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NOTES

Studies on the Reaction of n-Octane over Several Tellurium Loaded Zeolites

Several reports on the dehydrocyclization activity of tellurium loaded zeolites have appeared in the literature (*1–9*). These reports have covered several different aspects of the catalytic system, but none have addressed the mechanism of formation of aromatics containing fewer carbon atoms or a different carbon skeletal arrangement than the parent paraffin molecule. For instance, earlier studies have reported the formation of significant quantities of benzene formed during the aromatization of n-heptane and both benzene and toluene from the aromatization of n-octane (*9*) without a mechanistic explanation. We report here some reasonable mechanisms for these reactions along with previously unreported activity measurements over LiX, RbX, and CsX zeolites loaded with tellurium.

Li, K, Rb, and Cs zeolites were prepared by ion exchange of the Na form of Linde 13X zeolite. Ten successive exchanges with sodium zeolite and one equivalent of the desired alkali metal nitrate dissolved in water were performed at room temperature. A thorough drainage of the liquor with a filter/aspirator assembly followed each exchange. The liquor was changed three times per day in 4- to 16-h intervals. After 10 exchanges, the zeolites were washed once with water and once with methanol followed by drying overnight at 150°C. A sodium zeolite was also "prepared" in an analogous manner with 10 equivalents of sodium nitrate so as to assure that all the zeolites had a closely equivalent acidity caused by low levels of proton exchange with the zeolites and water as reported by Bolton (*10*).

A 10% Te on NaX zeolite by weight was prepared by ball milling elemental tellurium with NaX zeolite for 4 h. Similar catalysts with LiX, KX, RbX, and CsX were prepared but the weight percentage was varied so as to preserve the Te/alkali metal ratio obtained in the 10% Te/NaX zeolite. One hundred milligrams of the Te/NaX zeolite was used in one reactor; the others were filled with amounts of catalyst corresponding to equivalent numbers of cation sites.

Reactions were performed in an all-Pyrex recirculation batch reactor similar to those described by other laboratories (*11*, *12*) except that no mercury is used in this newer system. Catalysts were activated at 500°C in flowing hydrogen for 16 h followed by recirculation of 400 Torr H_2 for 4 h at 450°C in the recirculation reactor system with a liquid nitrogen trap to condense water.

After activation, the reactor was bypassed (still containing 400 Torr H_2), the liquid nitrogen trap thawed, and the remainder of the system evacuated. n-Octane (8 Torr), H_2 (400 Torr), and enough He to bring the system to atmospheric pressure were added to the system and allowed to mix for at least 1 h. At $t = 0$, the reactants were admitted to the reactor at 450°C.

Some time later, the reactor was bypassed to stop the reaction. Gaseous products through n-pentane were analyzed on a Carle 111H automated gas chromatograph attached to a Hewlett–Packard 3390A computing integrator for data reduction. Products heavier than n-pentane were analyzed on a Finnigan 1020 GC/MS/DS system fitted with a Bentone-34/SE-30 column for xylene separation. n-Pentane was used as

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an internal standard so that GC/MS/DS and gas chromatographic data could be linked together. n-Pentane was added to the reaction mixture (after the reactor was bypassed and after gaseous analysis) in known quantities prior to GC/MS/DS analysis. GC/MS/DS data were reduced by measuring the response to a selected ion for each compound. Using this method, amounts of all compounds of interest were measurable even though some components (e.g., hexane/hexenes) could not be separated chromatographically. Both the GC/MS/DS and chromatograph were calibrated with external standards prior to analysis.

After the activation procedure, each of the five catalysts was inspected for tellurium loss and color. A distinct trend was noted for each observation. The lighter the alkali metal, the more noticeable was the tellurium loss as evidenced by a silvery mirror formed just downstream from the heated zone of the reactor. The Te/LiX catalyst showed extensive Te loss. Approximately 50 mm of the 6-mm-i.d. Pyrex tubing exiting the heater was mirrored with Te. The Te/CsX had almost no perceptible loss. Also, the heavier the alkali metal, the more brilliant was the color and the redder the catalyst. The following colors were evident:

Te/LiX—deep, dark brown
Te/NaX—reddish brown
Te/KX—rusty red
Te/RbX—rouge
Te/CsX—magenta

Table 1 shows the raw results of the n-octane reaction over each catalyst. The reaction time, calculated n-octane conversion, and the corresponding first-order rate constant is also reported. The calculated conversion of n-octane does not include the conversion to the n-octenes which are assumed to be intermediates in the cyclization process and are probably in thermodynamic equilibrium with n-octane if the initial stage of the n-octane reaction is similar to the n-hexane reaction over Te/NaX (*6, 9*). The n-hexanes, n-heptenes, and n-octenes, though partially resolvable into individual components, are reported lumped together.

TABLE 1

Octane/Octene Free Product Distribution in Mole Percent

	LiX	NaX	KX	RbX	CsX
Methane	21.94	31.99	20.12	28.56	24.10
Ethane	10.98	15.13	14.10	22.72	28.04
Ethylene	0.63	0.00	7.77	2.54	0.00
Propane	8.39	5.88	4.07	7.74	11.14
Propylene	1.00	0.77	4.38	1.91	1.36
n-Butane	9.69	7.03	4.34	7.96	8.93
n-Pentane	7.84	4.52	1.82	5.20	0.00
n-Hexane	1.55	0.93	0.96	0.54	2.99
n-Hexenes	0.33	0.15	0.57	0.03	0.85
n-Heptane	0.01	0.00	0.00	0.00	0.26
n-Heptenes	0.00	0.00	0.00	0.00	0.03
2-Methylheptane	0.16	0.12	0.61	0.22	0.66
Benzene	5.90	6.66	5.80	2.63	4.30
Toluene	15.43	9.14	6.20	4.00	4.49
Ethylbenzene	7.23	8.79	13.79	7.14	5.55
p-Xylenc	1.36	0.72	0.48	0.50	0.59
m-Xylene	1.06	1.12	1.01	0.82	0.81
o-Xylene	6.47	7.04	13.93	7.48	5.96
Reaction time (h)	18.5	7.8	8.0	16.0	19.0
Conversion %	56	76	32	52	37
k (h^{-1})	0.044	0.183	0.048	0.046	0.024

Tables 2–4 contain other forms of the same data and are self-explanatory.

With the data presented, we would like to suggest mechanisms by which aromatic, skeletally isomerized aromatic, and cracked products are formed. We begin the discussion with the C_8 aromatics.

It is believed that the mechanism by which benzene is formed from n-hexane

TABLE 2

Mole Percentage of n-Octane Reacting to Form Cracked, Isomerized, or Aromatic Products

	LiX	NaX	KX	RbX	CsX
Cracked[a]	31.0	30.3	24.2	46.7	48.1
Isomerized[b]	0.3	0.2	1.1	0.5	1.5
Aromatic[b]	68.7	69.5	74.7	52.8	50.4

[a] Does not include methane and ethane formed during the production of toluene and benzene.

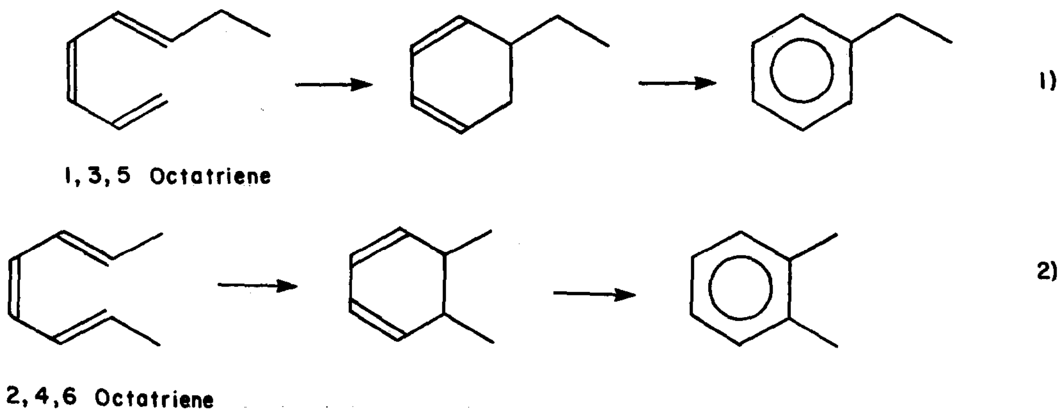
[b] The *m*- and *p*-xylenes are included in the aromatic products.

TABLE 3

Mole Percentage of C_8 Aromatic Products

	LiX	NaX	KX	RbX	CsX
Ethylbenzene	44.85	49.75	47.21	44.79	42.99
p-Xylene	8.44	4.07	1.64	3.14	4.57
m-Xylene	6.58	6.34	3.46	5.14	6.27
o-Xylene	40.14	39.84	47.69	46.93	46.17

over Te/NaX is (1) successive catalytic dehydrogenation of n-hexane to 1,3,5-hexatriene, (2) thermal cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene, and (3) catalytic dehydrogenation of 1,3-cyclohexadiene to benzene (*5, 6*). If we begin to construct a similar sequence for n-octane to aromatic products, the first stage is the successive dehydrogenation of n-octane to octatrienes or octatetraene. We note that many possibilities exist for isomers of octatriene, but the two completely conjugated octatrienes, 1,3,5-octatriene and 2,4,6-octatriene can conceivably cyclize and eventually give the two most abundant aromatic products which were observed, ethylbenzene and *o*-xylene; the mechanism being similar to the n-hexane reaction. Thus:



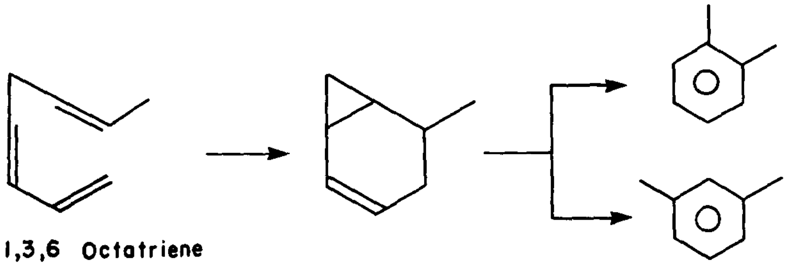
Mechanisms for the formation of *m*- and *p*-xylene present a slightly more difficult task. However, an investigation of the literature reveals that octatrienes, dimethyl-cyclohexadienes, bicyclo C_8 compounds, and cyclo C_8 compounds are interconvertible via *thermal*, homogeneous reactions in the temperature range of 300–500°C via a host of different reactions (e.g., 13, 14, 15, 16, 17, 18, 19). For instance, Cope *et al.* (*14*) report the thermal interconversion of 1,3,5-cyclooctatriene and bicyclo-[4.2.0]-octa-2,4-diene, and Pines and Kozlowski (*16*) report a mechanism by which 5-ethyl-1, 3-cyclohexadiene, 2,4,6-octatriene, 4,5-dimethyl-1,3 cyclohexadiene, and 2,5-dimethyl-1,3-cyclohexadiene are all interconvertible by thermal reactions in this temperature range. Clearly, a complete mechanistic picture of the thermal reactions which take place is beyond the scope of this paper. However, a simplified scheme which includes all the possible nonallenic n-octatrienes (other than 1,3,5- and 2,4,6-octatriene) and octatetraene (which of course can be formed from the successive dehydrogenation of n-octane) and which

TABLE 4

Mole Percentage of Aromatic Products

	LiX	NaX	KX	RbX	CsX
Benzene	15.75	19.90	14.07	11.65	19.82
Toluene	41.20	27.31	15.04	17.72	20.69
Ethylbenzene	19.31	26.26	33.46	31.63	25.58
p-Xylene	3.63	2.15	1.16	2.22	2.72
m-Xylene	2.83	3.35	2.45	3.63	3.73
o-Xylene	17.28	21.03	33.80	33.14	27.47

results in the observed products can be shown:



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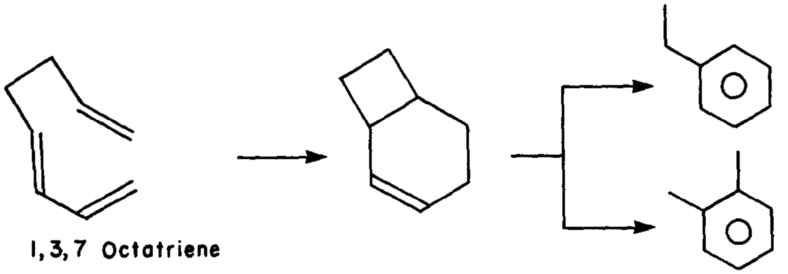

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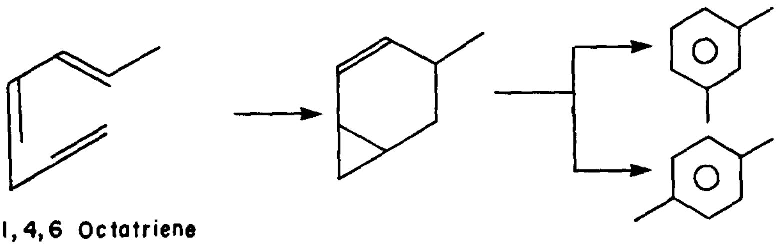

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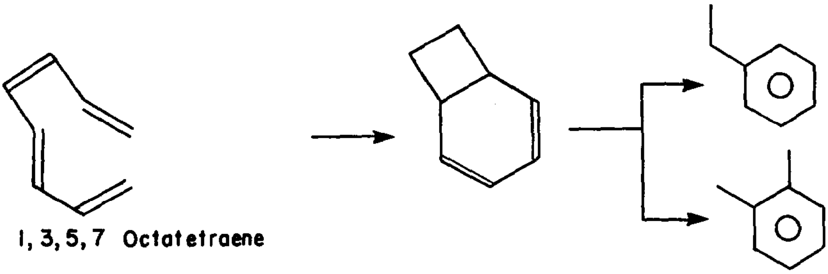

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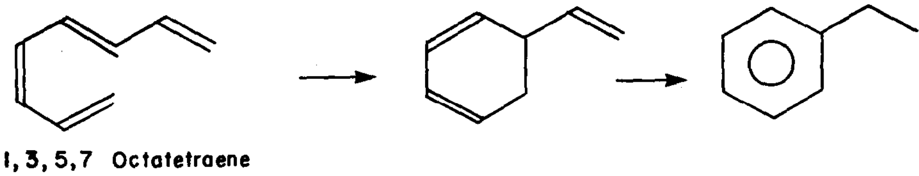
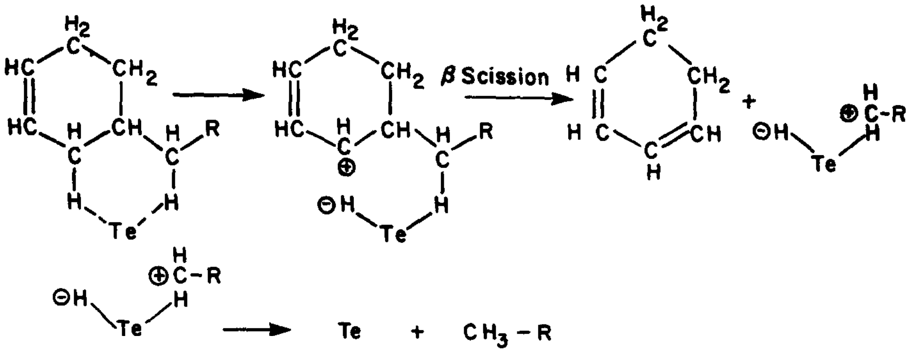


7)

In each of the above reactions, the first step is presumed thermal. Though these reactions can occur homogeneously, it is unlikely that desorption occurs before these electronic rearrangements occur. The second step may be thermal or catalytic though we would expect the majority to be catalytic since the catalyst shows a strong tendency for rapid dehydrogenation. We propose that pathways of this sort, i.e., successive dehydrogenation followed by thermal cyclization and catalytic or thermal dehydrogenation, are essentially exclusive routes to all C_8 aromatics from n-octane. Skeletally isomerized paraffins or olefins are essentially nonexistent in the products as shown in Table 2 and therefore, *p*- and *m*-xylene are not formed by a mechanism which includes paraffin or olefin skeletal isomerization before cyclization, nor does the catalyst directly promote cyclization. We may also strike down the possibility that the C_8 aromatics themselves undergo catalytic skeletal isomerization by referring to the experiments on dimethylcyclohexanes performed by Price (*9*). The 1,2-, 1,3-, and 1,4-dimethylcyclohexanes each gave the skeletally equivalent xylene exclusive of the other xylenes upon dehydrogenation over Te/NaX. Referring to Table 3, we note that each of five catalysts gave roughly equivalent distributions of C_8 aromatics though there are perceptible differences. We conclude that the final composition of the C_8 aromatics is strongly dependent on the rates of the thermal reactions that lead to cyclization.

Next, we would like to consider the mechanism by which benzene and toluene are formed from n-octane. The small amounts of n-hexane, n-hexenes, n-heptane, and n-heptenes indicate that benzene and toluene are not exclusively the products of these intermediates, though very small portions are. Thus, benzene and toluene must be formed from cyclic intermediates. Indeed, this proposition is consistent with the observation that toluene is observed during the reaction of dimethylcyclohexanes over Te/NaX (*9*). We propose a mechanism whereby hydride abstraction by tellurium from an allylic position within the ring produces a carbonium ion. The carbonium ion then undergoes β scission cracking yielding cyclohexadiene and leaving the electron deficiency with the side chain. The cyclohexadiene eventually becomes benzene upon dehydrogenation and the side chain picks up the hydride ion to become neutral. Thus:



Here, Te represents the tellurium active site proposed previously (*7*, *8*). Several other similar reactions could be envisaged. For instance, the ring could contain an extra methyl side group resulting in the ultimate formation of toluene. R- could be a hydrogen or a methyl group, or, the entire side chain could be an ethylene group. The ring could also contain another double bond. The particular cyclic olefin is chosen for the mechanism example because it is likely to exist since olefin isomerization is rapid (*9*) and because the allylic carbonium ion thus formed is comparatively stable. A β scission mechanism can also be written for opening the C_3 or C_4 side ring on the bicyclo octane systems (reactions 3–6). This particular mechanism also predicts the formation of toluene from the dehydrogenation of dimethylcyclohexanes as reported previously (*9*).

Some of the cracking products which were observed may be the result of homogeneous cracking reactions. Pines and Chen (*15*) report methane, ethane, and ethylene formed during the thermal reaction of the ethyl and dimethyl cyclohexadienes at 450–500°C. However, catalytic effects are clearly prominent in the cracking process yielding benzene and toluene since the five different catalysts do not give identical product distributions (Table 4). Also, Pines and Kozlowski (*16*) report only *m*-xylene and dimethylcyclohexadienes with the same skeletal structure as *m*-xylene from the thermal reaction of 5,5-dimethyl-1,3-cyclohexadiene at 500°C while Price (*9*) reports approximately a 3 to 1 ratio of *o*-xylene to *m*-xylene when 1,1-dimethylcyclohexane is reacted over Te/NaX at 520°C. One would expect nearly equivalent reaction products if thermal reactions of cycloolefinic intermediates were predominant.

A mechanism similar to the cyclic cracking reaction can be written to explain the cracking products which are not involved in benzene/toluene formation by simply imagining the ring structures presented above are opened. Notice that this type of mechanism does not include the opportunity for the parent molecule to take on a branched structure through methyl shift. This agrees with the observation that only negligible quantities of branched paraffins are formed.

Finally, we consider the difference in activity of the five catalysts. There are basically two types of effects that could be observed with the different alkali metals in the catalysts. The large sizes of the heavier alkali ions can contribute to steric effects particularly within the restrictive pore structure of the X zeolite. Also, electronic effects must come into play because of the distinctively different colors that the catalysts display.

The Te/NaX catalyst stands out as the most active in agreement with Mikovsky *et al.* (*3*) who reported that Te/NaX is more active than Te/KX. The Te/LiX catalyst probably suffered in activity due to a very large tellurium loss. But the lower activities of the other catalysts, particularly of the Te/CsX catalyst, cannot presently be quantitatively explained though steric factors may be important.

Referring to Table 2, we note that there is no strong trend in selectivity though Te/KX is the most selective in agreement with Mikovsky *et al.* (*3*). It appears that Te/LiX and Te/NaX belong in one group while Te/RbX and Te/CsX belong in a separate selectivity group. Mikovsky *et al.* (*3, 4*) argue for steric factors determining the higher selectivity of Te/KX over Te/NaX. The same argument would tend to indicate Te/RbX and Te/CsX catalysts would be still more selective than Te/KX. Thus, different effects must be prevalent in these catalysts.

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