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Aqueous Organic Chemistry. 1. Aquathermolysis: Comparison with Thermolysis in the Reactivity of Aliphatic Compounds

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The first report in this series describes a scoping study on a set of n-C_{10} aliphatic compounds with structures representative of those found in oil shale kerogens. 1-Decene underwent acid-catalyzed double bond isomerization and dimerization reactions, and 1-decyne was hydrated under aquathermolysis conditions. Acid-catalyzed aldol condensation reactions were observed for 1-decanal and 2-decanone, and the major products were α,β-unsaturated aldehydes and ketones. Decyl decanoate was four times more reactive with water than thermally at 250 °C and readily hydrolyzed to the corresponding carboxylic acid and alcohol. 1-Decanenitrile readily hydrated to 1-nonanecarboxamide, which then underwent further hydrolysis to 1-decanoic acid and ammonium hydroxide. The ammonium hydroxide will autocatalyze the hydrolysis of both the 1-decanenitrile and 1-decanamide. 1-Decylamine was converted thermally to the corresponding decanenitrile, and under aqueous conditions self-condensation took place to provide didecylamine and tridecylamine. The thermolysis of 1-decanethiol was found to be the source for hydrogen sulfide evolution during reaction to form dialkyl sulfides. In simulated maturation environments water can act as an amphoteric catalyst promoting ionic reaction pathways at high temperature for bonds that are not thermally labile. The presence of brine and clay facilitated the observed ionic chemistry and specific acid-catalyzed reactions. Reactivity is also facilitated by autocatalysis by water-soluble products.

Introduction

Transformations of organic compounds in aqueous environments are of significant interest and importance. Most of the world's fossil fuel resources have been naturally formed and modified under such conditions, but a detailed understanding of the formation and maturation pathways is still lacking. The potential economic incentives for the conversion and upgrading of fossil fuel resources by aqueous treatment rather than by conventional hydrogenation are enormous. Despite this scientific and economic importance, published work on the chemical reactions of organic molecules in aqueous environments is sparse and fragmentary. The investigations to be described in the present series of papers will cover reactions of aliphatic derivatives (part 1), molecules containing representative cross-links (part 2), and ethers and esters representative of those C–O cross-links found as components of coals and kerogens (part 3). A sister series of papers is concerned with aquathermolyses of benzenoid and heteroaromatic compounds.[1] In addition to water, experiments were also carried out in cyclohexane to differentiate thermal (radical) chemistry from aqueous (ionic) chemistry. Experiments in brine (10% NaCl) and clay-containing aqueous systems were run to simulate more closely the maturation environment and determine the effects of ionic strength and clay catalysis on reactivity.

A portion of petroleum seems to have been derived directly from biologically produced lipid precursors such as fats and waxes of their fatty acid derivatives[2-4] and from higher molecular weight precursors.[5-7]

It is generally believed that the immediate precursor for most of the naturally occurring liquid and gaseous hydrocarbons is kerogen, which is the predominant organic constituent of sedimentary rocks, such as shales.

Kerogen is a complex network of high molecular weight organic macromolecules, its precursors being largely algal and plant lipids that polymerize early in the diagenetic history of the sediment. Most of the deposited fatty acids and their derivatives that survived in the inorganic debris were quickly incorporated into the kerogen macromolecular network. The kerogen was in an aqueous environment as it was exposed to increasing temperature during burial. Progressive decarboxylation, dehydration, and carbon–carbon bond cleavage reactions occurred leading to the generation of alkane chains and fragments of polycyclic and heterocyclic nuclei. Many workers have postulated that a catalyst would have been required at these low temperatures to sufficiently lower the activation energies of these decomposition reactions.[8] The most obvious natural catalysts were the clay minerals of the matrix in which the kerogen was dispersed. With increasing depth and temperature, there was a loss of bituminous hydrocarbons, or petroleum. The petroleum formation (or liquid hydrocarbon) window was defined approximately by the temperature limits of 60–110 °C.[9]

The conversion of model compounds with clays to petroleum-like hydrocarbon mixtures has been carried out

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by a number of workers. Jurg and Eisma[10] reacted behenic acid (docosanoic acid) with bentonite clay in sealed tubes in the presence and absence of water at 200 °C for 89 and 760 h. They found significant hydrocarbon formation only in the presence of the clay catalyst. Without water, the ratio of n-butane to isobutane and pentane was much higher (ca. 40:1) than with water, indicating that water induced or provided conditions that favored carbocation chemistry. The proportion of saturated hydrocarbons was found to increase with time at the expense of unsaturated hydrocarbons, indicating that alkylations were taking place. Among the higher molecular weight hydrocarbons (C_{14}–C_{34}), there was a strong predominance of $C_{21}H_{44}$, the direct decarboxylation product of behenic acid.

Shimoyama and Johns[11] reacted behenic acid with calcium montmorillonite under anhydrous conditions at 200 and 250 °C for 50–500 h and obtained results similar to those of Jurg and Eisma.[10] In addition they found[12] that anhydrous calcium carbonate also promoted the degradation of the C_{19} and C_{22} fatty acids to alkanes at 250 °C. The most prominent product formed with $CaCO_3$ from the C_{22} acid was icosane resulting from the loss of a two-carbon unit. However, much of the consumed fatty acid was converted to a brown, insoluble, kerogen-like material. Henderson[13] showed that bentonite, in the presence of water at 375 °C, catalyzed the conversion (90%) of octacosane to an insoluble black carbonaceous material and small amounts of alkenes and aromatic hydrocarbons. In the absence of water, 1% of the octacosane was converted to other alkanes and aromatic hydrocarbons.

In 1979, Lewan et al.[14] pointed out that the rarity of olefins in natural crude oils as compared to the products of anhydrous pyrolysis or retorting of organic-rich shales indicated that these techniques do not duplicate the natural oil-generating processes.

Kaplan[15] reported that the presence of water during the 200–400 °C pyrolysis of Green River kerogen either enhanced the release of long-chain carboxylic acids (C_{10}–C_{32}) or reduced the rate of their thermal destruction. No correlation between the chain-length distribution of straight- or branched-chain carboxylic acids and their equivalent hydrocarbons in the kerogen pyrolyzates was observed. This suggested that decarboxylation was not an important mechanism for hydrocarbon generation during hydrous pyrolysis. However, carboxylic acids may have been subjected to decarboxylation once they were released into bitumen, especially in a clay-rich mineral matrix.

In order to understand the source of paraffins in petroleum crudes and the reactivity patterns of representative derivatized aliphatics, a systematic study was initiated on the following model compounds under aqueous conditions: 1-decene, 1-decyne, 1-decanal, 2-decanone, decyl decanoate, 1-decanenitrile, 1-decanol, 1-decylamine, 1-decanoic acid, methyl 1-nonyl sulfide, and 1-decyl methyl ether.

Experimental Section

Each of the 12 compounds was heated at 250 °C over 1.5–13.5 days in each of the following systems: (i) cyclohexane, (ii) water alone, (iii) water with calcium montmorillonite, (iv) 10% aqueous

Scheme I. General Pathways for Aquathermolysis Reactions of Aliphatic Compounds
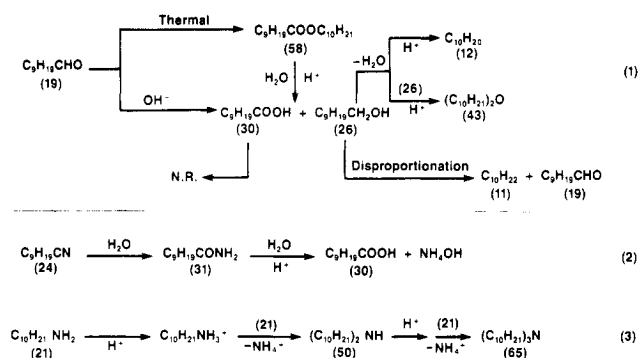
sodium chloride, and (v) 10% aqueous sodium chloride with calcium montmorillonite.

The starting material, decyl decanoate (58) was prepared in 99% purity following the literature procedure.[16] Other starting materials were commercially available and redistilled to achieve purities of >99%; see Table II.

General Procedure. The $C_{10}H_{21}X$ model compound (1.0 g, high purity) was charged into a glass-lined, 22-mL, 303SS Parr bomb. Deoxygenated water (7 mL, freshly prepared by bubbling nitrogen into distilled water for 1–1.5 h) was then charged into the nitrogen blanketed reactor vessel which was sealed using a Parr bomb screw-cap closure. The reactor was then kept nonagitated in a Techne fluidized sand bath (Model SBL-1) set at 250 °C for 1–13.5 days.

After the reaction period, the bomb was removed and allowed to cool to room temperature. It was then carefully opened under a nitrogen atmosphere. The entire mixture was transferred to a round-bottomed flask containing a Teflon stir bar. The walls of the glass liner and bomb cup were rinsed with 10 mL of diethyl ether which was added to the flask. The resulting mixture was stirred for 2 h, and the phases were allowed to separate. The organic layer was pipetted away from the aqueous layer and analyzed by gas chromatography (GC) and mass spectroscopy (MS).

The gas chromatographic behavior of all the compounds encountered in this work (starting materials and products) is summarized in Table I. Table IA records the source and mass spectral fragmentation patterns of the authentic compounds used, either as starting materials or for the identification of products. Tables IB and II record the mass spectra of the compounds for which samples were not available and which were identified by comparison with literature MS data (Table IB) or by deduction (Table II). Tables IA and IB along with a description of the mass spectral assignments of structures are available as supplementary material (see paragraph at end of paper regarding supplementary material).

Conversion Yields and Material Balance. All conversions and yields are given in terms of moles as a percentage of starting material. Internal standards were used to quantify conversion of the starting material, and the GC peak areas were corrected by response factors and then renormalized to omit material present in <0.1% concentration. Details on estimation of flame ionization detector (FID) response factors were discussed elsewhere.[17,18] The conversion of the areas to molar units was done by use of an equivalent weight factor (Table I). The experiments were duplicated and found to be reproducible within ±5%.

Results and Discussion

The major aquathermolytic pathways are summarized in Scheme I. These and other reactions are discussed in more detail below.

1-Decyl methyl ether and decanoic acid were unaf-

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Table I. Structure and Identification of Starting Materials and Products

no.	t_R, min	structure	mol wt	equiv wt	identification basis[a]	response factor
1	0.61	1-heptene	98	98	Table IA	0.96
2	0.69	1-octene	112	112	Table IA	0.96
3	0.73	2-octene	112	112	Table IB	0.96
4	0.99	1-nonene	126	126	Table IA	0.95
5	1.15	3-nonene	126	126	Table II	0.95
6	1.23	nonane	128	128	Table IA	0.95
7	1.25	4-nonene	126	126	Table IB	0.95
8	1.30	2-nonene	126	126	Table II	0.95
9	1.34	cyclohexanethiol	116	116	Table IB	0.72
10	1.90	2-decene	140	140	Table II	0.95
11	1.95	1-decene	140	140	Table IA	0.95
12	2.07	decane	142	142	Table IA	0.95
13	2.08	3-decene	140	140	Table II	0.95
14	2.10	4-decene	140	140	Table IB	0.95
15	2.15	5-decene	140	140	Table IB	0.95
16	2.25	1-decyne	138	138	Table IA	0.94
17	2.31	cyclohexyl methyl sulfide	130	130	Table IB	0.71
18	3.80	2-decanone	156	156	Table IA	0.78
19	4.10	1-decanal	156	156	Table IA	0.78
20	4.56	1-nonanethiol	160	160	Table IB	0.71
21	4.70	1-decylamine	157	157	Table IB	0.70
22	4.87	5-decanethiol	174	174	Table II	0.70
23	4.95	4-decanethiol	174	174	Table II	0.70
24	5.15	1-decanenitrile	153	153	Table IA	0.78
25	5.16	3-decanethiol	174	174	Table IB	0.70
26	5.20	1-decanol	158	158	Table IA	0.76
27	5.90	methyl 1-nonyl sulfide	174	174	Table IA	0.69
28	6.00	2-decanethiol	174	174	Table II	0.70
29	6.20	1-decanethiol	174	174	Table IA	0.70
30	7.00	1-decanoic acid	172	172	Table IA	0.32
31	8.88	1-nonanecarboxamide	171	171	Table IA	0.69
32	9.43	1-decenylcyclohexane	222	222	Table II	0.92
33	9.79	1-decylcyclohexene	222	222	Table IB	0.92
34	9.94	1-decylcyclohexane	224	224	Table IB	0.92
35	11.83	cyclohexyl 1-nonyl sulfide	242	242	Table II	0.67
36	12.45	9-nonadecene	266	133	Table II	0.90
37	12.89	(E)-$C_9H_{19}HC$=$C(CH_3)C_8H_{17}$	280	140	Table II	0.90
38	12.95	cyclohexyl 1-decyl sulfide	256	256	Table II	0.66
39	13.26	10-nonadecanol	284	142	Table II	0.72
40	13.38	cis-9-icosene	280	140	Table II	0.90
41	13.45	trans-9-icosene	280	140	Table IB	0.90
42	13.65	1,2'-dinonyl sulfide	286	143	Table II	0.65
43	14.14	1,1'-didecyl ether	298	149	Table IB	0.70
44	14.17	(Z)-$C_8H_{17}(CH_3)C$=$CHCOC_8H_{17}$	294	147	Table II	0.72
45	14.20	(Z)-$C_8H_{17}(CH_3)C$=$C(COCH_3)C_7H_{15}$	294	147	Table II	0.72
46	14.21	$C_9H_{19}CH(OH)CH(CHO)C_8H_{17}$	312	156	Table II	0.34
47	14.36	(E)-$C_8H_{17}(CH_3)C$=$C(COCH_3)C_7H_{15}$	294	147	Table II	0.72
48	14.50	(Z)-$C_9H_{19}CH$=$C(CHO)C_8H_{17}$	294	147	Table II	0.52
49	14.50	1,1'-dinonyl sulfide	286	143	Table IA	0.65
50	14.51	N,N'-didecylamine	297	148.5	Table II	0.65
51	14.87	4,4'-didecyl sulfide	314	157	Table II	0.64
52	14.90	(E)-$C_8H_{17}(CH_3)C$=$CHCOC_8H_{17}$	294	147	Table II	0.72
53	14.93	3,3'-didecyl sulfide	314	157	Table II	0.64
54	15.00	1,4'-didecyl sulfide	314	157	Table II	0.64
55	15.07	1,3'-didecyl sulfide	314	157	Table II	0.64
56	15.10	(E)-$C_9H_{19}CH$=$C(CHO)C_8H_{17}$	294	147	Table II	0.52
57	15.12	2,2'-didecyl sulfide	314	157	Table II	0.64
58	15.20	decyl decanoate	312	312	Table IA	0.55
59	15.27	1,2'-didecyl sulfide	314	157	Table II	0.64
60	15.56	1,1'-didecyl sulfide	314	157	Table II	0.64
61	17.16	1,3'-didecyl disulfide	346	173	Table II	0.38
62	17.43	1,2'-didecyl disulfide	346	173	Table II	0.38
63	18.05	1,1'-didecyl disulfide	346	173	Table IA	0.38
64	18.10	9-cyclohexylicosane	364	182	Table IB	0.85
65	20.00	N,N',N''-tridecylamine	437	145.7	Table II	0.60
66	20.59	1,4-dioctylbenzene	302	151	Table II	0.88
67	20.81	2,4-dioctyltoluene	316	158	Table II	0.88

[a] Tables IA and IB are in the supplementary material.

fected at 250 °C under both aqueous and thermal conditions for up to 13.5 days. The latter was unexpected based on previous reports.[10,11]

1-Decene (11) (Table III). At 250 °C, 1-decene (11) showed similar reactivity in cyclohexane (6.1% conversion), water (8.4% conversion), and 10% aqueous brine (10.8%

conversion). Under all these conditions, it underwent double bond migration to give 2- (10), 3- (13), 4- (14), and 5-decene (15). In addition to these products appreciable amounts of (E)-10- (37), cis-9- (40), and trans-9-icosene (41) were also formed via dimerization of 1-decene (11). In the presence of calcium montmorillonite, the isomeri-

Table II. Identification of Products from Mass Spectral Fragmentation Pattern

no.	compound	MW	fragmentation pattern m/z (% relative intensity, structure of fragment ion)
5	3-nonene	126	126 (5, M); 97 (60, M – C_2H_5); 83 (80, M – C_3H_7); 70 (50, M – C_4H_8); 69 (90, C_5H_9); 57 (40, M – C_5H_9); 56 (80, C_4H_8); 55 (100, M – C_5H_{11}); 43 (80, M – C_6H_{11}); 42 (35, C_3H_6); 41 (35, C_3H_5); 40 (60, C_3H_4)
8	2-nonene	126	126 (10, M); 97 (10, M – C_2H_5); 85 (60, M – C_3H_5); 71 (90, M – C_4H_7); 69 (25, C_5H_9); 58 (20, C_4H_{10}); 57 (100, M – C_5H_9); 43 (20, M – C_6H_{11})
10	2-decene	140	140 (15, M); 111 (25, M – C_2H_5); 97 (35, M – C_3H_7); 83 (35, M – C_4H_9); 69 (60, M – C_5H_{11}); 55 (100, M – C_6H_{13}); 41 (95, M – C_7H_{15})
13	3-decene	140	140 (20, M); 111 (5, M – C_2H_5); 97 (15, M – C_3H_7); 69 (50, C_5H_9); 55 (100, M – C_6H_{13}); 41 (95, M – C_7H_{15})
22	5-decanethiol	174	174 (5, M); 141 (15, M – SH); 140 (20, M – H_2S); 111 (25, C_8H_{15}); 97 (40, C_7H_{13}); 85 (30, C_6H_{13}); 71 (25, M – SC_5H_{11}); 70 (30, C_5H_{10}); 69 (30, C_5H_9); 57 (40, M – SC_6H_{13}); 56 (20, C_4H_8); 55 (80, C_4H_7); 47 (20, CH_2S); 43 (60, C_3H_7); 41 (100, C_3H_5)
23	4-decanethiol	174	174 (20, M); 173 (30, M – H); 141 (55, M – SH); 140 (15, M – H_2S); 115 (15); 97 (30, C_7H_{13}); 85 (60, C_6H_{13}); 83 (35, C_6H_{11}); 71 (40, M – SC_5H_{11}); 70 (50, C_5H_{10}); 69 (40, C_5H_9); 57 (50, M – SC_6H_{13}); 55 (40, C_4H_7); 43 (40, C_3H_7); 41 (100, C_3H_5)
28	2-decanethiol	174	174 (15, M); 140 (5, M – H_2S); 111 (10, C_8H_{15}); 97 (10, C_7H_{13}); 83 (30, C_6H_{11}); 70 (35, M – SC_5H_{12}); 69 (40, C_5H_9); 55 (70, C_4H_7); 41 (100, C_3H_5)
32	1-decenylcyclohexane	222	222 (20, M); 96 (35, C_7H_{12}); 83 (45, C_6H_{11}); 82 (30, M – $C_{10}H_{20}$); 81 (50, C_6H_9); 69 (30, M – $C_{11}H_{31}$); 67 (50, C_5H_7); 55 (100, C_4H_7); 41 (85, C_3H_5)
35	cyclohexyl 1-nonyl sulfide	242	242 (35, M); 159 (60, M – C_6H_{11}); 115 (15, M – C_9H_{19}); 55 (95, C_4H_7); 41 (100, C_3H_5)
36	9-nonadecene	266	266 (10, M); 125 (10, M – $C_{10}H_{21}$); 111 (15, C_8H_{15}); 97 (40, C_7H_{13}); 83 (40, C_6H_{11}); 69 (40, C_5H_9); 55 (65, C_4H_7); 43 (60, C_3H_7); 41 (100, C_3H_5)
37	(E)-$C_9H_{19}HC$=$C(CH_3)C_8H_{17}$	280	280 (5, M); 166 (5, M – C_8H_{18}); 154 (5, M – C_9H_{18}); 139 (15); 111 (30); 97 (35); 83 (30); 71 (25, C_5H_{11}); 57 (60, C_4H_9); 55 (45, C_4H_7); 43 (65, C_3H_7); 41 (100, C_3H_5)
38	cyclohexyl 1-decyl sulfide	256	256 (25, M); 173 (80, M – C_6H_{11}); 129 (15); 83 (30, M – $SC_{10}H_{21}$); 82 (30, C_6H_{10}); 81 (15, C_6H_9); 67 (60, C_5H_7); 55 (100, C_4H_7); 43 (25, C_3H_7); 41 (95, C_3H_5)
39	10-nonadecanol	284	284 (5, M); 283 (40, M – H); 155 (75, 283 – C_9H_{20}); 95 (25); 85 (15, C_6H_{13}); 81 (30); 71 (30, C_5H_{11}); 58 (35, C_4H_{10}); 57 (35, C_4H_9); 55 (40, C_4H_7); 43 (90); 41 (100, C_3H_5)
40	cis-9-icosene	280	280 (10, M); 138 (5, M – $C_{10}H_{22}$); 125 (10, C_9H_{17}); 111 (25, C_8H_{15}); 97 (40, C_7H_{13}); 83 (35, C_6H_{13}); 69 (40, M – $C_{15}H_{31}$); 67 (25); 57 (40, C_4H_9); 55 (55, C_4H_7); 43 (60, C_3H_7); 41 (100, C_3H_5)
42	1,2'-dinonyl sulfide	286	286 (20, M); 187 (30, M – C_7H_{15}); 159 (65, M – C_9H_{19}); 106 (40); 83 (25, C_6H_{11}); 69 (35); 55 (45, C_4H_7); 43 (60, C_3H_7); 41 (100, C_3H_5)
44	(Z)-$C_8H_{17}(CH_3)C$=$CHCOC_8H_{17}$	294	294 (15, M); 181 (5, M – C_8H_{17}); 141 (90, $^+COC_8H_{17}$); 123 (20); 82 (35); 71 (50); 67 (35); 57 (75, C_4H_9); 55 (45, C_4H_7); 43 (65, C_3H_7); 41 (100, C_3H_5)
45	(Z)-$C_8H_{17}(CH_3)C$=$C(COCH_3)C_7H_{15}$	294	294 (20, M); 181 (90, M – C_8H_{17}); 141 (30); 98 (20); 81 (25); 69 (35, M – $C_{15}H_{29}O$); 68 (25, C_5H_8); 56 (35); 55 (50, C_4H_7); 42 (60); 41 (100, C_3H_5)
46	$C_9H_{19}CH(OH)CH(CHO)C_8H_{17}$	312	312 (M$^{•+}$, not seen); 295 (10, M – OH); 155 (5, $^+COC_9H_{19}$); 125 (10, C_9H_{17}); 111 (15, C_8H_{15}); 97 (35, C_7H_{13}); 83 (35, C_6H_{11}); 69 (30, C_5H_9); 57 (40, C_4H_9); 55 (55, C_4H_7); 41 (100, C_3H_5)
47	(E)-$C_8H_{17}(CH_3)C$=$C(COCH_3)C_7H_{15}$	294	294 (5, M); 181 (100, M – C_8H_{17}); 98 (50, C_7H_{14}); 83 (25, C_6H_{11}); 69 (50, M – $C_{15}H_{29}O$); 55 (50, C_4H_7); 43 (40, C_3H_7); 41 (90, C_3H_5)
48	(Z)-$C_9H_{19}CH$=$C(CHO)C_8H_{17}$	294	294 (10, M); 195 (10, M – C_7H_{15}); 182 (10, M – C_8H_{16}); 155 (10); 97 (30, C_7H_{13}); 83 (30, C_6H_{11}); 69 (35, C_5H_9); 57 (30, C_4H_9); 55 (40, C_4H_7); 41 (100, C_3H_5)
50	N,N'-didecylamine	297	297 (5, M); 170 (70, M – C_9H_{19}); 55 (15, C_4H_7); 44 (100, Me(H)N$^+$=CH_2); 43 (25); 41 (35, C_3H_5)
51	4,4'-didecyl sulfide	314	314 (15, M); 257 (95, M – C_4H_9); 243 (60); 173 (35, M – $C_{10}H_{21}$); 83 (37, C_6H_{11}); 69 (30, C_5H_9); 57 (35, C_4H_9); 55 (45, C_4H_7); 43 (75); 41 (100, C_3H_5)
52	(E)-$C_8H_{17}(CH_3)C$=$CHCOC_8H_{17}$	294	294 (25, M); 181 (5, M – C_8H_{17}); 141 (90, $^+COC_8H_{17}$); 81 (35); 71 (60, C_5H_{11}); 67 (25, C_5H_7); 57 (80, C_4H_9); 55 (45, C_4H_7); 43 (65, C_3H_7); 41 (100, C_3H_5)
53	3,3'-didecyl sulfide	314	314 (35, M); 271 (80, M – C_3H_7); 173 (40, M – $C_{10}H_{21}$); 55 (60, C_4H_7); 43 (70, C_3H_7); 41 (100, C_3H_5)
54	1,4'-didecyl sulfide	314	314 (10, M); 257 (15, M – C_4H_9); 201 (10); 173 (40, M – $C_{10}H_{21}$); 83 (20, C_6H_{11}); 69 (30, C_5H_9); 58 (25, C_4H_{10}); 55 (45, C_4H_7); 43 (55); 41 (100, C_3H_5)
55	1,3'-didecyl sulfide	314	314 (25, M); 271 (85, M – C_3H_7); 173 (40, M – $C_{10}H_{21}$); 98 (15, C_7H_{14}); 83 (20, C_6H_{11}); 69 (30, C_5H_9); 57 (35, C_4H_9); 55 (60, C_4H_7); 43 (65, C_3H_7); 41 (100, C_3H_5)
56	(E)-$C_9H_{19}CH$=$C(CHO)C_8H_{17}$	294	295 (100, M + 1); 294 (45, M); 293 (10, M – H); 181 (15, M – C_8H_{17}); 167 (15); 137 (10); 95 (25); 81 (35); 55 (30, C_4H_7); 43 (50, C_3H_7); 41 (75, C_3H_5)
57	2,2'-didecyl sulfide	314	314 (15, M); 285 (60, M – C_2H_5); 215 (35); 173 (30, M – $C_{10}H_{21}$); 83 (25, C_6H_{11}); 69 (30, C_5H_9); 57 (35, C_4H_9); 55 (45, C_4H_7); 43 (75, C_3H_7); 41 (100, C_3H_5)
59	1,2'-didecyl sulfide	314	314 (10, M); 285 (30, M – C_2H_5); 201 (30); 173 (70, M – $C_{10}H_{21}$); 97 (10, C_7H_{13}); 83 (20, C_6H_{11}); 69 (25); 57 (30, C_4H_9); 55 (50, C_4H_7); 43 (65, C_3H_7); 41 (100, C_3H_5)
60	1,1'-didecyl sulfide	314	314 (30, M); 173 (100, M – $C_{10}H_{21}$); 97 (15, C_7H_{13}); 83 (30, C_6H_{11}); 69 (20, C_5H_9); 55 (50, C_4H_9); 41 (90, C_3H_5)
61	1,3'-didecyl disulfide	346	346 (35, M); 206 (85, M – $C_{10}H_{20}$); 173 (60, M – $SC_{10}H_{21}$); 85 (30, C_6H_{13}); 71 (30, C_5H_{11}); 57 (70, C_4H_7); 56 (40, C_4H_8); 42 (80, C_3H_6); 41 (100, C_3H_5)
62	1,2'-didecyl disulfide	346	346 (100, M); 206 (15, M – $C_{10}H_{20}$); 173 (40, M – $SC_{10}H_{21}$); 85 (30); 71 (30); 57 (60, C_4H_7); 56 (45); 42 (70); 41 (95, C_3H_5)
65	N,N',N''-tridecylamine	437	437 (5, M); 311 (10, M – C_9H_{18}); 308 (35); 196 (15); 170 (50, 311 – $C_{10}H_{21}$); 44 (100, MeHN$^+$=CH_2); 41 (80, C_3H_5)
66	1,4-dioctylbenzene	302	302 (50, M); 204 (45, M – C_7H_{14}); 105 (100, $C_8H_9^+$); 92 (35, $PhCH_3$); 91 (40, $PhCH_2$); 57 (20, C_4H_7); 43 (45, C_3H_7); 41 (85, C_3H_5)
67	2,4-dioctyltoluene	316	316 (90, M); 290 (15); 218 (25, M – C_7H_{14}); 119 (70, 218 – C_7H_{14}); 105 (50, $C_8H_9^+$); 91 (15); 57 (40, C_4H_9); 43 (85, C_3H_7); 41 (100, C_3H_5)

zation and to a lesser extent the dimerization reactions were enhanced. Conversion and extent of double bond isomerization increased with ionic strength and acidity of the system.

Table III. Products of 1-Decene Reactions at 250 °C for 5.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
10	2-decene	1.8	3.0	10.8	4.4	21.0
11	1-decene	93.9	91.6	79.2	89.2	63.1
13	3-decene	0.6	0.6	0.4	0.5	1.0
14	4-decene	0.2	0.3	3.0	1.7	11.5
15	5-decene	0.1	0.1	0.2	0.1	0.1
34	1-decylcyclohexane	1.3				
37	(E)-$C_9H_{19}CH{=}C(CH_3)C_8H_{17}$	0.3	1.8	2.2	1.7	1.6
40	cis-9-icosene	0.2	0.7	1.0	0.5	0.5
41	trans-9-icosene	0.7	1.9	3.1	1.9	1.2
64	9-cyclohexylicosane	0.8				

Table IV. Products of 1-Decyne Reactions at 250 °C for 2.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
1	1-heptene	1.3				
2	1-octene	4.6	0.7	0.6	0.6	0.2
3	2-octene	5.6		0.4	0.3	
4	1-nonene	5.7		0.6	0.2	
6	nonane	0.8		0.3		
10	2-decene	6.3	1.7	1.6	1.6	1.5
11	1-decene	11.8	2.7	5.6	2.4	1.7
16	1-decyne	27.8	92.8	80.4	87.0	73.3
18	2-decanone		2.0	10.4	7.9	23.1
32	1-decenylcyclohexane	2.3				
33	1-decylcyclohexene	5.6				
66	1,4-dioctylbenzene	23.2				
67	2,4-dioctyltoluene	5.0				

Table V. Products of 1-Decanal Reactions at 250 °C for 1.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
6	nonane	4.8	2.0	2.4	2.7	1.3
19	1-decanal	50.0	8.2	5.8	5.9	4.3
26	1-decanol	1.0	2.9	2.9	2.1	3.2
30	1-decanoic acid	2.7	4.4	12.8	12.5	14.9
36	9-nonadecene	0.3	1.0	1.3	1.2	1.1
39	10-nonadecanol	0.3	0.5	0.6	0.5	0.8
46	$C_9H_{19}CH(OH)CH(CHO)C_8H_{17}$	0.7	4.0	6.1	6.0	4.3
48	(Z)-$C_9H_{19}CH{=}C(CHO)C_8H_{17}$	2.0	5.6	4.2	4.1	3.0
56	(E)-$C_9H_9CH{=}C(CHO)C_8H_{17}$	29.9	64.6	58.0	58.2	61.3
58	decyl decanoate	8.3	6.8	5.9	6.8	5.8

1-Decylcyclohexane (34) (1.3%) and 9-cyclohexylicosane (64) (0.8%) were also formed in the cyclohexane run, presumably via thermal alkylation of the corresponding olefins by solvent.

1-Decyne (16) (Table IV). At 250 °C, for 2.5 days, 1-decyne (16) reacted much faster in cyclohexane (72.2% conversion) than in water (7.2% conversion) or in 10% aqueous brine (13.0% conversion). Thermolysis in cyclohexane yielded 1-heptene (1) (1.3%), 1-octene (2) (4.6%), 2-octene (3) (5.6%), 1-nonene (4) (5.7%), 2-decene (10) (6.3%), 1-decene (11) (11.8%), 1-decenylcyclohexane (32) (2.3%), 1-decylcyclohexene (33) (5.6%), 1,4-dioctylbenzene (66) (23.2%), and 2,4-dioctyltoluene (67) (5.0%) as major products. Only one isomer of the last two products was present, and each was assigned the structure of the least hindered isomer.

Formation of lower alkenes (heptene and octenes) indicated the possible elimination of acetylene and methylacetylene from 1-decyne (16), and these are the possible sources for the formation of 1,4-dioctylbenzene (66) (from acetylene and two molecules of 1-decyne) and 2,4-dioctyltoluene (67) (from methylacetylene and 1-decyne) via thermal cyclization. In the aqueous systems 1-decyne (16) underwent hydration to give 2-decanone (18) as the major product. The ionic hydration reaction was facilitated in

brine and especially in the more acidic clay systems.

1-Decanal (19) (Table V). 1-Decanal (19) reacted much faster under all the aquathermolysis conditions used (81–95% conversion) than in the cyclohexane run (50% conversion). The major products under all these conditions were nonane (6), 1-decanol (26), 1-decanoic acid (30), the aldol (46), α,β-unsaturated aldehydes (48 and 56), and decyl decanoate (58).

The aldol condensation can be acid or base catalyzed, and evidence for catalysis under aqueous conditions is clear. Under all thermolysis and aquathermolysis conditions, small amounts of aldol adduct (46) underwent decarbonylation to give 10-nonadecanol (39). 9-Nonadecene (36) was obtained by dehydration of 9-nonadecanol (39).

Under all conditions, more 1-decanoic acid (30) than 1-decanol (26) was produced, especially in the presence of calcium montmorillonite. A portion of the 1-decanoic acid (30) must be formed by direct oxidation of the 1-decanol (19) although some 1-decanoic acid and decanol may result from a Cannizzaro reaction as well as from hydrolysis of decyl decanoate (58). Decarbonylation of the 1-decanol (19) yielded an appreciable amount of nonane (6).

2-Decanone (18) (Table VI). Both thermolysis and aquathermolysis of 2-decanone at 250 °C for 5.5 days showed <2.0% conversion. Under all conditions, the four

Table VI. Products of 2-Decanone Reactions at 250 °C for 5.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca-mont	10% NaCl	10% NaCl Ca-mont
18	2-decanone	98.0	99.3	99.1	98.7	98.6
44	(Z)-$C_8H_{17}(CH_3)C{=}CHCOC_8H_{17}$	0.1	0.1	0.1	0.1	0.1
45	(Z)-$C_8H_{17}(CH_3)C{=}C(COCH_3)C_7H_{15}$	0.5	0.1	0.1	0.2	0.3
47	(E)-$C_8H_{17}(CH_3)C{=}C(COCH_3)C_7H_{15}$	0.5	0.3	0.3	0.6	0.3
52	(E)-$C_8H_{17}(CH_3)C{=}CHCOC_8H_{17}$	0.9	0.2	0.2	0.4	0.7

Table VII. Products of Decyl Decanoate Reactions at 250 °C for 1.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O
10	2-decene	1.7	5.6
11	1-decene	3.3	11.4
13	3-decene	1.7	4.5
14	4-decene	1.7	2.6
26	1-decanol	0.6	7.6
30	1-decanoic acid	11.8	46.8
43	1,1'-didecyl ether	3.3	2.3
58	decyl decanoate	75.9	19.2

possible isomeric α,β-unsaturated ketones (**44, 45, 47,** and **52**) were formed via aldol condensations and elimination. Aqueous conditions and the presence of calcium montmorillonite had no catalytic effect.

Decyl Decanoate (58) (Table VII). Thermolysis in cyclohexane for 1.5 days at 250 °C showed 24.1% conversion, and the major products were the decenes (**10, 11, 13,** and **14**) (8.4%), 1-decanoic acid (**30**) (11.8%), and 1-decanol (**26**) (0.6%). Some autocatalysis by water formed in the dehydration of decanol is suggested.

Aquathermolysis of decyl decanoate showed 80.8% conversion, and all the foregoing products were found in much increased quantities. Both thermolysis and aquathermolysis of decyl decanoate yielded an appreciable amount of didecyl ether (**43**) (via dehydration of 1-decanol). Decarboxylation of 1-decanoic acid (**30**) was not observed.

1-Decanenitrile (24) (Table VIII). At 250 °C, 1-decanenitrile (**24**) did not react thermally in cyclohexane, but it showed almost 99% conversion under all sets of aquathermolysis conditions. The major products were 1-decanoic acid (**30**) and 1-nonanecarboxamide (**31**).

1-Decanenitrile (**24**) underwent hydration to 1-nonanecarboxamide (**31**), which subsequently hydrolyzed to 1-decanoic acid (**30**). The ionic hydrolysis reaction was catalyzed by brine and in the presence of Ca–montmorillonite.

1-Decanol (26) (Table IX). 1-Decanol showed very little reaction at 250 °C, under all sets of conditions, but small amounts of nonane (**6**) and 1-decene (**11**) were formed. A very small amount of 1-decanal (**19**) and decane (**12**) was also formed via disproportionation. The alcohol alone was less reactive than suggested in the decanal (**19**) or decyl decanoate (**58**) systems.

1-Decylamine (21) (Table X). At 250 °C, a small amount of 1-decanenitrile (**24**) was formed in the cyclohexane run via thermal dehydrogenation. In water and 10% aqueous brine, 1-decylamine showed 8.2% conversion and the products were N,N'-di- (**50**) and N,N',N''-tridecylamine (**65**). In the presence of Ca-montmorillonite, the acid-catalyzed condensation reaction via decylammonium ion was very much accelerated. The ionic pathway was facilitated in 10% aqueous brine/Ca–montmorillonite (82.6% conversion).

Methyl 1-Nonyl Sulfide (27) (Table XI). Methyl 1-nonyl sulfide (**27**) showed very low reactivity (6–16%)

under aqueous conditions but was thermally more reactive (56.6% conversion) where major products were nonane (11.6%) and 1,1'-dinonyl sulfide (29.9%). There was no significant change in the reaction pathway observed at 250 °C, under all four sets of aquathermolysis conditions, and the only major product was 1,1'-dinonyl sulfide (**49**). An appreciable amount of nonane (**6**) and small amounts of 1-octene (**2**), 1-nonene (**4**), 2-nonene (**8**), and 3-nonene (**5**) were also formed thermally under all sets of conditions.

1-Decanethiol (29) (Table XII). At 250 °C, 1-decanethiol (**29**) reacted much faster in cyclohexane (66.5% conversion) than in neutral water (35.3% conversion). The major products from the cyclohexane run were decane (**12**) (8.8%), 1-decene (**11**) (4.7%), 2-decene (**10**) (2.7%), 2-decanethiol (**28**) (10.3%), 1,1'-didecyl sulfide (**60**) (9.9%), 1,2'-didecyl sulfide (**59**) (6.5%), 1,3'-didecyl sulfide (**55**) (4.1%), and 1,1'-didecyl disulfide (**63**) (3.9%). For the water run, the major products were decane (**12**) (3.6%) and 1,1'- (**60**) (13.9%) and 1,2'-didecyl sulfide (**59**) (9.9%). With Ca–montmorillonite there was no significant change in the reactivity observed (38–40% conversion), and once again the major products were decane (**12**), 1,1'-didecyl sulfide (**60**), and 1,1'-didecyl disulfide (**63**).

The various products obtained from 1-decanethiol (**29**) are explained as follows.

(i) 1-Decanethiol (**29**) was the source for the formation of 2- (**28**), 3- (**25**), 4- (**23**), and 5-decanethiol (**22**) via elimination addition of H_2S (Willgerodt type reaction).[19] 1- (**11**), 2- (**10**), and 3-Decene (**13**) were formed through loss of H_2S from the corresponding decanethiols **29, 28,** and **25,** respectively. Addition of 1-decanethiol (**29**) to 1-decene (**11**) gave 1,1'-didecyl sulfide (**60**).

(ii) Attack of 1-decanethiol (**29**) on 1- (**11**), 2- (**10**), 3- (**13**), and 4-decene (**14**) yielded 1,1'- (**60**), 1,2'- (**59**), 1,3'- (**55**), and 1,4'-didecyl sulfide (**54**), respectively. Similarly, addition of 2- (**28**), 3- (**25**), and 4-decanethiol (**23**) over 2- (**10**), 3- (**13**), and 4-decene (**14**) furnished 2,2'- (**57**), 3,3'- (**53**), and 4,4'-didecyl sulfide (**51**), respectively.

Conclusions

Reactions on a set of C-10 aliphatic compounds with structures representative of those found in oil shale kerogens showed that in simulated maturation environments *water acts as an amphoteric catalyst promoting ionic reactions at high temperature.* Classical acid- and base-catalyzed organic reactions take place in liquid water at high temperature and pressure over long periods of time. The observed reactivities of different functional groups parallel their abundance in oil shale kerogens, with the least reactive being most abundant (i.e., ethers and carboxylic acids).[21] The presence of brine and clay facilitated the observed ionic chemistry and specific acid-catalyzed reactions. Aliphatic olefins underwent acid-catalyzed double bond isomerization and dimerization reactions, and alkynes were hydrated under aquathermolytic conditions. These reactions were facilitated in brine and clay environments. *Aliphatic aldehydes and ketones underwent*

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Table VIII. Products of Decanenitrile Reactions at 250 °C for 2.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
24	1-decanenitrile	100	0.6	0.8	0.5	
30	1-decanoic acid		26.0	38.0	37.5	58.8
31	1-nonanecarboxamide		73.4	61.2	62.0	41.2

Table IX. Products of 1-Decanol Reactions at 250 °C for 13.0 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
6	nonane	0.2	0.3	0.1	0.2	0.2
11	1-decene		0.1	0.3	0.1	0.3
12	decane	0.2	0.2	0.3	0.3	0.4
19	1-decanal	0.1	0.2	0.4	0.2	0.3
26	1-decanol	99.5	99.2	98.9	99.2	98.8

aldol condensations, which can be acid catalyzed, forming dimeric products. Similarly, aliphatic amines underwent acid-catalyzed condensation reactions in water. The hydrolysis reactions of thermally unreactive nitriles, amides, and esters under aquathermolytic conditions were catalyzed in the presence of acidic clays and can be autocatalyzed by soluble hydrolysis products (e.g., ammonium hydroxide, acetic acid) even in pure water systems. In all cases, the aqueous ionic chemistry was distinguishable from purely thermal pathways observed in parallel control re-

Table X. Products of 1-Decylamine Reactions at 250 °C for 5.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
21	1-decylamine	99.6	91.8	61.2	91.8	17.4
24	1-decanenitrile	0.4				
50	N,N'-didecylamine		4.7	32.8	4.4	68.7
65	N,N',N''-tridecylamine		3.5	6.0	3.8	13.9

Table XI. Products of Methyl 1-Nonyl Sulfide Reactions at 250 °C for 13.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
2	1-octene	1.5	0.2	0.2	0.2	0.3
4	1-nonene	4.1	0.2	0.3	0.4	0.6
5	3-nonene	0.7	0.3	0.3	0.3	0.2
6	nonane	11.6	0.9	0.9	0.5	1.0
7	4-nonene	0.2				
8	2-nonene	0.9	0.4	0.1	0.2	0.2
17	cyclohexyl methyl sulfide	0.2				
20	1-nonanethiol	6.7				
27	methyl 1-nonyl sulfide	43.4	83.4	91.7	93.4	93.7
35	cyclohexyl 1-nonyl sulfide	0.2				
42	1,2'-dinonyl sulfide	0.6				
49	1,1'-dinonyl sulfide	29.9	14.6	6.5	5.0	4.0

Table XII. Products of 1-Decanethiol Reactions at 250 °C for 13.5 days

no.	solvent additive (1 mol equiv) structure	C_6H_{12}	H_2O	H_2O Ca–mont	10% NaCl	10% NaCl Ca–mont
6	nonane	1.1	2.0	4.0	4.2	3.7
9	cyclohexanethiol	0.5				
10	2-decene	2.7		0.2	0.4	0.5
11	1-decene	4.7	0.1	0.7	1.2	0.3
12	decane	8.8	3.6	5.1	6.2	6.7
13	3-decene	1.5			0.1	0.1
22	5-decanethiol	0.7				
23	4-decanethiol	1.5				
25	3-decanethiol	1.6		0.5	0.5	0.6
26	1-decanol			0.2	0.4	0.5
28	2-decanethiol	10.3	1.2	2.4	2.7	2.8
29	1-decanethiol	33.5	64.7	60.9	60.5	61.5
38	cyclohexyl 1-decyl sulfide	0.3				
51	4,4'-didecyl sulfide	0.2				
53	3,3'-didecyl sulfide	0.2		1.0	0.2	0.6
54	1,4'-didecyl sulfide	2.3	0.9			
55	1,3'-didecyl sulfide	4.1	2.3	0.7	0.8	1.0
57	2,2'-didecyl sulfide	2.0	0.6	2.4	1.0	2.1
59	1,2'-didecyl sulfide	6.5	9.9	7.9	2.5	2.3
60	1,1'-didecyl sulfide	9.9	13.9	11.7	10.2	10.5
61	1,3'-didecyl disulfide	1.4			0.1	0.2
62	1,2'-didecyl disulfide	2.3	0.1	0.8	0.7	0.9
63	1,1'-didecyl disulfide	3.9	0.7	1.5	8.3	5.7

actions carried out in anhydrous cyclohexane. Alkanes, alkyl ethers, alcohols, and sulfides were essentially unreactive under the aqueous conditions at 250 °C, but mercaptans reacted slowly to form sulfides with the evolution of hydrogen sulfide.[20]

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Supplementary Material Available: Text describing mass spectral assignments, Tables IA and IB listing properties (IA) and mass spectral fragmentation patterns (IA and IB), of compounds in this paper (11 pages). Ordering information is given on any current masthead page.