[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Comparison of Organic Inhibitors in Chain Reactions

BY KIA-KHWE JEU AND HUBERT N. ALYEA

In the oxidation of sodium sulfite inhibited by alcohols, and of benzaldehyde inhibited by anthracene, Bäckström and co-workers[1] established that the inhibitory process is accompanied by an induced oxidation of the inhibitor. This paper extends the investigation to types of reactions where such an inhibition mechanism seems improbable; for example, a polymerization carried out in a hydrogen atmosphere to the exclusion of oxygen. In place of a detailed study of products formed by one inhibitor in one reaction we have investigated the relative inhibitory effects of numerous classes of substances on several types of reactions: (1) the photo-polymerization of vinyl acetate, (2) the autoxidation of sodium sulfite, (3) the photolysis of hydrogen peroxide.

Our choice of inhibitors was limited by the necessity that they should represent as many different types of compounds as possible, were soluble in our reaction media, water or ethyl acetate, and did not absorb light in the spectral region used, 3000–4000 Å. The latter precautions eliminated any inhibition due to screening effect.[2]

Theoretical

All three reactions are chain reactions and have unimolecular velocity constants. The effect of various organic substances could, therefore, be expressed as relative inhibitory powers, k, in a velocity expression

$$\frac{dx}{dt} = k_1(1 - x)\left[1 + \frac{k_3}{k_2 + kC}\right] \qquad (1)$$

where dx is the fraction reacting in the interval dt and k_1 is the usual unimolecular constant. [1] is the primary step and $k_3/(k_2 + kC)$ is the probable number of links in a chain following the primary step. This probability is governed by k_3, the probability of continuing the chain; and $(k_2 + kC)$, the probability of breaking the chain by some constant factor, k_2, such as walls or impurities, or by the added inhibitor of concentration C.

With chains of any appreciable length the primary step in the reaction becomes negligible, and equation (1) reduces to

$$\frac{dx}{dt} = \frac{(1 - x)K}{k_2 + kC} \qquad (2)$$

Integrating this we obtain

$$1/t \ln \frac{1}{1 - x} = \frac{K}{k_2 + kC} \qquad (3)$$

(1) Alyea and Bäckström. THIS JOURNAL, **51**, 90 (1929); Bäckström and Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

(2) Anderson and Taylor, THIS JOURNAL, **45**, 650 (1923).

This equation will apply to photochemical as well as thermal reactions, provided that the reactant absorbs only a small fraction of the incident light, so that the number of chains started is proportional to $(1 - x)$. This condition is fulfilled in both the polymerization of vinyl acetate and the decomposition of hydrogen peroxide, so that equation (3) can be applied to both. The 5% vinyl acetate solutions we employed absorbed only 2% of the 3130 Å. light.[3] The 0.6 *M* hydrogen peroxide solutions absorbed as much as 50% of the 3132 Å. line[4] and a much smaller percentage of the 3340 and 3663 Å. lines, so that only an approximate agreement with equation (2) may be anticipated.

Experimental

Photopolymerization.—The reaction vessels and mercury lamp were immersed in a de Khotinsky thermostat at 75 ± 0.1°. A Cooper–Hewitt vertical mercury lamp was held in place inside a 2.5 × 25 cm. quartz tubing by an asbestos belt and calked with red lead-linseed oil. A small portion of the mercury reservoir projected from the bottom of the tubing, and was in direct contact with the water in the bath; the amount projecting was so adjusted that the lamp burned at 180 watts. The quartz tube was cemented in a brass collar in the center of a brass rack and tripod. On the periphery of the rack, and equidistant from the mercury lamp, eight holes were bored to accommodate eight Pyrex reaction vessels. Each vessel consisted of two parts: an outer tube 19 cm. long, the lower part 9 × 2 cm., the upper part 10 × 1.5 cm.; and an inner tube of 6 mm. o. d. tubing 37 cm. long with a stopcock 10 cm. from the upper end, below which was an enlargement ground to fit into the outer tube. The lower end was tapered and reached within 0.5 cm. of the bottom of the outer tube, whose contents were thereby well mixed and the gas space thoroughly flushed with hydrogen. The 16-cc. samples used in a run were completely exposed to the rays from the mercury lamp.

Pure vinyl acetate was supplied by the Union Carbide and Carbon Company and C. P. ethyl acetate by Merck and Company. They were simultaneously distilled in a hydrogen atmosphere in separate flasks on a water-bath at 80°. From the moment the distillation was begun to the time when all solutions were mixed and the polymerization measurements commenced, all operations were carried out in an atmosphere of tank hydrogen, to the complete exclusion of air.

8.45 cc. of the middle portion of the vinyl acetate distillate was diluted with 150 cc. of ethyl acetate; 15 cc. of this was mixed in a reaction vessel, with 1 cc. of inhibitor solution. Eight reaction tubes were filled in the same way and placed in the bath at the same time. Two always served as blanks and contained 1 cc. of ethyl acetate instead of 1 cc. of inhibitor solution. The ground joints were lubricated with completely polymerized vinyl acetate dissolved in ethyl acetate.

Merck C. P. or other products of equal quality were used without further purification in preparing the inhibitor solutions in 25.00-cc. lots by dissolving 0.02148 mole of inhibitor in ethyl acetate. This gave a concentration in the reaction vessel of one inhibitor to ten of vinyl acetate molecules. More dilute inhibitor concentrations were prepared by dilution of the 25-cc. lot. The initial vinyl acetate concentration was always 5% (0.536 molar).

At convenient time intervals during a polymerization run two 2-cc. samples were removed and their iodine values determined: 10 cc. of carbon tetrachloride, 2 cc. of un-

(3) Taylor and Vernon, THIS JOURNAL, **53**, 2537 (1931).
(4) Kornfeld, *Z. Phot.*, **21**, 66 (1922).

known, and 25 cc. of Wijs solution were allowed to stand in a glass-stoppered 500-cc. bottle for thirty minutes in the dark. Then 10 cc. of 10% potassium iodide solution and 200 cc. of water were added, and the iodide liberated by the remaining Wijs solution titrated at once with $N/10$ thiosulfate solution, starch emulsion being added toward the end.[5]

Wijs solution was prepared by bubbling chlorine gas through 13 g. of Merck resublimed iodine dissolved in one liter of glacial acetic acid until the halogen content was doubled.[6] The acetic acid should not contain reducing substances nor over 0.5% of water, since both affect the keeping quality of Wijs solution.

Autoxidation.—The apparatus and procedure for the thermal oxidation of sodium sulfite was identical with that used by Alyea and Bäckström,[1] except that ordinary distilled water and Merck C. P. anhydrous sodium sulfite were used without further purification. Decrease in sulfite concentration was followed by titration with 0.5 N sulfuric acid to P_H 4.3, using brom cresol green as indicator. Since the titration consists in changing SO_3^{--} to HSO_3^-, 5 cc. of 0.6 M sulfite requires 6 cc. of 0.5 N sulfuric acid. Standard aqueous inhibitor solutions were prepared containing 0.012 mole of inhibitor in 50 cc. of solution; 5 cc. of this added to 15 cc. of 0.8 M sulfite buffered with sulfuric acid gave a concentration of one inhibitor to ten sodium sulfite molecules. The initial sulfite concentration was always 0.6 molar.

Photolysis.—The apparatus was the same as in the photopolymerization except that the inner tube was replaced by a loosely fitting stopper. A stock solution of 50 cc. of Merck Superoxol diluted with 450 cc. of distilled water was used to prepare 0.8 molar hydrogen peroxide. For each run 15 cc. of the latter was mixed with 5 cc. of the aqueous inhibitor solutions described above. Two 1-cc. samples were removed from time to time during the run, and the peroxide content determined by titration with $N/10$ potassium permanganate in the usual way. The experiments were made at 75°, the initial peroxide concentration being 0.6 molar.

Results

Wijs Method for Following Polymerizations.—Not more than half of the Wijs solution should be consumed by the vinyl acetate, so that not more than 2 cc. of a 5% solution of vinyl acetate should be used in the directions above. Thus, with 5% solutions we obtained upon titrating 2-cc. samples an experimental iodine number of 294.2; with 4-cc. samples, 266.9. The theoretical iodine number is 294.9, showing that there was incomplete addition with the 4-cc. samples. Ethyl acetate does not react with Wijs solution; nor does the polymerized product, since sections cut from some solid photopolymerized vinyl acetate gave iodine values as low as 9.5 and 6.3, corresponding to 96 and 98% polymerized. In a few cases a blank titration and correction had to be applied for a small amount of Wijs solution reacting with the inhibitor. Wijs solution is rapid in action and keeps for months. It surpasses other methods which have been used in following the polymerization, especially since it is applicable to very dilute solutions. This, aside from obviating experimental difficulties of working with very viscous solutions, evades the danger of association in solutions

(5) Kolthoff and Furman, "Volumetric Analysis," Vol. I, p. 198; Buckwalter and Wagner, THIS JOURNAL, **52**, 5241 (1930); Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927).

(6) Sherman, "Methods of Organic Analysis," 2d ed., The Macmillan Co., New York, 1929, p. 152.

which according to Staudinger and Heuer[7] occurs in these solutions whenever the concentration exceeds a few per cent.

Confirmation of the Velocity Equation.—In all three reactions x is the fraction which has reacted after t hours. C is the ratio of the number of inhibitor to number of reactant molecules. Equation (3) may be written

$$\frac{k_2}{t} \ln \frac{1}{1-x} + \frac{kC}{t} \ln \frac{1}{1-x} = K \qquad (4)$$

For the photo-polymerization the wattage of the mercury lamp although constant throughout a single run varied between 170 and 200 watts from day to day. This necessitated a correction w the value of which was determined empirically by dividing the value of $x/2-x$ at the wattage used during the experiment by the value of $x/2 - x$ at 180 watts, the latter wattage being taken as standard. This introduced into equation (4), in which the expanded form $2x/2 - x$ is used in place of $\ln 1/1 - x$, gives

$$\frac{Kwt}{(kwt/2) + k_2 + kC} \qquad (5)$$

That this equation is satisfied over a large range of concentrations is shown for pyrogallol, hydroquinone and benzylamine in Tables I, II and III and in Fig. 1.

TABLE I

POLYMERIZATION INHIBITED BY PYROGALLOL

$k = 3200$; $w = 0.92$; $t = 3$ hours

$1/C$	kC	x Calcd. $\left(= \frac{0.22\ wt.}{0.11\ wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.378	0.380
5000	0.64	.270	.273
2500	1.28	.210	.176
1000	3.20	.126	.130
500	6.40	.076	.070
100	32	.018	.027
50	64	.009	.017
10	320	.002	.015

TABLE II

POLYMERIZATION INHIBITED BY BENZYLAMINE

$k = 130$; $w = 1.0$; $t = 3$ hours

$1/C$	kC	x Calcd. $\left(= \frac{0.22\ wt}{0.11\ wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.405	0.403
5000	.026	.399	.390
2500	.052	.392	.420
1000	.13	.375	.393
500	.26	.349	.349
100	1.3	.225	.235
50	2.6	.156	.158

(7) Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).

TABLE III

POLYMERIZATION INHIBITED BY HYDROQUINONE

$k = 1000$; $w = 0.86$; $t = 3$ hours

$1/C$	kC	x Calcd. $\left(= \frac{0.22\ wt}{0.11\ wt + 1.30 + kC}\right)$	x Observed
∞	0.0	0.358	0.362
2500	0.4	.286	.294
1000	1.0	.219	.222
500	2.0	.158	.159
100	10.0	.049	.059
50	20.0	.026	.063
10	100.0	.006	.008

For the oxidation of sodium sulfite, if the reaction is followed over small changes in x, the value of $1 - x$ in equation (2) remains essentially constant, and the equation reduces to that already shown by Bäckström[8] to be approximated in inhibited sulfite oxidation.

For inhibited photolysis, a thermal run was made in each case and deducted from the observed light rate to give the true photochemical rate. The uninhibited thermal rate was only 7% of the photochemical one. At a concentration of 1/500 all of the substances inhibited the normal thermal reaction with the exception of ethylamine. The latter accelerated[2] roughly in proportion to its concentration: 14-fold at 1/100, 4-fold at 1/500 and 1.2-fold at 1/2500. However, at no time did the thermal rate exceed the photochemical one, and with most inhibitors it was around 10% of the photochemical rate. At a concentration of one-tenth the thermolysis was accelerated 5-fold by pyrogallol, 4-fold by resorcinol, and 2.5-fold by hydroquinone, possibly due to reaction with the peroxide; so that this concentration was not used in evaluating their inhibitor powers. That a unimolecular equation is obeyed in the

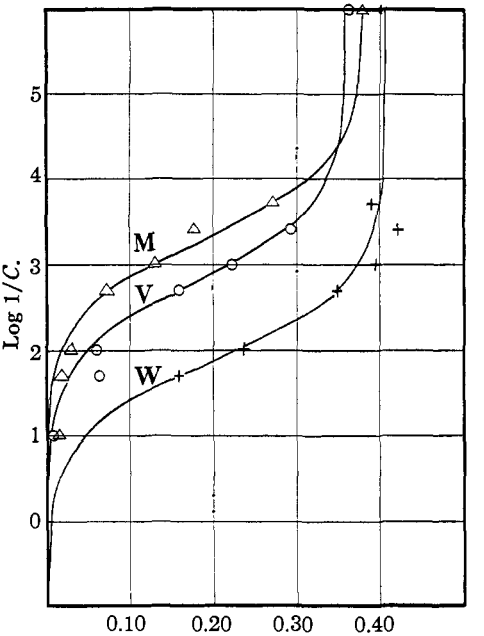

Fig. 1.—M, Pyrogallol ($W = 0.92$); V, hydroquinone ($W = 0.86$); W, benzylamine ($W = 1.00$). △ ○ + values observed; —— values calculated from $x = 0.22\ wt/(0.11\ wt + 1.30 + kC)$.

(8) Bäckström, THIS JOURNAL, **49**, 1460 (1927).

photochemical decomposition of pure or inhibited hydrogen peroxide at 75° is shown in Tables IV and V.

TABLE IV

PHOTOLYSIS OF HYDROGEN PEROXIDE IN UNINHIBITED SOLUTIONS AT 75°

t in hours	Photothermal	Thermal alone	Photo alone x	$1/t \log 1/(1-x)$
0.0	0.000	0.000	0.000	
0.6	.490	.028	.462	0.450
0.9	.678	.037	.641	.500
1.2	.800	.045	.755	.517
1.5	.880	.052	.828	.475
2.0	.945	.061	.884	.470
				Av. 0.482

TABLE V

PHOTOLYSIS OF HYDROGEN PEROXIDE INHIBITED BY VERONAL AT 75°

$1/C$	t in hours	Photothermal	Thermal alone	Photo alone x	$1/t \log 1/(1-x)$
100	0.3	0.137	0.007	0.130	0.223
100	.6	.262	.014	.248	.207
100	.9	.359	.022	.337	.196
500	.3	.222	.013	.209	.430
500	.6	.411	.027	.384	.352
500	.7	.507	.036	.471	.350
2500	.3	.261	.021	.240	.400
2500	.6	.486	.044	.442	.426
2500	.8	.602	.058	.058	.432

Evaluating the Relative Inhibitor Power k.—It is only possible to give k, k_2 and K in equation (4) numerical values by assigning one of them a definite value for some standard inhibitor. Experimentally, the results with powerful inhibitors were found to be most reproducible; of which pyrogallol was chosen as the standard, and assigned a k-value of 3200 for all three reactions. This number was chosen because ethyl alcohol, one of the weakest inhibitors known, was found thereby to assume a value of approximately unity. All substances, therefore, excepting those whose inhibitory powers were immeasurably small, have a value of k greater than unity.

For the polymerization of vinyl acetate, when $kC/t \ln 1/1 - x$ is plotted against $1/t \ln 1/1 - x$ for pyrogallol, all of the values fall along the same line, as shown in curve 1, Fig. 2. This conforms with equation (4) which indicates that when C approaches infinity $C/t \ln 1/1 - x = K$, and that when C is zero $k_2 = K/(1/t \ln 1/1 - x)$. Reading these values from the intercepts at the axes we obtain

$$K = 0.22 \text{ and } k_2 = 0.22/0.170 = 1.30$$

This method is extended to the other inhibitors by graphing $C/t \ln 1/1 - x$ against $1/t \ln 1/1 - x$ and then multiplying the ordinate values by

some constant, k, which brings the intercept at the ordinate up to 0.22. Examples are shown in Curve 1, Fig. 2, for hydroquinone and benzylamine.

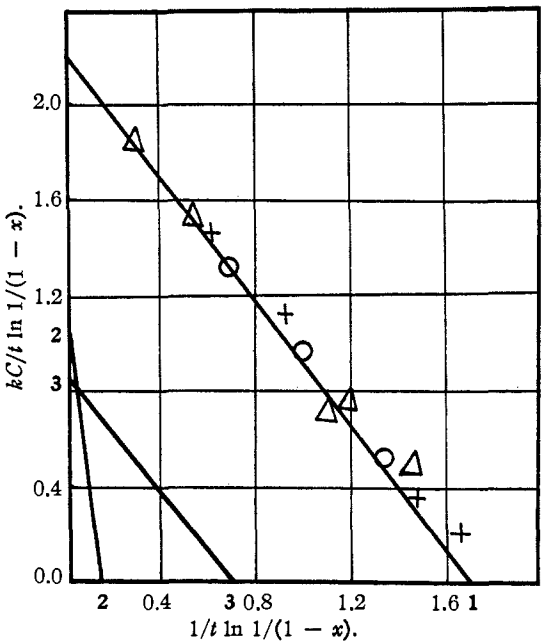

Fig. 2.—General curves for all inhibitors: Curve 1, photo-polymerization of vinyl acetate, 5% solution, in which the scale is increased ten-fold, the observed intercepts being 0.17 and 0.22; △ pyrogallol, ○ hydroquinone, + benzylamine; Curve 2, thermal autoxidation of sodium sulfite, 0.6 molar; Curve 3, photolysis of hydrogen peroxide, 0.6 molar.

The relative inhibitor powers so determined are given in Table VI and have been obtained from at least ten runs on each inhibitor. The intercept at the abscissa, which corresponds to the uninhibited rate, was strictly reproducible.

For the oxidation of sodium sulfite corrections must be applied. Unless there is extreme purification of the sulfite long induction periods are obtained. This difficulty is obviated by referring each run to exactly the same amount oxidized, a drop in sulfite concentration from 0.60 to 0.46 molar being taken as the standard. When this is done all experimental points for any given inhibitor lie along the same line when $C/t \ln 1/1 - x$ is plotted against $1/t \ln 1/1 - x$. The intercepts at the axes for these graphs are given in Table VII. It will be noticed that the intercept at the abscissa is not strictly reproducible, due to varying impurities in the sulfite. This was corrected for by assigning a standard value, 0.15, at the abscissa

TABLE VI

RELATIVE POWERS OF INHIBITORS IN VINYL ACETATE PHOTOPOLYMERIZATION

Inhibitor	Inhibitor constant k	Inhibitor	Inhibitor constant k
Benzene	2.3	Methyl oxalate	1.2
Ethyl alcohol	1.2	Ethylamine	45
Allyl alcohol	58	Benzylamine	130 ± 5
Benzyl alcohol	26		
Chloral hydrate	0.0	Phenol	16
		Hydroquinone	1000 ± 20
Propionic acids	0.0	Pyrocatechol	1400 ± 70
Benzoic acid	5.8	Resorcinol	29
		Pyrogallol[a]	3200 ± 175
Pyridine	12.0		

[a] This number taken as standard. The observed intercept at the abscissa for all curves is 0.170. The observed value for $C/t \ln 1/(1-x)$ at the intercept at the ordinate for each curve is $0.22/k$.

TABLE VII

RELATIVE POWERS OF INHIBITORS IN SULFITE OXIDATION

(No copper sulfate added)

Inhibitor	1/concentration range of inhibitor ($1/C$)	Intercepts Observed Absc.	Intercepts Corrected Ord.	Ordinate[a]	Inhibitory power k
Propionic acid	10–100	...	.....	.....	Accelerates slightly
Methyl oxalate	20–100	0.378	∞	.....	0.0
Benzoic acid	100–1000	.168	∞	.....	.0
Cocaine hydrochloride	500–1000	.120	∞	.....	.0
o-Cresol	20–500	.175	∞	.....	.0
Ethyl alcohol	0.5–50	.132	1.0000	1.130	.9
Chloral hydrate	10–500	.280	0.4360	0.2340	5
Phenol	10–500	.168	.0580	.0518	20
Acetoxime	10–500	.190	.0475	.0375	28
Resorcinol	5–500	.350	.0810	.0348	30
Acetamide	10–50	.135	.0300	.0333	32
Veronal	100–500	.320	.0710	.0333	32
Benzyl alcohol	10–100	.100	.0210	.0314	34
Pyridine	10–100	.156	.0200	.0192	55
Ethylamine	5–100	.200	.0140	.0105	100
Allyl alcohol	10–100	.290	.0185	.00955	110
Benzylamine	10–500	.330	.00648	.00295	360
Pyrocatechol	50–100	.0348	.000582	.....	1800
Pyrogallol	50–100	.055	.00033	.....	3200[b]
	500–2500	.140	.00076	.000082	(13000)
Hydroquinone	50–500	.0348	.000118	.....	9000
	1000–5000	.145	.000043	.000045	(24000)

[a] Corrected intercept at abscissa is 0.150 for all but the last three inhibitors. [b] This number taken as standard.

for the blank rate, $C = 0$, and correcting all curves to this standard so as to be comparable. The general curve is given in Fig. 2, Curve 2. It will be noticed also that the last three inhibitors at concentrations greater than 1/500 cut the abscissa at abnormally low values. For these the observed intercepts at the ordinate were used without correction. The values for k obtained from at least ten runs on each inhibitor are given in Table VII.

TABLE VIII

RELATIVE POWERS OF INHIBITORS IN SULFITE OXIDATION

(Accelerated by 5×10^{-6} molar $CuSO_4$)

Inhibitor	1/concn. range of inhibitor 1/C	Intercepts Observed Absc.	Ord.	Corrected ordinate[a]	Inhibitory power k	
Ethyl alcohol	0.5–1000	0.224	1.5000	1.0000	1.6	(0.9)[b]
Phenol	10–500	.263	0.1230	0.0704	23	(20)
Resorcinol	10–500	.250	.0970	.0582	27	(30)
Benzyl alcohol	10–1000	.230	.0815	.0532	30	(34)
Pyrocatechol	50–500	.110	.00097	....	1600	(1800)
	1000–5000	.250	.000204	.00012	3000	....
Pyrogallol	50–500	.063	.00050	....	3200	3200[c]
Hydroquinone	500–5000	.265	1.00010	.00058	28000	(24000)

[a] Corrected intercept at abscissa is 0.15 for all inhibitors.

[b] Values in absence of copper sulfate, taken from Table VII.

[c] This number taken as standard.

TABLE IX

RELATIVE POWERS OF INHIBITORS IN HYDROGEN PEROXIDE PHOTOLYSIS

Inhibitor	1/concn. of inhibitor 1/C	Intercepts Observed Absc.	Ord.	Corrected ordinate[a]	Inhibitory power k
Ethyl alcohol	10–20	0.732	0.0622	0.0598	130
Allyl alcohol	10–500	.672	.0525	.0550	150
Propionic acid	50–500	.770	.0143	.0131	640
Chloral hydrate	100–500	.460	.00690	.0106	790
Pyridine	10–500	.623	.00705	.00796	1040
Acetoxime	10–500	.802	.00875	.00770	1080
Veronal	100–2500	.985	.00945	.00678	1230
Methyl oxalate	50–100	.484	.00286	.00416	2000
Pyrogallol	100–2500	.825	.00304	.00260	3200[b]
p-Cresol	100–500	.664	.00140	.00149	5600
Benzyl alcohol	10–500	.705	.00124	.00124	6700
Pyrocatechol	100–2500	.691	.00099	.00101	8200
Hydroquinone	100–2500	.770	.00108	.00079	8400
Benzoic acid	500–2500	.904	.00109	.00085	9800
Resorcinol	500–1000	.691	.00076	.000775	11000
Phenol	500–1000	.737	.00077	.000737	11000
Cocaine hydrochloride	500	.705	.000691	.000691	12000
Benzylamine	500–2500	.857	.000815	.000671	12000
Ethylamine	500–2500	.830	.000488	.000410	20000

[a] The corrected intercept at the abscissa is 0.705 for all inhibitors. [b] This number taken as standard.

Some runs were also made on sodium sulfite solutions accelerated by 5×10^{-6} molar copper sulfate. The inhibitory powers for these solutions as given in Table VIII agree with the values in unaccelerated solutions.

For the photolysis of hydrogen peroxide there was no induction period, but a blank rate with a value of $1/t \ln 1/(1 - x) = 0.705$ was assigned (see Table IX, Curve 3, Fig. 2).

Photosensitization of Polymerization.—Taylor and Vernon[3] found that the quantum yield for vinyl acetate polymerization is unity at 2300 Å. and 2536 Å. but 1000 between 3000–4000 Å. The low value might be due to depolymerization occurring simultaneously and thereby masking the true polymerization rate; or to the light being absorbed by a photochemically inactive portion of the molecule, an "intra-molecular screening effect," analogous to the effective decrease in quantum yield with wave length in the decomposition of acetaldehyde.[9] A search was therefore made for photosensitizers to higher wave lengths at which these retarding effects might be nil. No attempt was made to weigh accurately the added sensitizer, our only intent being to discover one which gave a many-fold increase in rate. Semi-quantitative measurements in which the ratio of proposed sensitizer to reactant molecules ranged from 1:1 to 1:10 for liquids, and 1:20 to 1:10,000 for solids, the latter because of extremely low solubilities of some solids, showed the following. The reaction was accelerated from five to twenty per cent. by acetone, sodium benzoate, benzoyl peroxide, chloral hydrate, phosphoric acid, fuchsine, quinine sulfate, malachite green, propionic acid, anisole, chrysaniline, phthalic acid, and alizarin-indigo blue. Without effect, were eosin, phosphine 3R and thymol. The following were weak inhibitors, which reduced the normal rate to about half: bromindigo 2B, barbituric acid, phosphine, methyl oxalate, aniline violet, ethyl alcohol, guaiacol, erythrosine B, thiophene, benzene, acetamide, benzamide *p*-rosaniline, *m*-cresol, benzoic acid, benzophenone, indole, alizarin red S, caffeine, pyridine, indigo bengal, phenol, cyanin, benzyl alcohol, resorcinol, rosaniline, ethylamine, neo-indol, allyl alcohol, benzil, benzylamine, acetoxime and dinitronaphthol. The following were powerful inhibitors which reduced the rate to three per cent. or less of the normal rate: picric acid, quinoline, *o*-nitrotoluene, dimethylaniline, aniline, furfural, diethylamine, azobenzene, rhodamine B, *o*-nitrophenol, salicylic acid, α-nitronaphthalene, rhodinol, nitrobenzene, allyl isothiocyanate, pyrogallol, hydroquinone and pyrocatechol.

Discussion of Results

A summary of these results and other data in Table X at once emphasizes that the relative inhibitor powers are strikingly parallel in the oxidation and polymerization reactions, and that inhibitor power in the photoly-

(9) Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931).

sis, on the other hand, has nothing in common with them. Of all the inhibitors, hydroquinone alone absorbed above 3000 Å. and might well, therefore, sensitize as well as inhibit the photopolymerization; whereas such sensitization is precluded in the thermal sulfite oxidation. Therefore, k is larger in the latter. No explanation is offered for the exceptions pyridine and acetoxime, and the experimental discrepancies between Anderson and Taylor's and our values for benzoic acid and ethyl alcohol. Their value of about 20,000 was a limit of inhibitory power imposed by their experimental accuracy, and agrees well with our values when it is recalled that the concentration of their hydrogen peroxide, and, hence, the value k varied two-fold.

Let us return to the parallelism of inhibitory powers for the oxidation and polymerization. Assuming the function of the inhibitor is to receive and dissipate chain energy,[1] the relative inhibitor powers may be identical with the relative efficiencies of these twenty-odd substances in receiving excess energy from a "hot chain molecule." But collisions of the second kind are highly specific processes, and even though the excess energy of a hot polymerized and a hot oxidized molecule be identical, we should hardly anticipate identical collision efficiency, identical inhibitory powers. Another mechanism is possible: if the polymerization involves an initial peroxide step it may be inhibited in the same way as the peroxide stages in

TABLE X

RELATIVE POWERS OF INHIBITORS—SUMMARY

The values in columns 2, 3, 4, 7 are from this paper. Columns 5 and 6 were calculated from data in Raymond, *J. chim. phys.*, **28**, 316 (1931), and Anderson and Taylor, ref. 2.

		Oxidation			Photolysis	
Inhibitor	Polymerization, vinyl acetate	Na_2SO_3, no copper	Na_2SO_3 copper accelerated	Benzaldehyde photo	H_2O_2 Anderson and Taylor	H_2O_2 Jeu and Alyea
Chloral hydrate	0	5	..	..	.....	790
Propionic acid	0	0	..	..	.....	640
Methyl oxalate	1.2	0	..	..	700–1400	2000
Ethyl alcohol	1.2	0.9	1.6	..	2700–5400	130
Benzoic acid	5.8	0	..	..	0–100	9800
Phenol	16	20	23	20[a]	ca 20000	11000
Benzyl alcohol	26	34	30	..	3200–6400	6700
Resorcinol	29	30	27	..	.....	11000
Ethylamine	45	100	..	..	ca 20000	20000
Allyl alcohol	58	110	..	(2)	.....	150
Benzylamine	130 ± 5	360	..	..	ca 20000	12000
Pyrocatechol	1400 ± 70	1800	1600	..	.....	8200
Pyrogallol	3200[a]	3200[a]	3200[a]	..	.....	3200[a]
Hydroquinone	1000	9000	..	2930	.....	9400
Pyridine	12	55	..	..	.....	1040
Acetoxime	92	28	..	..	.....	1080

[a] This number taken as standard.

the sulfite oxidation. Such a mechanism might involve a competition for AO_2 by activated reactant A′ molecules

$$A' + AO_2 \longrightarrow O_2 + A_2$$

subsequent rapid polymerization giving rise to A_x, or by inhibitor molecules, B

$$B + AO_2 \longrightarrow BO_2 + A$$

whereby the formation of the polymer is prevented. This of course might give identical inhibitory powers corresponding with and proportional to the oxidizability of the inhibitors by peroxides. However, the only evidence to support this view is that benzoyl peroxide accelerates the polymerization.[10] For such a mechanism an extremely small amount of oxygen may be necessary and the large excess of oxygen used by Taylor and Vernon[3] might well lead to the inhibition which they report.

k_2, a Measure of Chain Length.—Pyrogallol, our most powerful inhibitor, was assigned a standard inhibitory power of 3200. Assume that a collision of a chain molecule with pyrogallol is as efficient in breaking the chain as a collision with a reactant molecule is in continuing the chain, and accordingly assign it an absolute inhibitory power of $k_a = 1 = k/3200$. Now when pyrogallol has reduced the uninhibited rate to half, kC will equal k_2. When k_a is used in place of k, $1/C$ will be half the chain length: thus to cut a one-thousand link chain at the five hundredth link requires a concentration of 1/500 of pyrogallol to reactant molecules. That is

$$\text{chain length} = 2/(k_aC) = 6400/kC = 6400/k_2$$

If an inhibitor more efficient than pyrogallol is found, it would increase the chain length by the factor (k for new inhibitor/3200), so that the assumption that pyrogallol is 100% efficient in breaking chains gives the value of a *minimum chain length*. This calculation has been carried out in Table XI for several measurements where the value k_2 is known.

TABLE XI

CALCULATION OF CHAIN LENGTH FROM k_2

Reaction	k_2	Chain lengths calculated ($=6400/k_2$)	Chain lengths probable
Polymerization of vinyl acetate 5% soln.	1.30	5000	2500
Autoxidation of sodium sulfate			
0.6 *M* Jeu and Alyea	7.04	900	1000–10000
Alyea and Bäckström	0.068	100000	100000
Bäckström	0.0059	1000000	100000
Photolysis of hydrogen peroxide 0.6 *M*	11.8	540 (2000)	1000

The values 1.30, 7.04, 11.8 are from this paper. Alyea and Bäckström's value[1] of $k_2 = 0.0012$, where k for benzyl alcohol was 1 and the concentration was expressed in moles of inhibitor per liter of 0.6 molar sulfite solu-

(10) See Conant and Peterson, THIS JOURNAL, **54**, 628 (1932), where a peroxide step is postulated for the polymerization of isoprene and for *n*-butyraldehyde at high pressures.

tion, gives in our units $0.0012 \times 34 \times 1.0/0.6 = 0.068$. Bäckström's[8] value of $k_2 = 0.00906$, where k for benzyl alcohol was 60 and concentration was expressed in moles per liter of 0.6 molar sulfite solution, gives in our units $0.00622 \times 34/60 \times 1/0.6 = 0.0059$. The value 2500 in the last column is a semi-quantitative quantum yield which we obtained by comparing the polymerization rate and light absorption of a 100% vinyl acetate solution for which Taylor and Vernon[3] obtained a quantum yield 1000, with the values for a 5% solution. The sulfite we used was not purified and exhibited long induction periods, and undoubtedly the chains were ten to a hundred-fold shorter than in Alyea and Bäckström's sulfite, for which they found chain lengths of 100,000, by induced oxidation of alcohols. Chains of 500 for hydrogen peroxide have been experimentally measured by Allmand and Style[11] and they postulated that they are considerably longer than this. A value 540 is obtained with 3200 for pyrogallol, but using a k of 12,000, which the more powerful amines and phenols possess, gives a minimum chain length of 2000 at 75°. The agreement is all that could be desired except in the case of Bäckström's sulfite measurements, in which different samples of sulfite used in the inhibited reaction and in the photochemical reaction, or even different reaction vessels, are sufficient to cause a several-fold change in reaction rate.

Summary

1. Photopolymerization of vinyl acetate may be followed by determining iodine numbers with Wijs solution.

2. A general equation $\frac{1}{t} \ln \frac{1}{1-x} = \frac{K}{k_2 + kC}$ represents the behavior for chain reactions of the first order in the presence of inhibitors. x is the fraction reacting during time t, K is composite of the number of chains initiated at $t = 0$ and the probability of continuing the chains; while $k_2 + kC$ is the probability of breaking the chains by a constant factor k_2 or by an inhibitor of concentration C and inhibitor power k.

3. The equation represents the photopolymerization of vinyl acetate, the thermal autoxidation of sodium sulfite and the photolysis of hydrogen peroxide.

4. Among sixteen representative inhibitors which include alcohols, esters, acids, amines, oximes, phenols, aldehydes, and alkaloids, the relative inhibitor power for a given substance is approximately identical in the polymerization of vinyl acetate and oxidation of sodium sulfite. In the photolysis of hydrogen peroxide, however, the values of k have no obvious relation to those in the other two reactions.

5. A maximum of twenty per cent. photosensitization to visible light was found for the polymerization among seventy organic substances tried.

(11) Allmand and Style. *J. Chem. Soc.*, 596 and 606 (1930).

6. Chain lengths agreeing with experimental values may be predicted from the values of k_2.

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The Photochemical Reaction between Quinine and Dichromic Acid. II. Kinetics of the Reaction

BY GEORGE S. FORBES, LAWRENCE J. HEIDT AND F. PARKHURST BRACKETT, JR.

This paper suggests a kinetic picture consistent with new data and with data already published.[1] The experimental methods have been described[1] except those followed (by the last-named author) at 208, and 254 mμ.

The only primary act (except possibly at 208 mμ) contributing to reduction of dichromic acid disclosed by our results is an activation of the quinine molecule or ion, Q to form Q*. In the secondary act a part of these activated molecules reduces dichromic acid. This picture could be amplified as follows. At the instant of excitation Q may be adjacent to molecules (or ions) of the other reactants, all within possibly effective ranges of distances and of orientations. That is, $n_1[Q] + n_2[H_2Cr_2O_7] + n_3[H^+] \rightleftharpoons$ potentially effective kinetic "clusters," to borrow Weigert's general designation.[2] Such clusters are conditioned by kinetic and electrostatic effects, and are in no sense stable complexes like uranyl oxalate. Photochemical reactivity, while varying with configuration, is practically independent of all activation energies except that of Q*. In a steady state and in a thin layer,

$$K_1\phi_q = [Q^*]_{cluster}/[Q^*]_{total} = K_2[Q^*]^{n_1}[H_2Cr_2O_7]^{n_2}[H^+]^{n_3}/[Q^*]$$

or

$$\log \phi_q + \log K_1/K_2 = (n_1 - 1)\log [Q^*] + n_2 \log [H_2Cr_2O_7] + n_3 \log [H^+]$$

where ϕ_q is net quantum yield referred to light absorbed by quinine and $[Q^*] = K'[Q]$ where K' depends, among other factors, upon the reaction cell used. K_1 is itself complex, involving factors such as $K_3e^{-\theta d/\theta_0 d_0}$ where θ_0 and d_0 indicate orientation and distance optimal for the secondary act.

If $[H_2Cr_2O_7]$ and $[H^+]$ are large compared with $[Q]$, or are held constant, $\log \phi_q = (n_1 - 1) \log [Q] +$ const. For correct evaluation of n_1, deviations from the reciprocity law had to be avoided by stopping down the front lens of the monochromator in each experiment to such an extent that the quinine in the first centimeter of the reaction mixture absorbed just as many quanta per minute, E_q, as in any other experiment in the series. As a consequence, $[Q^*]_{av.}$ was always the same in the layer thus

(1) Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).
(2) Weigert, *Z. physik. Chem.*, **102**, 416 (1922); **106**, 426 (1923).