conversion levels remains unexplained. In view of the large decrease of free energy for oxidation reactions, there cannot be any question of the extent of reaction being limited by equilibrium. A likely possibility is that the oxidation is inhibited by one of the intermediate products, however, too little is known of the process for an attempt to identify such an intermediate.

Table II

n-Hexane Conversion as a Function of Radiation Dose at 10^6 Rad./Hr. Intensity

Radiation dose abs., megarads	*n*-Hexane conversion, % 178°	205°
0.5	5.5	7.0
1.0	. .	17.0
2.0	9.5	. .
3.0	13.0	16.0
4.7	. .	15.5

Effect of Pressure.—At 205° and at a 2/1 mole ratio of *n*-hexane to oxygen, static experiments at 10^6 rad./hr. showed a considerable pressure effect. Increasing the total initial pressure from 3.4 to 10 atm. increased the *n*-hexane conversion from 17 to 40% with *G* values of about 6000 hexane molecules converted per 100 ev. The oxidation at 10 atm. remained a controlled reaction giving a low yield of carbon oxides corresponding to about 2% of the initial *n*-hexane concentration.

Composition of Products.—At temperatures higher than about 235°, large amounts of CO, CO_2 and water are formed. At 150–235°, the major products are oxygenated hydrocarbons obtained in a highly complex mixture. The four major products were unidentified epoxides of *n*-hexane containing 3- and 4-membered cyclic structures, 2,5-dimethyl tetrahydrofuran, acetone and methanol, in decreasing order of abundance. The presence of the cyclic ethers as major products agrees with the thermal oxidation results of Norrish and Bailey.[14]

The detailed mechanism of *n*-hexane oxidation in the presence of nuclear radiation is obviously very complex. However, it is of interest that radiation initiation can be used for achieving the controlled chain oxidation of hydrocarbons. This chain reaction is sensitive to radiation intensity, temperature and pressure. At some conditions it is very sensitive to the state of the reactor walls. Whether this radiation-induced reaction is a free radical chain process due to the radiation initiation or an entirely new kind of chain reaction propagated by ions, for example, is a question that cannot be answered on the basis of this work. In either case, it is important, since even if the reaction is only an accelerated thermal chain, controlled hydrocarbon oxidation chain processes are so difficult to achieve thermally that the radiation technique provides a useful initiation device for this area of hydrocarbon chemistry.

(14) H. C. Bailey and R. G. W. Norrish, *Proc. Royal Soc.* (*London*), **A212**, 311 (1952).

[Contribution from the Esso Research and Engineering Company, Linden, New Jersey]

Radiation-induced Carbonium Ion Reactions and the Chain Nature of Acid Catalyzed Isomerization

By P. J. Lucchesi, C. E. Heath and D. L. Baeder

Received March 2, 1960

Co-60 gamma rays and X-rays have been found to accelerate the rate of isomerization of *n*-hexane and methyl cyclopentane catalyzed by $AlCl_3$. This acceleration at 30–50° indicates a fairly long chain reaction, as evident from the high radiation yields observed with Co-60 radiation and the very high values (5×10^3) obtained with low intensity X-rays. The reaction is a chain reaction for both *n*-hexane and MCP even at conditions where little or no decomposition or disproportionation side reaction occurs. The results offer directly measured values of the chain length for these chain reactions and tend to support the chain carbonium ion mechanism for acid catalyzed isomerization.

Introduction

The skeletal isomerization of alkanes over acid catalysts such as activated aluminum chloride has been a commercially important chemical reaction for the past decade. It has also received considerable attention from the theoretical viewpoint. In this connection, there has been some controversy concerning the mechanism of isomerization. For example, in the case of *n*-butane one view[1,2] suggests essentially a molecular mechanism in which the activated complex is formed between catalyst and paraffin. In the field of the catalyst molecule (AlX_4^-, $HAlX_4$, etc.) there is a concerted, molecular rearrangement of the alkane without formation of a charged carbonium ion intermediate. However, Pines[3] has criticized this mechanism on the ground that pure HX/AlX_3 systems do not catalyze the isomerization of *n*-butane but require the presence of trace promoters such as olefins.[4]

The mechanism proposed to explain these effects, now widely applied to the isomerization of alkanes other than *n*-butane, considers the isomerization as a chain mechanism involving carbonium ions. These are normally written as free ions but they are, of course, associated with the catalyst.

$$RH + AlX_3 + \text{Initiator} \longrightarrow R^{\oplus}$$

$$CH_3CH_2CH_2CH_3 + R^+ \longrightarrow CH_3\,\overset{\oplus}{C}HCH_2CH_3 + RH$$

$$CH_3\overset{\oplus}{C}HCH_2CH_3 \longrightarrow (CH_3)_3C^{\oplus}$$

$$(CH_3)_3C^{\oplus} + CH_3CH_2CH_2CH_3 \longrightarrow \text{Isobutane} + CH_3\,\overset{\oplus}{C}HCH_2CH_3, \text{ etc.}$$

---

(1) J. D. Heldman, This Journal, **66**, 1789 (1944).

(2) T. M. Powell and E. G. Reid, *ibid.*, **67**, 1020 (1945).

(3) H. Pines, "Advances in Catalysis," Vol. I, Academic Press, Inc., New York, N. Y., 1948, pp. 201–255.

(4) H. Pines and J. D. Wackher, This Journal, **68**, 595 (1946).

Assuming the olefins added are initiators, one can calculate from the data presented by Pines that the isomerization is a chain reaction and, in fact, that the chain length increases with decreasing level of initiators by roughly the familiar inverse square root law.

Although the efficiency of trace amounts of olefins in initiating the reaction is good indirect evidence of a chain mechanism, a more direct confirmation would obviously be of interest.

With the advent of nuclear radiation, such a direct approach seems possible. The liquid phase radiolysis of pure liquid alkanes produces olefins and hydrogen at low degrees of conversion. At higher conversions the products cover a range of molecular weight above and below the parent alkane, but the product distribution is totally different from that obtained in the acid catalyzed isomerization of the same alkane. If nuclear radiation accelerated the rate of acid catalyzed isomerization of alkanes and if the observed radiation-induced reaction gave products similar to those obtained without radiation at the same degree of conversion, the reaction mechanism with and without radiation could be assumed to be the same. The observed radiation yield should then offer direct evidence for the chain nature of the ordinary acid catalyzed isomerization. Although the details of the initiation produced by nuclear radiation are very complex,[5] the radiation yield for acid catalyzed isomerization would be of great interest since a value below 10 would support a nonchain scheme while a value >10 would support a chain mechanism. Although unambiguous proof cannot be given, it will be shown that in the case of $AlCl_3$-catalyzed isomerization of *n*-hexane the results provide rather strong evidence that the ordinary catalytic isomerization is a long-chain process.

In this work, the effects of X-ray and Co-60 gamma irradiation have been measured for the $AlCl_3$ catalyzed isomerization of *n*-hexane and methyl cyclopentane. In the case of the radiolysis of *n*-hexane at low temperatures, Dewhurst has reported a nonchain process leading to a mixture of products of higher and lower molecular weight, including olefins.[6] Where possible, the radiation-induced isomerization products are compared with those obtained in the ordinary reaction at the same degree of conversion.

Experimental

The radiation sources used in this work were a Phillips X-ray diffraction unit and the 3200 curie Co-60 source at Esso Research. The Co-60 source has been described elsewhere.[7] The dosimetry was carried out using the Fe^{++}–Fe^{+++} system with an uncertainty (reproducibility) of ± 15% for both the Co-60 and X-ray work. The X-rays used (tungsten K alpha line) were produced at 55 k.v.p. and had an average energy of 2.8×10^4 ev., with a maximum energy of 4.5×10^4 ev. The Co-60 radiation, of course, consisted of the 1.17 and 1.33 Mev gammas emitted from this isotope per disintegration.

Phillips pure grade *n*-hexane (initially olefin free) and methyl cyclopentane were used with anhydrous $AlCl_3$ catalyst. Matched runs were made in batch vessels at constant temperature with and without radiation. To minimize spurious effects due to possible differences in purity, etc., the same source was used for reagents in the matched "blank" and radiation experiments. Results are reported as *G* values or molecules of reagent reacted per 100 ev. energy absorbed. This radiation yield is an integrated yield or the incremental conversion (radiation minus thermal conversion) per 100 ev.

Analyses of products were made by mass spectrometry and gas-liquid partition chromatography.

Results

n-Hexane Isomerization.—Co-60 and X-ray irradiation accelerated the rate of isomerization with radiation yields sufficiently high to establish the chain nature of the reaction even assuming complete energy transfer from the solid to the liquid reagent. Typical Co-60 data are given in Table I for the isomerization at 32°, which gave an integrated *G* value of 180 molecules *n*-hexane converted per 100 ev. Very similar results were obtained at 48° (total dosage 71×10^6 rad. at 1 megarad/hr.) with *G* values of 75. In these latter experiments, the higher temperatures and longer contact times gave considerable decomposition and disproportionation side reactions to butanes, pentanes and heptanes in both thermal blanks and radiation experiments. The products made with and without radiation were very similar, the major effect of irradiation being a greater degree of reaction for the same contact time. Since the products produced by the radiation-induced reaction are typical of those obtained in ordinary acid catalyzed isomerization of *n*-hexane, these data would indicate the mechanisms are similar. However, in order to show the two reactions are mechanistically similar, one would have to compare the products at similar degrees of conversion. The last column in Table I gives the detailed product distribution obtained at very similar conditions and at the same conversion of *n*-hexane. Although the products are not identical, the similarity between product spectra is apparent.

In the presence of low intensity X-ray initiation, and therefore at much reduced initiation rates, the chain length is greatly increased. Table II summarizes data obtained with X-ray induced isomerization.

In the foregoing work, the chain reactions measured were necessarily those of an isomerization reaction accompanied by the side reactions that are well known—disproportionation to butanes, pentanes and heptanes. It can be argued that the carbonium ion isomerization is only a long chain reaction when decomposition and other side reactions are present. In other words, the disproportionation could be an efficient chain reaction but "pure" isomerization might not. It is necessary, therefore, to measure the chain length of *n*-hexane isomerization at conditions where only isomerization occurs. In contrast to the olefin-initiated butane isomerization, we are not aware of any published data that would allow this estimate to be made in the case of hexane. Co-60 experiments were made at 48° using anhydrous $AlCl_3$ and *n*-hexane containing 8 wt. % methyl cyclopentane. This reagent is a well known inhibitor of decomposition and other side reactions

---

(5) M. Burton, "Annual Review of Physical Chemistry," Vol. I, Annual Reviews, Inc., Palo Alto, Calif., 1950, p. 113.

(6) H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1254 (1955).

(7) P. J. Lucchesi, B. L. Tarmy, R. B. Long, D. L. Baeder and J. P. Longwell, *Ind. Eng. Chem.*, **50**, 879 (1958).

TABLE I

EFFECT OF GAMMA RADIATION ON THE $AlCl_3$-CATALYZED ISOMERIZATION OF *n*-HEXANE

Temp., °C.	32	32	38
Catalyst/*n*-hexane wt. ratio	1.5	1.5	0.7
Radiation intensity, m rad./hr.	1	0	0
Dosage, megarad	47.5	0	0
Products, mole %			
H_2	0	0	0
CH_4	0	0	0
C_2H_6	0	0	0
C_2H_4	0	0	0
C_3H_8	0	0	0
C_3H_6	0	0	0
i-C_4H_{10}	25.8	0.09	16.1
n-C_4H_{10}	1.52	0	0
$(C_4H_8 + C_5H_{10} + C_6H_{12})$	0.23	0	0
n-C_5H_{12}	3.03	0	1.24
i-C_5H_{12}	18.2	0.09	14.9
n-C_6H_{14}	22.8	88.31	21.0
2,2-Dimethylbutane	6.8	0.86	13.6
2-Methylpentane + 2,3-dimethylbutane[a]	10.6	4.33	11.1
3-Methylpentane	3.79	1.73	3.71
2,4- + 2,2-Dimethylpentane[a]	1.52	2.60	2.50
2,3- + 3,3-Dimethylpentane[a]	3.03	1.73	5.0
2- + 3-Methylhexane[a]	1.52	0	2.48
n-Heptane	0.76	0	0.37
Others (unidentified C_8 and higher)	0.38	0.26	7.67
"G" molec. n-C_6H_{14} converted/100 ev.		200	

[a] Chromatographic analysis did not distinguish between these isomers.

TABLE II

EFFECT OF X-RAY IRRADIATION ON THE $AlCl_3$-CATALYZED ISOMERIZATION OF *n*-HEXANE AT 30°

Conditions	X-ray	Thermal
Time, hr.	16	16
$AlCl_3$/*n*-hexane wt. ratio	1.4	1.4
Conversion of n-C_6, mole %	62.6	5.0
Composition of total product, wt. %		
i-C_4H_{10}	12.48	0
n-C_4H_{10}	0.17	0
i-C_5H_{12}	12.48	0
n-C_5H_{12}	1.66	0
2,2-Dimethyl butane	5.82	0.017
2-Methyl pentane + 2,3-dimethyl butane[a]	12.48	0.87
3-Methyl pentane	4.14	0.43
n-Hexane	37.44	95.05
Heptanes	9.15	3.48
C_8+	4.16	0
G, molec. n-C_6H_{14} reacted/100 ev.	*ca.* 5000	

[a] Chromatographic analysis did not distinguish between these isomers.

in acid catalyzed isomerization.[3] At dose rates of 0.15×10^6 rad./hr. and dosages of 7.1 megarads, radiation accelerated the isomerization with *G* values of the order 130 and without any detectable products other than hexane isomers at *n*-hexane conversions of about 85%. Therefore, the chain nature of the isomerization is established at conditions where no side reactions occur.

Methyl Cyclopentane Isomerization.—As an example of the isomerization of "cyclic type" structures involving cyclic carbonium ions as intermediates, there is some interest in establishing the chain nature of the reaction for methyl cyclopentane. This compound is also of interest because it isomerizes rather cleanly to cyclohexane without extensive side reaction. As shown in Table III, the Co-60 accelerated isomerization of methylcyclopentane to cyclohexane is a selective chain reaction with *G* values of about 600 at 35°. The isomerization of methyl cyclopentane to cyclohexane is a well known acid catalyzed reaction.

TABLE III

EFFECT OF Co-60 IRRADIATION ON THE $AlCl_3$-CATALYZED ISOMERIZATION OF METHYL CYCLOPENTANE AT 35°

Catalyst MCP wt. ratio	1.34	1.34
Dosage, megarad/hr.	10.7	0
Intensity, megarad/hr.	0.15	0
Products, mole %		
Methylcyclopentane	39.83	88.14
Cyclohexane	55.93	11.76
Other[a]	4.24	0
"G," molecules reacted/100 ev.	600	

[a] Mostly heptanes and higher.

Discussion

As pointed out above, detailed knowledge of acid-catalyzed isomerization in the presence of high energy radiation, which can lead both to radiation-induced catalyst modifications and chemical reactions, is not available. However, from the comparison between radiation and "thermally" produced products, it seems reasonable to assume that radiation-induced isomerization gives direct evidence, and therefore important new knowledge, concerning the chain nature of the ordinary catalytic reaction. While the details of the radiation-produced initiation cannot be given, one can speculate that radiation produces chemical promoters in the reactants by a nonchain process. These promoters might be olefins, which then react in the acid system to form carbonium ions and chain initiators. It is interesting to note that the olefin content of the product from the Co-60 radiation-induced isomerization of *n*-hexane (0.23 mole %) is the same order of magnitude as that shown by Pines[3] to exert marked promotional effects in the isomerization of *n*-butane catalyzed by aluminum halides. Thus, in the case of $AlBr_3/HBr$ catalysis, increasing the butane concentration of *n*-butane from 0.08 to 0.56 mole % increased the yield of isobutane from 19 to 66% at 25°. Of course, it is possible, but we believe less likely, that the carbonium ions or the chain initiators are formed directly from radiation. At any rate, they are produced in a nonchain reaction so that the measured *G* value is a direct value of the chain length for isomerization. Assuming, for example, that three initiators are formed per 100 ev., then the true chain lengths would be *G*/3.

Although the reported values of the chain length are qualitative, they are to our knowledge the first measured values of the chain length for isomerization, especially at conditions where little side reaction occurs. In our opinion, these data support the chain carbonium ion mechanism as proposed by Pines rather than the various molecular mechanisms that have been advanced.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

Hydroxyl Spectra of *o-t*-Butylphenols

BY ROBERT F. GODDU

RECEIVED JANUARY 19, 1960

The free hydroxyl stretching vibration in most free phenols is observed close to 3608 cm.$^{-1}$. Most previously reported intramolecular interactions shift the band to lower frequency. However in 2,6-di-*t*-butyl-substituted phenols it is at 3643 cm.$^{-1}$. This is due to the interaction between two electropositive groups rather than between the hydroxyl proton and an electronegative group. In mono-*o-t*-butylphenols there are two free hydroxyl stretching bands which are attributed to two conformations of the hydroxyl group relative to the *t*-butyl group. One band is at the same frequency as found for hydroxyl groups in free phenols, the other is at the frequency of 2,6-di-*t*-butyl-substituted phenols. From the intensities of the two bands it is calculated that about 8% of the molecules are in the higher frequency configuration when the 6-position is free and about 17% are in the same form when a methyl group is in the 6-position. Data are included from both the 3600 cm.$^{-1}$ fundamental hydroxyl region and the 7100 cm.$^{-1}$ first overtone region.

The interaction between phenolic hydroxyl groups and *ortho* substituents was initially observed by Wulf, Liddel and Hendricks[1] in the 7100 cm.$^{-1}$ (1.4 μ) overtone hydroxyl stretching region. This interaction, observed as doublet hydroxyl bands in *ortho*-halo-phenols, was explained by Pauling[2] as being due to the existence of *cis*- and *trans*-orientations of the hydroxyl group which lies in the plane of the benzene ring. Recent work by Baker[3] in the fundamental hydroxyl stretching region has reaffirmed the earlier work and in addition explained more fully the observed frequency shifts.

In addition to *ortho*-halo substitution, shifts of the hydroxyl stretching band to lower frequencies are caused by a wide variety of intramolecular interactions. Many of these interactions are described by Flett[4] in his review of work on hydroxyl spectra. More recently Baker[5] and Baker and Shulgin[6] have discussed other types of intramolecular bonds in phenols. All of these interactions require coplanarity of the hydroxyl group and the benzene ring. Also all of these interactions were with an electronegative group and the shift of the hydroxyl band was to lower frequency.

A recent paper by the author[7] on the determination of phenolic hydroxyl gave considerable data on the free hydroxyl stretching band in the neighborhood of 3610 cm.$^{-1}$ (2.77 μ). It was noted that most free phenolic hydroxyl groups absorbed at 3608 ± 2 cm.$^{-1}$ (2.772 ± 0.001 μ). Notable exceptions included phenols in which di-*ortho* substitution was present. In particular, di-*o-t*-butyl substitution shifted the free hydroxyl band to higher frequency (3643 cm.$^{-1}$ or 2.745 μ). This shift is larger than that usually attributed to the electron donating effect of alkyl groups alone when in the *m*- or *p*-positions.[5] In the table of data included in this earlier paper were three mono-*o-t*-butyl-substituted compounds. These latter compounds had weak absorption bands at 3643 cm.$^{-1}$ (2.745 μ) and strong bands at 3608 cm.$^{-1}$ (2.772 μ). With the limited data on these mono-*ortho*-substituted isomers, it was not clear if the higher frequency band were real or possibly due to an impurity.

Discussion of Results

A considerable number of *t*-butyl-substituted phenols have now been investigated. A typical spectrum is in Fig. 1 and the data obtained in the fundamental hydroxyl region are in Table I.

The constancy of the fraction of the total absorptivity which is observed at 3642 ± 2 cm.$^{-1}$ (2.746 ±

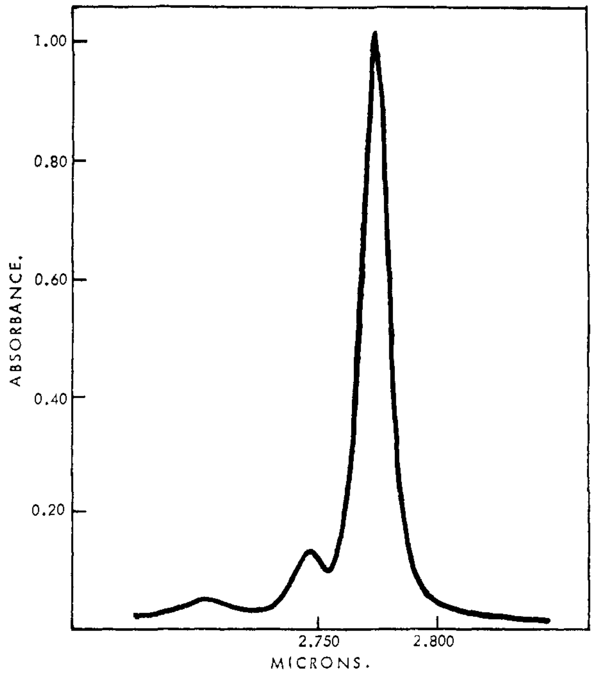

Fig. 1.—Hydroxyl spectrum of 2-*t*-butyl-5-methylphenol in the 2.75-μ region, 6.6 millimolar solution in carbon tetrachloride and run in 1-cm. cell.

---

[1] O. R. Wulf, U. Liddel and S. B. Hendricks, THIS JOURNAL, **58**, 2287 (1936).

[2] L. Pauling, *ibid.*, **58**, 94 (1936).

[3] A. W. Baker, *ibid.*, **80**, 3598 (1958).

[4] M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

[5] A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

[6] A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958).

[7] R. F. Goddu, *Anal. Chem.*, **30**, 2009 (1958).