Acrylate Monomers from Olefins via Tertiary Butyl Hypochlorite

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Synopsis

A variety of olefins were readily converted to acrylate monomers by combining them with *t*-butyl hypochlorite and acrylic or methacrylic acid at 25–65°C. The predominate product was the vicinal acyloxychloro derivative formed by addition at the olefinic double bond. By-products were the vicinal butoxychloro derivative and the still unsaturated chlorinated olefin. The main reaction was shown to occur by an ionic mechanism. 2-Chloro-1-methyl propyl methacrylate was isolated and identified as the main product of the reaction of 2-butene, methacrylic acid, and *t*-butyl hypochlorite. The crude olefin products readily homopolymerized and copolymerized with other vinyl monomers by incorporating free-radical initiators.
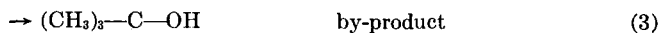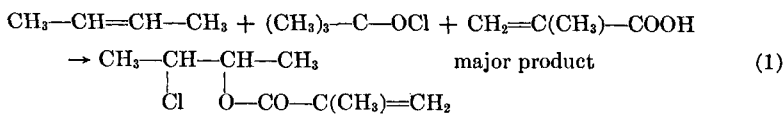
INTRODUCTION

The direct addition of anhydrous formic acid to the unsaturated carbons of various olefins was reported by Knight et al.[1] as a high-yield reaction. Acetic acid and higher molecular weight acids by comparison react only partially and produce several side-reaction products.

The formation of a chlorohydrin in the reaction of ethylene with dilute chlorine water was first successfully developed by Gomberg.[2] The product can be converted subsequently to a chlorohydrin ester. However, in formation of the chlorohydrin by this procedure HCl, Cl$_2$, and O$_2$ are always present, and these compounds also react at the olefinic double bonds. For many years it has been known[3] that when halogens are added to olefins in the presence of nonhalogen anions, derivatives of these anions may occur in the reaction products. Canterino and Baptist[4] describe the addition of chlorine to an olefin in the presence of an active solvent, acetic acid, to produce the vicinal acetoxychloro derivative. This reaction is partially effective, but a considerable quantity of dichlorinated product is formed, since both positive and negative chloride ions are present.

Harford was issued a patent[5] in 1936 that claims the preparation of chlorohydrin esters in reactions of olefins with tertiary alcohol hypochlorites and carboxylic acids. Since the alkyl hypochlorite contains only positive chlorine for attack at the double bond, dichlorination is eliminated, and the acrylate anion attaches to the resulting carbonium ion, forming a vicinal acyloxychloro product. Similar, more complete, studies were later reported by Irwin and Hennion.[6]

This previous work generated the idea that unsaturated compounds in general would react with alkyl hypochlorites plus vinyl carboxylic acids to form the vicinal vinylacyloxychloro derivatives. For example, 2-butene combined with tertiary butyl hypochlorite and methacrylic acid would react as follows:

$$CH_3—CH=CH—CH_3 + (CH_3)_3—C—OCl + CH_2=C(CH_3)—COOH$$

$$\rightarrow CH_3—\underset{\underset{Cl}{|}}{C}H—\underset{\underset{O—CO—C(CH_3)=CH_2}{|}}{C}H—CH_3 \qquad \text{major product} \qquad (1)$$

$$\rightarrow CH_3—\underset{\underset{Cl}{|}}{C}H—\underset{\underset{O—C—(CH_3)_3}{|}}{C}H—CH_3 \qquad \text{minor product} \qquad (2)$$

$$\rightarrow (CH_3)_3—C—OH \qquad \text{by-product} \qquad (3)$$

Logically, the tertiary butyl hypochlorite could also attack the unsaturation in the methacrylic acid, resulting in the formation of a vicinal methacryloxychloro methacrylic acid condensate. However, one would expect the ease of the hypochlorite reaction to vary in direct proportion to the electron density existing at the carbon–carbon double bond of the unsaturated compound. Since the methacrylic acid unsaturation is both terminal and conjugated with carbonyl unsaturation, its electron density is much lower than that of the 2-butene unsaturation. Consequently, in actuality only trace amounts of the methacrylic acid condensate form.

This general reaction provides a simple synthesis for preparing an acrylate (or substituted acrylate) monomer from unsaturated compounds. This paper describes the reaction of tertiary butyl hypochlorite and acrylic or methacrylic acid with a number of different olefins. It shows the ionic nature of the reaction and indicates the ease of performing addition reactions with olefins under mild conditions by using t-butyl hypochlorite.

RESULTS

Methacrylated 2-Butene

Table I presents the analytical data for the total reaction product mixture from a methacrylated 2-butene. The product composition, determined from chemical and physical analyses, is calculated as the mole per cent of various substituents on the butene. The calculations for total chlorine and for allylic chlorine are self-explanatory. The mole per cent butoxy substituent is calculated in one manner by subtracting the product saponification value from the sum of the value of the reactant methacrylic acid plus the value of the reactant t-butyl hypochlorite and comparing the difference with the original 2-butene reactant. This is based on the ability of alcoholic alkali to saponify all chlorine (allylic chlorine, vicinal dichloro-, and vicinal acyloxychloro) with the exception of chlorine vicinal to an alkoxy substituent. The mole per cent butoxy substituent is calculated a second way by subtracting the product t-butyl alcohol value (GLC method) from the reactant t-butyl hypochlorite value and comparing the difference

TABLE I
Methacrylated 2-Butene: Analyses and Product Composition

	Concn., mmoles	Calculated compns., mole-% substituent
Reactants		
2-Butene	700	
Methacrylic acid	930	
t-Butyl hypochlorite	700	
p-Cresol	2	
Total reaction product mixture, analyses:		
Total chlorine	715	715/700 = 102% chlorine
Allylic chlorine[a]	16	16/700 = 2% allylic chlorine
Saponification	1610	(1630-1610)/700 = 3% butoxy[b]
t-Butyl alcohol, GLC[c]	666	(700–666)/700 = 5% butoxy
Acidity	371	(930-371)/700 = 80% methacryloxy
Unsaturation, cat. H_2	910	no calculation
Vinyl unsat., NIR[d]	950	(950-371)/700 = 83% methacryloxy
Methacrylic acid, GLC[c]	410	(930-410)/700 = 75% methacryloxy

[a] Chloride reactive at room temperature with silver nitrate.[7,8]
[b] Based on inability of alcoholic alkali to saponify vicinal alkoxychloro substituents.
[c] Gas–liquid chromatography method.
[d] Near-infrared quantitative method.[9]

TABLE II
Methacrylated 2-Butene; Total Reaction Product Mixture

Component	Concn.,[a] mole-%	Concn., wt.-%
Methacrylic acid	53	16
t-Butyl alcohol	95	25
Methacryloxychlorobutane	80	50
Butoxychlorobutane	5	3
Allylic chlorobutene	2	<1
Nonallylic chlorobutene	13	5

[a] Based on moles of original 2-butene.

with the original t-butyl hypochlorite value.   The mole per cent methacryloxy substituent is calculated in three different ways: by subtracting the product acidity value from the reactant methacrylic acid value and comparing the difference with the original 2-butene reactant, by subtracting the product acidity value from the product total vinyl unsaturation value (NIR method) and comparing the difference with the original 2-butene reactant, and by subtracting the product methacrylic acid value (GLC method) from the reactant methacrylic acid value and comparing the difference with the original 2-butene reactant.

These data are summarized in Table II as the mole per cent of each component in the total reaction product (based on the original 2-butene) and as the weight per cent of each component.

A portion of the total reaction-product mixture was stripped on a rotary flash evaporator at 65°C. and 25 to 5 mm. in order to remove the *t*-butyl alcohol by-product.   This procedure resulted in a crude product consisting mainly of methacrylated butene and methacrylic acid.   Gas chromatography separated this crude product into seven components.   Integration of the areas under each peak gave estimates of the relative weight per cent of each separated component as recorded in Table III.   The components labeled *t*-butyl alcohol and methacrylic acid were identified by the corresponding retention times of high-purity samples of these two compounds. The other components were assigned probable structures based on the information presented in Table II.

TABLE III
Methacrylated 2-Butene: Vacuum-Stripped Crude Product,
Gas Chromatographic Analysis[a]

Component no.	Integration quantity, wt.-%	Adjusted quantity,[b] wt.-%	Assigned structure
1	0.14	1	*t*-butyl alcohol
2	0.66	1	minor impurity
3	0.43	1	minor impurity
4	15.4	10.5	methacrylic acid
5	4.7	3	chlorobutene
6	4.5	3	butoxychlorobutane
7	74.2	50	methacryloxychloro-butane
	100.0	67.5	

[a] Chromatographed directly on an Apiezon L column at 100°C.

[b] Values calculated on the basis of the weight per cent methacryloxychlorobutane in the total reaction-product mixture before vacuum-stripping.

The adjusted quantities in Table III are the calculated weight per cent of specific components in the total reaction-product mixture before vacuum-stripping.   These calculations are based on the premise that none of the methacryloxychlorobutane is volatilized.   It is evident from comparisons in Tables III and II that essentially all of the *t*-butyl alcohol was removed as desired, along with roughly one third of the methacrylic acid and one half of the chlorobutene material.   This gas chromatograph analysis substantiates the calculated product composition based on chemical analyses as presented in Table II.

Another portion of the total reaction-product mixture was purified by aqueous alkaline washing followed by vacuum fractional distillation (see under "Experimental").   Table IV compares the chemical analyses of the main constant boiling fraction with the corresponding theoretical analytical values for 2-chloro-1-methyl propyl methacrylate.   Agreement is excellent. The gas chromatogram of this purified fraction showed the presence of only one impurity (unidentified, estimated at 2 wt.-%).

TABLE IV
Methacrylated 2-Butene; Isolated Main Product

Analyses	Concn., mmoles/g.	Theory,[a] mmoles/g.
Total chlorine	5.80	5.66
Allylic chlorine	0.02	Zero
Acidity	0.01	Zero
Saponification	11.24	11.32
Unsaturation, cat. H_2	5.43	5.66
Vinyl unsat., NIR[b]	5.64	5.66

[a] Theoretical values for the compound 2-chloro-1-methyl propyl methacrylate.
[b] Near-infrared quantitative method.[9]

This isolated main product homopolymerized (see under Experimental) to a water-clear, hard, rigid solid. The casting had a flexural strength of 7480 psi and a flexural modulus of 396,000 psi with only 1.2 in. deflection. A Clash-Berg curve of elastic modulus versus temperature showed that the

TABLE V
Methacrylated 3-Heptene: Analyses and Product Composition

	Concn., mmoles	Substituent,[a] mole-%
Reactants:		
3-Heptene	500	
Methacrylic acid	500	
t-Butyl hypochlorite	500	
p-Methoxy phenol	0.2	
Total reaction-product mixture:		
Total chlorine	507	101 chlorine
Allylic chlorine	37	7 allylic[b]
Acidity	150	70 methacryloxy
Saponification	959	8 butoxy[c]
t-Butyl alcohol, GLC[d]	453	9 butoxy
Unsaturation, cat. H_2	642	28 non-vinyl
Vinyl unsat., NIR[e]	498	70 methacryloxy
Heptene derivatives mixture:[f]		
Total chlorine	502	100 chlorine
Allylic chlorine	40	8 allylic
Acidity	2	negligible
Saponification	797	11 butoxy
t-Butyl alcohol, GLC[d]	3	negligible
Unsaturation, cat. H_2	462	24 non-vinyl
Vinyl unsat., NIR[e]	341	68 methacryloxy

[a] Based on the 3-heptene.
[b] Chloride reactive at room temperature with silver nitrate.[7,8]
[c] Based on inability of alcoholic alkali to saponify vicinal alkoxychloro substituents.
[d] Gas–liquid chromatography method.
[e] Near-infrared quantitative method.[9]
[f] Obtained by aqueous, alkaline washing of total reaction product.

polymer was definitely thermoplastic. The T_4 value was 74°C., and the heat-distortion temperature at 66 psi was 66°C.

Other Acrylated Olefins

Table V presents the data for a methacrylated 3-heptene product. The product composition is determined as mole per cent substituents on the heptene, calculated from chemical and physical analyses. These analyses were made both on the total reaction-product mixture and on the heptene derivatives mixture, separated by aqueous alkaline washing of the total reaction-product mixture in order to remove the unreacted methacrylic acid reactant and the t-butyl alcohol by-product.

Various other olefins reacted, were recovered, and were analyzed as described for 3-heptene. Table VI presents a summary of the products formed in each case. The products are reported as mole per cent of specific olefin derivatives based on the total unsaturation of the original olefin.

TABLE VI
Acrylated Olefins: Product Composition

| | | Olefin derivatives formed,[a] mole-% | | | |
Olefin	Vinyl acid	Acryloxy-chloro	Butoxy-chloro	Allylic chloro	Nonallylic chloro
2-Butene	methacrylic	80	5	2	13
3-Heptene	methacrylic	69	9	8	14
3-Heptene	acrylic	75	7	7	11
1-Hexadecene	methacrylic	70	9	9	12
1-Octadecene	acrylic	68	10	9	13
Cyclooctene	acrylic	70	10	10	10
1,5-Cyclooctadiene	methacrylic	55	16	12	17
1,5-Cyclooctadiene	acrylic	53	16	11	18
Dicyclopentadiene	methacrylic	48[b]	14[b]	28[b]	10[b]
Styrene	acrylic	42	35	9	14

[a] Based on the total unsaturation of the original olefin.
[b] Based on one-half the total unsaturation in the dicyclopentadiene.

TABLE VII
Acrylated Olefin Homopolymers[a]

Crude olefin product	Homopolymer gross characteristics
Acrylated 3-heptene	clear, pale yellow, med. hard, brittle solid
Methacrylated 3-heptene	water-clear, hard, rigid solid
Methacrylated 1-hexadecene	clear, tacky, stringy, semisolid
Acrylated 1-octadecene	clear, tacky, stringy, semisolid
Acrylated cyclooctene	clear, pale yellow, flexible solid
Methacrylated 1,5-cyclooctadiene	clear, pale yellow, hard, brittle solid
Methacrylated dicyclopentadiene	black, soft gel; air-drying
Acrylated styrene	clear, pale yellow, flexible solid

[a] Formed by mixing the vinylated olefin with 0.5 wt.-% azobisisobutyronitrile, heating at 70°C. for 24 hr., and giving a postcure for 1 hr. at 100°C.

Dicyclopentadiene is the one exception. In this case only one-half mole of t-butyl hypochlorite and one-half mole of methacrylic acid were combined with 1 mole of dicyclopentadiene.
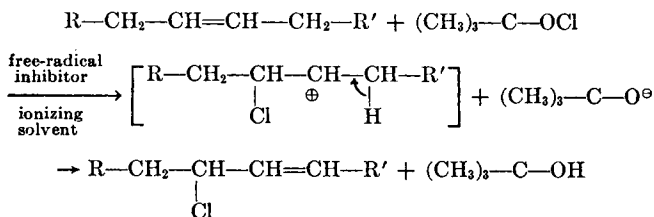
The separated crude olefin products were clear, faintly yellow, very low-viscosity fluids. All homopolymerized readily. Table VII records the gross physical characteristics of the homopolymers. Copolymers with styrene, methyl methacrylate, butyl acrylate, and vinyl acetate also formed.

DISCUSSION

In all preparations the major product was the desired acryloxychloro derivative of the olefin. One minor product was always the predicted butoxychloro derivative. A second, unpredicted, minor product was chlorinated olefin. This was determined by analyses of the separated olefin derivatives, which showed that 100 mole-% of the hypochlorite chlorine was attached to the olefin, yet olefinic unsaturation still remained. This remaining unsaturation was equivalent to the difference between the original olefinic unsaturation and that converted by addition reactions to the combined acryloxychloro and butoxychloro structures.

Walling and Thaler[10] have shown that t-butyl hypochlorite is an efficient free-radical allylic chlorinating agent when combined with olefins. We demonstrated the exclusively free-radical nature of this reaction by combining 1-octadecene, t-butyl hypochlorite, and p-methoxy phenol at room temperature in the light. No reaction occurred, and the t-butyl hypochlorite was recovered essentially quantitatively by distillation from the olefin. However, when acrylic acid was added to a similar olefin–hypochlorite–phenol mixture, an exothermic reaction occurred, and the products formed were comparable in analyses to those reported for 1-octadecene in Table VI.

It was first postulated that the chlorinated, olefinic, unsaturated derivative was all allylic chloro olefin, which had been formed by ionic attack of the olefin unsaturation by the positive t-butyl hypochlorite, followed by isomerization of the double bond and proton release, forming t-butyl alcohol by-product. Thus:

$$R-CH_2-CH=CH-CH_2-R' + (CH_3)_3-C-OCl$$

$$\xrightarrow[\substack{\text{ionizing} \\ \text{solvent}}]{\substack{\text{free-radical} \\ \text{inhibitor}}} \left[\begin{array}{c} R-CH_2-CH-CH-CH-R' \\ \overset{|}{C}l \quad \overset{\oplus}{} \quad \overset{|}{H} \end{array} \right] + (CH_3)_3-C-O^{\ominus}$$

$$\rightarrow R-CH_2-\underset{\underset{Cl}{|}}{CH}-CH=CH-R' + (CH_3)_3-C-OH$$

However, analyses showed that only a portion of the total chlorinated, olefinic, unsaturated derivative was allylic chlorinated. The analytical method determines chloride reactive at room temperature with silver nitrate.[7,8] Experience with purified compounds (allyl chloride and allylic

chlorinated heptene) has shown this analysis to be a valid measure of these allylic chloride compounds.

It is evident from Table VI that 10–15 mole-% of nonallylic chlorinated olefin is formed in every preparation. One could postulate that this occurs by migration of the unsaturation farther down the carbon chain of the aliphatic olefins before proton release. Another postulate is that vinylene chloride substituents are formed by ionic attack of the olefins by the t-butyl hypochlorite followed by proton release from the attacked carbon. It may be possible, as discussed by Shelton and Kosuga,[11] that competing reactions, which form products postulated by an ionic mechanism and products postulated by a free-radical mechanism, are occurring simultaneously. Further study is necessary before the structure of this nonallylic chlorinated olefin product can be definitely established.

EXPERIMENTAL

Materials

Methacrylic and Acrylic Acid. Rohm and Haas 99% purity commercial materials containing 0.025 and 0.020%, respectively, p-methoxy phenol.

2-Butene. Phillips Petroleum, 96% purity, commercial, 50:50 mixture of cis and $trans$ isomers.

3-Heptene. Phillips Petroleum, 95% purity, technical, mixed cis and $trans$ isomers.

1-Hexadecene and 1-Octadecene. Gulf, commercial, close-cut fractions, 99% mixed monoolefins.

Cyclooctene and 1,5-Cyclooctadiene. Columbia Carbon, 96 and 98% purity, commercial materials.

Dicyclopentadiene. Enjay, 95% purity, commercial material.

t-Butyl Hypochlorite. This was prepared as described in a United States patent.[12] The procedure is similar to that of Teeter and Bell[13] but is modified so as to minimize the concentration of free chlorine, hypochlorous acid, and hydrochloric acid by-products. The yields were 95–96% product, which were analyzed as 98–100% t-butyl hypochlorite by iodometric titrations for active chlorine. By adapting a procedure from Scott's "Standard Methods"[14] the analyses for $true$ t-butyl hypochlorite indicated 96–98% purity.

Preparation of Methacrylated 2-Butene

Methacrylic acid (80.4 g., 930 mmoles), $para$-cresol (0.23 g., 2 mmoles), and t-butyl hypochlorite (76.3 g., 700 mmoles) were combined at room temperature. 2-Butene gas (64.3 ml., 40.6 g., 700 mmoles) was bubbled slowly into this mixture while the exothermic reaction was maintained at 25 to 30°C. by external cooling. After all the 2-butene was added, the temperature was allowed to rise and was maintained at 45°C., until a negative active chlorine result for hypochlorite was obtained. This was the total reaction-product mixture.

A portion of the total reaction-product mixture was stripped on a rotary flash evaporator, first at 65°C. and 25 mm. and then at 65°C. and 5 mm. This vacuum-stripped crude product was used for gas chromatographic analysis.

A second portion of the total reaction-product mixture was dissolved in ethyl ether and washed with 8% aqueous disodium acid phosphate solution until alkaline, and then with distilled water until neutral (pH 6). para-Cresol (0.03 wt.-% of the estimated product) was added, and the washed material was fractionally vacuum-distilled through a 250 mm. indented Vigreaux column combined with a Claisen head. The main fractions (606 g. distilled between 40 and 43°C. at 1.3 to 1.2 mm.) were combined and redistilled to form the isolated 2-chloro-1-methyl propyl methacrylate (426 g. distilling at 34°C. and 0.5 mm. Hg with $n_D^{25} = 1.4426$). This procedure is typical of olefins that are gases at room temperature.

Preparation of Methacrylated 3-Heptene

A mixture of 3-heptene (49.0 g., 500 mmoles), methacrylic acid (43.3 g., 500 mmoles), and p-methoxy phenol (0.025 g., 0.2 mmole) was heated to 60°C. Tertiary butyl hypochlorite (54.5 g., 500 mmoles) was added slowly while the exothermic reaction was controlled at 65°C. by external cooling. When the exothermic reaction subsided, the temperature was maintained at 65°C. by heating, until the mixture gave a negative active chlorine result for hypochlorite. This was the total reaction-product mixture.

A portion of this total reaction-product mixture was dissolved in 2 vol. of ethyl ether and washed, first with 8% aqueous disodium acid phosphate solution until alkaline and then with distilled water until neutral (pH 6). para-Methoxy phenol (0.02 wt.-% of the estimated product) was added, and the ether solvent was removed by distillation on a rotary flash evaporator at 65°C. and 25 mm. The recovered residue was the separated heptene derivatives. This preparative procedure is typical of all the liquid olefins.

Polymerization Technique

The monomers were bulk-homopolymerized or copolymerized with commercial vinyl monomers by mixing with 0.5 wt.-% azobisisobutyronitrile as initiator and heating at 70°C. for 24 hr. This was followed by a postcure of 1 hr. at 100°C. Benzoyl peroxide was also an efficient initiator.

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