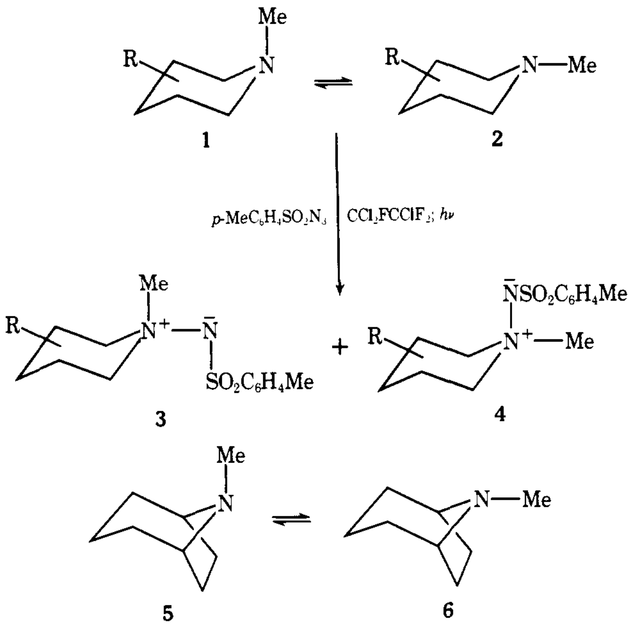

cyclohexane ($-\Delta G°_{305} = 1.70$ kcal mol^{-1} or $K = 17$). Tropane[11] (**5** ⇌ **6**) gave mixed aminimides in ratio 4.2:1 ($-\Delta G°_{300} = 0.86$ kcal mol^{-1} in CCl_2FCClF_2) and, by application of the kinetically controlled protonation procedure,[3,13] diastereoisomeric salts in ratio 5.8:1 ($-\Delta G°_{300} =$ 1.05 kcal mol^{-1} in CCl_2FCClF_2 or cyclohexane near the interface with aqueous sulfuric acid). Agreement between the two methods is satisfactory[14] in view of the obvious difference in physical conditions.

In application of the photochemical method, all bases (or mixtures of bases) were converted into aminimides by irradiation through Pyrex of solutions in CCl_2FCClF_2 containing *p*-toluenesulfonyl azide and a large excess of base, using a 450-W medium-pressure Hanovia lamp and a water-jacketed reaction cell with temperature controlled to ±2°. Yields of aminimide (based or decomposed azide) were typically 2-3% (8-9% with tropane); numerous by-products were evident, but under the experimental conditions chosen the high yields of by-products do not affect the quantitative conclusions on conformational equilibria.[4,15] Aminimides were readily isolated chromatographically and monitored by their characteristic ir spectra (strong bands at ca. 1090, 1130, and 1260 cm^{-1}). Rigorous checks with calibration mixtures (some in high ratios) indicated no tendency toward thermal or photochemical equilibration of products, and no loss of minor component during isolation procedures.

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(5) Standard deviations are about 10% of all ratios quoted.

(6) Two aminimides were observed with, unfortunately, some overlap of critical bands in the ^1H NMR spectrum of the mixture, but qualitatively in equal proportions. We interpret these as arising from axial addition of nitrene to one or other nitrogen atom of the piperazine. We had no similar problem in quantitative analysis of other aminimide mixtures.

(7) The difficulty of measuring high ratios by NMR spectroscopy (cf. ref 3 and comments thereon in ref 2) is eased considerably by the separate availability of the components of the mixtures. Both aminimides **3** and **4** (R = equatorial 4-*t*-Bu) were obtained from 1-amino-4-*tert*-butylpiperidine by successive treatments with methyl iodide, potassium *tert*-butoxide (in tetrahydrofuran), and *p*-toluenesulfonyl chloride; the 4-methyl analogues were similarly obtained. All new compounds have been characterized by elemental and spectroscopic analysis.

(8) So far as comparison is possible between results obtained by different methods on different models, our value accords with the highest previously recorded[3] ($-\Delta G°_{288} = 2.7 \pm 0.2$ kcal mol^{-1} to unspecified confidence limits) from kinetically controlled protonation of **1**, *cis*-3,5-trimethylpiperidine. We note that our *minimum* value is still correct even in the unlikely event that the nitrene is discriminatory between the conformers, with a higher rate constant for equatorial addition to the axial *N*-methyl conformer; this would lead to an observed product aminimide ratio lower than the reactant conformer ratio. The difficulty in *initial* bending of the axial *N*-methyl[2,9] group to relieve syn–axial interactions, relative to bending of *C*-methyl in axial methylcyclohexane, appears likely to be a substantial factor in the observed difference in conformational ratios for *N*-methylpiperidine and its hydrocarbon analogue.

(9) Cf. (for aliphatic analogues) G. Dellepiane and G. Zerbi, *Spectrochim. Acta, Part. A*, **24**, 2151 (1968); *J. Chem. Phys.* **48**, 3573 (1968); R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965), and (for qualitative theory) R. S. Nyholm and R. J. Gillespie, *Q. Rev., Chem. Soc.*, **11**, 339 (1957).

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(11) A crystalline hydrobromide shown[12] (x-ray analysis) to have equatorial *N*-methyl corresponded (NMR) to the major product of kinetically controlled protonation of tropine. By reasonable structural and spectroscopic (equatorial N-Me at higher field than axial N-Me) analogy, tropane also has preferred equatorial *N*-methyl.

(12) J. W. Visser, J. Manassen, and J. L. de Vries, *Acta Crystallogr.*, **7**, 288 (1954).

(13) We have independently developed the controlled proton-transfer procedure.[3]

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(15) Since the base is in large excess throughout each experiment, the ratio of aminimides derived from an *N*-methylpiperidine depends only on the base–conformer equilibrium ratio and the ratio of rate constants for conversion of the conformers into the corresponding aminimides. As indicated earlier, we believe that there is no kinetic selectivity between conformers in their conversion into aminimides, i.e., the rate-constant ratio for this reaction is unity. We note that it is *not* necessary for application of the method that rate constants for conversion of the individual conformers into by-products should also be equal.

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Tunneling Rotation of the Methyl Radical in the $CH_3COONa{\cdot}3D_2O$ Crystal

Sir:

Since Freed[1] theoretically predicted the quantum tunneling effect of the methyl group in radicals, several interesting experimental investigations[2] have been reported on the effect. However, these ESR studies on the quantum tunneling effect have been restricted to the systems for the methyl group in free radicals. In this paper, we wish to report the tunneling rotation of the methyl radical about the threefold symmetry axis of the molecule in a crystal.

We have measured temperature dependence of ESR spectra of the methyl radical produced by γ irradiation of a single crystal of $CH_3COONa{\cdot}3D_2O$ at temperatures below 77 K. The crystal was mounted in a quartz tube of high purity for the γ irradiation and the ESR measurements. The insertion type liquid helium Dewar[3] was used for the ESR measurements at the temperatures below 77 K. The temperature dependence could be examined for about 4 h until the sample temperature reaches 4.2 K, by keeping the crystal inside of the sample tube vacuo so that the thermal conduction might take place only through direct contact of the crystal with the glass wall. The ESR spectra shown in Figure 1b-e were observed during the first 2 h in the sample cooling process, and the spectrum of Figure 1f was observed during the last 2 h. After the sample temperature reached equilibrium with the liquid helium temperature, ESR absorption could not be observed for the sake of the microwave power saturation effect.

As Figure 1 shows, the γ irradiated crystal of

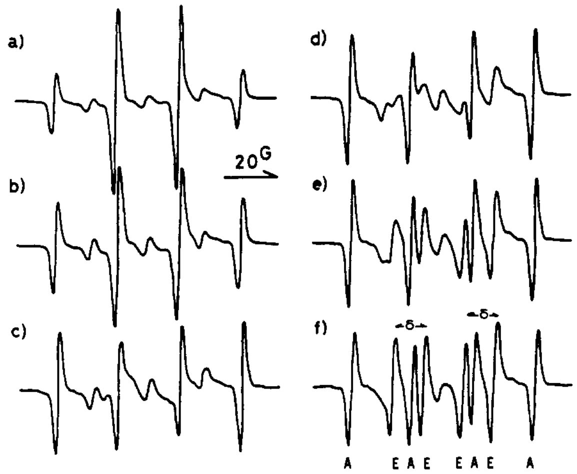

Figure 1. Temperature dependence of ESR spectra of the methyl radical produced by γ irradiation of $CH_3COONa \cdot 3D_2O$. The ESR spectra (a) was observed at 77 K and the spectra (b–f) were observed during the cooling process from 77 K to the liquid helium temperature in this order. Magnetic field is parallel to the *a* axis of the crystal. Weak triplet lines in (a) are due to the CH_2COO^- radical.

$CH_3COONa \cdot 3D_2O$ reveals well-resolved quartet lines with the isotropic hyperfine coupling constant of 22.4 G and small anisotropy less than 0.8 G at 77 K. This hyperfine pattern is apparently due to the methyl radical, produced by the γ irradiation.[4] As the temperature lowers, however, the drastic changes of the hyperfine pattern were observed; i.e., the relative intensities of the $M_I = \pm 1/2$ lines to the outside lines decrease monotonously with decreasing temperature and new lines appear on the both sides of each $M_I = \pm 1/2$ line. This variation in the hyperfine pattern was confirmed to be completely reversible by observing the changes of the ESR spectra by the spontaneous increase of temperature after evaporation of liquid helium.

The quartet lines observed at 77 K are the hyperfine pattern observed ordinarily for the methyl radical,[4] and the radical is considered to be freely rotating about its threefold symmetry axis at 77 K. However, at the lower temperature range where the drastic changes of the hyperfine structure were observed, the rotational motion of the methyl radical may be strongly restricted. If the potential barrier of the trapping site of the radical is represented by the threefold symmetry, the rotational oscillation state is expected to split into A and E symmetry components by the tunneling effect.[1,5] It is further expected that the large anisotropic proton hyperfine interaction will cause splitting of the E state through the tunneling rotation of the molecule, as the angular dependent proton hyperfine interaction in the tunneling rotating methyl group in radicals split its E state degeneracy.[1,5] The observed eight-line pattern in Figure 1f is apparently the one expected for this quantum tunneling rotation of the radical.

The observed splitting, δ, showed a large anisotropy; the splitting δ appreciably varied with crystal orientation in the magnetic field. For the rotation about the *a* axis of the crystal, the splitting changed from 2 to 13 G. If it is assumed that the E splitting[5] arises from the anisotropic proton hyperfine interaction, the splitting δ for the methyl radical is approximately calculated to be about 2 G at the minimum and 15 G at the maximum, by the use of anisotropy values for the methyl radical protons estimated from the theoretical calculation for the hyperfine interaction for a C–H fragment. The calculation of the δ splitting indicates good agreement with the observation. From these facts, it can be concluded that the observed ESR changes at the low temperatures are attributed to the quantum tunneling rotation of the methyl radical about its threefold symmetry axis in the $CH_3COONa \cdot 3D_2O$ crystal. Further work in this system is now in progress.

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Crossed Beams Chemistry: $Ba(^1S) + SO_2(^1A) \rightarrow BaO(^1\Sigma^+) + SO(^3\Sigma^-)$

Sir:

Smith and Zare[1] have recently reported the laser induced fluorescence spectrum of the $BaO(^1\Sigma^+)$ product of the Ba + SO_2 reaction. They have pointed out that production of SO product in its lowest singlet state ($a^1\Delta$) is forbidden by energy conservation in their experiment ($\Delta H = +13$ kcal/mol) so that the observed BaO product was ascribed to the spin-forbidden, bimolecular reaction

$$Ba(^1S) + SO_2(^1A) \rightarrow BaO(^1\Sigma^+) + SO(^3\Sigma^-) \qquad (I)$$

with $\Delta H = -4.1$ kcal/mol. Since strong violation of the Wigner spin conservation rule is a rare kinetic phenomenon,[1] we have studied this reaction in a crossed molecular beam apparatus and report our initial findings here.

The Ba beam, prepared by effusion from a molybdenum crucible at 1140–1170 K with an approximate thermal speed distribution, was intersected at 90° by an SO_2 nozzle beam (stagnation chamber temperature of 430 K and pressure of 280 Torr). Previous experience in this laboratory indicates that these conditions should produce translational and rotational relaxation in the expansion process resulting in a sharp SO_2 beam speed distribution (Mach number $\approx$ 11) centered at 0.67 km/s. Thus, the reactants collide with a well-defined collision energy, $E = \mu g^2/2 = 3.3$ kcal/mol, and little SO_2 internal excitation. The BaO products scattered from the beam intersection region (BIR) are detected by a quadrupole massfilter tuned to the BaO^+ mass setting after ionization in a Brink type electron-bombardment ionizer (EBI). This detector unit is rotated about the BIR, in the plane defined by the intersecting beams, in order to measure the laboratory (LAB) BaO product number density angular distribution, $N(\Theta)$.

Smith and Zare[1] produced the BaO by allowing a Ba atom beam to traverse a scattering chamber containing SO_2 at $\sim 10^{-4}$ Torr. Although these conditions would ordinarily