

ENCLOSURE (A)

Part II

THE IDENTIFICATION OF HYDROCARBONS BY THE USE OF RAMAN SPECTRA

The study of the Raman spectra of organic compounds, as pointed out by Dadieu & Kohlrausch (Ber., 63 (1930) 251, 1675), enables one to identify the substances in a mixture or in the pure state, by means of particular lines in the spectra of organic compounds with particular atomic groups. Various investigators in Japan have employed the Raman spectra for the identification of various hydrocarbons in gasolines and also to detect isomeric substances which were formed in the course of the chemical reaction of alcohols and hydrocarbons (as in the dehydration of n-butanol by the catalytic action with alumina).

The values of the force constant, f , calculated from the data of the Raman spectra for single, double and triple links are roughly proportional to the heat of the rupture of the links. Thus the Raman spectra have enabled the author to observe the behavior of organic compounds under the influence of heat. n-butanol from the market, B.P. 116-70°C, d_4^{20} 0.8098, n_D^{20} 1.3980 was converted, by the dehydration with alumina at 400°C, into n-butene, (of purity 94.7%) which passed over the phosphoric acid catalyst heated at 150°C, with space velocity 300 kg/1-hr and the product shows the physical constants d_4^{20} 0.7116, n_D^{20} 1.4013, M.W. 115, O.N. 90.8 & the Raman spectra. (Table IX(A)).

These Raman spectra of the reaction product were compared with those of 2, 3, 4 trimethyl pentane (T. TORIYAMA, J. Chem. Soc. Japan 64 (1943) 1423), 2, 2, 3 trimethyl pentane and also 2,2,4 trimethyl pentane (S. MIZUSHIMA, S. MORINO and OKAZAKI'S results). And it was assumed to be composed of:

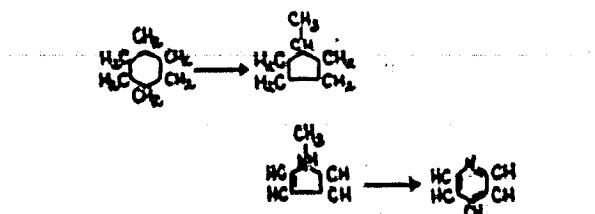
35 - 40% 2,3,4 trimethyl pentane
35 - 40% 2,2,3 trimethyl pentane
and 20 - 25% 2,2,4 trimethyl pentane

When n-butanol was dehydrated by TAKEDA with alumina at 350°C the product, after water cooling passed the receiver cooled with solid CO₂. The products distilled and their Raman spectra are shown in Table X(A).

These results were compared with those observed by Bourguet and Piaux (Bull. Soc. Chem. 2 (1935) 1958) of butene-1 and also of butene-2 by Gerschinowitz & Wilson (J. Chem. Phys., 6 (1930) 247). This comparison indicates that the product consists mostly of butene-1. (S. MIZUSHIMA, Y. MORINO, R. FUJISHIRO, K. OKAZAKI and Y. KAKIUCHI (1943), unpublished).

The direct-run gasoline from Sanga Sanga oil (O.N. 91.2 with 0.1% Pb.) was fractionated by SONODA, into 23 fractions (Table XI(A).) (Table XI(A)).

According to the author's opinion, the occurrence of cyclopentane derivatives, indene, 5-membered carbon ring, pyridine, quinoline, 6 membered carbon and nitrogen ring, in petroleum and coal tars, is due to the isomerization of cyclohexane derivatives and hydronaphthalenes, 6 carbon numbered ring, and pyrole derivatives, 5 carbon and nitrogen ring, under the influence of high temperature and high pressure.



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Based on this hypothesis, M. HAGIWARA, one of the author's co-workers, studied this problem. He has succeeded in converting cyclohexene and cyclohexene into methyl cyclopentane, and dehydronaphthalene into methyl indene respectively by subjecting them to high temperature and pressure in an autoclave.

He also reported the Raman spectra of these compounds used as an evidence for this chemical change (Tables XIII(A), XIII(A)).

(Refer also T. HAYASHI: Sci. P. Inst. Phys. Chem. Res., 23 (1934) 274.) The Raman shifts of indene appears to be smaller than that of 1,2-dihydronaphthalene.

It was noteworthy that a new base has been isolated by T. BOUCHI from Fushun shale tar (Bull. Soc. Chem. Japan 2 (1927) 176; 3 (1928) 227), which on analysis and examination of its physical (Bp. 199.8°, d₄²⁰ 1.029, n_D²⁰ 1.541, n_D²⁵ 1.536; M. R. 36.34) and chemical properties was concluded to probably have the structure of a "cyclopentano-pyridine" and was called pyridane. The molecular structure of this base was later confirmed by synthesis by American chemists.

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Table IX(A)
RAMAN SPECTRA OF THE ISOMERIZED PRODUCT OF n-BUTENE
(ν , cm⁻¹)

220	(o.d.)	1075	(3)
300-330	(4)	1100	(0)
347	(1)	1119	(2)
393	(1)	1159	(4b)
418	(0)	1183	(3b)
443	(16)	1205	(1)
470	(5)	1212	(1)
526	(3b)	1245	(3)
570	(4)	1265	(0)
610	(0)	1295	(3)
669	(26)	1319	(4)
688	(1)	1550	(4)
714	(6)	1435	
753	(10b)	1470	(10)
745	(4b)		
810	(4)		
834	(4)		
860	(6)		
700	(8)		
926	(6b)		
965	(6)		
976	(5)		
994	(0)		
1010	(10b)		
1035-1047	(8)		

* = weak, b = broad line, d = diffused line.

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Table X(A)
RAMAN SPECTRA OF THE DEHYDRATED PRODUCT OF α -BUTANOL
(ν , cm^{-1})

214	(0)	1293	(6)
387	(1)	1375	(3)
438	(3)	1417	(5)
500	(3)	1456	(4)
585	(0)	1640	(10)
633	(5)	1658	(2)
741	(0b)	1678	(2)
791	(1)	2729	(3)
832	(2)	2854	(4)
850	(4)	2875	(3)
868	(2)	2908	(6b)
910	(3)	2937	(?)
988	(2)	2970	(5)
1017	(3)	3001	(7b)
1065	(3)	3079	(5)
1258	(4)		

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Table XI(A)
RAMAN SPECTRA OF EACH FRACTION

Fraction (°C)	Yield (wt %)	
1. 19~30	3.88	It was confirmed to include 2 methyl butane 2% (wt.)
2. 30~35	2.38	It was confirmed to include 2 methyl butane 2% (wt.)
3. 35~40	0.55	n-pentane 2% (wt.)
4. 40~45	0.16	Cyclopentane 2% (wt.)
5. 45~50	0.21	2,2.-dimethyl butane 1% (wt.)
6. 50~55	0.40	2,3.-dimethyl butane 1% (wt.)
7. 55~60	0.68	2--methyl pentane 3% (wt.)
8. 60~65	2.77	3--methyl pentane 1% (wt.)
9. 65~70	5.30	n-hexane 3% (wt.)
10. 70~75	4.80	methyl cyclopentane 2% (wt.)
11. 75~80	3.69	2,2.-dimethyl pentane 1% (wt.)
12. 80~85	2.22	benzene 7% (wt.)
13. 85~90	1.69	Cyclohexane 6% (wt.)
14. 90~95	5.27	2,4.-dimethyl pentane 2% (wt.)
15. 95~100	8.88	3,3.-dimethyl pentane 1% (wt.)
16. 100~105	8.94	2--methyl hexane 1% (wt.)
17. 105~110	8.75	trans-1,2--dimethyl cyclopentane 2% (wt.)
18. 110~115	5.13	n-heptane 2% (wt.)
19. 115~120	2.08	methyl cyclohexane 11% (wt.)
20. 120~125	3.41	toluene 14% (wt.)
21. 125~130	4.66	1,3.-dimethyl cyclohexane 1,4.-dimethyl cyclohexane 4% (wt.) 2% (wt.)
22. 130~135	5.97	n-octane 3% (wt.)
23. 135~140	5.38	ethyl benzene 2% (wt.) p-xylene 2% (wt.) m-xylene 0% (wt.) o-xylene 1% (wt.)

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Table XIII(A)
RAMAN SPECTRA OF CYCLOHEXANE, CYCLOHELINE
AND METHYLCYCLOPENTANE

CyclohexaneCyclohexeneMethylicyclopentane

	176 (1)	
	273 (3b)	281 (1)
375 (1)	395 (5)	292 (5)
425 (2)	451 (2)	428 (2)
	494 (2)	530 (4)
	641 (1)	
	703 (2b)	
800 (8)	825 (8)	780 (3b)
	873 (2)	842 (5)
	905 (5)	886 (8)
	968 (3)	978 (4)
	1038 (2)	1017 (4)
1026 (5)	1066 (6)	1079 (4)
1155 (1)	1159 (10)	
1264 (6)	1220 (5)	1204 (2b)
	1247 (4)	1274 (2)
	1269 (3)	1310 (2b)
1344 (1)	1342 (2b)	1348 (1)
1437 (8)	1433 (6b)	
	1664 (6)	1453 (6b)
2659 (2)	2856 (6b)	2723 (6)
2691 (1)	2869 (3)	2965 (12b)
2883 (2)	2912 (6)	2921 (10b)
2938 (10)	2934 (6)	2956 (10b)

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Table XIII(A)
RAMAN SPECTRA OF DIHYDRONAPHTHALENE AND INDENE

1,2-dihydronaphthalene(ν₆ cm⁻¹)

3026
2760
1618
1554
1472
1375
1332
1280
1202
1145
1091
1020
933
865
726

indene

3038
2765
1589
1534
1443
1379
1343
1276
1190
1140
1099
1049
1003
984
881
710

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Table XIV(A)
RAMAN SPECTRA OF EACH FRACTION OF SANGA-SANGA GASOLINE (NO. 1)

	3000~3500	3500~4000	4500~5000	5000~5500	5500~6000	6000~6500
	219 (00)		216 (00)		222 (0)	225 (00)
275 (00)	275 (06)	271 (1)	275 (008)	275 (008)	260 (1)	
336 (1)	336 (8)	337 (0)	338 (16)	338 (26)	334 (86)	
369 (0)	365 (1)		363 (12)		365 (1)	
401 (6)	401 (7)	402 (5)	401 (12)	401 (2)	404 (1)	
463 (36)	464 (36)	464 (16)	467 (00)	445 (4)	445 (4)	
			478 (00)	478 (0)	478 (0)	
			505 (00)	504 (0)	506 (00)	
			550 (00)		528 (00)	
			548 (00)	548 (00)		
	662 (00)			607 (0)	607 (8)	
		692 (00)			674 (00)	
	709 (8)		712 (4)	712 (4)	712 (1)	
	738 (00)	732 (1)	730 (8)	730 (3)	728 (8)	
761 (2)	762 (8)			749 (1)	749 (1)	
766 (5)	766 (7)	766 (6)	766 (2)	767 (1)		
796 (6)	795 (4)	794 (1)	797 (1)	799 (00)		
843 (6)	841 (6)	841 (1)	814 (3)	815 (5)	801 (0)	
868 (5)	868 (6)	849 (8)	871 (8)	872 (0)	871 (1)	
	880 (4)	889 (7)			871 (6)	801 (46)
910 (8)	909 (36)	908 (1)	890 (76)	891 (6)		
	928 (00)		898 (00)	898 (0)		
964 (4)	964 (2)	964 (1)	967 (8)	967 (3)	961 (2)	
967 (1)	968 (2)	968 (1)	968 (1)	968 (3)	967 (3)	
1088 (1)	1088 (8)		1018 (1)	1018 (8)	991 (10)	
1089 (0)	1089 (8)	1088 (8)		1018 (00)	1017 (1)	
1078 (36)	1079 (8)	1079 (8)	1041 (8)	1038 (4)	1036 (8)	
1144 (6)	1145 (8)	1173 (8)	1073 (86)	1094 (26)	1074 (26)	
1145 (8)	1146 (8)	1146 (8)	1147 (8)	1148 (4)	1147 (4)	
1178 (16)	1179 (8)	1180 (1)		1178 (8)		
	1188 (16)	1188 (1)	1181 (26)	1181 (006)	1180 (46)	
1207 (16)	1208 (11)	1208 (8)	1208 (26)	1208 (46)	1208 (8)	
1204 (26)	1205 (11)	1205 (8)	1205 (26)	1205 (46)	1205 (8)	
1204 (1)	1205 (1)	1205 (8)	1205 (26)	1205 (46)	1205 (8)	
1428 (7)	1428 (8)	1428 (8)	1428 (26)	1448 (26)	1428 (8)	
1460 (8)	1470 (8)	1460 (8)	1461 (26)	1460 (26)	1460 (8)	
					1460 (8)	
2043 (06)	2043 (00)		2029 (00)	2029 (0)		
	2043 (26)		2029 (00)			
2720 (8)	2720 (8)		2710 (8)	2710 (8)	2710 (8)	
2727 (8)	2727 (8)	2729 (86)	2729 (8)	2729 (8)	2740 (36)	
2727 (16)	2727 (8)	2727 (8)	2727 (16)	2727 (8)	2727 (16)	
2727 (16)	2727 (8)	2727 (8)	2727 (16)	2727 (8)	2727 (16)	
2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	
2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	
2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	2727 (8)	

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Table XVI(A)
RAMAN SPECTRA OF EACH FRACTION OF SANGA SANGA GASOLINE (NO. 3)

95~100°C	100~105°C	105~110°C	110~115°C	115~120°C	120~125°C
216 (3)	215 (5)	214 (56)	218 (56)	217 (86)	154 (0)
221 (1)	220 (0)	216 (0)	228 (00)	227 (00)	224 (1)
221 (00)			228 (00)	228 (00)	227 (00)
308 (2)	311 (0)	309 (0)	309 (00)	312 (00)	310 (00)
348 (0)	346 (0)	345 (1)	345 (0)	340 (0)	340 (00)
365 (00)			371 (00)	373 (00)	374 (00)
405 (3)	406 (1)	403 (1)	407 (00)	409 (0)	410 (06)
448 (8)	445 (1)	446 (1)	418 (00)	420 (1)	418 (4)
464 (0)		468 (1)			457 (06)
496 (0)	494 (00)	495 (00)	495 (00)	495 (0)	474 (00)
520 (5)	520 (8)	520 (4)	521 (4)	520 (8)	518 (1)
544 (2)	544 (1)	545 (1)	545 (0)	544 (1)	543 (4)
622 (1)	624 (1)	622 (26)	623 (5)	621 (16)	
722 (0)	731 (0)	728 (1)	728 (1)	728 (1)	705 (1)
752 (0)				748 (1)	748 (3)
768 (6)	767 (4)	767 (8)	768 (1)	760 (8)	759 (3)
784 (5)	785 (5)	785 (6)	785 (8)	789 (8)	789 (6)
800 (1)		809 (00)	809 (1)	811 (1)	808 (00)
844 (5)	843 (8)	845 (8)	845 (1)	848 (00)	849 (80)
890 (16)	896 (00)	896 (1)	896 (1)	875 (00)	876 (80)
937 (1)	936 (00)	938 (00)		935 (00)	934 (70)
974 (8)	975 (1)	974 (8)	975 (8)	961 (00)	964 (86)
991 (1)	988 (00)	991 (00)	998 (00)	975 (00)	980 (80)
1003 (0)	1003 (10)	1008 (10)	1003 (10)	1002 (10)	1008 (7)
1030 (0)	1031 (5)	1029 (8)	1029 (7)	1029 (6)	1028 (5)
1058 (1)	1066 (0)	1066 (0)	1066 (8)	1056 (8)	1057 (6)
1081 (84)	1083 (06)	1086 (06)	1083 (04)	1128 (06)	1129 (16)
1126 (14)		1154 (8)	1154 (8)	1154 (1)	
1157 (14)		1154 (8)	1154 (8)	1154 (1)	1157 (8)
1160 (8)	1164 (18)				
1179 (0)	1178 (0)	1180 (1)	1178 (8)	1178 (1)	
1193 (8)					
1211 (8)		1203 (3)	1208 (8)	1208 (6)	1208 (5)
1244 (8)	1245 (1)	1244 (8)		1248 (8)	1248 (8)
1245 (8)	1245 (1)	1244 (1)		1244 (8)	1244 (8)
1253 (8)	1253 (8)	1254 (8)	1245 (00)	1244 (8)	1244 (8)
1264 (8)	1264 (1)	1267 (8)	1268 (8)	1266 (8)	1266 (8)
1265 (8)	1270 (1)	1278 (8)	1265 (8)	1270 (8)	1270 (8)
1278 (8)		1278 (8)			
1403 (0)		1408 (1)	1299 (8)		
1434 (8)		1441 (8)	1440 (8)	1440 (8)	1440 (8)
1447 (8)		1440 (8)	1440 (8)	1440 (8)	1440 (8)
1466 (8)		1466 (8)	1466 (8)	1466 (8)	1466 (8)
1497 (8)	1497 (8)	1496 (8)	1496 (8)	1494 (8)	1494 (8)
1527 (8)					
2044 (100)		2049 (8)	2049 (8)	2049 (8)	2049 (8)
2071 (100)		2074 (8)	2074 (8)	2074 (8)	2074 (8)
(8)					
2091 (8)		2097 (8)	2095 (8)	2094 (8)	2094 (8)
2129 (8)		2106 (8)	2106 (8)	2104 (8)	2104 (8)
2145 (8)		2141 (8)	2141 (8)	2141 (8)	2141 (8)
2176 (10)		2176 (8)	2176 (8)	2176 (8)	2176 (8)
2209 (8)		2209 (8)	2209 (8)	2209 (8)	2209 (8)
2241 (8)		2241 (8)	2241 (8)	2241 (8)	2241 (8)
2261 (8)		2261 (8)	2261 (8)	2261 (8)	2261 (8)
2281 (8)		2281 (8)	2281 (8)	2281 (8)	2281 (8)
2301 (8)		2301 (8)	2301 (8)	2301 (8)	2301 (8)

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