tity log $(K_\infty - K_t)$, where K_∞ and K_t are the reciprocals of the observed resistance at times ∞ and t, respectively, against t was made. The half-life was read from the graph. For the conductivity curves an accurately weighed amount of the acyl halide was added from a weight buret to the dimethylformamide (500 ml.) with stirring. The readings changed instantly to their final values except in the case of benzoyl chloride, where 1–2 minutes was required.

Qualitative Kinetics Measurements.—The experiments involving solutions of sodium perchlorate in the amides were carried out with 5–10% solutions of the salt. To 5–10 ml. of such a solution was added 2–4 drops of acid chloride and the rate of appearance of a white precipitate noted. The results are as follows (Table I).

TABLE I

Rapid denotes precipitation in <5 minutes; moderate, 5–30 minutes; slow > 30 minutes.

Acyl chloride	Dimethylformamide	Diethylcyanamide	Dimethylacetamide	N-Methylpyrrolidone	N-Methylacetamide
Benzoyl chloride	Rapid	No reacn.	Rapid	Slow	Slow
Ethyl chloroformate	Moderate	No reacn.	Rapid	Slow	Slow
Benzenesulfonyl chloride	Moderate	No reacn.	Mod.	Slow	Slow
Dimethylcarbamyl chloride	Very slow	......	...	..	..

A 5–10% solution of sodium perchlorate in acetonitrile was prepared, and to 10–15 ml. of this solution was added 2–4 drops each of acid halide and amide. The results for benzoyl chloride were as follows: dimethylformamide, formamide and N-methylpyrrolidone, rapid; N-vinylpyrrolidone and N-methylformanilide, moderate; dimethyl methanesulfonamide, tetramethylsulfamide, diethylcyanamide and hexamethylphosphoramide, negligibly slow.

Synthetic Experiments.—To 15 ml. of pure dimethylformamide was added 10 ml. of benzoyl bromide. The mixture solidified almost completely. It was filtered and washed with anhydrous ether under a nitrogen blanket. The precipitate weighed 12.67 g.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: N, 5.43. Found: N, 4.59, 4.58.

This material, 4.0 g., was slurried with 46 ml. of pure acetonitrile, in which it did not completely dissolve. Heat was absorbed. To this was added a solution of 2.88 g. of aniline in 46 ml. of acetonitrile. An exothermic reaction occurred and the solution became clear. It was evaporated overnight under a jet of nitrogen. The solid residue was taken up in 10 ml. of water, triturated, and filtered. It was washed twice more with 5-ml. portions of water and air-dried. There was obtained 2.59 g. (84.8%) of benzanilide, m.p. 158°.

Reaction of the crystalline salt with water was carried out by mixing the former, 2.0 g., in 10 ml. of water. After several hours at room temperature, the mixture was filtered and the precipitate was air-dried. There was obtained 0.75 g. (79.3%) of benzoic acid, m.p. 115–116°.

The preparation of acetyl bromide–dimethylformamide was carried out by slowly adding the amide (5 ml.) to the acid bromide (15 ml.) with chilling in ice under a nitrogen blanket. The adduct crystallized nicely from the excess acid bromide and was filtered and rinsed with ether.

Anal. Calcd. for $C_5H_{10}O_2NBr$: N, 7.15. Found: N, 7.31, 7.56.

Under these conditions the mixture remains colorless. If, however, the preparation is performed by adding the acid bromide to excess amide, the mixture rapidly turns a deep red color. This does not appear to be bromine, since pouring an aliquot into water and extracting with carbon tetrachloride does not extract the color. Styrene fails to decolorize the solution. The nature of the colored species is unknown.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Thermal Decomposition of Diol Dinitrites. II

BY LESTER P. KUHN, ROBERT WRIGHT AND LOUIS DEANGELIS

RECEIVED DECEMBER 15, 1955

The vapor phase decomposition of compounds having the formula $R_2C(ONO)(CH_2)_nC(ONO)R_2$, where R is H and methyl, and n is 1 through 4 has been studied. On the basis of the products formed, mechanisms have been proposed which have as their first step the cleavage of one nitrite group to form an alkoxy radical and nitric oxide. The fate of the unstable alkoxy radical depends upon the value of n and to a lesser extent upon whether R is H or methyl. When n is 1 and R is H and methyl, the alkoxy radical decomposes to olefin, aldehyde and nitrogen dioxide. When n is 2 and R is methyl, the radical yields ethylene, 2 moles of acetone and nitric oxide. When R is H and n is 2, 3 or 4 no cleavage of C–C bonds takes place. Instead a hydrogen transfer takes place yielding nitric oxide and a hydroxyaldehyde (α-hydrogen transfer) or nitrogen dioxide and hydroxyolefin (β-hydrogen transfer). The nature of the product requires that the hydrogen transfer be intra- rather than intermolecular which precludes the participation of nitric oxide as a hydrogen acceptor. The liquid phase decomposition of propane-1,3-diol dinitrite in paraffin oil solution differs from the gas phase reaction. The initially formed alkoxy radical does not undergo C–C cleavage. It abstracts a hydrogen atom from the solvent and the final product is propane-1,3-diol.

This is a continuation of Part I of this series in which the decomposition of various 1,2-diol dinitrites was described.[1] The present work is concerned with the vapor phase decomposition of compounds having the formula $R_2C(ONO)(CH_2)_nC(ONO)R_2$, where R is H or methyl and n is 1, 2, 3 and 4.

Experimental

All but one of the diol dinitrites were prepared by reaction of the diol with aqueous nitrous acid.[2] Two moles of 6 N hydrochloric acid were added slowly with mechanical stirring to an aqueous solution containing 1 mole of diol and 2.2 moles of sodium nitrite at 0°. Stirring was continued for 15 minutes after all the acid was added and the reaction mixture was poured into a separatory funnel. The aqueous layer was removed and the nitrite ester was washed with a 5% solution of sodium carbonate, dried over calcium chloride, and distilled. The dinitrite of 2,5-dimethyl-2,5-hexanediol was prepared by the addition of 2 moles of NOCl to an ether solution containing 1 mole of diol and 2 moles of pyridine at 0°. The ether solution was filtered, washed with dilute acid, and 5% sodium carbonate, and dried over calcium chloride. The product was purified by distillation. The physical constants and analytical data are given in Table I.

The vapor phase decompositions were performed by passing the vapor of the dinitrite in a stream of nitrogen through

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[1] L. P. Kuhn and L. DeAngelis, THIS JOURNAL, **76**, 328 (1954).

[2] L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," 24th edition, The Macmillan Co., New York, N. Y., 1943, p. 147.

TABLE I

PROPERTIES OF DINITRITES

Diol dinitrite	B.p. °C.	B.p. Mm.	d^{25}	n^{25}	Analyses, % Observed C	Observed H	Observed N	Calculated C	Calculated H	Calculated N
Propane-1,3-	46	42	1.130	1.3951	26.6	4.36	20.7	26.7	4.48	20.8
Butane-1,3-	52	41	1.0754	1.3968	32.7	5.51	18.7	32.4	5.4	18.9
Pentane-2,4-	56	33	1.0416	1.3978	37.0	6.08	17.1	37.0	6.15	17.2
Butane-1,4-	70	44	1.1659	1.4028	32.46	5.50	18.82	32.43	5.41	18.92
Hexane-2,5-	80	36	1.0296	1.4105	41.04	6.89	15.86	40.91	6.82	15.91
2,5-Dimethylhexane-2,5-	58	2	1.0077	1.4231	47.09	7.88	13.75	47.06	7.84	13.75
Pentane-1,5-	73	27	1.0706	1.4150	37.46	5.82	16.89	37.04	6.17	17.28
Hexane-1,6-	30	0.5	1.0449	1.4143	40.92	7.00	15.95	40.91	6.82	15.91

a reaction chamber which was held at a temperature of 300 to 320° in the manner previously described.[1] The residence time was about 10 seconds.

The analyses were carried out in the following manner. Nitrogen dioxide was determined spectrophotometrically at 4000 Å. The combined nitric oxide and nitrogen dioxide was determined by mixing a sample of gas with excess oxygen, which converts the nitric oxide to nitrogen dioxide, and analyzing for total nitrogen dioxide as before. Ethylene was measured by the intensity of its infrared band at 11.15 μ. For propylene the band at 11.0 and for carbon dioxide the band at 4.3 μ were used. Ethylene and propylene were determined in the presence of each other with an infrared spectrometer equipped with a LiF prism. The band at 3.200 was used for ethylene and the band at 3.425 was used for propylene. In all spectrophotometric analyses, calibration curves of log I_0/I *vs.* pressure were used. The extinction coefficient was not assumed to be constant. The total pressure of the gas in the absorption cell was always brought to atmospheric with nitrogen, or in the analysis for nitric oxide with oxygen.

Decomposition of 1,3-Diol Dinitrites.—Experiments were performed with a downstream pressure of either 760 or 5 mm. The results were the same in both cases. The products were collected in two traps. The first was cooled with Dry Ice and the second with liquid nitrogen. At the end of a run the trap contents were allowed to evaporate into an evacuated flask and the system was brought to atmospheric pressure with nitrogen. The gases were then analyzed. The decomposition of propane-1,3-diol dinitrite yielded a white solid in the Dry Ice trap which was identified as paraformaldehyde by its 2,4-dinitrophenylhydrazone, m.p. 166°; no depression with an authentic sample. The formaldehyde was determined quantitatively both by weighing the solid and by the bisulfite method.[3] The decomposition of butane-1,3-diol dinitrite and of pentane-2,4-diol dinitrite yielded only gaseous products. The infrared spectrum of the product indicated acetaldehyde, ethylene and propylene from the former and acetaldehyde and propylene from the latter. Acetaldehyde was determined by the intensity of its band at 3.75 μ. In order to obtain a derivative of acetaldehyde, runs were made at the conclusion of which the Dry Ice trap was kept cold until the system was brought to atmospheric pressure. From the liquid in the trap a 2,4-dinitrophenylhydrazone of acetaldehyde was obtained, m.p. 168°, which showed no depression when mixed with an authentic sample.

1,4-, 1,5- and 1,6-Diol Dinitrites.—A third trap cooled with the wet ice was used between the reaction chamber and Dry Ice trap. Because of their lower volatility, these compounds were held at 40 to 50° while the nitrogen was drawn through them. The downstream pressure was 2 mm. Butane-1,4-diol dinitrite yielded no nitrogen dioxide. Over 95% of the nitrogen appeared as nitric oxide. The infrared curve of the gaseous product showed that a trace of ethylene was present, its yield being less than 5%. The liquid which was found in the wet and Dry Ice traps was combined, taken up in ether, washed with dilute sodium carbonate, dried over sodium sulfate, and distilled. The product which boiled at 62–65° (13 mm.) was identified as γ-hydroxybutyraldehyde. Its infrared curve showed bands due to hydroxyl and aldehyde groups, and it formed a 2,4-dinitrophenylhydrazone, m.p. 120° (lit.[4] 120°), which gave no depression when mixed with an authentic sample. The liquid products before purification gave a 95% yield of the dinitrophenylhydrazone.[5] The yield of hydroxybutyraldehyde from dinitrite was 85–90%.

The decomposition of hexane-2,5-diol dinitrite was carried out in a similar manner. The yields of gaseous products were nitric oxide 95%, ethylene 20% and acetaldehyde 35%. The last was determined from the intensity of the band at 3.75 μ. The liquid product was worked up as described above. The product which boiled at 48–52° (1 mm.) was identified as 5-hydroxy-2-hexanone. Its semicarbazone melted at 151° (lit.[6] 151°). The yield of crude hydroxyhexanone was 70 to 80%.

The decomposition of 2,5-dimethylhexane-2,5-diol dinitrite yielded no liquid in the wet ice trap. From the liquid nitrogen trap, nitric oxide was obtained in 60% yield, ethylene in 70% yield, and a small amount of acetone. Acetone was obtained from the Dry Ice trap and was identified by its 2,4-dinitrophenylhydrazone, m.p. 120°, which showed no depression when mixed with an authentic sample.

The decomposition of pentane-1,5-diol dinitrite produced large amounts of nitrogen dioxide as well as nitric oxide. 4-Penten-1-ol in 20–30% yield was found in the wet ice trap as indicated by its infrared curve which was compared with the curve for the known material. It was further characterized by its α-naphthylurethan, m.p. 61° (lit.[7] 61°) which showed no depression with a known sample. The liquid in the Dry Ice trap was deep blue due to the presence of N_2O_3. A vigorous exothermic reaction occurred between the N_2O_3 and organic material when the trap was removed from the Dry Ice. In one experiment, the nitric oxide and nitrogen dioxide were destroyed by the addition of an ether solution of lithium aluminum hydride to the cold trap contents, and after working up the product a further quantity of 4-penten-1-ol was obtained. The infrared spectrum of the liquid nitrogen trap contents showed no significant amounts of organic material indicating that no cleavage of C–C bonds had occurred at this reaction.

The decomposition of hexane-1,6-diol dinitrite yielded less than 2% nitrogen dioxide and 60% of nitric oxide. From 9.3 g. of dinitrite there was formed in the wet ice trap 5 g. of liquid which was identified as 6-hydroxyhexanol by its 2,4-dinitrophenylhydrazone, m.p. 103–104° (lit.[8] 104–105°). The infrared spectrum of the liquid indicated the absence of hexane-1,6-diol and adipic aldehyde.

Liquid Phase Reactions.—Several experiments were carried out in which 10 ml. of propane-1,3-diol dinitrite dissolved in 200 ml. of white paraffin oil was heated at 125° for 48 hours in a nitrogen atmosphere. The gaseous products were collected over water. The only infrared active gases formed were nitric and nitrous oxides. Olefins were absent. The liquid reaction mixture was nitrite free and had turned dark. Extraction of the reaction mixture with water and distillation of the aqueous extract afforded a 60% yield of propane-1,3-diol, b.p. 214°, which was characterized as the bisphenylurethan, m.p. 137°. A mixed melting point with the known material gave no depression.

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(3) S. Siggia, "Quantitative Analysis *via* Functional Groups," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 21.

(4) R. Paul, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, 68 (1950).

(5) Reference 3, p. 31.

(6) Roy Adams and C. A. VanderWerf, THIS JOURNAL, **72**, 4368 (1950).

(7) J. Fakstorp, D. Raleigh and L. E. Schniepp, *ibid.*, **72**, 869 (1950). We are grateful to Professor H. R. Snyder of the University of Illinois for a sample of 4-penten-1-ol.

(8) C. D. Hurd and W. H. Saunders, Jr., THIS JOURNAL, **74**, 5324 (1952).

Results and Discussion

The vapor phase decomposition products from 1,3-diol dinitrite and yields are shown in Table II.

TABLE II

PRODUCTS OF 1,3-DINITRITE DECOMPOSITION

Diol dinitrite	Products and yield in moles per mole of dinitrite
Propane-1,3-	Ethylene 0.9, $NO + NO_2$ 1.9, formaldehyde 0.50–0.55, CO_2 0.35
Butane-1,3-	Ethylene 0.7, propylene 0.05, $NO + NO_2$ 1.8, acetaldehyde[a]
Pentane-2,4-	Propylene 0.95, $NO + NO_2$ 1.8, acetaldehyde 0.6

[a] Yield not determined.

In each of the three cases shown in Table II practically all of the nitrogen appeared as NO. Only small amounts of nitrogen dioxide were found. The observed results indicate that the decomposition can be represented by the equation

$$RCH(ONO)CH_2CH(ONO)R \longrightarrow NO + RCHO + NO_2 + RCH{=}CH_2$$

and that this is followed by a further reaction between the nitrogen dioxide and the aldehyde which reduces the former to nitric oxide and which destroys some of the latter. From the work of Pollard and co-workers[9] one would expect the reaction between nitrogen dioxide and formaldehyde to proceed largely according to the equation

$$CH_2O + 2NO_2 \longrightarrow CO_2 + H_2O + 2NO$$

with great rapidity at the temperature which we employ. This explains the appearance of carbon dioxide, the almost complete absence of nitrogen dioxide and the fact that only about a 50% yield of aldehyde is obtained.

If one assumes that the first step in the decomposition of 1,3-diol dinitrites is the breaking of the O–N bond, as is believed to be the case in the decomposition of mononitrites[10] and of 1,2-diol dinitrites,[1] then the following reasonable mechanism can be written to explain the formation of the observed products

$$RCH(ONO)CH_2CH(ONO)R \longrightarrow NO + RCH(ONO)CH_2CH(O\cdot)R$$

$$RCH(ONO)CH_2CH(O\cdot)R \longrightarrow RCH(ONO)CH_2\cdot + RCHO$$

$$RCH(ONO)CH_2\cdot \longrightarrow NO_2 + RCH{=}CH_2$$

Although the last two steps are written separately, it is quite possible that they occur simultaneously. This is the first instance in which a nitrite group has been found to cleave at the C–O bond instead of the O–N bond. The alternative reaction in which both O–N bonds break would yield ethylene oxide and formaldehyde from propane-1,3-diol dinitrite. No trace of ethylene oxide was found among the products.

Butane-1,3-diol dinitrite can decompose by two different routes. If the primary nitrite were to cleave first the products would be nitric oxide, nitrogen dioxide, formaldehyde and propylene

$$CH_3CH(ONO)CH_2C(O\cdot)H_2 \longrightarrow CH_2O + NO_2 + CH_3CH{=}CH_2$$

If the secondary nitrite were to cleave first the organic products would be acetaldehyde and ethylene

$$CH_3CH(O\cdot)CH_2C(ONO)H_2 \longrightarrow CH_3CHO + NO_2 + CH_2{=}CH_2$$

The relative amounts of ethylene and propylene obtained from the decomposition of butane-1,3-diol dinitrite as shown in Table II indicate that the second mode of reaction exceeds the first by a factor of about 14. This result could not have been predicted from the kinetic data for the decomposition of mononitrites[10] which show no significant difference in rates between primary and secondary nitrites.

In mineral oil solution the decomposition of propane-1,3-diol dinitrite differs from the vapor phase decomposition. From the decomposition in solution, no olefin was found in the gaseous products, and the dinitrite was converted to the diol in about 60% yield. This indicates that the initially formed alkoxy radical, instead of falling apart as it does in the vapor, abstracts a hydrogen from the solvent

$$CH_2(ONO)CH_2CH_2(ONO) \longrightarrow CH_2(ONO)CH_2CH_2O\cdot + NO$$

$$CH_2(ONO)CH_2CH_2O\cdot + SH_2 \longrightarrow CH_2(ONO)CH_2CH_2OH + SH$$

where SH_2 represents the solvent. This process is repeated for the second nitrite group. The fate of the solvent was not ascertained. The dehydrogenated molecules might yield dimers or olefins. That a hydrogen transfer reaction between a paraffin hydrocarbon and an alkoxy radical takes place readily has been clearly demonstrated.[11]

1,4-Diol Dinitrites.—The results of the decomposition of the 1,4-diol dinitrites are shown in Table III.

TABLE III

PRODUCTS OF DECOMPOSITION OF 1,4-DIOL DINITRATES

Diol dinitrite	Products and yield in moles per mole of dinitrite
Butane-1,4-	NO 1.9, γ-hydroxybutyraldehyde 0.9
Hexane-2,5-	NO 1.9, 2-hydroxyhexan-5-one 0.75, ethylene 0.2, acetaldehyde 0.35
2,5-Dimethylhexane-2,5-	NO 1.2, ethylene 0.7, acetone 1.3

These decompositions can be represented by two equations

$$RR'C(ONO)(CH_2)_2C(ONO)RR' \longrightarrow 2NO + R'CO(CH_2)_2C(OR)RR' \quad (1)$$

$$RR'C(ONO)(CH_2)_2C(ONO)RR' \longrightarrow 2NO + C_2H_4 + 2RR'CO \quad (2)$$

When R and R′ are H equation 1 correctly accounts for more than 90% of the reaction. When R and R′ are methyl the reaction proceeds according to equation 2. When R is H and R′ is methyl about 80% of the dinitrite decomposes according to equation 1 and about 20% according to 2. If we again assume that the initial step is the cleavage of the O–N bond to form NO and an alkoxy radical, then the following reasonable mechanism can

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[9] F. H. Pollard and R. M. H. Wyatt, *Trans. Faraday Soc.*, **45**, 760 (1949); F. H. Pollard and P. Woodward, *ibid.*, **45**, 767 (1949).

[10] (a) E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.* (*London*), **A146**, 388 (1934); (b) *J. Chem. Phys.*, **2**, 345 (1934); **3**, 394 (1935); (c) E. W. R. Steacie and W. M. Smith, *ibid.*, **4**, 504 (1936).

[11] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

be written to account for the observed products from butane-1,4-diol dinitrite

$$\mathrm{ONOCH_2CH_2CH_2CH_2ONO} \longrightarrow \mathrm{NO} + \mathrm{ONOCH_2CH_2CH_2CH_2O\cdot}$$
$$\mathrm{ONOCH_2CH_2CH_2CH_2O\cdot} \longrightarrow \mathrm{ONOCH\cdot CH_2CH_2CH_2OH}$$
$$\mathrm{ONOCH\cdot CH_2CH_2CH_2OH} \longrightarrow \mathrm{NO} + \mathrm{OCHCH_2CH_2CH_2OH}$$

The second step is an intramolecular hydrogen transfer from carbon to oxygen which is followed or accompanied by cleavage of the second O–N bond to form NO and the hydroxybutyraldehyde. In the decomposition of the 2,5-dimethylhexane-2,5-diol dinitrite there is no hydrogen on the carbon bearing the nitrite group and so the hydrogen transfer step does not take place. The initially formed alkoxy radical falls apart with cleavage of the C–C bonds in the following manner

$$\mathrm{(Me_2C(ONO)CH_2CH_2C(O\cdot)Me_2} \longrightarrow \mathrm{Me_2CO} + \mathrm{Me_2C(ONO)CH_2CH_2\cdot}$$
$$\mathrm{Me_2C(ONO)CH_2CH_2\cdot} \longrightarrow \mathrm{Me_2CO} + \mathrm{NO} + \mathrm{CH_2{=}CH_2}$$

The decomposition of hexane-2,5-diol dinitrite follows both paths, the hydrogen transfer being the more important by a factor of about 4.

The mechanism proposed for the decomposition of butane-1,4-diol dinitrite is similar to the mechanism originally proposed by Steacie[10] for the decomposition of mononitrites, the differences being that the decomposition of the dinitrite involves an intramolecular hydrogen transfer whereas in the decomposition of the mononitrites the transfer is intermolecular. The Steacie mechanism is

$$\mathrm{RCH_2ONO} \longrightarrow \mathrm{RCH_2O\cdot} + \mathrm{NO}$$
$$\mathrm{RCH_2O\cdot} + \mathrm{RCH_2ONO} \longrightarrow \mathrm{RCH_2OH} + \mathrm{RCH\cdot ONO}$$
$$\mathrm{RCH\cdot ONO} \longrightarrow \mathrm{RCHO} + \mathrm{NO}$$

If the hydrogen transfer step in the decomposition of butane-1,4-diol dinitrite were intermolecular, the products should include butane-1,4-diol and succinaldehyde as well as hydroxybutyraldehyde. The fact that no diol nor dialdehyde was found is strong evidence for the intramolecular nature of the hydrogen transfer step. The results of the decomposition of the higher diol dinitrites, which are discussed in succeeding paragraphs, also require an intramolecular hydrogen transfer. Recent work by Levy[12] indicates that nitric oxide is involved in the hydrogen transfer step of the decomposition of mononitrites. His mechanism may be formulated as

$$\mathrm{RCH_2ONO} \longrightarrow \mathrm{RCH_2O\cdot} + \mathrm{NO}$$
$$\mathrm{NO} + \mathrm{RCH_2O\cdot} \longrightarrow \mathrm{RCHO} + \mathrm{HNO}$$
$$\mathrm{HNO} + \mathrm{RCH_2O\cdot} \longrightarrow \mathrm{RCH_2OH} + \mathrm{NO}$$

Since the hydrogen transfer from an alkoxy radical to nitric oxide and from HNO to another alkoxy must be intermolecular, it must be concluded that the Levy mechanism is not applicable to the decomposition of diol dinitrites under our experimental conditions.

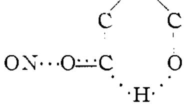
1,5- and 1,6-Diol Dinitrites.—The decomposition of pentane-1,5-diol dinitrite can be represented by the equation

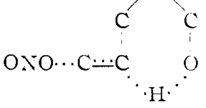
$$\mathrm{ONO(CH_2)_5ONO} \longrightarrow \mathrm{NO} + \mathrm{NO_2} + \mathrm{CH_2{=}CHCH_2CH_2CH_2OH}$$

Although the pentenol was isolated in only 30 to 40% yield, it is felt that the actual yield was somewhat higher. Some of the product was destroyed by reaction with nitrogen dioxide during the reaction and during the isolation procedure. The following reasonable mechanism accounts for the observed products

$$\mathrm{ONOCH_2CH_2(CH_2)_3ONO} \longrightarrow \mathrm{ONOCH_2CH_2(CH_2)_3O\cdot} + \mathrm{NO}$$
$$\mathrm{ONOCH_2CH_2(CH_2)_3O\cdot} \longrightarrow \mathrm{ONOCH_2CH\cdot(CH_2)_3OH}$$
$$\mathrm{ONOCH_2CH\cdot(CH_2)_3OH} \longrightarrow \mathrm{NO_2} + \mathrm{CH_2{=}CH(CH_2)_3OH}$$

Here again we have a hydrogen transfer from carbon to oxygen; however, this time it is from the β-carbon and leads to the formation of nitrogen dioxide and hydroxyolefin. The reason for the difference in products between the decomposition of the 1,5-dinitrite as compared with the 1,4-compound is made apparent by considering the transition states of the hydrogen transfer step


1,4-dinitrite


1,5-dinitrite

In each case a 6-membered ring is formed in the transition state. The hydrogen that is transferred is activated because the odd electron which it leaves on carbon can become paired with the odd electron that is left by the cleavage of the nitrite group. When the α-hydrogen is transferred the N–O bond breaks and the pairing of the odd electrons results in the formation of the aldehyde group. When the β-hydrogen is transferred the O–C bond breaks and the pairing of the electrons produces the olefin. The fact that nitrogen dioxide and olefins have never been observed among the decomposition products of mononitrites indicates that the α-hydrogen is more susceptible to transfer than the β-hydrogen. The hydrogen transfer step in the decomposition of the diol dinitrites, being intramolecular, requires a cyclic transition state, the size of whose ring also plays a part in determining which hydrogen, alpha or beta, will be transferred. The 6-membered ring appears to be preferred. The transfer of the normally more reactive α-hydrogen in the decomposition of the 1,5-diol dinitrite would require a 7-membered ring transition state. The preference for the 6-membered ring makes possible the transfer of the otherwise less reactive β-hydrogen.

The decomposition of hexane-1,6-diol dinitrite yields nitric oxide and 6-hydroxyhexanal. In this case the 6-membered ring transition state for the hydrogen transfer would require the transfer of a γ-hydrogen. This hydrogen is not activated by the second nitrite group since the odd electron that it would leave on carbon cannot become paired with the odd electron left by the cleavage of the nitrite, hence it is not transferred. The production of hydroxyaldehyde means that an α-hydrogen is transferred which in this case requires an 8-membered ring transition state.

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[12] Joseph B. Levy, Abstracts, 128th Meeting A.C.S., p. 33M (1955).