

In a representative experiment, titanium tetrachloride (0.5 mole equiv.) was added with cooling to an anhydrous benzene suspension of sodium benzyloxyde (generated *in situ* using oil-free sodium hydride). Potassium metal (1.0 mole equiv.) was added to the resulting pale olive-green suspension of the titanium-(IV) dichloride dialkoxide²; the mixture was refluxed briefly to disperse the metal, and then the whole was stirred for approximately 20 hr. in order to complete the reduction. The solvent was removed by distillation under a stream of nitrogen, and the black residue, presumed to be the titanium(II) dialkoxide,³ was heated from 100 to 140° until the color changed to light gray, indicating formation of titanium dioxide. Addition of ether, alcohol, and water, followed by filtration and evaporation, gave *bibenzyl* in 51% (v.p.c.) yield (based on recovered benzyl alcohol).

In other cases, results were varied and depended upon the structure of the alcohol, the nature of the solvent, and the character of the reducing agent employed. Under conditions similar to those described above, *allyl alcohol* was converted in 38% (v.p.c.) yield to *biallyl*. *Squalene* was produced in similar yield on carrying out the reduction sequence (glyme solvent) with *farnesol*. Attempts to produce coupled hydrocarbon from *n*-amyl alcohol and cyclohexylmethanol were unsatisfactory under the described conditions, in that at best only traces of the desired materials were detected. By the same method, phenol was converted (after final pyrolysis at 210–235° for 16 hr.) to a mixture of products, including biphenyl (2.5%) and other substances believed to be *o*-phenylphenol and *o,m,p*-terphenyls. The product nature and distribution in the phenol case are suggestive of a radical type decomposition in the final, thermal stage.

Our interpretation of the course of the over-all reaction rests in part on the following observations (experiments with benzyl alcohol, and benzene as solvent. (1) Refluxing of the titanium(IV) dichloride dialkoxide mixture without prior reduction afforded diphenylmethane in almost quantitative yield, a known reaction of this type of titanium derivative.⁴ (2) When sodium was utilized as the reducing agent, consumption of the metal was incomplete, and mixtures of bibenzyl, diphenylmethane, and benzyl alcohol ultimately resulted. This behavior is ascribable to titanium(III) species: extrusion of titanium dioxide leaves benzyl radical, which couples, and benzylcarbonium ion, which attacks solvent to give diphenylmethane. (3) Samples removed either before or after potassium reduction, but before heating, yielded on alcoholysis only benzyl alcohol, ruling out benzyl chloride as a participant. (4) If decomposition of the black organotitanium residue was interrupted and alcohol-water added, a blue or purple precipitate formed [Ti(II) → Ti(III)] which immediately turned white on contact with air [Ti(III) → Ti(IV)]. Large amounts of benzyl alcohol were recovered.

(2) Titanium compounds of this type are known and have been prepared in a similar manner: A. N. Nesmeyanov, E. M. Bratnina, and R. Kh. Freidlina, *Dokl. Akad. Nauk SSSR*, **94**, 249 (1954); *Chem. Abstr.*, **49**, 3000 (1955).

(3) Whether the alkoxide is mono- or polymeric is unknown.

(4) L. M. Bobinova and G. A. Razuvaev, *J. Gen. Chem. USSR*, **33**, 2329 (1963).

In further exploratory experiments, substitution of silicon species for titanium intermediates was attempted. By using silicon tetrachloride as reagent and glyme as solvent, but otherwise adhering to the original specified conditions, an *ca.* 2:1 mixture of toluene and bibenzyl was identified as product, along with starting material, benzyl alcohol. The nature of the reduced intermediates is obscure.

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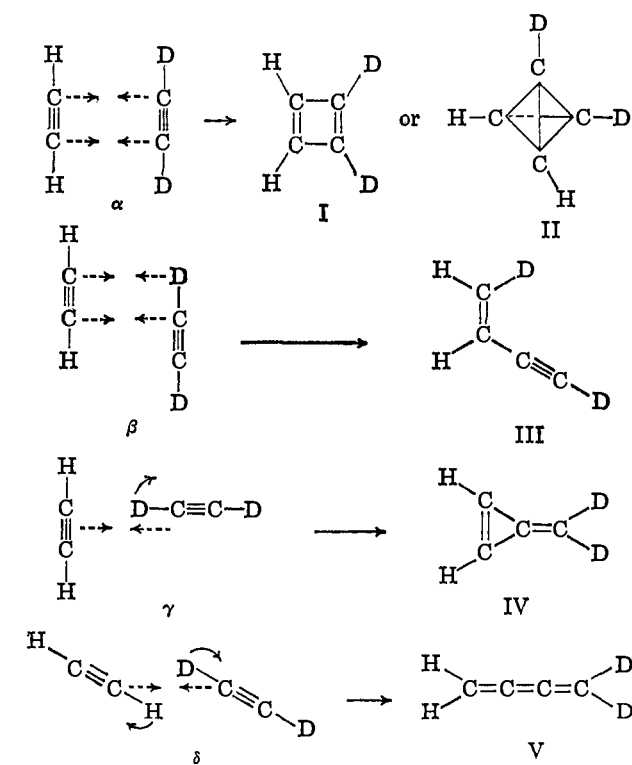
(5) National Science Foundation Fellow, 1962–1965.

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Structure of a Transient Dimer of Acetylene

Sir:

The following conclusions regarding the structure of a transient dimer of acetylene are based on measured rates of exchange between isotopically labeled species (H-D and C¹²-C¹³), as investigated under strictly homogeneous conditions in the gas phase, in high argon dilution. The kinetics indicate that the dimer is generated by the association of vibrationally excited monomers. Such an encounter may be schematically represented by α , β , γ , or δ leading to I–V. Our data



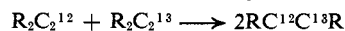
excluded all but one of these possibilities.

To place these experiments in proper context it is necessary to recall that the homogeneous gas phase reaction between acetylene and deuterium has been studied in a shock tube and its mechanism established.¹ Over the temperature range 1300–1665°K. the em-

(1) K. Kuratani and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 150 (1965).

(2) Note erroneous units given for (k_1k_3/k_2) at the conclusion of ref. 1. Also, the last two sentences of the paper are incorrect.

McOmie⁶ suggests that the exchange



may prove successful under the conditions of our experiment for properly selected substituents.

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(6) W. Baker and J. F. W. McOmie, ref. 5, p. 43.

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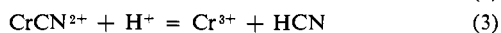
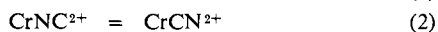
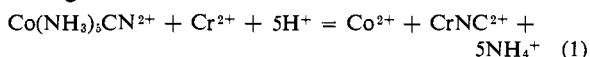
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Kinetics and Mechanisms of the Formation, Isomerization, and Aquation Reactions of the Isomeric Cyanochromium(III) Ions¹

Sir:

This communication describes the results of a kinetic study of the reaction of cyanopentaamminecobalt(III) and chromium(II) ions in acidic perchlorate solution in which a novel intermediate, the nitrogen-bonded isocyanochromium(III) ion, plays an important role. The over-all reaction occurs in three stages, which we interpret (as justified below) as corresponding to the three changes



Since each step is substantially slower than the preceding one, it has been possible to study the three processes in kinetically isolated circumstances. Under typical concentration conditions at 15°, the oxidation-reduction process (eq. 1) is essentially complete within 15–30 sec., the linkage isomerism of cyanide ion (eq. 2) within *ca.* 10 min., and the subsequent aquation (eq. 3) within several hours. It is this fortunate separation of rates which allows us to formulate this relatively detailed description of the reaction.

Oxidation-Reduction Stage. The rate of disappearance of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ was followed spectrophotometrically at its two wave lengths of maximum light absorption, 3270 and 4400 Å. Kinetic runs were carried out over concentration ranges $0.9\text{--}7 \times 10^{-3} M$ in each reactant at 15.0° in 1.00 *F* HClO_4 . The data follow the mixed second-order rate law

$$-d[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}]/dt = k_{\text{ox}}[\text{Co}(\text{NH}_3)_5\text{CN}^{2+}][\text{Cr}^{2+}] \quad (4)$$

with $k_{\text{ox}} = 61 \pm 6 M^{-1} \text{sec}^{-1}$.

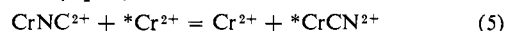
Linkage Isomerization Stage. The primary observations indicating that a second stage of reaction occurs were the continued appreciable changes in absorbance at some wave lengths over a period of several minutes after the primary reaction was essentially complete.²

(1) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 1727.

(2) At some wave lengths (*e.g.*, 3270 Å.), the absorbance falls sharply in the first stage, reaches a minimum, and then slowly rises to a steady value after 8–10 min.; at other wave lengths (*e.g.*, 4400 Å.), an initial sharp decrease in the first stage is noted, and the readings remain essentially constant during the succeeding several minutes; at still other

The data at 5200 Å., where the second stage of reaction exhibits the greatest changes in absorbance, proved the most accurate for kinetic analysis. These data fit a first-order rate equation, $-d \ln (A_\infty - A)/dt = k_i$. The value of k_i so calculated is independent of concentrations of products and of excess reactant, including chromium(II). The average value is $k_i = 9.2 \pm 0.5 \times 10^{-3} \text{sec}^{-1}$. We postulate that this second stage corresponds to a first-order isomerization reaction (eq. 2) with the associated rate equation $-d[\text{CrNC}^{2+}]/dt = k_i[\text{CrNC}^{2+}]$. The evidence that this reaction is, in fact, the isomerization is summarized in the next section.

The lack of dependence of rate upon the concentration (or presence) of chromium(II) ion leads to the particularly striking conclusion that the isomerization reaction does *not* proceed by involving chromium(II) ion in an electron-transfer process, in which the bridging CN^- ligand becomes bonded to chromium(III) *via* the carbon end (eq. 5). It should be noted also that



Halpern has observed the intermediate species $\text{Co}(\text{CN})_5(\text{NC})^{3-}$ in basic solution.³

Characterization and Identification of the Isomeric Cyanochromium(III) Ions. The identification of the ion CrCN^{2+} is based primarily on three observations: the behavior during ion-exchange elution (related to the net ionic charge), analysis of the cyanide/chromium ratio in the separated complex, and the absorption spectrum. The complex is absorbed onto Dowex 50W-X8 (50–100 mesh) cation resin, and is eluted by concentrations of electrolyte (generally 1 *F* NaClO_4) which will elute other ions of charge +2, including Co^{2+} in these solutions. The complex can be satisfactorily separated from other species, including Co^{2+} , by slow elution with 1 *F* NaClO_4 –0.01 *F* HClO_4 from cation-exchange resin in a water-jacketed column kept at 0°. Analysis of these solutions for the cyanide/chromium ratio led to the value 0.90 in two separate preparations. The spectrum of this ion resembles that of other $\text{Cr}(\text{OH}_2)_5\text{X}^{2+,3+}$ ions, with two peaks of comparable intensity. The absorption maxima occur at 5250 and 3930 Å., shifted more toward higher energies than those of other similar ions.⁴ This is quite reasonable for CrCN^{2+} , since CN^- causes a ligand field splitting considerably higher than other common ligands.

The rapid decomposition ($t_{1/2} = 1.28 \text{min.}$ at 15°) of the precursor of CrCN^{2+} has prevented our determining its composition and structure as firmly as we did for CrCN^{2+} . One indication that the ion is CrNC^{2+} is just that the product of its disappearance is the isomeric CrCN^{2+} ; in addition, it seems a reasonable product of the primary reaction of $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ and Cr^{2+} . A less subjective basis for this identification is its absorption spectrum. Extrapolation of the first-order absorbance change in the second stage of wave lengths (*e.g.*, 5200 Å.) the absorbance increases somewhat at the start, then continues to rise quite appreciably, reaching a steady value after 8–10 min. These observations are inconsistent with occurrence of a single reaction.

(3) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965).

(4) The long wave length absorption maxima (Å) of several ions $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+,3+}$, are: X = I⁻, 6500; Cl⁻, 6090; F⁻, 5950; H₂O, 5740; NCS⁻, 5700; NH₃, 5450. This order also represents increasing ligand field strength of X.