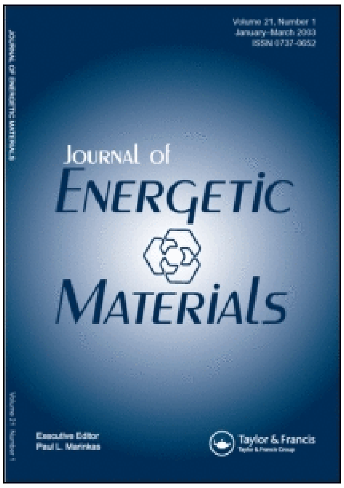

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EPR investigations of thermal decomposition of nitramines: II. Primary nitroxide radicals from HMX

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EPR INVESTIGATIONS OF THERMAL DECOMPOSITION OF NITRAMINES: II. PRIMARY NITROXIDE RADICALS FROM HMX

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ABSTRACT

The primary free radical produced by heating HMX in sulfolane is identified as the known nitroxide. The conditions for forming and observing this HMX-nitroxide show both similarities and differences with conditions observed for the related RDX-nitroxide.

INTRODUCTION

In Part I, the primary free radical produced by heating RDX in sulfolane was identified as the nitroxide[1]. As HMX is closely related to RDX, it was of interest to determine if a similar process occurs in heated HMX-sulfolane solutions. We confirm that the primary free radical from HMX under these conditions is the known HMX-nitroxide[2]. The behavior of the two nitroxides shows interesting differences, which are summarized.

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EXPERIMENTAL

Experiments were performed as described in Part I, with one exception. HMX dissolves in sulfolane less readily than RDX, and the preparation of solutions involved preliminary dissolution of HMX in sulfolane maintained at 60^{0}C.

RESULTS

At concentrations from 0.1M to saturated (@60^{0}C), HMX in sulfolane forms a free radical at 190^0-205^{0}C which we identify as the nitroxide (Figure 1). Both RDX- and HMX- nitroxides have been prepared previously by photolysis at room temperature or lower[2,3]. Comparison of EPR coupling constants for the same radical at low and high temperatures shows that, in both cases, the coupling of the alpha - methylene protons changes the most, with little variation in coupling constants with temperature for the ring nitrogens (either nitroxide-nitrogen or beta - nitrogens). This may be rationalized as a difference between "frontier" and "inner" groups in the molecules.

As previous workers observed, only two of the four methylene protons in HMX-nitroxide are involved in EPR coupling[2]. The intensity ratio is not simply 1:2:1, however, and additional weak lines can be observed at high signal intensities, to the left and right of Figure 1, Spectrum A. We take this to mean that free rotation exists for some - but not most - of the HMX-nitroxide molecules at ca. 200°C. In RDX-nitroxide, by comparison, all four methylene protons are equivalent[1-3].

The thermal preparation of HMX-nitroxide did not show the time-temperature inverse relationship observed for RDX-nitroxide. In the latter case, RDX-nitroxide in sulfolane could be produced in less than one minute at 170°C, and at lower temperatures (down to 120°C) by longer heating times (up to one hour). The HMX-nitroxide in sulfolane could not be produced below 190°C, even for heating times up to two hours (at 170-180°). Free radical production from HMX appears to occur rather sharply at 190°C, suggesting some molecular rearrangement is occurring (e.g., dimer to monomer).

As temperature and concentration were varied over the ranges described, no secondary radical was observed from HMX as with RDX[1]. Also, outgassing of HMX-nitroxide solutions becomes vigorous above 195°C, making it difficult to explore for a secondary radical. For RDX, the two-step radical sequence could be observed by varying concentration, with outgassing kept to a minimum by holding the temperature below 175-180°C. A similar ease of observation does not hold true for HMX.

Further experiments will determine if a second HMX radical is produced after outgassing, or in a different solvent.

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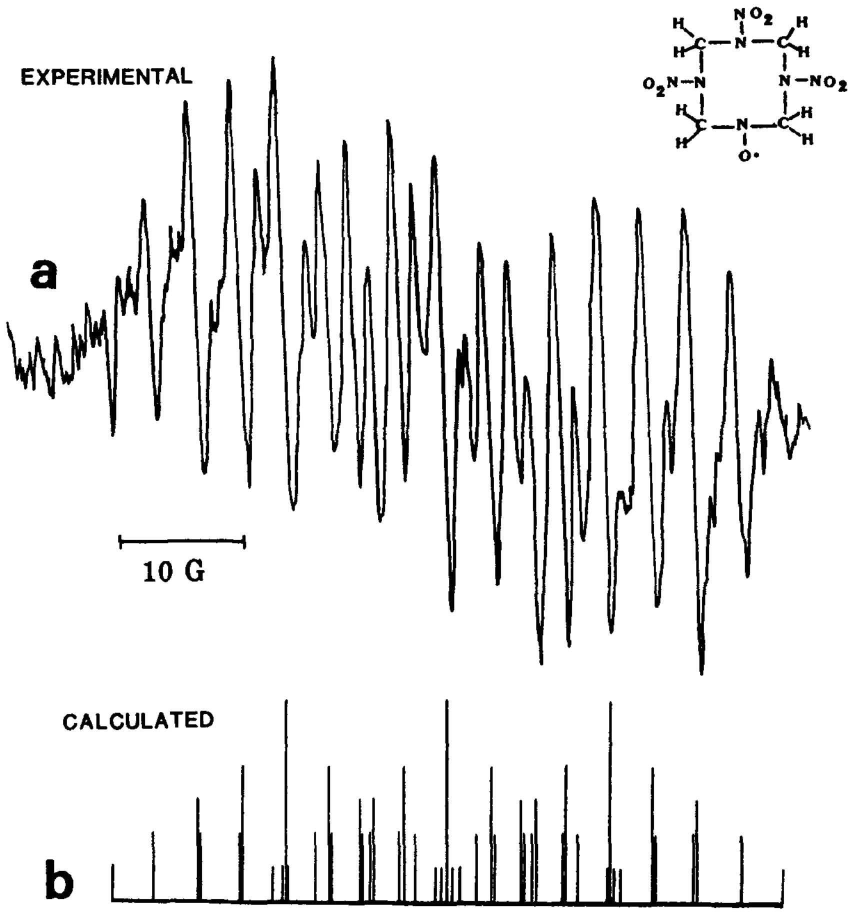

FIGURE 1

a. The first - derivative EPR spectrum of an 0.1M solution of HMX in sulfolane at 200^{0}C.

b. A calculated intensity spectrum for the nitroxide radical (as shown in 1a) using the following hyperfine coupling values:

Nuclei	Equivalent spins	Intensities	Hyperfine Coupling (Gauss)
N	1	1:1:1	12.8
H	2	1:2:1	7.0
N	2	1:2:3:2:1	3.4