

THE REACTION BETWEEN n-HEXANE AND DINITROGEN TETROXIDE INDUCED BY IONISING RADIATION*

J. FAŁĘCKI ^a, S. MINC ^a and T. URBAŃSKI ^b

^aInstitute of Nuclear Research, Polish Academy of Sciences,

^bInstitute of Technology,

Warszawa, Poland

Abstract—The irradiated mixture of n-hexane and dinitrogen tetroxide yields liquid (neutral and acidic) and gaseous products in appreciably greater quantities than it does without irradiation. In the reaction examined mainly acidic products were formed together with insignificant quantities of 1-nitrohexane.

SOME data on the reaction between inorganic salts of nitric acid and benzene in aqueous solution have been reported by Broszkiewicz, Minc and Zagórski.¹ The reaction was carried out in a sample chamber of the cobalt source. The authors found that under the reaction conditions nitrobenzene was formed and suggested that the reaction proceeded via an intermediate—nitrogen dioxide.

In further studies² on the course of the reaction in liquid phase between n-hexane and dinitrogen tetroxide, the solution of the two compounds was irradiated in the sample chamber mentioned above. It was hoped that under the conditions of ionising radiation, a new method of reacting paraffins with dinitrogen tetroxide could be developed which might contribute to the explanation of the nitration mechanism.

In order to compare the quantities of the products formed, the reaction was carried out in the presence or absence of air with n-hexane: dinitrogen tetroxide ratios of 6:1, 1:1 and 1:10.

At first the 6:1 and 1:10 solutions were irradiated and the products were examined. Results of the 50 hr reactions are presented in Table 1.

Then the reactions with the 1:1 mole ratio was carried out and the products were examined and identified. From the solution of the reagents two samples were prepared and sealed in a number of tubes. One sample was irradiated in

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¹ R. Broszkiewicz, S. Minc, Z. Zagórski: *Bull. Acad. Polon. Sci, Ser. Sci. Chim.* **8**, 103 (1960).

² J. Fałęcki, T. Ślebodziński, T. Urbański (in press).

TABLE 1. NITRATION OF n-HEXANE IN THE PRESENCE OF AIR

Product	n-hexane to N ₂ O ₄ ratio, 6 : 1	Yield, %	n-hexane to N ₂ O ₄ ratio, 1 : 10	Yield, %
Highly volatile acids	Irradiation time, 50 hr	0.75	Irradiation time, 50 hr	} 9.3
Non-volatile acids		1		
Highly volatile hydrocarbons and nitro compounds		2.1		} 9.7
Non-volatile nitro compounds		1.0		
n-Hexane recovered		93		
Total	97.85		<i>a</i> 19	

^a Not detectable.

the cobalt source and the other was left non-irradiated. Yields of the products formed based on n-hexane consumed (together with those obtained by the reaction carried out at 1 atm, i.e. on refluxing in unsealed tubes) are given in Table 2.

TABLE 2. NITRATION OF n-HEXANE BY DINITROGEN TETROXIDE, MOLE RATIO 1 : 1, IN THE ABSENCE OF AIR

Product	Yield, %		
	Irradiation time, 200 hr	Without irradiation	
		heating, ^a 143 hr	heating, ^{b,c} , 200 hr
Highly volatile acids	9.8	0.6	5.4
Non-volatile acids	10.1	2.5	4.1
Highly volatile hydrocarbons, esters and nitro compounds	8.5	2.4	2.8
1-nitrohexane	1	<i>d</i>	<i>d,e</i>

^a In sealed tubes.

^b Taken from (2).

^c In the presence of air, 1 atm.

^d Not detectable.

^e Not more than 0.05%.

Limited capacity of the sample chamber (about 3 l.) and the necessity of carrying out the reaction in sealed tubes (high vapour pressure of the reagents and strong corrosive properties of dinitrogen tetroxide) of small diameter (pressure of the gaseous reaction products) enabled to react only small quantities of the reagents.

When the reaction was carried out with dinitrogen tetroxide used in great excess, the yield of the products appreciably increased (calculated on n-hexane).

In view of a relatively large volume of the reaction mixture and large quantity of the gaseous products formed, the experiments were no longer continued.*

It was found that when the reaction was carried out under irradiation, only a primary nitroparaffin was formed. This was an unusual feature, as it is well known that at elevated temperatures secondary nitroparaffins are mainly formed.^{3,4} When the reaction occurred at low temperatures² secondary nitroparaffins were also detected.

EXPERIMENTAL

All m.ps. and b.ps. are uncorrected.

n-Hexane was purified by shaking with nitric acid ($d = 1.50$), freezing (m.p. -110° to -108°) and distillation (b.p. 68.0° – 68.2°).

Dinitrogen tetroxide was purified by fractional distillation (b.p. 21.8°) from elementary sulphur.

Solutions of dinitrogen tetroxide in *n*-hexane with various mole ratios were irradiated in the presence of air in sealed glass tubes in the sample chamber. The activity of the cobalt source (Gamma Cell 220) was 6600 C and the average dose was 120 r/sec.

Irradiation time ranged between 24 and 200 hr. When the solution was irradiated for more than 50 hr, the irradiation was occasionally interrupted to remove an excess of the gases formed. After the reaction was completed, the acidic and neutral products were separated and fractionated.

Nitration of n-hexane by dinitrogen tetroxide (mole ratio 1:1, Table 2). Dinitrogen tetroxide (46 g, 0.5 mole) was dissolved in *n*-hexane (42 g, 0.5 mole). The solution was poured into 24 tubes (ca. 4.0 ml in each tube, about 25 ml in capacity) and sealed. Twelve tubes were placed in the sample chamber of the cobalt source and the other tubes were left without irradiation. After the irradiation ended the unreacted reagents and a small quantity of the nitrogen oxides (containing most likely nitrous anhydride) had been removed, the products were separated by extracting aliphatic acids and acidic nitrogen compounds with aqueous sodium bicarbonate and dilute potassium hydroxide respectively. Under these conditions nitroparaffins and alkyl nitrates did not pass into the aqueous solution; however, alkyl nitrites hydrolysed progressively. The products were rectified under reduced pressure. The alkyl nitrates were detected by the Lunge

* The authors wish to point out that their work was interrupted and not renewed owing to a violent explosion which occurred in the course of one of the experiments.

This accounts for somehow unfinished experimental part of the paper.

³ H. B. Hass and E. F. Riley, *Chem. Revs.* **32**, 373 (1943).

⁴ T. Ślebodziński, T. Urbański *et al.* (in press).

method and the presence of 1-nitrohexane was verified by separation of the fraction boiling at the same point as did the standard 1-nitrohexane (Fluka), viz., $30^{\circ}/0.1$ mm., and having the refractive index ($n_D^{20} = 1.4225$) close to that of the standard 1-nitrohexane ($n_D^{20} = 1.4239$). The fraction gave a weak nitrolic reaction, characteristic of this nitroparaffin. The yield of the 1-nitrohexane obtained was about 1%.

