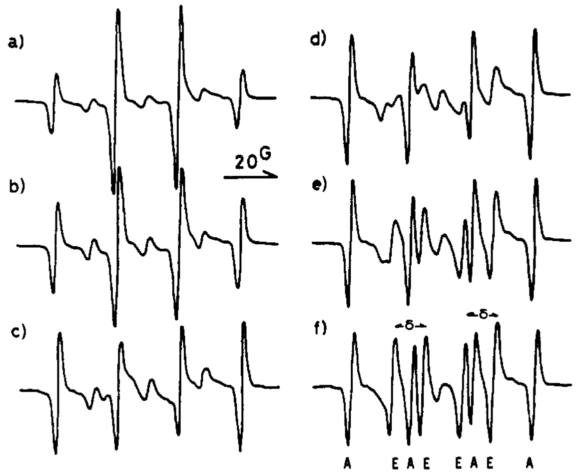

Figure 1. Temperature dependence of ESR spectra of the methyl radical produced by γ irradiation of $CH_3COONa{\cdot}3D_2O$. The ESR spectra (a) was observed at 77 K and the spectra (b–f) were observed during the cooling process from 77 K to the liquid helium temperature in this order. Magnetic field 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 $M_I = \pm\frac{1}{2}$ lines to the outside lines decrease monotonously with decreasing temperature and new lines appear on the both sides of each $M_I = \pm\frac{1}{2}$ 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

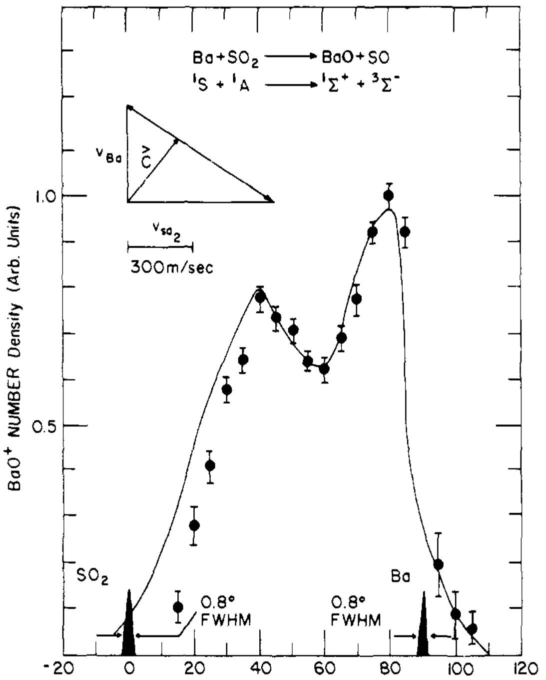

Figure 1. Data points show measured LAB BaO angular distribution from Ba + SO_2 reaction. Solid line shows a fit to the data for CM functions specified in eq 1–3. Also shown is a nominal velocity vector diagram indicating the relation of the center-of-mass velocity of the collision partners, C, to the velocities of the two beams.

assure single-collision-conditions (SCC), recent measurements by Wren and Menzinger[2] indicate an efficient three-body recombination of Ba with Cl_2 or Br_2 which persists into the micro-Torr region. However, our own observation of a copious BaO signal under rigorous SCC confirms Smith and Zare's assignment. Although our beam pressures at the BIR were unknown, they were too low to produce a detectable (< 0.005) attenuation of either beam by the other so that any three-body processes would be prohibitively inefficient. As a check against possible reaction of Ba with SO_2 dimers or higher polymers in the nozzle beam, the BaO^+ intensity measured at $\Theta = 75°$ (15° from the Ba beam) was observed to be approximately proportional (i.e., within 20%) to the SO_2 beam flux for a decrease in the nozzle stagnation pressure from 280 to 30 Torr; exact proportionality was not expected here owing to small changes in the SO_2 beam speed distribution and small EBI nonlinearity towards the intense SO_2 main beam. Furthermore, decreasing the nozzle stagnation temperature from 430 to 295 K produced only the small angular shift of the BaO distribution to be expected due to the change in the SO_2 speed distribution. Smith and Zare[1] report that the rate of reaction 1 is large, four times that of the spin-allowed Ba + CO_2 reaction. We find the peak in the BaO angular distribution from Ba + SO_2 to be nine times that from Ba + N_2O[3] for comparable nozzle stagnation chamber conditions (430 K and 280 Torr for SO_2, 475 K and 280 Torr for N_2O). Although comparison of peak LAB intensities from different reactions can be misleading owing to possible large differences in center-of-mass (CM) recoil functions, this observation qualitatively reinforces Smith and Zare's assignment of a large rate to reaction 1 so that its violation of the spin conservation rule cannot be lightly dismissed as a "heavy atom" effect.

Figure 1 shows the measured LAB angular distribution of BaO product. Also shown is a fit to CM BaO recoil angle, θ, and speed, u in km/sec, distributions obtained by averaging[4] the CM → LAB transformation over the (measured) Ba speed distribution, $\rho_1(v_1)$, and integrating over LAB BaO recoil speed, v:

$$N(\Theta) = \int_0^\infty \int_0^\infty dv\, dv_1 \rho_1(v_1) g(v/u^2) I(\theta) P(u) \qquad (1)$$

This particular fit was obtained with

$$P(u) = u^3 \exp[1.5(1 - (u/0.19)^2)] \qquad (2)$$

and

$$I(\theta) = (\sin\theta + \sin\delta)^{-1} \qquad (3)$$

where $\delta = 3°$ was inserted to prevent the singularities at 0° and 180°. We do not wish to emphasize the form of $P(u)$ here; it will be thoroughly characterized by TOF measurements of the scattered signal currently being pursued. However, we do wish to emphasize two points in relation to the form of $I(\theta)$ which can be fit to the data of Figure 1. We have been unable to fit any $P(u)$-$I(\theta)$ combination to the data unless $I(\theta)$ was constrained to be symmetric about $\theta = 90°$. This in turn implies that the reaction must proceed via formation of a $BaSO_2$ complex which persists for at least several rotational periods. Assuming a 50 Å^2 reactive cross section, Q_R, and "linear" Ba-O-S-O complex, $\tau_R \approx 2.5 \times 10^{-12}$ s. We are also unable to fit the sharp bimodal structure in $N(\Theta)$ unless $I(\theta)$ is forced to peak sharply at $\theta = 0°$ and 180° (e.g., eq 3). This is consistent with the large Q_R estimate and relatively weak BaO rotational excitation.[1]

Smith and Zare obtained a nonstatistical BaO internal energy distribution. This observation together with an early, erroneous report[4,5] of forward product scattering prompted them to propose a plausible mechanism wherein the reaction is initiated by the familiar electron transfer at large reactant separation (estimated as 3.5 Å) to give a singlet $Ba^+SO_2^-$ ion pair followed by a rapid singlet → triplet transition facilitated by the small expected splitting at large separations. However, this mechanism appears unlikely in view of the present finding because it would require a substantial binding energy for forming the $BaSO_2$ triplet state and would no longer account for the nonstatistical BaO internal excitation without additional assumptions. Rather, the present results provide a clear example of the mechanism advanced by Tully[6] and Zahr, Preston, and Miller[7] to account for quenching of $O(^1D)$ by N_2 and other facile, spin-forbidden processes. In this model, reaction I would be pictured as

$$Ba + SO_2 \underset{k_{-II}}{\overset{k_{II}}{\rightleftharpoons}} (BaSO_2)_s \qquad (II)$$

$$(BaSO_2)_s \xrightarrow{k_{III}} (BaSO_2)_t \rightarrow BaO + SO \qquad (III)$$

where the $(BaSO_2)_s$ singlet complex would be long-lived whereas the $(BaSO_2)_t$ triplet complex would immediately decompose. The rate of reaction I can be quite large (k_{II}) for only a modest singlet-triplet transition rate (k_{III}) provided that $k_{III} > k_{-II}$; the present data merely establishes that $k_{-II} < \tau_R^{-1}$. Moreover, the reaction energy need not be statistically distributed over product states. The product energy partitioning will be dependent upon the potential energy at which the singlet and triplet surfaces intersect as well as the energy dependence of k_{III}.

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Aromatic Substitution, XXXIX.[1] Varying Selectivity in Electrophilic Formylation of Toluene and Benzene

Sir:

Electrophilic aromatic acylations (Friedel-Crafts ketone syntheses) generally show high substrate and positional selectivity,[2] with predominant para substitution of toluene.[2] Friedel-Crafts type formylation reactions, such as the Gatterman-Koch reaction, also give nearly exclusive para substitution.[3]

In the preceding study of aromatic substitution, we have reported the observation of the fairly wide scope of selectivity obtainable in electrophilic acetylation and benzoylation reactions of aromatics with suitable substituted acyl halides.[4] In the case of formylation, of course, no substituent effects are possible in the formylating agent, but the nature of the formylating agent can be easily varied.

We now wish to report our studies of electrophilic formylation of benzene and toluene, showing the wide range of selectivity obtainable depending on the used formylating agents.

From the most frequently used formylation methods, the Gatterman-Koch reaction[5] shows the highest selectivity (data are summarized in Table I) reflected both in the observed high $k_{\text{toluene}}:k_{\text{benzene}}$ rate ratios (of 155-860), as well as a high degree of para substitution (88.7-96%). Gross's formylation with dichloromethyl methyl ether[6] is somewhat less selective ($k_T/k_B = 119$; 60.4% para substitution), as is the Gatterman synthesis using $Zn(CN)_2$ and $AlCl_3$.[5] Friedel-Crafts type formylation with formyl fluoride[7] (the so-called Olah aldehyde synthesis[8]) gives a much lower selectivity ($k_T:k_B = 34.6$ and 53% para substitution) indicating that the $HCOF-BF_3$ system produces a more reactive electrophile ($HCOF \cdot BF_3$ complex, but not necessarily a free formyl cation, HCO^+).

The lowest selectivity reaction studied was the $HF-SbF_5$ catalyzed formylation with CO in SO_2ClF solution at $-95°$, which gave a k_T/k_B ratio of 1.6, and an isomer distribution of 45% *o*-, 2.7% *m*-, and 52.1% *p*-tolualdehyde. Under the superacidic conditions studied, CO is protonated to give the rapidly equilibrating (with the solvent acid system) protosolvated formyl cation, an obviously very reactive electrophilic reagent. When the reaction is carried out at 0 °C using only excess aromatics as solvent, the selectivity becomes much higher giving an isomer distribution of 7.5% *o*-, 2.8% *m*-, and 89.8% *p*-tolualdehyde.

The formylation of hexadeuteriobenzene, C_6D_6, with $HCOF-BF_3$ shows a kinetic hydrogen isotope effect of $k_H/k_D = 2.68$, based on the comparison of the reactivity of $C_6H_6/CH_3C_6H_5$ and $C_6D_6/CH_3C_6H_5$. This isotope effect is similar to that observed in Friedel-Crafts acetylation and propionylation reactions, and indicates that the proton elimination step is at least partially rate determining. The low substrate selectivity formylation with $CO-HF-SbF_5$, however, shows no primary isotope effect.

For nearly a century Friedel-Crafts acylations were considered to give nearly exclusive para substitution of toluene.[2] The reason accounting for this fact was considered to be steric. Our increasingly better understanding of the mechanism of electrophilic aromatic substitution indicated that this is not necessarily the only reason. Para substitution is greatly favored if the transition state of highest energy of the reaction is intermediate arenium ion (σ-complex) like, where a para methyl group is more stabilizing than an ortho (and much more than a meta). When, however, the highest transition state is becoming increasingly "early" on the reaction path, the ratio of ortho/para substitution increases. Meta substitution always stays relatively low, generally less than 5-6%, varying with the reactivity of the reagent within this limit. It is rewarding to see this pattern now also in Friedel-Crafts type formylation reactions. In these reactions the involved substituting agents are obviously less space demanding than those of other acylation reactions. Steric effects consequently cannot be a very significant factor affecting selectivity, which is primarily reflected in the changing ortho/para isomer ratio. The methyl group always remains a predominately ortho-para directing substituent, even in very low substrate selectivity reactions and the meta isomer does not increase above 4%.

Besides mechanistic interest, our studies are also considered to eventually contribute to the extended preparative usefulness of Friedel-Crafts syntheses in obtaining previously not easily accessible isomers (such as *o*-tolualdehyde). Our studies are extended to the formylation of other substituted aromatics, and will be reported in full.

Table I. Electrophilic Formylation of Toluene and Benzene

					% tolualdehydes		
Formylating agent	Catalyst	Solvent	Temp, °C	k_T/k_B	Ortho	Meta	Para
CO	$HF-SbF_5$	SO_2ClF	−95	1.6	45.2	2.7	52.1
HCOF	BF_3	Excess aromatics	25	34.6	43.3	3.5	53.2
HCN−HCl	$AlCl_3$	Excess aromatics	25	49.1	39.9	3.7	56.4
$Zn(CN)_2-HCl$	$AlCl_3$	CH_3NO_2	25	92.8	38.7	3.5	57.8
$Zn(CN)_2-HCl$	$AlCl_3$	Excess aromatics	50	128	34.3	1.8	63.9
Cl_2CHOCH_3	$AlCl_3$	CH_3NO_2	25	119	35.8	3.8	60.4
CO + HCl	$AlCl_3Cu_2Cl_2$	Excess aromatics	25	155	8.6	2.7	88.7
CO + HCl	$AlCl_3$	Excess aromatics	0	319	6.6	0.8	92.6
CO + HF	BF_3	Excess aromatics	0	860	3.5	0.5	96.0