mensen reduction[12] of **6** and **7** to 4β-methyl-4α-carbomethoxycholestane (**8**), mp 95–97° (CH_3 on C-10: δ 0.90), and 4α-methyl-4β-carbomethoxycholestane (**9**), mp 79–80° (CH_3 on C-10: δ 0.68), respectively, and the demonstration that **9** was inert under basic hydrolysis conditions which sufficed to saponify **8**.[13]

Keto esters **5–7** were labeled by exchange with acidic tritium oxide in tetrahydrofuran[14] and then were reduced with lithium aluminum hydride to the desired diols **10** (mp 211–213°), **11** (mp 219–220°), and **12** (mp 209–210°), respectively.[15] Labeled sterols **1**, **3**, and **4** were prepared from their corresponding ketones by the same exchange–reduction sequence.

The results of incubations of these various labeled sterols are given in Table I. The most striking observation is that **11** is metabolized, but its 4β-hydroxymethyl epimer **12** is not. This result supports the involvement of a 4α-hydroxymethyl-4β-methyl sterol in cholesterol biosynthesis. Furthermore, the metabolism of **10** to cholestanol suggests that an analogous diol is an intermediate in the removal of the second C-4 methyl group from lanosterol.

Table I

Substrate[a]	% conversion to cholestanol
Dihydrolanosterol (**3**)	55.3 (cholesterol)
4,4-Dimethylcholestanol (**1**)	4.9
4,4,14α-Trimethylcholestanol (**4**)	0.0
4β-Methyl-4α-hydroxymethylcholestanol (**11**)	25.5 (+26.4% **13**)
4α-Methyl-4β-hydroxymethylcholestanol (**12**)	0.0
4α-Hydroxymethylcholestanol (**10**)	36.7

[a] Each substrate (46.5 nmol) was incubated aerobically with 4 ml of rat liver homogenate (N. L. R. Bucher and K. McGarrahan, *J. Biol. Chem.*, **222**, 1 (1956)). Products were isolated by saponification and extraction with ether. [^{3}H]Cholestanol and [^{3}H]4α-methylcholestanol (**13**) (F. Sondheimer and Y. Mazur, *J. Amer. Chem. Soc.*, **80**, 5220 (1958)) were characterized by (a) tlc mobility, (b) glpc retention time, (c) cocrystallization as the free sterol and as the acetate with authentic materials, and (d) demonstrated resistance to peracid treatment.

The reason why the results of this study are in apparent disagreement with those of Gaylor and Delwiche[3] is not obvious. These authors reported that lanosterol biosynthesized from [2-^{14}C]mevalonate yielded a 4-monomethyl sterol without loss of $^{14}CO_2$, whereas further metabolism of the monomethyl material to cholesterol released 1 equiv of $^{14}CO_2$. These findings were interpreted as indicating initial attack on the 4β-methyl group, since the 4α-methyl group has been found to be labeled with ^{14}C in all cases[16] of cyclic terpenoid natural products (soyasapogenol, gibberellic acid, and rosenonolactone) where the labeling pattern (from [2-^{14}C]mevalonate precursor) at C-4 has been determined. As an explanation for our discrepant results we have considered the possibility that Gaylor and Delwiche's reasonable assumption of labeling in the 4α-methyl group of lanosterol may have been incorrect. However, on the basis of a separate study[17] this explanation can be discounted. We cannot at present exclude an alternative possibility that the natural Δ^7 and Δ^8 substrates and the saturated substrates used in the present work are attacked by different enzymes, but this seems highly unlikely, particularly in view of the observed mutual inhibition of the metabolism of the natural and unnatural substrates. Further work is in progress in our laboratories that should clarify the situation.

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K. B. Sharpless, T. E. Snyder
Department of Chemistry, Stanford University
Stanford, California 94305

T. A. Spencer,[18] K. K. Maheshwari, Gabriele Guhn
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

R. B. Clayton
Department of Psychiatry, Stanford University School of Medicine
Stanford, California 94305

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Spatial Distribution of Trapped Electrons in Alkaline Ice Produced by Photoionization

Sir:

The detection and study of trapped electrons in γ-irradiated and photoionized ices[1] and organic solids[2,3] has aroused much current chemical interest. The spatial distribution of the trapped electrons and the separation distance between positive ions and electrons is an important but only partially solved problem. Paramagnetic relaxation experiments can give much information about the spatial distributions of trapped species in frozen solutions. We have previously obtained results demonstrating the existence and approximate size of the spatial inhomogeneities associated with trapped electrons which were generated by γ rays in alkaline ices.[4,5] We report here the paramagnetic relaxation characteristics of trapped electrons in alkaline ice produced by photoionization, and contrast the different spatial distributions produced by γ irradiation and photoionization.

Ferrocyanide ion is known to be easily ionized by ultraviolet light at 254 nm, and the trapped electrons can be detected in 8 *M* NaOH at 77°K.[6] Reagent grade

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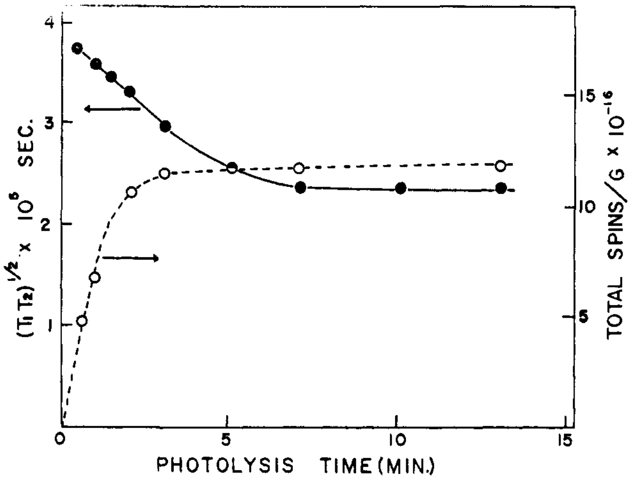

Figure 1. Characteristic relaxation time, $(T_1T_2)^{1/2}$, and spin concentration of e_t^- at 77°K in photoionized 10 *M* NaOH + 5 × 10^{-3} *M* $K_4Fe(CN)_6$.

potassium ferrocyanide (5 × 10^{-3} *M*) was dissolved in 10.0 *M* NaOH. Spherical samples were prepared as described previously.[4,5] Photoionization was carried out at 77°K by irradiating the samples at 254 nm in an epr dewar placed in a Rayonet photochemical reactor. Slow-passage progressive power saturation measurements were made at 77°K as described previously.[5]

We confirmed that the only observable, trapped paramagnetic species were electrons. The line width is 15 G between points of maximum slope. The epr line-shape parameter[5,7] is independent of photolysis time and averages 2.2. Thus we conclude that the line shape is essentially gaussian and that the saturation curves are due to inhomogeneous broadening. The most important results are the dependency of $(T_1T_2)^{1/2}$ on photolysis time. T_1 denotes the spin-lattice relaxation time and T_2 denotes the spin–spin relaxation time. $(T_1T_2)^{1/2}$ was calculated by Portis' and Castner's theoretical treatments for inhomogeneous lines.[5] The Portis $(T_1T_2)^{1/2}$ values are more complete and are plotted in Figure 1 together with the trapped electron yields. The number of trapped spins was measured by comparison with e_t^- in γ-irradiated 10 *M* NaOH at 77°K and using $G(e_t^-) = 2.1$.[1] $(T_1T_2)^{1/2}$ decreases while spin concentrations increase; at longer photolysis time both remain constant. The plateau in the spin concentration is partially caused by photobleaching of trapped electrons by visible light which is emitted from the mercury lamps. The plateau concentration corresponds to ionization of 5% of the ferrocyanide ions.

The most reasonable explanation for the observed behavior of $(T_1T_2)^{1/2}$ with photolysis time is that the electrons generated by photoionization are trapped with spatial uniformity in the alkaline ice matrix. For a uniform distribution of trapped electrons, the average distance between them decreases with increasing spin concentration and the spin–spin interactions become stronger, consequently reducing the spin–spin relaxation time, T_2. A uniform distribution is expected since the ferrocyanide ions are originally distributed uniformly in the matrix, and thus the mobile electrons will be generated uniformly. Once the spin concentration reaches steady state, the average interspin distance is expected to be constant, and thus $(T_1T_2)^{1/2}$ remains constant.

The photolysis results contrast strikingly with analogous paramagnetic relaxation results on trapped electrons generated by γ irradiation in the same matrix. In the γ-irradiated matrix $(T_1T_2)^{1/2}$ remains constant with dose to about 4 Mrads before it decreases.[5] This dose dependence of $(T_1T_2)^{1/2}$ was interpreted as due to nonuniform trapping. This different dose dependence found by photolysis strongly supports this contention.

$(T_1T_2)^{1/2}$ is 3.8 × 10^{-5} sec at short photolysis times in a photoionized matrix compared to 1.8 × 10^{-5} sec at short radiolysis times (0.4 Mrad) in a γ-irradiated matrix. Both values were measured in the present work under identical experimental conditions in order to make an accurate comparison. The difference is due mainly to changes in T_2; T_2 is smaller in the γ-irradiated matrix because the local spin concentration is greater. Further comparative studies on both T_2 and T_1 are in progress.

The paramagnetic relaxation of trapped hydrogen atoms in γ-irradiated, acid and neutral ices has also been previously reported.[8] $(T_1T_2)^{1/2}$ for H_t decreases with radiation dose at low doses and shows identical behavior with e_t^- produced by photoionization. This was interpreted as indicating a uniform spatial distribution of trapped hydrogen atoms which distribution was consistent with the H_t formation mechanism. The photolysis results confirm this interpretation and give over-all support to the validity of using the dose dependence of $(T_1T_2)^{1/2}$ as a method for study of the spatial distribution of trapped paramagnetic species.

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Hirotomo Hase, Larry Kevan
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044
Received August 29, 1968

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Trifluoroacetolysis of Neopentyl *p*-Toluenesulfonate. Evidence for Concerted Ionization and Rearrangement[1]

Sir:

Trifluoroacetolysis of 2-phenylethyl *p*-toluenesulfonate has recently been utilized to provide strong evidence for phenyl participation and for a phenonium ion intermediate.[2] We should like to report that solvolysis of neopentyl *p*-toluenesulfonate in this medium of low nucleophilicity and high ionizing power[3] provides evidence for methyl participation.

The neopentyl *p*-toluenesulfonate used was recrystallized material made from neopentyl alcohol by the procedure of Tipson.[4] The solvent purification and

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