

# The Relative Inhibitory Effect of Various Compounds on the Rate of Polymerization of Vinyl Acetate.

## II. Effect of Conjugated and Unconjugated Acetylenes and Olefins

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### Synopsis

The relative inhibitory effects of hexene-1, hexyne-1, *trans*-hexene-2, *cis*-hexene-2, hexyne-2, 1,5-hexadiene, 1,5-hexadiyne, 1,7-octadiyne, 1,8-octadiyne, 1-hexen-5-yne, 4-chloro-1,2-butadiene, chloroprene, 2,5-dimethyl-2,4-hexadiene, 2,4-hexadiyne, 2-methyl-1-buten-3-yne, styrene, ethynylbenzene, hydroquinone, and *p*-methoxyphenol on the bulk polymerization of vinyl acetate were measured. Polymerization was carried out at 70°C. in a test tube in the presence of benzoyl peroxide. A comparison was made of the magnitude of the inhibitory effect due to isolated and conjugated, double and triple bonds as well as cumulative double bonds. A brief comparison between aliphatic and aromatic compounds was also made.

The effect of certain organic compounds on the rate of polymerization of vinyl acetate was recently reported by this laboratory.<sup>1</sup> The investigation has now been extended to include both conjugated and unconjugated, acetylenic and olefinic, aliphatic hydrocarbons as well as a few aromatics. To obtain as great a difference in results as possible between compounds, the polymerization was carried out in a test tube immersed in a water bath at 70°C. (Method B<sup>1</sup>) rather than in a flask heated with a Glas-Col mantle (Method A<sup>1</sup>). Since some of the compounds studied were exceedingly weak inhibitors, the possibility of serious errors occurring due to the presence of minute concentrations of strongly inhibiting impurities was high. To reduce this possibility to a minimum, it was often necessary to purify the samples by passing them through one or two gas-liquid chromatographic columns.

### Experimental

A 10-ml. portion of vinyl acetate containing 0.0200 g. of benzoyl peroxide and a known amount of inhibitor was polymerized in a test tube immersed in a water bath at 70.0 ± 0.05°C. (Method B<sup>1</sup>). The vinyl acetate was commercial grade, Shawinigan Chemicals Ltd. material. Its absorbance

(undiluted) was 0.4–0.5 when measured with a Beckman DK-2 spectrophotometer in a 1 cm. cell against isoctane at 265  $m\mu$ .

The inhibitors are listed below in the same order as given in Table I. They were purified, and their purity determined with the following gas-liquid chromatographic (GLC) columns: (A) dimensions  $\frac{1}{2}$  in. I.D.  $\times$  20 ft., 18% tricresyl phosphate and 2% Carbowax-600 on firebrick C-22, 35–60 mesh, 60°C., carrier gas hydrogen, 300 ml./min.; (B) dimensions  $\frac{1}{4}$  in. I.D.  $\times$  6 ft., Perkin-Elmer "R," Ucon oil, 143°C., carrier gas helium, 35 ml./min.; (C) dimensions  $\frac{1}{2}$  in. I.D.  $\times$  20 ft., 20% Ucon oil LB 550X on firebrick C-22, 56°C.; carrier gas hydrogen, 300 ml./min.; (D) dimensions 1 in. I.D.  $\times$  20 ft., 20% Ucon oil LB 550X on C-22 firebrick, 110°C.; carrier gas helium, 400 ml./min.; (E) dimensions  $\frac{1}{4}$  in. I.D.  $\times$  12 ft., 15% Dow Corning silicone oil 704 on Fluoropak 80, 100°C., carrier gas helium, 33 ml./min.; (F) dimensions  $\frac{1}{4}$  in. I.D.  $\times$  20 ft., 20% Ucon oil LB 550X on C-22 firebrick, 100°C., carrier gas helium, 60 ml./min.; (G) dimensions  $\frac{1}{4}$  in. I.D.  $\times$  20 ft., 15% F & M mixture sorbitol-silicone oil X525 on Chromosorb W, 100°C., carrier gas helium, 40 ml./min.; (H) dimensions  $\frac{1}{4}$  in. I.D.  $\times$  6 ft., 10% hexadecanol on Fluoropak 80, 75°C., carrier gas helium, 40 ml./min.; (I) dimensions  $\frac{1}{2}$  in. I.D.  $\times$  20 ft., 15% F & M mixture sorbitol-silicone oil X525 on Chromosorb W, 47°C., carrier gas hydrogen, 300 ml./min.

Hexene-1, purchased from Phillips Petroleum Co., was purified by passage through column E at 30°C. Its purity appeared to be 99.95% from the chromatogram obtained with GLC column B at 60°C.

Hexyne-1 was prepared by reacting sodium acetylide with *n*-butyl bromide in liquid ammonia.<sup>2</sup> It was purified by using GLC column A, and its purity appeared to be over 99.9%.

Hexene-2 was obtained from Phillips Petroleum Co. The *cis* form was separated from the *trans* by passage three times through GLC column A. Both forms appeared to be over 99% pure by chromatography.

Hexyne-2 was prepared by brominating hexene-2 at  $-60^\circ\text{C}$ . and then dehydrobrominating with sodium amide in liquid ammonia.<sup>3</sup> It was purified by passage through GLC column A. Purity by chromatography appeared to be 99.99%.

1,5-Hexadiene was prepared by reacting allyl chloride with magnesium turnings in ether.<sup>4</sup> It was purified by distillation and gas-liquid chromatography. Its purity appeared to be 99.7% from the chromatogram obtained with GLC column B.

1,5-Hexadiyne was obtained by brominating 1,5-hexadiene and then dehydrobrominating with sodium amide in liquid ammonia.<sup>5</sup> The hexadiyne was purified by passage through GLC columns A and C. Its purity appeared to be 99.99% by chromatography. A second sample was purchased from Farchan Research Laboratories and it was similarly purified. It gave the same inhibition factor as the sample synthesized by the authors.

1,7-Octadiyne and 1,8-nonadiyne were purchased from Farchan Research

Laboratories and were purified by passage through GLC column D. The purity of the octadiyne appeared to be 99.75% and that of the nonadiyne 99.6%, as determined with GLC column E at 150°.

1-Hexen-5-yne was prepared by two methods. A 10% solution of 1,5-hexadiyne in methyl amyl acetate was hydrogenated with stirring at 20°C. and atmospheric pressure with the theoretical amount of hydrogen. 10.8% of 5% palladium on carbon, based on the weight of 1,5-hexadiyne, was used as catalyst. The yield and conversion to 1-hexen-5-yne were 35.6% and 16.3%, respectively. The crude was distilled to remove the diluent and then purified by passage through GLC columns D and E. Purity appeared to be almost 100% as determined with GLC column E. The purified product absorbed 97% of the theoretical amount of hydrogen and reacted with 92.2% of the theoretical amount of silver nitrate. In the second method of synthesis, 1,5-hexadiene (purchased from Aldrich Chemical Co.) was first partially brominated to 5,6-dibromo-1-hexene, and the latter was then dehydrobrominated with sodamide in liquid ammonia. A 33% solution of bromine in methyl cyclohexane was added dropwise over a period of 75 min. to stirred 1,5-hexadiene at -78°C. After standing overnight at 0°C. the crude was fractionally distilled. The dibromohexene was then dehydrobrominated with 110% of the theoretical amount of sodamide in liquid ammonia. The mixture was stirred for 3 hr. at -78°C., 1 hr. at -78 to -33°C., and 1¼ hr. at -32°C. The reaction was killed with 2% ammonium chloride solution. The organic layer was separated, distilled, and purified by passage through GLC columns C and E. From GLC columns F, G, and H, the purity appeared to be 99.95%.

A mixture of 4-chloro-1,2-butadiene and chloroprene was prepared by the reaction of monovinylacetylene with 37% hydrochloric acid at 20°C. in the presence of calcium chloride.<sup>6</sup> They were distilled in a short column at 220 mm. Hg absolute and purified by passage through GLC column I. From chromatography, the 4-chloro-1,2-butadiene appeared to be over 99.9% pure and the chloroprene 99.7% pure.

2,5-Dimethyl-2,4-hexadiene was generously supplied by Eastman Chemical Products Inc. It was distilled under high vacuum and appeared to be 99.98% pure, as determined with GLC column B.

2,4-Hexadiyne was prepared by adding the dry copper derivative of methyl acetylene to a boiling 12% solution of potassium ferricyanide in water and distilling the product as it formed.<sup>7</sup> The crude was purified by distillation, dried with Linde molecular sieves 4A, and appeared to be over 99% pure by chromatography. A second sample was purchased from K & K Laboratories and was used as received. It appeared to have a purity of 99.9% by chromatography and it gave the same inhibition factor as the material prepared by the authors.

2-Methyl-1-buten-3-yne was purchased from Aldrich Chemical Co. It was distilled under vacuum and appeared to be 99.8% pure by chromatography.

TABLE I Inhibition Factors and Ultraviolet Spectra of Various Compounds

Compound	Inhibition/ppm		Activity original V.A., sec.	Concn. range, ppm.	Synergism molar based on hexene-1 and hexyne-1	Ultraviolet spectrum <sup>a</sup>	
	Min.	Min. X mol. wt.				$\lambda_{max}$ , m $\mu$	$\epsilon_{max}$
Hexene-1	0.00203	0.170	982	0-6000			
Hexyne-1	0.00345	0.284	990	0-5000			
<i>trans</i> -Hexene-2	0.0069	0.581	970	0-2800			
<i>cis</i> -Hexene-2	0.0053	0.446	970	0-3600			
Hexyne-2	0.0051	0.42	919	0-3600			
1,5-Hexadiene	0.0092	0.756	990	0-1800	120	207 <sup>b</sup>	39
1,5-Hexadiyne	0.0385	3.01	969	0-400	430		
1,7-Octadiyne	0.0262	2.78	925	0-1000	390	208 <sup>b</sup>	40
1,8-Nonadiyne	0.00934	1.12	924	0-2800	100	209.7 <sup>b,c</sup>	22
1-Hexen-5-yne	0.0094	0.75	935	0-900	65		
4-Chloro-1,2-butadiene	0.0286	2.53	977	0-700	640	209 <sup>b</sup>	840
Chloroprene	0.521	46.1	974	0-42	13,400	222.4	19,600
2,5-Dimethyl-2,4-hexadiene	0.765	84.3	970	0-20	24,600	242.3	24,800
<i>trans</i> -1-Acetoxy-1,3-butadiene <sup>1</sup>	0.443	49.7	—	—	14,500	233.2	26,000
<i>cis</i> -1-Acetoxy-1,3-butadiene <sup>1</sup>	0.577	64.8	—	—	18,900	233.8	26,000
2,4-Hexadiyne	0.135	10.6	960	0-170	1,770	235.5 <sup>b</sup>	307
Diacetylene <sup>1</sup>	0.69	34.6	—	—	6,000	234.9 <sup>b</sup>	270
2-Methyl-1-buten-3-yne	0.69	45.6	919	0-36	9,950	225.7	8,620
<i>trans</i> -1,3,5-Hexatriene <sup>1</sup>	1.57	126.	770	0-12	24,600	255.4	52,000
Divinylacetylene <sup>1</sup>	1.33	104.	790	0-15	16,500	253	19,000
1,3-Butadienylacetylene <sup>1</sup>	1.34	104.5	—	—	16,600	252	26,300
Styrene	0.175	18.2	960	0-100	—	247.3	15,100
Ethynylbenzene	0.395	40.4	940	0-50	—	234.6	17,000
Hydroquinone	1.01	111.	842	0-40	—	298.8	3,030
<i>p</i> -Methoxyphenol	0.51	63.4	842	0-40	—	291.6	2,990

<sup>a</sup> Solvent was isoctane except in the case of hydroquinone and *p*-methoxyphenol where it was absolute ethanol.

<sup>b</sup> Subsidiary band. In all other cases, the main band is given. <sup>c</sup> Single determination.

Styrene was obtained from Dow Chemical Co. After high vacuum distillation, its purity appeared to be 99.8% as determined with GLC column B.

Ethynylbenzene was purchased from Farchan Research Laboratories and was distilled under vacuum. Its purity appeared to be over 99.9% from chromatography.

Hydroquinone, purified grade, was used as received from J. T. Baker Chemical Co.

*p*-Methoxyphenol was used as received from Eastman Kodak Co.

### Results

Known amounts of the compounds given in Table I were added to vinyl acetate and the time to reach a spontaneous boil determined. For the sake of completeness, a few compounds previously studied<sup>1</sup> were included in the table. In each case, the length of time to reach a spontaneous boil was plotted against the concentration of inhibitor. As in the previous investigation,<sup>1</sup> the initial part of the curve was found to be a straight line and its slope was taken as a measure of the inhibitory effect of the compound. The inhibition factor, expressed in minutes per ppm, was calculated as previously.<sup>1</sup>

As will be seen from Table I, a single terminal olefinic group (e.g., hexene-1) is a very weak inhibitor. A single internal double bond (e.g., hexene-2) appears to be stronger than a terminal double bond, the *trans* being slightly stronger than the *cis*. This is in contrast to previous results,<sup>1</sup> in which *cis*-1-acetoxy-1,3-butadiene was found to be stronger than the *trans* isomer. The addition of a second unconjugated, terminal double bond to the molecule enhances the inhibition somewhat (e.g., 120% for 1,5-hexadiene) over that due to the sum of two terminal double bonds. The enhancement of the inhibitory effect or percentage molar synergism, as given in Table I, was calculated from the following expression:

$$\frac{(\text{Molar inhibition factor of compound} - a \times 0.170 - b \times 0.284)}{(a \times 0.170 + b \times 0.284)} \times 100$$

The molar inhibition factor is expressed in (minutes per ppm)  $\times$  (molecular weight), *a* is the number of double bonds in the compound, *b* is the number of triple bonds, 0.170 is the molar inhibition of a single terminal double bond, and 0.284 the molar inhibition of a single terminal triple bond. When the second double bond is conjugated, the synergism increases to 13,000–25,000 (e.g., chloroprene, 2,5-dimethyl-2,4-hexadiene, *cis*- and *trans*-1-acetoxy-1,3-butadiene). The addition of a third conjugated double bond (e.g., 1,3,5-hexatriene) increases the molar inhibition factor by an additional 50% but the percentage synergism remains the same.

A single terminal acetylenic group (e.g., hexyne-1) is also a very weak inhibitor but appears to be somewhat stronger than a terminal olefin. A

single internal acetylene (e.g., hexyne-2) appears to be stronger than a terminal (cf. olefins). Addition of a second terminal, unconjugated triple bond to the molecule gives a relatively high synergesis (e.g., 430% for 1,5-hexadiyne). However, as the two acetylenic groups become further separated in the molecule, the synergesis gradually decreases (e.g., 1,7-octadiyne and 1,8-nonadiyne). When the second triple bond is conjugated, the synergesis increases to 1800–6000% (e.g., diacetylene and 2,4-hexadiyne). In contrast to olefinic compounds, the terminal diyne, diacetylene, appears to be several times stronger than the nonterminal diyne, 2,4-hexadiyne.

A terminal olefinic group together with an unconjugated terminal acetylene (e.g., 1-hexene-5-yne) has a synergesis of the same order as that possessed by two terminal, unconjugated, double bonds. However, when the double and triple bonds are conjugated, the synergesis increases to about 10,000% (e.g. 2-methyl-1-buten-3-yne). The inhibition factor for 2-methyl-1-buten-3-yne (b.p. 34–34.5°C.) was found to be considerably higher than that for monovinylacetylene (b.p. 6°C.). Previously it was reported that the inhibition factor for monovinylacetylene was considerably lower than that predicted from calculations, perhaps due to its boiling out during the polymerization.<sup>1</sup> The inhibition factor now obtained for the vinylacetylenic structure from 2-methyl-1-buten-3-yne is within 10% of that calculated. When another conjugated double bond is added to the molecule (e.g., divinylacetylene and 1,3-butadienylacetylene) both the inhibition factor and the synergesis greatly increase in value.

Cumulative double bonds (e.g., 4-chloro-1,2-butadiene) have a synergesis intermediate between that of two isolated and two conjugated double bonds. From previous work, this was, perhaps, not unexpected.

When a vinyl or ethynyl group is conjugated with benzene, the inhibitory effect is many times greater than when it is combined with a saturated hydrocarbon chain. However, the effect of the benzene ring is equivalent to less than one conjugated double bond (e.g., styrene and ethynylbenzene).

Hydroquinone and *p*-methoxyphenol, which are used commercially as stabilizers for vinyl acetate, were found to be strong inhibitors. Since hydroquinone is almost twice as strong as *p*-methoxyphenol, the inhibition factor appears to be a function of the number of hydroxyl groups. The inhibition factor is also influenced by the relative position of the hydroxyls on the benzene ring and by the other substituent groups present.<sup>8</sup> Hydroxyls combined with saturated aliphatic chains are, of course, almost without inhibitory effect.

The fact that certain strong aliphatic inhibitors (e.g., divinylacetylene) have high extinction coefficients in the ultraviolet has been used as the basis for a convenient method for determining their concentration in vinyl acetate.<sup>9</sup> In the case of conjugated aliphatic polyenes and enynes, it has already been shown that the inhibition factor increases with the number of conjugated unsaturated groups.<sup>1,10</sup> From Figures 1 and 2 it will be seen that there appears to be a rough relationship between the molar inhibition

factor, and the molar extinction coefficient or the wavelength of the main ultraviolet absorption band. From the few aromatic compounds studied, a similar relationship for aromatics could not be established.

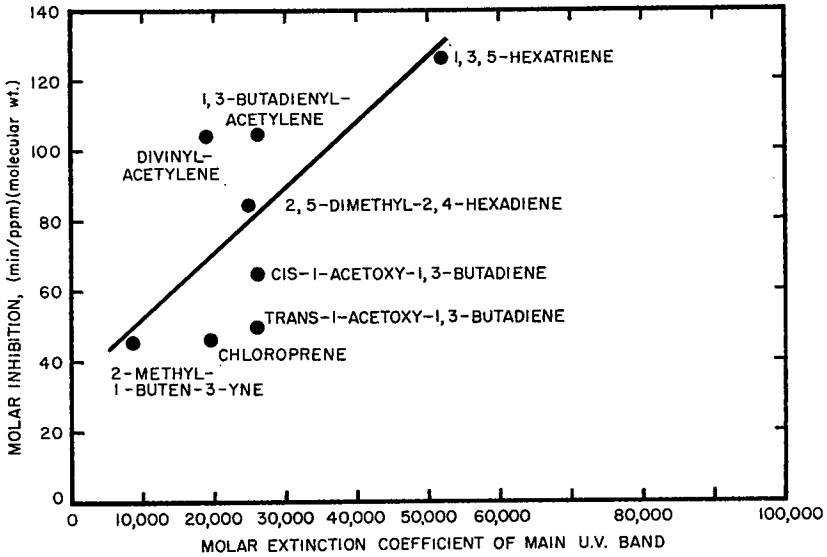


Fig. 1. Time delay in spontaneous boiling of vinyl acetate, (min./ppm.) × (molecular weight) vs. molar extinction coefficient of main ultraviolet absorption band of various polyenes and enynes.

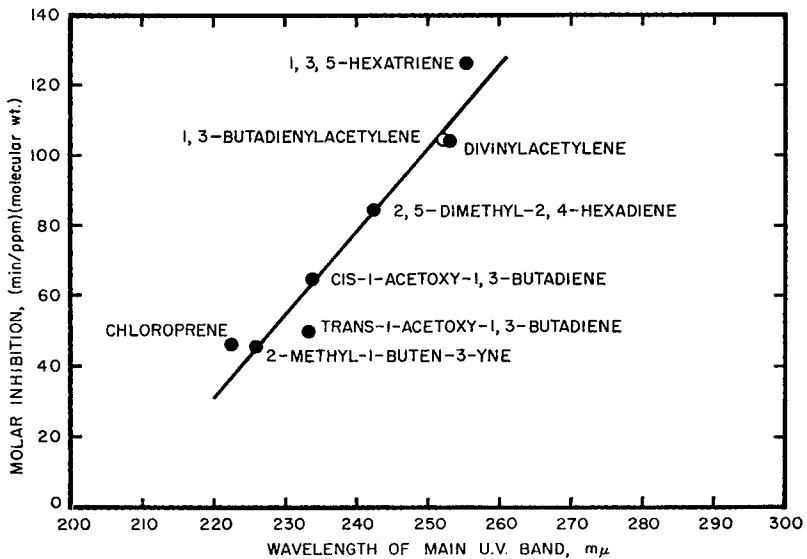


Fig. 2. Time delay in spontaneous boiling of vinyl acetate, (min./ppm.) × (molecular weight), vs. wavelength of main ultraviolet absorption band, mμ, of various polyenes and enynes.

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### Résumé

On a mesuré les effets relatifs d'inhibitor de l'hexène-1 de l'hexyne-1, du *trans*-hexène-2, du *cis*-hexène-2, de l'hexyne-2, du 1,5-hexadiène, du 1,5-hexadiyne, du 1,7-octadiyne, du 1,8-octadiyne, du 1-hexène-5-yne, du 4-chloro-1,2-butadiène, du chloroprène, du 2,5-diméthyl-2,4-hexadiène, du 2,4-hexadiyne, du 2-méthyl-1-butène-3-yne, du styrène, de l'éthynylbenzène de l'hydroquinone et du *p*-méthoxyphénol sur la polymérisation en bloc de l'acétate de vinyle. On a effectué la polymérisation à 70°C dans un tube à essai en présence de peroxyde de benzoyle. On a comparé l'importance de l'effet inhibiteur dû aussi bien à des liaisons doubles et triples conjuguées ou isolées qu'à des doubles liaisons cumulatives. On a également comparé des composés aliphatiques et aromatiques.

### Zusammenfassung

Es wurde die relative Inhibitorwirkung von Hexen-1, Hexin-1, *trans*-Hexen-2, *cis*-Hexen-2, Hexin-2, 1,5-Hexadien, 1,5-Hexadiin, 1,7-Octadiin, 1,8-Octadiin. 1-Hexen-5-in, 4-Chlor-1,2-Butadien, Chloropren, 2,5-Dimethyl-2,4-Hexadien, 2,4-Hexadiin, 2-Methyl-1-buten-3-in, Styrol, Äthynylbenzol, Hydrochinon und *p*-Methoxyphenol auf die Polymerisation von Vinylacetat in Substanz bestimmt. Die Polymerisation wurde bei 70° in einem Reagenzglas in Gegenwart von Benzoylperoxyd durchgeführt. Die Inhibitorwirkung von isolierten und konjugierten Doppel- und Dreifachbindungen sowie von kumulierten Doppelbindungen wird verglichen. Ausserdem wurde kurz ein Vergleich zwischen aliphatischen und aromatischen Verbindungen angestellt.

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