

# OXIDATION OF CYCLOHEXANE BY OZONIZED OXYGEN IN THE PRESENCE OF NITROGEN OXIDES

V. D. Komissarov and É. M. Kuramshin

UDC 542.943:547.592.12:546.214

Alkyl nitrates are obtained by the esterification of alcohols with nitric acid [1]. They are also formed by the reaction of  $N_2O_5$  with saturated hydrocarbons [2, 3]. In this case nitration of the hydrocarbon proceeds in parallel with the nitrooxidation and the yield of the nitrate reaches 75 mole % [2]. Still another method for the nitrooxidation of hydrocarbons with  $N_2O_4$  (or NO) and ozonized oxygen is proposed in the present paper. The relation between the composition of the products and the reaction conditions was studied on the example of cyclohexane.

## EXPERIMENTAL METHOD

The experiments were run in a glass thermostatted reactor equipped with a reflux condenser. The ozonized  $O_2$  and nitrogen oxides (NO or  $N_2O_4$ ) were added separately. The feed rate of the ozonized  $O_2$ , containing 2.2% of  $O_3$ , was 6 liters/h, while the volume of the cyclohexane was 40 ml. The feed rate of the nitrogen oxides,  $v_{N_2O_4}$  and  $v_{NO}$ , was varied from 1 to 5 liters/h. An efficient magnetic stirrer was used for the mixing. The reaction time was 2 h.

The cyclohexyl nitrate ( $RONO_2$ ) and nitrocyclohexane ( $RNO_2$ ) were identified via the elemental analysis and IR spectral data after their isolation from the reaction mixture by preparative GLC. The amounts of  $RONO_2$ ,  $RNO_2$ , cyclohexanol (ROH), and cyclohexanone ( $R=O$ ) in the solution were determined quantitatively by GLC (25% poly(ethylene glycol adipate) deposited on Chromatone, helium as the carrier gas, 100°C, and a flame-ionization detector).

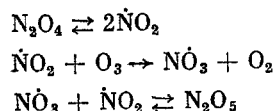
The methods for  $O_3$  analysis and cyclohexane purification are described in [4].

## DISCUSSION OF RESULTS

Under our experimental conditions the main reaction products were  $RONO_2$  and  $RNO_2$  (Tables 1 and 2). The selectivity of the process in  $RONO_2$  is quite dependent on the ratio of the feed rates of the gases; it is maximum (80-84 mole %) at  $v_{N_2O_4} = 1.5$  (40°) and  $v_{NO} = 3.0$  liters/h (20°). Besides the indicated products, ROH,  $R=O$ , and adipic acid are also formed: the latter accumulates in amounts that do not exceed the yield of cyclohexanone (the acid deposits in the precipitate during experiment).

The reaction proceeds at a fast rate, which is actually determined by the  $O_3$  feed rate. When using  $N_2O_4$ , the total yield of the products when based on consumed  $O_3$  is 125-130% at 40°, and ~150% at 60°. When NO is used the yield drops to 75-90%.

The kinetics and mechanism of the oxidation of  $\dot{NO}_2$  and RH by ozone, and also the reactions of  $N_2O_5$  with RH and of the radicals  $RO_2$  with  $\dot{NO}_2$ , and also with each other, have been studied in considerable detail [2-7]. This makes it possible to postulate that the mechanism of the process in a system containing RH,  $N_2O_4$ ,  $O_3$ , and  $O_2$ , is a combination of the following steps:



Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 700-701, March, 1975. Original article submitted August 20, 1974.

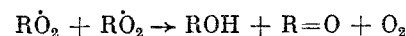
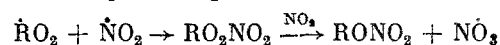
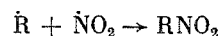
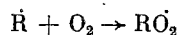
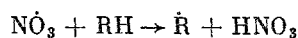
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TABLE 1. Effect of  $N_2O_4$  Feed Rate on Composition of Reaction Products

T., °C	$\nu_{N_2O_4}$ , l/h	Concentration of product, M			
		RONO <sub>2</sub>	RNO <sub>2</sub>	ROH	R=O
20	1,5	0,11	0,05	0,03	0,02
	1,0	0,09	0,004	0,03	0,04
40	1,5	0,32	0,06	0,004	0,004
	4,0	0,24	0,09	—	—
60	2,0	0,32	0,13	0,007	0,005

TABLE 2. Effect of NO Feed Rate on Composition of Reaction Products

T., °C	$\nu_{NO}$ , l/h	Concentration of product, M			
		RONO <sub>2</sub>	RNO <sub>2</sub>	ROH	R=O
20	3,0	0,17	0,02	0,003	0,005
	4,0	0,13	0,03	0,003	0,004
	4,8	0,09	0,04	traces	traces
60	4,8	0,10	0,10	0,002	0,004



The adipic acid is probably formed by the oxidation of cyclohexanone [7]. It should be mentioned that the chain oxidation of cyclohexane, with chain propagation, by the reaction:  $RO_2 + RH \rightarrow ROOH + \dot{R}$  practically does not go at 20–60° [4].

## CONCLUSIONS

1. A method was proposed for the preparation of alkyl nitrates by the reaction of saturated hydrocarbons with ozonized oxygen and nitrogen oxides ( $N_2O_4$ , NO).
2. The relation between the composition of the oxidation products of cyclohexane and the reaction conditions was studied.

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