The Effect of Some Non-bridging Ligands on the Cr(II)-Cr(III) Oxidation[1]

BY JOHN B. HUNT AND JOSEPH E. EARLEY

The relative efficiency of Cr(II) catalysis of the formation of the Cr(III) complexes of a number of anionic ligands has been studied by visual and ion exchange techniques. Semiquantitative results indicate that the order of catalytic efficiency is the same as the order of stability of the resulting complexes; EDTA > pyrophosphate > citrate ∼ phosphate > fluoride > tartrate > thiocyanate > sulfate. This is interpreted as a non-bridging ligand effect on the Cr(II)-Cr(III) electron exchange reaction.

It has been established[2] that the mechanism of an important class of oxidation reactions of metallic ions in aqueous solutions involves the action of ligands as bridging groups between oxidant and reductant. Studies of the effect of the nature of the bridging group have been made[3] and it has been demonstrated[4] that ligands in positions other than the bridging position also exert an effect on the rate of the oxidation. The effect of anions in solution on the rate of oxidation reactions which proceed by a mechanism other than the bridge mechanism has been studied.[5] Recently, Irvine[6] has published a study of the effect of modification of the nature of the ligands on the rates of a series of peroxydisulfate oxidations of metal complexes which seems certain to involve a more complicated mechanism.

The present study was undertaken to obtain information on the effect of altering the nature of non-bridging ligands on the rates of oxidation reactions which occur via the bridge mechanism. Ligand effects of the type studied are of considerable importance in synthesis[7] and other areas, but were first studied under the present aspect by Taube[4] who observed that pyrophosphate and other anions increased the rate of oxidation of Cr(II) by Co(III) species and that the anion was incorporated into the product Cr(III) complex along with the bridging group. Milburn and Taube[8] performed semiquantitative experiments which indicated that similar results were obtained when Cr(III) was substituted for Co(III) as oxidizing agent. A kinetic study of the effect of pyrophosphate ion on the rate of the Cr(II)-Cr(III) electron exchange is being carried out.[9] Since the reduction of Cr(III) regenerates the reducing agent, this reaction is easily followed as the Cr(II) catalysis of the formation of the Cr(III) pyrophosphate complex. The fact that both Co(III) and Cr(III) are inert to ligand substitution[10] under the conditions used indicates that this effect is not due to the action of

anions as bridging groups but is a non-bridging ligand effect.

In the present investigation, preliminary semiquantitative information concerning the effect of various types of non-bridging ligands on the Cr(II)-Cr(III) oxidation was sought by measuring the relative efficiency of Cr(II) catalysis of the formation of the Cr(III) complexes of several ligands.

Experimental

Hexaquochromium(III) perchlorate was prepared by the reduction of CrO_3 by formic acid.[11] Excess formic acid was removed by boiling. The product was recystallized once from dilute $HClO_4$ and twice from deionized water to yield needle-shaped crystals. Cr(III) perchlorate stock solutions were prepared by dissolving an appropriate amount of chromic perchlorate in dilute $HClO_4$ and diluting carefully to volume while the pH was being adjusted to 3.0. In order to minimize olation, i.e., the formation of polymeric chromium species,[12] the pH adjustment was effected by the slow dropwise addition of dilute NaOH solution into a solution which was being continuously and vigorously stirred by means of a magnetic stirrer. By this method, it was found possible to prepare solutions of pH 3.0 which did not appear to have any of the green tinge characteristic of olated solutions. The chromium concentration of stock solutions was determined spectrophotometrically as chromate after alkaline peroxide oxidation.[13] The molar extinction coefficient for chromate at 374 mμ was found to be 4,800.

Chromous perchlorate solutions were prepared by the electrolytic reduction of hexaquochromium(III) perchlorate in dilute $HClO_4$. Concentrations of Cr(II) were determined by reaction with a measured excess of standard iodine solution followed by back-titration with standard sodium thiosulfate. Stock solutions of the ligands of interest were prepared from the appropriate AR sodium salts. Ionic strength was regulated by the use of sodium perchlorate prepared from AR $HClO_4$ and Na_2CO_3. The distilled water used in the preparation of all solutions had been further purified by passing through a mixed bed ion exchange column.

Visual colorimetric observation of the catalyzed rate of complex formation was supplemented by experiments in which the products of the reaction were separated using ion exchange resins. The conditions for these experiments were: [Cr(III)], 0.021 g. ion/l.; [ligand], 0.0194 g. ion/l.; [Cr(II)], 3×10^{-4} g.-ion/l.; pH 3.0; ionic strength 1.0; temperature 25.0°. These conditions represent a [Cr(III)]/[ligand] ratio of 3/2 and favor almost exclusive formation of the 1/1 complex. Reactions were carried out in 25 ml. Erlenmeyer flasks, sealed with soft rubber serum stoppers. The reaction solutions were purged of oxygen by the passage of a stream of oxygen-free nitrogen for at least ten minutes before mixing and addition of Cr(II). During purging, the solutions were suspended in a 25.0° water-bath. The reactions were initiated by the introduction of chromous perchlorate solutions by means of a calibrated hypodermic syringe. Blank runs in which no chromous catalyst was added were carried out in all cases. At appropriate intervals aliquots were withdrawn from the reaction vessel under a stream of nitrogen. These aliquots

(1) Taken from a M.S. Thesis by John B. Hunt, submitted to the Graduate School of Georgetown University, June, 1960.

(2) (a) H. Taube, Can. J. Chem., 37, 129 (1959). (b) H. Taube in Advances in Inorganic Chemistry and Radiochemistry," Vol. I, H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, Inc., New York, N. Y., 1959.

(3) (a) A. E. Ogard and H. Taube, THIS JOURNAL, 80, 1084 (1958). (b) D. L. Ball and E. L. King, ibid., 80, 1091 (1958).

(4) H. Taube, ibid., 77, 4481 (1955).

(5) B. R. Baker, F. Basolo and H. M. Neuman, J. Phys. Chem., 63 371 (1959).

(6) D. H. Irvine, J. Chem. Soc., 2977 (1959).

(7) S. M. Jörgensen, J. pract. Chem., 2, 20, 105 (1879).

(8) R. Milburn and H. Taube, unpublished observations.

(9) J. Earley and H. Taube, to be published.

(10) H. Taube, Chem. Revs., 50, 69 (1952).

(11) C. Postmus and E. L. King, J. Phys. Chem., 59, 1208 (1955).

(12) C. L. Rollinson in "Chemistry of the Coördination Compounds," J. C. Bailar, Ed., Reinhold Publishing Co., New York, N. Y., 1956.

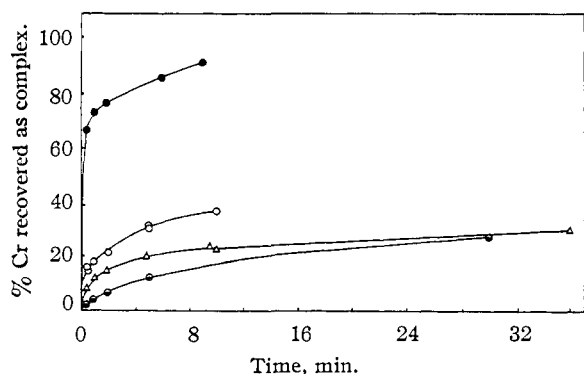(13) G. W. Haupt, J. Research Natl. Bur. Standards, 48, 414 (1952)

Fig. 1.—Formation of Cr(III) complexes by Cr(II) catalysis–faster ligands: ●, EDTA; O, pyrophosphate; ◒, fluoride; △, citrate.

were quenched by exposure to air and then placed on an ion exchange column in order to separate the products of the reaction from unreacted starting materials.

Ion exchange columns were 1 cm. in diameter and were packed with Dowex 50 × 8. The eluting solution was aqueous $HClO_4$. It was found possible to choose a column length and acid strength such that essentially quantitative recovery of the complex species was obtained without causing significant elution of uncomplexed Cr(III).[14] In the case of the phosphate complex no separation could be effected by the resin, probably due to polymerization.

An attempt was made to determine the degree to which the Cr(III) complex of thiocyanate ion may have been formed in the quenching process.[15] Cr(II) and thiocyanate stock solutions were mixed and allowed to come to equilibrium at 25°. Aliquots were withdrawn, air oxidized and run through ion exchange columns. Approximately 25% of the initial Cr(II) was recovered as the thiocyanato Cr(III) complex. This is in rough agreement with the amount of Cr(II) thiocyanate complex which could be expected to be present under the conditions employed in these experiments.[16]

Results and Discussion

After a preliminary survey of a large number of ligands, the following anions were chosen for investigation; citrate, ethylenediaminetetraacetate (EDTA), fluoride, phosphate, pyrophosphate, sulfate, tartrate and thiocyanate. A number of ligands which formed relatively unstable chromium complexes in acid solutions, such as Cl^- and ligands coördinating through basic nitrogen atoms were found not to participate in the reaction.

Under the experimental conditions employed in the visual colorimetric experiments, the rates of the reactions varied greatly. Reaction was virtually complete in the time of mixing in the case of the EDTA and was very rapid for pyrophosphate samples, but several hours were required for significant reaction to occur in the case of thiocyanate. The order of decreasing speed of reaction was found to be: EDTA > pyrophophsate > tartrate ~ phosphate > citrate > fluoride > sulfate > thiocyanate.

The results of the experiments using resins to separate products are shown in Figs. 1 and 2. The amount of complex recovered gives a more reliable estimate of the progress of the reaction than visual observation. The data presented in these figures indicate that the order of effectiveness

(14) E. L. King and E. B. Dismukes, THIS JOURNAL, 74, 1674 (1952).

(15) A. Anderson and N. A. Bonner, ibid., 76, 3826 (1954).

(16) K. B. Yatsimirskii and T. I. Fedorova, Izvest Vysshykh, Ucheb. Zavendenii, Khim i. Khim Tekhnol., 40 (1958); C. A., 53, 1977 (1959).
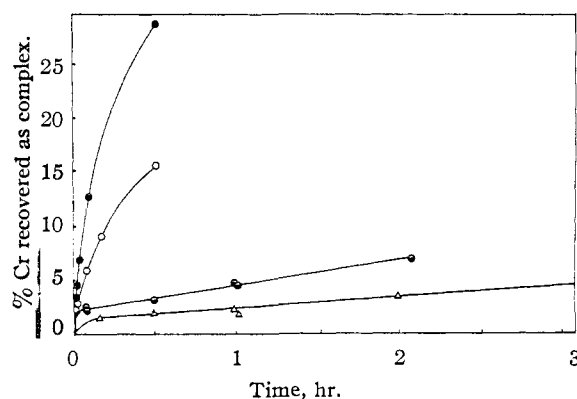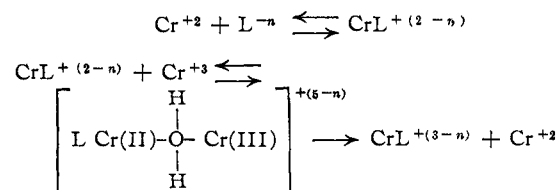
Fig. 2.—Formation of Cr(III) complexes by Cr(II) catalysis–slower ligands: ●, fluoride; O, tartrate; ◒, thiocyanate; △, sulfate.

of the ligands in promoting Cr(II)–Cr(III) electron transfer is EDTA > pyrophosphate > citrate > fluoride > tartrate > thiocyanate > sulfate. The differences between the orders of reactivity observed in these two series of experiments is attributed to the inability of visual observations to take account of the details of the spectra of the complexes.

No attempt was made to interpret the rate data in terms of a rate law. The reactions probably involve rather complex hydrogen ion dependences and the buffering action of the aquated chromium ion and the basic ligands was not sufficient to maintain the pH of the solutions at a constant value for more than the initial portion of the reaction. Blank runs indicated that the formation of the complex by the uncatalyzed path was much slower than the catalyzed reaction in all cases and did not interfere. The formation of complex during the quenching process could not have contributed to the observed reaction in any significant degree due to the small concentration of Cr(II). It appears that the order observed in the ion exchange measurements is a measure of the tendency of the ions in question to form Cr(III) complexes under the influence of Cr(II) catalysis. This, in turn, is regarded as a measure of the extent to which these ligands exert a non-bridging ligand effect on the Cr(II)–Cr(III) oxidation.

In view of the evidence which supports the bridge formation mechanism for Cr(II)–Cr(III) reactions, the following sequence of steps may be considered a likely mechanism for the Cr(II) catalysis of the formation of Cr(III) complexes (coördinated water molecules omitted)

$$Cr^{+2} + L^{-n} \underset{\longrightarrow}{\overset{\longleftarrow}{}} CrL^{+(2-n)}$$

$$CrL^{+(2-n)} + Cr^{+3} \overset{\longleftarrow}{\longrightarrow}$$
$$\left[L\ Cr(II)\text{-}\overset{\displaystyle H}{\underset{\displaystyle H}{O}}\text{-}Cr(III) \right]^{+(5-n)} \longrightarrow CrL^{+(3-n)} + Cr^{+2}$$

Differences in the stabilities of the Cr(II) complexes would be expected to effect the rate of the catalytic reaction. According to the postulated mechanism, the concentration of the reducing agent would dependent on the stability constant of the Cr(II)–ligand complex. A recent study[16]

of the stability of the Cr(II)–SCN⁻ complex indicates that under the conditions of our experiments about 20% of the Cr(II) present existed in complexed form. Since the EDTA reaction appears to be much more than five times faster than the SCN⁻ reaction, it seems that the differences in rates cannot be primarily due to differences in concentrations of the reducing agent. The effect of the ligand on the electronic energy levels of the metal atoms in the bridged complex is an important effect which is difficult to evaluate precisely.[17]

The free energy change for the catalytic reaction in question is directly related to the stability constant of the Cr(III) complex formed by the reaction. Unfortunately, there is little data on stability constants of either Cr(III) or Cr(II) complexes,[18] owing to the slow approach to equilibrium characteristic to the former and to the sensitivity of the latter to air oxidation. The ability of EDTA to form extremely stable complexes is well known; there is evidence[19] that pyrophos-

phate ion forms more stable complexes with +3 ions than does phosphate. Citrate appears to form more stable complexes than does tartrate.[18] The thiocyanato complex of Cr⁺³ has been shown to have a stability constant[11] which is less than that measured for the corresponding fluoro complex.[20] The sulfato complex is much less stable than the phosphato complex.[21]

The observed order of increasing rate of catalytic reactions is the same as the apparent order of stabilities of the Cr(III) complexes involved. This indicates that the rates of reactions of this type may be related to the free energy change for the reaction as was found to be the case in the more complex oxidations studied by Irvine.[6]

(17) (a) R. A. Marcus, Can. J. Chem., 37, 155 (1959).

(18) J. Bjerrum, et al., Eds., "Stability Constants," The Chemical Society (London), 1957.

(19) S. Mayer and S. D. Schwartz, This Journal, 72, 5106 (1950).

(20) A. S. Wilson and H. Taube, ibid., 74, 3509 (1952).

(21) A. Holroyd and J. E. Salmon, J. Chem. Soc., 269 (1956).

The Thermal Decomposition of 2,2'-Azoisobutane[1]

By Joseph B. Levy and B. K. W. Copeland

The thermal decomposition of gaseous 2,2'-azoisobutane has been studied over the temperature range 180–220°. The principal reaction products were isobutane and nitrogen. Small amounts of methane and 2,2,3,3-tetramethylbutane were also found. A brown solid deposit was invariably formed on the walls. Good first-order kinetics were observed and the temperature dependence of the rate measured. The activation energy of the reaction was found to be 42.8 kcal./mole and the frequency factor 2.2×10^{16} sec.⁻¹. In the presence of added nitric oxide, a blue product believed to be 2-methyl-2-nitrosopropane was formed and isobutene and nitrous oxide were observed as products. Experiments with added isobutene showed that it was consumed in the reaction. The significance of these results is discussed and a mechanism for the reaction proposed.

Introduction

The synthesis of 2,2'-azoisobutane and its thermal decomposition in dioctyl phthalate solution containing dihydroanthracene as a hydrogen donor have been described by Farenhorst and Kooyman.[2] It seemed that this compound should be a good source of t-butyl radicals since the decomposition temperature indicated was low, 200°, and nitrogen should be the only product other than t-butyl radicals. The thermal decomposition of 2,2'-azoisobutane in the gas phase was, therefore, investigated and the results are reported here.

Experimental

Chemicals.—The synthesis of 2,2'-azoisobutane was carried out as described by Farenhorst and Kooyman.[2] The

product was fractionated through a short Vigreux column and the product boiling at 108–109° was that used in the experiments. The density was d^{20}_4 0.7617 compared to d^{20}_4 0.7670.[2] A sample of 2,2,3,3-tetramethylbutane was supplied through the kindness of Dr. Kenneth Greenlee of the Department of Chemistry of the Ohio State University. The nitric oxide used in this work was purchased from the Matheson Company, Inc., and certified as 99.0% pure. It was purified further by bulb-to-bulb distillation on the vacuum line. The material used condensed to a white solid. The isobutene and isobutane used in these experiments were Matheson Company C.P. grade, 99.0 % minimum and were used without further treatment.

Procedure for the Kinetics and Product Studies.—The reaction vessels used were spherical glass bulbs of 300 cc. nominal capacity. They were fitted with mercury manometers for the kinetic runs and with break-tips for runs in which product analyses were to be carried out. The volume exterior to the thermostat in the kinetic runs was of the order of 1–2 cc.

The bulbs were filled on a vacuum line. In most cases 2,2'-azoisobutane, at room temperature, was allowed to vaporize into the evacuated bulb until the vapor pressure, about 22 mm. was reached. The bulb contents were then condensed in the bulb bottom by means of a cold bath and the bulb sealed off with a torch. In larger scale experiments, a reservoir bulb of known volume was filled with 2,2'-azoisobutane at its vapor pressure, the contents transferred,