

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

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A number of investigations of limited scope concerning the effect of certain compounds on the rate of polymerization of vinyl acetate have been made.<sup>1-18</sup> However, to make a quantitative correlation of results for even these compounds is difficult, owing to differing experimental conditions. Because of the technical importance of knowing the relative inhibitory effects of various types of compounds on vinyl acetate, this investigation was undertaken. Some of these compounds have been reported previously in the literature as being present in small concentrations in commercial monomer.

The compounds were first investigated by means of a modification of the polymerization (activity) test previously described<sup>8</sup> (Method A). The use of controlled heating with a Glas-Col mantle, according to a method introduced by Henning and Godfrey of Shawinigan Resins Corporation, resulted in much greater reproducibility than had been previously obtained. Deviations never exceeded  $\pm 1.5\%$  and were usually less than  $1\%$ , although a great deal of practice was required to obtain the latter degree of reproducibility. In dealing with very pure samples of vinyl acetate, it has been found that reproducibility and differentiation can be improved by use of a test (Method B) in which only one tenth as much benzoyl peroxide catalyst is used as is used in Method A and the reaction tube is immersed in a liquid bath at  $70^{\circ}\text{C}$ . A few of the compounds were studied by means of this test as well as by Method A.

### EXPERIMENTAL

#### Method A

The polymerization test was carried out as follows. 0.400 g. of reprecipitated Eastman-Kodak

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benzoyl peroxide was placed in a very clean 100-ml. Pyrex round-bottomed flask (Corning) with a female 24/40 standard tapered joint. (The actual capacity of the flask was 125 ml.) Vinyl acetate (21.4 ml. 20 g. at  $20^{\circ}\text{C}$ .) was pipetted into the flask and the flask was shaken to dissolve the peroxide. A Liebig condenser (500 mm. length  $\times$  12-13 mm. i.d., Fisher catalogue no. 7-721) with a male 24/40 standard tapered joint was attached. The condenser was filled with water at room temperature and the flow was stopped. A 125-ml. Glas-Col mantle (originally at room temperature) was heated for exactly 45 sec. and placed under the flask. (The voltage on the mantle had been adjusted so that the heat supplied would cause the first drop of condensate to fall after  $120 \pm 3$  sec.) The stop watch was started at the instant the first drop fell. Heating was continued thereafter for exactly 15 sec., and then the mantle was quickly removed and an empty beaker placed around the flask to shield it from drafts. The stop watch was stopped when the vinyl acetate came to a spontaneous boil.

The boiling should begin sharply. Particles of dust or impurities in the benzoyl peroxide cause a series of small boils which makes it impossible to obtain a definite end point. Practically all commercial samples of benzoyl peroxide were found unsatisfactory and had to be reprecipitated by pouring a filtered, saturated, C.P. chloroform solution of the peroxide into 3 or 4 times as great a volume of filtered C.P. methanol. Immediately after completion of the test, the flask and condenser should be rinsed out with acetone three times and dried with a current of cool air from a hair drier. If it is desired to run a series of tests, the mantle must be cooled to room temperature with a blast of air for at least 12-15 min.; otherwise poor checks are obtained. The values are dependent on the atmospheric pressure. For pure vinyl acetate

the delay in spontaneous boiling per mm. Hg fall in pressure is approximately 0.5 sec.

### Method B

Exactly 0.02000 g. of reprecipitated benzoyl peroxide was placed in a 6 in.  $\times$  1 in. test tube, and 10 ml. of the sample was pipetted in. A glass tube (250 mm.  $\times$  10 mm. i.d.) fitted with a cork was attached to the test tube to act as an air condenser. The entire assembly was placed in an insulated water bath which was maintained at  $70.0 \pm 0.05^\circ\text{C}$ . by means of a Bronwill constant temperature circulator. The position of the test tube was adjusted so that the top of the sample was 1 in. below the surface of the water bath. The time required for the sample to come to a spontaneous boil was recorded. If it is desired to reuse the test tube, ethyl acetate should be added and stirred immediately after the boil, and then the tube should be rinsed with acetone. The results did not appear to be affected by small changes in atmospheric pressure.

The various compounds investigated were obtained or prepared as follows.

The acetaldehyde was refined material obtained from Shawinigan Chemicals Ltd. stills and was used without further purification. Its analyzed purity was better than 99%.

Acetone, purchased from Standard Chemicals Ltd., was dried with Linde Molecular Sieves No. 4A and redistilled.

1-Acetoxy-1,3-butadiene was prepared by reaction of crotonaldehyde and acetic anhydride in the presence of potassium acetate.<sup>19</sup> Examination by infrared spectroscopy indicated that the product was a mixture of *cis* and *trans* forms.<sup>20</sup> By repeated distillation in a column (6 ft. long  $\times$  1 in. i.d., packed with  $\frac{1}{4}$  in. Berl saddles) at 34 mm. Hg absolute, samples composed of at least 90% of one form or the other were obtained. Physical properties, infrared and ultraviolet spectra, and some chemical reactions have already been reported.<sup>20</sup>

1,3-Butadienylacetylene, divinylacetylene, and monovinylacetylene were prepared by circulating acetylene through an aqueous solution of cuprous chloride, ammonium chloride, and hydrochloric acid and were distilled by use of the high-vacuum, low-temperature technique.<sup>21,22</sup> 1,3-Butadienylacetylene (1,3-hexadiene-5-yne) and monovinylacetylene were purified by regeneration from their copper salts. The purity of these compounds was checked by taking their infrared, ultraviolet, and mass spectra.

Mallinckrodt analytical reagent grade carbon disulfide was used without further purification.

Commercial Shawinigan Chemicals Ltd. crotonaldehyde was redistilled and a center cut boiling at  $101.8^\circ$  (uncorr.) (755 mm.) was used.

Diacetyl, purchased from Brickman and Co., was distilled in a Podbielniak column at a pressure of 161 mm. Hg abs. A center fraction boiling at  $50.8^\circ$  (uncorr.) was dried with Linde Molecular Sieves No. 4A and redistilled by use of the high-vacuum, low-temperature technique.

Diacetylene was prepared by the reaction of 1,4-dichloro-2-butyne with sodium hydroxide in ethyl alcohol at  $80^\circ$  and was purified by gas chromatography.<sup>23</sup>

Divinyl sulfide was prepared by the dehydration of thiodiglycol with potassium hydroxide pellets at  $195\text{--}230^\circ$ .<sup>24</sup> It was purified by distillation in a Podbielniak column under reduced pressure (b.p. =  $42.5^\circ$  (uncorr.) at 150 mm. abs.;  $n_D^{20} = 1.5076$ ). Its purity was checked by taking infrared, ultraviolet, and mass spectra.

*Trans*-1,3,5-hexatriene was prepared by adding sodamide to a solution of allyl chloride in liquid ammonia.<sup>25</sup> The crude was purified by high-vacuum, low-temperature distillation followed by gas chromatography. The purity was not established. Ultraviolet extinction coefficients of the three maxima in isoöctane (obtained with a Beckman DK-2 instrument) were  $\epsilon 265.7 \text{ m}\mu = 43,000$ ,  $\epsilon 255.4 \text{ m}\mu = 52,000$  and  $\epsilon 246.3 \text{ m}\mu = 38,000$ . From its infrared and ultraviolet spectra, the product appeared to be essentially the *trans* form.<sup>32</sup>

One sample of thiophene was used as received from the Matheson Co. It had an exceeding strong mercaptan odor and contained 0.3% carbon disulfide. Another sample was prepared by the reaction of succinic anhydride with phosphorus pentasulfide at  $140^\circ$ .<sup>26</sup> The crude product was purified by shaking with caustic solution, digestion with sodium, and distillation through a short column. It had a mild odor and contained 0.1% carbon disulfide.

Commercial toluene was shaken with concentrated sulfuric acid, separated, and distilled.

Commercial Shawinigan Chemicals Ltd. vinyl acetate of specification grade was redistilled in a column 6 ft. long, 1 in. i.d., packed with  $\frac{1}{4}$  in. Berl saddles, and a center fraction was taken. The optical density of undiluted monomer at  $265 \text{ m}\mu$  with isoöctane in the 1 cm. reference cell was 0.40–0.42.

Vinyl propionate obtained from Carbide and

Carbon Chemicals Ltd. was distilled, and a center cut boiling at 56.8° (uncorr.) at 198 mm. abs. was taken.

### RESULTS

Known amounts of various compounds of high purity were added to redistilled vinyl acetate and the time to reach a spontaneous boil was determined by Method A. The values are plotted in Figure 1. It will be noted that in every case the first portion of the curve is, within the limits of experimental error, a straight line. The slope of the straight portion of the curve is a measure of the relative inhibitory effect of each compound; the values of the slopes (in the form of inhibition fac-

tors) are given in Table I. The inhibition factor is arbitrarily defined as the number of seconds or minutes by which very pure vinyl acetate is made less active (i.e., by which its spontaneous boiling is delayed) by addition of one part per million (w/w) of the compound.

Saturated aldehydes were found to be exceedingly weak inhibitors, about one order stronger than saturated ketones. Both these types of saturated compounds are usually considered to be chain-transfer agents.<sup>3,7,18</sup> Unsaturated aldehydes (e.g., crotonaldehyde) are one to two orders stronger than saturated ones (on a molar basis) and are usually considered to be retarders.<sup>13</sup> Generally, it was found that those compounds with inhibition

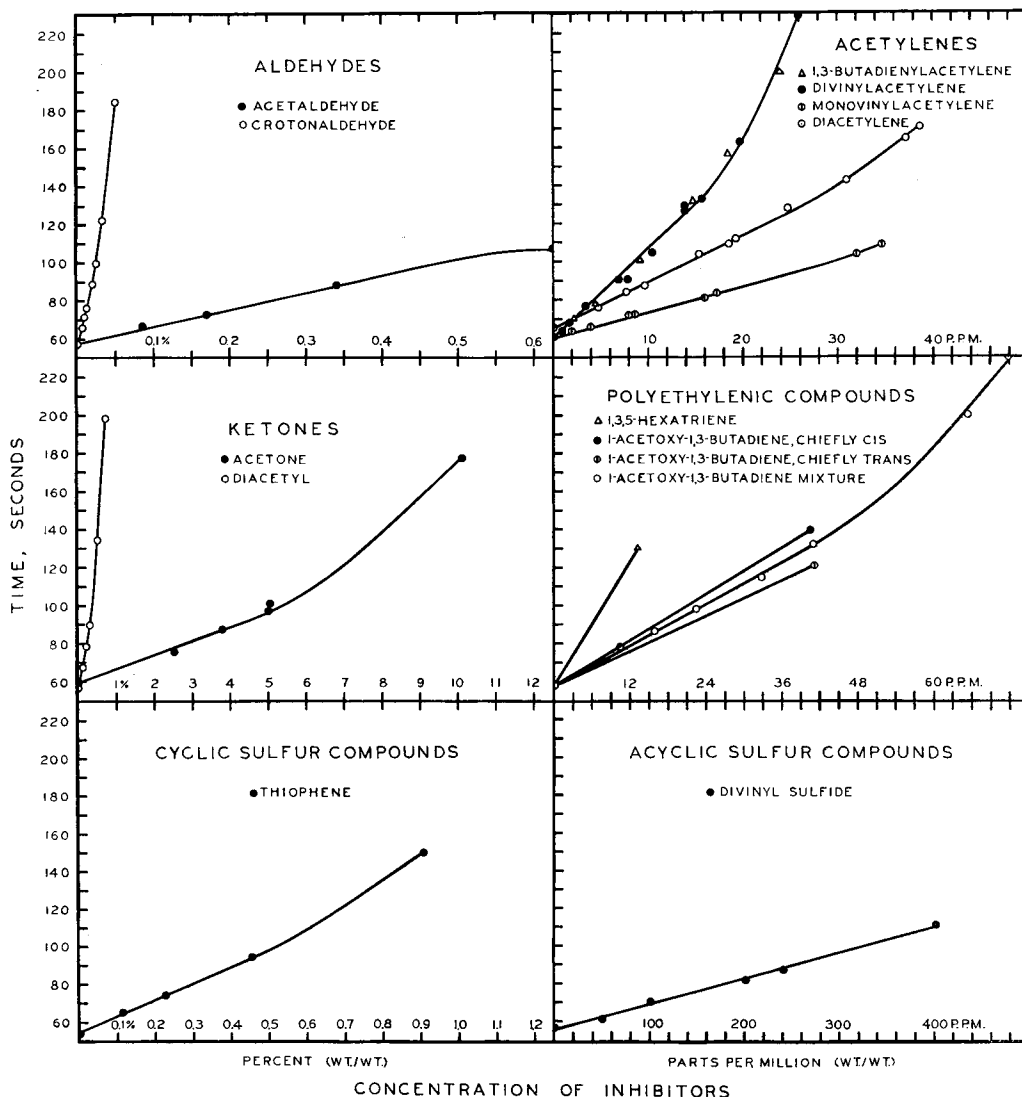


Fig. 1. Time lapse (sec.) until spontaneous boiling of vinyl acetate, vs. concentration of various compounds added.

TABLE I  
 Inhibition Factors of Various Compounds

Compound	Method A				Method B		Comments
	Inhibition factor, sec./ppm	Activity of original vinyl acetate, sec.	Pressure, mm. Hg	Range of concentration	Inhibition factor, min./ppm	Activity of original vinyl acetate, min.	
Acetaldehyde	0.0090	57.3	755	0-0.35%	—	—	—
Acetone	0.00074	59.8	752	0-0.5%	0.0011	12.8	—
1-Acetoxy-1,3-butadiene	2.02	57.5	751	0-40 ppm	—	—	a
	1.55	57.5	753	—	—	—	b
Benzene	—	—	—	—	0.00	12.8	—
1,3-Butadienylacetylene	4.67	57.3	753	0-13 ppm	—	—	—
Carbon disulfide	0.00	—	—	0->103 ppm	—	—	c
Crotonaldehyde	0.161	56.4	764	0-200 ppm	0.062	12.9	—
Diacetyl	0.0108	56.9	753	0-0.28%	—	—	—
Diacetylene	2.42	65.0	745	0-22 ppm	—	—	—
Divinylacetylene	4.65	59.2	750	0-16 ppm	1.33	13.2	—
Divinyl sulfide	0.135	56.4	762	0->400 ppm	—	—	e,d
	0.150	—	—	—	—	—	e
1,3,5-Hexatriene	5.5 <sup>f</sup>	—	—	—	1.57	12.8	g
Monovinylacetylene	1.35	59.2	751	0-30 ppm	—	—	—
Thiophene	0.0088	54.0	758	0-0.5%	—	—	—
Toluene	0.00	—	—	0->0.42%	—	—	e
Vinyl propionate	0.00	—	—	0->1.75%	—	—	e

<sup>a</sup> Chiefly *cis* form.

<sup>b</sup> Chiefly *trans* form.

<sup>c</sup> Not investigated sufficiently to get full range.

<sup>d</sup> First 12 hr.

<sup>e</sup> After 1-2 days.

<sup>f</sup> Calculated from results obtained by Method B.

<sup>g</sup> From infrared and ultraviolet spectra, essentially *trans* form.<sup>32</sup>

factors of the order of 0.01 sec./ppm or less are usually classed as chain-transfer agents rather than inhibitors or retarders.

Diacetyl, a diketone, was found normally to act as a chain-transfer agent, when in a fresh solution. However, on standing in diffuse light in stoppered bottles, most samples (containing from 0.06 to 1.0% diacetyl) polymerized within 12 days. Samples kept in the dark did not polymerize within 3 months. However, an identical sample which had been blown with oxygen for 30 min. did polymerize in the dark after 2 to 3 months. Since dye-sensitized photopolymerizations have previously been observed with various vinyl compounds including vinyl acetate,<sup>27-30</sup> there seems little doubt that such a mechanism was responsible for those polymerizations occurring in diffuse light. However, in the case of the sample which had been blown with oxygen and kept in the dark, it is very probable that a different activation agent was responsible. Peroxide was found in old samples of diacetyl that were stored in bottles sealed under an atmosphere of air. Although freshly distilled di-

TABLE II

Compound	Relative molar inhibition
(1) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	3.63
(2) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	4.41
(3) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$	3.65
(4) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{OAc}$	2.0 (~50% <i>cis</i> ) 2.26 (>90% <i>cis</i> )
(5) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$	0.70
(6) $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	1.21

acetyl was found, by the ferrous sulfate-ammonium thiocyanate test, to contain very little, if any, peroxide, it is not unreasonable to suppose that after several months enough peroxide formed to initiate the polymerization.

All the conjugated polyacetylenic and polyethylenic compounds were found to be strong inhibitors. The greater the number of conjugated unsaturated groups, the greater the inhibition (both on a weight and on a molar basis). A relationship between the number and arrangement of the double and triple bonds in a compound and

the magnitude of its inhibiting effect on acrylonitrile was previously suggested.<sup>8</sup> As will be shown this same relation has been found to hold, in part at least, for vinyl acetate.

Let  $-\text{C}=\text{C}-$  conjugated with  $-\text{C}\equiv\text{C}-$  be  $a$ , and let  $-\text{C}=\text{C}-$  conjugated with  $-\text{C}=\text{C}-$  be  $b$ . Referring to Table II, subtract (1) from (2):

$$2b - 2a = 4.41 - 3.63 = 0.78$$

$$\therefore a = b - 0.39$$

From (2),

$$2b = 4.41$$

$$\therefore b = 2.2$$

$$\therefore a = b - 0.39 = 2.2 - 0.39 = 1.8$$

Substituting the above values for  $a$  and  $b$  in (3),

$$b + a = 2.2 + 1.8 = 4.0$$

This is in fair agreement with the experimental value, being within 10%. From (4), the value of  $b$  is 2.0, which is an approximate confirmation of the value calculated from (2).

A value for  $-\text{C}\equiv\text{C}-$ , ( $c$ ) can be obtained as follows:

$$\text{From (1)} \quad 2a + c = 3.63$$

$$(2) \quad 2b = 4.41$$

$$(3) \quad a + b + c = 3.65$$

Solving,  $a = 2.18$ ,  $b = 2.20$ , and  $c = -0.73$ .

For acrylonitrile,  $c$  was found to be  $-0.5$ ,<sup>8</sup> but this value is not directly comparable. If the relative inhibition of divinylacetylene on vinyl acetate were assumed to be the same as for acrylonitrile, i.e., 1.5,<sup>8</sup> then the value of  $c$  would be  $-0.3$ . Similarly, if the value for butadienyacetylene were assumed to be 3.0, as in the case of acrylonitrile,<sup>8</sup> then  $c$  would be  $-0.6$ .

The experimental value for the inhibition factor of monovinylacetylene was much lower than that predicted from the above calculations i.e.,  $2.18 - 0.73 = 1.45$ . Since monovinylacetylene boils at  $6^\circ$ , there is some possibility that part of it boiled out of the vinyl acetate during the test, thus giving only a partial effect. Since it was shown in the calculations above, as well as in the previous investigation on acrylonitrile,<sup>8</sup> that greater inhibition was due to the 1,3-butadienyl structure than to the vinylacetylenic structure, it would have been expected that diacetylene would be weaker than vinylacetylene. However, this was not the case, and a study of more polyethylenic and polyacetylenic compounds, including higher-boiling derivatives of

monovinylacetylene and diacetylene, will obviously be necessary in order to clarify the picture.

Divinyl sulfide was the only compound studied that had two unconjugated ethylenic groups. It was found to be a weak inhibitor when compared with those containing two or more conjugated, unsaturated groups. Its low inhibitory activity is undoubtedly due to the lack of conjugation of the vinyl groups, since other compounds, such as 1-acetoxy-1,3-butadiene, which have two conjugated ethylenic groups were found to be strong inhibitors.

Exceedingly little inhibition, if any at all, appears to be traceable to sulfur in organic compounds. The inhibition caused by 104 p.p.m. of carbon disulfide was too small to be measurable. Thiophene was also found to be such a weak inhibitor that even if it were assumed that all its activity was due to the sulfur, the sulfur activity would still be very small.

Linkages  $-\text{HC}=\text{CH}-$  in cyclic compounds appear to have very little activity. Benzene and toluene were inert and thiophene was very weak. These compounds appear to be chain-transfer agents.<sup>31</sup>

A difference between *cis* and *trans* isomers was observed. Gradually changing inhibition factors were obtained with consecutive, distilled fractions of 1-acetoxy-1,3-butadiene.<sup>20</sup> Physical properties, chemical analyses, and mass, infrared, and ultraviolet spectra indicated the presence of *cis* and *trans* isomers. In all the distillation fractions studied, the highest inhibition factor obtained was 2.02 sec., ppm (chiefly *cis*) and the lowest was 1.55 (chiefly *trans*).

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## Synopsis

The relative inhibitory effects of acetaldehyde, acetone, 1-acetoxy-1,3-butadiene, benzene, 1,3-butadienylacetylene, carbon disulfide, crotonaldehyde, diacetyl, diacetylene, divinylacetylene, divinyl sulfide, 1,3,5-hexatriene, monovinylacetylene, thiophene, and toluene on the bulk polymerization of vinyl acetate were measured. Two polymerization tests utilizing different concentrations of benzoyl peroxide catalyst were used. Experimental details of the tests, inhibition factors and curves, and general conclusions regarding the magnitude of the inhibition caused by various organic functional groups are given.

## Résumé

On a mesuré l'effet inhibiteur relatif de l'acétaldéhyde, de l'acétone, du 1-acétoxy-1,3-butadiène, du benzène, du 1,3-butadiénylacétylène, du sulfure de carbone, du crotonaldéhyde, du diacétyl, du diacétylène, du divinylacétylène, du sulfure de divinyle, du 1,3,5-hexatriène, du monovinylacétylène du thiophène et du toluène sur la polymérisation en bloc de l'acétate de vinyle. On a fait deux essais de polymérisation en employant différentes concentrations de peroxyde de benzoyle comme catalyseur. On donne les détails expérimentaux de ces essais, les facteurs inhibiteurs et les courbes obtenues ainsi que les conclusions générales concernant l'importance de l'inhibition causée par les différents groupes fonctionnels organiques.

## Zusammenfassung

Die relative Inhibitorwirkung von Acetaldehyd, Aceton, 1-Acetoxy-1,3-butadien, Benzol, 1,3-Butadienylacetylen, Schwefelkohlenstoff, Crotonaldehyd, Diacetyl, Diacetylen, Divinylacetylen, Divinylsulfid, 1,3,5-Hexatrien, Monovinylacetylen, Thiophen und Toluol auf die Polymerisation von Vinylacetat in Substanz wurde bestimmt. Polymerisationsversuche mit zwei verschiedenen Benzoylperoxydkonzentrationen wurden ausgeführt. Angaben über experimentelle Details der Versuche, über Inhibitionsfaktoren und -kurven werden gemacht und allgemeine Schlüsse auf die Grösse der durch verschiedene organische funktionelle Gruppen verursachte Inhibierung gezogen.

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