# Thermal Decomposition of Nitrate Esters[1]

## Michael A. Hiskey, Kay R. Brower, and Jimmie C. Oxley*

*Department of Chemistry, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801*
*(Received: April 2, 1990; In Final Form: July 17, 1990)*

Rates of thermal decomposition and solvent rate effects have been measured for a series of nitrate esters. The alkoxy radicals formed by homolysis together with some of their further degradation products have been stabilized by hydrogen donation. Internal and external return of nitrogen dioxide have been demonstrated by solvent cage effects and isotope exchange. Radical-stabilizing substituents favor β-scission. Dinitrates in a 1,5 relationship behave as isolated mononitrates. Dinitrates in a 1,3 or 1,4 relationship exhibit intramolecular reactions. Tertiary nitrate esters in diethyl ether undergo elimination rather than homolysis.

## Introduction

The esters of nitric acid have long been used as explosives and propellants, and their thermal decomposition products and kinetics have been studied as a means to evaluate the thermal hazards of these compounds. The thermal decomposition of ethanol nitrate was examined by a number of researchers, and it was proposed that the first, and rate-determining, step was the reversible loss of $NO_2$:[2-5]

$$RCH_2O-NO_2 \leftrightarrow RCH_2O^{\bullet} + NO_2$$
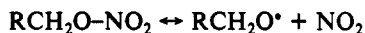
Griffiths, Gilligan, and Gray[6] investigated 2-propanol nitrate pyrolysis and found it exhibited more β-cleavage than primary nitrate esters. It yielded nearly equal amounts of 2-propanol nitrite and acetaldehyde, as well as small amounts of acetone, nitromethane, and methyl nitrite (Figure 1). Homolytic cleavage of the RO–$NO_2$ bond would form the 2-propoxy radical, which could subsequently react with nitric oxide to produce 2-propanol nitrite. It could also eliminate methyl radical to form acetaldehyde and methyl-derived products; or it could be converted to acetone by oxidization or loss of a hydrogen atom.

Dinitrates of butanediol were investigated by Powling and Smith.[7] They found that 1,4-butanediol dinitrate, following cleavage of one $NO_2$ moiety, decomposed to formaldehyde, nitrogen dioxide, and ethylene, whereas 2,3-butanediol dinitrate gave acetaldehyde in place of formaldehyde and ethylene. A similar intramolecular decomposition to gaseous products has been proposed for nitroglycerin.[8] The mechanism of thermolysis of pentaerythritol tetranitrate (PETN) is complex and poorly understood; however, Ng, Field, and Hauser[9] have postulated a mechanism based on time-of-flight mass spectrometric results which involves the formation of the tertiary tris(nitroxymethyl)methyl radical.

In this paper the thermal decomposition rates have been measured and mechanisms proposed for selected primary, secondary, and tertiary mononitrates (1-pentanol nitrate, 3-buten-1-ol nitrate, ethanol nitrate, neopentanol nitrate, 2-phenylethanol nitrate, 2-propanol nitrate, cyclohexanol nitrate, 2-methyl-2-

propanol nitrate, and 2-methyl-2-butanol nitrate). In addition, the mechanisms of thermolysis of the multiple nitrates 1,4-butanediol dinitrate, 1,5-pentanediol dinitrate, 2,2-dimethyl-1,3-propanediol dinitrate, nitropentaglycerin [1,1,1-tris(hydroxymethyl)ethane trinitrate], and pentaerythritol tetranitrate (PETN) have been studied. Figure 2 depicts the nitrate esters.

We have been able to shed light on decomposition pathways of nitrate esters by use of hydrogen-donor solvents capable of capping radical intermediates. This is a convenient method of stabilizing intermediates for identification. It also diverts the oxides of nitrogen from further complicating the course of degradation. The reversibility of $NO_2$ homolysis has been demonstrated by solvent cage effects and isotopic labeling experiments. To shed light on the timing of the loss of $NO_2$ and $CH_2O$ from primary alkanol nitrates, certain nitrate esters leading to stabilized alkyl radicals were designed in order to favor concerted fragmentation. Nitrate esters with multiple nitrate ester moieties were also examined. The effect of α-substitution was studied by using nitrate esters of varying degrees of substitution.

## Experimental Section

1-Pentanol nitrate, ethanol nitrate, neopentanol nitrate, 1,4-butanediol dinitrate, 1,5-pentanediol dinitrate, and 2,2-dimethyl-1,3-propanediol dinitrate were prepared with mixed acid according to the method of Pattison and Brown.[10] The preparation of 3-buten-1-ol nitrate was previously reported by Hiskey and Oxley.[11] Treatment of 2-phenylethyl chloride with $AgNO_3$ formed 2-phenylethanol nitrate in accord with the methods of Pattison and Brown[10] and Baker and Heggs.[12] 2-Propanol nitrate and cyclohexanol nitrate were prepared via acetyl nitrate as described by Soffer, Parotta, and DiDomenico.[13] Tertiary nitrates were made by metathesis or direct esterification.[14] Nitropentaglycerin and PETN were both prepared with 99% $HNO_3$ following the methods of Colson[15] and Davis.[16] Methyl neopentanol-$d_9$ nitrate-^{15}N was made by treating nitric-^{15}N acid with methylneopentanol-$d_9$, prepared from acetone-$d_6$.[1]

The thermal decompositions were performed using 10 wt % solutions of the nitrate esters sealed in glass capillary tubes. The primary, secondary, and multiple nitrates were dissolved in tetralin (1,2,3,4-tetrahydronaphthalene), benzene, toluene, or o-xylene and heated at temperatures ranging from 140 to 225 °C. Tertiary nitrates were thermolyzed in diethyl ether at much lower temperatures. Specific solvents and temperature ranges are listed in

(1) Taken in part from the Ph.D. thesis of M. A. Hiskey.
(2) Phillips, L. *Nature* **1947**, *160*, 753. Phillips, L. *Nature* **1950**, *165*, 564.
(3) Pollard, F. H.; Wyatt, R. M. H.; Marshall, H. S. B. *Nature* **1950**, *165*, 564–565. Pollard, F. H.; Marshall, H. S. B.; Pedler, A. E. *Trans. Faraday Soc.* **1956**, *52*, 59–67.
(4) Levy, J. B. *J. Am. Chem. Soc.* **1954**, *76*, 3254–3257. Levy, J. B. *J. Am. Chem. Soc.* **1954**, *76*, 3790–3793.
(5) Adams, G. K.; Bawn, C. E. H. *Trans. Faraday Soc.* **1949**, *45*, 494–499.
(6) Griffiths, J. F.; Gilligan, M. F.; Gray, P. *Combust. Flame* **1975**, *24*, 11–19. Griffiths, J. F.; Gilligan, M. F.; Gray, P. *Combust. Flame* **1976**, *26*, 385–393.
(7) Powling, J.; Smith, W. A. W. *Combust. Flame* **1958**, *2*, 157–170.
(8) Waring, C. E.; Krastins, G. *J. Phys. Chem.* **1970**, *74*, 999–1006.
(9) Ng, W. L.; Field, J. E.; Hauser, H. M. *J. Chem. Soc., Perkin Trans.* **1976**, *6*, 637–639.

(10) Pattison, F. L. M.; Brown, G. M. *Can. J. Chem.* **1956**, *34*, 880–883.
(11) Hiskey, M. A.; Oxley, J. C. *J. Energ. Mater.* **1989**, *7*(3), 199–205.
(12) Baker, J. W.; Heggs, T. G. *Chem. Ind.* **1954**, 464.
(13) Soffer, L. M.; Parotta, E. W.; DiDomenico, J. *J. Am. Chem. Soc.* **1952**, *74*, 5302.
(14) Michael, A.; Carlson, G. H. *J. Am. Chem. Soc.* **1954**, *76*, 4522.
(15) Colson, R. *Mem. Poudres* **1948**, *30*, 43–58.
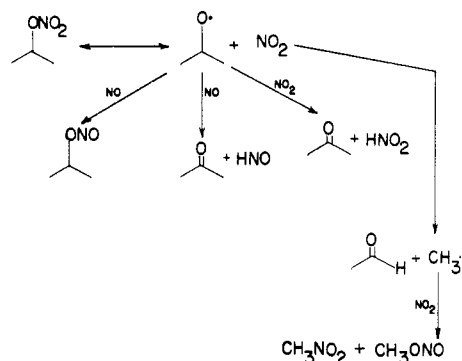(16) Davis, T. L. *The Chemistry of Powder and Explosives*; Angriff: Hollywood, CA; 1943; p 279.

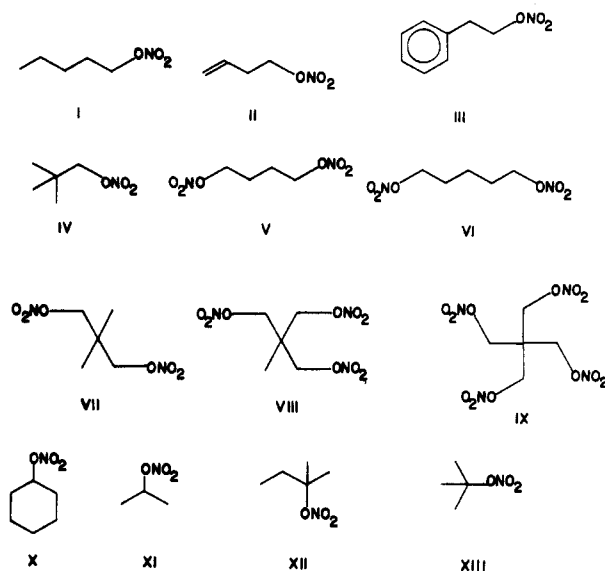**Figure 1.** Thermal decomposition of 2-propanol nitrate (ref 6).



**Figure 2.** Structures of the nitrate esters studied in this work: (I) 1-pentanol nitrate; (II) 3-buten-1-ol nitrate; (III) 2-phenylethanol nitrate; (IV) neopentanol nitrate; (V) 1,4-butanediol dinitrate; (VI) 1,5-pentanediol dinitrate; (VII) 2,2-dimethyl-1,3-propanediol dinitrate; (VIII) nitropentaglycerin; (IX) pentaerythritol tetranitrate; (X) cyclohexanol nitrate; (XI) 2-propanol nitrate; (XII) 2-methyl-2-butanol nitrate; (XIII) tert-butyl nitrate.

Table I. Activation volume was measured by methods previously described[17] except that a mercury seal was used to isolate the reaction mixture from the pressurizing fluid. Gas-phase decompositions were performed in flame-sealed test tubes approximately 1.3 mm in diameter (i.d.) and 90 mm long with about 0.1 g of reactant. That the reaction was gas phase was determined by visual observation of the partially decomposed sample; no liquid was visible when the sample was first removed from the heated bath.

Kinetics of thermal decomposition were followed by gas chromatography [a Tracor 565 equipped with a 30-m SPB-5 (0.25 mm i.d.) capillary column] using a flame-ionization detector and the reaction solvent as the internal standard. Product identification was accomplished by gas chromatography (Hewlett-Packard 5890) with mass-selective detector (GC-MS) or a Perkin Elmer 1700 Fourier transform infrared (FTIR) spectrophotometer. A commercial package (Perkin Elmer Model 1700) was used to interface the Hewlett-Packard gas chromatograph with the Perkin Elmer infrared spectrometer to perform GC-FTIR experiments. Products were identified by comparison of spectra and retention times to those of authentic samples. No rigorous attempt was made to quantify the products of reaction. Percentages reported for products are relative to each other, based on GC-MS total ion currents; typically, reaction products were determined on samples decomposed for one to three half-lives.
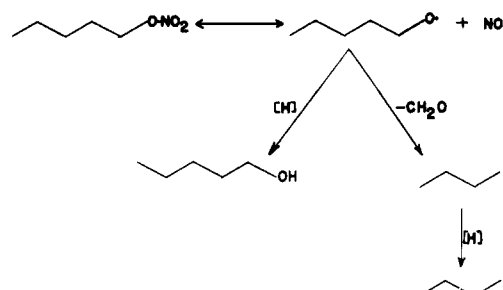
(17) Pajak, J.; Brower, K. R. J. *Energy Fuels* **1987**, *1*, 363–366.



**Figure 3.** Thermal decomposition of 1-pentanol nitrate.

## Results and Discussion

Decomposition of all the nitrate esters followed a first-order rate law to a high degree of reaction ($\sim$90%). This is ascribed to homolytic cleavage of the $RO-NO_2$ linkage as the rate-determining step in the thermal decomposition. Reaction in solution was not faster than in the vapor state, and it seems probable that the solvent played no direct chemical role in the rate-determining step. Activation energies and preexponential factors are tabulated in Table I. Only those products derived from the nitrate ester are described and discussed in detail. Oxidation products of the solvent were also observed. For example, tetralin-based reaction products detectable by GC-MS were naphthalene, 3,4-dihydro-1(2H)-naphthalenone, and 1,2,3,4-tetrahydro-1-naphthol.

*Reversibility of NO₂ Loss.* It has been postulated that the first step in nitrate ester thermolysis involves reversible cleavage of the $RO-NO_2$ bond. This hypothesis is based on the observation that $NO_2$ added to the gas-phase thermolysis of ethanol nitrate retarded the decomposition.[2-4] We have shown by two methods that the cleavage is reversible. The first involves the effect of solvent viscosity on the rate of thermolysis of pentanol and neopentanol nitrate. In Table II, the solvents used in thermolysis are listed in order of decreasing viscosity. It is evident that a significant increase in the rate of reaction accompanies decrease in solvent viscosity. This increase in rate can be attributed to faster separation of RO• and $NO_2$ by diffusion from the solvent cage.

The reversibility of homolysis was further demonstrated by use of an isotopic labeling technique. A small amount of ¹⁵N-labeled ethanol nitrate was sealed in a test tube with $NO_2$ gas and heated at 175 °C for 30 min. The contents of the tube were then examined by GC-MS. The condensate contained nitromethane, methanol nitrite, and small amounts of acetic acid and ethanol nitrate. Approximately 1/3 of the unreacted ethanol nitrate retained the original ¹⁵N label [$m/z = 77$ ($CH_2\!=\!O\!-\!{}^{15}NO_2)^+$], and 2/3 was unlabeled. This showed that exchange of the $NO_2$ group is faster than subsequent decomposition of the ethoxy radical.

*Timing of NO₂ and CH₂O Loss.* To test whether or not the loss of $NO_2$ and $CH_2O$ can be concerted, a number of primary nitrate esters were examined, and certain ones leading to stabilized alkyl radicals were designed in order to favor concerted fragmentation.

*1-Pentanol Nitrate (I).* 1-Pentanol nitrate was chosen as a representative primary nitrate ester. 1-Pentanol (98%) and n-butane (2%) were the only two identifiable products of complete thermolysis in tetralin. These products suggested the reaction mechanism shown in Figure 3. The mechanism involves reversible formation of the n-pentoxy radical. The n-pentoxy radical abstracts hydrogen from the solvent and concurrently undergoes β-scission to yield butane by way of butyl radical. An activation energy of 168.7 kJ/mol and a frequency factor of $9.31 \times 10^{15}$ s⁻¹ were found. According to transition-state theory, the entropy of activation is 50.8 kJ/(mol·K). This high positive entropy of activation is typical of homolytic first-order dissociation and is comparable to Levy's value for ethanol nitrate decomposition of 62.8 J/(mol·K).[4] The volume of activation determined for 1-pentanol nitrate in a tetralin solution (10 wt %) at 160 °C was +17 ± 3 mL. This value is outside the usual range (3–10 mL) for homolytic reactions at normal temperatures but is appropriate for reaction at 160 °C. Homolysis of bibenzyl at 400 °C has an

TABLE I: Thermolysis Conditions, Activation Energies, Preexponential Factors, and Products for a Variety of Nitrate Esters

| nitrate esters | thermolysis solvent | temp range, °C | activn energy, kJ/mol | log $A$, $s^{-1}$ | products |
|---|---|---|---|---|---|
| 1-pentanol nitrate | tetralin | 154–194 | 169 | 16.0 | |
| neopentanol nitrate | tetralin | 154–194 | 166 | 15.8 | |
| neopentanol nitrate | gas | 175 | | | |
| 3-buten-1-ol nitrate | tetralin, toluene, o-xylene | 150–195 | 159 | 15.0 | |
| phenylethanol nitrate | tetralin | 150–195 | 149 | 13.7 | |
| phenylethanol nitrate | toluene, o-xylene | 150–195 | | | |
| 1,4-butanediol dinitrate | tetralin | 140–190 | 189 | 18.8 | |
| 1,5-pentanediol dinitrate | tetralin | 140–190 | 199 | 20.0 | |
| 2,2-dimethyl-1,3-propanediol dinitrate | tetralin | 140–190 | 139 | 13.4 | |
| nitropentaglycerin | benzene | 190 | | | |
| pentaerythritol tetranitrate | benzene | 185 | 165[21] | 16.1[21] | |
| cyclohexanol nitrate | tetralin | 155–195 | 180 | 17.4 | |
| 2-propanol nitrate | tetralin | 155–195 | 191 | 15.2 | |
| 2-methyl-2-butanol nitrate | ether | 70–120 | 110 | 13.4 | |
| tert-butyl nitrate | ether | 70–120 | 127 | 15.2 | |



TABLE II: Rate Constants of Thermolysis of Neopentanol and 1-Pentanol Nitrate in a Variety of Solvents

| | | rate constants × $10^4$, $s^{-1}$ | |
|---|---|---|---|
| solvent | viscosity,[a] cP | 1-pentanol nitrate, 174 °C | neopentanol nitrate, 175 °C |
| triacetin | 28 | 1.29 | 3.83 |
| 1-pentanol | 4 | 2.54 | |
| 1-butanol | 4 | | 4.70 |
| decalin | 3 | 2.28 | 5.59 |
| tetralin | 3 | 2.35 | 4.74 |
| cyclohexane | 1 | 3.34 | 4.95 |
| cyclopentane | 0.5 | 4.77 | 7.35 |
| cyclohexane (gas phase) | ~0 | 7.60 | 15.5 |

[a] At 25 °C.

activation volume of +31 mL, which is attributed to the great increase of free volume with temperature.[18]

*3-Buten-1-ol Nitrate (II).* In an effort to encourage β-cleavage, several nitrate esters, which would possibly yield stabilized alkyl radicals upon β-scission, were thermolyzed. The first of these was 3-buten-1-ol nitrate, in which β-cleavage would yield the allyl

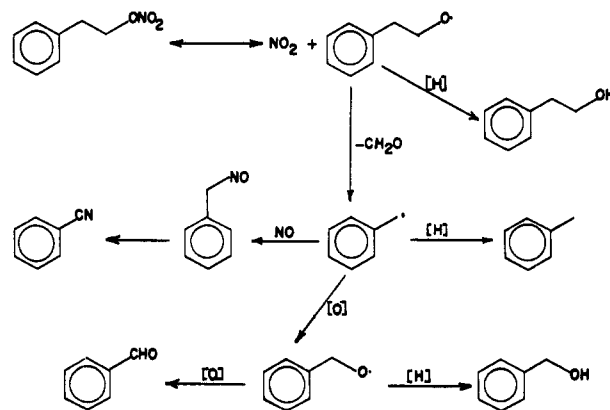(18) Brower, K. R. *J. Org. Chem.* **1980**, *45*, 1004–1008.



Figure 4. Thermal decomposition of 2-phenylethanol nitrate in tetralin.

radical. However, neither products derived from the allyl radical nor propylene itself could be detected by GC-MS. Evidently the fate of the alkoxy radical is not affected by the double bond at the end of the chain. The only product obtained was 3-buten-1-ol.

*2-Phenylethanol Nitrate (III).* 2-Phenylethanol nitrate was also designed to produce a stabilized alkyl radical upon β-scission. But upon thermolysis in tetralin, the parent alcohol, 2-phenyl-ethanol (30%), was again a significant product. Lesser amounts
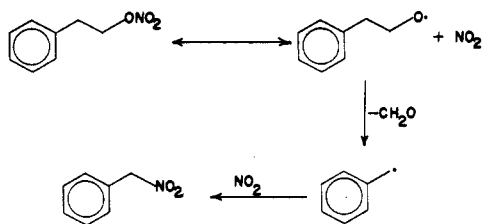
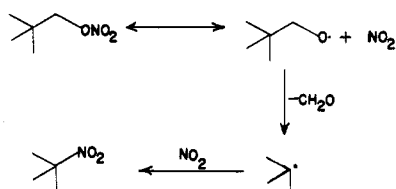**Figure 5.** Thermal decomposition of 2-phenylethanol nitrate in toluene or *o*-xylene.



**Figure 6.** Thermal decomposition of neopentanol nitrate.

of β-scission products, benzonitrile (25%), benzaldehyde (25%), benzyl alcohol (20%), and toluene (1%), were also produced. The scheme depicted in Figure 4 is proposed.

The formation of parent alcohols in the thermolyses of 1-pentanol nitrate, 3-buten-1-ol nitrate, and 2-phenylethanol nitrate show that in these thermolyses $NO_2$ and $CH_2O$ loss is not concerted. However, when 2-phenylethanol nitrate was decomposed in thermolysis solvents less reducing than tetralin, such as toluene or *o*-xylene, formaldehyde was lost faster than the alkoxy radical could scavenge hydrogen. The resulting alkyl radical scavenged $NO_2$ to form phenylnitromethane (55%) (Figure 5). Small amounts of benzonitrile (25%) and benzaldehyde (20%) were also detected.

*Neopentanol Nitrate (IV).* In a variety of solvents neopentanol nitrate yielded almost exclusively the tertiary nitroalkane, 2-methyl-2-nitropropane. Occasionally, small amounts (<1%) of neopentanol were observed. 2-Methyl-2-nitropropane undoubtedly arose by rapid β-scission of the neopentoxy radical yielding the more stable *tert*-butyl radical. The *tert*-butyl radical then combined with external $NO_2$ to yield the nitroalkane by the mechanism shown in Figure 6. In support of this mechanism, formaldehyde was detected in the GC-FTIR scan of the thermolysis mixture. Since no neopentanol was found, it appears that the neopentoxy radical losses formaldehyde much more rapidly than the pentoxy, butenoxy, or phenylethoxy radicals. This is undoubtedly due to the stability of the *tert*-butyl radical.

Since 2-methyl-2-nitropropane was almost the only product of neopentanol nitrate thermolysis, it initially appeared that this reaction might involve the concerted breaking of the nitrogen-oxygen and the carbon–carbon bond. However, the presence of a small amount of neopentanol in the solution thermolysis and trimethylacetaldehyde in the gas-phase thermolysis showed the neopentoxy radical had a brief existence. Furthermore, the solvent viscosity effect also argues against a concerted fragmentation because such fragmentation would not be reversible and thus would be insensitive to solvent cage effects.

The timing of the thermolysis of neopentyl nitrate was further tested by means of a crossover experiment. A mixture of unlabeled neopentanol nitrate and methylneopentanol-$d_9$ nitrate-$^{15}N$ was heated together in tetralin. GC-MS examination of the products indicated that almost complete scrambling of both labels produced approximately equal amounts of each isotopomer of 2-methyl-2-nitropropane (Figure 7). This showed that the *tert*-butyl radical did not exclusively combine with the $NO_2$ derived from the same parent neopentanol nitrate; the radical has a long enough lifetime to migrate and combine randomly with $NO_2$ in solution.

The gas-phase decomposition of neopentyl nitrate (10%) in cyclohexane at 175 °C produced a variety of products not found in the condensed-phase thermolysis, including small amounts of trimethylacetaldehyde, 2-methyl-2-propanol nitrite, 2,2,3,3-tetramethylbutane, 2-methyl-2-butanol nitrate, and formaldehyde,
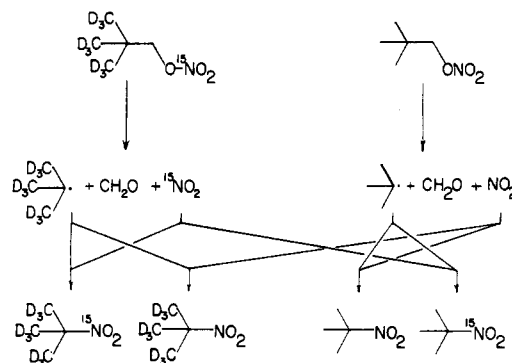


**Figure 7.** Crossover experiment with neopentanol nitrate and methylneopentanol-$d_9$ nitrate-$^{15}N$.
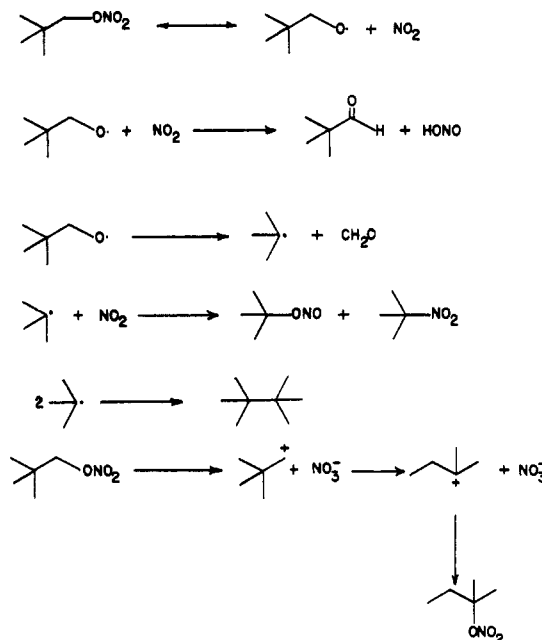


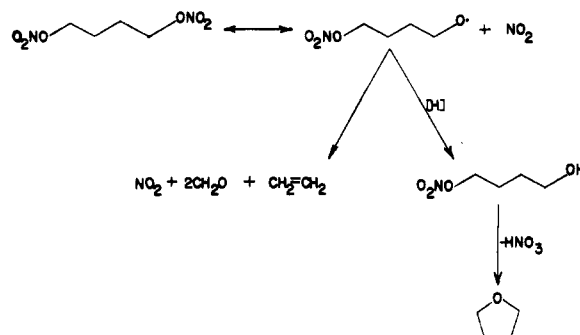**Figure 8.** Gas-phase thermal decomposition of neopentanol nitrate.



**Figure 9.** Thermal decomposition of 1,4-butanediol dinitrate.

in addition to the major product, 2-methyl-2-nitropropane. Apparently, in the gas phase, the radicals have longer lifetimes than in solution (Figure 8).

*Multiple Nitrate Esters.* The question of the timing of the intramolecular homolyses becomes more interesting when several nitrate ester moieties are contained within the same molecule.

*1,4-Butanediol Dinitrate (V).* Two products resulted from the thermolysis of 1,4-butanediol dinitrate; the major one was ethylene. The thermal decomposition mechanism proposed by Powling and Smith would account for this product.[7] However, the formation of a small amount of tetrahydrofuran (30%) suggests that molecular fragmentation may be stepwise rather than concerted. Loss of $NO_2$ produces an alkoxy nitrate radical, which can decompose to ethylene, $NO_2$, and formaldehyde or be reduced to the nitrate alcohol, which then ring-closes to tetrahydrofuran (Figure 9).
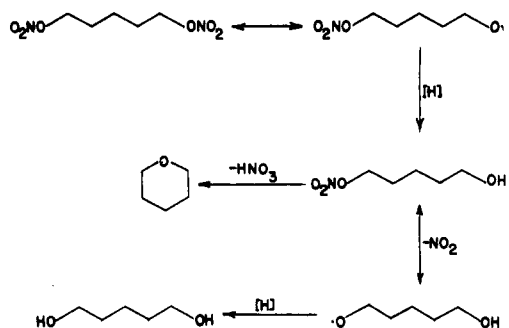
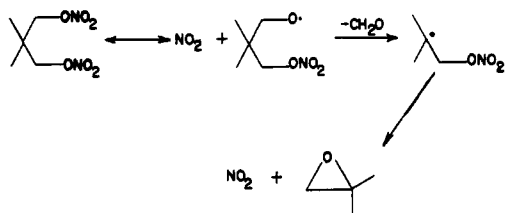**Figure 10.** Thermal decomposition of 1,5-pentanediol dinitrate.



**Figure 11.** Thermal decomposition of 2,2-dimethyl-1,3-propanediol dinitrate.
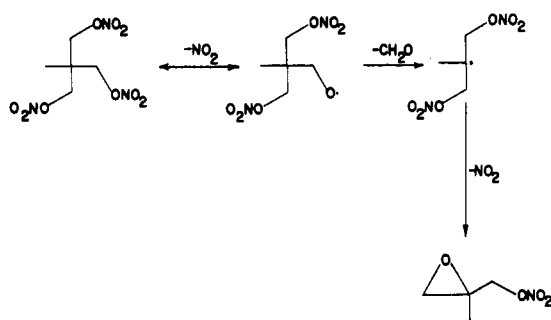


**Figure 12.** Thermal decomposition of nitropentaglycerin.



**Figure 13.** Thermal decomposition of PETN.



**Figure 14.** Thermal decomposition of cyclohexanol nitrate.

*1,5-Pentanediol Dinitrate (VI).* 1,5-Pentanediol dinitrate yielded two products—the parent diol, the major product, and a small amount of tetrahydropyran (5%). The thermal decomposition pathway was stepwise reduction of each alkoxy radical as illustrated in Figure 10. The presence of the additional methylene group (compared to 1,4-butanediol dinitrate) completely suppressed the formation of olefins.

*2,2-Dimethyl-1,3-propanediol Dinitrate (VII).* Upon thermolysis in tetralin, 2,2-dimethyl-1,3-propanediol dinitrate yielded a single product, 2,2-dimethyloxirane. A plausible mechanism is shown in Figure 11. This mechanism is somewhat similar to that of neopentanol nitrate in that, after loss of $NO_2$, rapid $\beta$-cleavage yields the more stable tertiary carbon-centered radical. At this point, rather than combining with external $NO_2$, the radical loses nitrogen dioxide and cyclizes.

*Nitropentaglycerin (VIII) and Pentaerythritol Tetranitrate (IX).* Nitropentaglycerin [1,1,1-tris(hydroxymethyl)ethane trinitrate] decomposed thermally in benzene to yield a single condensed-phase organic product 2-methyl-2-nitroxymethyloxirane, identified by GC-MS. This product, a substituted oxirane, would have been predicted by analogy with the single product derived from 2,2-dimethyl-1,3-propanediol dinitrate thermolysis. In this case, however, the additional nitrate ester present in nitropentaglycerin was retained to yield 2-methyl-2-nitroxymethyloxirane. The proposed mechanism is illustrated in Figure 12.

The production of the oxirane as the only thermolysis product shows that decomposition of an alkoxy radical to an alkyl radical is favored if a stabilizing structural feature is present, as in *tert*-butyl radical. If this effect applies to pentaerythritol tetranitrate (PETN), it should undergo a double ring closure to yield a spiro-ketal as shown in Figure 13. However, a brown-yellow, viscous liquid with infrared absorbances at 1725 and 1100–1025 cm$^{-1}$ was the only condensed-phase product obtained from
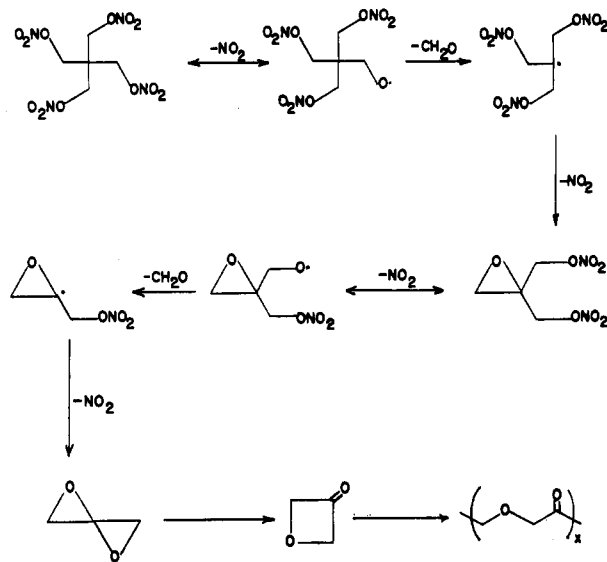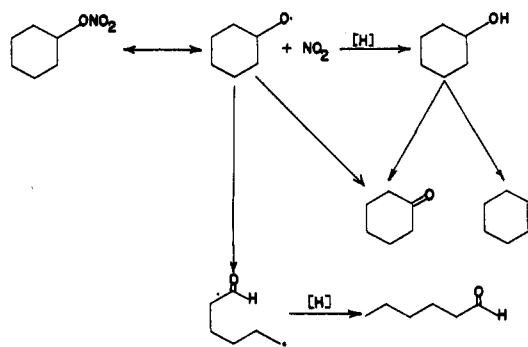
thermolysis of PETN in benzene. The literature revealed that the proposed spiro-ketal would ring-expand to 3-oxetanone.[19] In turn, 3-oxetanone would readily polymerize under the experimental conditions to the polyketo oxetane (Figure 13).[20] This polymer is described as a viscous liquid of low degree of polymerization, with a carbonyl absorbance at 1724 cm$^{-1}$ as well as a broad ether absorbance at 1111–1024 cm$^{-1}$. These absorbances do not prove PETN decomposes in this manner but strongly suggest this scheme.

*The Effect of α-Carbon Substitution.* We have seen that 1-alkanol nitrates eliminate formaldehyde to an extent dependent on the stability of the resulting alkyl radical. It remains to be seen whether secondary and tertiary nitrates will show analogous behavior with corresponding tendencies to eliminate aldehyde or ketone.

*Secondary Nitrate Esters: Cyclohexanol Nitrate (X) and 2-Propanol Nitrate (XI).* Thermal decomposition of cyclohexanol nitrate resulted in formation of the cyclohexyloxy radical. The products, cyclohexanol (70%), cyclohexanone (10%), and cyclohexene (10%), can be traced to it (Figure 14). A small amount (<10%) of 1-hexanal was also found by GC-MS. Ring cleavage of the cyclohexyloxy radical produced the open-chain aldehyde radical, which abstracted hydrogen from the solvent to form 1-hexanal. 2-Propanol nitrate has been shown to undergo $\beta$-scission and eliminate acetaldehyde in the gas phase in a fashion similar to ring opening and aldehyde formation by cyclohexanol nitrate.[6] However, we found that thermolysis of 2-propanol nitrate in tetralin yielded 2-propanol and small amounts of propylene. Both of the secondary nitrate esters give alkoxy radicals, which

(19) Crandall, J. K.; Machleder, W. H.; Sojka, S. A. *J. Org. Chem.* **1973**, *38*, 1149.

(20) Woitowicz, J. A.; Polak, R. J. *J. Org. Chem.* **1973**, *38*, 2061–2066.
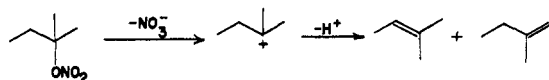
**Figure 15.** Thermal decomposition of 2-methyl-2-butanol nitrate.

abstract hydrogen from the solvent more readily than they undergo $\beta$-scission.

*Tertiary Nitrate Esters: 2-Methyl-2-butanol Nitrate (XII) and 2-Methyl-2-propanol Nitrate (XIII).* Tertiary nitrates deviated from the preceding pattern. Since both 2-methyl-2-butanol nitrate and 2-methyl-2-propanol nitrate exhibited low thermal stability, they were not distilled from the reaction solvent diethyl ether. Thermolysis of 2-methyl-2-butanol nitrate in diethyl ether over a temperature range of 70–110 °C gave nitric acid and the isomeric pentenes 2-methyl-2-butene and 2-methyl-1-butene with the more substituted olefin favored. The activation energy (127.2 kJ/mol) is about 42 kJ/mol lower than that found for primary and secondary nitrates (Table I). This lower activation energy signals a change in mechanism. The tertiary nitrate esters could eliminate nitric acid by a cyclic mechanism (E1) similar to that of the well-known acetate ester pyrolysis, Cope elimination, and Chugaev reaction; but in such cases, the product distribution usually follows the Hofmann rule. In this case, it appears the Saytzeff rule applies since 2-methyl-2-butene is preferentially formed (Figure 15). 2-Methyl-2-propanol nitrate also eliminates nitric acid and yields isobutylene as the only organic product.

*Kinetics.* Table I lists the activation energies and frequency factors for the thermal decomposition of the nitrate esters. The decomposition of all the primary and secondary nitrate esters have approximately the same activation energy (170 kJ/mol). The tertiary nitrates in diethyl ether have activation energies which are much lower; this has been attributed to an E1 mechanism operating in their decomposition. Among the primary and secondary nitrate esters, there is no dependence of the activation energy on the number of nitrate ester moieties, the degree of substitution on the $\alpha$- or $\beta$-carbon, or the relative placement of the nitrate esters. This is reasonable since the rate-determining step is homolytic cleavage of the RO–NO$_2$ bond of the ester. The chemistry occurring after this cleavage is highly dependent on the number of nitrate esters originally present, the substitution on the $\alpha$- and $\beta$-carbon, and the placement of the original nitrate ester groups relative to each other. The frequency factors of 1,4-butanediol dinitrate and 1,5-pentanediol dinitrate are relatively high compared to other eliminations. Robertson observed this phenomenon for nitrate esters and attributed it to chain reactions.[21] However, in the case of these high boiling dinitrates, it is more likely due to experimental error resulting from some decomposition in the gas chromatographic column.

**Conclusions**

From this thermal decomposition study, three general principles can be drawn.

1. The rate-determining step in nitrate ester thermolysis is usually homolytic cleavage of the RO–NO$_2$ bond, but tertiary nitrates undergo E1 reaction on heating in diethyl ether.

2. The presence of radical-stabilizing substituents on the $\beta$-carbon determines the rate and extent of $\beta$-scission and elimination of formaldehyde.

3. In compounds containing more than one nitrate ester, the orientation has a marked effect on the reaction products. The thermolysis of compounds of this sort results in ring closure or sequential elimination of NO$_2$ and CH$_2$O if the nitrate esters are in close proximity.

(21) Robertson, A. J. B. *J. Soc. Chem. Ind.* **1948**, *67*, 221–224.

# Low-Temperature Absolute Rate Constants for the Reaction of Atomic Sodium with Ozone and Nitrous Oxide

## D. R. Worsnop,* M. S. Zahniser, and C. E. Kolb

*Center for Chemical and Environmental Physics, Aerodyne Research, Inc., 45 Manning Road, Billerica, Massachusetts 01821 (Received: May 23, 1990; In Final Form: December 3, 1990)*

The bimolecular reaction between atomic sodium and ozone has been measured between 293 and 216 K, yielding a rate constant of $(7.9 \pm 2.1) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 293 K with a temperature dependence given by $(1.6 \pm 0.7) \times 10^{-9}$ exp$[-(195 \pm 110)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The bimolecular rate constant for the reaction of atomic sodium with nitrous oxide has also been measured at 294 and 218 K, yielding values of $(1.1 \pm 0.3) \times 10^{-12}$ and $(2.1 \pm 0.5) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. These values compare well with recent low-temperature measurements from other laboratories. The kinetic results for the Na + O$_3$ reaction are compared with earlier results and discussed in terms of their impact on the atomic sodium nightglow in Earth's mesosphere.

**Introduction**

The reaction between atomic sodium and gaseous ozone is a key process in controlling the structure of the atomic sodium layer produced by meteor ablation in Earth's mesosphere[1-6] and is the initial step for both Chapman's 1939 model of the atomic sodium nightglow[7-11] and his 1955 explanation of long-lived visible meteor trails.[12-15]

(1) Liu, S. C.; Reid, G. C. *Geophys. Res. Lett.* **1979**, *6*, 283.

(2) Kirchhoff, V. W. J. H.; Clemesha, B. R.; Simonich, D. M. *J. Geophys. Res.* **1989**, *86*, 6892.

(3) Kirchhoff, V. W. J. H.; Clemesha, B. R. *J. Geophys. Res.* **1983**, *88*, 442.

(4) Sze, N. D.; Ko, M. K. W.; Swider, W.; Murad, E. *Geophys. Res. Lett.* **1982**, *9*, 1187.

(5) Thomas, L.; Isherwood, M. C.; Bowman, M. R. *J. Atmos. Terr. Phys.* **1983**, *45*, 587.

(6) Swider, W. *Planet. Space Sci.* **1986**, *34*, 603.

(7) Chapman, S. *Astrophys. J.* **1939**, *90*, 309.

(8) Clemesha, B. R.; Kirchhoff, V. W. J. H.; Simonich, D. M. *J. Geophys. Res.* **1978**, *83*, 2499.

(9) Kirchhoff, V. W. J. H.; Clemesha, B. R.; Simonich, D. M. *J. Geophys. Res.* **1979**, *84*, 1323.

(10) Swider, W. *J. Geophys. Res.* **1986**, *91*, 6742.

(11) Newman, A. L. *J. Geophys. Res.* **1988**, *93*, 4067.

(12) Chapman, S. In *Aurora and Airglow*; Armstrong, E. B., Dalgarno, A., Eds.; Pergamon: Oxford, U.K., 1955; p 204.

(13) Baggaley, W. J. *Nature (London)* **1975**, *257*, 567.

(14) Baggaley, W. J. *Nature (London)* **1977**, *267*, 376.