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Reaction of 2-Nitropropane with Nitrogen Dioxide in Gas Phase

by

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Continuing our work [1] on possibility of the formation of polynitroalkanes when paraffins are nitrated with an excess of nitrogen dioxide in a gas phase, we examined now the action of nitrogen dioxide on 2-nitropropane to find out whether 2,2-dinitropropane could be formed that way.

According to Levy [2], a prolonged nitration of paraffins with nitrogen dioxide at 200—250° can yield a mixture of mono- and dinitroalkanes, containing 20—50% dinitro compounds. Denton and co-workers [3], when nitrating 2-nitropropane with nitric acid at 210—230°, obtained 2,2-dinitropropane. On the contrary, McClearly and Degering [4], when acting on mononitroalkanes with nitrogen dioxide at much higher temperature (400—420°) neither obtained dinitro compounds nor recovered the starting nitroalkanes.

To solve the existing controversy, we examined the products formed by acting on 2-nitropropane with an excess of nitrogen dioxide at 300° and higher, considering that still higher temperatures may decompose dinitro compounds.

The liquid products leaving the reaction tube were composed of:

1) unreacted 2-nitropropane in quantity 54—68% of this substance used for the reaction, the lower yield being obtained at higher temperatures;

2) nitromethane and nitroethane in a yield of 4—7% and 1.4—2.5%, respectively, the yield being lower at higher temperature;

3) 3-nitroprop-1-ene in a yield of *c.* 3%;

4) formaldehyde and oxalic adic in a yield of 0.1—0.2% and *c.* 1%, respectively.

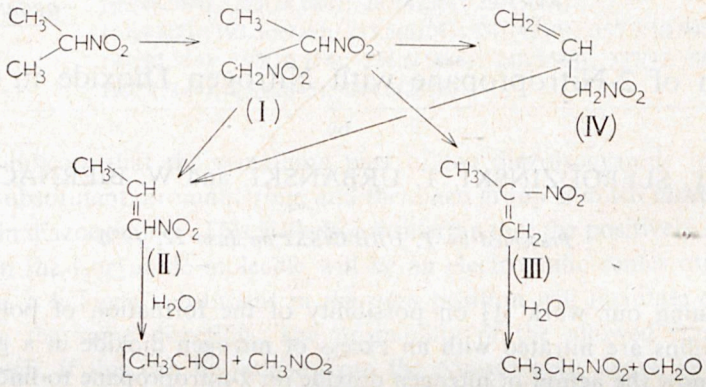
(All yields are given in relation to the 2-nitropropane used for the reaction).

We could not detect 2,2-dinitropropane in the products of the reaction. The formation of 3-nitroprop-1-ene, nitromethane and formaldehyde, could be explained by admitting the formation of 1,2-dinitropropane (I) which, upon the loss of HNO_2, could yield three nitroolefines: 1-nitroprop-1-ene (II), 2-nitroprop-1-ene (III) and 3-nitroprop-1-ene (IV).

Note. The paper forms contribution XCII to The Chemistry of Nitroparaffins and Part VI to The Nitration of Paraffins.

It is likely that (II) could also be formed from (IV) through its isomerization at a high temperature.

Compound (II) could yield nitromethane and (undetected) acetaldehyde, and (III) could be responsible for the formation of nitroethane and formaldehyde, according to the scheme:



We also suggest that acetaldehyde was eventually transformed into oxalic acid through the following sequence of reactions:

$$CH_3CHO \xrightarrow{HONO} ONCH_2CHO \rightarrow HON = CH\,CHO \xrightarrow{H_2O} OHC \cdot CHO + [NH_2OH]$$

(hydroxylamine was not detected and we only postulate its formation);

$$\begin{matrix} CHO \\ | \\ CHO \end{matrix} \xrightarrow{[O]} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Experimental

2-*Nitropropane* (Fluka, A. G. Chemische Fabrik, Buchs S. G.) was distilled, the fraction boiling within the range 119—120° was used.

The nitration was carried out in the same apparatus as in one of our previous papers [5] using two temperatures: 300° and 360°C and the molar ratio of 2-nitropropane:nitrogen dioxide 1:2. A few reactions were carried out at a ratio of 1:5 giving the same results. To avoid gas explosions, nitrogen was added in the proportion: reacting gas mixture:nitrogen 50:50.

The condensed products were collected from a few reactions at 300° and 360°C and mixed to obtain 144 g and 112 g, respectively.

Oxalic acid dihydrate (0.2—0.5 g) crystallized out from the oily products. It was identified by its m.p. 98.5—102° (no depression when mixed with a standard sample); $C_2H_2O_4 \cdot 2H_2O$ requires: 19.05% C, 4.8% H; found: 19.15% C; 4.9% H.

The oily product was washed with water containing some urea (to decompose nitrogen dioxide and nitrous acid). Subsequently the oily layer was washed with a saturated aqueous sodium hydrogen carbonate. Ether was added to obtain a better separation of the oily layer.

Aqueous solutions. The combined aqueous solutions were analyzed and the following products were identified.

Formaldehyde was characterized as its 2,4-dinitrophenylhydrazone (0.4—1.0 g), m.p. 157°C unchanged when mixed with a standard sample; $C_7N_6N_4O_4$ requires: 26.7% N,; found: 26.4% N.

Oxalic acid in the form of dihydra te, 2.1 g, identical with that isolated directly from the oily layer, as above.

Oily product. The organic oily layer was dried over sodium sulphate, ether was evaporated and the product was distilled. Three fractions were collected. Composition and identification is given in the Table.

TABLE

Fraction	b.p.	Components	Yields on 2-nitropropane used when nitrated at		Identified as	Analyses, % N		
			300°	360°		for the formula	Calcd.	Found
I	to 105°	Nitromethane	7.0	4.0	N,N′-diphenyl-C-nitroformazan, m.p. 149—151°	$C_{13}H_{11}N_2O_5$	26.0	26.3
II	105—120°	Nitroethane	2.5	1.4	1-nitroethanal-*p*-bromophenylhydrazone, m.p. 130—133°	$C_8H_8BrN_3O_2$	16.3	16.8
		2-Nitropropane	68	54	2-*p*-bromophenylazo-2-nitropropane, m.p. 92—93.5°	$C_9H_{10}BrN_3O$	15.4	15.5
III	>120° und undistilled residue	Nitroolefines, total: 3-nitroprop-1-ene: and their polymers	9.0 3	8.5 3	nitropropyl-2-enalphenylhydrazone, m.p. 96—97°	$C_9H_9N_3O_2$	22.0	21.8

Nitromethane, *nitroethane*, and *2-nitropropane* were identified as their products of the reaction with benzenediazonium or *p*-bromobenzenediazonium chloride according to the method previously described [6].

3-Nitroprop-1-ene (IV) was isolated by collecting the fraction distilling between 126—131° in agreement with the literature [7]. It reacted with bromine and showed the presence of the primary nitro group. $C_3H_5NO_2$ requires: 16.1% N, found: 16.5% N.

Compound (IV) was also condensed with benzenediazonium chloride to yield nitropropylen-2-alphenylhydrazone, m.p. 96—97° in agreement with the literature [8]. M.p. was unchanged when mixed with the standard sample; $C_9H_9N_3O_2$ requires: 21.9%, N, found: 21.8%.

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