In a representative experiment, titanium tetrachloride (0.5 mole equiv.) was added with cooling to an anhydrous benzene suspension of sodium benzyloxide (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) \rightarrow Ti(III)] which immediately turned white on contact with air $[Ti(III) \rightarrow Ti(IV)]$. Large amounts of benzyl alcohol were recovered.

(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-

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

K. Kuratani and S. H. Bauer, J. Am. Chem. Soc., 87, 150 (1965).
 Note erroneous units given for (k₁k₃/k₂) at the conclusion of ref. 1. Also, the last two sentences of the paper are incorrect.

³²⁷⁸ Journal of the American Chemical Society | 87:14 | July 20, 1965

pirical rate is given by

$$-\frac{\mathrm{d}(\mathrm{C}_{2}\mathrm{H}_{2})}{\mathrm{d}t} = k_{\mathrm{p}}(\mathrm{C}_{2}\mathrm{H}_{2})^{0.24}(\mathrm{D}_{2})^{1.0}(\mathrm{Ar})^{0} \qquad (1)$$

with

$$k_{\rm p} = 8 \times 10^7 \exp(-33,800/RT)$$

(mole/l.)^{-0.24} sec.⁻¹ (2)

Further, it was established that

$$d(C_2HD)/dt \approx 2[d(C_2D_2)/dt] \approx - \frac{2}{3}[d(C_2H_2)/dt]$$
 (3)

Expression 1 and relation 3 may be accounted for on the basis of a mechanism in which two types of complexes are generated: a loose species designated by $C_2H_2 \cdot D_2$, and a tightly bound species designated by $C_2H_2D_2^*$, which resembles a highly excited ethylene with V_d symmetry. Thus

Reduction of the experimental results according to this mechanism gives magnitudes for

$$\frac{k_1 k_3}{k_2} = 2.8 \times 10^7 \exp(-32,500/RT) \text{ sec.}^{-1} \quad (4)$$

and

$$\alpha = 3.9 \times 10^{6} \text{ mole}^{-1} \text{ cm.}^{3}$$

where

$$\alpha \equiv \frac{k_2}{k_{-1} + 0.75k_3} \tag{5}$$

The combinations of rate constants in (4) and (5) may be resolved² by introducing reasonable estimates for the unknown k values. Let $k_{-1} \approx k_3$; then $k_2/k_3 \approx 8 \times 10^6 \text{ mole}^{-1} \text{ cm}.^3$, and $k_1 \approx 2 \times 10^{14}$ $\exp(-32,500/RT) \text{ mole}^{-1} \text{ cm}.^3 \text{ sec}.^{-1}$. Further, since a maximum value for $k_2 \approx 10^{14} \text{ mole}^{-1} \text{ cm}.^3 \text{ sec}.^{-1}$, the corresponding maximum for $k_3 \approx 10^7 \text{ sec}.^{-1}$. The unimolecular rate for destruction of $C_2H_2 \cdot D_2$ is $(k_3 + k_{-1})(C_2H_2 \cdot D_2)$; hence, its minimum (natural) lifetime is of the order of $10^{-7} \text{ sec}.^3$.

Using a single pulse shock tube, mixtures of acetylene and dideuterioacetylene were heated to temperatures in the range 1200–1800 °K. for dwell times of about 1.3 msec. Small amounts of diacetylene were detected when shock temperatures were above 1700 °K.; below 1600 °K. neither HD or diacetylene could be detected. The limits of sensitivity are 0.04% for HD and 0.7% for C₄H₂ of the acetylene subjected to shock. At reaction temperatures 1600 °K. and below, the reclaimed acetylene could be accounted for to better than 1% of that present in the initial mixture. This imposes an upper limit on possible conversion to C₆H₆, C₈H₈, etc. If the reaction 2C₂H₂ \rightarrow C₄H₃ + H were to occur to a substantial extent, hydrogen would be detectable under the conditions of our experiment. This was not the case. The power rate law for the H-D exchange reaction is

 $\frac{\mathrm{d}(\mathrm{C}_{2}\mathrm{D}\mathrm{H})}{\mathrm{d}t} = k_{\mathrm{p}}(\mathrm{C}_{2}\mathrm{H}_{2})^{0.25}(\mathrm{C}_{2}\mathrm{D}_{2})^{0.5}(\mathrm{Ar})^{0.55}$

(6)

$$k_{\rm p} = 1.7 \times 10^7 \exp(-30,500/RT) \ ({\rm mole/l.})^{-0.25} \ {\rm sec.}^{-1}$$
(7)

To account for this rate expression again, consider the generation of a loose and a tight complex $[C_2H_2 \cdot C_2D_2]$ and $C_4H_2D_2^*$, respectively] and make the additional assumption that the loose complex $[C_2H_2 \cdot C_2D_2]$ cannot be produced unless one of the acetylene molecules had been previously *vibrationally excited* by collision, in this case with argon, since that species is present in the highest concentration.

$$C_{2}D_{2} + Ar \stackrel{k_{-}eD}{\longrightarrow} C_{2}D_{2}^{(v)} + Ar$$

$$C_{2}H_{2} + Ar \stackrel{k_{-}eH}{\longrightarrow} C_{2}H_{2}^{(v)} + Ar$$

$$C_{2}D_{2}^{(v)} + C_{2}H_{2} \stackrel{k_{-1}}{\longrightarrow} C_{2}D_{2} \cdot C_{2}H_{2} \text{ etc.}$$

The essential difference between the $(C_2H_2 + D_2)$ reaction and the $(C_2H_2 + C_2D_2)$ reaction is then a difference in the type of activation required for the formation of the loose complex. A detailed report on this kinetic study will be submitted shortly.

The occurence of a rapid H-D exchange with a relatively low activation energy eliminates structures IV and V. The transition states which permit H-D atom scrambling in IV and V require complicated and closely synchronized motions of the hydrogen atoms. To ascertain which of the remaining structures best describes the $C_4H_2D_2^*$ complex, we compared the rate law for C^{13} - C^{12} exchange in the reaction

$$C_2{}^{13}H_2 + C_2{}^{12}H_2 \longrightarrow 2C{}^{13}C{}^{12}H_2$$

with that found for $(C_2H_2 + C_2D_2)$. Single pulse shock tube experiments on several mixtures of C^{13} - C^{12} labeled acetylenes, under conditions identical with those used for the H–D studies, gave *no exchange*. The limit of sensitivity for $C^{12}C^{13}$ exchange is about 1% (of the acetylene present), whereas under comparable conditions 25% H–D exchange occured for $(C_2H_2 + C_2D_2)$. The structure of the tight complex is therefore an excited vinylacetylene type (III) which preferentially dissociates either to $(C_2H_2 + C_2D_2)$ or to $2C_2HD$. Only at temperatures above 1700°K. is there an indication of dissociation to $(C_4HD + HD)$.

The energized species generated in these experiments is approximately 135 kcal./mole above the enthalpy of the elements (reduced to 0°K.). At that temperature, $\Delta H_{\rm f}$ ° (vinylacetylene) has been estimated at 75 kcal./ mole.⁴ Thus, it appears that the approximately 60 kcal./mole available in the loose complex is not sufficient to surmount the potential barrier for conversion to a cyclobutadiene conformation. Study of the reviews on cyclobutadiene by Craig⁵ and Baker and

⁽³⁾ It is interesting to note that in the unimolecular decomposition of ethylene [G. B. Skinner and E. M. Sokoloski, J. Phys. Chem., 64, 1020 (1960)] the vibrationally excited $C_2H_4^*$ has a comparably long lifetime: $k_u^{\infty} = 10^{8.87} \exp(-46,400/RT) \sec^{-1}$.

⁽⁴⁾ M. Cowperthwaite and S. H. Bauer, J. Chem. Phys., 36, 1743 (1962).

⁽⁵⁾ D. P. Craig, "Non-Benzenoid Aromatic Hydrocarbons," D. Ginsburg, Ed., Interscience Publishers Inc., New York, N. Y., 1959, p. 1.

McOmie⁶ suggests that the exchange

 $R_2C_2^{12} + R_2C_2^{13} \longrightarrow 2RC^{12}C^{13}R$

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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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

$$Co(NH_{3})_{5}CN^{2+} + Cr^{2+} + 5H^{+} = Co^{2+} + CrNC^{2+} + 5NH_{4}^{+}$$
(1)

$$CrNC^{2+} = CrCN^{2+}$$
 (2)

$$CrCN^{2+} + H^{+} = Cr^{3+} + HCN$$
 (3)

Since each step is substantially slower than the preceeding one, it has been possible to study the three processes in kinetically isolated circumstances. Under typical concentration conditions at 15° , the oxidationreduction 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 $Co(NH_3)_5CN^{2+}$ was followed spectrophotometrically at its two wave lengths of maximum light absorption, 3270 and 4400 Å. Kinetic runs were carried out over concentration ranges $0.9-7 \times 10^{-3}$ *M* in each reactant at 15.0° in 1.00 F HClO₄. The data follow the mixed second-order rate law

$$- d[Co(NH_3)_5CN^{2+}]/dt = k_{ox}[Co(NH_3)_5CN^{2+}][Cr^{2+}]$$
(4)

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

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 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

$$CrNC^{2+} + *Cr^{2+} = Cr^{2+} + *CrCN^{2+}$$
 (5)

Halpern has observed the intermediate species Co- $(CN)_{5}(NC)^{3-}$ in basic solution.³

Characterization and Identification of the Isomeric Cyanochromium(III) Ions. The identification of the ion CrCN²⁺ 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 $1 F \text{ NaClO}_4$) which will elute other ions of charge +2, including Co²⁺ in these solutions. The complex can be satisfactorily separated from other species, including Co²⁺, by slow elution with 1 F NaClO₄-0.01 F HClO₄ 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 $Cr(OH_2)_5 X^{2+}$, 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 CrCN²⁺, since CN⁻ causes a ligand field splitting considerably higher than other common ligands.

The rapid decomposition $(t_{1/2} = 1.28 \text{ min. at } 15^{\circ})$ of the precursor of CrCN²⁺ has prevented our determining its composition and structure as firmly as we did for CrCN²⁺. One indication that the ion is CrNC²⁺ is just that the product of its disappearance is the isomeric CrCN²⁺; in addition, it seems a reasonable product of the primary reaction of Co(NH₃)₃CN²⁺ and Cr²⁺. 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).

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

⁽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 \$-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

⁽⁴⁾ The long wave length absorption maxima (Å) of several ions $Cr(H_2O)_5X^{2+}$, $^{3+}$, are: $X = I^-$, 6500; Cl^- , 6090; F^- , 5950; H_2O , 5740; NCS⁻, 5700; NH₃, 5450. This order also represents increasing ligand field strength of X.