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A Study on the Stereo-Anisotropy of the CN*(B,A) Radical Formation in the Reaction of Acetonitrile with Metastable Excited Ar Atom by Use of the Oriented CH_3CN Molecular Beam

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An orientation-dependence of the CN*(B,A-X) radical formation was observed in the reaction of Ar(^{3}P) with the oriented CH_3CN. The experimental results were analyzed on the basis of a hard-sphere model and gave the ratio of reaction cross sections of σ_h(heads configuration)/σ_t(tails configuration) as 2.8±1.2, showing a large stereo-anisotropy in the formation of the CN* radicals.

To probe what really happens during a chemical reaction is one of the current interest in reaction dynamics. In some cases, a picture of the electronic orbital overlap affords an insight into this problem. An approach by means of chemical excitation using the oriented melecular beam may provide a sort of selection in collisional geometry at the initial step of chemical reaction.[1,2] In this letter, we present an experimental finding of a large orientation-dependence of the CH_3CN molecule in the CN* formation observed in the title reaction.

The oriented beam apparatus in which the 60-cm hexapole inhomogeneous electric field is installed with an axial beam-stop of 1.5 mm in diameter was used.[2] A supersonic beam of acetonitrile with the stream velocity of v_s=685±10 ms^{-1} and the translational temperature of T_t=57±5 K crosses the Ar(^{3}P) supersonic beam with v_s= 589±10 ms^{-1} and T_t=27±3 K, and the CN* chemiluminescence from the beam-intersection zone was observed. The polarity of the uniform electric field of $\approx$150 Vcm^{-1} was switched periodically in order to alter the collisional geometry from the random,

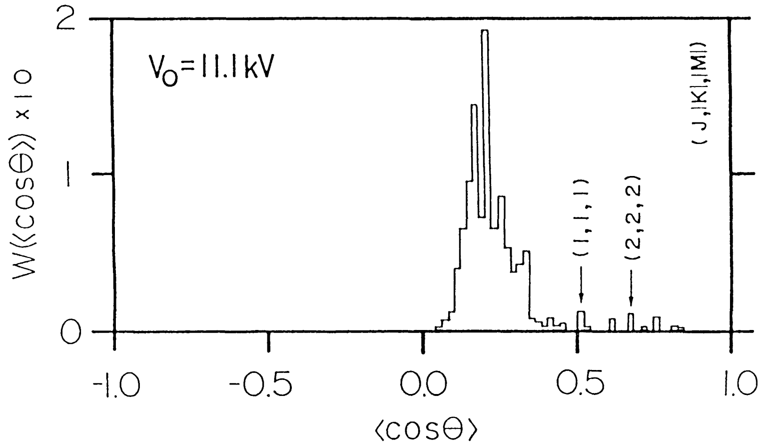

Fig. 1. The <cos θ> distribution of CH_3CN after the hexapole state-selection at 11.1 kV. The distribution was simulated by the trajectory calculation (see text). The parentheses (J,|K|,|M|) is a set of three rotational quantum numbers for symmetric top.

Table 1. The orientation-dependence of the CN* chemiluminescence. The intensities were averaged over 410 sets of 100 pulsed signals.

Polarity of Uniform field	Emission intensity
Positive	36.5±3.2 (I_+)
Negative	26.4±3.1 (I_-)
None	31.7±3.2 (I_r)

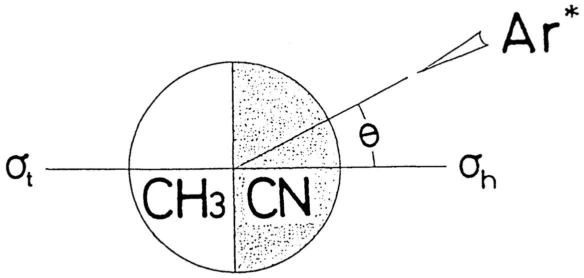

Fig. 2. A hard-sphere model for the CH_3CN molecule.

the head, and the tail configurations. The rotational temperature of the supersonic beam of CH_3CN was determined to be 57 ± 10 K by the trajectory simulation for the observed focusing curve.[3,4] The histograms of the <cos θ> ($\langle\cos\theta\rangle \equiv KM/J(J+1)$) distribution of CH_3CN in Fig. 1 shows no population at <cos θ>=0 as the result of the beam-stop and the ensemble average of $\overline{\langle\cos\theta\rangle}$ was 0.228 at V_0=11.1 kV. The emission intensities of CN* at the three collisional geometries are listed in Table 1. This result clearly shows that the attacks at the CN-end give greater CN* formation than the attacks at the methyl-end(i.e. $I_+ > I_-$). For a quantitative expression of reaction probability, a hard-sphere model is adopted in which a molecule is divided into two parts and the reaction cross sections are given as σ_h and σ_t, respectively as shown in Fig. 2. The ratio of σ_h/σ_t was found to be 2.8±1.2 as the result in the present study.

At the step of electron exchange in the collision of Ar(^3P) with CH_3CN like in the Penning ionization,[5] the extent of the orbital overlap between the target molecule and the projectile atom may be regarded as an appropriate measure of exchange efficiency. We tentatively suggest on the present reaction that the $7a_1$ molecular orbital of acetonitrile is a candidate at the initial stage of electron exchange, since the $7a_1$ orbital has characters of nonbonding at the CN group while of bonding at the C-C bond,[6] thus the removal of a covalent electron from the C-C bond may accelerate the bond-breaking and to form the CN* fragment more. For further discussion, it should be necessary to obtain more accurate orientational opacity function.

References

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