactive dialkyl-substituted cyclopropylcarbinyl dinitrobenzoate previously reported.

The basis for this enhanced reactivity is as yet undefined, but it is interesting to note that recent formulations of the cyclopropyl carbonium ion impute some double bond character to the bond joining the two carbon atoms β to the site of ionization. In the present instance, such a formulation (XI[13] or XII[3]) imparts partial benzenoid character to the norcaradiene six-membered ring.



XI



XII

Acknowledgment. We are grateful to the National Science Foundation and to the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

[22] The dilatometric technique which was able to detect 0.01% bicyclic valence tautomer in cyclooctatetraene failed to detect norcaradiene in cycloheptatriene [R. Huisgen, *Angew. Chem.*, 76, 928 (1964)]. By utilizing standard bond energies, Doering and Willcott estimate that norcaradiene is less stable than cycloheptatriene by 11–14 kcal/mole: W. von E. Doring and M. R. Willcott, III, unpublished calculations; M. R. Willcott, Ph.D. Thesis, Yale University, 1963.

G. Dann Sargent, Nancy Lowry
Department of Chemistry, Amherst College
Amherst, Massachusetts 01002

Steven D. Reich
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received July 24, 1967

Oxygen Isotopic Fractionation in the Reduction of Aquotetraamminechromium(III). Evidence for a *trans* Effect

Sir:

It has been suggested by a number of authors that the rearrangement of bonds to nonbridging ligands may be an important part of the activation process for some inner-sphere redox reactions.[1,2] Very recently Pennington and Haim[3] suggested that the large difference in the rates of reactions of the *cis* and *trans* isomers of some bis(ethylenediamine)chromium(III) complexes with chromium(II) could be explained by assuming that the bond to the ligand *trans* to the bridging group had to be stretched to make the activated complex. Several years ago, Taube and co-workers[2,4] began seeking direct experimental evidence for such bond rearrangements in the form of isotopic fractionation measurements. Green, Schug, and Taube[4] measured nitrogen isotopic fractionation factors for the reactions of a number of cobalt(III)–ammine complexes with aquochromium(II) ion and concluded that stretching of cobalt–nitrogen bonds was not important in the reactions studied. Their results are not surprising in retrospect, in view of the small difference in bond distances between cobalt(II) and cobalt(III) ammines.[5] A more substantial difference in geometry exists between the complexes of chromium(II) and chromium(III) with weak field ligands,[6] and it seemed to us that measurements of isotopic fractionation for atoms bound to chromium(III) would constitute a more meaningful test of the bond-stretching hypothesis.

We have measured the fractionation of O^{16} compared to O^{18} in the reaction of *trans*-chloroaquotetraamminechromium(III) ion with aquochromium(II) ion. The reaction under study is actually the chromium(II)-catalyzed loss of ammonia from the chromium(III) complex, the main net change being described by

$$(NH_3)_4Cr(OH_2)Cl^{2+} + 4H_3O^+ \longrightarrow 5NH_4^+ + (H_2O)_5CrCl^{2+} \quad (1)$$

It is generally accepted that the catalysis of such reactions by chromium(II) involves an electron-transfer reaction as the rate-determining step.[1,2] That net replacement of chloride is not observed is taken to be evidence that the redox reaction is of the inner-sphere type.

The salt *trans*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ was mixed with $Cr(ClO_4)_2$ in *ca.* 2 *M* $HClO_4$ and allowed to react for two or more half-times. The reaction was quenched, and the unreacted *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was retrieved. The ratio $[O^{18}]/[O^{16}]$ was determined for the *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ before reaction and for the complex retrieved from the reaction mixture. It was found that the $[O^{18}]/[O^{16}]$ ratio increased steadily with the extent of reaction. From these ratios we calculate that the kinetic isotopic fraction factor $(d \ln [O^{16}])/(d \ln [O^{18}]) = k_{O^{16}}/k_{O^{18}} = 1.016 \pm 0.001$, where $k_{O^{16}}$ and $k_{O^{18}}$ represent the rate constants for ions of the complex containing O^{16} and O^{18}, respectively.

Preliminary data have also been obtained for the reaction of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ with Cr^{2+}, and these allow an upper limit to be set for the fractionation factor for the *cis* complex, namely, $k_{O^{16}}/k_{O^{18}} \leqq 1.007$.

The isotope fractionation data indicate that *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ reacts with Cr^{2+} 1.6% faster when the water molecule *trans* to the bridge contains O^{16} than when the water molecule contains O^{18}. Thus a substantial stretching of the bond to the *trans* ligand

---

[1] N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966).

[2] H. Taube, *Advan. Inorg. Chem. Radiochem.*, 1, 1 (1959).

[3] D. E. Pennington and A. Haim, *Inorg. Chem.*, 5, 1887 (1966).

[4] M. Green, K. Schug, and H. Taube, *ibid.*, 4, 1184 (1965).

[5] M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

[6] L. E. Orgel, "An Introduction to Transition-Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 59.

must occur in the formation of the activated complex. Our results for the *cis* isomer imply that the stretching of bonds to ligands *cis* to the bridging group is much less important. It would appear then that the chromium(III) complex undergoes tetragonal distortion in the formation of the activated complex, so that the activation process resembles in many respects Orgel's description[7] of the reaction of $Co(NH_3)_5Cl^{2+}$ with Cr^{2+}.

We have also measured the kinetics of the reactions of both isomers with Cr^{2+}, and we find that both reactions obey rate laws of the form

$$\text{rate} = k[Cr^{2+}][Cr(NH_3)_4(OH_2)Cl^{2+}] \qquad (2)$$

For the *cis* isomer $k = 0.098\ M^{-1}\ \text{sec}^{-1}$ at 25.0° and $E_a = 10.7$ kcal/mole; for the *trans* isomer $k = 0.89\ M^{-1}\ \text{sec}^{-1}$ at 25° and $E_a = 10.1$ kcal/mole. The difference in rates for the two isomers is much smaller than reported by Pennington and Haim[3] for the analogous ethylenediamine complexes. In the case of the ethylenediamine complexes, it may be necessary to change the conformation of the chelate rings in order to form the activated complex for the *cis* isomer, whereas the ligands of the ammine complexes may move independently of each other.

---

(7) L. E. Orgel, *Inst. Intern. Chim. Solvay, X^e Conseil Chim.*, 289 (1956).

Sr. J. M. DeChant, J. B. Hunt
Department of Chemistry, The Catholic University of America
Washington, D. C.

Received September 1, 1967

A Coordination Compound of Diethyldipyridylnickel with Acrylonitrile. A Polymerization Catalyst of Acrylonitrile

Sir:

Previously we reported the isolation of ethylnickel,[1,2] -iron,[1] and -cobalt[1b,2] complexes from mixed catalyst systems of metal acetylacetonates, diethylaluminum monoethoxide, and dipyridyl. These complexes catalyze the conversion of butadiene to oligomers on one hand and acrylonitrile to high polymers on the other.[1b,c] Polymerization of acrylonitrile takes place at room temperature with catalytic amounts of these complexes yielding white polyacrylonitrile with molecular weights of the order of 10^5. Although the infrared spectra of these polymers are similar to those obtained using a radical initiator, the mechanism of polymerization seems to be different from the ordinary radical-initiated polymerization. Styrene, methyl methacrylate, and vinyl chloride are not polymerized with these complexes; copolymerization of acrylonitrile with butadiene gave only a homopolymer of acrylonitrile. These facts suggest a specific interaction of acrylonitrile with the transition metal complexes. We could isolate an orange coordination compound of acrylonitrile with diethyldipyridylnickel (I) at low temperatures as an active species for acrylonitrile polymerization.

The adduct is extremely sensitive to air and stable only at low temperature. Over about −10° *in vacuo* it releases acrylonitrile, leaving the starting material I. The adduct was prepared and the amount of acrylonitrile contained determined as follows.

Acrylonitrile was distilled *in vacuo* into a flask containing dark green crystals of I (0.972 g, 3.56 mmoles) at −78°. The mixture was stirred for several hours until all the solid became orange. The excess acrylonitrile was removed by evaporation at 10^{-4} mm at −78° for 40 hr. The orange solid which remained was then warmed to room temperature *in vacuo*. The volatile matter was condensed with liquid nitrogen and shown to be acrylonitrile (0.180 g, 3.39 mmoles) by infrared and gas chromatography. The green residue (0.980 g, 101% of the original weight) was crystallized from acetone and proved to be the starting material I by infrared comparison and analytical data.

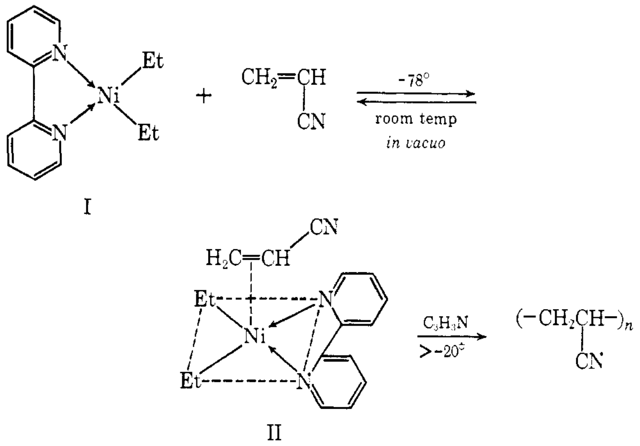
Anal. Calcd for $C_{14}H_{18}N_2Ni$: C, 61.61; H, 6.62; N, 10.25. Found: C, 61.8; H, 6.73; N, 10.3.

The orange 1:1 acrylonitrile adduct, II, dissociates in ether solution at −78° yielding a green solution of I. The adduct is an active catalyst for the polymerization of acrylonitrile, but not of styrene or butadiene.

Whereas I is thermally quite stable, interaction of acrylonitrile with I at room temperature causes immediate fission of the ethyl–nickel bonds, releasing a gas composed mainly of *n*-butane, with small amounts of ethane and ethylene. By reaction of I with acrylonitrile in ether at room temperature, relatively stable red crystals of composition $Ni(dipy)(CH_2{=}CHCN)_2$ were isolated.

Anal. Calcd for $C_{16}H_{14}N_4Ni$: C, 59.85; H, 4.40; N, 17.45. Found: C, 59.8; H, 4.51; N, 17.5.

The infrared spectrum of the red complex (KBr disk) showed a sharp $\nu_{C\equiv N}$ absorption band at 2169 cm^{-1} and the absence of absorption bands due to vinyl groups. This fact indicates that acrylonitrile may be coordinated with the nickel atom in the red complex through the vinyl groups as in the acrylonitrile–nickel complexes prepared by Schrauzer.[3] The mode of coordination of acrylonitrile with the nickel atom in the orange adduct II is not known, due to the instability of the complex. However it seems reasonable to assume that acrylonitrile is coordinated with the nickel



---

(1) (a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, **87**, 4652 (1965); (b) Preprint, International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, 1966, I-102; (c) submitted for publication.

(2) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Am. Chem. Soc.*, **88**, 5198 (1966); *J. Organometal. Chem.* (Amsterdam), **6**, 572 (1966).

(3) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); H. P. Fritz and G. N. Schrauzer, *Chem. Ber.*, **94**, 650 (1961). The $\nu_{C\equiv N}$ band at 2175 cm^{-1} of $Ni(CH_2{=}CHCN)_2(PPh_3)_2$ obtained by Schrauzer may be compared with that for our complex $Ni(dipy)(CH_2{=}CHCN)_2$.