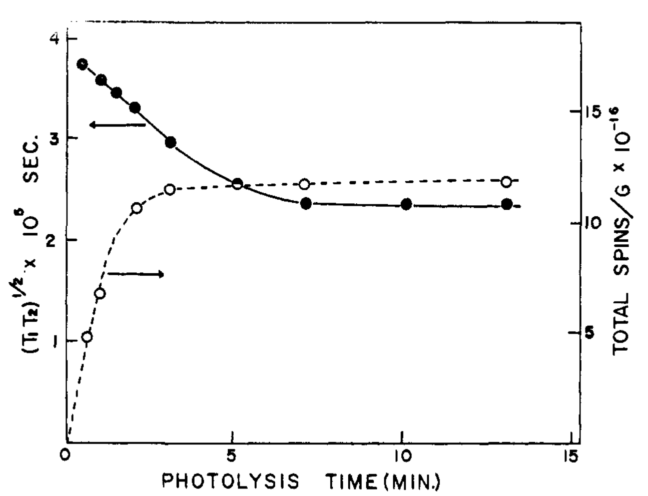

Figure 1. Characteristic relaxation time, $(T_1T_2)^{1/2}$, and spin concentration of e_t^- at 77°K in photoionized 10 *M* NaOH + 5 × 10^{-3} *M* $K_4Fe(CN)_6$.

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.

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission and the Air Force Rocket Propulsion Laboratory. This is AEC Document No. COO-1528-26.

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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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(1) This work was supported in part by National Science Foundation Grant GP-3890.

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(3) For leading references see: P. E. Peterson, R. J. Bopp, D. M. Cherli, E. L. Curran, D. E. Dillard, and R. S. Kamat, *ibid.*, **89**, 5902 (1967); and P. E. Peterson and J. F. Coffey, *Tetrahedron Letters*, 3131 (1968).

(4) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

composition were similar to those used by Peterson as was the uv spectrophotometric procedure for rate determinations.[5] The buffered trifluoroacetolysis rate of neopentyl *p*-toluenesulfonate at 75.0° was 8.5×10^{-5} sec^{-1}. There was some yellowing and decomposition during the solvolysis, but the major, volatile product was *t*-amyl trifluoroacetate.

The significance of these results can be best seen by comparing the solvolyses of ethyl, 2-phenylethyl, and neopentyl *p*-toluenesulfonates in three commonly used solvolysis media and in trifluoroacetic acid.

Table I. Solvolysis Rates (Relative to Neopentyl *p*-Toluenesulfonate in Acetic Acid) as a Function of Solvent at 75°[a]

Reactant	Ethanol	Acetic acid	Formic acid	Trifluoroacetic acid[b]
CH_3CH_2OTs	356	9.2	226	6.4
$C_6H_5CH_2CH_2OTs$	85	3.4	952	10,500
$(CH_3)_3CCH_2OTs$	0.2	1.0	227	1,018

[a] For all rates except trifluoroacetolysis of neopentyl *p*-toluenesulfonate see: S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952); S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953); and ref 2. [b] Rates in trifluoroacetic acid in buffered solution.

The first point of interest is the striking rate enhancement of neopentyl *p*-toluenesulfonate relative to ethyl *p*-toluenesulfonate, a factor of 159 for the buffered trifluoroacetolysis.[6] Ethyl *p*-toluenesulfonateh as no alkyl group to provide anchimeric assistance to ionization. The solvolysis rate of ethyl *p*-toluenesulfonate is usually enhanced through displacement by solvent; however, trifluoroacetic acid is a solvent of low nucleophilicity and high ionizing power, a combination which accentuates SN1 and diminishes SN2 reactions.[7] It therefore appears that the rate of ionization of neopentyl *p*-toluenesulfonate is significantly enhanced, relative to ethyl *p*-toluenesulfonate, due to methyl participation during ionization with concomitant formation of the tertiary substituted product.[8]

It is also of interest to look at the relative rates of each individual *p*-toluenesulfonate as the solvent changes from trifluoroacetic acid to ethyl alcohol, *i.e.*, as the solvents progress from low nucleophilicity and high ionizing power to high nucleophilicity and low ionizing power. For displacement reactions with ethyl *p*-toluenesulfonate, formic acid offers the most effective combination of ionizing power and nucleophilicity,[2] with ionizing power decreasing on going to acetic acid without a compensating increase in nucleophilicity. The rate of ethyl *p*-toluenesulfonate increases in ethyl alcohol due to the increase in nucleophilicity and decreases in trifluoroacetic acid due to the decrease in nucleophilicity. Thus, the solvolysis rate of ethyl *p*-toluenesulfonate is more sensitive to nucleophilicity than to ionizing power when compared with the other two systems; *i.e.*, SN1 is much less important than SN2. 2-Phenylethyl *p*-toluenesulfonate, on the other hand, can benefit both from an increase in nucleophilicity and in ionizing power since the solvolysis rate can be enhanced by solvent displacement or by phenyl participation and it is reasonable that the rate would be increased, relative to acetic acid, in going either to ethyl alcohol or to formic and trifluoroacetic acids. In neopentyl *p*-toluenesulfonate solvent participation is sterically prohibited, so that solvolysis rate is only a function of the ionizing power of the solvolysis medium; therefore, the rates progressively increase from ethyl alcohol to trifluoroacetic acid.

Turning to the question of the role of alkyl participation during ionization of neopentyl *p*-toluenesulfonate in media other than trifluoroacetic acid, it is anticipated that, as the ionizing power of the solvolysis medium is decreased, the need for assistance in ionization increases. This means that assistance from internal displacement, *i.e.*, methyl participation, should become even more important as one changes solvent from trifluoroacetic acid to formic and acetic acids.[9]

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(5) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

(6) A similar enhancement has been reported for solvolysis in concentrated sulfuric acid: P. C. Myhre and K. S. Brown, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstract P-194.

(7) (a) In 2-phenylethyl *p*-toluenesulfonate, there is no SN2 component in trifluoroacetic acid; however, the extent of SN2 with ethyl *p*-toluenesulfonate in trifluoroacetic acid is uncertain (see ref 2). This implies that the transition-state energy in the neopentyl solvolysis is lowered through methyl participation by at least 2 kcal in trifluoroacetic acid. (b) Inductive effects are amplified in trifluoroacetic acid relative to formic and acetic acids, and this would somewhat reduce the enhancement due solely to methyl participation, *i.e.*, $\rho_I = -15.7$ for trifluoroacetolysis, -7.79 for formolysis, and -5.72 for acetolysis (see ref 2 and 5).

(8) Nordlander has used similar reasoning to show phenyl participation in 2-phenylethyl *p*-toluenesulfonate. See ref 2.

(9) The view has recently been presented that ionization and rearrangement are sequential during the acetolysis of simple neopentyl systems: J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nichols, *J. Amer. Chem. Soc.*, **88**, 4475 (1966). One, of course, might question the validity of comparing adamantylcarbinyl *p*-toluenesulfonate directly with neopentyl *p*-toluenesulfonate: W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968).

(10) National Institutes of Health Predoctoral Fellow, 1966–1968.

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Received July 8, 1968

Synthesis of Porphyrins. Deoxophylloerythroetioporphyrin[1]

Sir:

Deoxophylloerythroetioporphyrin (DPEP) (I) has been generally accepted as the predominant porphyrin in crude oil; however, mass spectral studies suggest that a number of homologs are also present.[2] The isocyclic ring in DPEP and the resulting steric interactions have made synthesis of such porphyrins related to chlorophylls extremely difficult. Two syntheses of I have been reported;[3,4] both involve condensation of the same dipyrrylmethenes, gave extremely low yields (*ca.* 0.03%), and reported different electronic spectra for the product. A third preparation of DPEP has recently been reported[5] from pheophytin in *ca.* 0.5%

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(1) This research was supported in part by Grant AI-04888 from the National Institutes of Health, U. S. Public Health Service.

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