Thermal Desorption of C_6–C_9 n-Alkenes from the Surface of Zeolite HY*

R.V. JASRA, B.D. BHATT, V.N. GARG and S.G.T. BHAT*

Research Centre, Indian Petrochemicals Corporation Ltd., P.O. Petrochemicals, Baroda 391346 (India)

ABSTRACT

The nature of the species formed during the adsorption and thermal desorption of 1-hexene, 1-heptene, 1-octene and 1-nonene from HY zeolite was studied by temperature-programmed desorption coupled with mass spectrometry. Various transient species desorbed include alkenes, dienes, trienes, alkanes and aromatics. From the identification of these species, the mechanism of the formation of aromatics and the nature of carbonaceous deposits formed during alkene conversion are proposed.

INTRODUCTION

The formation of carbonaceous material during hydrocarbon cracking on acidic catalysts is believed [1] to occur via alkene intermediates, which have been shown [2, 3] to be responsible for the initiation of cracking reactions. Alkenes adsorbed on the acidic surface give rise to aromatics which in turn are believed to act as coke precursors [4, 5]. However, there are conflicting reports on the nature and formation of aromatic species. Blackmond et al. [6] could not obtain conclusive evidence for the presence of aromatics in their studies on the conversion of 1-hexene on zeolite HY by FT-IR spectroscopy. On the other hand, Eberly [7] reported that aromatics were formed at temperatures above 473 K when 1-hexene was exposed to HY zeolite followed by gradual heating in a high-temperature infrared cell. Similar results have also been reported by Venuto and Habib [8].

In earlier studies [9] on alkene desorption from acidic clays we found that thermal desorption studies coupled with mass spectrometry gives valuable information on the molecular species formed during a surface reaction. In this work, temperature-programmed desorption of chemisorbed species from the surface of HY zeolite was studied, following the adsorption of 1-hexene, 1-

---

*IPCL Communication No. 111.

heptene, 1-octene and 1-nonene. Identification of desorbed transient species was attempted using an on-line mass spectrometer. The results provide additional clues to the nature of species that are formed during cracking reactions and the pathways of the formation of coke and coke precursors.

EXPERIMENTAL

HY zeolite was prepared from NaY (SK-40, Union Carbide, U.S.A.) by ion exchange with ammonium chloride followed by calcination of the resulting ammonium form of Y zeolite. The degree of ion exchange was determined by measuring sodium in the original and exchanged zeolite sample by atomic absorption spectrometry and was found to be 75%. The NH_4 Y was calcined at 723 K for 8 h to give HY. Prior to the alkene adsorption/desorption experiment, the zeolite sample was activated at 623 K at 10^{-3} Torr for 4 h and cooled to ambient temperature. The sample was then saturated with the vapour of the alkene under study. A small amount (ca. 10 mg) of the saturated sample was mounted on the direct insertion probe of the mass spectrometer, which had the facility for programmed heating. The mass spectrometer used was a Hewlett-Packard Model 5985B GC–MS instrument having a data processing system and an NBS Library Search Facility. The probe was inserted in the mass spectrometer and the sample was subjected to temperature-programmed desorption under the following conditions: ionization mode, electron impact; ionizing energy, 70 eV; ion source temperature, 473 K; pressure, 10^{-6} Torr; mass range, 50–300 a.m.u.

The temperature was increased at a constant rate of 10 K/min from ambient to 573 K and maintained at the latter temperature for 10 min. The desorption profile, in the form of a temperature vs. total ion abundance curve, was analysed further for individual molecular species.

RESULTS AND DISCUSSION

The thermal desorption profiles of the alkenes from the surface of HY as a function of temperature are shown in Fig. 1. The ordinate gives the total ion abundance, which corresponds approximately to the number of molecular species desorbed at any given temperature. The desorption profiles of 1-hexene and 1-heptene show two peaks and that of 1-octene shows three well defined peaks. With 1-nonene, however, the two high-temperature peaks seem to have merged into a broad band. The fragmentation patterns of the molecules desorbing at various temperatures are given in Tables 1–4. The prominent desorption peaks at the initial stages of desorption consist of C_{10} and higher alkenes, alkanes up to C_9 and traces of C_8 and C_9 dienes and cycloalkenes. No aromatics are observed at this stage. With increase in the temperature of desorption, the relative abundance of alkenes decreases but those of alkanes and
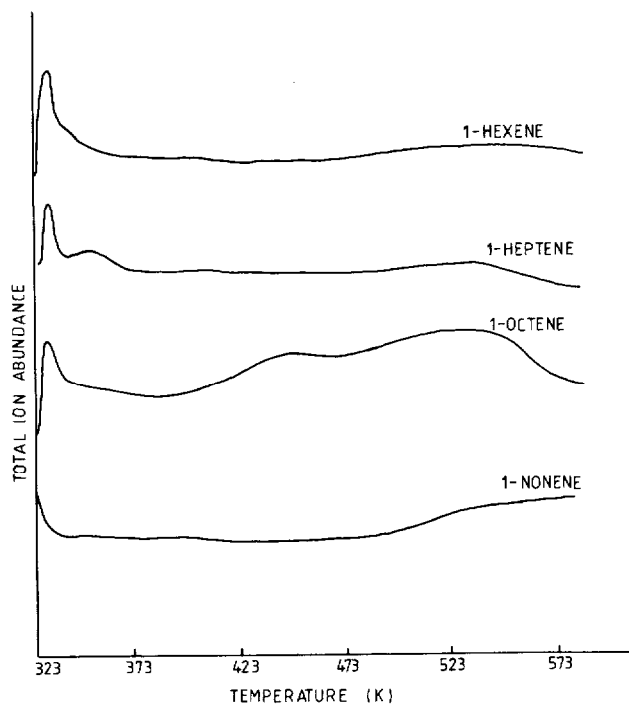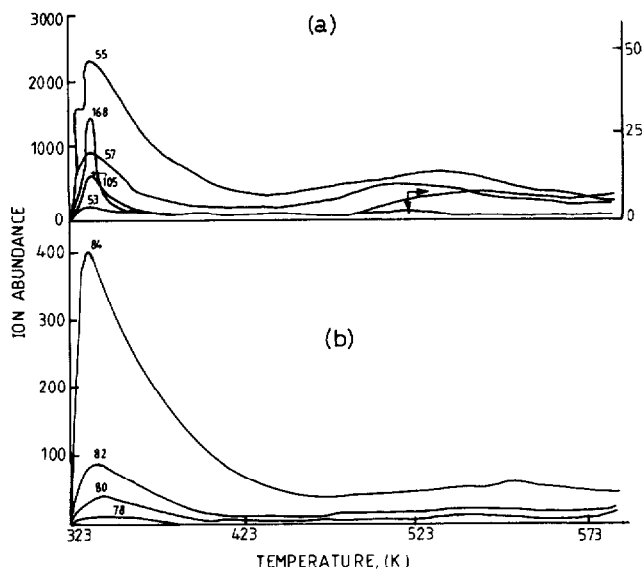
Fig. 1. Total ion profiles of C_6–C_9 alkenes.

Fig. 2. Selected ion monitoring (SIM) profile of 1-hexene desorption products. (a) Products as a class, viz., alkanes, alkenes, dienes and aromatics. (b) Products with C_6 alkenes, dienes, trienes and aromatics.

TABLE 1

Mass fragment		Relative abundance at			Mass fragment		Relative abundance at		
m/z	Ion	310 K	490 K	550 K	m/z	Ion	310 K	490 K	550 K
*Alkanes**					*Dienes/cycloalkenes***				
57	$C_4H_9^+$	35	78	95	53	$C_4H_5^+$	10	17	18
71	$C_5H_{11}^+$	15	40	50	67	$C_5H_7^+$	12	22	20
85	$C_6H_{13}^+$	12	25	30	81	$C_6H_9^+$	10	15	12
99	$C_7H_{15}^+$	5	5	6	95	$C_7H_{11}^+$	5	18	12
113	$C_8H_{17}^+$	1	2	5	96	$C_7H_{12}^+$	–	6	4
127	$C_9H_{19}^+$	1	2	2	109	$C_8H_{13}^+$	Traces	12	3
128	$C_9H_{20}^+$	–	–	2	110	$C_8H_{14}^+$	Traces	5	5
*Alkenes/cycloalkanes***					123	$C_9H_{15}^+$	Traces	5	–
55	$C_4H_7^+$	100	100	100	124	$C_9H_{16}^+$	Traces	2	–
56	$C_4H_8^+$	15	45	52	*Trienes/cyclodienes*§				
69	$C_5H_9^+$	95	70	55	51	$C_4H_3^+$	Traces	5	5
70	$C_5H_{10}^+$	15	30	34	65	$C_5H_5^+$	Traces	4	5
83	$C_6H_{11}^+$	40	25	20	79	$C_6H_7^+$	Traces	7	6
84	$C_6H_{12}^+$	10	17	14	80	$C_6H_8^+$	Traces	2	–
97	$C_7H_{13}^+$	30	20	15	93	$C_7H_9^+$	Traces	3	3
111	$C_8H_{15}^+$	20	10	6	107	$C_8H_{11}^+$	Traces	2	3
112	$C_8H_{16}^+$	10	6	6	*Aromatics*§§				
125	$C_9H_{17}^+$	10	5	3	77	$C_6H_5^+$	Traces	6	6
126	$C_9H_{18}^+$	5	5	4	78	$C_6H_6^+$	Traces	1	–
139	$C_{10}H_{19}^+$	5	–	–	91	$C_7H_7^+$	Traces	4	6
140	$C_{10}H_{20}^+$	–	2	–	105	$C_8H_9^+$	Traces	1	3
168	$C_{12}H_{24}^+$	5	2	–	119	$C_9H_{11}^+$	–	1	2
195					133	$C_{10}H_{13}^+$	–	–	2
209		Traces			145	$C_{10}H_{15}^+$	–	–	4
252					159	$C_{12}H_{17}^+$	–	–	2

*Alkanes up to nonane with traces of higher alkanes.

**Alkenes/cycloalkanes up to C_{12} plus traces of C_{18} cycloalkanes.

***Dienes/cycloalkanes up to C_9.

§Trienes/cyclodienes up to C_8.

§§Benzene and higher aromatics including traces of alkenyl- or cycloalkylbenzene compounds.

aromatics increase. Tables 1–4 also show that, in general, the relative amounts of aromatics formed increase with increase in the chain length of the starting alkene.

Fig. 2 shows the desorption profiles of the various products during the reaction of 1-hexene on HY. Fig. 2a shows the desorption of alkanes (m/z 57), alkenes (m/z 55), aromatics (m/z 105), dienes (m/z 53) and the dimer of 1-hexene (m/z 168). Fig. 2b shows the desorption of 1-hexene (m/z 84), hexadiene (m/z 82) and benzene (m/z 78). These profiles were constructed from the total ion abundance profiles (Fig. 1) by the selected ion monitoring programme of the GC–MS computer. Similar profiles were also obtained for 1-heptene, 1-octene and 1-nonene and are shown in Figs. 3–5.

TABLE 2

Mass spectra of various species formed during desorption of 1-heptene

Mass fragment		Relative abundance at			Mass fragment		Relative abundance at		
m/z	Ion	330 K	470 K	570 K	m/z	Ion	330 K	470 K	590 K
*Alkanes**					*Dienes/cycloalkenes****				
57	$C_4H_9^+$	75	93	81	53	$C_4H_5^+$	9	15	2
58	$C_4H_{10}^+$	4	5	4	54	$C_4H_6^+$	5	7	7
71	$C_5H_{11}^+$	44	43	41	67	$C_5H_7^+$	26	23	19
72	$C_5H_{12}^+$	25	3	–	68	$C_5H_8^+$	9	8	7
85	$C_6H_{13}^+$	26	27	21	81	$C_6H_9^+$	28	22	14
86	$C_6H_{14}^+$	2	2	–	82	$C_6H_{10}^+$	10	10	5
99	$C_7H_{15}^+$	8	7	6	95	$C_7H_{11}^+$	30	22	9
100	$C_7H_{16}^+$	1	3	3	96	$C_7H_{12}^+$	10	7	4
113	$C_8H_{17}^+$	5	2	3	109	$C_8H_{13}^+$	15	12	4
114	$C_8H_{18}^+$	1	2	–	110	$C_8H_{14}^+$	5	5	–
127	$C_9H_{19}^+$	3	–	–	123	$C_9H_{15}^+$	8	5	–
128	$C_9H_{20}^+$	1	–	–	124	$C_9H_{16}^+$	4	3	–
141	$C_{10}H_{21}^+$	2	–	–	137	$C_{10}H_{17}^+$	4	3	–
142	$C_{10}H_{22}^+$	1	–	–	138	$C_{10}H_{18}^+$	2	1	–
155	$C_{11}H_{25}^+$	1	–	–	151	$C_{11}H_{19}^+$	2	2	–
191	$C_{13}H_{27}^+$	Traces	–	–	*Trienes/cycloalkynes*§				
*Alkenes/cycloalkanes***					65	$C_5H_5^+$	4	4	7
55	$C_4H_7^+$	100	100	100	66	$C_5H_6^+$	1	2	3
56	$C_4H_8^+$	24	52	52	79	$C_6H_7^+$	13	8	8
69	$C_5H_9^+$	85	68	58	80	$C_6H_8^+$	2	2	–
70	$C_5H_{10}^+$	26	32	35	93	$C_7H_9^+$	7	3	3
83	$C_6H_{11}^+$	53	25	19	94	$C_7H_{10}^+$	1	1	4
84	$C_6H_{12}^+$	15	13	16	107	$C_7H_{11}^+$	3	2	–
97	$C_7H_{13}^+$	46	17	10	108	$C_8H_{12}^+$	2	–	–
98	$C_7H_{14}^+$	15	11	9	*Aromatics*§§				
111	$C_8H_{15}^+$	22	10	5	77	$C_6H_5^+$	6	7	7
125	$C_9H_{17}^+$	11	5	–	78	$C_6H_6^+$	1	2	–
126	$C_9H_{18}^+$	7	3	–	91	$C_7H_7^+$	8	5	8
139	$C_{10}H_{19}^+$	5	2	–	105	$C_8H_9^+$	3	2	6
140	$C_{10}H_{20}^+$	3	2	–	106	$C_8H_{10}^+$	–	2	–
154	$C_{11}H_{22}^+$	2	1	–	119	$C_9H_{11}^+$	–	–	6
168	$C_{12}H_{24}^+$	2	–	–	133	$C_{10}H_{13}^+$	–	–	5
224	$C_{18}H_{36}^+$	Traces			145	$C_{11}H_{13}^+$	–	–	7
					159	$C_{12}H_{15}^+$	–	–	4

*Alkanes up to C_{13} and traces of higher alkanes.

**Alkenes up to C_{12} and traces of higher alkenes.

***Dienes/cycloalkenes up to C_{10} and traces of higher cycloalkenes.

§Trienes/cycloalkynes up to C_8.

§§Benzene, toluene, xylenes and higher aromatics above C_{12} and traces of alkenyl- or cycloalkyl-benzene compounds.

TABLE 3

Mass spectra of various species formed during desorption of 1-octene

Mass fragment		Relative abundance at			Mass fragment		Relative abundance at		
m/z	Ion	330 K	380 K	623 K	m/z	Ion	330 K	380 K	623 K
*Alkanes**					*Dienes/cycloalkenes****				
57	$C_4H_9^+$	58	100	100	53	$C_4H_5^+$	10	10	13
71	$C_5H_{11}^+$	35	52	40	67	$C_5H_7^+$	17	8	8
85	$C_6H_{13}^+$	12	28	24	81	$C_6H_9^+$	12	6	5
99	$C_7H_{15}^+$	2	6	6	95	$C_7H_{11}^+$	8	4	3
113	$C_8H_{17}^+$	2	4	2	96	$C_7H_{12}^+$	3	3	2
114	$C_8H_{18}^+$	1	1	2	109	$C_8H_{13}^+$	3	4	1
127	$C_9H_{19}^+$	1	2	2	123	$C_9H_{15}^+$	Traces	2	–
141	$C_{10}H_{21}^+$	1	2	2	124	$C_9H_{16}^+$	Traces	1	–
155	$C_{11}H_{23}^+$	1	1	1	*Trienes/cycloalkynes*§				
169	$C_{12}H_{25}^+$	–	–	1	65	$C_5H_5^+$	3	4	4
*Alkenes/cycloalkanes***					66	$C_5H_6^+$	2	2	2
55	$C_4H_7^+$	100	96	69	79	$C_6H_7^+$	6	6	5
56	$C_4H_8^+$	34	44	47	80	$C_6H_8^+$	1	1	–
69	$C_5H_9^+$	90	63	33	93	$C_7H_9^+$	1	2	2
70	$C_5H_{10}^+$	41	37	28	107	$C_8H_{11}^+$	1	1	2
83	$C_6H_{11}^+$	58	37	28	*Aromatics*§§				
84	$C_6H_{12}^+$	25	18	11	77	$C_6H_5^+$	4	4	6
97	$C_7H_{13}^+$	35	20	12	78	$C_6H_6^+$	1	1	2
98	$C_7H_{14}^+$	12	9	6	91	$C_7H_7^+$	3	4	9
111	$C_8H_{15}^+$	22	12	6	92	$C_7H_8^+$	–	3	2
112	$C_8H_{16}^+$	15	12	4	103	$C_8H_7^+$	–	2	2
125	$C_9H_{17}^+$	6	3	1	104	$C_8H_8^+$	–	3	–
126	$C_9H_{18}^+$	8	4	1	105	$C_8H_9^+$	1	2	10
139	$C_{10}H_{19}^+$	4	2	–	106	$C_8H_{10}^+$	1	3	3
140	$C_{10}H_{20}^+$	6	3	–	115	$C_9H_7^+$	1	–	3
153	$C_{11}H_{21}^+$	2	1	–	116	$C_9H_8^+$	–	–	1
154	$C_{11}H_{22}^+$	3	2	–	117	$C_9H_9^+$	–	–	3
167	$C_{12}H_{23}^+$	1	1	–	119	$C_9H_{11}^+$	–	–	9
168	$C_{12}H_{24}^+$	1	1	–	120	$C_9H_{12}^+$	–	–	4
224	$C_{16}H_{32}^+$	2	–	–	128	$C_{10}H_8^+$	–	–	1
					133	$C_{10}H_{13}^+$	–	–	4
					145	$C_{11}H_{13}^+$	–	–	3
					148	$C_{11}H_{16}^+$	–	–	1
					159	$C_{11}H_{15}^+$	–	–	2

*Alkanes up to nonane with traces of higher alkanes.

**Alkenes/cycloalkanes up to C_{12} and cyclic dimers.

***Dienes/cycloalkenes up to C_9.

§Trienes up to C_6 and traces of higher trienes/cycloalkenes.

§§Benzene, toluene, xylenes and higher aromatic at around 623 K.

TABLE 4

Mass spectra of various species formed during desorption of 1-nonene

Mass fragment		Relative abundance at		Mass fragment		Relative abundance at	
m/z	Ion	328 K	580 K	m/z	Ion	328 K	580 K
*Alkenes**				*Dienes/cycloalkenes***			
57	$C_4H_9^+$	38	100	53	$C_4H_5^+$	14	11
58	$C_4H_{10}^+$	4	5	54	$C_4H_6^+$	14	6
71	$C_5H_{11}^+$	24	58	67	$C_5H_7^+$	27	21
72	$C_5H_{12}^+$	5	4	68	$C_5H_8^+$	17	7
85	$C_6H_{13}^+$	20	36	81	$C_6H_9^+$	19	17
86	$C_6H_{14}^+$	2	3	82	$C_6H_{10}^+$	18	–
99	$C_7H_{15}^+$	5	11	95	$C_7H_{11}^+$	13	14
100	$C_7H_{16}^+$	–	2	96	$C_7H_{12}^+$	11	9
113	$C_8H_{17}^+$	3	5	109	$C_8H_{13}^+$	5	7
114	$C_8H_{18}^+$	–	2	110	$C_8H_{14}^+$	3	6
127	$C_9H_{19}^+$	3	4	123	$C_9H_{15}^+$	5	2
128	$C_9H_{20}^+$	Traces		124	$C_9H_{16}^+$	5	3
141	$C_{10}H_{21}^+$	Traces		137	$C_{10}H_{17}^+$	–	2
155	$C_{11}H_{23}^+$	Traces		138	$C_{10}H_{18}^+$	–	–
*Alkenes/cycloalkanes***				*Trienes/cycloalkynes*§			
55	$C_4H_7^+$	88	85	65	$C_5H_5^+$	5	5
56	$C_4H_8^+$	59	51	66	$C_5H_6^+$	2	2
69	$C_5H_9^+$	100	66	79	$C_6H_7^+$	7	7
70	$C_5H_{10}^+$	78	40	80	$C_6H_8^+$	2	2
83	$C_6H_{11}^+$	71	25	93	$C_7H_9^+$	3	3
84	$C_6H_{12}^+$	44	23	107	$C_8H_{11}^+$	–	2
97	$C_7H_{13}^+$	53	31	*Aromatics*§§			
98	$C_7H_{14}^+$	10	14	77	$C_6H_5^+$	7	6
111	$C_8H_{15}^+$	12	20	78	$C_6H_6^+$	26	2
112	$C_8H_{16}^+$	4	9	91	$C_7H_7^+$	3	6
125	$C_9H_{17}^+$	11	6	105	$C_8H_9^+$	–	5
126	$C_9H_{18}^+$	24	3	106	$C_8H_{10}^+$	–	2
139	$C_{10}H_{19}^+$	3	2	119	$C_9H_{11}^+$	–	4
140	$C_{10}H_{20}^+$	2	3	120	$C_9H_{12}^+$	1	2
154	$C_{11}H_{22}^+$	4	2	128	$C_{10}H_8^+$	–	2
168	$C_{12}H_{24}^+$	2	2	133	$C_{10}H_{13}^+$	–	2
				145	$C_{10}H_{15}^+$	–	2

*Alkanes up to C_9 and traces of naphthenes.

**Alkenes/cycloalkanes up to C_{13}.

***Dienes/cycloalkenes up to C_{10}.

§Trienes up to C_6 and traces of higher cycloalkynes.

§§C_9 aromatics, naphthalenes, cycloalkylaromatics, alkenyl aromatics.

Fig. 3. Selected ion monitoring profile of 1-heptene desorption products. (a) Products as a class, viz., alkanes, alkenes, dienes and aromatics. (b) Products with C_7 dienes, trienes and aromatics.

Fig. 4. Selected ion monitoring profile of 1-octene desorption products. (a) Products as a class, viz., alkanes, alkenes, dienes and aromatics. (b) Products with C_8 alkenes, dienes, trienes and aromatics.

The fragmentation pattern of the desorbed molecules in the initial region (around 310 K) of the profile shows that the parent alkenes give rise to a series of product alkenes of different chain length (C_4–C_{12}), alkanes, di- and trienes, cyclic hydrocarbons and traces of dimers and trimers of the respective alkenes. As the mass spectrometer could not be operated at a.m.u. below 50 it cannot
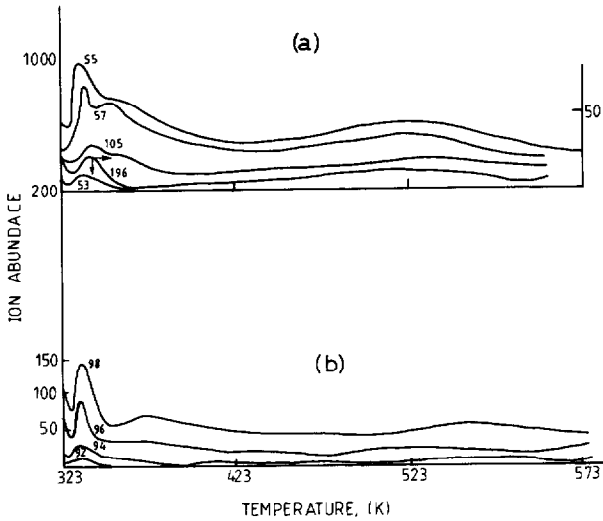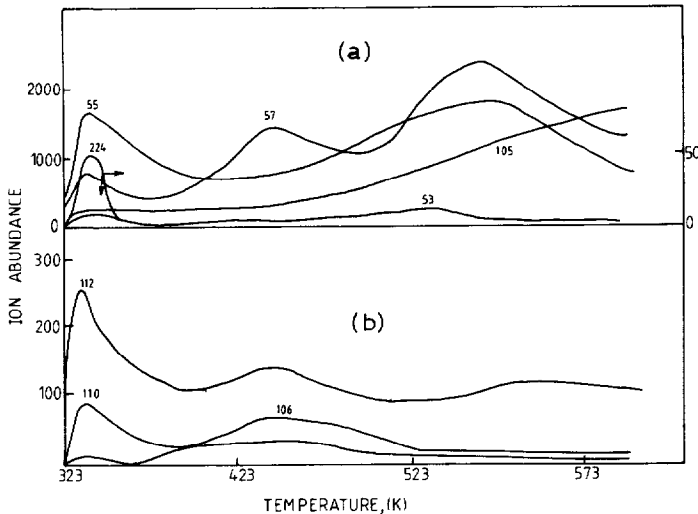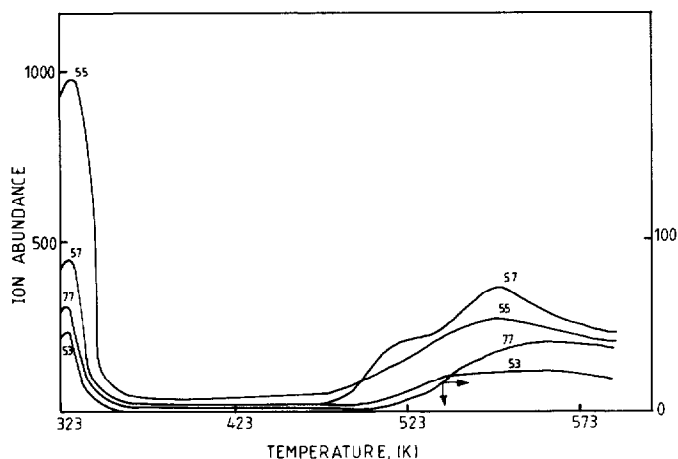
Fig. 5. Selected ion monitoring profile 1-nonene desorption products as a class, viz., alkanes, alkenes, dienes and aromatics.

be said with certainty whether C_1, C_2 and C_3 products were also formed during desorption. Nevertheless, the formation of higher homologues of the alkenes suggests that the dimerization–cracking mechanism is operative, as suggested by Abbot and Wojciechowski [4], who also noted the absence of C_1 and C_2 species during the cracking of 1-hexene on HY. It is interesting that this region, which generally represents the desorption of physically adsorbed molecules, consists of a large number of molecules resulting from hydrogen transfer and cracking reactions. It shows that the cracking, dimerization and recombination of cracked products take place readily at ambient temperature. Owing to the high vacuum applied (10^{-6} Torr), the reaction products are readily desorbed below 350 K. With increase in temperature and depletion of the alkene concentration, the oligomerization ceases but cracking and hydrogen transfer reactions as shown in eqn. (1) still take place:

$$2C_n H_{2n} \longrightarrow C_n H_{2n+2} + C_n H_{2n-2} \tag{1}$$

This is inferred from the presence of fragments corresponding to m/z 57, 71, 85, etc., representing alkane molecules, and $m/z = 56$, representing a C_4 alkene fragment (Tables 1–4). The other products of hydrogen transfer reactions are dienes/cycloalkenes, trienes and aromatics. The formation of these hydrogen-deficient and aromatic molecules is always associated with the formation of a saturated molecule, which means that no pure dehydrogenation or dehydrocyclization reactions involving the evolution of molecular hydrogen occur. This observation substantiates the results of Abbot and Wojciechowski [4], who noted that no hydrogen was formed during the catalytic cracking of 1-hexene on HY at moderate severities.

The length of the hydrocarbon chain has a significant effect on the nature

of the products of desorption, particularly at higher temperatures. With 1-hexene (Fig. 2a and b) the desorbed products at elevated temperature (e.g., the peak at 573 K) are richer in alkene species (m/z 55) than alkanes (m/z 57). Significant amounts of dienes (m/z 53) are also seen. However, very small amounts of aromatics (m/z 77) are noted (Fig. 2a). Similarly, 1-hexene (m/z 84), hexadiene (m/z 82) and hexatriene (m/z 80) are seen in significant amounts, but benzene (m/z 78) is not found at all at this stage. Similar observations are made with 1-heptene desorption (Fig. 3a and b), heptene (m/z 98), heptadiene (m/z 96) and heptatriene (m/z 94) being observed, but no toluene (m/z 92) (Fig. 3b). Interestingly, fragments of higher aromatics (m/z 105) are noticed. With 1-octene (Fig. 4), it can be seen that large amounts of alkanes (m/z 57) and substantial amounts of octene (m/z 112), *octadiene/dimethyloctene* (m/z 110) and xylenes (m/z 106) are desorbed around 423 K. The desorption products at higher temperature (573 K) consist mainly of cracked alkenes, alkanes and higher aromatics (Fig. 4a). The behaviour of 1-nonene is similar to that of 1-octene, with C_9 aromatics being formed in significant amounts (Table 4). The aromatics formed during 1-nonene adsorption probably need higher temperatures for desorption. Consequently, in contrast to 1-octene, we find a poorly resolved desorption band above 500 K. It is also interesting that 1-hexene and 1-heptene give rise to trienes in significant amounts whereas 1-octene does not produce the corresponding triene (m/z 108). In fact, as can be seen from Tables 2–4, no triene larger than C_7 is observed in any of the experiments. These results lead to the conclusions that aromatics and other cyclic products are more readily formed with increase in chain length, particularly above C_7, and that the cyclization probably takes place at the diene stage followed by rapid hydrogen transfer to give aromatics.

The aromatic nature of the molecular growth on the zeolite surface can be seen from closer examination of Fig. 4a and Table 3. As the temperature increases, the overall desorption diminishes, but the desorption of higher aromatics continues at a steady rate. Above 570 K condensed rings such as those of indene (m/z 146), dihydroindene and their derivatives (m/z 118, 145) and alkenylbenzene derivatives (m/z 150, 149) are also formed. Such aromatic molecules are held strongly and are not completely removed even by heating above 673 K under vacuum as reported by Eberly [7]. The aromatic molecules, being basic in nature, are chemisorbed on the strong acid sites of zeolites. These species act as coke precursors. In fact, coke formation has been correlated with the basicity of aromatic molecules [10] and the aromatic content of the feedstock [9]. The aromatic molecules tend to grow on the surface through alkylation and condensation reactions with unsaturated species chemisorbed on the neighbouring active sites. These molecules tend to form coke through further hydrogen transfer reactions. The increasing alkane content (m/z 57) in the desorption products, despite the depletion of the alkenes in the high-temperature region of the desorption profile (Tables 3–5), leads to the above conclu-

sion. This mechanism is also favoured by a higher acid site density of zeolites, as reported [8, 11, 12]. Although the nature of carbon in coke is subject to some controversy [6, 12], we feel that the coke progressively becomes more hydrogen deficient through the hydrogen transfer reactions. Furthermore, analysis of coke extract has shown the presence of a large number of aromatic compounds which are rarely found in the main reaction products [13]. These data support our view that during alkene conversion on zeolites the main reaction products and coke are formed through independent reaction pathways. The total coke formed may reach a plateau with respect to time [6, 12], but its nature probably constantly undergoes changes. Based on the mass spectral evidence obtained in this study, the network of reactions leading to the formation of various intermediates and products may be represented as shown in Scheme 1.

Alkene ⟶ diene ⟶ triene

Cracked products

Oligomers

Coke

Cycloalkane ⟶ Cycloalkene

Cycloalkyne

Polynuclear aromatics

Aromatics ⟶ Alkylated aromatics
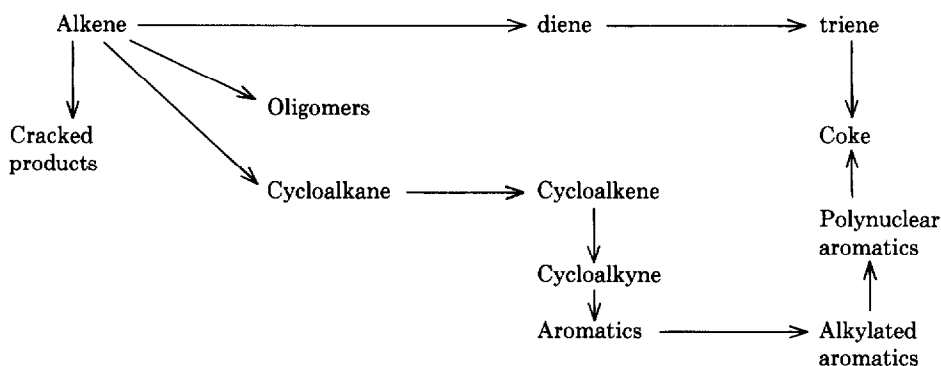
In conclusion, the formation of coke during the conversion of alkenes over acidic zeolite catalysts involves transient aromatic species, confirming literature reports on the aromatic nature of the carbonaceous deposits. The tendency to form aromatics on the surface increases with increasing number of the aliphatic hydrocarbon chain.

REFERENCES

1   L.B. Ryland, M.W. Tamele and J.N. Wilson, in P.H. Emmett (Editor), Catalysis, Vol. 7, New York, 1960, p. 1.
2   M.L. Poutsma, in J.A. Rabo (Editor), Zeolite Chemistry and Catalysis, ACS Monograph, 171, 1976, p. 529.
3   P.B. Weisz, Chemtech., August (1973) 498.
4   J. Abbot and B.W. Wojciechowski, Can. J. Chem. Eng., 63 (1985) 247, 278, 451, 462.
5   P.B. Venuto, L.A. Hamilton and P.S. Landis, J. Catal., 2 (1966) 484.
6   D.G. Blackmond, J.G. Goodwin and J.E. Lester, J. Catal., 78 (1982) 34, 247.
7   P.L. Eberly, J. Am. Chem. Soc., 35 (1963) 12.
8   P.B. Venuto and E.T. Habib, Jr., Fluid Catalytic Cracking with Zeolite Catalysts, Marcel Dekker, New York, 1979.
9   R.V. Jasra and S.G.T. Bhat, in T.S.R. Prasada Rao (Editor), Adv. Catal. Sci. & Technol., Wiley Eastern, 1985, p. 423.
10 W.G. Appleby, J.W. Gibbson and G.M. Good, Ind. Eng. Chem. Process Des. Dev., 2 (1962) 102.
11 B.C. Gates, J.R. Katzer and G.C.A. Schuit, Chemistry of Catalytic Processes, Academic Press, New York, 1973.
12 D. Eisenbach and E. Gallei, J. Catal., 56 (1979) 377.
13 K.W. McLaughlin and R.G. Anthony, A.I.Ch.E. J., 31 (1985) 929.