Organic Process Research & Development **2002**, *6*, 394−400

Lecture Transcripts

Catalytic Oxidation of Acenaphthene and Its Derivatives in Acetic Acid

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Abstract:

The chemistry of formation of products of acenaphthene oxidation in the presence of the catalyst containing both manganese and cobalt bromides under batch conditions is discussed. The main reaction products are acenaphthene quinone, acenaphthenol-9, *trans*-acenaphthylene glycol, naphthalide, and naphthalic anhydride. The sequence of reactions leading to the final products is established. It is shown that the main oxidation product in the presence of the manganese-based catalyst is naphthalic anhydride, and the main product in the presence of the cobalt-based catalyst is acenaphthene quinone. The process and engineering techniques providing for the high overall and fractional yields of the desired products are discussed.

Introduction

Liquid-phase air or oxygen oxidation of alkyl-substituted aromatic hydrocarbons in the presence of a catalytic system containing both cobalt and manganese salts and bromide anion is a well-established method in organic process industries for the production of various chemicals. As a general rule, the kinetics and mechanisms of industrially important reactions are subjected to a thorough investigation. Then a generally accepted reaction concept is formed on the basis of these studies. Such a concept allows predicting the influence of different factors on a reaction course and product composition. On our opinion, the above-mentioned oxidation reactions constitute an exception from this usual practice. A lot of journal and patent publications including comprehensive Partenheimer review[1] are devoted to the topic. According to the opinion of the immense majority of investigators the reaction proceeds by the radical-chain mechanism, where the catalytic species (transient metal ion in its highest or lowest oxidation state) participate in the initiation step and catalyse hydroperoxide decomposition to radicals, thus causing degenerate chain branching. The chain termination occurs either by the quadratic recombination of peroxide radicals or linearly on the metal ion. The interaction of peroxyl ($ROO^{\bullet}$) or peracyl ($R'C(O)OO^{\bullet}$) radicals with the starting hydrocarbon or reaction intermediates provides for the chain propagation. At first glance this scheme seems sensible and self-consistent; however, it contradicts some of the experimental findings. Should it be true, then the fractional yield of different oxidation products would be independent of the nature of the catalyst metal ion, as the products would rather be formed in the chain propagation steps without the catalyst participation. Nevertheless, it is noted in ref 1, p 118, that in the ethyl benzene oxidation in acetic acid in the presence of Co bromide catalyst mainly acetophenone is formed, and in the presence of Mn bromide catalyst the main product is benzoic acid. We have found also that the oxidation of acenaphthene and its derivatives in aliphatic acids in the presence of Co−Br catalyst leads to acenaphthene quinone, and in the presence of Mn−Br catalyst the main product is naphthalic anhydride.[2,3] These findings can be rationalised if one assumes that the oxidation chain length is close to unity and that the product composition is determined in the interaction of a metal ion with a substrate. In this case the metal ion is a true catalyst participating in a nearly every act of the product formation and not just the initiator of a radical generation. This conclusion is further confirmed by the fact that in the oxidation of toluene in the presence of transient metal ions the rates of initiation and product accumulation are practically equal.[4]

In our opinion the concept of the nonchain mechanism of acenaphthene oxidation is more to the point than that of the radical-chain concept. Its application in developing the processes of manufacturing acenaphthene quinone, naphthalic anhydride, their derivatives, and naphthalene tetracarboxylic acid allowed us to run the reactions under milder conditions and obtain higher fractional yield.

Oxygen-containing products of the acenaphthene oxidation are used in the manufacture of dyes, luminophores, and thermostable polymers.[5]

Results and Discussion

The oxidation of acenaphthene by oxygen to naphthalic anhydride in the presence of cobalt and manganese bromide catalyst was studied earlier.[3,4] The compositions of catalytic

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Published on Web 06/19/2002

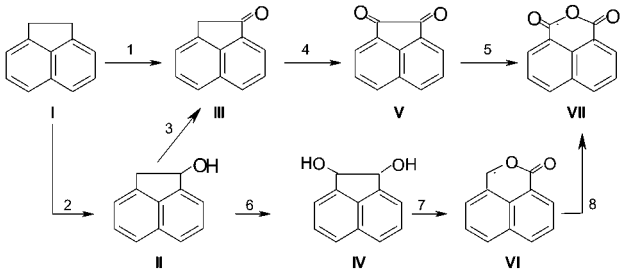
10.1021/op0100448 CCC: $22.00

Table 1. **Compositions of catalytic systems employed in the acenaphthene oxidation**

$Co(OAc)_2 \cdot 2H_2O$, mol·L^{-1}	$Mn(OAc)_2 \cdot 2H_2O$, mol·L^{-1}	KBr, mol·L^{-1}	catalytic system designation
0.016	0.002	0.020	"cobalt" catalyst
0.002	0.016	0.020	"manganese" catalyst

systems employed are listed in Table 1. In this work the same classification of catalytic systems would be used consistently; that is the catalytic system with [Co]/[Mn] ratio > 1 would be called a "cobalt" catalyst and vice versa—a "manganese" catalyst.

The main reaction products were identified, and the sequence of their formation was established. The general reaction scheme is shown below.



Acenaphthene quinone **V** is the final oxidation product in the presence of the mixed cobalt−manganese catalyst with the predominant cobalt component (a "cobalt" catalyst), whereas in the presence of the catalyst with the predominant manganese component (a "manganese" catalyst) the final product is naphthalic anhydride **VII**. Moreover, in the presence of a cobalt catalyst the rate of reaction 3 strongly exceeds the rate of reaction 6, thus preventing the contamination of the final product with impurities **IV** and **VI**. If manganese acetate is the predominant component of the catalytic system, then not only is reaction 5, the oxidation of quinone **V** to anhydride **VII**, accelerated, but the concentration of unreactive side products **IV** and **VI** is also increased. Thus, if the desired product is quinone **V**, then one should apply "cobalt" catalyst, whereas when the desired products are acids or anhydrides, then the predominant component of the catalytic system should be manganese. Generally, cobalt is more active in the breaking of C−H bonds, whereas manganese is more active in the breaking of C−C bonds. This bond breaking is realised by one-electron transfer from an oxidised hydrocarbon molecule to a catalytic cation in its highest oxidation state.

The bromide ion incorporated in the coordination sphere of the catalytic cation accelerates this electron transfer. Thus, it is evident that if acids are the desired products, then the mixed catalyst should be used, as its components are active in the different stages. Possibly, cobalt is more active in reactions 1, 2, 3, 4, and manganese is more active in steps 5, 6, and 8. One must note that the activation energies of the slow reactions 5, 7, and 8 are significantly higher than those of the others. Therefore it is preferable to obtain acenaphthene quinone **V** at relatively low temperatures, and naphthalic anhydride **VII** at the higher ones, thus lowering the concentrations of side products **IV** and **VI**.

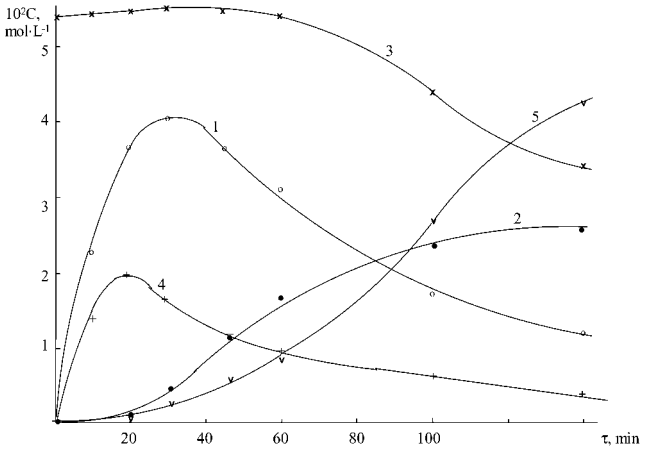


Figure 1. **The oxidation of acenaphthene in the presence of naphthalide at 105 °C. Initial concentrations, (mol·L^{-1}): [acenaphthene] = 0.067; [naphthalide] = 0.054; [$Co(OAc)_2$] = 0.016; [$Mn(OAc)_2$] = 0.002; [KBr] = 0.020. Oxidant gas: oxygen. The concentration profiles for acenaphthene and acenaphthenol-9 are omitted. (1) Acenaphthenone, (2) acenaphthene quinone, (3) naphthalide, (4) *trans*-acenaphthylene glycol, (5) naphthalic anhydride.**

The rate of benzylic oxidation in acetic acid in the presence of metal bromide catalysts depends on the current $[M^{3+}]/[M^{2+}]$ ratio (M is the transient catalytic metal).[2,6,7] It should be noted that in our case the addition of aldehyde or ketone results in the increase in Co^{3+} and Mn^{3+} concentrations, whereas the addition of alkohols lowers them. The effect of acenaphthene quinone addition was studied in the slowest reaction 8 of the oxidation of naphthalide **VI** to anhydride **VII**. The reaction was run at 105 °C. Under these conditions pure naphthalide remained unchanged for 6 h, its concentration (0.054 mol·L^{-1}) is unchanged, and no anhydride or other products are formed. Due to this the naphthalide oxidation was run in the presence of acenaphthene (Figure 1) Acenaphthene and acenaphthenol-9 **II** (their concentration profiles are omitted in the graph) are consumed during first 20 min. It is seen that the consumption of naphthalide **VI** begins only when appreciable amounts of acenaphthene quinone **V** are present in the reaction mixture. It seems that **V** somehow accelerates the reaction. This assumption was further confirmed in experiments on acenaphthene oxidation with acenaphthene quinone addition (Figure 2). It is seen that at high concentrations of quinone **V** the rate of naphthalide consumption is increased.

Therefore, to increase the overall reaction rate, one can choose to carry out the process in a semibatch mode, adding rapidly oxidised acenaphthene to the reaction mixture. Thus, the concentration of acenaphthene quinone **V** is kept stationary even at the slowest final steps of the process, and concentrations of inhibiting byproducts are lower than those in the batch mode.

Taking all these considerations into account, we have developed the methods of manufacturing acenaphthene quinone, naphthalic anhydride, and some of their derivatives

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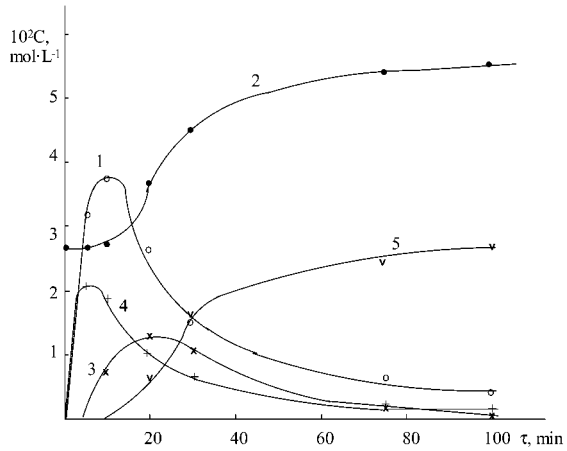


Figure 2. **The oxidation of acenaphthene in the presence of acenaphthene quinone at 105 °C. Initial concentrations, (mol·L^{-1}): [acenaphthene] = 0.067; [naphthalide] = 0.054; [Co(OAc)$_2$] = 0.016; [Mn(OAc)$_2$] = 0.002; [KBr] = 0.020. Oxidant gas: oxygen. The concentration profiles for acenaphthene and acenaphthenol-9 are omitted. (1) Acenaphthenone, (2) acenaphthene quinone, (3) naphthalide, (4) *trans*-acenaphthylene glycol, (5) naphthalic anhydride.**

Table 2. **Results of the acenaphthene oxidation with the recycle of the mother liquor[a]**

recycle no.	acenaphthene load, g	yield of the sediment, g	content of products in the sediment, mol %		product yields, mol %	
			V	**VII**	**V**	**VII**
0	7	4.4	80	20	42.2	10.1
1	7	6.5	74	26	58.0	18.9
2	7	6.8	65	35	53.2	26.8
3	7	6.5	60	40	47.0	29.0
4	7	4.1	58	42	28.0	19.8

[a] [Co(OAc)$_2$]$_0$ = 0.077 mol·L^{-1}; [Mn(OAc)$_2$]$_0$ = 0.008 mol·L^{-1}; [KBr]$_0$ = 0.050 mol·L^{-1}; w_f = 20 g·(h·L)$^{-1}$; t = 65 °C.

in a semibatch mode using selective catalytic systems and the same equipment.

The Combined Production of Acenaphthene Quinone and Naphthalic Anhydride. The solubilities of acenaphthene quinone **V** and naphthalic anhydride **VII** in the reaction mixture are significantly lower than those of other reaction components. The mother liquor after the separation of sediments of acenaphthene quinone **V** and naphthalic anhydride **VII** contains intermediate products and catalyst components; therefore, its recycle is desirable. In the subsequent experiments we studied the influence of the number of recycles, Mn/Co ratio, and acenaphthene feed rate w_f on the yield of the reaction products. The aim was to maximize the yield and content of acenaphthene quinone in the raw product. The results are listed in Tables 2 and 3.

These experiments showed that the number of mother-liquor recycles should not exceed three due to the decrease in the acenaphthene quinone yield. Under these conditions it is possible to obtain acenaphthene quinone in a 50% yield together with 20−22% yield of naphthalic anhydride.

Synthesis of Naphthalic Anhydride. One can expect that increases in the reaction temperature and Mn/Co ratios should lead to an increase in the yield of naphthalic anhydride together with the subsequent decrease in the partial yield of

Table 3. **Results of the acenaphthene oxidation at the different feed rates[a]**

feed rate g·(h·L)$^{-1}$	acenaphthene load, g	yield of the sediment, g	product yields, mol %	
			V	**VII**
10	28	24.9	29.6	41.9
15	28	24.6	49.8	22.5
17.5	28	24.9	54.5	19.2
20	28	24.2	50.1	21.2
30	7	17.9	31.7	20.6

[a] [Co(OAc)$_2$]$_0$ = 0.077 mol·L^{-1}; [Mn(OAc)$_2$]$_0$ = 0.008 mol·L^{-1}; [KBr]$_0$ = 0.050 mol·L^{-1}; number of recycles = 3; t = 65 °C.

Table 4. **Results of the acenaphthene oxidation at the different feed rates[a]**

feed rate g·(h·L)$^{-1}$	acenaphthene load, g	yield of the sediment, g	product yields, mol %	
			V	**VII**
10	24	26.5	11.3	86.0
15	24	27.6	7.4	89.7
20	24	27.9	5.8	90.5
33	24	25.3	13.1	82.1

[a] Co(OAc)$_2$]$_0$ = 0.008 mol·L^{-1}; [Mn(OAc)$_2$]$_0$ = 0.077 mol·L^{-1}; [KBr]$_0$ = 0.050 mol·L^{-1}; number of recycles = 3; t = 105 °C.

acenaphthene quinone. The synthesis of naphthalic anhydride by the acenaphthene oxidation was run at 110 °C with three mother liquor recycles. The values of w_f and [Mn^{2+}]/[Co^{2+}] ratio providing for the maximal yield of **VII** and the lowest content of admixtures of **V** were determined experimentally. The results are listed in Table 4. Under the optimal conditions the yield of naphthalic anhydride is about 90%, and the amount of the acenaphthene quinone impurities is about 2−3 mol %. In our opinion, further increase in the reaction temperature (requiring pressurised equipment) would result in both higher overall process rate and naphthalic anhydride partial yield.

Oxidation of Acenaphthene Derivatives. Some anhydrides that can be obtained by oxidation of 4-substituted acenaphthene derivatives, particularly 4-chloro, 4-nitro, and 4-acetyl, are used in the production of dyes and monomers (Scheme 1).

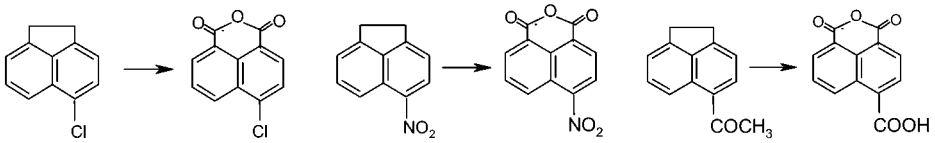
The preliminary experiments showed that the synthesis of 4-chloronaphthalic (**VIII**), 4-nitronaphthalic (**IX**), and 4-carboxynaphthalic (**X**) anhydrides by the oxidation of the corresponding acenaphthene derivatives is virtually possible. The process conditions providing for the maximum product yields were determined by varying reaction temperature, [Mn^{2+}]/[Co^{2+}] ratio, and w_f. The operating oxidation conditions are listed in Table 5.

The quality of the obtained products was confirmed by the HPLC and GLC analysis and by determination of the melting points. Results are presented in Table 6.

Another acenaphthene derivative is acenaphthalic acid (**XI**): a key intermediate in the synthesis of naphthalene tetracarboxylic acid used in the production of high-quality dyes and heat-proof polymers (Scheme 2).

It is reasonable to suppose that this oxidation should be carried out in the presence of manganese bromide catalysts. Oxidation of **XI** under atmospheric pressure leads to just

Scheme 1



VIII IX X

Table 5. **Operating conditions for the oxidation of acenaphthene and its derivatives**

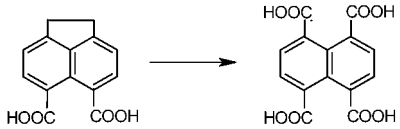
reaction product	*t*, °C	[Mn]+[Co], [Br], mol·L^{-1}	[Mn]/[Co]	w_f, g·(h·L)$^{-1}$	number of recycles	yield, mol %
V + VII	65	0.085/0.050	1/(10−13)	17−18	3	(48−50) + (20−22)
VII	105	0.175/0.114	(10−25)/1	15−25	3	89−90
VIII	100	0.180/0.100	(4−7)/1	12−14	−	89−93
IX	100	0.120/0.120	(14−16)/1	11−13	−	54−56
X	80	0.120/0.060	(5.5−6.5)/1	12−13	2	75−80

Table 6. **Melting points of product samples**

reaction product	mp, °C experimental	mp, °C lit.[7]	product content, % mass (by GLC and HPLC[a])
acenaphthene quinone	260−262	261−263	98
naphthalic anhydride	270−273	272−274	97
VIII	215−216	215−216	98
IX	219−221	220−221	99
X	273−275	274−275	97

[a] Only main component was determined.

Scheme 2



XI XII

two products: dicarboxyacenaphten-9-ol, **XIII**, and dicarboxyacenaphthenone, **XIV**. That is possibly due to the inactivation of the acenaphthene structure by two carboxylic groups (Figure 3). It is evident that high temperature and, consequently, high pressure are necessary for obtaining the tetracarboxylic acid. The oxidation of **XI** under 293 psi and 140 °C produced the desired product **XII** (Figure 4). The analysis of the reaction mixture and the profiles of reactant consumption and product accumulation showed that the reaction proceeds along the following pathway (Scheme 3).

Compound **XI** is poorly soluble in acetic acid even at high temperatures (less than 0.04 mol·L^{-1}), so that the reactor specific capacity in the commercial process would be very low. Thus, the oxidation of **XI** was carried out in the suspension with the overall formal concentration 0.40 mol·L^{-1}. In this case, the starting reactant would dissolve in the course of its consumption, making the process essentially semibatch just as in the acenaphthene oxidation. The high process temperature (160 °C) permits the use of gases with the low oxygen content as oxidants. The process is more explosion-proof when the oxygen content in the oxidant gas is 10%. The mother liquor obtained after filtering off the products and stripping off some of the acetic acid

Scheme 3

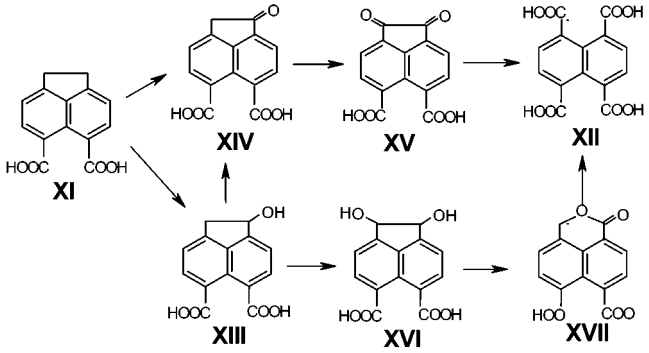


Table 7. **Oxidation of XI with the manganese catalyst[a]**

concentrations, mol·L^{-1} Co	Mn	Br	oxidation time, h	oxidant gas	content of **XII** in the sediment, mol %
0.004	0.04	0.04	2	air	83.8
0.004	0.04	0.04	2	oxygen	95.4
−	0.04	0.04	2	oxygen	51.8
−	0.04	0.04	4	oxygen	94.4
b	0.04	0.04	4	10%O_2 + 90%N_2	95.0

[a] t = 140 °C, p = 293.92 psi, [**XI**]$_0$ = 0.04 mol·L^{-1}. [b] t = 160 °C, p = 293.92 psi, [**XI**]$_0$ = 0.40 mol·L^{-1}

with water can be recycled. No inhibition was observed after two recycles. The obtained sediment contains 95% mass of **XII**. This product can be used for the production of the fast red dye by condensation with *o*-phenylenediamine in acetic acid without additional purification.

The results of oxidation of **XI** with the manganese catalyst are listed in Table 7.

Conclusions

1. The methods of controlled synthesis of acenaphthene quinone/naphthalic anhydride by acenaphthene oxidation in acetic acid with metal bromide catalyst under normal pressure have been developed. In the presence of the "cobalt" catalyst the main product is acenaphthene quinone; in the presence of the "manganese" catalyst naphthalic anhydride predominates.

2. The developed catalytic system allows obtaining anhydrides of chloro-, nitro-, and carboxy-substituted naph-

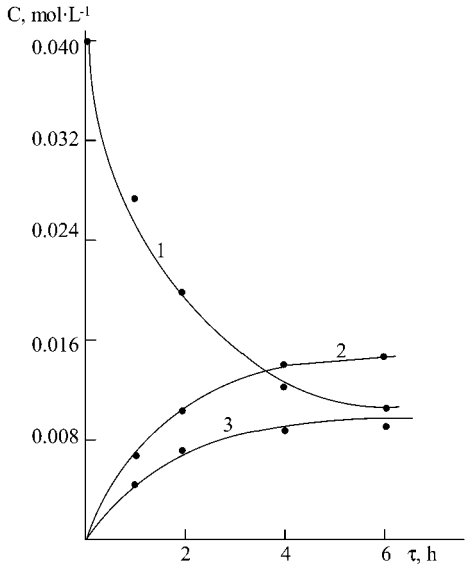


Figure 3. **Oxidation of acenaphthalic acid under atmospheric pressure at 100 °C. Initial concentrations, (mol·L^{-1}): [acenaphthalic acid] = 0.04; [Co(OAc)$_2$] = 0.004; [Mn(OAc)$_2$] = 0.04; [NaBr] = 0.04. (1) Acenaphthalic acid, (2) dicarboxyacenaphthenol-9, (3) dicarboxyacenaphthenone. Oxidant gas: air.**

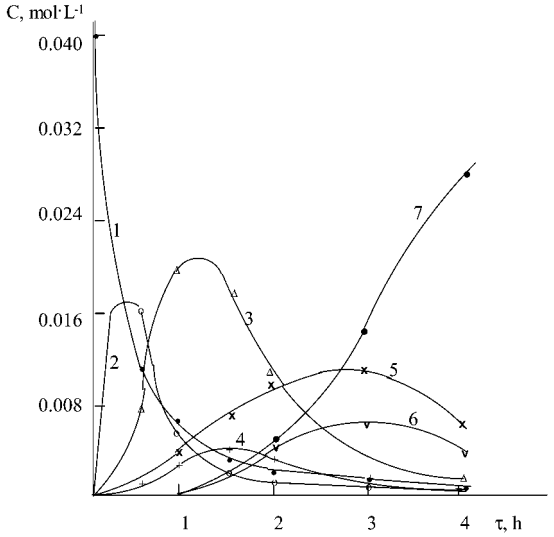


Figure 4. **Oxidation of acenaphthalic acid under increased pressure (293.92 psi) at 140 °C. Initial concentrations, (mol·L^{-1}): [acenaphthalic acid] = 0.04; [Co(OAc)$_2$] = 0.004; [Mn(OAc)$_2$] = 0.04; [NaBr] = 0.04. (1) Acenaphthalic acid, (2) dicarboxyacenaphthenol-9, (3) dicarboxyacenaphthenone, (4) dicarboxyacenaphthylene glycol, (5) dicarboxyacenaphthene quinone, (6) dicarboxynaphthalide, (7) naphthalene tetracarboxylic acid. Oxidant gas: air.**

thalic acids by oxidation of the respective acenaphthene derivatives.

3. Naphthalene tetracarboxylic acid was obtained in high yield by the oxidation of acenaphthalic acid under high pressure in the presence of manganese bromide catalyst.

Experimental Section

Experimental Setup. The oxidation of acenaphthene and its derivatives was carried out both under atmospheric and increased pressure by air or oxygen. Catalytic system employed consisted of aqueous solutions of Co(OAc)$_2$·2H$_2$O, Mn(OAc)$_2$·2H$_2$O, and KBr.

The Oxidation under Atmospheric Pressure was carried out in the glass stirred reactor (Figure 5a) in a batch or semibatch mode. Oxygen was used as the oxidant gas. The reactor was a cylinder of 100−150 mL volume (1) equipped with a turbine stirrer (2), oxidant gas inlet (3), baffles (4), and a contact thermometer (5). In the semibatch mode the setup was additionally equipped with a heated batch meter of the starting materials (6) and a solvent distilling-off unit (7) to keep the reaction volume constant. A motor with a controlled stirring speed drove the turbine stirrer, the reactor was heated by means of a Nichrome coil (8), and the reactor temperature was kept constant at ±0.5 °C by a contact thermometer and a relay (9). All the experiments were carried out using efficient agitation (stirring speed > 1000 rpm and oxidant gas flow rate > 600 mL/min).

Typical Run under Atmospheric Pressure. The overall volume of the solvent (acetic acid) was 100 mL. Half of this volume was charged into the reactor, and then calculated amounts of catalyst components and acenaphthene were added. The rest of acetic acid was added, heating was turned on, and an inert gas was fed into the reactor. After the reaction mixure reached the necessary temperature, the oxygen was fed into the reactor, and inert gas was turned off. This moment was assumed as the start of the reaction. In a typical run the load was:

acenaphthene $C_{12}H_{10}$	0.0975 mol·L^{-1}
cobalt acetate Co(OAc)$_2$·2H$_2$O	0.002 mol·L^{-1}
manganese acetate Mn(OAc)$_2$·2H$_2$O	0.016 mol·L^{-1}
potassium bromide KBr	0.020 mol·L^{-1}

After 200 min the heating and oxygen feed were turned off, and the reaction mixture was unloaded and analysed. The following identified products were obtained:

acenaphthene	0
acenaphthenone	0.0090 mol·L^{-1}
trans-acenaphthylene glycol	0.0123 mol·L^{-1}
naphthalide	0.0110 mol·L^{-1}
naphthalic anhydride	0.0454 mol·L^{-1}

The summary product concentration is 0.0952 mol·L^{-1} that corresponds to 97.6 mol % yield of identified products.

The Oxidation of Acenaphthalic Acid under Increased Pressure was carried out in the titanium-made setup (Figure 1b). It consisted of the jacketed titanium-made column (1) equipped with cooler-separator (2), sparger of an oxidant gas (usually air) (3), and a sample valve (4). The temperature was kept constant in the limits of ±2 °C by circulation of the silicone oil as the heat carrier. The reactor temperature and pressure were monitored by a thermocouple (5) and a pressure gauge (6). The reaction mixture in the amount of 300 mL was charged through the charge hatch (7). The efficient agitation was ensured by keeping the oxidant gas flow rate above 2 standard L/min.

Typical Run in Pressurised Reactor. The reaction mixture was prepared separately in a round-bottomed flask with a mechanical stirrer and a reflux condenser. The flask was charged with 250 mL of acetic acid, necessary amounts of acenaphthalic acid, and catalyst components. The mixture was heated at 80 °C, stirred until all catalyst was dissolved

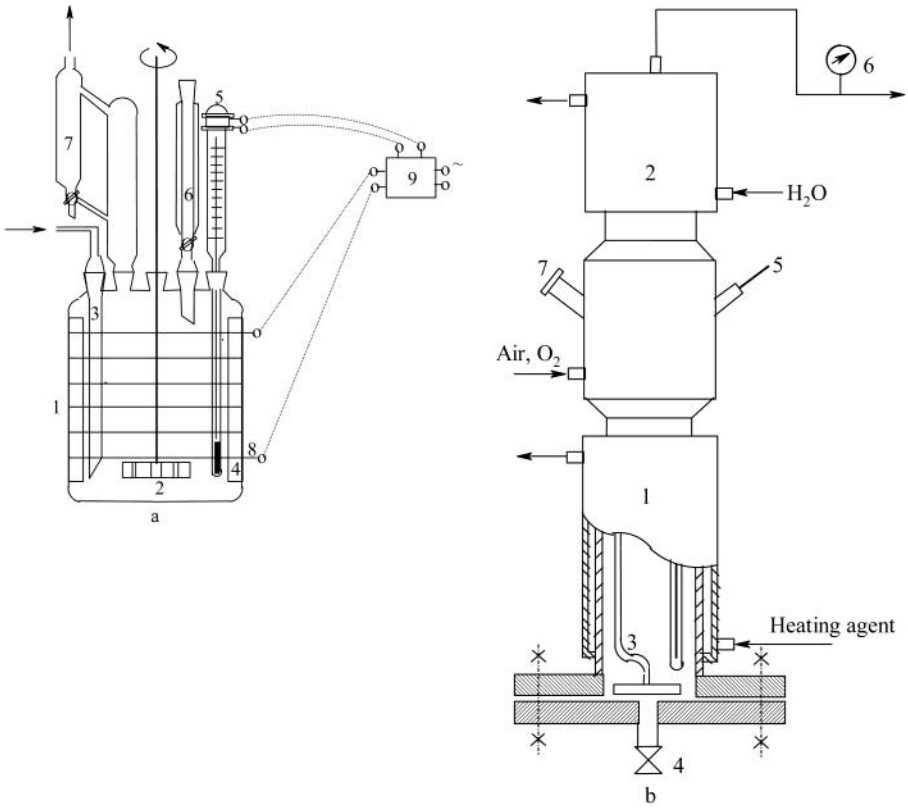


Figure 5. **The experimental setups for the oxidation of acenaphthene and its derivatives under atmospheric (a) and increased (b) pressure.**

and was quantitatively transferred to the reactor through the charge hatch. The heating of the column was turned on, and argon was passed through the reaction mixture. After the reaction temperature was reached, argon was turned off, and air was fed into the reactor. This moment was assumed as the start of the reaction. In a typical run the load was:

acenaphthalic acid $C_{12}H_{10}O_4$	0.400 mol·L^{-1}
cobalt acetate $Co(OAc)_2 \cdot 2H_2O$	0.004 mol·L^{-1}
manganese acetate $Mn(OAc)_2 \cdot 2H_2O$	0.040 mol·L^{-1}
potassium bromide KBr	0.040 mol·L^{-1}

After 120 min the heating and air feed were turned off, and the reaction mixture was unloaded and analysed. The following identified products were obtained:

acenaphthalic acid	0
dicarboxyacenaphthene quinone	0.068; 0.040 mol·L^{-1}
naphthalene tetracarboxylic acid	0.331 mol·L^{-1}

The summary product concentration is 0.40 mol·L^{-1} that corresponds to 99.8 mol % yield of identified products.

Analytical Procedure. Acenaphthene and the products of its oxidation: acenaphthylene, acenaphthol-9, acenaphthenone, acenaphthene quinone, *trans*-acenaphthylene glycol, naphthalide, and naphthalic anhydride were determined by GLC using a "Tsvet-100" gas chromatograph with FID. Analysis conditions: 1 m × 3 mm i.d. glass column packed with INERTON-Super (0.2−0.25 mm) coated with 5% DS-550 and 1% neopentyl glycol adipate. Injector temperature 250 °C, temperature programming from 115 to 210 °C at 3 °C/min, carrier gas (nitrogen) flow rate 35−40 mL/min. 3,3′,4,4′-Tetramethylbenzophenone was added to samples as the internal standard. The standard analysis error was ±5−6 mol %.

4-Chloroacenaphthene and 4-chloronaphthalic anhydride were determined by GLC using a "Tsvet-100" gas chromatograph with FID. Analysis conditions: 2 m × 3 mm i.d. glass column packed with INERTON-Super (0.1−0.125 mm) coated with 5% DS-550. Injector temperature 250 °C, column temperature 195 °C, carrier gas (nitrogen) flow rate 35−40 mL/min. The concentrations were determined using absolute calibration by peak heights; the standard analysis error was ±5−6 mol %.

4-Acetylnaphthene was determined by GLC using the "Tsvet-100" gas chromatograph with FID. Analysis conditions: 1 m × 3 mm i.d. glass column packed with INERTON-Super (0.2−0.25 mm) coated with 5% DS-550 and 1% neopentyl glycol adipate. Injector temperature 250 °C, column temperature 205 °C, carrier gas (nitrogen) flow rate 35−40 mL/min. The standard analysis error was ±5−6 mol %.

4-Nitrophthalic, 4-acetylnaphthalic, and 4-carboxynaphthalic anhydrides were determined by HPLC on a "Tsvet-304" chromatograph with UV detector. Analysis conditions: stainless steel column 200 mm × 6 mm i.d. packed with Silasorb C2 (10 μm), wavelength 254 nm, eluent H_2O/AcOH (98:2 w/w), eluent rate 1 mL/min. The concentrations were determined using absolute calibration by peak heights; the standard analysis error was ±5−6 mol %.

The products of acenaphthalic acid oxidation were determined by reversed-phase HPLC on a "Milikhrom" chromatograph with UV detector. Analysis conditions: stainless steel column 50 mm × 2 mm i.d. packed with

Silasorb C18, wavelength 250 nm, eluent MeCN/H_2O/H_3PO_4 (28:72:0.2 w/w), eluent rate 100 μL/min. Sample volume 0.4−2 μL. The concentrations were determined using absolute calibration by peak heights; the standard analysis error was ±4 mol %.

Product Isolation Procedure. Acenaphthene quinone, naphthalic anhydride, and 4-carboxynaphthalic anhydride were filtered off after the reaction, washed by distilled water, and treated with the 20% solution of sodium bisulfite taken in one equivalent with respect to quinone at 90−100 °C for 3 h. The hot solution of the bisulfite compound was then filtered off at 80 °C. Acenaphthene quinone can be obtained by the acidic decomposition of the bisulfite compound.

Another procedure was applied for the isolation of 4-chloronaphthalic and 4-nitronaphthalic anhydrides due to their high solubility in the reaction mixture. The reaction mixture containing 4-chloronaphthalic anhydride was filtered; the filtrate was diluted with an equal volume of water and acidified by hydrochloric acid. The obtained sediments were combined, and the desired product was obtained as the disodium salt after treatment with Na_2CO_3 solution.

4-Nitrophthalic anhydride was isolated by stripping off acetic acid under reduced pressure; the obtained mixture was treated by the aqueous carbonate solution in the presence of the activated charcoal. After filtering off the charcoal the anhydride was isolated by acidification of the disodium salt by hydrochloric acid.

Acknowledgment

We express our thanks to Dr. Felix Sirovski for his help in preparation of the paper.

Received for review May 30, 2001.

OP0100448