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ALUMINUM CHLORIDE SOLUTIONS IN NITROPARAFFINS

Catalysts for Hydrocarbon Reactions

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Anhydrous aluminum chloride dissolves readily in nitromethane, nitroethane, and the two nitropropanes yielding solutions which, in contrast to those in alcohols, ethers, and ketones, are catalytically active. The active component of the solution is the addition complex, $AlCl_3 \cdot RNO_2$. The nitroparaffin solutions of aluminum chloride are miscible with benzene; the nitroparaffins thus are solubilizers for the metal chloride in the hydrocarbon. Homogeneous phase alkylation may be accomplished by contacting the clear solution with an olefin or alkyl halide. In a two phase system, to permit the recycling of the catalyst, the catalyst layer may be salted out by adding sodium chloride. The solutions of aluminum chloride in the nitroparaffins may be used also for the alkylation of isoparaffins with olefins. The solutions are not soluble in paraffins and are available for recycling. Higher reaction temperatures are necessary than those that are used with unmodified aluminum chloride. Data for the alkylation of isobutane with propene are discussed. When isopropyl chloride is brought into contact with isobutane in the presence of unmodified aluminum chloride, the principal reaction is reduction of the alkyl chloride to propane. If, on the other hand, a solution of aluminum chloride in nitromethane is used as catalyst, reduction of the isopropyl chloride is markedly decreased and alkylation of isobutane to heptane occurs. The nitroparaffin solutions of aluminum chloride effected virtually no isomerization of *n*-pentane or methylcyclopentane.

CERTAIN properties of anhydrous aluminum chloride lessen its usefulness as a catalyst for hydrocarbon conversions. It is often excessively active initially and catalyzes undesirable side reactions such as cracking or autodestructive alkylation. It forms addition compounds (lower layer sludge) with aromatic and olefinic hydrocarbons (present as reactants or formed during the reaction) which usually result in a decrease in the activity and life of the catalyst. Frequently it is advantageous, both in industrial processes and in laboratory syntheses, to use a catalyst which has uniform activity and a constant physical state. Fluid aluminum chloride catalysts become the logical choice because loss of the original crystalline form is apparently inherent in all but a few reactions. Furthermore, the liquid catalyst permits more efficient utilization of the aluminum chloride; there is no loss in activity because of the coating of catalyst particles with sludge.

The fluid aluminum chloride catalysts which have been described previously have usually been addition compounds, such as make up the lower layer complex, and uncombined aluminum chloride. Mixtures of aluminum chloride and certain metal chlorides—e.g., antimony trichloride—in the liquid state also are active catalysts. Nitrobenzene has been used as solvent for aluminum chloride in a few isolated cases. Other organic compounds such as chloroparaffins (methyl chloride and tetrachloroethane) and carbon disulfide also have been used but have the disadvantage that they dissolve only a small amount of the metal halide; thus the use of large proportions of the solvent is necessary. On the other hand, aluminum chloride is highly soluble in ethers, ketones, and alcohols, but the resulting solutions are catalytically inactive, at least for the alkylation of hydrocarbons.

Nitroparaffins also have high solvent power for anhydrous aluminum chloride; solutions containing more than 50% by weight of the metal halide are obtainable. In the present investigation it was discovered that unlike the ether, ketone, and alcohol solutions, these nitroparaffin solutions are excellent catalysts, particularly for alkylation reactions. This paper describes the results obtained with nitromethane, nitroethane, and the two nitropropanes as solvents.

CATALYST SOLUTIONS

The active component of the solutions of aluminum chloride in the nitroparaffins is not aluminum chloride as such but rather the addition compound, $AlCl_3.RNO_2$. This was shown by evaporating a nitromethane solution of aluminum chloride under reduced pressure. The residue, which was catalytically active, was a yellow-brown solid; the weight of the solid indicated that it consisted of equimolecular proportions of aluminum chloride and nitromethane. In this connection it is significant to contrast the nitroparaffin solutions with the ether, ketone, and primary alcohol solutions which were mentioned above. All four types of compounds form monomolecular addition complexes (usually crystalline compounds of low melting point) which are catalytically active (*9*). Aluminum chloride monomethanolate, for example, is an excellent catalyst for the alkylation of isoparaffins with olefins and has the advantage over pure aluminum chloride in that it produces high yields of primary products accompanied by a minimum of by-products (*8*). Solutions of the aluminum chloride monomethanolate in excess methanol, however, are catalytically inert. Indeed, even the solid product of the reaction of aluminum chloride with two molecular proportions of methanol —that is, $AlCl_3.2CH_3OH$—is not an alkylation catalyst. Similarly, aluminum chloride monoetherates and aluminum chloride monoketonates lose their catalytic activity when dissolved in ethers and ketones, respectively. In direct contrast to these, the aluminum chloride–nitroparaffin complexes retain their activity even with a large excess of nitroparaffin solvent.

Table I. Propylation of Benzene

Expt. No.	$AlCl_3$, g.	Catalyst and Reactants RNO_2 R—	g.	C_6H_6, g.	C_3H_6, g.[a]	Max temp, ° C.	Isopropylbenzene Mono g.	[b]	%[c]	Di g.	[b]	%[c]	Higher g.	[b]
1	4	CH_3	5.7	55	12	40	20	30	59	8	11	34	3	4
2	1	CH_3	2.3	80	15	43	26	27	61	10	10	35	5	5
3	5	C_2H_5	5.7	80	24[d]	47	31	32	45	16	16	35	7	7
4	5	iC_3H_6	7.5	40	6	..[e]	9.5	19	55	4.5	9	39	3	6

[a] Determined by increase in weight of absorber.
[b] Grams of product per mole of benzene charged.
[c] Per cent of theoretical based on propene absorbed.
[d] Experiment was carried out in two parts: 9 grams of propene were absorbed during 3 hours with absorber in an ice-water bath; an additional 15 grams were absorbed during 1 hour with absorber in a bath at 30° C., and maximum reaction temperature of 47° C.
[e] Not determined; bath at room temperature.

It is, of course, essential that the solvent be stable in the presence of aluminum chloride under the reaction conditions. Tests showed that nitromethane, for example, can be distilled from aluminum chloride with relatively little decomposition. The distillation temperature (100° C.) is substantially higher than the temperatures used in most of the hydrocarbon conversions in the presence of the catalyst solutions.

Aluminum Chloride–Nitromethane Complex. Evidence was obtained which indicated that the catalysts that are actually involved when nitroparaffin solutions of aluminum chloride are used are addition complexes. Aluminum chloride (3.699 grams, 0.028 mole) was dissolved in 10 grams of nitromethane at 0° C. and the resulting yellow solution was evaporated under 3 mm. of mercury pressure at a maximum (final) temperature of 70° C. The residue was a yellow-brown solid weighing 4.982 grams. The increase in weight corresponded to 0.021 mole of nitromethane, a value which was presumably somewhat low owing to loss of hydrogen chloride as moisture was not rigidly excluded. The residue was soluble in benzene and the solution so obtained reacted with isopropyl chloride to yield isopropylbenzene.

Action of Aluminum Chloride on Nitromethane. A solution of 5 grams (0.038 mole) of aluminum chloride in 25 ml. (28 grams) of nitromethane was placed in a 50-ml. flask under a 14-inch total reflux column and slowly distilled. The yellow solution began to turn brown when the temperature reached about 40° to 50° C. and was almost black at 100° C. Little decomposition occurred until 21.5 ml. of nitromethane had distilled over at 100° to 101° C. (n_D^{20} 1.3817) and the flask temperature had reached 120° to 130° C. At this point there was a vigorous reaction and the material in the flask was converted to a dark tar. This reacted vigorously when treated with water. The amount of unrecovered nitromethane was 3.5 ml. or 4 grams (0.066 mole).

CATALYST SOLUTIONS IN BENZENE

When a nitroparaffin solution of aluminum chloride is added to benzene, a single clear solution is obtained. The nitroparaffin may be considered to be a solubilizer for aluminum chloride in aromatic hydrocarbons. It makes possible the solution of almost any desired quantity of aluminum chloride in benzene. Pure benzene will dissolve only 0.72% by weight of aluminum chloride at 80° C. Benzene containing a minor amount of nitroparaffin can at room temperature dissolve aluminum chloride in an amount at least equal to the weight of the nitroparaffin.

The solid complex, $AlCl_3.CH_3NO_2$, remaining after the excess nitromethane is evaporated from a solution of aluminum chloride in nitromethane is soluble in benzene and the solution thus obtained contains active catalyst. The complex contains more than twice as much aluminum chloride by weight as nitromethane.

The aluminum chloride may be dissolved in the nitroparaffin before the benzene is added or the aluminum chloride and the nitroparaffin may be added separately to the aromatic hydrocarbon. It is often advantageous to add the aluminum chloride to the solution of the nitroparaffin in the aromatic hydrocarbon to avoid the possibility of overheating the catalyst; solution of aluminum chloride in the nitroparaffin is an exothermic process. The heat evolved can be decreased greatly by cooling the nitroparaffin to 0° C. or lower before mixing it with the aluminum chloride.

Nitroparaffins as Solubilizers for Aluminum Chloride in Benzene. When 3 grams (0.022 mole) of aluminum chloride were shaken with 40 grams of benzene at room temperature there was no visible evidence that any had dissolved. After addition of 0.25 gram of nitromethane, partial solution occurred and the benzene turned yellow. Addition of 0.35 gram more of nitromethane caused about 30 to 50% of the aluminum chloride to dissolve; a final addition of 1.10 grams resulted in complete solution of the chloride. A total of 1.70 grams or 0.028 mole of nitromethane was added; this indicated that equimolecular complex between aluminum chloride and nitromethane was formed.

Similarly, the addition of 1.0 gram of 2-nitropropane to a mixture of 3 grams (0.022 mole) of aluminum chloride and 40 grams of benzene caused the solution of about one half of the aluminum salt, the remainder going into solution after addition of 1.0 gram more of 2-nitropropane. The resulting clear solution was red. It is significant that a total of 2 grams or 0.022 mole of 2-nitropropane brought about the solution of an equimolar amount of aluminum chloride.

ALKYLATION OF BENZENE WITH PROPENE

Alkylation of benzene can be accomplished readily at about room temperature by bubbling propene through the solution of aluminum chloride and nitroparaffin in benzene. Practically quantitative yields of propylated benzene based on the propene absorbed are obtained (Table I). The reaction product consists of a single phase; the use of nitroparaffins thus makes it possible apparently for the first time, to study the alkylation reaction in a homogeneous, liquid phase. In working up the product, the aluminum chloride is removed by washing with water; the nitroparaffin may be extracted with dilute alkali or it may be recovered in part during the distillation of the water-washed product. Nitromethane is fairly soluble in water.

The various nitroparaffins do not seem to yield equally active catalyst solutions. Nitromethane and nitroethane are approximately equally effective but the secondary nitroparaffin, 2-nitropropane, yields solutions which are less active.

Experiment 2 in Table I was carried out to show one of the advantages of the nitroparaffin solvents—namely, that they permit the efficient use of small amounts of aluminum chloride. With only 0.007 mole of aluminum chloride dissolved in 1.0 mole of benzene, there were obtained about 0.2 mole of monoisopropylbenzene, 0.06 mole of diisopropylbenzene, and 0.02 mole of more highly alkylated product. Even more propene could have been absorbed had it been desired to continue the experiment.

Benzene (55 grams, 0.71 mole) was added to the pale yellowish solution prepared by dissolving 4 grams of aluminum chloride in 5 cc. of nitromethane. The resulting clear yellow solution (cooled to 0° C.) was placed in a spiral-type gas absorption bottle (*2*) and propene was bubbled through it. The reaction temperature rose to room temperature during 1 hour and then to 40° C. during the next 1.5 hours. About 12 grams (0.29 mole) of propene were absorbed. The clear yellow product was washed with water, then with dilute sodium hydroxide (in sufficient excess to dissolve the precipitated aluminum hydroxide) and finally dried over anhydrous potassium carbonate. The almost water-white product was distilled through a 14-inch total reflux column (*10*). There were obtained 20 grams (0.17 mole) of isopropylbenzene, 8 grams (0.05 mole) of diisopropylbenzene (boiling chiefly at 203° to 209° C.), and 2.5 grams of higher boiling material. The isopropylbenzene was characterized as the diacetamino derivative, melting point 214° to 215° C. (*4*).

The results of this and similar experiments in which nitroethane and 2-nitropropane were used as solubilizers for the aluminum chloride in the benzene are summarized in Table I. The solution of aluminum chloride in 2-nitropropane was yellow and when benzene was added, a red solution resulted. This turned yellow when the propene was bubbled in.

ALKYLATION OF BENZENE WITH ETHYLENE

As is the case with most alkylation catalysts, the nitroparaffin solutions of aluminum chloride were less active for the ethylation of benzene than for its propylation. Small amounts of ethylbenzene were formed when ethylene was bubbled through a solution of aluminum chloride and nitromethane in benzene under the conditions which gave good yields of isopropylbenzene with propene. Ethylation did occur when the solution was heated with ethylene under pressure, particularly in the presence of hydrogen chloride promoter.

Only a small amount of ethylbenzene was obtained when ethylene was bubbled through a benzene solution of nitromethane and aluminum chloride under the conditions used in the alkylations with propene described above. Improved results were obtained by carrying out the reaction under superatmospheric pressure, particularly in the presence of hydrogen chloride as promoter. A glass liner containing a solution of 8 grams of aluminum chloride and 10 grams of nitromethane in 80 grams of benzene was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity. Hydrogen chloride (3 grams) was pressed in, ethylene was added to a pressure of 40 atmospheres, and the autoclave was rotated at room temperature for 1 hour and then heated at 40° C. for 4 hours and finally at 65° C. for 3 hours. Distillation of the washed reaction product yielded 12 grams of monoethylbenzene and 6 grams of more highly alkylated material.

A lower yield (3 grams) of alkylation product was obtained when the above experiment was repeated, but without the addition of hydrogen chloride.

ALKYLATION OF BENZENE WITH DIISOBUTYLENE

Depolyalkylation accompanied the alkylation reaction when diisobutylene (chiefly a mixture of the 2,4,4-trimethylpentenes) was added to a solution of aluminum chloride and 2-nitropropane in benzene at 40° to 45° C.; *tert*-butylbenzene was obtained in 6% yield. The remainder of the product apparently consisted of a mixture of high molecular weight alkylbenzenes and some polymer.

Diisobutylene (boiling point 100° to 120° C., chiefly a mixture of the 2,4,5-trimethylpentenes) was added in small portions to a clear red solution of 10 grams of aluminum chloride and 15 grams of 2-nitropropane in 80 grams of benzene. The addition of only 0.5 gram of the olefin caused the red solution to turn yellow. A total of 32 grams (0.28 mole) of diisobutylene was added in 5- to 10-gram batches with intermittent manual shaking. The temperature of the solution was maintained at 35° to 40° C. by cooling the reaction flask with water. After setting overnight (16 hours) the reaction solution was again deep red; this indicated, perhaps, the complete reaction of the olefin. The product was washed with water, dried, and distilled. A small amount (4.5 grams, 6% yield) of *tert*-butylbenzene was obtained; it was characterized by its diacetamino derivative, melting point and mixed melting point 207° to 208° C. (*4*). The major product, 38 grams, boiled above 240° C.; n_D^{20} 1.4861.

ALKYLATION OF BENZENE WITH CYCLOPROPANE

n-Propylbenzene was formed when cyclopropane was bubbled into a solution of aluminum chloride in nitromethane and benzene at 20° to 50° C. There was no evidence of the presence of isopropylbenzene in the product. *n*-Propylbenzene was the only isomer obtained also when aluminum chloride alone was used as catalyst at 71° C. (*3*).

Cyclopropane was bubbled into a solution of 5 grams of aluminum chloride in 5.7 grams of nitromethane and 62 grams of benzene, first at room temperature for 4 hours and then at 50° C. for 2 hours. About 2 grams of the cycloparaffin were absorbed at the lower temperature and about 4 grams at the higher. The product, a clear yellow solution, was worked up in the manner described above. There were obtained 12 grams (70% yield) of propylbenzene and 2.5 grams of higher boiling product. The diacetamino derivative of the propylbenzene was obtained as white feathery needles, melting point 208° to 209° C., this proved that the hydrocarbon was *n*-propylbenzene. No hexagonal crystals of the diacetaminoisopropylbenzene were found when the crystals were observed with a polarizing microscope (*4*).

ALKYLATION OF BENZENE WITH ALKYL CHLORIDES

Isopropylbenzenes were formed in good yields when a clear solution of isopropyl chloride, a nitroparaffin, and aluminum chloride in benzene was permitted to stand at room temperature for several hours. With nitromethane or 2-nitropropane as solubilizer and using 0.5 mole of isopropyl chloride per mole of benzene, there was obtained a 41 to 46% yield of isopropylbenzene and a 31% yield of diisopropylbenzene.

The primary alkyl chloride, *n*-propyl chloride was less reactive than isopropyl chloride. With 2-nitropropane as solubilizer and a temperature of from room temperature to 70° C., propylbenzene was formed in only 4% yield. This product was shown to be isopropylbenzene rather than *n*-propylbenzene; isomerization accompanied the alkylation because of the relatively high reaction temperature (*3*).

A clear red solution of 40 grams of *n*-propyl chloride, 5 grams of 2-nitropropane, and 5 grams of aluminum chloride in 80 grams of benzene was permitted to stand at room temperature for 18 hours, during which a slow evolution of hydrogen chloride occurred. The solution then was heated at 60° to 70° C. for 1 hour; there was little additional formation of hydrogen chloride. The product (114 grams) was washed with ice water, dried, and distilled. There were obtained, besides unreacted *n*-propyl chloride, benzene, and 2-nitropropane, about 2.5 grams (4%) of a propylbenzene fraction which yielded a diacetamino derivative consisting of hexagonal prisms only (melting point 215° C.); this proved that the hydrocarbon was isopropylbenzene unadmixed with more than traces of *n*-propylbenzene (*4*).

Isopropyl chloride (40 grams, 0.51 mole) was added to a solution of 5 grams of aluminum chloride and 5 grams of a nitroparaffin in 80 grams (1.0 mole) of benzene at 0° C. The resulting solution was permitted to stand at room temperature overnight (20 hours) and then was washed, dried, and distilled. With nitromethane as solubilizer there were obtained 28 grams (46% yield) of isopropylbenzene, 13 grams (31% yield) of diisopropylbenzene, and 4 grams of residue. With 2-nitropropane as solutizer the respective yields were 25 grams (41%), 13 grams (31%), and 4 grams.

ALKYLATION OF BENZENE IN PRESENCE OF NITROMETHANE SOLUTIONS OF ALUMINUM CHLORIDE-SODIUM CHLORIDE

Alkylation of benzene in the presence of dissolved aluminum chloride and a nitroparaffin has obvious advantages because of the intimacy of contact between catalyst and reactants and is of theoretical interest because it permits the study of alkylation as a homogeneous phase catalytic reaction. On the other hand, it has the disadvantage that the catalyst cannot be recycled because it is dissolved in the product. This disadvantage can be overcome however, by salting out the catalyst solution by adding an alkali or alkaline earth metal chloride. Sodium chloride, for example, is insoluble in nitromethane but is soluble in nitromethane solutions of aluminum chloride; approximately 1 mole of the salt dissolves for each mole of aluminum chloride present; formation of sodium aluminum tetrachloride ($NaAlCl_4$) apparently occurs. The resulting solution is insoluble in benzene and separates as a deep-red lower layer. Alkylation takes place less readily with this two-phase system than with the solubilized aluminum chloride. Higher reaction temperatures are necessary; this is in agreement with previously reported weakening effect of sodium chloride on aluminum chloride (*1*).

TABLE II. ALKYLATION OF ISOBUTANE WITH PROPENE

Expt. No.	5	6	7	8	9	10	11	12	13	14	15	16[a]
Nitroparaffin	Nitromethane						$EtNO_2$	1-Nitropropane				i-$PrNO_2$
Hydrogen chloride, g.	3.5	3.5	3.8	3.7	11	3.8	3.6	3.5	10	3.5	3.7	1.8
Reaction Temp., ° C.	0.7	22	35	70	74	82	75	50	50	65	88	75
Pressure, lb./sq. in. gage												
At beginning of run	..[b]	47	64	159	180	174	107	68	85	102	200	..[b]
At end of propene addition	..[b]	51	63	148	132	155	121	80	71	100	168	80
One hour later	..[b]	38	53	97	120	112	97	60	50	95	170	..[b]
Products, g.												
Condensable gas[c]	228[d]	189	203	128	141[e]	162[f]	192	190	180	170	199[g]	64
Upper layer	27	49	45	82	102	79	38	55	48	63	59	24
Catalyst layer[h]	56	56	59	55	58	58	57	60	64	59	39[i]	30
Loss	0	16	3	45	9	11	23	5	18	18	13	12
Products, wt. % of C_3H_6												
Liquid hydrocarbon, C_5+	55	120	110	200	210	190	75	130	110	150	90[j]	80
Gasoline (200° C. end point)	17	36[k]	44	190	200	180[l]	48	56	54	97	75	..[m]
Heptanes	..	8	9	105	96	100	10	10	13	33	42	1
Octanes	2	15	6	29	50	37	10	21	19	25	19	12

[a] Experiment carried out in glass liner in rotating autoclave. Charge: 70 g. isobutane, 31 g. propene, and 10 g. of aluminum chloride dissolved in 19 g. of 2-nitropropane.

[b] Too low to be read on gage.

[c] Chiefly unreacted isobutane, but propane, propene, and pentane were also sometimes present; propene content footnoted only if present in more than 1.5% concentration; propane content was determined in only a few cases.

[d] Includes 7% propene.

[e] Includes 11% propane.

[f] Includes 4.8% propane.

[g] Includes 3% propene.

[h] Brown, fluid.

[i] Wet, cokelike granules.

[j] Also, 14 g. of 1-nitropropane.

[k] End point 175° C.

[l] End point 185° C.

[m] Distillation discontinued at 125° C. because hydrogen chloride was evolved.

Cumene was obtained in 14% yield when a mixture of propene, benzene, and sodium chloride and aluminum chloride dissolved in nitromethane was heated at 60° C. in a rotating autoclave. The addition of hydrogen chloride promoter resulted in an increased yield (55%). When isopropyl chloride was used instead of propene, the yield was 43%.

To a solution of 5 grams (0.038 mole) of aluminum chloride in 10 ml. of nitromethane there were added 2 grams (0.034 mole) of sodium chloride. The resulting clear yellow solution was added to 80 grams of benzene in a glass liner for an 850-cc. rotating autoclave; a deep red lower layer (12 ml.) separated. The mixture was cooled to −78° C., 20 grams of propene were added, and the liner was sealed into the autoclave. Nitrogen was charged to 30 atmospheres pressure and the autoclave was heated at 60° C. for 4 hours. The liquid reaction product consisted of 88 grams of upper layer and 12 grams of light-yellow fluid catalyst layer which reacted vigorously when treated with water. Distillation of the washed upper layer yielded 8 grams (14% based on the propene charged) of isopropylbenzene and 6 grams of higher boiling material. A higher yield (55%) of isopropylbenzene was obtained when the experiment was repeated under the same conditions except for the addition of 2.5 grams of hydrogen chloride promoter.

In a third experiment, the catalyst solution was heated at 60° C. with a solution of 80 grams of benzene and 40 grams of isopropyl chloride. The catalyst was recovered in the form of 15 grams of tan fluid lower layer. The upper layer yielded 26 grams (43%) of isopropylbenzene and 12 grams of higher-boiling material.

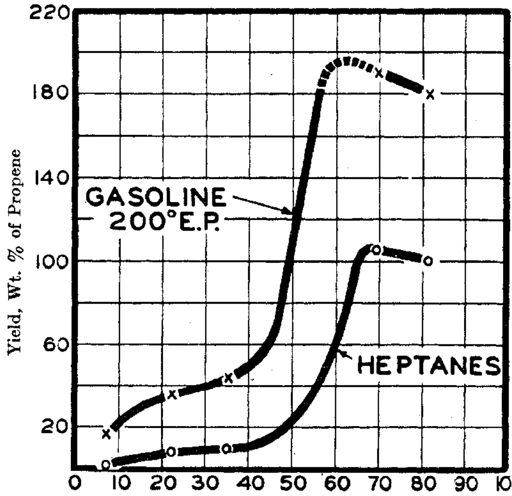

Figure 1. Alkylation of Isobutane with Propene in Presence of Aluminum Chloride Dissolved in Nitromethane

ALKYLATION OF ISOPARAFFINS WITH PROPENE

Alkylation of isobutane with propene took place in excellent yield in the presence of aluminum chloride dissolved in nitromethane. Use of nitroethane or 1-nitropropane as solvents gave fair to good yields of alkylated products whereas rather poor yields were obtained in the presence of solutions in 2-nitropropane. The catalyst solutions are not soluble in the hydrocarbon product and therefore may be separated and recycled.

Results of typical batch experiments on the alkylation of isobutane with propene are summarized in Table II. Under the most favorable conditions used, the yield of liquid product was 210% by weight of the propene charge. The theoretical yield of heptane is 238%; that of octane formed by hydrogen exchange reaction is 271%.

The experiments were carried out in a 1-liter stainless steel autoclave equipped with a rotary-type sealed stirrer. The catalyst (20 grams of aluminum chloride dissolved in 40 grams of the nitroparaffin) was weighed into a nickel liner which was then sealed into the autoclave. Isobutane (300 cc., 165 grams) was added from a calibrated charger and hydrogen chloride from a small weighed bomb. A solution of 40 grams of propene in 45 grams of isobutane was then added during 2 hours to the stirred mixture of isobutane, hydrogen chloride, and catalyst solution. The product was stirred for an additional hour, after which the gaseous material was passed through a soda lime tower and collected in a trap cooled in a dry ice–acetone bath. The autoclave was opened, the liquid product was separated from the catalyst layer, washed, dried, and distilled. The results of a series of such experiments are presented in Table II.

The catalyst layer was recovered as a brown mobile liquid in all experiments except the one in which 1-nitropropane was used as catalyst at 88° C. In that experiment, a cokelike catalyst layer was obtained; much of the nitropropane was recovered from the hydrocarbon layer. In the other alkylations, the catalyst solution underwent relatively little change. Unlike pure aluminum chloride, these catalyst solutions showed no appreciable increase in weight after the reaction; instead, there was usually a slight loss of nitroparaffin which dissolved in the hydrocarbon layer.

The effect of reaction temperature on the yield of alkylation product is shown in the results with nitromethane as solvent (Figure 1). A marked change occurred somewhere between 35° and 70° C. At the higher temperature the yield of liquid product was twice as much as that at the lower; the yield of product boiling in the gasoline range (200° C. end point) was four times as much and of heptanes more than ten times as much.

The composition of the alkylate was investigated by redistilling the combined product of experiments 8, 9, and 10. The data obtained are summarized in Table III and shown graphically in Figure 2. The results of the analysis of some of the fractions by means of their Raman spectra also are presented in the table. As is to be expected from the mechanism of the reaction (*7*, *8*), the heptane product consisted principally of 2,4- and 2,3-dimethylpentane.

The presence of 2,2,4-trimethylpentane in the octane product was shown by the Raman analysis. The higher-boiling octane fractions were not analyzed, but, based on the physical properties, it seems probable that they consisted chiefly of other trimethylpentanes (particularly 2,3,4-trimethylpentane). The formation of the octane undoubtedly occurred largely by reactions which may be indicated as follows (*8*):

$$C_3H_6 + HCl \longrightarrow i\text{-}C_3H_7Cl \tag{1}$$

$$i\text{-}C_4H_{10} + i\text{-}C_3H_7Cl \longrightarrow t\text{-}C_4H_9Cl + C_3H_8 \tag{2}$$

$$t\text{-}C_4H_9Cl \rightleftharpoons i\text{-}C_4H_8 + HCl \tag{3}$$

$$t\text{-}C_4H_9Cl + i\text{-}C_4H_8 \rightleftharpoons C_8H_{17}Cl \tag{4}$$

$$C_8H_{17}Cl + i\text{-}C_4H_{10} \longrightarrow C_8H_{18} + t\text{-}C_4H_9Cl \tag{5}$$

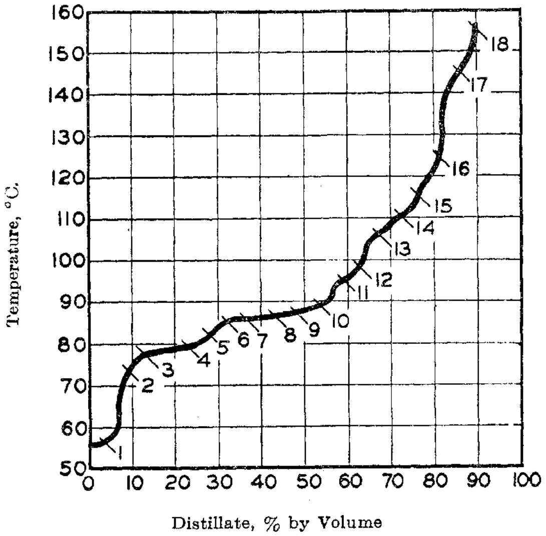

Figure 2. Redistillation of Product of Alkylation of Isobutane with Propene

Combined material from experiments 8, 9, and 10

The over-all reaction may be written:

$$2\ i\text{-}C_4H_{10} + C_3H_6 \longrightarrow C_8H_{18} + C_3H_8 \tag{6}$$

Its net effect is one of hydrogen transfer with resultant conversion of the propene to propane, and of isobutane to octane. Propane was found in the reaction product of experiment 10, for example, in an amount (0.14 mole) equivalent to the amount (0.14 mole) of octane formed. In experiment 9 the yields of propane and of octane were 0.28 and 0.18 mole, respectively.

ALKYLATION OF ISOPARAFFINS WITH ISOPROPYL CHLORIDE

It has been rather well established that paraffins and naphthenes (unlike aromatic hydrocarbons) undergo little condensation with alkyl chlorides when treated with aluminum chloride; instead intermolecular hydrogenation occurs. The alkyl halide is reduced to the corresponding paraffin and hydrogen chloride. The hydrogen is furnished by the original paraffin or naphthene, which is thereby converted either to paraffinic or naphthenic self-condensation product or to unsaturated hydrocarbon combined with the aluminum chloride in the lower layer. The over-all reaction is similar to that discussed with regard to the formation of propane during alkylation with propene.

Thus, for example, Nenitzescu and Ionescu (*6*) found that the reaction of cyclohexane with various alkyl and acyl halides (ethyl bromide, *n*- and isopropyl chloride, isobutyl chloride, cyclohexyl chloride, acetyl chloride, butyryl chloride, and benzoyl chloride) in the presence of aluminum chloride, yielded a mixture of hydrocarbons, $C_{12}H_{22}$, including dimethylbicyclopentyl. This product was not obtained by the reaction of cyclohexane and aluminum chloride alone or in the presence of hydrogen chloride, nitrobenzene, or olefins; the alkyl and acyl halides act as hydrogen acceptors.

Nenitzescu and Dragan (*5*) reported further that the reaction of *n*-heptane with propyl chloride, for example, in the presence of aluminum chloride gives a 90% yield of propane; the heptane undergoes only a small amount of decomposition to lower molecular weight paraffins, being converted principally to high-boiling cycloparaffins as well as the olefinic compounds found in the lower layer.

Similarly, as may be seen from the data presented in Table IV, the reaction of isobutane with isopropyl chloride in the presence of unmodified aluminum chloride results in the formation of 60 to 90% (depending on the temperature) of the propane available by the reduction of the alkyl chloride. The isobutane was converted by the formation of *tert*-butyl chloride (or isobutylene or *tert*-butyl carbonium ion) to octane (and products of its destructive alkylation) and catalyst complex (compare Equations 1 to 5, inclusive). On the other hand, no reaction at all occurred, when isobutane was heated at 70° C. with aluminum chloride and hydrogen chloride (experiment 23).

Analogous results were obtained with isopentane. Isopropyl chloride was converted to propane in 90% yield (experiment 26). Heating the isopentane with aluminum chloride and hydrogen chloride caused it to undergo autodestructive alkylation yielding higher-boiling isoparaffins and isobutane but no propane; less catalyst complex was formed (experiment 27).

It would be expected that similar reactions would occur in the presence of the nitroparaffin solutions of aluminum chloride. It was surprising, therefore, to find that alkylation of isobutane occurred when it was heated at 60° to 70° C. with isopropyl chloride in the presence of a nitromethane solution of aluminum chloride. Less than 30% of the isopropyl chloride was reduced to

TABLE III. REDISTILLATION OF PRODUCT FROM ALKYLATION OF ISOBUTANE WITH PROPENE

Charge		
Expt. No.	B.p., ° C.	Vol., Cc.
8	58–175	71
9	53–175	66
10	40–175	86

Distilled through Stedman-packed column

Cu'	B.P., ° C.	Vol., Cc.	Vol. %	n_D^{20}	Raman Analysis[a]
	28–56	10	4.6	1.3730	
2	56–74	10	4.6	1.3771	
3	74–78	10	44.8	1.3814	
4	78–79	21		1.3820	2,4-dimethylpentane
5	79–82	10		1.3830	
6	82–85	10		1.3869	
7	85–86	10	1.3887	1.3887	
8	86–87	13		1.3891	Mixture of 40% 2,4-dimethylpentane and 60% 2,3-dimethylpentane
9	87–88	11		1.3900	
10	88–89	12		1.3908	
11	89–95	10	4.6	1.3911	2,2,4-trimethylpentane
12	95–98	10	23.0	1.3916	
13	98–106	10		1.3939	
14	106–110	10		1.3971	
15	110–115	10		1.4010	
16	115–124	10		1.4011	
17	124–145	10	4.6	1.4066	
18	145–155	10	4.6	1.4188	
Bottoms		20	9.2		

[a] Raman analyses by C. R. Sandburg, University of Chicago; he reported that a maximum of 10% of other hydrocarbons might possibly have been present in the samples but were not found, their Raman lines not showing up on the spectrograph due to fluorescence of the samples.

propane. The liquid product consisted of a mixture of paraffins; heptanes and octanes were formed in largest amounts. The yield of liquid product was higher than that obtained in the presence of unmodified aluminum chloride, but it was lower than that obtained with propene as alkylating agent (the latter difference in yield may have been due in part to the difference in experimental procedure).

Table IV. Reaction of Isoparaffins with Isopropyl Chloride

Expt. No.	17	18	19	20	21	22	23	24	25	26	27	28
Isoparaffin	Isobutane							Isopentane				
Reactants, g.												
Isoparaffin	100	100	102	109	0	101	100	100	100	100	100	100
Isopropyl chloride	40	40	40	81	80	40	0	40	50	40	0	0
Catalyst, g.												
Aluminum chloride	7	8	7	10	7	8	8	10	10	8	8	10
Nitromethane	15	0	15	20	15	0	0	15	12	0	0	15
Hydrogen chloride	0	0	0	0	0	0	20	0	2	0	16	16
Temperature, ° C.	30	40	60	70	60	70	70	70	70	40	40	70
Products, g.												
Hydrocarbon	118	105	115	153	0	108	100[a]	120	127	120	94	99
Catalyst layer	25	20	23	38	87[b]	21	8[c]	30	35	23	11	24
Hydrogen chloride[d] + loss	19	23	26	24	15	20	20	15	12	15	19	18
Products, wt. % of C_3H_6[e]												
Propane[f]	2	60	28	28	0	90	0	15	20	90	0	...
Liquid hydrocarbon[g]	25	75	130	100	0	70	0	180	122	126	150[h]	0
Heptane	12	12	39	35	0	14	0	28	19	28	23[h]	0
Octane	..	33	41	20	0	19	0	42	51	16	12[h]	0
Hydrocarbon in catalyst layer	14	56	5	18	...	60	0	23	48	70	14[h]	0
Products, moles/mole C_3H_6[e]												
Propane	0.02	0.60	0.28	0.28	0	0.90	0	0.15	0.20	0.90	0	0
Heptane	0.05	0.05	0.16	0.15	0	0.06	0	0.13	0.06	0.12	0.10[h]	0
Octane	...	0.12	0.15	0.07	0	0.07	0	0.16	0.15	0.06	0.04[h]	0

[a] Isobutane.
[b] Hydrolysis yields 52 g. of isopropyl chloride (65% of charge).
[c] Crystalline.
[d] Theoretical amount available from 40 g. isopropyl chloride charge is 19 g.
[e] On basis of propene available from isopropyl chloride.
[f] Per cent of theory.
[g] Of higher boiling point than charged isoparaffin.
[h] Calculated on basis of 40 g. of isopropyl chloride charge, merely for purposes of comparison; product consisted of 32 g. of material boiling higher than isopentane (included 5 g. heptane, 2.5 g. octane).

The difference between the action of aluminum chloride as such and aluminum chloride dissolved in nitromethane seems to be that in the latter case the isopropyl chloride dissolves in the liquid catalyst and is dehydrohalogenated to propene. *tert*-Butyl chloride, formed by the hydrogen-chlorine exchange between part of the isopropyl chloride and isobutane, then can add to propene and thus eventually yield heptane as a primary product. In the absence of propene—that is, when the reduction to propane is more rapid than the dehydrochlorination to propene as seems to be the case when unmodified aluminum chloride is used—the *tert*-butyl chloride is converted to octane and catalyst complex in the manner discussed previously.

The reaction of isopentane with isopropyl chloride at 70° C. in the presence of the nitromethane solution of aluminum chloride yielded octane as the major product. Propane was formed in only 15 to 20% yield.

Little or no reaction occurred when either the isopentane or the isopropyl chloride was heated at 60° to 70° C. with the nitromethane solution of aluminum chloride. Hydrogen chloride was added as promoter in the former case.

Isopropyl chloride was weighed into a glass liner and cooled to −78° C. Isobutane or isopentane and aluminum chloride (as such or dissolved in nitromethane) were added and the liner was sealed into an Ipatieff-type rotating autoclave of 850-cc. capacity. Hydrogen chloride, if desired, was then charged from a small weighed bomb. Nitrogen was added to a total pressure of 30 atmospheres and the autoclave was rotated at the desired temperature for 4 hours. It then was allowed to stand overnight, after which the gaseous and liquid products were separated and treated in the same manner as were the products from the propene alkylations described. The results are summarized in Table IV.

ISOMERIZATION OF SATURATED HYDROCARBONS

In contrast to their effectiveness as catalysts for the alkylation of aromatics and isoparaffins, the nitroparaffin solutions of aluminum chloride seem to be inactive for the isomerization of paraffins and naphthenes. Not more than 2% isomerization of *n*-pentane occurred when the alkane was heated at 100° to 125° C. with a solution of aluminum chloride in nitromethane or 2-nitropropane. The addition of hydrogen chloride had little effect. Similarly, little isomerization of heptane occurred at 75° C. in the presence of hydrogen chloride and aluminum chloride dissolved in nitromethane.

As the isomerization of methylcyclopentane to cyclohexane takes place more readily than does that of *n*-pentane, the isomerization of this naphthene in the presence of a nitromethane solution of aluminum chloride was investigated. It was found that no isomerization (certainly less than 2%) occurred under conditions which yielded at least 40% of cyclohexane when unmodified aluminum chloride was used as catalyst.

Isomerization of Paraffins. The experiments were carried out in glass liners in the rotating autoclave; the paraffin was heated for 4 hours with the catalyst solution under 50 atmospheres initial nitrogen pressure. No isopentane was obtained when 50 grams of *n*-pentane were heated at 125° C. in the presence of a solution of 5 grams of aluminum chloride in 5 grams of nitromethane. Similarly little or no isomerization occurred when the *n*-pentane was treated at 100° C. with a solution of 4 grams of aluminum chloride in 4 grams of 2-nitropropane using 5 grams of hydrogen chloride as promoter.

n-Heptane underwent no more than 2% conversion when 50 grams of the compound were heated at 75° C. with 2 grams of hydrogen chloride and a solution of 5 grams of aluminum chloride in 11 grams of nitromethane.

Isomerization of Methylcyclopentane. A mixture of 20 cc. of methylcyclopentane and a solution of 5 grams of aluminum chloride in 10 cc. of nitromethane was shaken at room temperature for 10 minutes. A small portion (0.3 cc.) of the upper layer was removed, washed with a few drops of water, and dried over potassium carbonate. Its refractive index (n_D^{20} 1.4100) was identical with that of the original methylcyclopentane.

The mixture of catalyst and napthene then was heated at 40° C. for 2 hours with occasional shaking; there fractive index of a sample at the end of that time was 1.4096. The catalyst had turned from yellow to dark brown.

The mixture was refluxed finally (72° C.) for 2 hours. Distillation of the washed hydrocarbon product (n_D^{20} 1.4102) showed that 90% boiled at 71.5° to 72.0° C., n_D^{20} 1.4100. The residue had a refractive index of 1.4130.

The product obtained by treating 10 cc. of methylcyclopentane with 3 grams of aluminum chloride alone at 40° C. for 2 hours and at 72° to 74° C. for 2 hours had a refractive index of 1.4170. Since the refractive indexes of methylcyclopentane and cyclohexane are 1.4099 and 1.4264, respectively, it was estimated that about 40% isomerization had occurred.

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