241. cis-trans-*Isomerism in Octahedral Groups.*

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The proportions in which *cis*- and *trans*-isomeric groups of formulæ MA_2B_4, MA_3B_3, and MA_4B_2 may be expected to form in the same reaction are discussed on a geometrical basis, and a branched reaction of a special type is suggested for which a partial interpretation of P in the expression for the velocity constant $k = PZe^{-E/RT}$ may be given. The method is only applicable to reactions in which A and B are groups of such a type that the octahedral bonds of the metal atom M are not broken and the reaction consists of addition or subtraction of a group distant from M in a complex MA_nB_{6-n}. Facts relating to the alkylated ferrocyanides and cobalticyanides are in general agreement with the hypothesis.

Many compounds are known in which alternative arrangements of groups attached by six octahedral bonds to a central atom can give rise to isomerism. Decisions as to the configuration of the isomers produced in a given reaction based on chemical evidence are open to objection. It has often been supposed that compounds prepared by substitution of a group, occupying two co-ordination positions, by two separate groups occupying one each must be *cis*-isomers; *e.g.*, the carbonatotetramminocobaltic ion $[Co(NH_3)_4CO_3]^+$ should give the *cis*-form of the dichlorotetrammine complex $[Co(NH_3)_4Cl_2]^+$ on reaction with hydrochloric acid. However, it has been recognised that such arguments may lead to erroneous conclusions : in the case quoted, both *cis-* and *trans*-forms are produced. Whenever a group is substituted, a bond to the central atom is temporarily broken and rearrangement may occur. This must happen in the case of the complex ion of Erdmann's salt $[Co(NH_3)_2(NO_2)_4]^-$, which is known to be *trans-* although the chemical evidence would lead one to suppose it was *cis-* (Wells, *Z. Krist.*, 1936, **95**, 74). Further, in some cases the bonds are very easily broken and rearrangement of the complex to form the other isomer may take place; *e.g.*, the dichloropropylenediamine ion $[Co\ pn_2Cl_2]^+$ readily changes over from the *trans-* to the *cis*-form in neutral solution, but the addition of a trace of acid causes a reversal of the reaction. In these circumstances it is not possible to predict what proportions of the isomers will be formed in a particular reaction.

In contrast to these compounds there is a case of isomerism discovered by Hartley (J., 1913, **103**, 101) where it seems possible to draw conclusions as to the mechanism of production of the isomers. Tetramethyl ferrocyanide exists in α- and β-forms which have been shown (preceding paper) to be *cis-* and *trans-* respectively. Both are obtained in the same reaction, *viz.*, elimination of two molecules of methyl chloride by the action of heat on hexamethyl ferrocyanogen chloride $[Fe(CH_3{\cdot}NC)_6]Cl_2$. The *cis*(α)-form is produced in much larger quantity than the *trans-*. The yields obtained by Hartley were in the ratio of about 10 to 1; this ratio is not quite accurate, since it depends on the efficiency of a difficult separation, and some of the β will have been left in the reaction mixture, but there is no doubt that several times as much α- as β- is formed.

A simple explanation of the predominance of the *cis*-isomer may be given. In the hexamethyl ferrocyanogen chloride decomposition we are not dealing with a molecule which splits off some of its groups at the metal atom but only with the removal of two terminal methyl groups linked through two other atoms to the metal, and there is no reason to suppose that, in the reaction, any of the six strong octahedral bonds of the iron is broken. The CN groups will therefore be left, without rearrangement, in the places where they are formed. In support of this is the stability of the two isomers, both of which may be heated to high temperatures without change from one to the other. If two groups are to be removed simultaneously from the corners of an octahedron, there are four times as many ways of doing this to give the *cis*-form as there are for the *trans-*, since there are twelve edges of the octahedron to three solid diagonals. If one terminal methyl is first removed, the complex will retain its octahedral form, and the subsequent removal of any one of four methyl groups gives the *cis*-isomer but the removal of the fifth methyl gives the *trans-*. It is necessary to consider these two cases separately, since the reaction is most likely to proceed by successive removals, and it may be objected that the five methyl groups are not equivalent in their relation to the apex of the octahedron from which the first methyl group has been taken. Although this is true geometrically, it does not seem likely that the probability of breaking a particular nitrogen–methyl bond will be very much affected by it since the molecule as a whole is electronically still highly symmetrical. Any effect transmitted through bonds applies equally to all five groups, and it is improbable that other effects such as dipole interaction, which falls off very rapidly with increasing distance, will have a large influence, since the nearest terminal methyl groups are over 6 A apart, and even the nitrogen atoms are separated by nearly 4·5 A. Further, if such effects were to operate, it seems most probable that they would lead to the formation of the *trans*-isomer, owing to the mutual repulsion of similar groups. It may therefore reasonably be assumed that the rate of removal is about the same for all methyl groups, and therefore in this case the purely geometrical probability is mainly responsible for the large proportion of the *cis*-isomer obtained.

If this explanation is correct, similar results may be expected in other reactions of the same type. Few of these are known, but they are in general agreement with expectation. Hölzl, Hauser, and Eckmann (*Monatsh.*, 1927, **48**, 71) prepared tetraethyl ferrocyanide by an analogous reaction and obtained only one isomer. The failure to find the second isomer is not of great significance, since the earlier workers except Hartley did not find the β-form of tetramethyl ferrocyanide, and these authors apparently did not succeed in obtaining Hartley's β-form. From its solubility relationships they conclude that the tetraethyl compound obtained corresponded to the α-form of tetramethyl ferrocyanide. They also prepared tetrapropyl ferrocyanide by the action of *n*-propyl iodide on silver ferrocyanide. Precisely similar arguments apply to the addition of groups to an existing octahedral complex such as takes place in this reaction. There are four times as many ways of obtaining the *cis*-isomer MA_2B_4 (or MA_4B_2) from MA_6 as there are ways of obtaining the *trans*-form, and it is therefore expected that the *cis*-form will again predominate. Only one isomer was obtained, and Hölzl concludes from its solubility relationships and reaction with ferric chloride that it corresponds to the α-form of tetramethyl ferrocyanide.

A slightly different case is the formation of trimethyl cobalticyanide, $Co(CH_3NC)_3(CN)_3$, from silver cobalticyanide and methyl iodide. There are eight ways of adding three methyl groups to give the *cis*-compound, corresponding to the eight faces of the octahedron, and twelve ways of adding them to give the *trans*-form, and it would therefore be expected that one form would not predominate above the other to such an extent as in the case of tetramethyl ferrocyanide, the ratio being 1·5 : 1 instead of 4 : 1. In the experiment, about equal quantities of the two isomers were obtained in the same reaction (Hartley, J., **1914**, **105**, 521).

A consideration of other possibilities of the same type is summarised in the following table for octahedral complexes. It is applicable only to cases where the metal bonds are not broken, and only distant parts of the six arms are affected.

	Reaction product and proportions of isomers expected (*cis* : *trans*).		
Initial substance.	MA_2B_4.	MA_3B_3.	MA_4B_2.
MA_6	4 : 1	1 : 1·5	4 : 1
MA_5B	4 : 1	1 : 1·5	4 : 1
MA_4B_2 (*cis*)	5 : 1	1 : 1	—
MA_4B_2 (*trans*)	2 : 1	0 : 1	—
MA_3B_3 (*cis*)	1 : 0	—	1 : 0
MA_3B_3 (*trans*)	2 : 1	—	2 : 1

The ratios in the above table are independent of the intermediate steps taken by the reaction provided it be assumed, as in the example considered earlier, that at all stages the probability of removal (or addition) of a particular terminal group is unaffected by its position relative to the changes already made.

It would be of interest to investigate the course of a reaction of this type in a more quantitative way, *e.g.*, in solution if suitable substances could be found. A particularly good test would be provided by a comparison of the behaviour of *cis*- and *trans*- MA_4B_2 reacting to give MA_2B_4. The products would be the same in both reactions but the ratios of *cis* to *trans* should differ widely, being 5 : 1 and 2 : 1, respectively.

If such a reaction may be regarded from the standpoint of the collision theory, the velocity constant is given by $k = PZe^{-E/RT}$, and in a branched reaction the relative numbers of molecules reacting according to the different paths will depend on differences in P and E. In this case the constants for the two branches may be written $k = P_1P_2Ze^{-E/RT}$ and $k' = P_1'P_2Ze^{-E/RT}$; the rigid restrictions introduced as to the nature of the reaction and the equivalence for reaction purposes of all the terminal links concerned (*e.g.*, all the $N-CH_3$ links in the tetramethyl ferrocyanide reaction) are virtually equivalent to requiring the energy of activation E and the factor P_2 to be the same for both branches. The factors P_1 and P_1' then depend only on the geometry of the molecules involved in the reaction and are in the ratios given in the table. This reaction, as far as the author is aware, is the only type so far suggested in which a geometrical effect in P may be stated in precise terms. The particular reaction that has suggested this idea is not convenient for accurate measurement, since the methyl chloride is only eliminated from tetramethyl ferrocyanogen chloride by heating the solid under diminished pressure, but it is suggested that any similar substances prepared should be considered as possible means for testing this effect.

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[*Received, May 22nd*, **1939**.]