arguments about θ are not occasioned by mathematical artifacts, the first step of the vision process is likely to be a cis–trans photoisomerization reaction that can be described as a "through-space" charge separation[21] where the isomerization leads to separation of the positively charged Schiff base nitrogen and a negatively charged group of the protein[6,22] (Figure 3). The high quantum yield of the visual pigment indicates that the protein eliminates the excited-state barrier; this might involve proton transfer between two acids.[13]

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Catalysis of Hydrogen Production in Irradiated Aqueous Solutions by Gold Sols[1]

Sir:

In conjunction with the efforts to devise energy storage systems, it is often noted that many radicals which thermodynamically are capable of water reduction (or oxidation) to hydrogen (or oxygen) lack the kinetic stability to follow that course and would react via other pathways (such as disproportionation or dimerization) long before any detectable reaction with water occurs. Recent reports indicate, however, that redox catalysts may participate in the diversion of photochemically or thermally produced radicals or short-lived oxidation states of inorganic complexes from their energy-wasting back-electron-transfer reaction, dismutation, or dimerization reactions to the more profitable pathway of water decomposition.[2,3] Furthermore, it was recently shown by Henglein[4] that 2-propanol radicals will produce hydrogen in the presence of silver colloids rather than recombine. To this end we would like to present some results which indicate that aqueous solutions of gold sols may also serve as efficient catalysts for such a reaction.

Table I. Dose and Dose Rate Effect on $G(H_2)$ in the Aqueous 2-Propanol, Acetone, and Gold Sols

solutions[a]	dose rate, krad/min	dose, krad	$G(H_2)$[b]
c	1.55–16	7.75–32	1.10
	1.55	7.75	1.31
	1.55	10.85	1.65
	1.55	15.5	2.17
	1.55	31.0	2.62
d	1.55	31.0	1.05
	16	16	4.22
	16	24	3.94
	16	32	4.28
	16	48	4.43
d	16	32	1.02
	0.56	25.2	1.94[e]
	1.55	24.8	2.04[e]
	3.2	25.6	2.25[e]
	16	24	4.00[e]

[a] Unless otherwise stated deaerated 0.13 M 2-propanol and 0.13 M acetone, 5.4×10^{-4} M in Au and initial sodium citrate concentration of 3.9×10^{-3} M. [b] Molecular hydrogen yields in molecules/100 eV. Accuracy is ±0.1 *G* units. [c] As given in *a* without the gold and citrate components. [d] After coagulation and filtration of the gold. See ref 12. [e] For the sake of uniformity, these were normalized to a dose of 25 krad assuming linear dose dependence (<5% correction).

The 2-propanol radical in the present system was produced by γ-irradiation of aqueous solutions containing 0.13 M 2-propanol and 0.13 M acetone. The gold was chosen as the catalyst since the wealth of available information on these colloids[5] provides a means of production of the colloid under controlled conditions in a reliable, reproducible, and predictable manner. Furthermore, the size and shape of the gold colloids can be varied over a wide range.

In the above-mentioned solutions, reactions 1–4 will convert

$$H_2O \rightsquigarrow e_{aq}^- \ (G = 2.8),\quad H\ (G = 0.65),\quad OH\ (G = 2.8),\quad H_2\ (G = 0.45),\quad H_2O_2\ (G = 0.7) \qquad (1)$$

$$H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2COH \qquad (2)$$

$$OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH \qquad (3)$$

$$e_{aq}^- + (CH_3)_2CO \xrightarrow{H^+} (CH_3)_2COH \qquad (4)$$

all the radicals produced by γ-irradiation[6a] into the 2-propanol radical, thus producing a one-radical system.[6b] Although the latter radical has a low enough redox potential to reduce water to hydrogen,[7] such a reaction does not occur in homogeneous solutions and these radicals usually decay by a radical-radical dismutation of dimerization reaction.[8] As mentioned above, it was recently observed that silver colloids catalyze hydrogen production by this radical.[4] The yield of molecular hydrogen in the absence of the catalyst is therefore equal to $G_{H_2} + G_H = 1.1$. This was indeed found to be the case in our solutions also (in the absence of the catalyst) and was used in the latter experiments as the reference system.[9]

In Table I we summarize some of our results on the effect of the gold sols[10] on the hydrogen yield at different doses and dose rates. As can be seen in Table I, a substantial increase in the yield of hydrogen, $G(H_2)$, can be achieved. If all of the alcoholic radicals would be used up in the hydrogen-producing reaction

$$2(CH_3)_2\dot{C}OH \xrightarrow{(Au)_c} 2(CH_3)_2CO + H_2 \qquad (5)$$

then the maximum yield expected would be $G(H_2) = G_{H_2} + G_H + (G_{e_{aq}^-} + G_{OH} + G_H)/2 = 4.2$. This yield could be obtained in the higher dose rate experiments[11] (Table I). Since values close to the calculated $G(H_2)$ could be obtained, we conclude that very little, if any, oxidation of $(CH_3)_2\dot{C}OH$ by the radiolytically produced H_2O_2 occurs, either by direct or by gold-catalyzed reaction.[15] The ultimate proof that the gold particles do participate in reaction 5 (which does not occur in its absence) comes from the yield of H_2 in radiolysis of the standard solution after coagulation of the gold.[12a] Since this coagulation removes exclusively the gold particles, the decrease in $G(H_2)$ to its value in the absence of the catalyst stresses its indispensable role in the hydrogen production. No radiation-induced coagulation could be observed in any of our experiments. In fact, spectral analysis of the irradiated solutions revealed only a slight blue shift (~2 nm) and a <5% increase in the absorption at the 520-nm absorption band even at the highest doses and dose rates of irradiation used here.[12b]

That the origin of the added yield of H_2 is primarily from the water is evident from the isotopic composition of the hydrogen obtained on irradiation (dose rate, 16 krad/min; dose, 48 krad) of 2-propanol-d_8 and acetone-d_6 in H_2O. The experimentally obtained composition in the absence of gold is 42% H_2, 57% HD, 1% D_2 (the calculated values: 41% H_2 and 59% HD). The composition in the presence of the sol is 77% H_2, 23% HD, <0.5% D_2 (calculated: 84% H_2, 16% HD). Apparently the contribution from the methyl hydrogens is rather minor.[16]

The effect of dose and dose rates should provide some insight into the processes leading to the hydrogen production. Firstly, we note that at low dose rate $G(H_2)$ increases with the total dose and, secondly, high dose rates enhance the formation of molecular hydrogen. The first effect may indicate some competition of reaction 5 with a product of the sol-producing procedure (possibly unreacted Au(III) or acetone dicarboxylate[13]). More plausibly, some of the molecular hydrogen probably adsorbs on the gold aggregates and is not removed by our measuring apparatus. Measurements on authentic hydrogen samples indicate that this effect can indeed occur in our system and will at least partially explain the dose effect. The significance of both adsorption and reaction decrease as the aggregates saturate and the destructive reactant is consumed during the irradiation.

More interesting is the rather unexpected effect of the dose rate. Apparently the rate of the rate-limiting step in the hydrogen-producing reaction is dependent on the steady-state concentration of the radical, $[R]_{ss}$, in a kinetic order higher than 1. The upper limit for $[R]_{ss}$ can be calculated from the dose rate and the rate constant for the bulk radical–radical reaction at the highest dose rate used. This yields $[R]_{ss} = 2.8 \times 10^{-8}$ M, which would correspond to a half-life time of 0.018 s for the radical. On the other hand, the concentration of the aggregates is $[(Au)_c] = 2.74 \times 10^{-10}$ M[14] (and thus the aggregation number is 1.97×10^6). Under our experimental conditions of dose rate and aggregate size, $[(Au)_c]$ is thus $\ll [R]_{ss}$. The rate constant for the gold particles to encounter the radicals can be estimated from the Smoluchowski equation (assuming diffusion coefficient of 2×10^{-5} cm^2 s^{-1} for the radical and $r = 2 \times 10^{-6}$ cm for the aggregate) to be 3.0×10^{11} M^{-1} s^{-1}. The half-life for the gold particles to experience these encounters under the above-mentioned conditions would be 8.3×10^{-5} s. Clearly, during the time required for half of the radicals to react with one another in a bulk reaction, most of the aggregates will suffer many encounters with the radicals and will thus be able to accumulate adsorbed radicals (or their deposited electrons).[17] Since we concluded above that the rate-determining step in the hydrogen production is of at least an order of 2 in $[R]_{ss}$, the processes of diffusion to the aggregate cannot be the rate-determining step. We therefore tend to believe at this stage that the reaction which leads to the hydrogen production involves two radicals while adsorbed on the particle. Such a reaction can exhibit a rather high kinetic order.

In conclusion, it was demonstrated here that finely dispersed gold particles would catalyze hydrogen formation from a radical which would otherwise disporportionate or dimerize in a diffusion-controlled reaction. In the particular example studied here, the effect of the radiation is to produce hydrogen from water (reaction 4 followed by 5) with a yield close to that theoretically possible, with the conversion of 2-propanol into acetone (reactions 2 and 3 followed by 5). The net decomposition of water to hydrogen is therefore $G(-H_2O \rightarrow H_2) = H_{H_2} + \frac{1}{2}G_{e_{aq}^-} = 1.85$. Rather unexpectedly and somewhat disappointing is the observation that high-energy fluxes favor the hydrogen-production process over low-energy flux conditions.

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(6) (a) *G* is the yield of the appropriate species in units of molecules/100 eV. All solutions are deaerated by bubbling Ar through the solutions for 15 min. All the usual precautions common in radiation-chemical studies were undertaken. Hydrogen yields were determined on a Van Slyke gas chromatograph apparatus. No detectable amounts of other gases were observed. Dose rates were determined using a Fricke dosimeter. See also note 9. (b) No other component of the system, including any reasonable oxidation product introduced by the sol production procedure, could effectively compete for the primary radicals under our experimental conditions in an H_2-producing reaction. See the following NBS specific rate tables: Farhataziz and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 59** (1977); M. Anbar, Farhataziz, and A. B. Ross, *ibid.*, **No. 51** (1975); M. Anbar, M. Bambenek, and A. B. Ross, *ibid.*, **No. 43** (1973).

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(9) Dose rates of 0.56–16 krad/min were used and total dose delivered ranged from 5 to 50 krad. If $G(H_2)$ would reach a value of 5 molecules/100 eV, the maximum concentration of H_2 would be 2.5×10^{-4} M, which is still below the solubility of H_2 in water at 1 atm. No evolution of hydrogen gas from the water is expected and all yields reported are those of H_2 soluble in the water.

(10) In the preparation of the gold sols, we followed the procedure of Turkevich et al.[5] for their "standard" solution of gold-citrate sol with the only exception that twice the concentration of both chloroauric acid and sodium citrate were always used. The pH of the sol solution was 6.4 ± 0.2. No deterioration of our standard solution was detected for at least 2 weeks after preparation. The standard solution, when diluted 1:10, showed change in size of the particles and was less stable.

(11) The calculated $G(H_2)$ was taken for dilute solution. Actually, in this system some increase in these values should be expected owing to some scavenging of radicals in the radiolytical spur by the relatively high concentrations of 2-propanol and acetone.

(12) (a) Coagulation was achieved by addition of 5×10^{-2} M Na_2SO_4 and filtration of the gold precipitate. (b) This also indicates the catalytic role of the gold when the total amount of H_2 produced is considered.[9]

(13) Since no absorption of the original chloroauric acid was observed, the concentration of Au(III) is very small. On the other hand, a radical produced by reduction of acetone dicarboxylate would be expected to react in a way similar to the 2-propanol radicals.

(14) The following known quantities were used for this calculation: the density of gold, 19.3 g/cm^3; the radius of the aggregate,[5] 2×10^{-6} cm; total Au concentration, 5.4×10^{-4} M; atomic weight of gold, 197.

(15) It was, however, noticed that, depending on the age of the sol, the maximum

yield may drop by as much as 1.5 molecules/100 eV.

(16) Such β-hydrogen abstraction by reduced cadmium cations was, however, suggested: M. Kelm, J. Lilie, and A. Henglein, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1132 (1975); M. Freiberg and D. Meyerstein, *ibid.*, **73**, 622 (1977).

(17) This calculation would predict that ~50% of the radicals will encounter the gold aggregate while 50% combine. The results at high dose rate indicate that, under the present experimental conditions, recombination is no more a competing reaction. Probably [(Au)$_c$] or the diffusion rate constant are underestimated. As expected from these considerations, a decrease in [(Au)$_c$] by half hardly affected the yield.

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A Convenient One-Step Synthesis of 2,2-Disubstituted Oxetanes from Ketones

Sir:

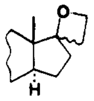
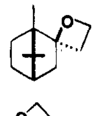
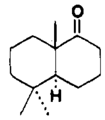
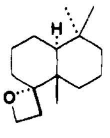
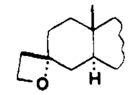
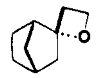
Oxetanes are useful intermediates in organic synthesis which undergo substitution nucleophilic bimolecular ring opening with a variety of good nucleophiles.[1,2] The synthesis and chemistry of oxetanes has been reviewed.[3] The synthesis of 2,2-disubstituted oxetanes from aromatic ketones is accomplished most often by the Paterno–Büchi reaction via a photochemical [2 + 2] cycloaddition reaction.[4] However, the preparation of 2,2-disubstituted oxetanes **4** from aliphatic ketones **1** (Scheme I) normally requires a multistep sequence of reactions employing a Reformatsky reaction (Zn/BrCH$_2$CO$_2$Et) or Rathke reaction (LiCH$_2$CO$_2$-*t*-Bu) followed by reduction (LiAlH$_4$), selective esterification (*p*-TsCl or MsCl, pyridine) and base-induced ring closure (NaH or KO-*t*-Bu).[5] Heretofore no simple, straightforward single-step synthesis of oxetanes **4** had been devised or published.

Recently, Johnson and co-workers[6] reported that the sodium anion of dimethyl *N*-(*p*-toluenesulfonyl)sulfoximine (**2**)[7] acts as a nucleophilic methylene-transfer reagent with ketones. According to their general reaction method, depicted in Scheme I, 1.1 equiv of anion **2** are generated by 1.1 equiv of each sodium hydride and the parent sulfoximine[7] in dimethyl sulfoxide (DMSO in Scheme I), followed by the addition of ketone **1** (1 equiv) and stirring at room temperature (20–25 °C) overnight. Under these conditions ketones **1** are smoothly converted into epoxides **3** in good yields. As a matter of fact epoxides **3** with axial carbon–oxygen bonds are formed with a high degree of stereoselectivity in the case of cyclohexanones, both with reagent **2** and with dimethylsulfoxonium methylide in Me$_2$SO.[8e,9]

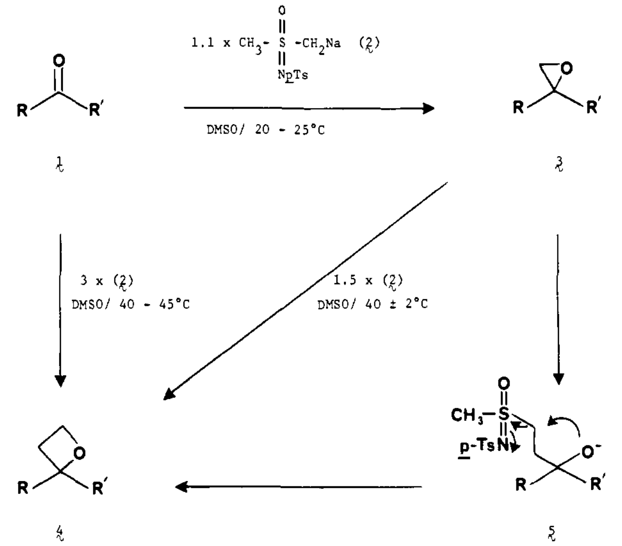
We recently had an occasion to utilize this elegant method on a hindered cyclopentanone intermediate. Estrone 3-methyl ether (**6**) was used as a model for carrying out this methylene-transfer reaction. In an effort to optimize yields, ketone **6** was added to 3 equiv of reagent **2** in Me$_2$SO and allowed to stir at 45 ± 2 °C for 20 h. After workup and examination of the infrared (IR) and nuclear magnetic resonance (NMR) spectral data of the product, it was apparent that no carbonyl group or epoxide protons were present. However, the NMR spectrum of the product did display a multiplet (overlapping triplets) at δ 4.28 (-CH$_2$O-) and the mass spectrum exhibited a parent ion at M^+/z 312 which is 28 mu greater than the starting ketone. These data, together with the combustion analysis, confirmed the fact that oxetane **6** (actually a 64:36 ratio of β:α C–O bonded diastereomers, respectively; see Table I) was the structure of the product.

Repetition of these experimental conditions with ketones **6–20** affords the respective oxetane products cleanly in 46–96% yield (see Table I). Cyclohexanones, such as 4-*tert*-butylcyclohexanone (**8**) and 3-cholestanone (**10**), afford single oxe-

Table I

	Ketone	Oxetane	Reaction Conditions time (h)	temp (°C)	Yields (%) isolated
6[5g,h]	estrone-3-methyl ether		20	45 ± 2	96
7[8b]	camphor		16	43 ± 2	59
8[9]	4-*t*-butylcyclohexanone		16	40 ± 2	69
9[8c]			20	45 ± 2	79
10[9]	3-cholestanone		20	45 ± 2	78
11[8d]	norcamphor		20	40 ± 2	46
Other Ketones Converted to Oxetanes					
12	bicyclo[3.3.1]non-9-one		20	40 ± 2	68
13[5d,e]	cyclohexanone		20	40 ± 2	47
14	cycloheptanone		20	45 ± 2	63
15	cyclooctanone		20	45 ± 2	59
16	cyclononanone		20	45 ± 2	65
17	cyclodecanone		20	45 ± 2	61
18	cyclopentadecanone		20	45 ± 2	72
19	2-undecanone		20	45 ± 2	49
20	2-tridecanone		20	45 ± 2	51

Scheme I



0002-7863/79/1501-6135$01.00/0