J. Am. Chem. Soc. **1981**, *103*, 1059-1066

to be relatively slow as it requires disruption of the interaction between water and the ligand, in addition to partial desolvation of the metal. Similarly, the dissociation process would be assisted by interaction between water molecules and the donor atoms of the ligand bridges. The deviation of the water values in Figure 4 presumably also has a common origin.

Thus, it seems likely that differences between the results in water and those in the other solvents studied may be best interpreted in terms of specific hydrogen-bonded interactions between water and the ligands rather than effects arising from the bulk structure of water. That the effect is not simply an artifact due to an inappropriate DN for H_2O is supported by the observation that a "corrected" DN which fits the linear correlation in Figure 6 is not applicable in Figure 7.

In absolute terms the formation rates are high, particularly considering the relative inflexibility of the ligands, and the fact that during the overall process of complex formation all of the solvent molecules in the immediate vicinity (inner coordination sphere) of the cations must be replaced. The rates are also relatively independent of solvent and for (2,2,2) and (2,2,1) cryptates in poorly solvating media (e.g., MeOH, EtOH, Pc) are generally close to the rates of solvent exchange in the inner coordination sphere of the cations. Substantial variations in charge densities of the cations can, however, lead to somewhat more drastic variations in rate. This is particularly apparent from a comparison of Ca^{2+} and Na^+ rates and to a lesser extent from the rates of formation of Li^+ cryptates compared with those of the other alkali metal cations. Weaver and co-workers[26] have considered the effect of charge density on cryptate formation rates in water and find even larger effects for 3+ cations. It must be remembered, however, that the total solvation energy of Ca^{2+} is some 1000 kJ mol^{-1} higher than that of Na^+ and even that of Li^+ is more than 100 kJ mol^{-1} higher than Na^+.[27] Thus even a relatively small amount of desolvation of these high charge density cations on formation of the transition state can lead to quite large energy barriers.

Finally, it is of interest to see how the results for naturally occurring macrocyclic antibiotics such as valinomycin and the macrotetralides[5,28] compare with those of the cryptands. Many of the results for these systems have been obtained in methanol, because of problems of low solubility and low complex stability in water. High complex formation rates, of the order of 10^7–10^8 $M^{-1}\ s^{-1}$, have been found by using various relaxation techniques. It is quite possible, in view of the results for the cryptands, that these high rates may be at least partially due to the poor solvating ability of methanol and that significantly lower results might be expected in water. In water, as discussed above, not only more effective cation solvation but also H-bonded interactions with the ligands cause lower formation rates in the case of cryptates. Measurements of the formation rate constants for some valinomycin complexes of alkali metal ions in methanol–water mixtures[5] suggest that similar effects may be operating for these complexes. Thus the value of k_f for the K^+ complex of valinomycin in methanol is $3.5 \times 10^7\ M^{-1}\ s^{-1}$, in 90% MeOH–$H_2O$ is $1.3 \times 10^7\ M^{-1}\ s^{-1}$, in 80% MeOH–$H_2O$ is $5.5 \times 10^6\ M^{-1}\ s^{-1}$, and in 70% MeOH–$H_2O$ is $1.3 \times 10^6\ M^{-1}\ s^{-1}$. There is a clear tendency to lower k_f values with increasing water content of the solvent.

Acknowledgment. We thank the SRC for a grant and the British Council and the National University of Mexico for financial support to J.G.-R.

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Storage of Electrons in Aqueous Solution: The Rates of Chemical Charging and Discharging the Colloidal Silver Microelectrode

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Abstract: Conductometric methods were applied to study the electron transfer from 1-hydroxy-1-methylethyl radicals, $(CH_3)_2COH$, to colloidal silver particles and the reduction of water by electrons stored on the silver particles. The charging reaction is diffusion controlled and takes place within milliseconds. The rate of the discharge reaction depends on the number of electrons stored on one silver particle. This reaction requires seconds or even minutes in solutions of pH 3.7. In the stationary state, up to 1 C of electrons (or 10^{-5} mol of electrons) could be stored per liter of solution, each silver particle carrying about 450 electrons under these conditions. The total electrical capacity of a 2.5×10^{-4} M colloidal silver solution was determined as about 1 F/L, the specific capacity of the silver particles as 43 $\mu F/cm^2$ of surface. The storage of electrons is also proven by their transfer to a compact mercury electrode in contact with the colloidal solution. Potential changes of about 0.3 V of this electrode were measured. A few properties of the microelectrode such as its absorption spectrum, its sensitivity toward oxygen, and its efficiency in combination with various stabilizers for catalyzing the reduction of water by radicals are also reported.

(1) Introduction

Colloidal silver[1-3] and colloidal gold[4-7] have recently been found to catalyze novel reactions of free radicals in aqueous solution. These reactions include the decomposition of water to yield hydrogen and the multielectron reduction of dissolved substances. The most important step in the postulated mechanism[1] is the storage of electrons on the colloidal particles as the free radicals transfer electrons to them. The stored electrons are then used to carry out the various reduction processes. Equations 1 and 2

$$m(CH_3)_2COH + Ag_n \rightarrow Ag_n^{m-} + m(CH_3)_2CO + mH^+ \tag{1}$$

$$Ag_n^{m-} + 2H_2O \rightarrow Ag_n^{(m-2)-} + H_2 + 2OH^- \tag{2}$$

describe the processes of charging colloidal silver particles by

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1-hydroxy-1-methylethyl radicals and of discharging them by water molecules (n = agglomeration number of the colloid). Reaction 2 may be regarded as an electrochemical process at a silver microelectrode charged by the chemical electron-transfer process 1.

In our previous studies, the radicals were produced by continuous γ-irradiation. The solution of the silver sol which was present at some 10^{-4} M contained 0.1 M acetone and 0.2 M 2-propanol. It is well-known from many studies in radiation chemistry that γ-irradiation produces 1-hydroxy-1-methylethyl radicals almost exclusively under these conditions. The occurrence of reaction 2 was inferred from the observed hydrogen yield and its dependence on various parameters such as the pH and the concentration of added substances. However, a number of questions was still left open such as the following ones. (1) How fast do $(CH_3)_2COH$ radicals transfer electrons to the colloidal microelectrode? Is the rate of transfer dependent on the number of electrons already having been picked up by the silver particles? (2) What is the rate of reduction of water as a function of the number of electrons on a colloidal particle? And, in connection with this question, for how long a time can electrons be stored on colloidal silver particles? (3) Electrons may always be regarded as the base form of the hydrogen atom. The question arises whether or not part of the electrons on a silver particle are converted into adsorbed hydrogen atoms H(ads) according to the equilibrium

$$\mathrm{Ag}_n^{m-} + \mathrm{H}^+ \rightleftharpoons \mathrm{Ag}_n^{(m-1)-} + \mathrm{H(ads)} \qquad (3)$$

The present pulse radiolysis study was undertaken in order to find answers to the above questions. As reactions 1 and 2 are accompanied by changes in the hydrogen ion concentration of the solution, they could be studied conductometrically. Highly sensitive pulse radiolysis equipment was required as the concentration of radicals produced in a single pulse had to be kept very low in order to avoid radical–radical deactivation before the radical–colloid reaction occurred. The radical concentration per pulse was of the order of 10^{-8} M, and the signals were averaged over several pulses. In addition to the pulse radiolysis experiments in the microseconds to seconds range, continuous irradiation experiments in the minutes range were carried out, in which the buildup of the stationary charge on the silver particles and the discharge after irradiation were observed via conductivity changes. It may also be mentioned that no changes in conductivity were observed when an acetone plus 2-propanol-containing solution was irradiated in the absence of the colloid.

(2) Experimental Section

(2.1) Preparation of the Solutions. Colloidal silver was prepared by γ-irradiation of silver perchlorate solutions which were degassed by evacuation first with a water pump and then with an oil pump. The irradiation occurred during 2 h at a dose rate of 5×10^4 rad/h as described in the previous studies.[1-3] The solutions also contained 0.1 M acetone and 0.2 M 2-propanol as well as small amounts of a stabilizer for the colloidal silver. After the irradiation, the solutions were allowed to age for 1 h.

Sodium polyvinyl sulfate (PVS-Na), polyacrylic acid (PAS), and sodium lauryl sulfate (NaLS) were tried as stabilizers. The efficiency of the colloidal metal–stabilizer system was checked by measuring the H_2 yield produced by 1-hydroxy-1-methylethyl radicals. This yield, referred to as the excess hydrogen yield, was the observed H_2 yield minus the yield measured in the absence of the catalyst. When all organic radicals transfer an electron to the silver particles, a maximum excess hydrogen yield of 3.0/100 eV arises. However, the hydrogen peroxide which is also produced by irradiation may lower this yield down to 2.2/100 eV.[1,3] As will be shown in section 3.1, sodium polyvinyl sulfate turned out to be the most efficient stabilizer. It was therefore used in all further experiments.

(2.2) Electron Microscopy. A drop of the colloidal solution was put on a commercial carbon film (S160, Agar Aids) and the aqueous solvent evaporated at 80 °C within 5 min.

The film was inserted into a Siemens electron microscope and the pictures were taken at an enlargement of 40 000. The silver particles which partly were clustered had practically spherical shape. The silver particles were identified by their refractive pattern in the electron microscope.

(2.3) Irradiation and Conductometric Techniques. Irradiations were carried out with the pulsed electron beam of a 4-MeV Van de Graaff generator. The duration of the pulses was 5, 15, and 50 ns. The irradiation vessel that contained 50 cm^3 of the solution had a side arm with two pairs of platinum electrodes (0.5 × 0.5 cm; 0.5-cm distance). One pair was irradiated at a distance of 40 cm from the exit window of the accelerator. The electron beam was wide enough as to irradiate homogeneously the solution in the electrode pair and the surroundings. The other pair of electrodes was carefully shielded. It served as reference for the conductivity measurements with an ac bridge, the frequency of which was 10^7 s^{-1}. The details of the bridge have previously been described.[8] The bridge was operated by a quartz-stabilized oscillator delivering 40 V of output with a very low noise factor.

The output signal of the bridge was amplified, digitized by a Biomation 8100 transient recorder, and processed by a PDP 11/40 computer which also controlled the triggering of the accelerator. Every other trigger signal was used to record the base line (without irradiation), which was subtracted from the recorded signals. The time range covered by this setup was from 10 μs to 10 s.

For longer times of observation, trains of pulses at a frequency between 1 and 20 cycles/s were applied for irradiation times of many minutes. The output of the ac bridge was plotted on a strip chart recorder. The absorbed dose rate of the solution was between 10^4 and some 10^5 rad/h. In some of the experiments, continuous γ-irradiation at the same dose rate was used, the results being the same.

(2.4) Potential Measurements. Irradiations were also carried out with a vessel, in which the colloidal solution was in contact with a mercury and a platinum electrode. The whole vessel was γ-irradiated at a dose rate of 10^5 rad/h. The potential between the two electrodes was measured by using a dc microvoltmeter with an inner resistance of 1 M Ω. Experiments were also carried out with solutions that did not contain the colloid. They were irradiated at a dose rate, which produced the same stationary radical concentration as in the experiments with the colloidal solutions. Negligibly small potential changes (<0.1 V) were observed under these conditions.

(2.5) Determination of Radical Concentrations and Stored Charges. In order to determine the radical concentration produced by one pulse of the electron beam, we placed 1 cm^3 of a solution of 5×10^{-3} M of tetranitromethane containing also 1 M of acetone and 2-propanol into the irradiation position of the conductivity cell. Some thousand pulses were applied, and the optical absorbance of the irradiated solution at 350 nm was measured. The anion of nitroform that is formed in tetranitromethane solution according to eq 4 absorbs here with $\epsilon = 1.4 \times 10^4$ M^{-1} cm^{-1}. The concentration of $C(NO_3)^-$ found is thus a measure of the concentration of radicals produced.[9]

$$(\mathrm{CH_3})_2\mathrm{COH} + \mathrm{C(NO_2)_4} \rightarrow \mathrm{C(NO_2)_3^-} + \mathrm{H^+} + (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{NO_2} \qquad (4)$$

The NO_2 radical produced in reaction 4 reacts with water within milliseconds.[10]

$$\mathrm{NO_2} + {}^1/_2\mathrm{H_2O} \rightarrow \mathrm{H^+} + {}^1/_2\mathrm{NO_3^-} + {}^1/_2\mathrm{NO_2^-} \qquad (5)$$

Two hydrogen ions and two anions are thus formed for each $(CH_3)_2COH$ radical. By comparing the conductivity signal of a tetranitromethane solution with that of the colloidal silver solution (taken under identical conditions, i.e., the same dose rate and the same irradiation vessel), one may calculate the concentration of hydrogen ions formed in the latter via reaction 1. This concentration is equal to the concentration of electrons stored on the silver particles. Any consumption of those electrons would lead to OH^- ions which would in turn consume H^+ ions. The stored charge on the silver particles is then $[H^+]/F$ in coulomb per liter, where F is the Faraday constant.

(3) Experimental Results

(3.1) Some Properties of Colloidal Silver. In these studies, sodium polyvinyl sulfate (PVS-Na) was used as stabilizer of the colloid. In order to study its efficiency, we measured the excess hydrogen yield produced by 1-hydroxy-1-methylethyl radicals at various concentrations of the stabilizer as earlier described.[1] The results are shown in Figure 1, where $G(H_2)$ is plotted vs. the

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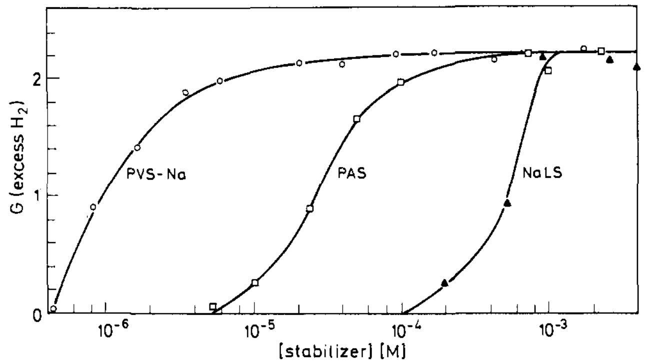

Figure 1. Excess hydrogen yield (observed yield minus 1.04/100 eV, the yield in the absence of catalyst) in the γ-irradiation of a colloidal silver solution as a function of the concentration of three stabilizers (2.5 × 10^{-4} g-atom/L of Ag, 0.1 M acetone, 0.2 M 2-propanol).

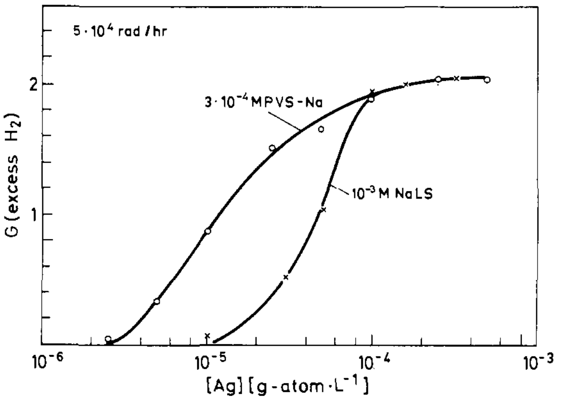

Figure 2. Excess hydrogen yield as a function of the silver concentration for solutions containing sodium polyvinyl sulfate or sodium lauryl sulfate as stabilizer.

stabilizer concentration. The figure also contains results obtained with polyacrylic acid ($\bar{M}$ = 80 000) and sodium lauryl sulfate. It can be seen that much lower concentrations of PVS-Na are required for producing a colloid of full catalytic activity.

Several other observations were made which show that the PVS-Na-stabilized colloid is much more efficient than the NaLS-stabilized colloid used in the previous studies. Figure 2 shows how the yield of excess hydrogen depended on the silver concentration. Below 10^{-4} g-atom/L, the decrease in yield was less pronounced for the colloid stabilized by PVS-Na. It was further observed that the yield of H_2 depended little on the dose rate in the range between 1 × 10^4 and 4 × 10^5 rad/h, while a significant decrease in yield had been observed for the NaLS-stabilized colloid at high dose rates.[1] The maximum absorption of the presently used colloid was at 378–380 nm, while the NaLS-stabilized colloid absorbed between 380 and 395 nm. The half-height width of the absorption band was 27 nm, while it amounted to 35–40 nm in the previous studies. All these observations indicate that the colloid produced in the presence of PVS-Na consists of smaller particles than the one stabilized by NaLS.

It is also noteworthy that the PVS-Na-stabilized colloid was very sensitive toward oxygen. Figure 3 shows the changes in the absorption band of the colloid upon standing in contact with air for various periods of time. The band became smaller and broader, and it shifted toward slightly longer wavelengths. At the same time the conductivity of the solution decreased; i.e., hydrogen ions were consumed. After the sample that had been in contact with air for 20 h was evacuated and γ-irradiated for 2 h, the high and narrow band of the colloid was reestablished. Oxygen apparently oxidizes the colloidal particles, the rate of reaction being larger for the smaller particles being present in the original size distribution. This effect made it difficult to determine the size of the particles by electron microscopy, as some contact with air during the preparation of the samples could not be avoided. The radius of the particles found by electron microscopy must therefore be expected to be too large and can only be regarded as an upper limit.

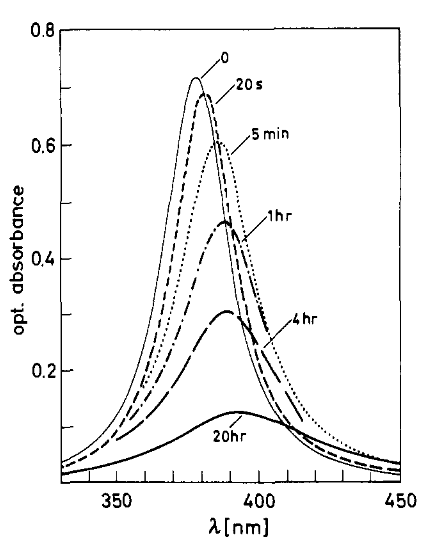

Figure 3. Absorption band of a colloidal silver solution at various times after the admission of air (2.5 × 10^{-4} g-atom/L of Ag, 1.5 × 10^{-4} M PVS-Na, 0.1 M acetone, 0.2 M 2-propanol).

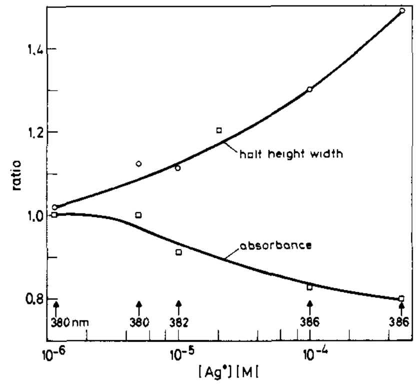

Figure 4. Absorbance, half-height width, and wavelength of the absorption band of colloidal silver as a function of the concentration of added $AgClO_4$ (the ratios of the Ag^+ containing to the Ag^+ free solution are plotted).

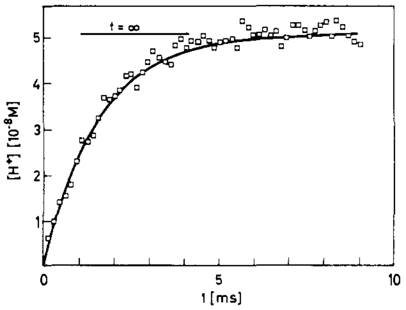

Figure 5. Buildup in H^+ concentration as a function of time (average over four pulses, each of which produced 5 × 10^{-8} M of radicals). The curve was calculated for a first-order process ($t = \infty$, assumed final conductivity; half-height time = 1.2 ms). The silver solution had been prepared by γ-irradiation of 2.5 × 10^{-4} M $AgClO_4$, 2 × 10^{-4} PVS-Na, 0.1 M acetone and 0.2 M 2-propanol for 2 h and aging for 1 h (pH 3.7).

Silver ions influence both the height and width of the absorption band of colloidal silver. These effects are illustrated by Figure 4. $AgClO_4$ was added in various concentrations to a solution of colloidal silver under the exclusion of air. The ratios of the absorbance and the width of the band in the presence and absence of Ag^+ ions are plotted vs. the Ag^+ concentration. The position of the maximum of the band is indicated by the numbers at the arrows. When a solution to which Ag^+ ions had been added was

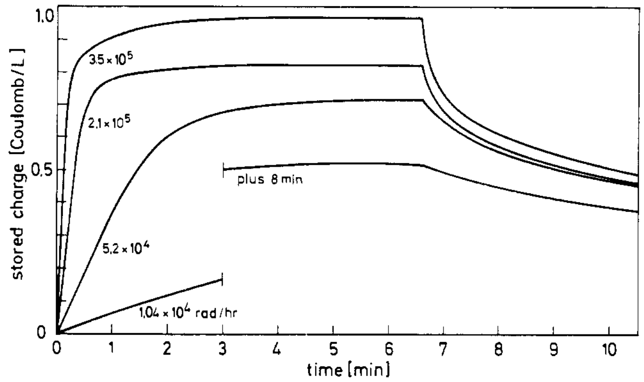

Figure 6. Stored charge in an irradiated solution of colloidal silver as a function of time. Irradiation was finished at 6.5 min with the exception of the experiment at 1.05 × 10^4 rad/h, when irradiation ended at 14.5 min.

further irradiated, the sharp 380-nm band was reestablished, its height being higher by the amount of added silver. The influence of the Ag^+ ions is explained by an adsorption of ions at the colloidal particles.

(3.2) Rate of Electron Transfer from Radicals to Colloidal Silver. In a solution containing 0.1 M acetone and 0.2 M 2-propanol, the radicals are formed within less than 10^{-8} s after application of a pulse of radiation. Figure 5 shows how the conductivity of the solution or the concentration of H^+ ions increased within milliseconds after the pulse. The solution contained the colloid at 2.5 × 10^{-4} g-atom/L and PVS-Na at 2 × 10^{-4} M. The mean particle radius of the colloid as determined by electron microscopy was 7 nm.

The points in Figure 5 are averages over four pulses, each of which produced radicals at a concentration of 5 × 10^{-8} M. The time interval between the pulses was 1 s. The curve in Figure 5 was computer calculated for a first-order process. Its shape did not change when weaker pulses that produced radical concentrations down to 5 × 10^{-9} M were used. This shows that no second-order component contributed to the increase in conductivity, i.e., that no radical–radical deactivation occurred. The half-height time of 1.2 ms can therefore be attributed to the reaction of the radicals with the colloidal particles. A dilution by a factor of 3 resulted in an increased half-height time of 3.8 ms in accordance with this conclusion. It was only at much stronger pulses (producing radical concentrations of several 10^{-7}–10^{-6} M) that the half-height time gradually became shorter.

The final conductivity signal remained constant at longer times till the end of the available time range of 10 s. It is concluded that the discharge reaction 2 occurred at much longer times. This reaction was consequently studied by using continuous irradiation techniques in the minute range, as described in section 3.3. In the pulse radiolysis experiments, reaction 1 was further investigated by using a greater number of pulses up to 64 which were applied with a frequency of 10 s^{-1}. Under these circumstances, most of the radicals transferred their electron to silver particles already carrying electrons deposited from the preceding pulses. No change in the curve of Figure 5 was observed. This result shows that the rate of electron transfer from 1-hydroxy-1-methylethyl radicals to silver particles does not depend on the number of electrons already present on the colloidal particle.

(3.3) Conductivity Measurements under Continuous Irradiation. When a solution of colloidal silver was continuously irradiated with either weak pulses of high energy electrons or γ-rays (dose rates of some 10^4–10^5 rad/h), the conductivity increased until a stationary value was reached after several minutes. This increase is explained by the charging of the silver particles via the electron-transfer reaction 1. In the stationary state the rates of reactions 1 and 2 are equal. Reaction 2 leads to a decrease in conductivity as the OH^- ions formed in this reaction rapidly react with hydrogen ions. As soon as the irradiation was stopped, the conductivity decreased. This decrease is attributed solely to reaction 2.

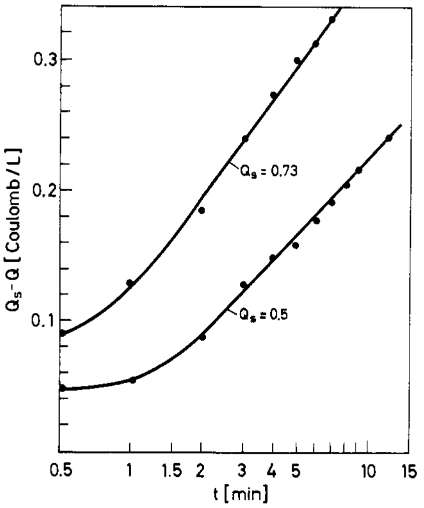

Figure 7. A plot of $Q_s - Q_{(t)}$ vs. ln *t* from the data in Figure 6 at the lower dose rates.

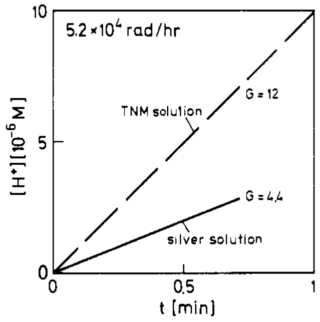

Figure 8. H^+ concentration as a function of time in the γ-irradiation of a solution of tetranitromethane and of a solution of colloidal silver.

Typical curves for the dependence of the conductivity of the solution as a function of time during and after irradiation are shown by Figure 6. Instead of plotting the conductivity on the ordinate, the stored charge in 1 L of solution is given. It was calculated as described in section 2.5. As expected, the charge Q_s stored in the stationary state became larger with increasing dose rate, i.e., with increasing rate of charging the storage system. Stored charges close to 1 C/L of solution were reached in the stationary state which corresponded to a concentration of stored electrons of about 10^{-5} M. The decay of the charge after irradiation became slower with time. This decay could not be described by first- or second-order kinetics. Figure 7 shows a diagram where the difference $Q_s - Q_{(t)}$ is plotted vs. the logarithm of the time *t* for two Q_s values. It can be seen that a linear relationship of the type

$$Q_{(t)} = Q_s - a \ln t \qquad (6)$$

exists for longer times (*a* = constant). At shorter times, $Q_s - Q_{(t)}$ is larger than expected from this relation.

Because of the logarithmic dependence, the storage of electrons on the colloidal particles at concentrations of micromoles per liter for relatively long times is possible. The low rate of the discharge could also be recognized by a simple visual observation. The colloidal solutions which were under vacuum developed gas bubbles of hydrogen even at 10 min after the irradiation.

Figure 8 shows the increase in the hydrogen ion concentration for a tetranitromethane solution irradiated for short times. H^+ ions are formed here with a radiation chemical yield of 12/100 eV. Furthermore, the figure shows the corresponding increase for a colloidal silver solution irradiated at the same dose rate. The yield is 4.4/100 eV, i.e., smaller than the yield of 6.0 with which 1-hydroxy-1-methylethyl radicals are produced. This is understood in terms of the molecular hydrogen peroxide that is produced by radiation with G = 0.8. H_2O_2 consumes two electrons and two

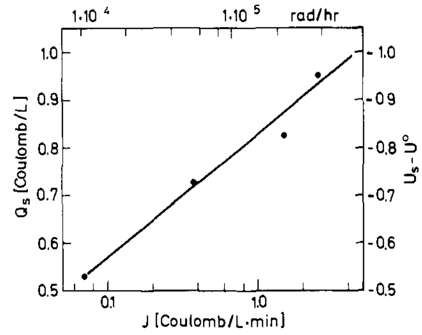

Figure 9. Semilogarithmic plot of the stationary charge Q_s (from the data in Figure 6) vs. the rate J of charge transfer (lower abscissa) or dose rate (upper abscissa). The ordinate scale on the right side gives the calculated potential difference $U - U^0$ (see section 4.3).

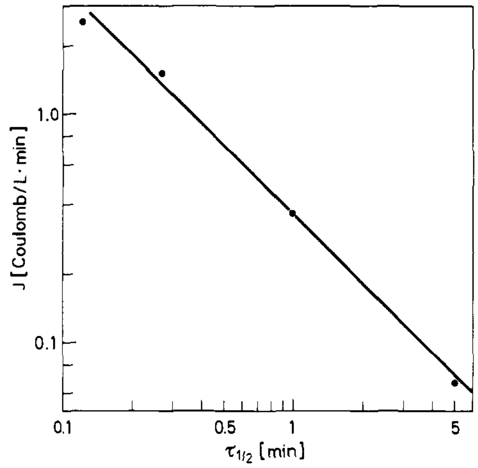

Figure 10. Relation between the time required for the storage of half the charge Q_s and rate of charging.

protons in its reaction with stored electrons, thus diminishing the H^+ yield by 1.6/100 eV.

Q_s, the stationary charge in 1 L of solution, is plotted in Figure 9 as a function of the dose rate or J, the rate of charge transfer to the colloidal particles in C/(L min). The straight line obtained in this semilogarithmic plot indicates a relation of the form of eq 7, where b and c are constants.

$$Q_s = b + c \ln J \qquad (7)$$

The description of the buildup of stored charges during irradiation is finally completed by Figure 10, where $\tau_{1/2}$, the time required to store $Q_s/2$ charges, is plotted on a double log scale vs. the rate J. The linear relation obtained indicates that $\tau_{1/2}$ is proportional to J^{-1}.

H^+ ions are known to facilitate the reduction of water. Figure 11 shows the effect of the H^+ concentration on the Q vs. t curves during and after irradiation. As it was expected, the stationary charge Q_s decreased with increasing H^+ concentration, i.e., with increasing rate of the discharge reaction. As can be recognized from the straight line obtained in the semilogarithmic plot of Figure 12, a relation of the type

$$Q_s = d - f \ln\,[H^+] \qquad (8)$$

describes the quantitative dependence of Q_s on $[H^+]$ (d and f = constants).

(3.4) Potential Measurements under Continuous Irradiation. γ-Irradiation leads to a change in the potential of a mercury electrode in contact with the colloidal solution. Figure 13 shows how the potential of this electrode becomes more negative as a function of the time of irradiation. A stationary potential change of about −0.3 V was reached after several minutes. After irradiation, the potential slowly became more positive again.

These effects are rationalized in terms of the transfer of electrons from the charged silver particles to the mercury electrode.

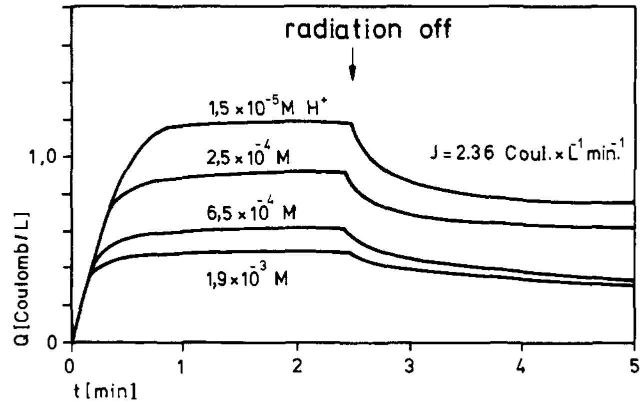

Figure 11. Stored charge as a function of time at various H^+ concentrations of the solution (2.5 × 10^{-4} M Ag, 0.1 M acetone, 0.2 M 2-propanol).

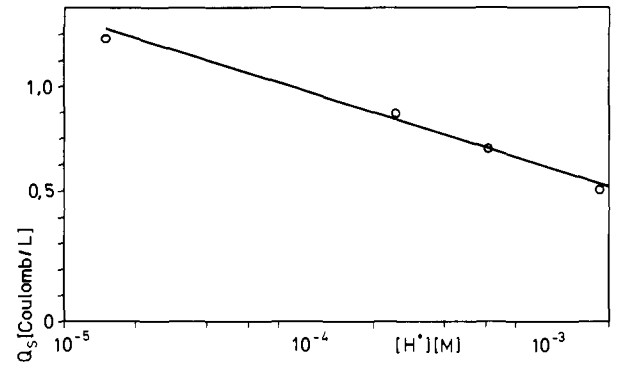

Figure 12. Stationary charge Q_s as a function of the H^+ concentration.

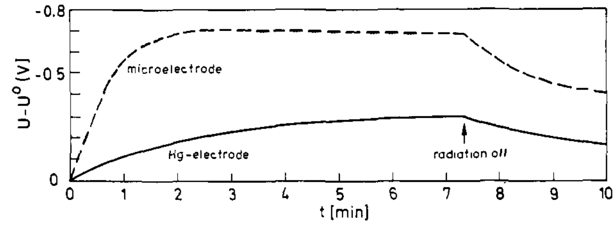

Figure 13. Potential increase as a function of time: full line, measured for a mercury electrode in the colloidal solution; dashed line, calculated for the microelectrode. The composition of the solution was the same as in the experiment of Figure 11, plus 5 × 10^{-3} M sodium perchlorate. The solution was irradiated under an atmosphere of pure argon.

Electron transfer will also occur on the platinum counter electrode. However, the fate of the transferred electrons will be different on these two electrodes because of their different overpotentials for the evolution of hydrogen. The electrons on the platinum electrode will rapidly be used to produce hydrogen, the result being a more or less constant potential of this electrode. The electrons on the mercury electrode will remain there and build up a more negative potential.

(4) Discussion

(4.1) Kinetics of Charging the Microelectrode. Electron transfer from organic radicals to a compact metal electrode in solution has been observed in polarographic studies for short-lived free radicals.[11] It has been found that 1-hydroxyalkyl radicals may react in a two-step mechanism: The radical is first adsorbed and then oxidized. These two steps were observed at relatively high negative potentials of the mercury electrode, i.e., under conditions where the second step was retarded. The possibility of a two-step mechanism in the reaction of 1-hydroxy-1-methylethyl radicals with colloidal silver has also been discussed.[1]

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[11] Henglein, A. *Electroanal. Chem.* **1976**, *9*, 163–244.

$$\text{adsorption} \quad (CH_3)_2COH + Ag_n \rightarrow (CH_3)_2COH\text{–}Ag_n \quad (9)$$

$$\text{electron transfer} \quad (CH_3)_2COH\text{–}Ag_n \rightarrow (CH_3)_2CO + H^+ + Ag_n^- \quad (10)$$

If the time required for the electron-transfer step was comparable to the time of adsorption, a pulse radiolysis experiment would yield a sigmoidal curve for the increase in conductivity with time and the sigmoidal character of the curve would become more pronounced with increasing concentration of the colloidal particles. On the other hand, if the adsorption step was rate determining, an exponential curve would be expected and the half-height time of the rise should be proportional to the inverse concentration of the colloid.

The experiments in section 3.2 prove that the latter conditions are fulfilled. It can thus be said that the time of the electron-transfer step 10 is much shorter than the time for the adsorption of the radical. Reaction 10 certainly becomes slower with increasing number of electrons on a silver particle (picked up in the preceding pulses). Our finding of a constant overall reaction rate shows that reaction 10 is still not rate determining even when the silver particles carry negative charges. This seems understandable in terms of the high negative standard reduction potential of −1.5 V of the 1-hydroxy-1-methylethyl radical.[12] It provides sufficient driving force to make the transfer reaction fast even at a cathodically charged microelectrode.

These conclusions make one suspect that the reaction between $(CH_3)_2COH$ radicals and colloidal silver particles occurs at a diffusion-controlled rate. Smoluchowski's equation allows one to calculate the relation between the rate of a diffusion-controlled reaction and the radius of the colloidal particles at a given overall concentration of the colloid. The rate of reaction is

$$k_d[Ag_n] = (\ln 2)/\tau \quad (11)$$

(τ = observed half-height time of the exponential increase). k_d, the diffusion-controlled rate constant for encounters between radicals and colloidal particles, is

$$k_d = 4\pi(6.03 \times 10^{20})DR \quad (12)$$

(in mol/L), where D is the diffusion coefficient of the radical and R the radius of the colloidal particles. The concentration of the colloidal silver particles is

$$[Ag_n] = C_0/n \quad (13)$$

where C_0 is the overall concentration in g-atom/L and n their mean agglomeration number. The latter is connected to the radius R by the relation

$$n = (245 \times 10^{21})R^3 \quad (14)$$

if the particles are assumed to be spherical.[1] Using $D = 10^{-5}$ cm^2/s and $C_0 = 2.5 \times 10^{-4}$ g-atom/L, one obtains the relation

$$R = 1.05 \times 10^{-5}\sqrt{\tau} \quad (15)$$

We may now calculate τ by using the radius of 7×10^{-7} cm found by electron microscopy. The time of 4.4 ms obtained is about 4 times longer than the observed time of 1.2 ms (Figure 5). This discrepancy is probably due to the changes in the size of the colloidal particles during the preparation of the samples for electron microscopy as pointed out in section 3.1. It seems safer to calculate an upper radius of the colloidal particles from the observed time τ. $R = 3.6 \times 10^{-7}$ cm is obtained in this way. With this value of R, an agglomeration number n = 11 430 is calculated. The concentration $[Ag_n]$ of the silver particles in the experiments of Figures 5 and 6 is calculated as 2.19×10^{-8} M, the surface of one colloidal particle as 1.63×10^4 Å^2, and the total surface of the colloidal particles in 1 L of solution as 2.2×10^4 cm^2.

(4.2) The Conversion of Stored Electrons into Adsorbed Hydrogen Atoms. The yield of hydrogen ions in the irradiation of colloidal silver solutions at short times (where the stored charge was much lower than Q_s) was found as 4.4/100 eV (Figure 8). As has been pointed out in section 3.3, this yield corresponds to the one expected, assuming that no transferred electrons were converted into hydrogen atoms. It can thus be said that the forward reaction of the equilibrium of eq 3 is a very slow process. Adsorbed hydrogen atoms have been postulated as intermediates of the reduction of water and of N_2O and NO_3^- at cathodically charged silver particles.[1,3] This postulate is still valid. One may, however, question, whether the equilibrium of eq 3 is fully established in those reactions. If a hydrogen atom reacts faster with a molecule in the solution than according to H(ads) → $H^+ + e_{Ag_n}^-$, the equilibrium will not be established.

(4.3) Kinetics of the Discharge of the Microelectrode. The case may first be considered in which the colloidal particles have acquired a total charge Q_0 measured in C/L of solution. No further charging shall occur during the discharge process of eq 2. This reaction may be regarded as a cathodic electrode reaction with a rate constant

$$k = k_{0e}^{-(\alpha F/RT)(U-U^0)} \quad (16)$$

where F is Faraday's equivalent, α is the transfer coefficient of reaction 2 ($\alpha < 1$), and U^0 and U are the potentials of the colloidal particles before and after charging with electrons. The potentials refer to a zero potential in the bulk of the solution. The constant k_0 shall refer to 1 cm^2 of surface of the colloidal particles. Its dimension is in cm^{-2} s^{-1}, if the rate of reaction 2 is expressed as

$$\frac{d[H_2]}{dt} = \frac{-dQ_{(t)}}{dt}\frac{1}{nF} = A[H_2O]k \quad (17)$$

where $n = 2$ is the number of electrons transferred in one elementary process. A is the total surface of the colloidal particles in 1 L of solution, and $Q_{(t)}$ is the charge per liter at time t. The potential difference $U - U^0$ caused by the charge Q is

$$U - U^0 = -Q/C \quad (18)$$

where C is the electrical capacity of the colloidal particles in 1 L of solution. The differential rate law may now be written as

$$\frac{-dQ}{dt} = nFA[H_2O]k_0e^{(\alpha F/RTC)Q} \quad (19)$$

and its integrated form is

$$e^{-(\alpha F/RTC)Q} - e^{-(\alpha F/RTC)Q_0} = \frac{RTC}{\alpha}nk_0A[H_2O]t \quad (20)$$

At longer times, eq 20 can be approximated by neglecting the second term on the left side

$$Q = \frac{RTC}{\alpha Fn}\left(\ln\frac{\alpha}{RTCk_0A[H_2O]} - \ln t\right) \quad (21)$$

One recognizes from eq 19 that the rate constant decreases with decreasing number of particles of one reactant (i.e., of the electrons) and from eq 21 that the rate of reaction decreases more rapidly with time than that of any reaction of higher order in homogeneous solution. The logarithmic time dependence found experimentally at longer times is well explained (compare eq 6 and 21).

The continuous irradiation experiments may now be dealt with. A stationary charge Q_s is acquired by the colloidal particles at sufficiently long irradiation times. In the stationary state, the discharge rate $-dQ/dt$ is equal to the rate J (in C/L and unit time) of charge transfer from the radicals to the colloidal particles. Under these conditions, a stationary charge

$$Q_s = \frac{RTC}{\alpha F}\ln J - \frac{RTC}{\alpha F}\ln k_0nFA[H_2O] \quad (22)$$

is obtained from eq 19, which explains the dependence of Q_s on J according to eq 7. If it is assumed that the rate k_0 is proportional to the concentration of H^+ ions, eq 22 will also be able to rationalize the experimentally found relation of eq 8. The slope of the Q_s vs. ln J curve is

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[12] Butler, J.; Henglein, A. *Radiat. Phys. Chem.* **1980**, *15*, 603–612.

$$s = RTC/\alpha F \qquad (23)$$

The growth of Q with time until Q_s is reached is described by the differential equation

$$\frac{dQ}{dt} = J - k_0 nFA[H_2O]e^{(\alpha F/RTC)Q} \qquad (24)$$

or its integrated form

$$t = \frac{1}{J}\left[Q - \frac{RTC}{\alpha F}\ln\left(J + nFA(H_2O)k_0e^{(\alpha F/RTC)Q}\right) + \frac{\alpha F}{RTC}\ln\left(J + nFA[H_2O]k_0\right)\right] \qquad (25)$$

This equation can be approximated by

$$t = Q/J \qquad (26)$$

for small values of Q. As Q_s was relatively little dependent on J, an almost linear relationship between $\tau_{1/2}$ and J^{-1} could be expected where $\tau_{1/2}$ is the time required for storing a charge of $Q_s/2$. The results in Figure 10 are explained this way.

The slope of the straight line in Figure 9 is obtained as 0.113 C/L. The transfer coefficient α of the cathodic reduction of water is close to 0.5.[13] The capacity of the colloidal silver microelectrode in the experiment of Figure 9 is thus obtained from eq 23 as

$$C = \frac{s\alpha F}{RT} = 0.94 \text{ F/L} \qquad (27)$$

The potential difference $U - U^0$ can now be calculated as

$$U - U^0 = -Q/0.94 \qquad (28)$$

For $Q = Q_s$, one calculates potential differences between about −0.5 and −1.0 V for the range of the Q_s values in Figure 9. $U_s - U^0$ is plotted on the right ordinate scale of this figure. Note that this potential difference is not identical with the standard redox potential of the electrons on the silver electrode. The latter has been determined by chemical experiments as −0.63 V[2,3] under conditions where the dose rate was 5 × 10^4 rad/h. $U_s - U^0$ is about −0.77 V under these conditions as may be read from Figure 9. It thus seems that the potential U^0 of the uncharged silver particles is close to +0.1 V on the standard redox potential scale. This finding is in agreement with recent observations about the electron exchange between uncharged colloidal silver particles and various free radicals and stable electron donors or acceptors.[14]

The above quantities, i.e., Q, C, and U, are macroscopic ones that characterize the colloidal silver microelectrode as a whole. We may now proceed to a calculation of the microscopic values for single colloidal particles using the properties of the latter as given in the last paragraph of section 4.1.

The specific capacity of the silver particles is obtained as

$$C_{spec} = C/A = 43\ \mu\text{F cm}^{-2} \qquad (29)$$

Double-layer capacities of this order of magnitude have often been observed for compact metal electrodes.[15] We can thus draw the conclusion that the colloidal silver microelectrode behaves like a macroscopic electrode.

The number of electrons residing on one colloidal particle is

$$N_e = \frac{Q}{F[Ag_n]} \qquad (30)$$

Using $[Ag_n] = 2.19 \times 10^{-8}$ M, one calculates $N_e = 450$ for the highest Q_s value of 0.95 C/L obtained in the experiments of Figure 9 and $N_e = 250$ for the lowest Q_s value of 0.53 C/L. By dividing the square area of the surface of one colloidal particle, 1.63 × 10^4 Å^2, by N_e, one obtains the respective areas of 36 and 65 Å^2 available for one electron on the surface of the silver particles. The constant k_0 is finally calculated from the data in Figure 9 as 4.6 × 10^{-17} cm^{-2} s^{-1} at $[H^+] = 2.5 \times 10^{-4}$ M.

From the decay curves in Figure 6 one can recognize that about 300 electrons can readily survive on one silver particle for at least 1 min, time enough to use them for a chemical experiment after the irradiation has ceased.

(4.4) The Radiation-Driven Galvanic Silver Cell. The maximum potential between the mercury and the platinum electrode in the experiment of Figure 13 may be estimated as follows: at the dose rate of 1 × 10^5 rad/h, the potential difference $U_s - U^0$ in the stationary state is 0.8 V (Figure 9). As U^0 is about 0.1 V, U_s = −0.7 V is obtained for the mercury electrode on the standard potential scale. The potential of the platinum electrode will be the standard potential for the decomposition of water corrected by a small overpotential of maybe 0.1 V. The pH of the solution in Figure 13 was 3.7. During irradiation, the Pt electrode was surrounded by small hydrogen bubbles. Under these circumstances, the potential for the evolution of hydrogen was −0.22 V. With an overpotential of 0.1 V, a potential of −0.3 V of the Pt electrode is calculated. The maximum potential of the Hg electrode that could be expected under these conditions is −0.7 + 0.3 = −0.4 V. The potential of about −0.3 V found in the experiments of Figure 13 is only a little smaller.

The dashed curve in Figure 13 describes the time dependence of the potential $U - U^0$ of the colloidal microelectrode. It was calculated from the conductivity data, i.e., the Q vs. t curve, as described in section 4.3. A comparison with the potential of the mercury electrode (full line in Figure 13) shows that the latter reached its stationary potential much more slowly than the microelectrode. Furthermore, the decay of the potential after irradiation did not show the typical ln t dependence but was of exponential shape. These effects are explained by a long characteristic time for the charging and discharging of the outer electrode system. This time is determined by the capacity of the mercury electrode and the high ohmic resistance of the circuit.

(5) Final Conclusions

The results of the present conductometric investigations complete a picture that had already been sketched from the chemical product analysis in the previous studies: colloidal silver behaves electrochemically like a compact electrode. Electrons can be transferred to it, be stored, and be further transferred to acceptors. A new type of electrochemical investigation now becomes possible, in which the powerful methods of fast kinetics of reactions in homogeneous solution can be applied. Furthermore, the products are formed in quantities large enough for chemical analysis, while many electrochemical studies are based only on the measurement of currents. The rate of reaction at a compact electrode is often limited by the buildup of a diffusion layer; this restriction obviously does not occur when a colloidal microelectrode is used.

On first sight, the storage of electrons on silver particles for a relatively long time seems surprising. However, it is known from electrochemical potential jump experiments[16] that the formation of adsorbed hydrogen atoms according to eq 3 is rather slow at a silver electrode. In the cases of some other electrode materials such as gold and platinum, this reaction is much faster. Similar observations on the hydrogen evolution at colloidal particles of these metals are being reported elsewhere.[7]

The use of microelectrodes for the storage of electrons and subsequent pairwise transfer to acceptors should be advantageous in studies of redox processes where a good yield with respect to the initiating radiation or light is desired. In pairwise electron transfer at an interface, the formation of energy-rich intermediates can be avoided in contrast to sequential one-electron transfers in solution. Storage systems for electrons are for example of interest in solar photochemistry.[17] Suspensions of small particles of semiconductors which absorb light have recently been used to

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initiate chemical reactions in solution.[18] While the present studies do not overlap with these experiments, they complement them in a wider frame of microelectrode chemistry in solution.

Colloidal metals are known to catalyze the reduction of various organic compounds by molecular hydrogen.[19] The present studies may contribute to a more detailed knowledge of the mechanism of such reduction processes. In our experiments, electrons are transferred from a donor to the colloid, transformed into adsorbed hydrogen atoms (eq 3), molecular hydrogen being the final product. A catalyzed reduction by hydrogen may proceed via the same elementary reactions in the opposite direction. H_2 is adsorbed at the colloid, dissociated into adsorbed atoms, which are in equilibrium with electrons on the colloid. The electrons are finally transferred to the substrate.

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The Conformations and Energetics of Simple Ylids

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Abstract: The electronic structures of the simplest ylids of nitrogen, oxygen, phosphorus, and sulfur have been determined from ab initio molecular orbital theory at the Hartree–Fock–SCF level. The calculations were carried out by using basis sets of double-ζ quality with polarization functions added to the heavy atoms and s and p diffuse functions added to carbon. Full-geometry optimization was performed by using both point-wise searches and gradient methods. Rotation barriers about the X–S bond were determined to be 2.3, 5.6, 0.2, and 21.2 kcal/mol for X = N, O, P, and S, respectively. Energies for the internal proton-transfer reaction to form the ylid from its most stable isomer were determined to be 68.7, 86.5, 57.8, and 81.7 kcal/mol for X = N, O, P, and S, respectively. Simple physical arguments for these values are presented. The charge distributions of the ylids are also discussed.

Introduction

Ylids are extremely useful synthetic intermediates.[2] Although much is known about the details of the chemistry of these species, little is known about their electronic[3] and molecular[4] structure and thermodynamic properties. For the simplest ylids, with only hydrogens as substituents, an unequivocal molecular structure is available only for the phosphorus ylid.[3b,d,e] In order to provide quantitative information about the molecular structure, relative energetics, and conformational preferences of the simplest ylids of N, O, P, and S (**1**–**4**), we have examined the electronic structure of these compounds by using ab initio molecular orbital theory.

All calculations were done by using the program HONDO (version 5) with contracted Gaussian orbitals.[5] The basis sets were of double-ζ quality with polarization functions added to the heavy atoms.[6] Since the methylene group is nominally a carbanion, an additional set of diffuse s and p functions were added to the carbon basis set to allow for a proper description of anionic character at this center.[7] Geometry optimization was carried out for two conformations of each of the four ylids studied by using both point-wise searches and gradient methods.[8] Both types of

Table I. Dipole Moments and Ionization Potentials for Nonzwitterionic Isomers

molecule	μ^a	$\mu(\text{exptl})^{a,b}$	IP^c	$\text{IP(exptl)}^{c,d}$
CH_3NH_2	1.63	1.31	10.53	8.97
CH_3OH	2.01	1.69	12.22	10.83
CH_3PH_2	1.16	1.10	9.81	9.72
CH_3SH	1.79	1.53	9.64	9.44

[a] Dipole moment in Debye. [b] Experimental value.[11] [c] Ionization potential in eV. [d] Experimental value.[12]

Table II. Geometry-Optimized Parameters for the Ylids **1a**–**4a**

parameter[a]	N	O	P	S
$r(\text{C-S})^{b,c}$	1.591	1.870	1.668	1.646
	(1.538)	(1.587)	(1.762)	(1.801)
θ(HCH)	106.6	106.2	120.4	121.8
	(103.6)	(96.7)	(109.2)	(117.7)
θ(HCX)	101.0	95.1	119.2	119.2
θ(HXH)	107.5	110.2	99.8	93.9
	(109.5)[d]	(120.0)	(109.5)[d]	(105.4)

[a] Bond lengths in Å and bond angles in deg. [b] Values in parentheses are the values taken from ref 14. [c] The C–X bond lengths for the nonzwitterionic isomers are, X = N, 1.474; O, 1.427; P, 1.863; and S, 1.819. [d] Constrained values in parentheses from ref 14.

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(7) The diffuse carbon functions are ζ_s : 0.04548 and ζ_p = 0.034[5a] The basis sets are summarized as follows: H, (4)/[2]; C, (10,6,1)/[4,3,1]; N and O, (9,5,1)/[3,2,1]; P and S, (11,7,1)/[6,4,1].

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