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Abstract

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REDUCTION OF MONOOLEFINIC HYDROCARBONS BY ALKALI METALS IN LIQUID AMMONIA

Until recently it was believed that hydrogen "at the moment of liberation" can reduce only those double bonds $> C = C <$ that are conjugated either with other double bonds or with an aromatic nucleus.

In recent years, a number of facts have been established concerning the reduction of an isolated olefinic bond by so-called hydrogen at the moment of liberation. Thus, Haspill and Romer ([1]) observed that metallic cesium can add to ethylene, and that the resulting compound, under the influence of water vapor, is converted into ethane. Kazanskii and Gostunskaya ([2,3]), by means of the hydrogen liberated during decomposition of calcium hexaammine according to the equation
$Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + 2H$, partially reduced 2-methylbutene-1, 2-methylbutene-2, 2,5-dimethylhexene-2, 2,5-dimethylhexene-3, and cyclohexene. Orchin ([4]), with co-workers, partially reduced hexene-1 by the action of sodium dissolved in liquid ammonia in the presence of methyl alcohol. Benkeser ([5,6]) and co-workers obtained saturated hydrocarbons by treating cyclohexene and decene-5 with lithium in a medium of the simplest aliphatic amines.

Kraus ([7,8]), and subsequently Barton and Ingold ([9]) and Berg ([10]), proposed that the reaction of addition of hydrogen to a double bond under the action of sodium dissolved in liquid ammonia should be regarded as an ionic reaction. According to Kraus and Berg, the first stage of the reaction is the addition of one or two electrons, the source of which is the metal dissolved in ammonia, to the double bond:

$$> C = C < + 2\bar{e} \rightarrow > \bar{C} - \bar{C} < \qquad \text{(a)}$$

In the second stage, protons are added to the carbanion formed; their source may be ammonia, amines, alcohol, and other protolytic agents:

$$> \bar{C} - \bar{C} < + 2H^+ \rightarrow > CH - CH < \qquad (\ )$$

Simultaneously with the reduction, a side reaction involving hydrogen evolution may also occur:

$$2H^+ + 2\bar{e} \rightarrow H_2 \qquad (\ )$$

In the present work we investigated the influence of the nature and structure of the olefin, the nature of the metal and of the alcohol, on the rate of the reduction reaction of monoolefins of the aliphatic series in liquid ammonia. The objects of study were monoolefins of normal structure: pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, octene-2, and heptene-3. As metal reducing agents, Na, Li, and K were used; as donors

protons, methyl and ethyl alcohols were added. Na in liquid ammonia in the presence of methyl alcohol reduces pentene-1, hexene-1, and heptene-1 comparatively readily (with an average yield of about 40%); octene-1 is reduced more slowly (with a yield of 20%); nonene-1 and decene-1 are reduced with considerably greater difficulty (yields 3-6%), and for them reaction (c) proceeds more noticeably; olefins with a double bond removed from the end of the chain (heptene-3 and octene-2) are not reduced at all. Increasing the concentration of methyl alcohol leads to increased evolution of free hydrogen (reaction (c)) and to a decrease in the yield of saturated hydrocarbon. When methyl alcohol is replaced by the less acidic ethyl alcohol (its dissociation constant is 100 times smaller than that of methyl alcohol) ([11], [12]), the reduction reaction proceeds faster. Nonene-1 and decene-1 under these conditions are reduced by 20 and 8%, respectively.

If K or Li is used as the reducing agent in liquid ammonia in the presence of methyl alcohol, the monoolefins listed are reduced more slowly than in the presence of Na under the same conditions. However, their relative activity in the reduction reaction does not correspond to their position in the electromotive series in liquid ammonia. This series is as follows ([13]): Na < K < Li.

The more intense evolution of free hydrogen by potassium and lithium should decrease the rate of reduction of the olefins studied, since the rate of their reduction is less than the rate of the competing reaction of free hydrogen evolution.

Experimental Part

Pentene-1 (b.p. 30.0°/760 mm, n_D^{20} 1.3718, d_4^{20} 0.6411) and heptene-1 (b.p. 93.7°/760 mm, n_D^{20} 1.3995, d_4^{20} 0.6965) were obtained from allyl chloride and the corresponding Mg alkyl halide. Hexene-1 (b.p. 63.2°/760 mm, n_D^{20} 1.3876, d_4^{20} 0.6735), heptene-3 (b.p. 95.7-95.8°/760 mm, n_D^{20} 1.4048, d_4^{20} 0.7002), octene-1 (b.p. 121.3°/760 mm, n_D^{20} 1.4092, d_4^{20} 0.7155), octene-2 (b.p. 124.7-125.2°/760 mm, n_D^{20} 1.4140, d_4^{20} 0.7215), nonene-1 (b.p. 146.6°/760 mm, n_D^{20} 1.4158, d_4^{20} 0.7292), and decene-1 (b.p. 170.7°/760 mm, n_D^{20} 1.4215, d_4^{20} 0.7410) were prepared by pyrolysis of the acetates of the corresponding alcohols. Their constants agree with the most reliable literature data ([14]).

Method for the Reduction of Olefins and Investigation of the Reaction Products

The reaction was carried out in a three-necked flask of 0.5-liter capacity, equipped with an efficient stirrer, a thermometer, a tube for introducing gaseous ammonia reaching to the bottom of the flask, and a short tube

connected to a drying bottle filled with pieces of solid potassium hydroxide. The flask was cooled in a Dewar vessel with a mixture of dry ice and ethyl alcohol.

The reduction of olefins was carried out by two methods.

Method A. Into a flask containing 150 ml of liquid ammonia, with vigorous stirring, the metal was introduced in small pieces (0.2 gram-atom) until a homogeneous solution was formed. Then, at −35 to −37°, a solution of the hydrocarbon in alcohol (0.1 mole of hydrocarbon and 0.25 mole of alcohol) was added dropwise over 40 min. Stirring was continued for another hour at the same temperature; during this time practically all the metal had time to react, and the evolution of free hydrogen ceased 50–60 min after the start of the reaction. Then 12–20 ml of ether was added to the flask (in the case of pentene-1, hexene-1, and heptene-1, ordinary ether was replaced by dibutyl ether), and with strong cooling and stirring ···

slow decomposition of the reaction mixture with ice was carried out, followed by partial neutralization of the ammonia with carbonic acid. The ether layer was washed with water, dilute hydrochloric acid, and again with water, and dried over $CaCl_2$. After distillation of the ether, the hydrocarbon fraction was distilled over sodium from a Favorskii flask or on a 40-theoretical-plate column and examined. The percentage of reduction was calculated from the change in refractive index and the bromine number, determined by the method of Kaufmann–Halpern–Vinogradova ([15]).

Method B. The hydrocarbon and alcohol were placed in a flask with liquid ammonia (the same amounts as in the experiments by method A), and metal (0.2 gram-atoms) was introduced in small pieces through the neck of the flask, with vigorous stirring, over the course of 40 min. The subsequent procedure was as in method A.

In all experiments the result of the reduction did not depend on the order in which the reagents were added.

Results of the reduction of monoolefins

Pent-1-ene, hex-1-ene, and hept-1-ene were reduced both by method A and by method B; oct-1-ene, non-1-ene, and dec-1-ene only by method B. The refractive indices and bromine numbers of the reduction products in the presence of methyl alcohol are given (Table 1).

Table 1

Hydrocarbon	Na + NH_3 + CH_3OH			K + NH_3 + CH_3OH			Li + NH_3 + CH_3OH		
Hydrocarbon	n_D^{20}	bromine number	% reduction	n_D^{20}	bromine number	% reduction	n_D^{20}	bromine number	% reduction
Pent-1-ene	1.3655	144.2	43	1.3697	196.8	13	1.3670	157.0	32
Hex-1-ene	1.3883	113.8	40	1.3882	168.1	11	1.3850	149.3	23
Hept-1-ene	1.3946	101.2	38	1.3984	149.5	9	1.3975	140.2	15
Oct-1-ene	1.4067	113.8	20	1.4081	131.9	7	1.4079	130.4	9
Non-1-ene	1.4150	119.5	6	1.4151	120.4	5	1.4154	124.6	2
Dec-1-ene	1.4210	110.5	3	1.4212	112.0	2	1.4216	116.0	0

All hydrocarbons were also reduced with sodium in liquid ammonia and in the presence of ethyl alcohol (Table 2).

Table 2

Hydrocarbon	Na + NH_3 + CH_3CH_2OH		
Hydrocarbon	n_D^{20}	bromine number	% paraffin
Pent-1-ene	1.3651	128.3	45
Hex-1-ene	1.3820	111.2	42
Hept-1-ene	1.3942	95.9	41
Oct-1-ene	1.4058	101.0	30
Non-1-ene	1.4135	102.0	20
Dec-1-ene	1.4206	106.0	8

As is evident from these data, in the presence of ethyl alcohol the reduction proceeds more deeply.

Hept-3-ene and oct-2-ene were subjected to reduction with Na and K in liquid ammonia with the addition of methyl and ethyl alcohol. In all experiments

the bromine numbers of the reaction products changed almost not at all in comparison with the starting hydrocarbons, which indicates that reduction did not take place. A certain decrease in the values of n_D^{20} and d_4^{20} could also be explained by partial conversion of cis-olefins into trans-olefins ([16]), since the starting hydrocarbons, in all probability, were mixtures of these stereoisomeric forms. The experimental data and constants of the corresponding trans isomers are given in Table 3.

To determine whether migration of the double bond toward the center occurs in α-olefins, which could reduce the yield of their reduction products, we reduced 0.5 mole of heptene-1 and 0.5 mole of octene-1 with Na in liquid ammonia with the addition of methyl alcohol.

Table 3

Hydrocarbon	Before experiment: n_D^{20}	Before experiment: d_4^{20}	Before experiment: bromine number	After experiment: n_D^{20}	After experiment: d_4^{20}	After experiment: bromine number	Literature data for trans-isomers (15): n_4^{20}	Literature data for trans-isomers (15): d_D^{20}
Heptene-3	1.4048	0.7002	162.9	1.4046	0.6992	161.4	1.4043	0.6981
Octene-2	1.4140	0.7215	142.5	1.4133	0.7210	141.5	1.4132	0.7199

During fractionation on an 80 theoretical-plate column, no unsaturated fractions with boiling points corresponding to heptene-2 (98°), heptene-3 (95.7°), octene-2 (125°), or octene-3 (123°) were isolated from the reduction products. Fractions corresponding to the starting olefins and to their reduction products—*n*-heptane and *n*-octane—were obtained.

The results of the fractionation are given in Table 4.

Table 4

Hydrocarbon	Fraction I: b.p., °C	Fraction I: n_D^{20}	Fraction I: bromine number	Fraction III: b.p., °C	Fraction III: n_D^{20}	Fraction III: d_4^{20}	Fraction III: bromine number
Heptene-1	93.7–93.7	1.3993	161.8	98.5	1.3873	0.6882	2
Octene-1	121.3–121.4	1.4086	141.6	125.6	1.3976	0.7021	0.8

Conclusions

1. In the reduction of α-olefins by alkali metals in liquid ammonia with the addition of alcohol, the yield of saturated hydrocarbons decreases with increasing molecular weight of the olefin.
2. Olefins with the double bond in the β- and γ-positions were not reduced under the conditions studied.
3. Of the three alkali metals used, Li, Na, and K, Na proved to be the most active in the reduction reaction.
4. Replacement of methyl alcohol by the less acidic ethyl alcohol in the reduction of olefins of composition C_5–C_{10} increased the yield of saturated hydrocarbons.

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