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A Carbon-14 Tracer Study of the Dehydrocyclization of *n*-Heptane

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n-Heptane containing *n*-heptane-4-C^{14} was dehydrocyclized over unsupported chromia and two different chromia-alumina catalysts in an effort to learn more about the intermediate(s) formed on the catalyst surface during cyclization. The relative radioactivity in the methyl position and ring positions 1, 2, and 3 was determined. These results are compared to the results expected from mechanisms proposed by previous workers. The results of this study can be interpreted to support the Twigg mechanism if some isomerization reaction is allowed. A possible reaction path is proposed which can explain the C^{14} distribution obtained experimentally for cyclization of *n*-heptane-1-C^{14} and *n*-heptane-4-C^{14}.

INTRODUCTION

Investigations of the dehydrocyclization of paraffins (*1*) using C^{14}-labeled hydrocarbons (*2–5*) have indicated that the reaction mechanism is more complex than those proposed by Twigg (*6*), Herington and Rideal (*7*), and Pitkethly and Steiner (*8*). For the dehydrocyclization of *n*-heptane-1-C^{14} the latter mechanisms predict 50% of the radioactivity will be present in the methyl group of the toluene produced. Wheatcroft, using 1-heptene-1-C^{14}, felt he had demonstrated the validity of this type reaction mechanism. Later Mitchell, using *n*-heptane-1-C^{14} found only 25% radioactivity in the methyl group and postulated three possible explanations: (a) a bicyclo intermediate, (b) ring expansion and contraction of the adsorbed intermediate, and (c) an adsorbed cycloheptane intermediate. Pines and Chen found the activity in the methyl group of the toluene was dependent on the catalyst used; they concluded that the reaction proceeded to some extent through an adsorbed cycloheptane intermediate which was free to "roll around" on the catalyst surface.

It could be decided whether the cycloheptane or the bicyclo species was an intermediate if the amount of radioactivity in the various ring positions could be measured. The cycloheptane intermediate free to "roll around" on the surface would predict equal activity in all ring positions and the methyl position. The bicyclo intermediate would give more activity in certain positions than other ones; the positions containing C^{14} activity would depend on the position of the C^{14} in the original *n*-heptane.

For this study *n*-heptane-4-C^{14} was chosen since this would only give activity in one position for the Twigg mechanism and because the C^{14} is located in the middle of the heptane chain it would not be as subject to isomerizations such as proposed by Turner and Warne.

EXPERIMENTAL

Catalysts. The two chromia-alumina catalysts were prepared by the method employed by Pines and Chen (*9*) to prepare their chromia-alumina-A and -B catalysts. The unsupported chromia was prepared by

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forming the gel from a chromium nitrate–ammonium acetate solution by adding ammonium hydroxide and heating until gel formation (*10*).

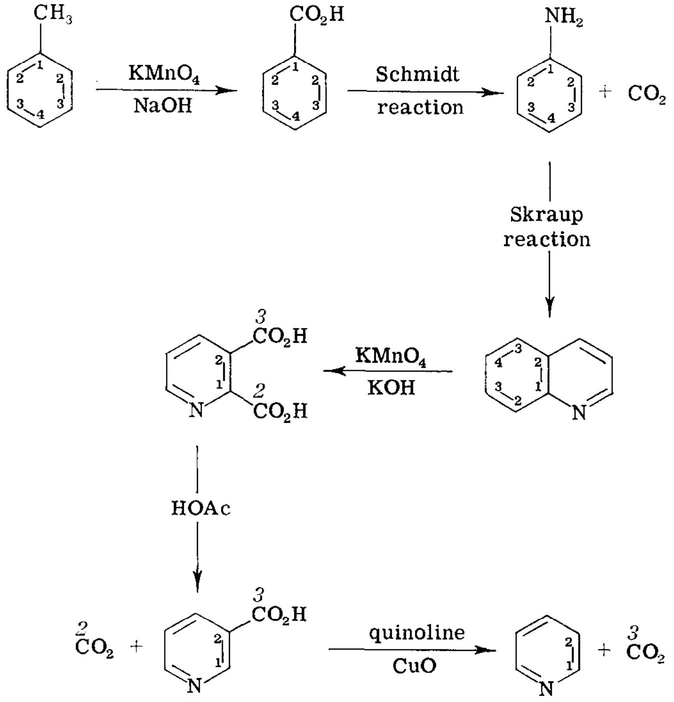
***n*-Heptane-4-C^{14}.** This material was synthesized by hydrogenation of the 3-heptene-4-C^{14} which results from the thermal decomposition of C^{14}-labeled 4-heptyl acetate (*11*). The 4-heptyl acetate was prepared from 4-heptanol-4-C^{14} which had been prepared from sodium formate-C^{14} and propyl magnesium bromide. 1-Heptene and 2-heptene isomers could not be detected in the 3-heptene by gas chromatography or infrared analysis.

Cyclization procedure. The reaction was carried out in a conventional flow-type reaction apparatus. The reactant was passed over 6 ml of catalyst (20-mm diameter reaction tube) at 500°C in a nitrogen carrier gas. The nitrogen was passed through a bubbler containing heptane at 0°C at a rate such that 1 ml of reactant per hour passed over the catalyst. The chromia-alumina catalyst was activated by heating to 500°C in nitrogen, then passing hydrogen over it for 1 hr before the reaction run was started. The unsupported chromia was activated by flushing it with hydrogen for 15 min at room temperature; hydrogen was passed over it while heating to 400°C during a 3-hr period, held at this temperature for 1 hr, and then slowly heated to 500°C and kept at this temperature for 1 hr before beginning the reaction run. The different activation procedure was used for unsupported chromia to prevent, as much as possible, the "glow" phenomenon.

The catalyst activity was determined by passing unlabeled heptane over the catalyst under conditions identical to those used for the C^{14}-labeled heptane runs. The activity was determined for a fresh catalyst from the same catalyst preparation as was used for the run with the labeled heptane.

The liquid products were collected at 1-hr intervals. They were diluted with an unlabeled heptane-toluene mixture and separated by chromatography on silica gel.

Ring degradation—method and discussion of method. The over-all degradation scheme is as follows (the numbers at the different carbon positions refer to the carbon position in the original toluene):



The toluene fraction of the reaction products was oxidized to benzoic acid by alkaline permanganate. The benzoic acid was decarboxylated by two different methods: (a) heating at 260°C in a quinoline–copper oxide mixture and (b) by the Schmidt reaction (*12*). The carbon dioxide for each decarboxylation was trapped in sodium hydroxide and collected as barium carbonate.

Pines and Chen employed the copper oxide–quinoline decarboxylation in their study using n-heptane-1-C^{14} and concluded that an uncertainty of 3% could be allowed for their assay data, i.e., isotope discrimination for this reaction was absent or at least small. As shown in the Results section there is good agreement between the two decarboxylation methods employed in this study. Thus it was assumed that the Schmidt reaction gave little, if any, isotope discrimination.

The aniline formed by the Schmidt reaction was extracted with chloroform from the reaction mixture after neutralization with ammonium hydroxide. The chloroform was washed with water and dried by passing through filter paper. The aniline was precipitated from the chloroform by the addition of concentrated sulfuric acid. The addition of an excess of acid is to be avoided as it is adsorbed by the aniline sulfate precipitate and makes separation difficult.

The Steinberg and Sixma (*13*) scheme proceeds by the nitration of the toluene to the three nitrotoluene isomers and then oxidation to the corresponding nitrobenzoic acids. These isomers are then separated by countercurrent solvent extraction. Now if the degradation scheme outlined at the beginning of this section is followed for the *ortho* isomer one obtains carbon dioxide from the ring positions 1 and 4 for the decarboxylation of quinolinic and nicotinic acids, respectively; in addition the *para* isomer yields carbon dioxide from the ring positions 3 and 2 from the decarboxylation of the quinolinic and nicotinic acids, respectively. This then would enable one to calculate the activity of each ring position directly from experimentally measured data. The nitration, oxidation to nitrobenzoic acid, and separation of isomers was replaced by the Schmidt reaction for the present investigation because only about 3 g of toluene was available from each cut and this was not enough material for the preferred Steinberg and Sixma method.

The quinoline was prepared from aniline by mixing aniline sulfate with nitrobenzene, ferrous sulfate, boric acid, anhydrous glycerol, and concentrated sulfuric acid in such amounts that the final mixture had the same composition as Steinberg and Sixma used for their Skraup reaction. The flask was heated gently until a vigorous exothermic reaction began; after the initial reaction subsided somewhat the temperature was maintained at 160°C for 4 hr. The mixture was then neutralized with ammonium hydroxide and an excess of 20–30 ml of concentrated ammonium hydroxide was added. The quinoline was removed from the mixture by steam distillation and extracted from the distillate with chloroform. The chloroform was washed with water and then dried; the quinoline was then precipitated by addition of concentrated sulfuric acid. This precipitation is slow and requires several hours; again an excess of sulfuric acid is to be avoided. The extraction and precipitation steps are necessary because glycerol also steam distills and so much oxalate is produced in the next step that the desired quinolinic acid could not be recovered.

The quinoline is oxidized to quinolinic acid with alkaline permanganate. The degradation from this point on was identical to the scheme developed by Steinberg and Sixma; the amounts of reagents were adjusted to give the same ratio of reagents as were used by Steinberg and Sixma. The yield of barium carbonate for the two decarboxylations and the van Slyke combustion of nicotinic and quinolinic acid was in the range of 96–103% of the theoretical amount.

Unfortunately the modified method used for this study does not allow for the calculation of the activity in the C-4 position. (The abbreviations C-1, C-2, C-3, and C-4 will be used to designate the ring positions 1, 2, 3, and 4, respectively.) The quinoline produced by the Skraup reaction is formed from the aniline sulfate and also from the nitrobenzene. The quinoline formed from the nitrobenzene causes the C^{14} activity in the quinoline to be different from the C^{14} activity in the aniline relative to the original toluene. Thus the C^{14} activity of the aniline cannot be used to calculate the total activity present in the quinoline. Some of the nitrobenzene is reduced to aniline during the Skraup reaction; thus the quinoline sulfate is contaminated by an unknown amount of unlabeled aniline sulfate and not enough quinoline was produced to attempt a purification of the material. This then eliminates the combustion of aniline sulfate to obtain the total ring activity.

It is seen from the reaction scheme that, if the amine group replaces the carboxyl group without migration around the ring, the quinolinic acid contains only C^{14} from positions C-1, C-2, and C-3. It is also noted that the decarboxylation of quinolinic acid gives carbon dioxide containing activity from C-2 only; likewise decarboxylation of nicotinic acid yields carbon dioxide containing activity from C-3 only. This allows the calculation of the ratio of activity in C-2 to C-3 directly from experimentally determined values.

The activity distribution among C-1, C-2, and C-3 using nicotinic acid to obtain the "total activity" was calculated from the activities of the barium carbonate from the decarboxylations of nicotinic and quinolinic acids, and the total activity from the combustion of nicotinic acid. The nicotinic acid contains one carbon from C-1, C-2, and C-3 positions along with three inactive carbon atoms not originally in the toluene ring. Now the activity of C-3 will be in the barium carbonate from the decarboxylation of the nicotinic acid; the activity of C-2 will be in the barium carbonate from the quinolinic acid decarboxylation. However, half of the original activity in the C-2 and C-3 positions was lost when the quinoline was oxidized to quinolinic acid; therefore the activity of the barium carbonate obtained from the decarboxylations must be doubled to represent the activity of these positions in the original toluene molecule. The barium carbonate from the complete combustion of the nicotinic acid will contain the activity of C-1, half of the activity of C-2, and half of the activity of C-3. To get the total activity of these three ring positions in the original toluene, the activity of the barium carbonate from the decarboxylations of the nicotinic and quinolinic acids must be added to six times the activity of the barium carbonate from the combustion of the nicotinic acid. The activity of the nicotinic acid must be multiplied by 6 because there are five inactive carbon atoms in each molecule with an active carbon. The per cent activity in C-2 or C-3 is the activity in the barium carbonate from the decarboxylation corresponding to these positions divided by the total activity of the three positions times 100. The activity of the C-1 will then be 100% minus the per cent activity in C-2 and C-3. Similar reasoning enables one to calculate these percentages using quinolinic acid to obtain the total activity in the three positions.

Run 3, Cut 4 activities (counts/10 min/100 mg $BaCO_3$) are typical of the amount of activity present in the ring degradation products. The counts/10 min activity was 128 for $BaCO_3$ from quinolinic acid decarboxylation, 2660 for $BaCO_3$ from nicotinic acid decarboxylation, and 488 for $BaCO_3$ from the van Slyke combustion of nicotinic acid. For the same run the $BaCO_3$ from the decarboxylation of benzoic acid activity was 92 counts/10 min and the $BaCO_3$ from combustion of benzoic acid was 874. Note that since these activities are based on $BaCO_3$ weight the activity for the decarboxylation must be divided by 7 before calculating the percentage activity in the methyl position. Three duplicate samples were prepared from the $BaCO_3$ from the decarboxylation of benzoic acid for Run 3, Cut 1; the activities obtained for these samples were 207, 208, and 198 counts/10 min. Two duplicate samples were prepared from a standard 0.045 μcurie/g $BaCO_3$ and the activities measured for these samples were 4350 and 4480 counts/10 min.

The radioactivity of the $BaCO_3$ was

measured by a Packard TriCarb liquid scintillation spectrometer. Each sample was counted four times for a 10-min period each time.

RESULTS AND DISCUSSION

The order of activity for the three catalysts was in the same order as obtained by Pines and Chen. For unsupported chromia the toluene content was 95% for the first-hour cut and decreased to 14% for the third-hour cut; for chromia-alumina (alumina from aluminum isopropoxide) the toluene yield was 70% for the first-hour cut and fell to 55% for the fourth-hour cut; for chromia-alumina (alumina from sodium aluminate) the toluene yield was 53% for the first-hour cut and dropped to 44% for the fourth-hour cut.

TABLE 1

ACTIVITY IN METHYL POSITION

Sample	% C^{14} activity by HN_3 decarboxylation	% C^{14} activity by CuO-quinoline decarboxylation
Run 3[a] Cut 1	2.0	1.6
Cut 2	—	1.7
Cut 3	0.8	1.3
Cut 4	1.0	1.2
Run 4[b] Cut 1	1.9	1.6
Cut 2	1.7	1.2
Cut 3	—	1.0
Cut 4	1.3	1.0
Run 6[c] Cut 1	3.7	3.1
Cut 2	1.8	0.7
Cut 3	0.6	0.3

[a] Run using chromia-alumina (alumina from aluminum isopropoxide).

[b] Run using chromia-alumina (alumina from sodium aluminate).

[c] Run using unsupported chromia.

The radioactivity found in the toluene methyl group for the two decarboxylation methods is presented in Table 1. The agreement between the two methods is seen to be reasonably close. It is noted that the methyl activity appears to decrease as the reaction time increases. Also the highest activity in the methyl group, for the cut at the end of the first hour, was obtained for the toluene formed over the unsupported chromia. In Table 2 the ratio of activity of the C-2 to C-3 position and the activity in C-1, C-2, and C-3 are presented.

These results cannot be accounted for using the mechanisms postulated by either Mitchell or by Pines and Chen. With a bicyclo intermediate 50% of the radioactivity would be present in the ring position 1 and the other 50% would be in ring position 3. The activity for ring position 1 given in Table 2 has a large experimental error because the value depends upon the difference between two large, nearly equal numbers. However, the minimum ratio of activity of ring position 1 to ring position 3 is approximately 1:5; the average ratio

TABLE 2

ACTIVITY DISTRIBUTION IN THE AROMATIC RING

Sample	Ratio[d] C-2:C-3	C-1[e] (%)	C-2[e] (%)	C-3[e] (%)
Run 3[a] Cut 1	1:21.2	−0.5 (−1.4)	4.5 (4.6)	96.0 (96.8)
Cut 3	1:19.7	12.1 (21.4)	4.2 (3.8)	83.7 (74.8)
Cut 4	1:20.8	2.7 (4.9)	4.5 (4.4)	92.8 (90.7)
Run 4[b] Cut 1	1:7.0	11.5 (23.5)	11.0 (9.5)	77.5 (67.0)
Cut 2	1:13.7	16.1 (27.7)	5.7 (4.9)	78.2 (67.4)
Cut 4	1:21.2	9.5 (18.5)	4.1 (3.7)	86.4 (77.8)
Run 6[c] Cut 1	1:12.3	6.6 (12.7)	7.0 (6.6)	86.4 (80.7)
Cut 2	1:6.5	1.7 (−17.2)	2.3 (16.5)	96.0 (100.7)
Cut 3	1:58.5	8.0 (15.3)	1.5 (1.4)	90.5 (83.3)

[a-c] See footnotes *a-c*, Table 1.

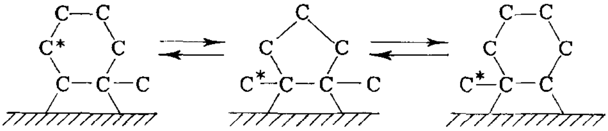
[d] Ratio of the counts/10 min/100 mg $BaCO_3$ for the CO_2 from the decarboxylation of quinolinic and nicotinic acids.

[e] C-1, C-2, and C-3 refer to ring positions 1, 2, and 3 respectively. Numbers in parentheses are based on the total activity based on quinolinic acid.

is 1:13. Thus, while there may be a large absolute error in the numbers, they do show that the activity ratio of ring position 1 to ring position 3 is far less than the 1:1 ratio required by the bicyclo intermediate. The elimination of this species as the intermediate is in agreement with the results of Pines and Chen.

The cycloheptane intermediate as proposed by Mitchell and extended by Pines and Chen likewise does not explain these results. If this intermediate is involved in the major reaction path the activity of each ring position and the methyl position must be nearly equal. This distribution of radioactivity is not obtained in the present study. The maximum activity in the methyl group is obtained for the first cut over the unsupported chromia catalyst and is only 3.7 and 3.1 as determined by the two decarboxylation methods. This is about one-fourth of the activity predicted by the cycloheptane intermediate. Indeed most of the cuts contained less than 15% of the activity predicted by this intermediate.

The rapid ring contraction–expansion between a five- and six-membered ring cannot explain the C^{14} distribution for *n*-heptane-4-C^{14} cyclization. If 1-heptene-4-C^{14} is adsorbed and cyclized by simple ring closure all C^{14} will be in the ring position three. If 2-heptene-4-C^{14} is adsorbed and cyclized and then undergoes the rapid isomerization shown below the toluene would be labeled in the methyl group and the ring position 3 only. Thus, even assuming that 1- and 2-heptene-4-C^{14} cyclize at the same rate leads to 25% methyl-labeled toluene. Thus this isomerization can be eliminated as contributing greatly to the over-all reaction.



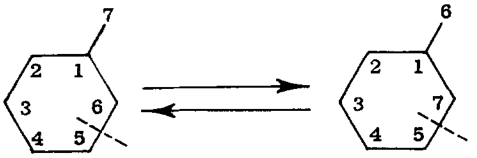
Likewise no great difference is observed for the C^{14} distribution in the toluene obtained over the three different catalysts. This is in marked contrast to the case of *n*-heptane-1-C^{14} as obtained by Pines and Chen. Indeed Table 1 shows the highest C^{14} activity in the methyl position is obtained for Cut 1 from the run using unsupported chromia catalyst. Also no significant difference is noted for the two chromia-alumina catalysts in the amount of C^{14} in the methyl position of the toluene formed with these catalysts.

However, it appears that the ratio of ring position 2 to ring position 3 activity does show a significant difference for the three catalysts. For Run 3 using chromia-alumina catalyst (alumina from aluminum isopropoxide) the ratio seems to be constant at about 1:20. For Run 4 using chromia-alumina (alumina from sodium aluminate) the ratio is seen to increase from 1:7 for Cut 1 to 1:21 for Cut 4. This indicates that there is considerable deviation from a Twigg-type mechanism or considerable contribution from an isomerization reaction for this catalyst for Cut 1 and that this decreases rapidly with reaction time until the fourth cut ratio is the same as the ratio obtained over the other chromia-alumina catalyst. Over chromia alone the toluene yield for Cuts 2 and 3 was low; consequently the ratio is based on low C^{14} activity and little significance is attached to the ratio for Cuts 2 and 3. From the ratio of Cut 1 it appears that chromia alone would fall between the two chromia-alumina catalysts for the radioactivity isomerization to ring position 2. Thus, in agreement with Pines and Chen, the alumina support does seem to have some effect on the C^{14} distribution, particularly in the initial periods of the reaction.

The results of the present investigation can be explained by the mechanism proposed by Twigg, etc., more satisfactorily than by any mechanism proposed to date. This reaction path would require all of the C^{14} to be located in ring position 3 and

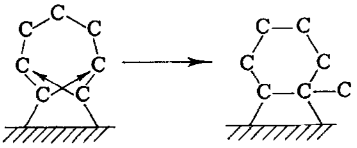
Tables 1 and 2 show this to be more nearly the case. However, there is enough C^{14} activity in the other positions to require some toluene to be formed by alternate mechanism(s) or isomerization of the adsorbed species or the toluene after formation.

Turner and Warne passed methylcyclohexane-7-C^{14} and methylcyclohexane-1-C^{14} over a chromia-alumina catalyst. With the former reactant nearly all (96.3%) of the C^{14} remained in the 7 position. With the latter 99.4% of the C^{14} remained in the ring; however, only 86.2% was in the original ring position after dehydrogenation. They attribute this to (a) a migration of the methyl group around the ring and (b) the isomerization reaction

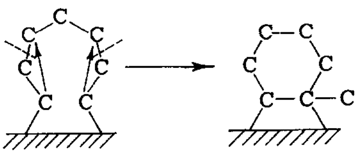


If the Twigg mechanism is assumed to apply for *n*-heptane-4-C^{14} cyclization, it is necessary for the methyl group to migrate about the ring before the above isomerization takes place. This is necessary to obtain C^{14} in the methyl position. This side reaction cannot be explicitly ruled out on the basis of our experimental results; however, it is seen that there is more C^{14} in the methyl position in the present case (where the C^{14} originally is assumed to be in ring position 3) than where the C^{14} was in the ring position 1 in methylcyclohexane. Thus it does not seem likely that this is the scheme whereby the C^{14} is distributed to positions other than ring position 3.

Considering these results and those obtained by previous workers it seems reasonable to search for a mechanism which is similar to the Twigg mechanism but which allows for low C^{14} activity in the methyl group of toluene when *n*-heptane-1-C^{14} is the reactant. One such mechanism is for the *n*-heptane to be attached to the catalyst surface by carbon atoms 1 and 7. This adsorbed species would not be free to "roll around" on the surface as proposed by Pines and Chen. Then cyclization could be effected by the two schemes shown below (each arrow represents a possible path for ring closure; dashed lines indicate bonds to be broken):



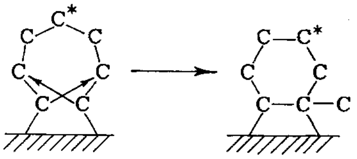
(a)



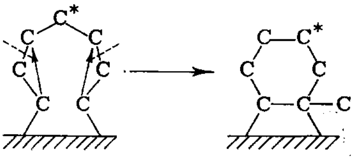
(b)

The reaction path (a) will produce toluene labeled in the same position as would the Twigg mechanism for *n*-heptane labeled in any of the four positions. However, reaction path (b) may give rise to the same or quite different distributions, depending on the position of the C^{14} in the starting material.

For *n*-heptane-4-C^{14} the two paths yield toluene labeled in the same position, ring position 3, as shown below



(a)



(b)

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