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The Peroxide-induced Addition of Acetic Acid to Olefins

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The peroxide-induced addition of acetic acid to ethylene gave straight-chain fatty acids, such as butyric, hexanoic, octanoic, decanoic, lauric, myristic, and palmitic acids. Some α-branched-chain fatty acids were also formed. Di-*t*-butyl peroxide (DTBP) was an effective initiator in forming fatty acids. To obtain the 1 : 1-telomer acids, it was preferable that a 20—10 : 1 : 0.25 (mol) mixture of acetic acid, ethylene, and DTBP be heated at 150°C for 6 hr. Straight-chain fatty acids were also obtained by the reaction of acetic acid to 1-olefins under similar conditions.

The radical addition to 1-olefins gives anti-Markownikoff's products,[1] and α-branched-chain fatty acids are generally formed by the addition of fatty acids to 1-olefins.[2-4] It is expected that straight-chain fatty acids can be obtained by the radical addition of acetic acid to ethylene or 1-olefins. However, the removal of a hydrogen atom from the α-position of acetic acid is much more difficult than that of other fatty acids.[2,3,5,6] Consequently, the yields of the addition products of acetic acid to olefins are generally poor.[5,6] A few papers[3,5,7,8] have reported on the addition of acetic acid to olefins. However, the addition of acetic acid to ethylene has been considered in only two patents.[6,9] Therefore, the details of the reaction have not been made clear.

In the present study, in order to find preferable conditions for the formation of fatty acids, the acidic products of the radical addition of acetic acid to ethylene and 1-olefins under various conditions were investigated. The peroxides used were di-*t*-butyl peroxide (DTBP), *t*-butyl hydroperoxide (TBHP), benzoyl peroxide (BZPO), and dilauroyl peroxide (DLPO). The reaction was carried out in an autoclave, and the products were identified by GLC, GC–MS, and IR, and determined by GLC.

When BZPO or DLPO was used in the reaction temperature range of 60—180°C, no fatty acids were formed. When DTBP or TBHP was employed, however, the addition product was a mixture of acidic and neutral substances, and DTBP was the best initiator for the reaction forming fatty acids. No succinic acid formed by the radical dimerization of acetic acid was found in any products, although a small amount of succinic acid was obtained by heating acetic acid with DTBP in the absence of an olefin.

In the case of the addition of acetic acid to ethylene, no acidic product was separated from the reaction mixture, because butyric acid formed by the reaction is easily soluble in water. However, the compositions of the acidic products could be determined by GLC. The addition product contained acetic, butyric (1 : 1-telomer), 2-ethylbutyric, hexanoic, (2 : 1-telomer), 2-ethylhexanoic, octanoic (3 : 1-telomer) 2-ethyloctanoic, decanoic (4 : 1-telomer), lauric (5 : 1-telomer), myristic (6 : 1-telomer), and palmitic (7 : 1-telomer) acids, various hydrocarbons, and a small amount of an ester

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Table 1. Addition of acetic acid to ethylene

	Molar ratio			Reaction		Yield from 1 kg of acetic acid (g)									
						Fatty acid									Neutral product
						Straight-chain									
Run No.	AcOH	C_2H_4	Peroxide (A, DTBP) (B, TBHP)	Temp. (°C)	Time (hr)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	Total	Branched-chain	Total	
1	20	1	A 0.25	150	6	5.9	4.5	2.6	1.9	1.2	0.8	16.9	12.1	30.0	3.4
2	10	1	A 0.25	130	6	6.0	3.4	1.9	1.4	0.7	0.3	13.7	14.2	27.9	16.1
3	10	1	A 0.15	150	6	1.5	1.5	1.4	0.7	0.5	0.1	5.7	4.5	10.2	7.9
4	10	1	A 0.20	150	6	7.2	4.0	2.5	1.4	0.5	0.3	15.9	13.5	29.4	9.7
5	10	1	A 0.25	150	4	6.7	2.8	1.7	0.9	0.3	0.1	12.5	9.1	21.6	8.8
6	10	1	A 0.25	150	6	8.5	4.1	2.6	1.5	0.9	0.4	18.0	13.1	31.1	10.3
7	10	1	A 0.25	150	11	5.3	6.3	2.6	1.9	1.2	0.5	17.8	17.9	35.7	14.3
8	10	1	A 0.25	170	6	8.1	4.8	2.4	1.3	1.0	0.4	18.0	14.8	32.8	13.8
9	10	1	A 0.25	190	6	8.5	4.6	1.9	1.1	0.5	0.2	16.8	13.8	30.6	16.5
10	5	1	A 0.25	150	6	4.4	4.1	3.5	1.6	0.9	0.4	14.9	16.2	31.1	28.0
11	3	1	A 0.25	150	6	7.3	6.1	4.3	2.6	1.6	0.4	22.3	21.9	44.2	53.0
12	10	1	B 0.25	150	6	7.2	3.0	2.2	1.9	1.3	0.7	16.3	13.5	29.8	22.5
13	10	1	B 0.25	170	6	6.7	3.2	2·0	1.8	1.4	0.9	16.0	15.2	31.2	26.7

a) Small amounts of palmitic acid were detected except Runs 3, 5, and 9.

of acetic acid. 2-Ethylbutyric, 2-ethylhexanoic, and 2-ethyloctanoic acids are presumably formed by the adition of butyric, hexanoic, and octanoic acids respectively to ethylene. 2-Ethylhexanoic acid may also be formed by the addition of ethylene to a radical formed by the addition of butyric acid to ethylene. The ester of acetic acid may be formed by the ionic addition of acetic acid to ethylene.[10]

The reaction conditions and the yields of the addition products of acetic acid to ethylene are shown in Table 1. The best yield of straight-chain fatty acids was given by Run 11 (the conversion of ethylene to straight-chain fatty acid: 7.0%), but very large amounts of neutral substances were also formed in this case. On the other hand, the autoclave was a little injured at reaction temperatures above 70°C. Judging from the conversions of ethylene, the yields of the products, and the reaction time and the temperature, the conditions of Runs 1 and 6 are preferable (the conversions of ethylene to straight-chain fatty acids were 35.2% in Run 1 and 17.2% in Run 6).

The telomerization for the formation of fatty acids with reasonable yields required 20—25 mol % of a peroxide to olefin; the amount of the peroxide was much larger than the amount employed usually as an initiator. This fact shows that the kinetic chain lengths are rather short.

The addition of acetic acid to 1-olefins was carried out under conditions similar to those in the case of Run 6, and the acidic and neutral products were separated from each other. The acidic addition product of acetic acid to 1-octene was a mixture of hexanoic, heptanoic, 3-methylnonanoic (Markownikoff's product), decanoic (1 : 1-telomer), 4-hexyldodecanoic 2 : 1-telomer), and 4,6-dihexyltetradecanoic (3 : 1-telomer) acids. It is noteworthy that Markownikoff's product[11] and lower fatty acids were also formed, although their yields were quite low.

Gas chromatograms of the acidic addition products of acetic acid to other 1-olefins resembled that of the acidic addition product of acetic acid to 1-octene. Thus, the formations of 1 : 1-, 2 : 1-, and 3 : 1-telomers, and of small amounts of lower fatty acids and Markownikoff's products, were observed. The following acids (1 : 1-telomers) with purities of more than 95% could be obtained from the acidic products of the addition of acetic acid to the corresponding 1-olefins by distillation or recrystallization: octanoic (from 1-hexene), decanoic (from 1-octene), lauric (from 1-decene), myristic (from 1-dodecene), palmitic (from 1-tetradecene), stearic (from 1-hexadecene),

Table 2. Conversion of 1-olefin in addition of acetic acid to 1-olefin

Acetic acid : 1-olefin : DTBP=10 : 1 : 0.25 (mol)
Reaction temperature : 150°C. Reaction time: 6 hr.

	Conversion of 1-olefin (%)				
	Telomer				Neutral product
Olefin	1 : 1	2 : 1	3 : 1	M*[a]	
1-Hexene	28.9	10.0	4.1	0.3	40.8
1-Octene	28.3	9.7	2.5	0.5	45.7
1-Decene	30.7	8.7	2·8	0.6	46.6
1-Dodecene	29.6	6.0	2.1	0.8	45.5
1-Tetradecene	28.5	6.1	1.7	0.8	48.2
1-Hexadecene	28.9	6.0	—	0.8	47.0
1-Octadecene	26.7	4.9	—	0.7	44.4

a) M: Markownikoff's product

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[10] G. I. Nikishin, R. I. Mustafaev, and A. D. Petrov, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, **1963**, 359.

[11] V. D. Vorob'ev and G. I. Nikishin, *ibid.*, **1966**, 138; G. I. Nikishin, M. G. Vinogradov, and R. V. Kereselidze, *ibid.*, **1967**, 1624; D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964); G. I. Nikishin, M. G. Vinogradov, and R. V. Kereselidze, *Zh. Org. Khim.*, **2**, 1918 (1966).

and eicosanoic (from 1-octadecene) acids.

The conversions of 1-olefins are shown in Table 2. Allen *et al.* obtained decanoic acid in a 70% yield from a 300 : 1 : 0.15 (mol) mixture of acetic acid, 1-octene, and DTBP.³⁾ Although the yield based on the moles of 1-octene employed was very high, only 6.7 g of decanoic acid were obtained from 1 kg of acetic acid under the above conditions. According to the conditions shown in Table 2, however, 81.2 g of decanoic acid were obtained from the same amount of acetic acid. Therefore, the present conditions were preferable practically.

Dimers and trimers of the 1-olefins employed and esters of acetic acid were found in the neutral products.

Experimental

GLC was carried out with a Hitachi Gas Chromatogram 063 equipped with dual columns (3 mm × 2 m) packed with 15% SE 30-Chromosorb WAW (70→300°C, 10°C/min) or 20% DEGS-Chromosorb WAW (50→220°C, 10°C/min).

GC-MS was carried out with a Shimadzu LKB-9000 Gas Chromatograph-Mass Spectrometer with a column packed with 15% SE 30-Chromosorb WAW, and the ionization intensity was 70 eV.

The IR spectra were measured in a liquid film with a Hitachi EPI-S2 Infarared Spectrophotometer, a sodium chloride cell being used.

Identification of Products. The acidic products were identified by deriving them into their butyl esters, and by comparing the retention times of the esters in GLC with those of authentic esters using two columns packed with SE 30 and DEGS. In the cases of the addition products of acetic acid to ethylene, both butyl and amyl esters of the products were used in order to distinguish between acidic and neutral substances. In addition, the correction factor for GLC and mass spectrum of each butyl ester were measured.

The derivation into butyl and amyl esters was done as follows: Ten milliliters of 1-butanol or 1-pentanol containing 0.2 ml of sulfuric acid was added to 1 g of a sample, and the solution was warmed for 1 hr on a water bath. Then, a solution saturated with both sodium carbonate and sodium chloride was added to the reaction mixture until the mixture was free from sulfuric acid; the upper layer of the mixture was then ready to submit to GLC.

The neutral products were analyzed by means of GLC and IR without pretreatment.

Materials. The purity of ethylene was more than 99%. Each gas chromatogram of acetic acid and 1-olefins showed a single peak. The 1-olefins used were 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The peroxides were all commercial products.

Addition of Acetic Acid to Ethylene. A typical procedure (Run 6) was as follows: Ninety milliliters of acetic acid and 5.70 g of DTBP were put in a 200-ml autoclave, after which ethylene was fed into the autoclave until the pressure gauge showed 36 kg/cm² at 20°C (the pressure was calculated by presuing that ethylene was an ideal gas and that it was insoluble in acetic acid). When stirring was begun, the pressure quickly dropped to 13.5 kg/cm². The reaction mixture was heated at 150°C under stirring. The pressure rose to 26 kg/cm² with an increase in the temperature, and then it gradually decreased to 18 kg/cm². After 6 hr, the reaction mixture was cooled and distilled to remove most of the unreacted acetic acid.

A part of the residue was esterified for identification. Most of the residue was dissolved in ether, and the ethereal solution was washed successively with water, a 5% aqueous potassium carbonate solution, and water. The ethereal solution was dried over anhydrous sodium sulfate, and the ether was distilled off to obtain neutral substances.

The conversions of ethylene and the yields of fatty acids were calculated from the results of GLC, and the amounts of the residue and neutral substances.

Addition of Acetic Acid to 1-Olefins. A mixture of acetic acid (2.0—1.5 mol), and 1-olefin, and DTBP (molar ratio, 10 : 1 : 0.25) was stirred in a 200-ml autoclave at 150°C for 6 hr. Then, unreacted acetic acid was distilled off from the reaction mixture, and the residue was dissolved in ether. The ethereal solution was washed successively with water, a 5% aqueous potassium carbonate solution, and water. After being dried over anhydrous sodium sulfate, the ether was distilled off to obtain neutral product. The washings obtained above were combined and then acidified with hydrochloric acid. The acidic product separated from the washings was extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. The ether was distilled off, and acidic product was thus obtained. A part of the acidic product was esterified to make identification possible.

The isolation of 1 : 1-telomer acids from the acidic products was carried out by distillation (C_8—C_{12} acids) or by three recrystallizations (C_{14}—C_{20} acids) from petroleum benzin (bp 60—85°C).

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