CHEMISTRY LETTERS, pp. 407-408, 1990.

Dissimilar Stereo-Anisotropy of the CN*(B,A) Radical Formation in the Reaction of Ar(^{3}P) and CD_3CN as Compared with CH_3CN

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Dissimilar orientation-dependence of the CN* chemiluminescence as compared with the CH_3CN system was observed in the reaction of Ar(^{3}P) with the oriented CD_3CN. The ratio of $\approx$ 1.8 of the CN*(B,A) emission cross sections for the head-on to the tail-end attacks was obtained by use of the hard-sphere model, indicating isotope effects on the branching ratio in the deuteration of CH_3CN.

In our previous paper on the CH_3CN/Ar* system, it is shown that the CN-end attack is more efficient in the CN* formation than the methyl-end attack by a factor of three.[1] In the case of the CD_3CN/Ar* system, however, the dissimilar orientation-dependence of the CN* chemiluminescence was observed. Tabayashi and Shobatake have observed the enhanced reaction cross section of the CN* formation in the CD_3CN/Ar* system as compared with the CH_3CN/Ar* system, and implied the branching competition.[2] It is therefore worthy to investigate key factors on this enhancement in the CN* emission.

The oriented beam apparatus has been described elsewhere.[3] The supersonic beam of CD_3CN with the stream velocity of 660 ms^{-1} and the rotational temperature of 57 K was focused via the hexapole inhomogeneous field. It was then oriented via the uniform field at the beam intersection. Thus the oriented CD_3CN encounters the Ar* atom at the specified orientations. The CN* emission was measured by the gated photon-counting with the simultaneous background subtraction.[4]

The emission intensities of CN* at three collisional geometries are listed in Table 1. By use of the quantal orientational distribution of $W(r \cdot E)$ for the CD_3CN

Table 1. The orientation-dependence of the CN* chemiluminescence.

Polarity of uniform field	Emission intensity[a] (count/pulse)
Positive(the CN-end)	0.82
Negative (the methyl-end)	0.67
None (random orientation)	0.73

a) The emission intensity is the average over 30000 pulses. The gate time was 2.8 ms. The estimated standard deviation is 0.08.

beam at the 11.1 kV hexapole voltage, the ratio of the cross sections in the hard-sphere model was obtained as 1.8 ± 1.1, showing the CN-end attack as the favored orientation. Since the relative emission intensities for the randomly oriented CD_3CN and CH_3CN were measured in this experiment, the relative emission cross sections, σ_h(H and D) and σ_t(H and D) can be compared, where the H and D in parentheses stand for the CH_3CN and the CD_3CN system, respectively. As shown in Fig. 1 with the solid lines for CD_3CN and with the dashed lines for CH_3CN, the reactive ratio is given as follows, $\sigma_t(H) : \sigma_h(H) : \sigma_t(D) : \sigma_h(D) = 1 : 3.1 : 2.6 : 4.6$.

From the measurement of the branching fractions in the $CH_3X(X=CH_3,OH)/Ar^*$, Balamuta and co-workers have showed that the major process of deexcitation is the atomization to produce the hydrogen atoms.[6] In the CH_3CN/Ar^* system, the CN* chemiluminescence channel yields only a few percent of the total quenching cross section of ≈160 Å^2,[7] and the value of which may be similar in the CD_3CN/Ar^* system. The isotope effect in the C-D vibration can disfavor the rate of the bond-breaking for the atomization. As a result, the branching to the competing channel of chemiluminescence can be enhanced. This chemiluminescent enhancement could be accelerated especially in the case of the methyl-end attack. The internal excitation of the products and the translational energy release, however, may be taken into account in the future studies.

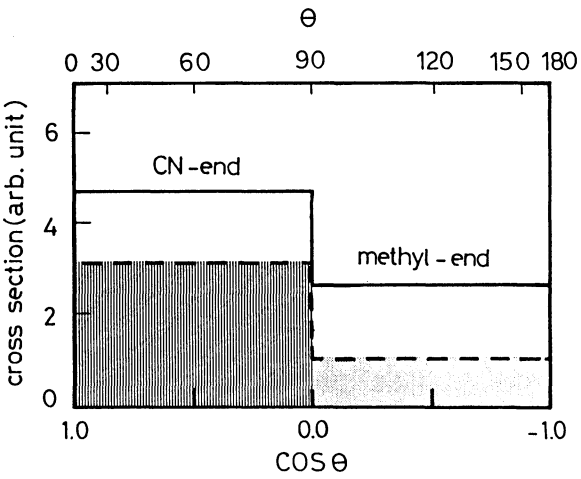

Fig. 1. The reaction cross sections for the CN* formation as a function of the angle of attack, θ.

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(Received November 20, 1989)