tion was required for 80% reaction of the same EHDP solution in the absence of hydrogen peroxide.

Effect of Excess Oxygen.—The rate of EHDP rearrangement in the presence of oxygen is about twice as fast as the rearrangement when no oxygen is added during irradiation and nearly 5 times as fast as when the oxygen concentration is decreased by nitrogen bubbling during irradiation. This is shown in Figure 1.

Product Study.—The phosphonate portion of EHDP is rearranged to orthophosphate, based on orthophosphate chemical analysis and ^{31}P nmr data. Based on chemical analyses, orthophosphate is also produced by MDP photolysis.

The infrared spectrum shows the presence of a carbonyl function and carbon–hydrogen bonds in the organic reaction product(s). The ^1H nmr spectra show a regular decrease in the triplet signal characteristic of EHDP (τ 7.9) and the appearance of a singlet resonance signal at τ 7.5. In the interval between 50 and 75 hr of irradiation, the EHDP signal disappears, leaving the τ 7.5 peak as the signal from the product. This τ 7.5 peak at 5% concentration in D_2O with a TMS capillary is identified as acetic acid.

Discussion

The rate of rearrangement for EHDP, which contains the hydroxyl group, is faster than that for MDP which does not have this structural feature. Though the presence of the hydroxyl group leads to a faster rearrangement rate, perhaps by stabilizing an intermediate, it cannot be the only structural feature that leads to rearrangement. If the phosphonate is not ionic, as in the tetramethyl ester of MDP, or if the phosphorus bonded to carbon is not in a high oxidation state, as in dimethyldodecylphosphine oxide (DDPO), no reaction occurs.

The primary photochemical processes of hydrogen peroxide are described in ref 11. In aqueous solution and in the energy region produced by mercury lamps, hydrogen peroxide undergoes homolytic dissociation of the peroxide bond to produce two hydroxyl radicals. Thus, hydroxyl radicals from hydrogen peroxide are probable species during these photolysis experiments. Calvert and Pitts also reported that the photolysis of water in all wavelength regions leads to hydroxyl radicals and hydrogen atoms though the energy state of the hydroxyl radical and the quantum yield of this reaction depends on the wavelength of light used for irradiation.

These primary photochemical processes reported to occur in aqueous solution and in the presence of hydrogen peroxide indicate that hydroxyl radicals will be important consequences of this photolysis experiment and support our experimental observations that hydrogen peroxide promotes the reaction but is not required for rearrangement.

It is not possible to define a reaction mechanism on the basis of the data reported here. The accelerative effect of hydrogen peroxide and oxygen on the reaction rate suggests that hydrogen atom abstraction is not as important to the photolysis of diphosphonates as it is reported to be for ethyl dihydrogen phosphate. Acetic acid is tentatively identified as the predominant organic residue. No direct evidence of acetaldehyde or paraldehyde as precursors to acetic acid was found.

Acknowledgment.—The discussions with Drs. P. J. Kropp and D. E. O'Conner during this study were very helpful and the assistance of Mr. W. B. Gehling in the experimental work is gratefully acknowledged.

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Some Observations on Ligand-Exchange Reactions of Bis-1,2-Dithiolene Complexes

BY A. L. BALCH[1]

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Recent studies have shown that ligand-exchange reactions can be effected between bis-1,2-dithiolene complexes in poorly coordinating solvents.[2,3] At room temperature these exchange reactions are generally slow for planar complexes. The sluggishness of these reactions was first demonstrated for nickel complexes[3] and the data in Table I show that exchange is also slow in the case of planar complexes of copper, gold, palladium, and platinum.

Information on the dithiolene ligand-exchange for some five-coordinate adducts[4] of the type (base)-$CoS_4C_4R_4^-$ is also set out in the table. The presence of additional base serves to retard the rate of attainment of equilibrium, but, within experimental error, the excess base does not affect the position of equilibrium. Similar results were obtained for the analogous five-coordinate iron adducts, but quantitative, reliable data are not available because of the susceptibility of the apical bases to oxygenation.[5]

Exchange reactions involving the dimeric bis-dithiolene complexes of iron and cobalt, which have the structure shown in Figure 1,[6] occur in two steps which require, respectively, seconds and hours to reach equilibrium. Figure 2 shows the region of the $Co_2S_8C_8R_8^{2-} \rightleftarrows Co_2S_8C_8R_8^- + e^-$ wave for a solution pre-

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TABLE I

RESULTS OF DITHIOLENE-EXCHANGE REACTIONS

Complex I	Complex II	Electrochemical process	$E_{1/2}$(I), V	$E_{1/2}$(II), V	$E_{1/2}$(mixed), V	% mixed species	Time,[a] days
$CuS_4C_4(CF_3)_4{}^-$	$CuS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 2-$	+0.41	−0.08	+0.18	61	15
$AuS_4C_4(CF_3)_4{}^-$	$AuS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 0$	+1.34	+1.68	...	<5[b]	74
$NiS_4C_4(CF_3)_4{}^-$	$NiS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 2-$	−0.05	+0.37	...	<5[b]	72[b]
		$1- \rightleftarrows 0$	+1.01	+1.38	...		
$NiS_4C_4(CF_3)_4{}^-$	$NiS_4C_4(CN)_4{}^{2-}$	$1- \rightleftarrows 2-$	−0.05	+0.37	+0.15	18	50
		$1- \rightleftarrows 0$	+1.01	+1.38	+1.19		
$PdS_4C_4(CF_3)_4{}^-$	$PdS_4C_4(CN)_4{}^{2-}$	$1- \rightleftarrows 2-$	+0.21	+0.56	+0.40	16	27
		$1- \rightleftarrows 0$	+1.04	+1.39	+1.22		
$PtS_4C_4(CF_3)_4{}^-$	$PtS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 2-$	+0.02	+0.30	...	<5[b]	99[b]
		$1- \rightleftarrows 0$	+0.93	+1.28	...		
$PtS_4C_4(CF_3)_4{}^-$	$PtS_4C_4(CN)_4{}^{2-}$	$1- \rightleftarrows 2-$	+0.02	+0.30	...	<5[b]	30[b]
		$1- \rightleftarrows 0$	+0.93	+1.28	...		
$(C_6H_5)_3PCoS_4C_4(CF_3)_4{}^-$	$(C_6H_5)_3PCoS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 0$	+0.40	+0.75	+0.58	55	5
						58[c]	45[c]
$(C_6H_5)_3AsCoS_4C_4(CF_3)_4{}^-$	$(C_6H_5)_3AsCoS_4C_4(CN)_4{}^-$	$1- \rightleftarrows 0$	+0.46	+0.77	+0.63	58[d]	2[d]
						58[e]	5[e]

[a] Time required until no further change was observed in polarography of solutions initially 1.0×10^{-3} mM in complex I and in complex II. [b] No observable exchange within the time listed. [c] Exchange run in the presence of 1.01 mM excess triphenylphosphine. [d] Exchange run in the presence of 75 mM excess triphenylarsine. [e] Exchange run in the presence of 190 mM excess triphenylarsine.

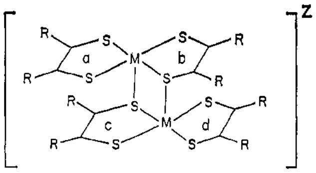


Figure 1.—Idealized representation of the structure of the dimeric dithiolene complexes of cobalt and iron. In order to describe mixed-ligand species the symbol [$^{ab}{}_{cd}$] will be used to denote the ligand positions within the dimer.

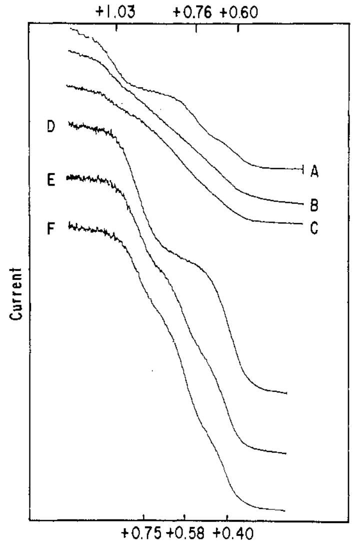


Figure 2.—Polarograms of an equimolar mixture of $Co_2S_8C_8(CF_3)_8{}^{2-}$ and $CoS_8C_8(CN)_8{}^{2-}$: A, within 2 min of mixing; B, after 80 min; C, after 300 min. Polarograms D, E, and F result from addition of $(C_6H_5)_3As$ to the original mixture after (D) 2 min, (E) 80 min, and (F) 300 min. The voltage and arbitrary current scales used for A, B, and C differ from those used for D, E, and F.

pared from equimolar amounts of the cyano- and perfluoromethyl-substituted species. Three distinct waves are clearly discernible in the polarograms recorded immediately after mixing (Figure 2A). About 1 min was required for mixing the solutions and recording the polarogram. Within this time equilibrium among the three species detected appears to be established, since no change in the three wave heights is noted in the succeeding few minutes. The wave with a half-wave potential of +0.60 V is identified with the oxidation of $Co_2S_8C_8(CF_3)_8{}^{2-}$ while the wave at +1.03 V is due to the oxidation of $Co_2S_8C_8(CN)_8{}^{2-}$. The wave at +0.76 V is not present in the polarogram of either of these species alone; consequently it must be assigned to a new mixed-ligand species. Over a period of 5 hr, the polarogram due to this solution gradually converts into that shown in Figure 2C. The overall wave height due to oxidation of all of the $Co_2S_8C_8R_8{}^{2-}$ species does not change, but the wave becomes broadened and the structure of distinct waves is lost. Polarograms recorded at times beyond 5 hr show no further change.

Additional information about the course of the ligand-exchange process is gained by adding triphenylphosphine or triphenylarsine to the mixture of dimeric complexes after different time intervals. Since dithiolene exchange is slow for (base)$MS_4C_4R_4{}^-$ in the presence of excess base, the addition of base serves to quench the ligand-exchange process. Addition of base to the $Co_2S_8C_8(CF_3)_8{}^{2-}$–$Co_2S_8C_8(CN)_8{}^{2-}$ mixture within 2 min after mixing results in the polarogram seen in Figure 2D. No (base)$CoS_4C_4(CF_3)_2(CN)_2{}^-$ can be detected, although a mixed-ligand dimer was detected prior to the addition of base. When base is added to the original $Co_2S_8C_8(CF_3)_8{}^{2-}$–$Co_2S_8C_8(CN)_8{}^{2-}$ mixture after 5 hr, the resulting solution contains (Figure 2F) 22% (base) $CoS_4C_4(CF_3)_4{}^-$, 56% (base)$CoS_4C_4(CF_3)_2(CN)_2{}^-$, and 22% (base)$CoS_4C_4(CN)_4{}^-$. The percentage composition does not depend on the base used and does not change if the original mixture is quenched after a longer time interval. Quenching the original mixture at time intervals of less than 5 hr reveals the expected gradual growth in concentration of (base)-$CoS_4C_4(CF_3)_2(CN)_2{}^-$.

Similar behavior is observed with other mixtures of cobalt and iron bis dithiolenes. Of particular importance is the observation, immediately after mixing, of three waves in the region in which the oxidation of $M_2S_8C_8R_8^{2-}$ is expected to occur. For a mixture of $Fe_2S_8C_8(CF_3)_8^{2-}$ and $Fe_2S_8C_8(CN)_8^{2-}$ the half-wave potentials are +0.71 V (oxidation of $Fe_2S_8C_8(CF_3)_8^{2-}$), +1.06 V (oxidation of $Fe_2S_8C_8(CN)_8^{2-}$), and +0.85 V (oxidation of a new mixed-ligand species). A mixture of $Co_2S_8C_8(CF_3)_8^{2-}$ and $Fe_2S_8C_8(CN)_8^{2-}$ also exhibits three waves with half-wave potentials of +0.59 V (oxidation of $Co_2S_8C_8(CF_3)_8^{2-}$), +1.06 V (oxidation of $Fe_2S_8C_8(CN)_8^{2-}$), and +0.76 V (oxidation of a mixed complex). In both cases the three distinct waves are gradually transformed into a broad wave similar to that in Figure 2C; about 5 hr is required in both cases to complete this transformation.

The dimeric, dianionic iron- and cobalt-dithiolene complexes are known to undergo some dissociation into monomeric species in solution;[6] this dissociation most likely involves cleavage of the two long extraplanar M–S bonds of the dimer. There are ten possible dimeric complexes (excluding optical isomers) that can be formed from a mixture of $M_2S_8C_8(CF_3)_8^{2-}$ and $M_2S_8C_8(CN)_8^{2-}$. Figure 3 shows these ten complexes and their relationship to the three possible monomeric complexes under the restriction that the dimers dissociate and associate through extraplanar M–S bonds.

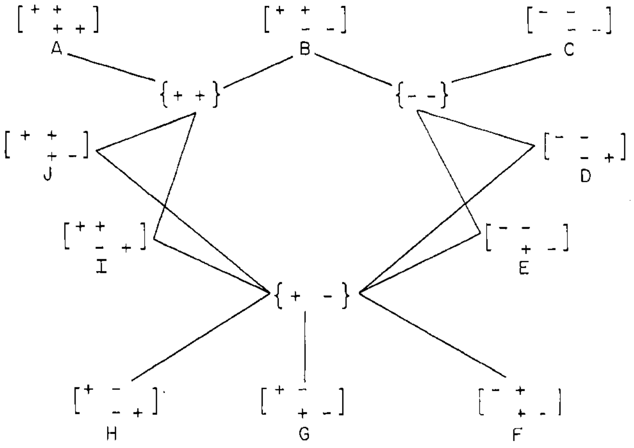
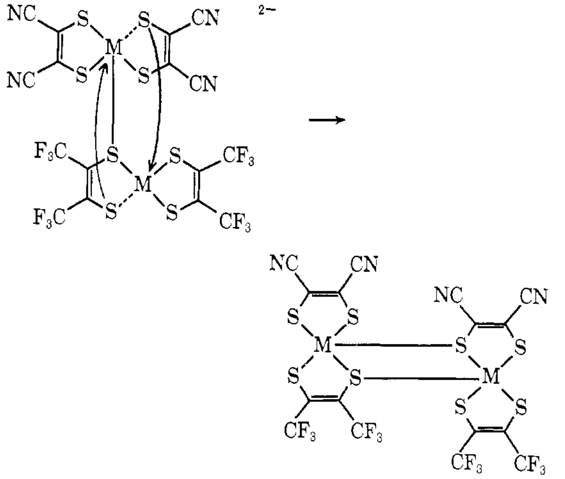


Figure 3.—A diagram which shows the relationship between all possible dimeric complexes, $[{}^{ab}{}_{cd}]$ (lettered A–J), derived from a nixture of $[M_2S_8C_8R_8]^{2z}$ and $[M_2S_8C_8R'_8]^{2z}$ and the monomeric complexes, (ab) or (cd), of the type $[MS_4C_4R_4]^z$. This diagram pertains only to the case in which the dimer–monomer reaction is effected by cleavage of the two extraplanar M–S bonds in the dimer. The two distinct ligands are denoted by + and −.

The initial observations of the exchange reaction of the dimer complexes are consistent with the formation of a single mixed-ligand dimer, $M_2S_8C_8(CN)_4(CF_3)_4^{2-}$, with the structure B. Association of two dissimilar monomers results in the formation of B exclusively. This mechanism can only equilibrate the three dimers A, B, and C; no other dimers can be formed since there is no path available for the formation of the mixed-ligand monomer $MS_4C_4(CF_3)_2(CN)_2^-$. Consequently only three dimeric species are observed in the first, rapid stage of the exchange. The reaction of triphenylphosphine or triphenylarsine with this mixture is likely to occur by one or two routes, neither of which is expected to form any (base)$MS_4C_4(CN)_2(CF_3)_2^-$. The base may react with the dissociated monomers; the absence of the mixed-ligand monomer $MS_4C_4(CF_3)_2(CN)_2^-$ ensures that no mixed-ligand adduct can be formed through this path. Alternately or in addition, the base may attack the intact dimer.[6a] Direct attack on the dimer would most probably cause rupture of the two extraplanar M–S bonds; from a mixture of dimers A, B, and C this mechanism would also not be capable of producing the mixed-ligand adduct.

The second, slower phase of exchange involves a more extensive reorganization mechanism. The gradual broadening and loss of structure seen on the polarographic waves in Figure 2A, B, and C can be ascribed to the formation of all ten possible dimers. Since ligand exchange is very much slower in the case of unassociated, planar monomers, the next step probably involves the mixed-ligand dimer B as an intermediate.[7] Two attractive pathways can be proposed for this step. One involves an intramolecular isomerization of B into G, eq 1. This rearrangement, in combination with the previous mechanism for cleavage, can generate the remaining isomers. Notice, however, that the internal conversion (eq 1) is restricted to effecting the single geometrical isomerization B ⇄ G. No other geometrical isomerziation can be effected by simply interchanging the two bridging ligands. Rearrangements involving interchange of bridging and terminal ligands would undoubtedly have higher activation energies than the isomerization B ⇄ G. Alternately another, slower cleavage mechanism may allow B to dissociate into two mixed-ligand monomers directly. Combination of



(1)

[6a] Note Added in Proof.—A recent report indicates that this reaction in acetone solution proceeds by attack of base on the dissociated monomer in the case of $Co_2S_8C_8(CN)_8^{2-}$: H. G. Tsiang and C. H. Langford, *Can. J. Chem.*, **48**, 2776 (1970).

[7] We consider that complete dissociation of a dithiolene ligand as a mechanism for exchange is unlikely because of the poor donor properties of the solvent medium. Any dithiolene dissociation must be slower than the dimer–monomer equilibrium because only a single new species is detected in the first step of the exchange reactions.

the two cleavage mechanisms can then generate the ten dimeric complexes. No new mechanism is required to account for the formation of (base)$MS_4C_4(CF_3)_2(CN)_2^-$ upon addition of base once $MS_4C_4(CF_3)_2(CN)_2^-$ or the dimers D–J are formed.

Dithiolene exchange in the case of the base adducts appears to involve dissociation with exchange occurring *via* the mechanism already proposed for the bis-dithiolene dimers. Accordingly, the addition of base should suppress dissociation and slow ligand exchange as is observed. The fact that triphenylphosphine inhibits exchange more effectively than does triphenylarsine accords well with the greater stability (toward dissociation) of the phosphine adduct.[4] An alternate means for exchange could involve, initially, dimerization of base adducts by formation of extraplanar M–S bonds. Such dimerization has been proposed to explain the solid-state properties of the neutral complex $(C_6H_5O)_3PCoS_4C_4(CF_3)_4$.[4] Base inhibition of this mechanism could be ascribed to the formation of six-coordinate bis adducts which could not undergo dimerization. However this mechanism is unlikely because no evidence has been found for bis adducts $(\text{base})_2MS_4C_4R_4^-$ in these systems.

Finally some comments on mixed-metal dimers are in order. Clearly our results indicate that, in solution, a dimer of the type $CoFeS_4C_4R_4^{2-}$ will be in rapid equilibrium with $Co_2S_8C_8R_8^{2-}$ and $Fe_2S_8C_8R_8^{2-}$; consequently attempts to isolate mixed-metal, dianionic dimers will probably be fruitless. Attempts to detect mixed-metal dimers polarographically with a single type of dithiolene ligand have been unsuccessful because the polarography of these complexes is only very slightly dependent on the metal. Direct polarographic observation of the dimer $CoS_4C_4(CF_3)_4FeS_4C_4(CN)_4^{2-}$ with structure B has been possible; the half-wave potential for its oxidation is +0.76 V. Similar attempts at detecting $CoS_4C_4(CN)_4FeS_4C_4(CF_3)_4^{2-}$ were thwarted by the rapid onset of the second reorganization reaction. These exchange reactions require both a dimeric species and rapid dimer–monomer equilibrium. Since the extent and kinetics of disproportionation or dissociation of the oxidized dimers $M_2S_8C_8R_8^{-1,0}$ have not been determined, these factors may allow for the isolation of mixed-metal species in these oxidation states.

Experimental Section

The ligand-exchange reactions were followed by the polarographic technique developed by Davison, *et al.*[2] Dichloromethane solutions for exchange studies were prepared so that the initial concentration of each of the exchanging species was 1.00 m*M*. Periodically aliquots of these solutions were withdrawn, mixed with the supporting electrolyte, and diluted with dichloromethane for polarographic measurements. For a typical exchange reaction only the waves (for a particular redox step) due to the parent complexes $MS_4C_4(CF_3)_4^-$ and $MS_4C_4(CN)_4^-$ were observed initially, but slowly the height of those waves decreased as the height of a new wave, positioned between the initial waves, increased. There was, however, no change in the total wave height due to all species and consequently no loss of electroactive species. These observations are similar to those reported by Davison, *et al.*[2] The new wave is ascribed to the mixed-ligand species $MS_4C_4(CF_3)_2(CN)_2^-$.

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3-Trimethylamino-3-beryl-1,2-dicarba-*closo*-dodecaborane(12) and Related Species

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The reconstruction of the 1,2-dicarba-*closo*-dodecaborane(12) icosahedron from the reaction of the (3)-1,2-dicarbollide ion [(3)-1,2-$B_9C_2H_{11}^{2-}$] with phenylboron dichloride

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + C_6H_5BCl_2 \longrightarrow 3\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{11} + 2Cl^-$$

has been described.[2,3] The similar reaction of $BeCl_2$ with the (3)-1,2-dicarbollide ion

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + BeCl_2 \longrightarrow 3\text{-}BeCl\text{-}1,2\text{-}B_9C_2H_{11}^- + Cl^-$$

in the presence and absence of donor solvents failed to insert a Be atom into the open face of the (3)-1,2-dicarbollide ion under all conditions attempted. However, since the expected 3-BeCl-1,2-$B_9C_2H_{11}^-$ icosahedral species would be isoelectronic with the known $B_{11}CH_{12}^-$ ion,[4] due to the isoelectronic relationship of B–B and Be–C atomic pairs,[5] further work was successfully undertaken and briefly reported elsewhere.[5] This note describes these initial results in greater detail.

Results and Discussion

Earlier work[6] had illustrated the existence of a highly acidic $B_9C_2H_{13}$ species which resulted from the protonation of the (3)-1,2-$B_9C_2H_{12}^-$ ion. This species may be formally considered to be a diprotonated (3)-1,2-dicarbollide ion, and, as such, one might expect (3)-1,2-$B_9C_2H_{13}$ to react with metal alkyls to produce 2 mol of alkane through protolysis of metal–alkyl bonds with insertion of the metal into the open face of the icosahedral fragment. In the case of beryllium alkyls, the intervention of a donor solvent, :L, would probably be required to stabilize the product. Thus, dialkylberyllium etherates appeared to be the reagents of choice with which to test the proposed reaction sequence

$$(3)\text{-}1,2\text{-}B_9C_2H_{13} + BeR_2\cdot 2(O(C_2H_5)_2) \xrightarrow{C_6H_6-(C_2H_5)_2O} 2RH + 3\text{-}BeO(C_2H_5)_2\text{-}1,2\text{-}B_9C_2H_{11} + (C_2H_5)_2O$$

Accordingly, diethyl- and dimethylberyllium diethyl etherates were allowed to react with (3)-1,2-$B_9C_2H_{13}$ in benzene solution containing added diethyl ether. One mole of alkane was rapidly produced upon mixing the reagents at room temperature and additional alkane was evolved upon the removal of solvent at 50°. The resulting white crystalline product (mp 120–121°) was

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