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Ya. T. Eidus, B. K. Nefedov, I. P. Yakovlev, and A. V. Lobzova

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Abstract

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Ya. T. Eidus, B. K. Nefedov, I. P. Yakovlev, and A. V. Lobzova

ALKYLATION OF CYCLOHEXENE UNDER THE CONDITIONS OF THE DESTRUCTIVE HYDROPOLYMERIZATION REACTION OF ISOBUTYLENE

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The reaction of destructive hydropolymerization of isobutylene proceeds when an equimolecular mixture of it with H_2 is passed over a Co–clay catalyst at 190° and atmospheric pressure ([1]). In this process, 2-methylalkanes are formed (2-methylbutane, 2-methylpentane, 2-methylhexane, etc.) and the corresponding alkenes. With an excess of isobutylene in the initial mixture with H_2, dimers, trimers, and the products of their hydrogenation are formed. It has been shown that the formation of 2-methyl-substituted hydrocarbons cannot be explained by transformations of the isobutylene dimer (2,4,4-trimethylpentene-1) and, apparently, is due to the reaction of destructive hydrogenation of isobutylene with formation of surface radicals, which subsequently interact with isobutylene and the products of its transformation.

It was shown earlier ([2]) that, under the same conditions, cyclohexene in a mixture with CO and H_2 is methylated by CH_2 radicals formed by the reduction of carbon monoxide with hydrogen. Therefore, upon adding cyclohexene to a mixture of isobutylene and hydrogen, one could also expect its alkylation by radicals formed during the destructive hydrogenation of isobutylene, thereby confirming the previously proposed scheme for this reaction.

Experimental Part

The apparatus and procedure for carrying out the experiments did not differ from those described earlier ([1]). Isobutylene and cyclohexene were synthesized as in previous works ([1,2]). The initial cyclohexene had b.p. 82°/760 mm, n_D^{20} 1.4465, d_4^{20} 0.8099. Literature data for cyclohexene ([3]): b.p. 82.97°/760 mm, n_D^{20} 1.44654, d_4^{20} 0.81096. The experiments were carried out over a Co–clay catalyst ([4]) at 190° and atmospheric pressure. The catalyst volume in the reaction glass tube, 10 mm in diameter, was 30 ml. Cyclohexene entered the reaction zone from an automatic burette. The collected catalyzate was dried over calcium chloride, freed by fractionation from gases (C_1—C_4), and distilled

on a column packed with copper triangular turns, with an efficiency of 60 theoretical plates. Analysis of the catalyzate fractions was carried out qualitatively and semiquantitatively from the spectra of combination light scattering. In individual cases, ultraviolet absorption spectra were used. The intensities of the lines were evaluated visually on a ten-point scale. Interpretation of the spectra obtained was performed using literature data on the combination-scattering spectra of hydrocarbons ([5]). The reaction off-gas and the gases distilled from the liquid catalyzate were analyzed by a chromatothermographic method. Before studying the behavior of cyclohexene in a mixture with isobutylene and hydrogen, experiments were carried out with binary mixtures: cyclohexene–hydrogen and isobutylene–hydrogen.

Table 1

Experiment no.	Catalyst sample no.	Duration of experiment, h	Cyclohexene passed, ml	Passed H_2, l (N.T.P.)	Passed isobutylene, C_4H_8, l (N.T.P.)	Volumetric feed rate, h^{-1}, initial cyclohexene	Volumetric feed rate, h^{-1}, H_2	Volumetric feed rate, h^{-1}, isobutylene, C_4H_8	Gas contraction, %	Catalyst yield**, %	Collected H_2, l (N.T.P.)	Collected CH_4, l (N.T.P.)	Collected C_2H_4 and C_2H_6, l (N.T.P.)	Collected C_3H_6 and C_3H_8, l (N.T.P.)	Collected iso-C_4H_8, C_4H_{10}, l (N.T.P.)	Collected iso-C_4H_{10}, l (N.T.P.)
1*	1	20	46.6	32.7	0.0	0.08	54.5	—	33.4	80.3	21.8	—	—	—	—	—
2*	2	51	167.0	74.7	0.0	0.11	48.8	—	47.0	90.0	29.8	7.2	0.6	0.4	—	0.7
3*	1	21.5	44.2	32.4	22.3	0.07	50.3	34.6	50.2	98.5	9.7	1.0	0.7	1.3	—	12.8
4*	1	8.5	0.0	11.0	11.2	—	43.2	44.0	56.2	12.9***	1.3	0.4	0.4	0.7	0.1	5.9
5	1	29.5	57.4	35.9	37.1	0.07	40.6	42.0	43.6	104.0	5.2	0.6	0.8	1.5	6.4	24.2
6	1	26.5	0.0	37.9	38.2	—	47.8	48.2	49.6	3.8***	3.6	0.8	0.6	1.8	1.6	27.7
7*	2	34	128.4	78.1	31.2	0.13	76.7	30.5	42.0	101.5	22.6	10.1	4.5	3.0	—	21.0

* Before the experiment the catalyst was regenerated at 450° for 4 h.
** Based on the initial cyclohexene.
*** Yield based on the isobutylene passed.

Cyclohexene–hydrogen mixture. Two experiments were carried out (Table 1, experiments 1 and 2) at molar ratios of cyclohexene to hydrogen of 1 : 3.2 and 1 : 2.0, respectively. The ratio of hydrocarbons C_1 : C_2 : C_3 : C_4 in the exit gas of experiment 2 was 1 : 0.08 : 0.05 : 0.09. The cyclohexene passed was converted into hydrocarbons C_1-C_4 to the extent of 5.5%. The liquid catalyzates of experiments 1 and 2 had, respectively, d_4^{20} 0.7770 and 0.7795; n_D^{20} 1.4280 and 1.4300. They were distilled on a column in amounts of 35 and 156 ml, respectively, into 4 fractions. Fractions 1 with b.p. 38.5-73°, constituting 3-4 vol.% of the catalyzate and having n_D^{20} 1.4190 and 1.3970, d_4^{20} 0.7551 and 0.7174, were products of cyclohexene decomposition. Fractions

2 (b.p. 74-80°, n_D^{20} 1.4368 and 1.4460, d_4^{20} 0.7889 and 0.8090; yield 14.4 and 33.3 vol.%) had constants—specific gravity and refractive index—whose values are higher than in the preceding and subsequent fractions. This is explained by the fact that, as was shown earlier ([2]), azeotropic mixtures of benzene with cyclohexane and benzene with cyclohexene fall into these fractions. Benzene is formed by the reaction of irreversible catalysis from cyclohexene ([6]): $3C_6H_{10} \rightarrow C_6H_6 + 2C_6H_{12}$.

Indeed, in the Raman spectrum of fraction 2 of experiment 2, frequencies characteristic of benzene were found ($\Delta\nu$ cm^{-1}: 608 (2), 992 (10), 1178 (2), 1586 (2), 1606 (1), etc.) and of cyclohexane ($\Delta\nu$ cm^{-1}: 802 (9), 1030 (3), 1268 (5), 1445 (4), etc.). Fractions 3 (b.p. 79.5-82°, n_D^{20} 1.4268 and 1.4265, d_4^{20} 0.7785 and 0.7788, yield 75.6 and 52.0 vol.%) were practically pure cyclohexane ($\Delta\nu$ cm^{-1}: 428 (2), 802 (10), 1030 (6), 1158 (2), 1268 (5), 1445 (4), etc.). Literature data for cyclohexane ([3]): b.p. 80.738°/760 mm, n_D^{20} 1.42623, d_4^{20} 0.77855. Finally, fractions 4, constituting 3.4-4.5% of the entire catalyzate and having n_D^{20} 1.4324 and 1.4430, d_4^{20} 0.7802 and 0.7959, boiled above the initial cyclohexene, with an upper boiling-temperature limit up to 130°. Quantitative spectral measurements showed that fraction 4 of experiment 2 contains ~80% methylcyclohexane ($\Delta\nu$ cm^{-1}: 445 (1), 546 (1), 770 (5), 844 (2), etc.) and toluene ($\Delta\nu$ cm^{-1}: 522 (2), 787 (4), 1004 (10), 1210 (3), 1605 (2), etc.), and about 10% cyclohexane, whose presence may be judged from the frequency 802 (1)* cm^{-1}.

Isobutylene-hydrogen mixture. Two experiments were carried out (Table 1, experiments 4 and 6) with an equimolecular mixture of isobutylene and hydrogen on a regenerated (experiment 4) and on a surface not regenerated after experiment 5 (see below) contact surface (experiment 6). From Table 1 it is seen that on the regenerated

* The remaining frequencies of cyclohexane cannot be identified, since the corresponding lines are overlapped by the lines of methylcyclohexane and toluene.

on the surface the destructive hydropolymerization reaction of isobutylene proceeds with a yield of liquid polymerizate of 12.9% of the isobutylene passed, and on the non-regenerated one with a yield of up to 3.8%. In this case the principal reaction is hydrogenation of isobutylene to isobutane. Along with this, methane, ethane, propane, *n*-butane, and isopentane are present in the off-gas, which indicates the occurrence of a hydrocracking reaction. The ratio of hydrocarbons $C_1 : C_2 : C_3 :$ iso-C_4 in the off-gas was $1 : 1 : 1.6 : 14.5$ in experiment 4 and $1 : 0.8 : 2.4 : 35.9$ in experiment 6.

The mixture cyclohexene—isobutylene—hydrogen. Three experiments were carried out with the ternary mixture (Table 1, experiments 3, 5, and 7). The ratio of isobutylene to hydrogen in the initial gas mixtures was 0.68, 1.03, and 0.4; the molar cyclohexene content was 14.9, 14.6, and 20.2%, respectively. Experiments 3 and 7 were carried out on regenerated contact (regeneration was performed every 15-20 hr), and experiment 5 on non-regenerated contact. In the off-gases of these experiments, along with the main components—hydrogen, isobutane, and

isobutylene–methane, ethane, and propane were present in ratios of 1 : 0.6 : 1.3 in experiment 3, 1 : 1.3 : 2.5 in experiment 5, and 1 : 0.45 : 0.29 in experiment 7. The yield of liquid catalyzates based on cyclohexene passed was 98.5 vol.% in experiment 3, 104 vol.% in experiment 5, and 101.5 vol.% in experiment 7. From the catalyzate of experiment 3 (n_D^{20} 1.4350, d_4^{20} 0.7828, bromine number 3.4), fractionation on a 32-ml column gave 1.6% (by volume) of a fraction with b.p. 31.7–49° (n_D^{20} 1.3690), 43.8% of a fraction with b.p. 61–78.7° (n_D^{20} 1.4465, d_4^{20} 0.7969), which was a mixture of benzene ($\Delta\nu$ cm^{-1}: 608 (4), 992 (10), 1178 (3), 1586 (2), etc.) and cyclohexane ($\Delta\nu$ cm^{-1}: 802 (10), 1030 (6), 1268 (5), 1445 (5), etc.); 39.4% of a fraction with b.p. 78.8–81.7° (n_D^{20} 1.4274, d_4^{20} 0.7786), which was cyclohexane ($\Delta\nu$ cm^{-1}: 428 (2), 802 (10), 1030 (9), 1268 (7), 1445 (7), etc.), and, finally, 11% of a fraction boiling above cyclohexane (b.p. 86.2–110.7°, n_D^{20} 1.4305, d_4^{20} 0.7806). From the catalyzate of experiment 5 (n_D^{20} 1.4335, d_4^{20} 0.7813, bromine number 28.5), analogous fractions were obtained, with the sole difference that fraction 3 was a mixture of cyclohexane and cyclohexene. The content of the high-boiling residue with an end boiling point of 112.5° (n_D^{20} 1.4240, d_4^{20} 0.7606) was 14.0%. The catalyzate of experiment 7 (n_D^{20} 1.4310, d_4^{20} 0.7676), distilled in an amount of 90 ml, contained the same fractions as the preceding two. The content of the fraction of the high-boiling residue with an end boiling point of 135° (n_D^{20} 1.4449, d_4^{20} 0.7964) in this catalyzate was 7.8%. To determine the composition of the fractions with b.p. above cyclohexene and cyclohexane, fraction 4 from experiments 3 and 5 were combined and, in an amount of 15 ml, subjected to dehydrogenation catalysis ([7]) at 310° and a space velocity of 0.84 hr^{-1} over a Pt/C catalyst prepared according to Zelinskii and Turova-Polyak ([6], pp. 150, 224). After three passes, 9.4 ml of catalyzate were obtained, boiling in the range 83–120° and having n_D^{20} 1.4870 and d_4^{20} 0.8531.

These constants indicate a high content of aromatic hydrocarbons in it. The dehydrogenate gave a positive reaction for toluene by the Eidus–Fedichkina method ([8]). By the method of combinational light scattering, benzene was detected in it ($\Delta\nu$ cm^{-1}: 608 (7), 992 (10), 1178 (5), 1586 (4), etc.) and toluene ($\Delta\nu$ cm^{-1}: 522 (2), 787 (3), 1030 (2), 1210 (2), 1382 (1), etc.). In addition, the spectrum contains frequencies 895 (1) and 1450 (2), which apparently belong to ethylcyclopentane.

Fraction 4 of the catalyzate of experiment 7 was subjected directly to spectral investigation. It was found that this fraction consists of $\sim$ 80% methylcyclohexane ($\Delta\nu$ cm^{-1}: 546 (1), 770 (3), 844 (1), etc.) and toluene ($\Delta\nu$ cm^{-1}: 522 (1), 787 (3), 1004 (10), 1210 (2), etc.), i.e., of the methylation products of the initial cyclohexane, and of $\sim$ 10% cyclohexane ($\Delta\nu$ cm^{-1}: 802 (1)).

From the data presented it is evident that, in the presence of hydrogen at 190° and atmospheric pressure over a Co–clay catalyst, cyclohexene is mainly hydrogenated to cyclohexane and undergoes the reaction of irreversible catalysis; to some extent, the reaction of alkylation of cyclohexene by CH_2 radicals formed during its hydrocracking also takes place. In the presence of isobutylene and hydrogen, cyclohexene undergoes alkylation 3.5–4 times more extensively than

in a mixture with hydrogen alone. This result indicates that an additional source of alkylation is isobutylene.

Evidently, in accordance with the scheme of destructive hydropolymerization of isobutylene that we proposed earlier, in the presence of H_2 a portion of the molecules of the latter decomposes on the catalyst surface with the formation of radicals, which interact with the added cyclohexene, forming methyl derivatives. Under the same conditions, but in the absence of cyclohexene, the radicals obtained from isobutylene interact with the initial isobutylene, giving 2-methyl-substituted hydrocarbons.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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REFERENCES CITED

1. Ya. T. Eidus, B. K. Nefedov, DAN, 127, 1029 (1959); 124, 111 (1959); Izv. AN SSSR, OKhN, 1960, 125.

2. Ya. T. Eidus, N. I. Ershov, Izv. AN SSSR, OKhN, 1955, 704.

3. F. D. Rossini, B. J. Mair, A. J. Streiff, *Hydrocarbons of Petroleum*, translated under the editorship of S. R. Sergienko, L., 1957.

4. Ya. T. Eidus, N. I. Ershov, K. V. Puzitskii, I. V. Guseva, Izv. AN SSSR, OKhN, 1960, 975.

5. G. S. Landsberg, P. A. Bazhulin, M. M. Sushchinskii, *Fundamental Parameters of the Combination Scattering Spectra of Hydrocarbons*, Publishing House of the Academy of Sciences of the USSR, 1956.

6. N. D. Zelinsky, Selected Works, 2, 1941, pp. 191, 220, 150, 224.

7. B. A. Kazanskii, A. L. Liberman, T. F. Bulanova, V. A. Aleksanyan, Kh. E. Sterin, DAN, 95, 17 (1954).

8. Ya. T. Eidus, T. L. Fedichkina, Izv. AN SSSR, OKhN, 1940, 275, 282.

Note: Figure translations are in progress. See original paper for figures.