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Reaction of Carbocations Derived from Alkanes with Carbon Monoxide in HF-SbF$_5$ Superacid

Norihiko YONEDA,* Yukio TAKAHASHI,[†] Tsuyoshi FUKUHARA, and Akira SUZUKI
Department of Applied Chemistry, Faculty of Engineering, Hokkaido University,
Sapporo 060

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Alkanes readily react with CO and H$_2$O in HF–SbF$_5$ at 30 °C under atmospheric pressure and give considerably different product distributions from those in the usual Koch-Haaf reaction. When using C$_5$- or C$_6$-alkanes with tertiary C–H bonds, a considerable amount of secondary carboxylic acids are produced by the reaction of CO with secondary alkyl cations. Such cations may appear as transient intermediates in the course of the carbon skeletal isomerization of initially formed tertiary cations. For the straight-chain alkanes, the protonolysis at C–C bonds initiated the reaction to give fragment alkyl cations. This resulted in the formation of carboxylic acids with a lower number of carbon atoms than the starting alkanes. Intermolecular hydride shift between the fragment cations and the starting alkanes occurred at the same time to form a large amount of carboxylic acids with the alkyl group of the same number of carbon atoms as the starting alkane. On the other hand, for alkanes with more than seven carbon atoms, β-scission occurs exclusively to produce C$_4$–, C$_5$–, and C$_6$–carboxylic acids.

Ionization of alkanes to the corresponding alkyl cations in superacid media such as FSO$_3$H–SbF$_5$ and HF–SbF$_5$ has been well investigated.[1)] The reaction of alkyl cations thus obtained with nucleophiles such as benzene[2)] and carbon monoxide[3)] has also been described. Paatz and Weisgerber reported that the reactions of isopentane, methylcyclopentane or cyclohexane with carbon monoxide in the presence of HF–SbF$_5$ at room temperature under atmospheric pressure gave C$_6$- or C$_7$-acids along with some ketones.[4)] The reaction is highly interesting, especially because of the mild reaction conditions.[5,6)] However, no extensive studies of the reaction have been reported to date. We have therefore undertaken a detailed study, using alkanes with various skeletal structures in order to clarify the reaction of alkyl cations derived from the alkanes with carbon monoxide in superacidic media.[7)]

In this report, we shall discuss the reaction, initiated by the ionization of σ-bonds in alkanes, followed by trapping with carbon monoxide and quenching with water to give carboxylic acids. Our discussion will be based on the detailed analysis of the composition and isomer distribution of the products.

Experimental

Materials. Pure alkanes and carbon monoxide were of commercially available and were used without further purification. SbF$_5$ and anhydrous hydrogen fluoride were distilled, twice and once, respectively.

General Procedure of Carboxylation. A solution of HF–SbF$_5$ (5:1 molar ratio, ca. 20 ml) was placed in a 100-ml Kel-F three-necked reaction vessel under vigorous stirring at an appropriate temperature. The substrate (5—20 mmol) was added dropwise during 15 min to the acid solution, while carbon monoxide was introduced at a constant flow rate of 20 ml min^{-1} at 30 °C. After the reaction was completed, the resulting solution was hydrolyzed with ice-water, and the product obtained after usual work-up[8)] were identified by means of GLC, GC-mass, IR, NMR spectrometry, and by comparison with authentic samples.

Carboxylic Acids as Authentic Samples. Propanoic acid (**1**), 2-methylpropanoic acid (**2**), 2,2-dimethylpropanoic acid (**3**), 2-methylbutanoic acid (**4**) and 2,2-dimethylbutanoic acid (**8**) are commercially available. 2-Methylpentanoic acid (**5**),[21)] 2-ethylbutanoic acid (**6**),[21)] 2,3-dimethylbutanoic acid (**7**),[22)] 2,2-dimetylbutanoic acid (**8**),[23)] 2,2,3-trimethylbutanoic acid (**9**),[24)] 2-ethyl-2-methylbutanoic acid (**10**),[15)] 2,2-dimethylpentanoic acid (**11**),[15)] 2-ethyl-3-methylbutanoic acid (**12**),[25)] 2,3-dimethylpentanoic acid (**13**),[26)] 2-methylhexanoic acid (**14**),[27)] 2-ethylpentanoic acid (**15**),[28)] 2,3,3-trimethylbutanoic acid (**16**),[29)] 2,4-dimethylpentanoic acid (**17**)[30)] and 2,2,3,3-tetramethylbutanoic acid (**18**),[31)] were prepared according to Hussey's[9)] or/and Creper's[10)] methods and identified with the aid of IR, NMR, and MS. All products were liquid except for **18** (mp 198—199 °C, lit,[30)] 198.5—199.5 °C) and exhibited reasonable spectra. These were esterified with diazomethane.[8)] The retention times and volumes of GLC (Hitachi FID-063, Column: Silicon DC-550. 45 m, 150 °C) of these methyl esters were appropriate as a means of qualitative and quantitative identification for the products.

Results and Discussion

The results of the reaction of C$_5$- and C$_6$-alkanes with carbon monoxide are shown in Tables 1 and 2. Tables 1 and 2 indicate that the isomer distribution of the major products (C$_6$–acids and C$_7$–acids) are independent of the individual skeletal structures of the starting alkanes under the same conditions. A considerably high yield of secondary carboxylic acids are found in the products. In a marked contrast, it was reported that tertiary carboxylic acids were exclusively produced from nonbranched alkenes or alcohols in the Koch–Haaf carboxylation using usual strong acids such as H$_2$SO$_4$.[11)] It is likely that the reaction of branched C$_5$- and C$_6$-alkanes is readily initiated by

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[†] Present address: Department of Industrial Chemistry, Kitami Institute of Technology, Kitami 090.

Table 1. Carboxylation of C_5- and C_6-Alkanes

Alkane	Total yield	Composition and distribution of carboxylic acids/%									
	%	C_3-Acid	C_4-Acid	C_5-Acids		C_6-Acids				C_7-Acids	C_8-Acids
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**		
Pentane	53	3	26	14		57				Some	—
				25	75	12	11	38	39		
2-Methylbutane	55	Some	Some	4		96				Some	—
				67	33	13	11	38	38		
Hexane	69	2	10	18		5				65	Some
				13	87	11	10	41	39		
2-Methylpentane	61	—	Some	3		3				94	—
				67	33	10	9	41	40		
3-Methylpentane	66	—	Some	4		3				93	—
				20	80	10	10	40	40		
2,3-Dimethylbutane	63	—	4	Some		5				91	—
						9	9	40	42		
2,2-Dimethylbutane	57	—	Some	10		15				75	—
				80	20	10	11	39	40		

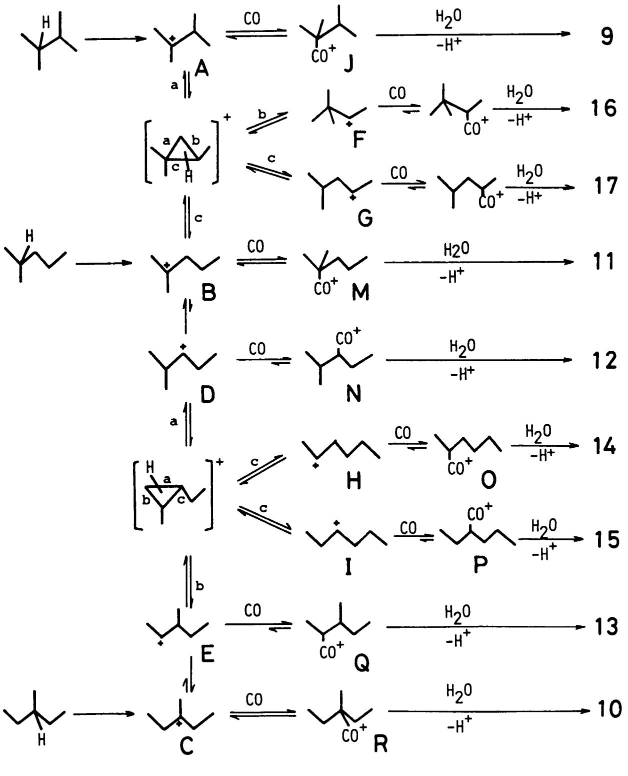
Reaction conditions: Reaction time, 1 h; reaction temp, 30 °C; alkane, 20 mmol; SbF_5/alkane molar ratio, 2; HF/SbF_5 molar ratio, 5.

Table 2. Isomer Distribution of C_7-Acids in the Carboxylation of Hexanes[a)]

Substrate	React. time	Isomer distribution of C_7-acids/%									Sec./tert. ratio
	h	Tert. acids			Sec. acids						
		9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	
Hexane	1.0	12	9	12	15	11	4	7	25	5	67/33
2-Methylpentane	1.0	10	9	10	16	12	5	7	26	5	71/29
3-Methylpentane	1.0	10	9	11	16	13	5	7	24	5	70/30
2,3-Dimethylbutane	1.0	10	9	11	16	12	5	7	26	5	70/30
2,3-Dimethylbutane	1.0	11	9	12	16	12	4	7	25	4	68/32
Hexanes[b)]	0.2	15	20	20	10	7	3	3	19	3	45/55
Hexanes[b)]	0.5	13	16	15	14	10	3	5	22	3	56/44
Hexanes[b)]	1.0	10	9	11	16	13	5	7	24	5	70/30
Hexanes[b)]	3.0	7	8	8	17	13	5	8	28	7	75/25
Hexanes[b)]	5.0	6	8	8	18	12	6	9	28	7	78/22

a) Reaction conditions: See footnote in Table 1. b) 3-Methylpentane. 2-Methylpentane and 2,3-dimethylbutane gave almost the same results.

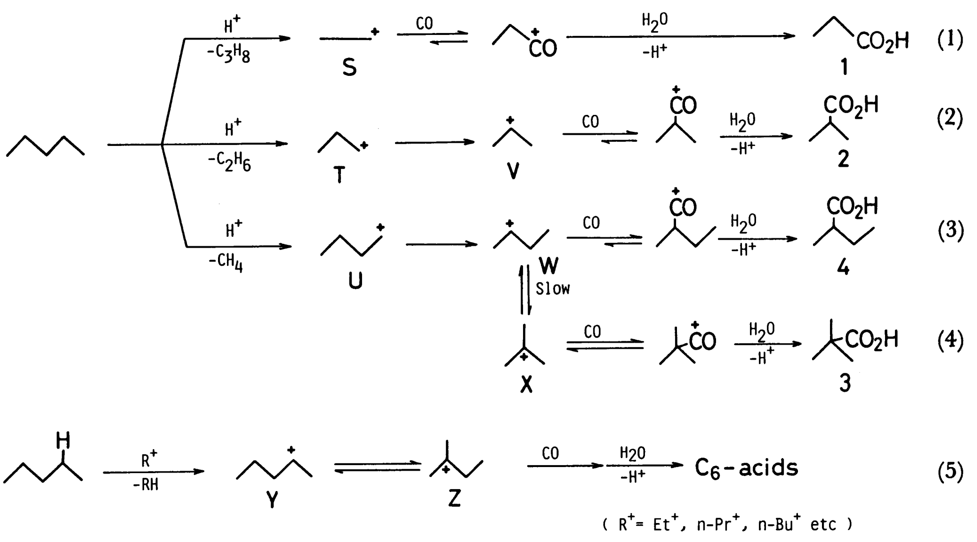
protonolysis[12] at their tertiary C–H bonds to give the corresponding tertiary alkyl cations which in turn undergo skeletal isomerization via secondary alkyl cations.[13] The alkyl cations under the present conditions seem more electrophilic[14] than those expected in the reaction of alkenes, alcohols or alkyl halides under the Koch–Haaf conditions. The Koch–Haaf conditions usually require either high temperature and pressure or a high concentration of carbon monoxide achieved by use of copper(I) carbonyl catalyst under highly acidic conditions.[15,16] These alkyl cations can react with carbon monoxide to form acyl cations which give the corresponding carboxylic acids by quenching with water as shown in Scheme 1. When the reaction time is longer, as is the case with the reaction of hexanes as shown in Table 2, the ratio of secondary carboxylic acids **12**—**17** to tertiary ones **9**—**11** is increased and the isomer distributions in the product seem to attain an equilibrated state after 3 h. Tertiary alkyl cations, **A**–**C** in Scheme 1, derived from starting alkanes (2-methylpentane, 3-methylpentane and 2,3-dimethylbutane) rearrange rapidly to reach an equilibrium with each other which can be observed by NMR as demonstrated by Brouwer.[13] Secondary alkyl cations **D**–**I** may form as transient intermediates in the course of the rearrangement of initially formed tertiary alkyl cations to other tertiary skeletal ones. Although spectroscopic attempts to observe the formation of such secondary cations in superacids were unsuccessful.[17] These alkyl cations may be in a high concentration and/or have a sufficiently long life time in a HF-SbF$_5$ solution to bring about the reaction with carbon monoxide. Thus, isomer distributions of carboxylic acids found in the initial stage of reaction depend largely on the equilibrium mixtures of these isomeric alkyl cations **A**–**I** including the secondary ones. On the other hand, when the reaction time is longer, an actual increase in the ratio of the secondary carboxylic acids **12**—**17** to tertiary ones **9**—**11** occurs. This seems unreasonable because of the rearrangement from more stable tertiary carbocations to less stable secondary ones is unlikely. This would probably result from the equilibration of alkanoyl cations **J**–**R**.[18,19]



Scheme 1.

For straight chain C$_5$- or C$_6$-alkanes, on the other hand, the protonolysis at carbon–carbon bonds takes place to give fragment alkyl cations **S**–**T** and C$_1$-—C$_4$-alkanes where the protonolysis at secondary C–H bonds in the substrate is preferred as shown in Scheme 2. The fragment alkyl cations **S**–**U** thus formed are responsible for the preferred formation of carboxylic acids **1**—**4** with the alkyl group of a lower number of carbon atoms than the starting alkanes (Eqs. 1—4). They are also responsible for the ionizaton of starting alkanes by the abstraction of hydride ion at secondary C–H bonds which in turn produced carboxylic acids with the alkyl group with the same number of carbon atoms as in the starting alkanes (Eq. 5). Thus, compared with the reaction of branched C$_5$- and C$_6$-alkanes, a considerably large amount of gaseous hydrocarbons, i.e., methane, ethane, propane and butanes were observed in these reactions.

The isomer distribution of C$_6$- and C$_7$-carboxylic acids are the same as that in the reaction of branched alkanes. As shown in Table 1, however, there is a distinction among the isomer distributions of C$_5$-carboxylic acids produced in the reactions of C$_5$- and C$_6$-alkanes. This can be explained by the slow occurrence of the skeletal isomerization of butyl cations arising from suitable protonolysis at carbon–carbon bonds in the substrates compared to those of pentyl, **Y** and **Z**, or higher alkyl cations as demonstrated by Brouwer.[13]

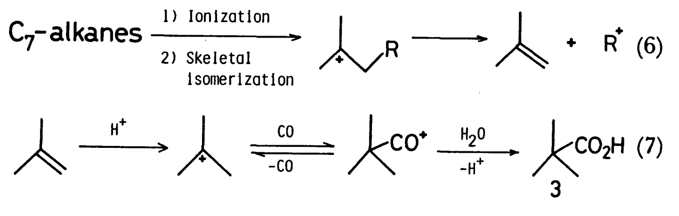


Scheme 2.

Table 3. Carboxylation of C_7-, C_8-, and C_9-Alkanes

Alkane	Total yield %	Composition and distribution of carboxylic acids/%											
		C_3-Acid	C_4-Acid	C_5-Acids			C_6-Acids					C_7-Acids	C_8-Acids
		1	**2**		**3**	**4**		**5**	**6**	**7**	**8**		
Heptane	80	Some	47	48	90	10	5	17	10	35	38	Some	Some
3-Methylhexane	98	—	4	92	96	4	4	12	10	36	42	Some	—
2,4-Dimethylpentane	92	—	79	21	98	2	Some					Some	Some
2,3-Dimethylpentane	94	—	70	28	98	2	2	13	10	33	44	Some	Some
2,3,4-Trimethylbutane	102	—	65	35	99	1	Some					Some	Some
Octane	90	Some	6	87	90	10	7	15	10	37	38	Some	Some
2,4,4-Trimethylpentane	102	—	—	100	100	—	—					—	—
Nonane	75	Some	34	31	87	13	33	12	10	40	38	2	—

Reaction conditions: See footnote in Table 1.



Scheme 3.

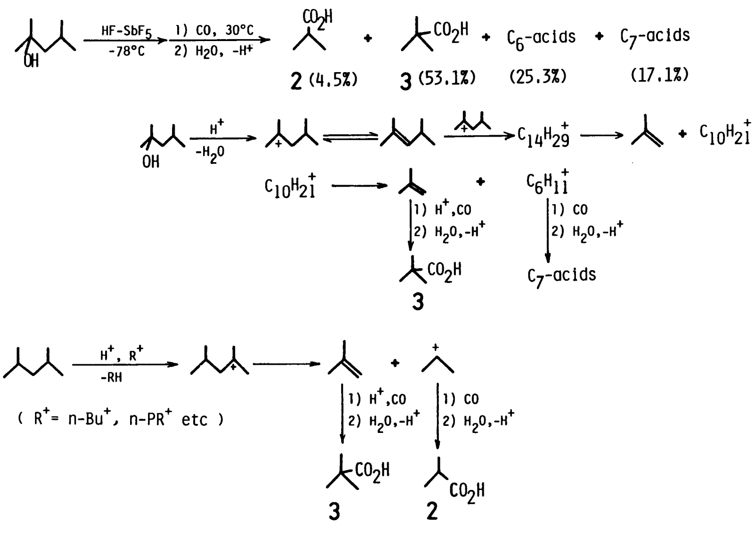
In contrast to C_5- or C_6-alkanes, the reactions of such substrates having seven or eight carbon atoms gave C_4- and/or C_5-carboxylic acids almost exclusively, as shown in Table 3. In other words, these alkanes can give a small amount of C_8-, C_9- or C_{10}-carboxylic acids with an alkyl group of the same number of carbon atoms of starting alkanes. From the product distribution, these alkanes, as shown in Eqs. 6 and 7 in Scheme 3, were ionized in the same fashion as those in the case of C_5- or C_6-alkanes. They gave alkyl cations which easily undergo exclusive β-scission and produce fragment alkyl cations R^+ and 2-methylpropene resulting from the preferential formation of **3** under the present reaction conditions. Interestingly, the product distribution obtained in the reaction of C_7-alkanes is quite different from those found in the reaction of alcohols or halides having the same carbon skeletal structure as alkanes under the same reaction conditions. 2,4-Dimethyl-2-pentanol, for example, reacted with carbon monoxide and water to give a considerable amount of C_6- and C_7-carboxylic acids together with C_4- and C_5-carboxylic acids. This is in contrast with the product distribution in the reaction of 2,4-dimethylpentane which yielded 79% of **2** and 21% of **3** without any other products under the same conditions as shown in Scheme 4. C_7-alkyl cations, which were formed in the reaction of the alcohols in a $HF-SbF_5$ solution, may be abundant and may give rise to oligocondensation to produce such alkyl cations which have fourteen or more carbon atoms. These oligocondensed alkyl cations undergo β-scission to give *t*-butyl cation and C_6-cations which in turn gave C_5- and C_7-carboxylic acids, respectively. C_6-acids may arise from C_5-alkyl cations derived from another β-scission process of these or other oligocondensed alkyl cations. 2,4-Dimethylpentane, on the other hand, may be ionized slowly to yield the alkyl cation, because mass transfer between acid and the hydrocarbon phase is a rate-determining step. Such an alkyl cation may take place in a limited oligocondensation with each other. Thus, β-scission of the alkyl cation may take place predominantly to produce 2-methylpropene and isopropyl cation which in turn gave C_4- and C_5-carboxylic acids.

Another characteristic feature in the reaction of C_7-alkanes is the product compositions which differ from each other as shown in Table 4. The exact reaction pathway giving these product distributions is not clear, but fragment alkyl cation R^+ (*t*-butyl or isopropyl cation), produced by β-scission of parent alkyl cations, may play an important role in the formation of C_5- and C_4-carboxylic acids and also in the ionization of the starting alkanes. This resulted in

Table 4. Products Found in Gaseous Phase in the Carboxylation of Tertiary C_7 Alkanes

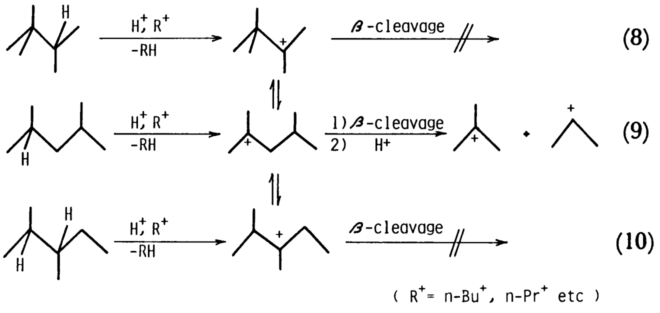
Substrate	Products found in the gaseous phase/%				
	Isobutane	Butane	Propane	Ethane	Methane
3-Methylhexane	Some	1	90	8	Some
2,4-Dimethylpentane	82	Some	17	Some	—
2,3-Dimethylpentane	68	—	27	4	Some
2,2,3-Trimethylbutane	60	—	39	Some	Some

Reaction conditions: See footnote in Table 1.

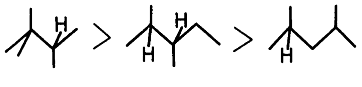


Scheme 4.

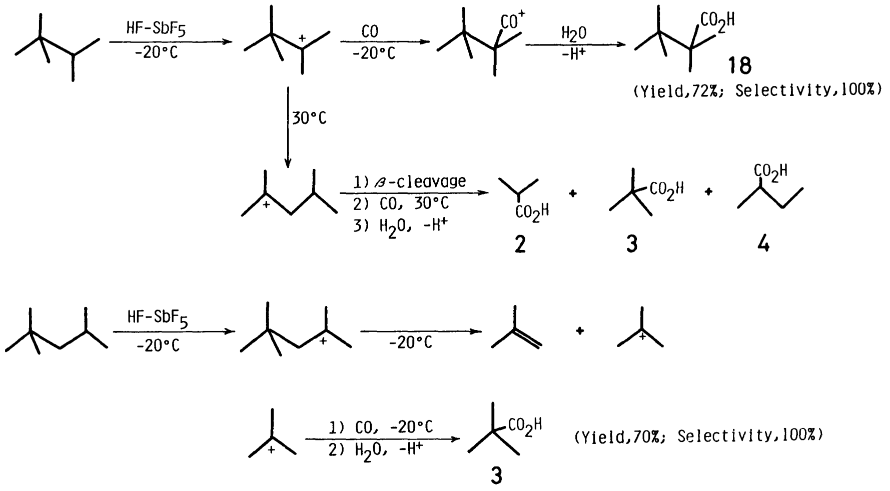
the formatiom of C$_7$-alkyl cations, and then propane and isobutane are produced by the intermolecular hydride ion transfer reaction as shown in Scheme 5. For C$_7$-alkanes, other than 2,4-dimethylpentane, initially formed C$_7$-alkyl cations must be rearranged in such an alkyl cation to give isopropyl and *t*-butyl cations by β-scission, since initially formed C$_7$-alkyl cations have unfavorable skeletal structures for β-scission reaction (Eqs. 8 and 10). The preferential formation of **2** prior to **3** and isobutane prior to propane in the reactions of 2,4-dimethylpentane, 2,3-dimethylpentane, and 2,2,3-trimethylbutane (Tables 3 and 4) are observed. *t*-Butyl cation, formed in Eq. 9, seems to play a much more important role to undergo intermolecular hydride abstraction from the starting C$_7$-alkanes in preference to that undergone by isopropyl cation in Eq. 9. Such a predominant occurrence of hydride abstraction with *t*-butyl cation may be attributed to the equilibrations in the reaction of these alkyl cations and carbon monoxide. Namely, the equilibrium of the reaction of isopropyl cation and carbon monoxide to produce isobutyryl cation leans far toward the isobutyryl cation compared to the reaction of *t*-butyl cation and carbon monoxide to produce pivaloyl cation[18] as seen in Eqs. 2 and 4 in Scheme 2. By these equilibrations, *t*-butyl cation may always exist in a higher concentration than isopropyl cation in the reaction mixture. The hydride abstraction of the substrate with the *t*-butyl cation (R$^+$) may proceed in Eqs. 8—10. On the other hand, in the case of C$_7$-alkanes, there is a much higher steric hindrance against the intermolecular hydride abstraction with *t*-butyl cation, than with the isopropyl cation. Such a steric hindrance may be expected in the following C$_7$-alkanes order.



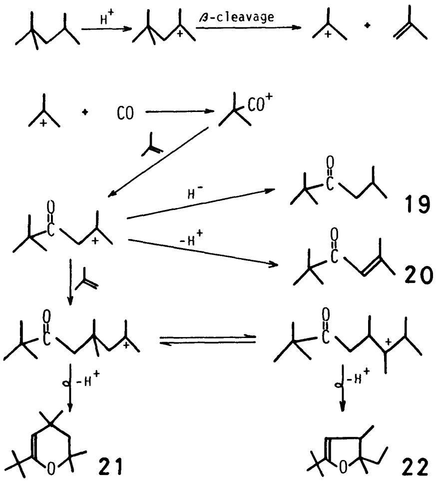
Scheme 5.



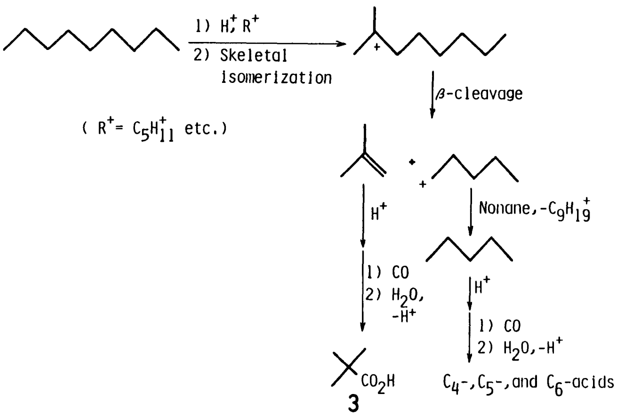
Thus, this steric factor renders the ratio of the products, i.e., between **2** and **3** or between isobutane and propane in these reactions variable as shown in



Scheme 6.



Scheme 7.



Scheme 8.

Tables 3 and 4. The preferred formation of **3** in the reaction of 2- or 3-methylhexane is still unclarified. However, judging from the preferred formation of propane in this case, it seems that the β-scission of the alkyl cations derived from these alkanes can afford *s*-propyl cation which is a highly reactive electrophile and can readily attack the tertiary C–H bond in the starting alkane.

In general, the lower the reaction temperature, the β-scission of alkyl cations is more difficult. The exclusive formation of **18** was observed in the reaction of 2,2,3-trimethylbutane in good yield at −20 °C as shown in Scheme 6. However, in the reaction of 2,2,4-trimethylpentane, initially formed 1,1,3,3-tetramethylbutyl cation undergoes the reaction involving the β-scission remarkably even at −20 °C to give *t*-butyl cation and 2-methylpropene which in turn reacts with carbon monoxide to yield **3** exclusively.

As shown in Scheme 7, when 2,2,3-trimethylpentane is in excess relative to SbF_5 (alkane/SbF_5 molar ratio 2, HF/SbF_5 molar ratio 10), ketones (**19**/(20%), **20**/(31%)) and cyclic ethers (**21**+**22**/29%) were produced together with **3** and 2-methylpropane.[20] A large amount of 2-methylpropene was formed from the β-scission of initially formed 1,1,3,3-tetramethylbutyl cation may react directly with pivaloyl cation resulting in the formation of these ketones and cyclic ethers.

In the reaction of nonane, a large amount of C_6-carboxylic acids together with C_4- and C_5-carboxylic acids were formed as shown in Table 3. The principal reaction path accompanied with β-scission of initially formed alkyl cation may be again well accounted for in the product composition as shown in Scheme 8. The intermolecular hydride ion shift between the substrate and primary pentyl cation produced by the β-scission of the initially formed alkyl cation will give rise to pentane and C_9-alkyl cations. Pentane, thus formed, could react with carbon monoxide and water to yield C_4-, C_5-, and

C_6-carboxylic acids. Hence, the product composition in the reaction of nonane exhibited an almost similar product composition that was observed in the reaction of pentane itself as shown in Table 1. The only difference in the composition is that it has a relatively high distribution of **3** which may have arisen mostly from the reaction of 2-methylpropene formed by the β-scission of C_9-alkyl cations.

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