[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Thermal Decomposition of Dinitrites. I. Vicinal Dinitrites

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RECEIVED AUGUST 17, 1953

A study, based upon analysis of products, has been made of the thermal decomposition of vicinal dinitrites. In the vapor phase the decomposition can be represented by the equation RCH(ONO)–CH(ONO)R = 2NO + 2RCHO. A mechanism has been proposed for the reaction. In the liquid phase decomposition, 70% of the dinitrite can be accounted for by the equation 2RCH(ONO)–CH(ONO)R = 2NO + RCO–COR + RCHOH–CHOHR. Only 8% of the dinitrite decomposes according to the equation given for the gas phase reaction. The mechanism of the predominant reaction of the liquid phase decomposition is believed to be the same as that of the decomposition of mononitrites as given by previous workers.

It is a well-known fact that compounds containing two functional groups show markedly greater reactivity in certain types of reactions than compounds containing only one functional group, *e.g.*, rearrangement of pinacols *vs.* alcohols. Although an extensive literature exists on this so-called neighboring group effect, it appears that for the most part only those reactions which proceed by an ionic mechanism have been studied. In this paper and in subsequent ones the behavior of compounds containing two functional groups which decompose by a free radical mechanism will be described. Dinitrites have been chosen for study because these compounds are fairly easily prepared and because the decomposition of mononitrites is quite straightforward and appears to be fairly well understood.[1,2] In the present paper we report the vapor phase decomposition of the following compounds: propane-1,2-dinitrite, butane-2,3-dinitrite, *cis*- and *trans*-cyclohexane-1,2-dinitrite. The second of these has also been decomposed in the liquid phase.

Experimental

The dinitrites were prepared from the corresponding diols by a standard procedure.[3] Their physical constants and analytical data are given in Table I. The inhalation of these substances produces headaches. They should be handled in a hood.

TABLE I

PROPERTIES OF DINITRITES

Compound	B.p. °C.	B.p. Mm.	d^{20}	n^{20}	Observed C, %	Observed H, %	Observed N, %	Calculated C, %	Calculated H, %	Calculated N, %
Propane-1,2-dinitrite	45	84	1.107	1.3880	26.87	4.50	20.88	26.87	4.48	20.89
Butane-2,3-dinitrite	42	50	1.066	1.3938	32.64	5.42	18.88	32.43	5.41	18.92
cis-Cyclohexane-1,2-dinitrite	46	4	1.096	1.4442	41.39	5.72	15.89	41.38	5.75	16.09
trans-Cyclohexane-1,2-dinitrite	65	6	1.172	1.4395	41.45	5.72	15.99	41.38	5.75	16.09

The vapor phase decompositions were performed by passing the vapor of the dinitrite in a stream of nitrogen through a tube heated to 260–280° at such a rate that the residence time was about 5 seconds. Some experiments were performed with a downstream pressure equal to one atmosphere, in other experiments the pressure was held at 5 mm. Nitrogen (Matheson prepurified, min. purity 99.9%) was passed through a flowmeter, a drying tube, a tube containing the sample which was surrounded by a bath held at 30°, a reaction chamber of 80-ml. volume contained in a furnace, and finally a series of traps immersed in either Dry Ice or liquid air. The tube containing the sample was weighed before and after a run to determine the weight of material used.

Propane-1,2-dinitrite was decomposed in the above manner. At the end of the run the remaining sample was cooled with Dry Ice to prevent further evaporation. The liquid air was removed from the trap and the condensed material was allowed to evaporate into an evacuated flask. The trap was then immersed in a Dry Ice-bath and the residual gas was flushed out with nitrogen. The infrared spectrum of the gas showed that it consisted of NO and a trace of N_2O. The NO was further identified by conversion to NO_2 when mixed with air. The traps were allowed to come to room temperature. The Dry Ice trap contained a liquid and a solid. The latter was found to be paraformaldehyde, *p*-nitrophenylhydrazone derivative, m.p. 181°. In this and all other cases mixed melting points were taken with authentic specimens. No depression was observed. The liquid in both the liquid air and Dry Ice traps was acetaldehyde; *p*-nitrophenylhydrazone m.p. 128°. The traps were free of nitrite and NO_2. Another experiment was performed to determine the yield of aldehyde which was measured by the bisulfite method.[4] From 4 g. (0.03 mole) of dinitrite there was obtained 0.052 mole of aldehyde corresponding to an 87% yield.

Butane-2,3-dinitrite was decomposed in a similar manner and the products, which were found to be acetaldehyde and NO, were separated and analyzed. NO was determined by oxidizing a measured fraction of the gas to NO_2 and determining the latter colorimetrically. From 0.072 mole of dinitrite there was obtained 0.141 mole of NO corresponding to a 98% yield.

The product obtained from *cis*-cyclohexane-1,2-dinitrite was found from its infrared curve to be practically pure adipic aldehyde which was further characterized by conversion to its dioxime, m.p. 185°. The weight of the aldehyde in the trap corresponded to a 70% yield, but the actual yield was higher because some of the product had condensed in the tube leading to the trap and this was not included in the yield. Identical results were obtained with the *trans* compound. NO was determined qualitatively but not quantitatively in this instance.

The liquid phase decomposition was carried out by refluxing 70 g. (0.47 mole) of butane-2,3-dinitrite in a slow stream of nitrogen for 24 hours. At the end of this time the liquid had turned dark and was nitrite free. The gases were allowed to pass through a Dry Ice trap. The contents of the trap which contained a small amount of N_2O_3 (blue color) were dissolved in water. Urea was added to destroy the nitrous acid, and the resulting solution was analyzed quantitatively for acetaldehyde by the dimedon method and for biacetyl by reaction with hydroxylamine and a nickel salt.[5] An 8% yield of acetaldehyde (0.075 mole) was obtained, assuming that two moles of acetaldehyde are formed

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[1] (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).

[2] F. O. Rice and E. L. Rodowskas, THIS JOURNAL, **57**, 350 (1935).

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

[4] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 10.

[5] H. Meyer, "Nachweis und Bestimmung Organische Verbindungen," J. Springer, Berlin, 1933, p. 75.

per mole of dinitrite. The amount of biacetyl in the trap was 0.001 mole. The reaction mixture was distilled through a 12-inch Vigreux column. The first fraction, b.p. 80–100° was biacetyl, plus a small amount of water, and was found to contain 0.082 mole of pure biacetyl. The second fraction weighed 2 g., b.p. 70–80° (21 mm.). The infrared curve showed that it was largely butane-2-ol-3-one; semicarbazone m.p. 200°. The third fraction, b.p. 87–90° (21 mm.), weighed 19 g. (0.22 mole). This was identified as butane-2,3-diol from its infrared spectrum; bisphenylurethan m.p. 198°. There was a small amount of high-boiling residue which was not identified.

Results

The vapor phase decomposition of the four dinitrites may be represented by the equation

$$\mathrm{RCH(ONO)\text{-}CH(ONO)R = 2NO + 2RCHO} \quad (1)$$

The products and yields are shown in Table II.

TABLE II

PRODUCTS FROM DINITRITE DECOMPOSITION

Compound	Products and % yield
Propane-1,2-dinitrite	NO, formaldehyde and acetaldehyde 87
Butane-2,3-dinitrite	NO 98, acetaldehyde 88
cis-Cyclohexane-1,2-dinitrite	NO, adipic aldehyde >70
trans-Cyclohexane-1,2-dinitrite	NO, adipic aldehyde >70

The liquid phase decomposition of butane-2,3-dinitrite yielded the following products: acetaldehyde, 0.16; biacetyl, 0.17; butan-2-ol-3-one, 0.05; butane-2,3-diol, 0.46. The numbers indicate the moles of product per mole of dinitrite. The low yield of acetaldehyde shows that the liquid phase decomposition proceeds according to equation 1 to only a small extent. The major part of the reaction may be represented by (2)

$$\mathrm{2RCH(ONO)\text{-}CH(ONO)R = 2NO + RCO\text{-}COR + RCHOH\text{-}CHOHR} \quad (2)$$

The liquid phase reaction is not as clean-cut as the vapor phase reaction. Small but observable amounts of water and NO_2 were formed. According to 2, equal amounts of biacetyl and butane-2,3-diol should have been obtained. The larger amount of the latter may be due to its formation by a secondary reaction such as hydrolysis of the dinitrite. Alternatively, the biacetyl originally formed may have been destroyed by a secondary reaction.

Discussion

The decomposition of mononitrites, either in the gas phase at not too low pressures[1,2] or in the liquid phase,[6] is believed to proceed according to the scheme

Mechanism 1

$$\mathrm{RCH_2ONO = RCH_2O\cdot + NO}$$
$$\mathrm{RCH_2O\cdot + RCH_2ONO = RCH_2OH + RCH(ONO)\cdot}$$
$$\mathrm{RCH(ONO)\cdot = RCHO + NO}$$

Although more recent work has cast some doubt upon the validity of the second step,[7] there seems to be little doubt that the first step is the breaking of the O–N bond. If one assumes that the first step in the decomposition of the dinitrites is also the cleavage of the O–N bond, then the results of the vapor phase decomposition can reasonably be explained by the sequence

Mechanism 2

$$\mathrm{RCH(ONO)\text{-}CH(ONO)R = RCH(O\cdot)\text{-}CH(ONO)R + NO}$$
$$\mathrm{RCH(O)\text{-}CH(ONO)R = RCHO + RCH(ONO)\cdot}$$
$$\mathrm{RCH(ONO)\cdot = RCHO + NO}$$

Although the second and third steps of mechanism II are written as separate steps, they may occur simultaneously. The products obtained by the liquid phase decomposition indicate that under these circumstances mechanism 2 is relatively unimportant and that mechanism 1 predominates. It is concluded, therefore, that the unstable initially formed alkoxy radical, $\mathrm{RCH(O\cdot)\text{-}CH(ONO)R}$, can react in two different ways: it can fall apart to yield two molecules of aldehyde and one NO, as it does in the gas phase, or it can abstract a hydrogen atom from another molecule to yield the alcohol and a new radical, as it does in the liquid phase.

The vapor phase decomposition is reminiscent of the cleavage of glycols by lead tetraacetate

$$\mathrm{RCHOH\text{-}CHOHR + Pb(OAc)_4 = 2RCHO + 2AcOH + Pb(OAc)_2}$$

It has been suggested that this fraction also proceeds *via* an alkoxy radical, $\mathrm{RCH(O\cdot)\text{-}CHOHR}$.[8]

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[6] N. Kornblum and E. Oliveto, THIS JOURNAL, **71**, 226 (1949).

[7] J. B. Levy, *ibid.*, **75**, 1801 (1953).

[8] J. Cordner and K. Pausacker, *J. Chem. Soc.*, 102 (1953).