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Solar Energy Conversion by Water Photodissociation

Transition metal complexes can provide low-energy cyclic systems for catalytic photodissociation of water.

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There are two fundamental ways for converting solar energy into useful energy: (i) thermal conversion, in which the solar radiation is degradated to heat in the absorbing system, and (ii) quantum conversion, in which the solar radiation is used to cause some kind of photochemical or photoelectric process in the absorbing system. In this article, we discuss some aspects of the photochemical conversion of solar energy by simple, nonbiological systems.

Any endothermic photochemical reaction represents a conversion of light energy into chemical energy. A kinetically stable photoproduct must be considered as a "fuel" since it can be stored, transported, and then converted to other chemical species with evolution of energy. Therefore, direct conversion of solar radiation into chemical energy is, in principle, a very useful conversion mode since it remedies the major defects of solar energy, namely its low density and intermittency.

In looking for a photochemical process to be used as a solar energy conversion system, some obvious restrictions must be taken into consideration: (i) the solar radiation that reaches the surface of the earth has a defined wavelength distribution (see Fig. 1); (ii) the infrared radiation is not useful for generating photochemical reactions since it cannot cause electronic excitation; (iii) the ecological equilibrium of our planet must not be perturbed; and (iv) the system to be used must be as economical as possible. Taking these restrictions into account, we can state eight requirements for systems to be used for the photochemical conversion of solar energy. These requirements, which have been discussed in detail elsewhere (*1*), are as follows:

1) The electronic absorption spectrum of the system must overlap the emission spectrum of the sun.

2) Upon absorption of solar radiation, the system must be able to undergo an endothermic photoreaction.

3) The endothermic photoreaction must be followed by other (thermal or photochemical) reactions which must lead the system to its original state (in other words, the process must be a closed cycle).

4) The quantum yield of the endothermic photoreaction must be as high as possible.

5) At least one of the exothermic reactions involved in the cycle must take place under controlled conditions (useful reaction).

6) The useful reaction should return as large a portion as possible of the solar energy absorbed.

7) The reactants of the useful reaction should be suitable for storage and transportation.

8) The system must be as economical as possible.

Each photochemical system involving the splitting of water and then the recombination of gaseous (g) molecular hydrogen and oxygen

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) + 58 \text{ kcal} \quad (1)$$

satisfies requirements 5, 6, and 7 (*2–4*). However, as we will see later, the direct photodissociation of water cannot take place with solar radiation since water does not satisfy the first requirement.

We will try to show that this basic difficulty can be theoretically overcome by using properly devised systems in which transition metal complexes are used as "catalysts." At the same time, our discussion will provide an example of the type of approach that should be used in dealing with the problem of the photochemical conversion of solar energy by nonbiological systems (*5*).

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Direct Photodissociation

The electronic absorption spectrum of water does not overlap the solar spectrum at the surface of the earth (see Fig. 1), so that the system "water" does not satisfy the first requirement. The lowest energy for the unimolecular dissociation of water is 116 kcal/mole, and corresponds to the formation of molecular hydrogen and ground state atomic oxygen (Fig. 1). The lowest electronic excited state ($^3B_1$) of water was reported to be at about 100 kcal/mole by some authors (*6*) and as low as about 80 kcal/mole by others (*7*). Such a low-lying excited state would be a bound state, and it could play some role in the photochemistry of water. However, recent experiments (*8*) as well as theoretical calculations (*9*) indicate that the $^3B_1$ state cannot be lower than 116 kcal/mole. Thus, it is clear that solar radiation can cause water photodissociation neither directly nor via electronic energy transfer processes.

On the other hand, it is well known that the heat of dissociation of gaseous water into molecular hydrogen and molecular oxygen is only 58 kcal/mole, which means that, potentially, about 16 percent (*10*) of the solar energy could be stored in splitting water by one-photon processes. As shown in Fig. 1, the excess energy needed for direct photodissociation is due to the formation of radicals. Since radicals cannot be stored (requirement 7), their production is a sheer waste of energy from the photochemical conversion point of view. The only chemical energy that can be stored from water dissociation is that corresponding to the heat of combustion of molecular hydrogen with molecular oxygen (useful reaction, requirement 5)—that is, 58 kcal/mole. Thus, one problem in the photochemical conversion of solar energy using water as a substrate is finding systems in which water dissociation takes place without formation of intermediate radical species.

In some respects, the situation is similar to that of the thermochemical dissociation of water. Direct thermal splitting of water requires temperatures around 2500°C, which are well above the temperature ranges of present-day nuclear reactors (*4*). Thus, several research groups are looking for catalytic thermochemical cycles in which water splitting is achieved in several steps, each of which requires heat at temperatures available in commercial nuclear reactors (*4*). Similarly, splitting of water by direct photolysis requires high-energy photons, which are not available from solar radiation, but catalytic photodissociation processes may be carried out by lower-energy photons. The problem is devising appropriate chemical systems in the light of the requirements stated above.

Simple Chemical Cycles

A very simple system for catalyzed photodissociation of water can be based on a couple X^+/X having a standard reduction potential $E^0 > 1.23$ volts. Here X^+ and X are oxidized and reduced forms of a chemical species X. With such a couple, if X is able to reduce water in a photochemical step (reaction 2), water is dissociated, since X^+ is able to oxidize water in a thermal process (reaction 3).

C1 system

$$X + H_2O \xrightarrow{h\nu} X^+ + H + OH^- \quad (2)$$

$$\underline{X^+ + \tfrac{1}{2}H_2O \rightarrow X + H^+ + \tfrac{1}{4}O_2} \quad (3)$$

$$\tfrac{1}{2}H_2O \xrightarrow{h\nu} H + \tfrac{1}{4}O_2$$

A system of this type, which we call a C1 system, would satisfy requirements 2 and 3. However, it cannot satisfy requirement 1. A simple calculation shows that the threshold energy (*11*) for the C1 cycle is 86 kcal/$Nh\nu$, where $Nh\nu$ is Avogadro's number of photons; therefore, only photons having wavelength lower than 332 nm can be used. The energy needed for the C1 cycle is thus much lower than that needed for the direct photodissociation, but still exceedingly high for solar energy conversion (Fig. 1). Specifically, a calculation based on the wavelength distribution of solar radiation shows that at most about 1 percent of the solar energy would be stored. In practice, of course, things are even worse: for the Ce^{4+}/Ce^{3+} couple (*12*), the lowest-energy absorption band (of aqueous Ce^{3+}) is at about 250 nm, and the quantum yield of the photoreaction (requirement 4) is less than 10^{-3}.

Another cyclic system for water photodissociation can be formulated as

C2 system

$$Y + H_2O \xrightarrow{h\nu} Y^- + H^+ + OH \quad (4)$$

$$\underline{Y^- + H_2O \rightarrow Y + OH^- + \tfrac{1}{2}H_2} \quad (5)$$

$$H_2O \xrightarrow{h\nu} \tfrac{1}{2}H_2 + OH$$

In this case, the Y/Y^- couple must have $E^0 < 0$ volt for the thermal reaction to be possible. The threshold energy for this process (78 kcal/$Nh\nu$, 367 nm) is lower than that of the C1 system, but it is still too high for substantial solar energy conversion (Fig. 1). Experiments on this cycle have been carried out using the Eu^{3+}/Eu^{2+} couple (*13*) and the Cr^{3+}/Cr^{2+} couple (*14*). Only radiation at or below 254 nm was effective, and the quantum yields were very low.

The advantage of the C1 and C2 systems over direct photodissociation is that only one radical is formed (Fig. 1). However, the threshold energies of these cycles are still too high for solar energy conversion. Furthermore, there are problems connected with the intimate mechanisms of

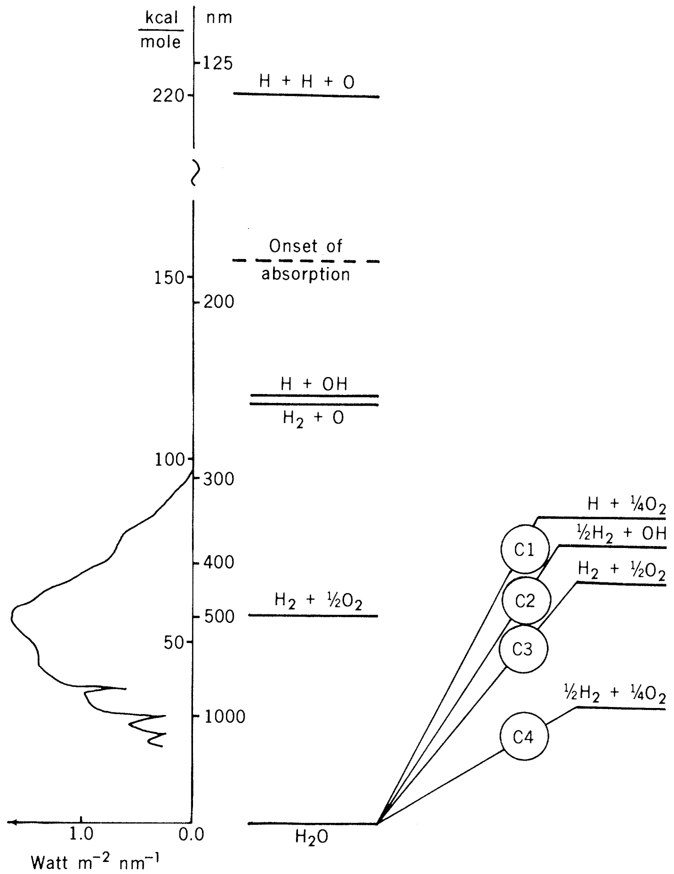

Fig. 1. Energy level diagram showing the energies of unimolecular dissociation and the onset of the electronic absorption spectrum for gaseous water. The threshold energies of some closed-cycle processes for the "catalyzed" photodissociation of liquid water are also shown. At the left, the spectral distribution of solar radiation at sea level with air mass $m = 1$ is shown. [Data from (*25*)]

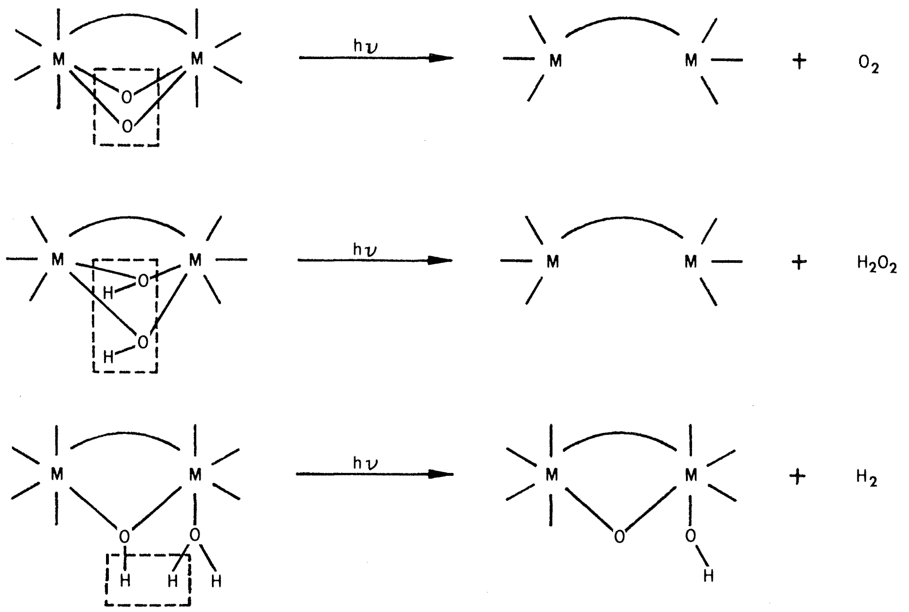

Fig 2. Schematic representation of the photochemical evolution of O_2, H_2O_2, and H_2 from binuclear transition metal complexes.

the "overall" reactions 3 and 5 (these problems, however, cannot affect the threshold energies of the cycles). There are also experimental difficulties, such as those connected with the need to have gaseous oxygen and hydrogen evolved separately. Finally, the quantum yield is very low. This is probably because in the primary photoreactions (reactions 2 and 4) the oxidized (or reduced) catalyst and the corresponding water-derived radical (H or OH) are formed close to each other in a solvent cage, so that a geminate recombination is very probable.

In conclusion, the formation of water-derived radicals not only imposes threshold energies so high that requirement 1 cannot be satisfied, but is also very bad for the efficiency of the system.

A hypothetical formulation of a cycle which does not involve water-derived radicals is

C3 system

$$Z + H_2O \xrightarrow{h\nu} ZO + H_2 \qquad (6)$$

$$ZO \rightarrow Z + \tfrac{1}{2}O_2 \qquad (7)$$

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2$$

In this cycle, there is a photochemical reaction in which two electrons are transferred from the catalyst to water with direct formation of molecular hydrogen, followed by a spontaneous thermal reaction which again involves the transfer of two electrons with formation of molecular oxygen. The threshold energy for dissociation of liquid water is 68 kcal/$Nh\nu$ (420 nm), and thus the situation is somewhat better than in the previous cycles (see Fig. 1). It can be shown that, theoretically, 6 percent of the solar energy can be stored by a system having such a threshold energy. In this case radicals are not formed in the photochemical step, so that back thermal reactions should be much less important than in the previous cases, and it should be easier to meet requirement 4. Other difficulties, of course, are still present—in particular it is difficult to formulate a real cycle of this type. For example, a two-electron transfer from a simple species like a metal ion to water can hardly be caused by a photon having such a small amount of energy.

Cycles Involving Binuclear Complexes

We have already suggested (*5*) that the formation of water-derived radicals can probably be avoided, as is required in cycles of the C3 type, if the catalyst and the substrate are arranged in appropriate molecular structures, such as in a binuclear coordination compound. The idea is that in a suitable molecular arrangement formation of molecular oxygen, hydrogen peroxide, or molecular hydrogen is possible in the excited state without intermediate formation of oxygen atoms, hydroxyl radicals, or hydrogen atoms. Schematic examples of these processes are given in Fig. 2.

It should be kept in mind that, in order to have a cyclic system (requirement 3), the reduced or oxidized catalyst must be able to undergo some reaction which must ultimately lead it back to its original structure. Although it is not easy to design a real cycle involving a binuclear complex, some specific requisites can be anticipated. For example, the two metal atoms should be tied together into a macrocyclic ligand so as to avoid breaking the molecular structure. Moreover, the photoreaction should transfer a number of electrons which is the minimum needed for avoiding radical formation. This last point can be illustrated on the basis of the following three schemes, each of which is assumed to involve only one photon.

$$[\text{Cat-}O_2]_{\text{ox}} \xrightarrow{h\nu} [\text{Cat}]_{\text{red}} + O_2$$

$$[\text{Cat}]_{\text{red}} + 2H_2O \rightarrow [\text{Cat-}O_2]_{\text{ox}} + 2H_2$$

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2\,(136 \text{ kcal}/Nh\nu, 210 \text{ nm})$$

$$[\text{Cat-}(OH)_2]_{\text{ox}} \xrightarrow{h\nu} [\text{Cat}]_{\text{red}} + H_2O_2$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

$$[\text{Cat}]_{\text{red}} + 2H_2O \rightarrow [\text{Cat-}(OH)_2]_{\text{ox}} + H_2$$

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2\,(68 \text{ kcal}/Nh\nu, 420 \text{ nm})$$

$$[\text{Cat-}H_2]_{\text{red}} \xrightarrow{h\nu} [\text{Cat}]_{\text{ox}} + H_2$$

$$[\text{Cat}]_{\text{ox}} + H_2O \rightarrow [\text{Cat-}H_2]_{\text{red}} + \tfrac{1}{2}O_2$$

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2\,(68 \text{ kcal}/Nh\nu, 420 \text{ nm})$$

We can see that the threshold energy is 210 nm when the primary photoreaction must transfer four electrons to give molecular oxygen, whereas it is 420 nm if two electrons only are transferred to yield hydrogen peroxide or molecular hydrogen. It should also be noted that the complexity or the number of the dark reactions needed to lead the system back to its original structure very likely increases with the number of electrons transferred in the photoreaction.

In the light of the above discussion, the di-μ-oxotetrakis(2,2′-bipyridine)dimanganese(III,IV) complex, $(\text{bipy})_2\text{Mn}O_2\text{Mn}(\text{bipy})_2^{3+}$, which has been discussed (*15, 16*) as a possible oxygen-generating catalyst in the photodecomposition of water, can hardly enter in a useful cyclic system. If this complex undergoes photolysis according to reaction 8 (*15*)

$$[(\text{bipy})_2\text{Mn}O_2\text{Mn}(\text{bipy})_2]^{3+} \xrightarrow{h\nu} O_2 + \text{unknown reduced products} \qquad (8)$$

which formally involves the transfer of four electrons from the oxygen ligands to the metals, the binuclear structure most probably breaks into two different reduced fragments. The oxidation of these two fragments would involve a very complicated reaction sequence, and it is extremely unlikely that such a sequence would result in the formation of the original binuclear complex. On the other hand, if we assume that the complex does not break in the primary photoreaction, the oxidation of the reduced complex would require the transfer of four electrons to the oxidizing species, with the insertion, between the manganese atoms, of two oxygen atoms taken from two water molecules. This again seems to be an extremely complicated reaction for a nonbiological system. The design and synthesis of suitable binuclear complexes is an exciting challenge to chemists, and in this regard we believe that attempting to imitate natural processes is not the best way of using chemists' talent.

Cycles Involving Hydrido Complexes

Very interesting cycles for the catalyzed photodissociation of water can be formulated with metal-hydrido complexes. The first example shown below belongs to the C3 type previously discussed.

C3′ system

$$cis\text{-}ML_nH_2^{z+} \xrightarrow{h\nu} ML_n^{z+} + H_2 \tag{9}$$

$$ML_n^{z+} + H_2O \longrightarrow ML_n^{(z-2)+} + 2H^+ + \tfrac{1}{2}O_2 \tag{10}$$

$$\underline{ML_n^{(z-2)+} + 2H^+ \longrightarrow cis\text{-}ML_nH_2^{z+}} \tag{11}$$

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2$$

A *cis* dihydrido complex, $ML_nH_2^{z+}$ (where M = metal and L = ligand), is assumed to liberate molecular hydrogen on irradiation, thus giving a ML_n^{z+} complex. This complex oxidizes water spontaneously and then undergoes diprotonation to yield the original dihydrido complex. Depending on the specific nature of the catalyst, every one of the three steps or even two of them can be photochemical. In the last case, the threshold energy (68 kcal/*Nhν* for the one-photon cycle) is lower (see below).

Another cycle involving hydrido complexes may be schematized as follows:

C4 system

$$ML_n + H^+ \xrightarrow{h\nu} ML_nH^+ \tag{12}$$

$$ML_nH^+ \longrightarrow \tfrac{1}{2}[ML_n]_2^{2+} + \tfrac{1}{2}H_2 \tag{13}$$

$$\underline{\tfrac{1}{2}[ML_n]_2^{2+} + \tfrac{1}{2}H_2O \longrightarrow ML_n + H^+ + \tfrac{1}{4}O_2} \tag{14}$$

$$\tfrac{1}{2}H_2O \xrightarrow{h\nu} \tfrac{1}{2}H_2 + \tfrac{1}{4}O_2$$

In this cycle a complex is assumed to give its monohydrido derivative on irradiation. Then there is a bimolecular reaction of the monohydrido complex yielding molecular hydrogen and a dimer containing a metal-metal bond. Dimer dissociation and reduction of the two fragments would form molecular oxygen and give back the original complex. It should be pointed out that since two photons are used to split one water molecule, the threshold energy of the C4 cycle is only 34 kcal/*Nhν* (841 nm), so that, theoretically, 40 percent of the solar energy can be stored. In general, each system that utilizes two photons to split a water molecule can convert a large fraction of solar energy. In order to have a cycle of this type, either two photons must be absorbed simultaneously by the catalyst (which is impossible for a low-density photon source such as solar radiation), or two consecutive reactions must be driven by light against a gradient of chemical potential (*17*), or intermediate compounds must be formed in the photochemical reaction which are sufficiently stable to react with each other (as is supposed to happen in the C4 cycle).

To our knowledge, no attention has been paid as yet to cycles involving hydrido complexes. These complexes, which were thought to be very unstable and strange molecules for many years, have now been shown to exhibit, in several cases, high stability and a wide range of chemical reactions (*18*). Their photochemistry is practically unexplored, but the photochemical production of H_2 on irradiation of *cis*-$Co(phen)(PR_3)_2H_2^+$ (where phen = 1,10-phenanthroline and R = alkyl radical) has already been observed (*19*).

$$cis\text{-}Co\,(phen)\,(PR_3)_2H_2^+ \xrightarrow{h\nu} Co\,(phen)\,(PR_3)_2^+ + H_2 \tag{15}$$

This reaction is just that needed in the C3′ system (reaction 9). Moreover, the *cis*-$Co(AA)(PR_3)_2H_2^+$ complexes (where AA is a chelate ligand) are colored (requirement 1) and their dissociation is presumably endothermic (requirement 2). Other reactions relevant to the C3′ system, and specifically to reaction 11, are known. They are the thermal diprotonation of some complexes[for example (*20*)

$$ArMo\,(PR_3)_3 + 2H^+ \longrightarrow ArMo\,(PR_3)_2H_2^{2+} \tag{16}$$

where Ar stands for aromatic hydrocarbon] and numerous thermal and photochemical oxidative additions.

Some experimental knowledge is also available concerning the reactions involved in the C4 type cycle and its possible modifications. The "thermal" analog of reaction 12, the protonation reaction, is one of the usual routes for preparing hydrido complexes (*18*). A photochemical version of reaction 13 has already been reported (*21*)

$$2HIr(PF_3)_4 \xrightarrow{h\nu} H_2 + (PF_3)_4Ir\text{-}Ir(PF_3)_4 \tag{17}$$

Finally, the photochemical version of reaction 14, photoinduced metal-metal bond cleavage, has been obtained for several complexes (*22*). Much work is still needed to find hydrido systems that satisfy all the requirements stated in the introduction.

Conclusions

The basic concepts for direct and catalyzed photodissociation of water have been summarized. Water dissociation in closed-cycle processes based on endothermic photochemical reactions offers a potential solution to the solar energy conversion problem. Transition metal complexes, whose excited state chemistry is extremely rich (*23, 24*) although mostly unexplored, are, in principle, suitable "catalysts" for cycles of this type. The most interesting cycles are those involving metal hydrido complexes or binuclear complexes in which the two metal atoms are bound into a macrocyclic ligand. Systematic investigations of the photochemistry of transition metal complexes with the aim of designing suitable systems for solar energy conversion have long-range promise and merit further consideration.

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Doctorates Granted to Women and Minority Group Members

What changes have there been in recent years in numbers and in distribution among fields of study?

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Current emphasis on affirmative action in recruiting new faculty members focuses attention on those universities from which appropriately qualified young holders of doctorates are most likely to be obtained. Most of these universities are members of the Association of American Universities (AAU). The 46 AAU universities (*1*) within the United States have awarded 75 percent of all doctorates awarded to date in this country, and are currently awarding about 60 percent of the yearly total. In quality, too, the AAU universities are a select group. They include 89 percent of all graduate departments rated as "distinguished" or "strong" in the 1969 Roose-Andersen survey (*2*).

Clearly the AAU institutions offer a rich hunting ground for beginning faculty members. It is therefore of interest to know their current record and trends in providing doctoral education to women and to members of the principal minority groups. To obtain that information, we asked the graduate dean of each member university to supply information on the number of doctorates (Ph.D., Ed.D., D.B.A., D.M.A., and so on, but not M.D., D.D.S., D.V.M., D.Th., or J.D.) conferred in each field from 1 July 1969 to 1 July 1972 and the number expected to be conferred in each field from 1 July 1972 to 1 July 1975, and also to show the numbers in each field and time period awarded to women, to minority women, and to minority men. The four minority groups—American Indian, Asian American, Black, and Spanish origin—were defined in accordance with the instructions of the Department of Health, Education, and Welfare concerning affirmative action programs (*3*).

All AAU members except McGill University and the University of Missouri supplied data. Not every university could supply all the information asked for, but the gaps were relatively few and were filled by adding proportionate estimates. Figures and percentages reported below are therefore either actual or estimated totals for the 46 AAU universities in the United States (including the Berkeley and Los Angeles campuses of the University of California). Data concerning each university were sent to its graduate dean for verification.

The data are summarized by fields in Table 1. Several conclusions can be drawn from that table:

1) The total number of doctorates from AAU institutions is expected to be essentially the same in 1972–75 as in 1969–72; the figures show an increase of less than 0.1 percent. This slight increase is much smaller than the 20 percent increase projected by the U.S. Office of Education (*4*) for all doctoral degrees from all U.S. universities. However, it is consistent with a recent report of the American Council on Education (*5*) which included figures or estimates for the "top 20" universities in the country. In these 20 universities, the average number of doctorates in 1972–73 and 1974–75 (the first and third years of our second 3-year period) is projected to be 0.7 percent greater than the number in 1971–72 (the final year of our first 3-year period). It seems clear that for the immediate future the AAU universities are not increasing their total number of doctorates significantly above the 1969–72 level.

2) The small total increase is the net result of four substantially larger changes in the representation of women and minority group members (recapitulated in Table 2).

3) A number of individual fields show substantial increases or decreases. Some that increased more than 10 percent are applied mathematics, business administration, fine arts, psychology, and foreign languages. Those that decreased more than 10 percent are mathematics, chemistry, engineering, biochemistry, and physics.

4) The individual fields differ very substantially in the percentages of doctorates awarded to women and to minority members. For women, the percentage of doctorates for the entire 6-year span is less than 10 percent in each of the following fields. Note that the fields included in this list (and also the three following lists) are more finely divided than those of Table 1. The figure in parentheses is the 6-year total of doctorates from the AAU institutions; a field is not listed if its total is less than 100.

Geography (1042)	9%
Astronomy (500)	8
Economics (3372)	8
Mathematics (3356)	8
Religion (608)	8
Computer science (958)	6
Applied mathematics (1562)	5
Geology (1530)	4
Agriculture (1856)	3
Atmospheric science (201)	3
Business administration (2373)	3
Physics (5621)	3
Engineering (all branches) (11,912)	1
Operations research (100)	1

In contrast, women received more than 25 percent of the doctorates in the 6-year span in each of the following fields:

Home economics (121)	79%
Art history (302)	53
Romance languages (2026)	46
Germanic languages (893)	40
Comparative literature (332)	40
Social work (978)	38
Health sciences (1651)	34
English (5470)	34
Speech (1409)	33

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