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

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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 $\dot{N}O_2$ and RH by ozone, and also the reactions of N_2O_5 with RH and of the radicals $R\dot{O}_2$ with $\dot{N}O_2$, 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:

$$N_2O_4 \rightleftarrows 2\dot{N}O_2$$
$$\dot{N}O_2 + O_3 \rightarrow N\dot{O}_3 + O_2$$
$$N\dot{O}_3 + \dot{N}O_2 \rightleftarrows N_2O_5$$

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

T., °C	$v_{N_2O_4}$, l/h	Concentration of product, M			
		$RONO_2$	RNO_2	ROH	R=O
20	1,5	0,11	0,05	0,03	0,02
	1,0	0,09	0,001	0,03	0,04
40	1,5	0,32	0,06	0,001	0,001
	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	v_{NO}, l/h	Concentration of product, M			
		$RONO_2$	RNO_2	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	0,001

$$\dot{NO}_3 + RH \rightarrow \dot{R} + HNO_3$$
$$\dot{R} + O_2 \rightarrow R\dot{O}_2$$
$$\dot{R} + \dot{N}O_2 \rightarrow RNO_2$$
$$\dot{R}O_2 + \dot{N}O_2 \rightarrow RO_2NO_2 \xrightarrow{NO_2} RONO_2 + \dot{NO}_3$$
$$R\dot{O}_2 + R\dot{O}_2 \rightarrow ROH + R{=}O + O_2$$

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: $R\dot{O}_2 + RH \rightarrow ROOH + \dot{R}$ 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.

LITERATURE CITED

1. R. Boschan, R. T. Merrow, and R. W. Dolah, Chem. Rev., 55, 485 (1955).
2. A. I. Titov and N. V. Shchitov, Dokl. Akad. Nauk SSSR, 81, 1085 (1951).
3. J. C. D. Brandt, J. Am. Chem. Soc., 77, 2703 (1955).
4. L. G. Galimova, V. D. Komissarov, and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 307 (1973).
5. H. S. Johnston and D. M. Yost, J. Chem. Phys., 17, 386 (1949).
6. C. W. Spicer, A. Villa, H. H. Wiebe, and J. Heicklen, J. Am. Chem. Soc., 95, 13 (1973).
7. N. M. Émanuel, E. T. Denisov, and Z. K. Maizus, Chain Oxidation Reactions of Hydrocarbons in the Liquid Phase [in Russian], Nauka (1965).