

# Thermal Decomposition of Isomeric Nitropropenes: A Photoelectron Spectroscopic Study

W. S. Chin, C. Y. Mok, and H. H. Huang\*

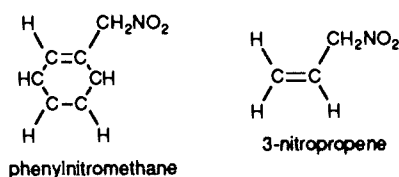
Contribution from the Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511. Received June 9, 1989

**Abstract:** The thermal decomposition of the three isomers of nitropropene has been investigated in a flow system at low pressures, by using the characteristic bands of the photoelectron spectra of the products for their identification. Of the three isomers, 1- and 2-nitropropene decomposed to give products analogous to those found in the thermolysis of nitrostyrenes, implying some similarities in mechanism. On the other hand, 3-nitropropene gave similar products as 3-propenyl nitrite, indicating the isomerization of the nitro compound to the nitrite form as a probable first step for decomposition.

Among the analytical techniques used for the investigation of gaseous reactions, photoelectron spectroscopy offers some unique advantages.<sup>1</sup> For example, only a small amount of a sample is required, identification of products can be made readily if the species exhibit characteristic spectral bands, and semistable species can be detected and their properties studied.

In a previous study,<sup>2</sup> we have applied photoelectron spectroscopy to follow the pyrolysis of gaseous phenylnitromethane. The compound was found to decompose through two different processes. At low temperatures water and benzonitrile were detected, whereas at high temperatures, water, nitric oxide, benzaldehyde, and a small amount of carbon monoxide were observed. A free-radical mechanism was proposed to account for the high-temperature mode, whereas the initial intramolecular rearrangement to *aci*-phenylnitromethane followed by its dissociation was proposed as the likely path for the reaction at low temperatures.

In view of the similarity in structure between phenylnitromethane and 3-nitropropene, we have carried out the pyrolysis



of the latter compound in the hope that its structural simplicity may make it a better candidate for the study of reaction mechanisms. To examine the importance of structural variation on reactivity, we have also carried out the pyrolysis of the other isomers 1- and 2-nitropropene.

While the thermal decomposition of nitroalkanes has been a subject of intensive investigation, relatively few studies have been made on the behavior of nitroolefins.<sup>3</sup> On the other hand, interest in energetic materials has led to a number of theoretical and semiempirical MO calculations related to the decomposition of simple nitroolefin molecules.<sup>4</sup> Experimental results on the pyrolysis of the nitropropenes should provide useful comparisons to these studies.

In this paper we report the results of a pyrolysis study on the nitropropenes. For comparison 3-propenyl nitrite was also examined. The reactions were followed by on-line recording of photoelectron spectra; the various products were readily characterized by their fingerprint bands. The technique allowed us to

detect readily such isomeric species as isocyanic acid and fulminic acid. Some significant variations in reaction pattern arising from differences in reactant structure were also observed.

## Experimental Section

HeI photoelectron spectra were recorded on a Leybold-Heraeus UPG-200 spectrometer. The resolution was in the range of 17–25 meV. Calibrations were carried out with the argon <sup>2</sup>P doublet lines and with the <sup>3</sup>Π peak due to nitric oxide where applicable.

Pyrolysis was carried out in a flow system, in which the heated part consisted of a 45-cm long quartz tubing with inner diameter of 1.2 cm. To improve thermal contact a portion of the tubing about 6 cm long was packed lightly with quartz wool. Heating was applied through a temperature-controlled tube oven 30 cm in length. One end of the quartz tubing was connected to the inlet system of the spectrometer via a metal cone and glass socket joint, at a distance of about 28 cm away from the ionization chamber. The pure compound was vaporized under reduced pressure and introduced by a standard glass vacuum line without any carrier gas through this heated zone by the vacuum pump system of the spectrometer. The vacuum system was supported by two turbopumps with pumping speeds of 145 and 450 L/s, respectively, backed by a rotary pump with a pumping speed of 4.58 L/s. Progress of the pyrolysis was monitored by on-line recording of the photoelectron spectrum of the heated gas.

A liquid nitrogen cold trap placed downstream from the quartz tubing was sometimes employed to trap the condensables. To measure the spectra of the individual products, the components in the trapped mixture were released through differential vaporization, by using a cold bath of liquid N<sub>2</sub>/EtOH mixture.

3-Nitropropene was prepared from the reaction of allyl bromide with silver nitrite.<sup>5</sup> The other two isomers were prepared from the dehydration of the corresponding β-nitroalcohols.<sup>6</sup> 3-Propenyl nitrite was synthesized by reacting allyl alcohol with nitrous acid.<sup>7</sup> The compounds prepared were purified through vacuum distillation. The NMR spectrum of the 1-nitropropene prepared was found to agree with that expected for the *trans* configuration.<sup>8</sup>

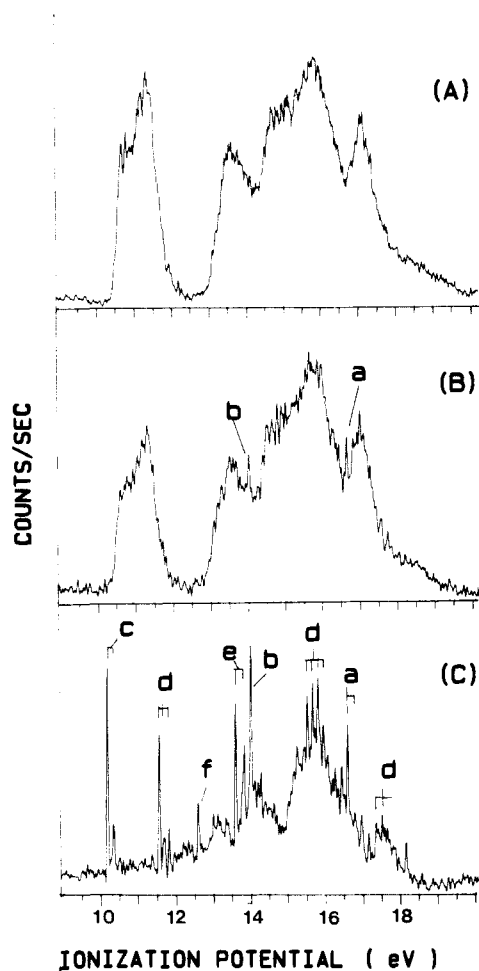
## Results and Discussion

**Changes Observed in Pyrolysis.** The pyrolysis experiments were usually performed at a pressure of 0.6–1.0 mbar in the flow tube, and about 0.1–0.2 g of material was pyrolyzed during a period of 2–3 h. During pyrolysis, as the temperature was gradually increased, the ionization bands of the parent compound diminished; simultaneously, new bands due to products emerged and became more and more prominent. At the end of a run, there were usually some carbonaceous materials deposited on the quartz wool.

**1-Nitropropene.** The spectral changes during pyrolysis of 1-nitropropene are shown in Figure 1. The first sign of change was noted at ca. 500 °C with the appearance of the sharp peaks due to the states <sup>3</sup>Π of NO<sup>+</sup> and <sup>2</sup>Σ of CO<sup>+</sup> at 16.56 and 14.01 eV,

(1) Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427.  
 (2) Mok, C. Y.; Kok, L. Y.; Chin, W. S.; Huang, H. H. *J. Mol. Struct.* **1988**, *175*, 429.  
 (3) Batt, L. *Chemistry of Amino, Nitroso, and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: Chichester, U.K., 1982; Vol. 2.  
 (4) (a) Cox, J. R.; Hillier, I. H. *Chem. Phys.* **1988**, *124*, 39. (b) Turner, A. G. *J. Phys. Chem.* **1986**, *90*, 6000. (c) Turner, A. G.; Davis, L. P. *J. Am. Chem. Soc.* **1984**, *106*, 5447.

(5) Bordwell, F. G.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3116.  
 (6) Buckley, G. D.; Scaife, C. W. *J. Chem. Soc.* **1947**, 1471.  
 (7) Noyes, W. A. *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1943; Collect. Vol. II, p 108.  
 (8) Baskov, Y. V.; Urbanski, T.; Witanowski, M.; Stefaniak, L. *Tetrahedron* **1964**, *20*, 1519.



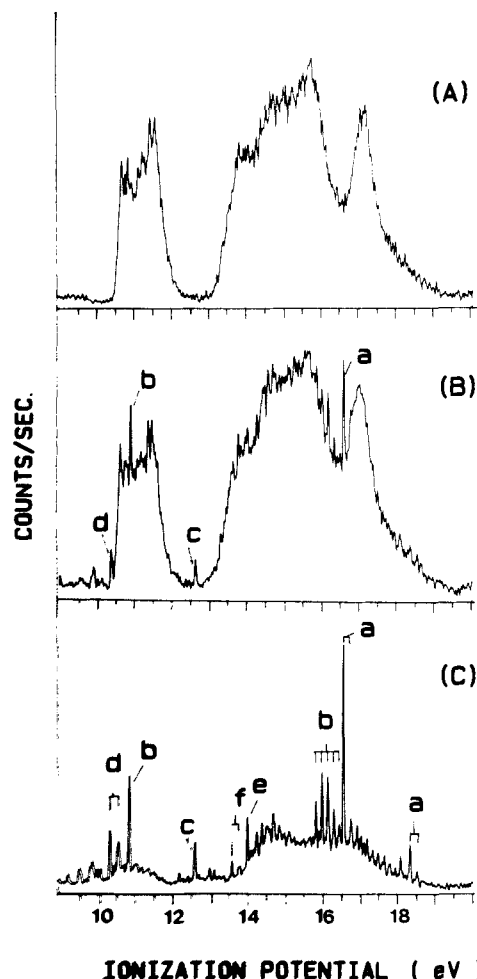
**Figure 1.** Spectral changes during pyrolysis of 1-nitropropene: (A) room temperature, (B) 500 °C, and (C) 700 °C. Products: a, NO; b, CO; c, CH<sub>3</sub>CHO; d, HNCO; e, HCN; and f, H<sub>2</sub>O. CO<sub>2</sub> is found through differential vaporization.

respectively.<sup>9</sup> At 700 °C pyrolysis was complete. From the positions and structure of the new bands, CH<sub>3</sub>CHO, HCN, H<sub>2</sub>O, and isocyanic acid HNCO were identified as the products in addition to CO and NO. A minor product, CO<sub>2</sub>, was only detected through differential vaporization.

When pyrolysis was carried out without quartz wool packing for the flow tube, the three bands due to HNCO were not detected; instead four bands at 10.8, 15.9, 17.8, and 19.1 eV due to fulminic acid HCNO were observed.<sup>10</sup>

**2-Nitropropene.** Figure 2 shows the changes during the pyrolysis of 2-nitropropene. The peak at 16.56 eV due to NO could be observed at 550 °C, indicating the occurrence of decomposition. At 600 °C, although the extent of reaction was small, the spectral features showed the presence of three other products, viz. formaldehyde, methyl acetylene, and water. Reaction was virtually complete at 700 °C, and the composite spectrum showed the presence of CO and CO<sub>2</sub> as additional products. A minor product, CH<sub>3</sub>CN, could only be detected through differential vaporization.

**3-Nitropropene.** 3-Nitropropene decomposed at slightly lower temperatures than the other two isomers, as shown in Figure 3. At 400 °C the bands due to NO and CO were visible, and C<sub>2</sub>H<sub>4</sub>



**Figure 2.** Spectral changes during pyrolysis of 2-nitropropene: (A) room temperature, (B) 600 °C, and (C) 700 °C. Products: a, NO; b, HCHO; c, H<sub>2</sub>O; d, CH<sub>3</sub>CCH; e, CO; and f, CO<sub>2</sub>. CH<sub>3</sub>CN is found through differential vaporization.

**Table I.** Pyrolysis Products of the Decomposition of Nitropropenes and 3-Propenyl Nitrite

	main	minor
1-nitropropene	CH <sub>3</sub> CHO, HCN HNCO, HCNO <sup>a</sup> CO	NO, H <sub>2</sub> O CO <sub>2</sub>
2-nitropropene	CH <sub>3</sub> CCH, NO HCHO	CH <sub>3</sub> CN, CO H <sub>2</sub> O, CO <sub>2</sub>
3-nitropropene	C <sub>2</sub> H <sub>4</sub> , NO CO	CH <sub>2</sub> =CHCHO C <sub>3</sub> H <sub>6</sub> , H <sub>2</sub> O CO <sub>2</sub>
3-propenyl nitrite	CH <sub>2</sub> =CHCHO C <sub>2</sub> H <sub>4</sub> , NO CO	H <sub>2</sub> O, N <sub>2</sub> O

<sup>a</sup> Observed when flow tube was not packed with quartz wool.

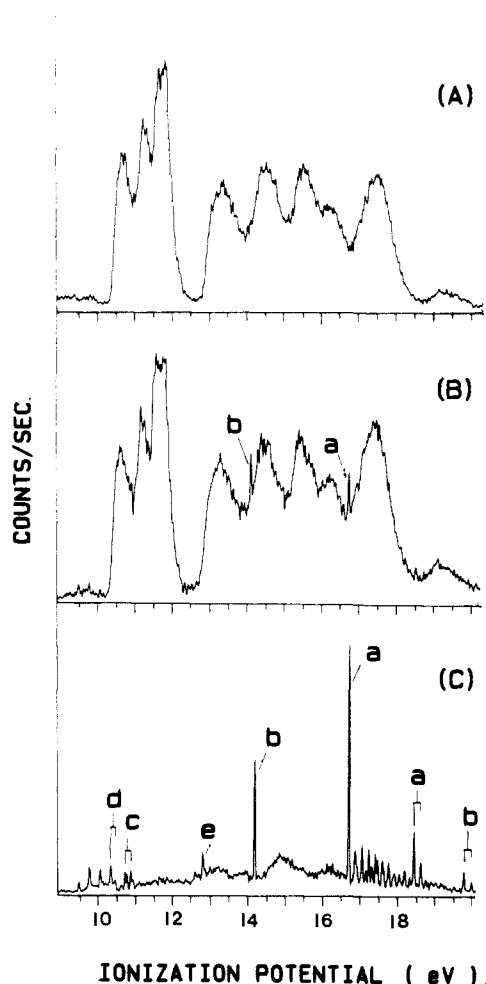
could be detected through differential vaporization. Decomposition was complete at 550 °C, and the spectral features showed the presence of propenal and water, in addition to the three products mentioned. Propene and CO<sub>2</sub> were also confirmed by differential vaporization.

**3-Propenyl Nitrite.** 3-Propenyl nitrite decomposed to essentially the same products as 3-nitropropene but at lower temperatures. The changes are shown in Figure 4. Detectable changes commenced at 300 °C with the appearance of the NO and CO bands. Substantial changes occurred at 350 °C, and at 400 °C decomposition was complete. Propenal was one of the major products; a minor product, N<sub>2</sub>O, was confirmed through differential vaporization.

Table I summarizes the products formed during pyrolysis of the four compounds. The products were approximately classified

(9) The PE spectra of individual products were compared with those reported in the literature especially the following references: (a) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of Hel PE Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981. (b) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley Interscience: London, 1970.

(10) The spectra of HNCO and HCNO were obtained after the individual species were separated by differential vaporization. They compared well with those published in the following references: (a) Eland, J. H. D. *Phil. Trans. Roy. Soc. London* 1970, A268, 87. (b) Bastide, J.; Maier, J. P. *Chem. Phys.* 1976, 12, 177.

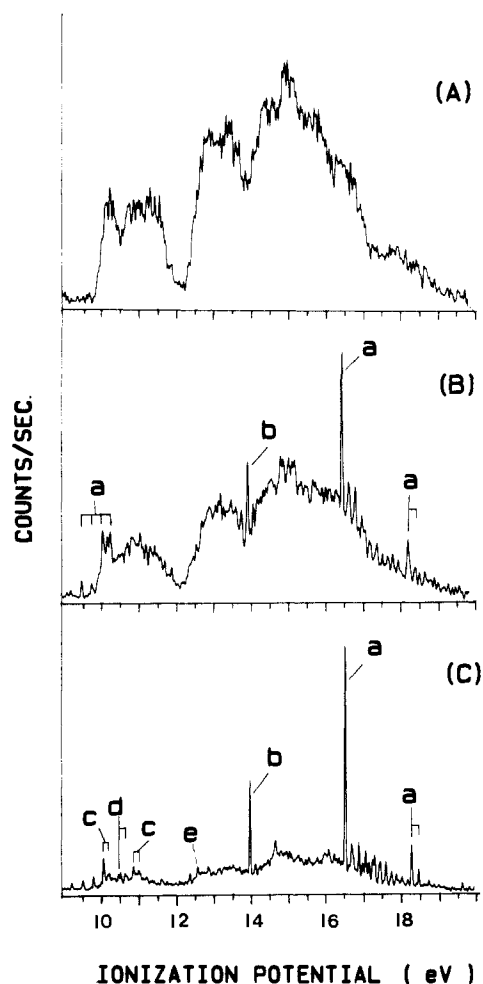


**Figure 3.** Spectral changes during pyrolysis of 3-nitropropene: (A) room temperature, (B) 400 °C, and (C) 550 °C. Products: a, NO; b, CO; c, C<sub>2</sub>H<sub>4</sub>; d, CH<sub>2</sub>=CHCHO; e, H<sub>2</sub>O. CO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> are confirmed through differential vaporization.

as main and minor. The classification was made on the basis of either the peak heights corrected by the relative spectral responses of the species, as determined by using authentic samples, or the vapor pressures of individual components released during differential vaporization.

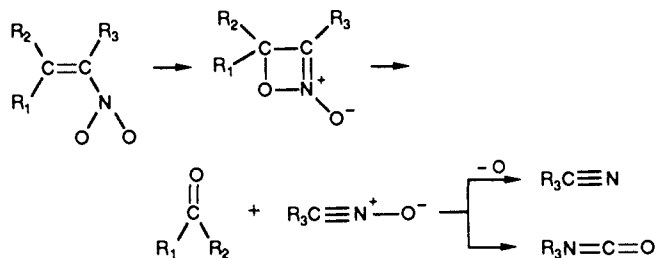
**Mechanism of Decomposition.** Table I shows that the three nitropropenes decomposed into rather different products, indicating the variation in reaction pattern brought about by differences in the position of substitution of the nitro group. However, the following observations can be made. First, 1- and 2-nitropropene both yielded an aldehyde of lower carbon number and a cyanide, implying a common reaction pathway. Secondly, the similarity in the products obtained for 3-nitropropene and 3-propenyl nitrite suggests the possibility that decomposition of the former compound involves its isomerization to the nitrite form as the first step. Since the nitrite decomposed at lower temperatures, it would not be detected at the decomposition temperatures of the nitro compound.

The formations of CH<sub>3</sub>CHO, HNCO, and HCN from 1-nitropropene and CH<sub>3</sub>CCH, CH<sub>3</sub>CN, and HCHO from 2-nitropropene are reaction patterns parallel to those observed by Kinstle et al.<sup>11</sup> They reported that pyrolysis of  $\beta$ -methyl- $\beta$ -nitrostyrene at very low pressures and at 500–600 °C in a flow tube gives benzaldehyde, acetonitrile, and methyl isocyanate as main products. Under similar conditions  $\beta$ -nitrostyrene gives benzaldehyde, a polymer, and hydrogen cyanide as products. A few other nitrostyrenes also give analogous products.<sup>11</sup> It was proposed that the reactions proceed through a cyclic intermediate formed by intramolecular addition of the nitro group to the C=C



**Figure 4.** Spectral changes during pyrolysis of 3-propenyl nitrite: (A) room temperature, (B) 350 °C, and (C) 400 °C. Products: a, NO; b, CO; c, CH<sub>2</sub>CHCHO; d, C<sub>2</sub>H<sub>4</sub>; and e, H<sub>2</sub>O. N<sub>2</sub>O is confirmed through differential vaporization.

double bond, and subsequent decomposition of the intermediate leads to the observed products.<sup>11</sup> The polymer obtained from



$\beta$ -nitrostyrene was attributed to polymerization of isocyanic acid, HNCO, although the acid itself was not detected as a product. A similar four-center transition state was suggested for the decomposition of *N*-nitrocarbamates.<sup>12</sup>

The above mechanism can also account for the changes observed for 1- and 2-nitropropene. For 1-nitropropene, isocyanic acid was observed when the flow tube was packed with quartz wool, while fulminic acid was found in the absence of such packing. Theoretical calculations<sup>13</sup> have shown that among the various CHNO isomers isocyanic acid is the most stable and that the rearrangement of fulminic acid to isocyanic acid is an energetically feasible process. Experimental evidence for such rearrangement has been reported for bulkier nitrile oxides.<sup>14</sup> Our results indicate

(12) White, E. H.; Dolak, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 3790.

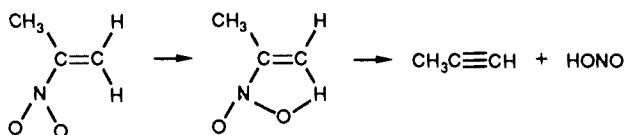
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(14) Grundmann, C.; Datta, S. K. *J. Org. Chem.* **1969**, *34*, 2016.

(11) Kinstle, T. H.; Stam, J. G. *J. Org. Chem.* **1970**, *35*, 1771.

that the fulminic acid–isocyanic acid rearrangement was apparently influenced by heterogeneous conditions.

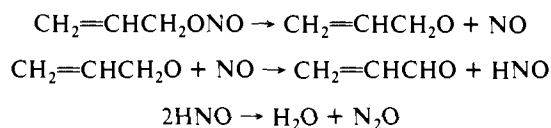
It should be noted that the formation of methyl acetylene occurred only in the pyrolysis of 2-nitropropene, and no acetylene product was formed in the reaction of 1-nitropropene. Likewise, for pyrolysis of nitrostyrenes, methylphenylacetylene was detected as a product from  $\beta$ -methyl- $\beta$ -nitrostyrene, but the corresponding phenylacetylene was not observed for  $\beta$ -nitrostyrene.<sup>11</sup> The reaction probably involves elimination of HNO<sub>2</sub> through a cyclic transition state. It seems that the presence of the adjacent methyl



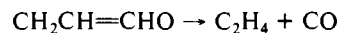
group, which renders the nitro group more electron-rich, is essential to the reaction. A five-center elimination was also proposed for the formation of propene in the thermolysis of 2-nitropropane.<sup>15</sup>

The presence of carbon monoxide in the pyrolysis of 1-nitropropene can at least partly be attributed to secondary reactions such as the decomposition of acetaldehyde.<sup>16</sup>

As pointed out earlier, the decomposition of 3-nitropropene probably involves the conversion to the nitrite form as the first step. Theoretical prediction<sup>17</sup> and experimental evidence<sup>18</sup> for such initial conversion have been reported in the case of the decomposition of nitromethane. As for the decomposition of nitrites, there have been many studies on alkyl nitrites.<sup>3</sup> It has been generally established that alkyl nitrites are a clean source of alkoxy and alkyl radicals. The decomposition reaction normally proceeds through the initial breaking of the CO–NO bond to yield an alkoxy radical and nitric oxide. The alkoxy radical further splits into an alkyl radical and a carbonyl compound of lower carbon number.<sup>3</sup> In the case of 3-propenyl nitrite, the only carbonyl compound found was 3-propenal, which was probably formed through the following steps:



The other two major products C<sub>2</sub>H<sub>4</sub> and CO could come from the decomposition of propenal:



However, when we pyrolyzed a commercial sample of propenal by using the same experimental setup, it was found that although the products were indeed C<sub>2</sub>H<sub>4</sub> and CO, the reaction proceeded only at temperatures higher than 800 °C. It thus appears that the formation of these two products in the pyrolysis of 3-propenyl nitrite must involve some other pathways. Further investigation would be needed for a better understanding of this aspect of the reaction.

Semiempirical molecular orbital calculations have been made for a number of reaction modes for *cis*-1-nitropropene, which was used as a model compound for 2,4,6-trinitrotoluene.<sup>4c</sup> The reactions considered were intramolecular and intermolecular hydrogen transfer from the methyl to the nitro group, intramolecular and intermolecular oxygen insertion from the nitro to the methyl group, nitro–nitrite rearrangement, and nitro group removal. The results show that among these reactions the processes that require low enthalpies of activation are (1) intramolecular hydrogen transfer, (2) nitro–nitrite rearrangement, and (3) nitro group removal.<sup>4c</sup> None of the three favored reactions would lead to the formation of isocyanic or fulminic acid. While it is expected that reaction 1 would take place more readily for *cis*- than for *trans*-1-nitropropene, no such preference is expected for reactions 2 and 3. For *trans*-1-nitropropene, the reaction observed in the present study apparently involves a lower enthalpy of activation than any of the above three reactions, if enthalpy change is the dominant rate-determining factor.

The interpretation of the PE spectra of the nitropropenes in terms of their electronic structure shall be discussed and published in a separate paper later.

**Registry No.** H<sub>2</sub>C=CHCH<sub>2</sub>NO<sub>2</sub>, 625-46-7; O<sub>2</sub>NCH=CHCH<sub>3</sub>, 3156-70-5; H<sub>2</sub>C=C(NO<sub>2</sub>)CH<sub>3</sub>, 4749-28-4.

(15) Smith, T. E.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 1305.

(16) Ho, S. K. *Proc. Roy. Soc. London Ser. A* **1963**, *276*, 278.

(17) Dewar, M. J. S.; Ritchie, J. P. *J. Org. Chem.* **1985**, *50*, 1031.

(18) Wodtke, A. M.; Hints, E. J.; Lee, Y. T. *J. Phys. Chem.* **1986**, *90*, 3549.