ton's results, were constructed as follows. The values of the dissociation constant of acetic acid were corrected for the ionization of the acid, {log $K_{HAc} - \sqrt{\mu}$} was plotted *vs.* μ, and values of K_{HAc} were read off from the curve at those ionic strengths at which K_{HCac} was measured. The curves of Fig. 1 show log (K_{HCac}/K_{HAc}) thus found for the soutions[11] where M_{NaCac} (and M_{NaAc}) $\leqq \mu/5$.

Application of the method of least squares to the data of Chase for cacodylic acid (smoothed values, $\mu < 2.0$), and the data of Kilpatrick, Chase and Riesch for acetic acid, gave

$$\log (K_{HCac/HAc}) = \bar{2}.476 - 0.024\mu \text{ in KCl soln.}$$

The curve obtained using the data of Harned and Hickey for acetic acid is not linear; as drawn, the intercept is $\bar{2}.482$. Application of the method of least squares to Morton's data gave

$$\log (K_{HCac}/K_{HAc}) = \bar{2}.479 + 0.005\mu \text{ in NaCl soln.}$$

$$\log (H_{HCac}/K_{HAc}) = \bar{2}.481 - 0.012\mu \text{ in BaCl}_2 \text{ soln.}$$

These intercepts may be compared with log 0.0308 = $\bar{2}$.489 determined colorimetrically. The average of the electrometric and colorimetric results at 25° is $\bar{2}$.484 which is probably correct to 0.01; the dissociation constant of cacodylic acid computed from this figure is 5.33×10^{-7}.

Figure 1 and Tables II and III show that the change of K_A with μ closely parallels that for acetic acid, which indicates that cacodylic acid is present in aqueous solution as neutral molecule, rather than as zwitterion.

Acknowledgment.—The writer wishes to thank Dr. E. F. Chase for kindly permitting the publication of Table III. She also wishes to thank Dr. L. C. Riesch for preparing the ethylene acetal.

Summary

At 25°, the basic strength of cacodylic acid was found by a kinetic method to be 37.3 at $\mu = 0.03$, and the acid strength, which was determined both colorimetrically and (by Chase) electrometrically, to be $5.33 \pm 0.10 \times 10^{-7}$ at $\mu = 0$. The figure for the acid strength is in satisfactory agreement with the results of Morton.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 14, 1949

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[11] Morton's data in potassium and magnesium sulfate solution are not included because of involvement of the sulfate-bisulfate equilibrium.

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Rate Constants in Free Radical Polymerizations. II. Vinyl Acetate[1]

BY M. S. MATHESON, E. E. AUER, ELLEN B. BEVILACQUA[2] AND E. J. HART[3]

The absolute rate constants of vinyl acetate polymerization have previously been measured both by Burnett and Melville[4] and by Swain and Bartlett[5] through the use of the rotating sector technique, but the results are in disagreement. More recently the viscosity method of Bamford and Dewar has been applied to vinyl acetate[6] with results in fair agreement with those of Swain and Bartlett.

In the first paper of this series the application of the rotating sector to the measurement of the rate constants in methyl methacrylate[7] polymerization was described. We have now applied the method to vinyl acetate in an attempt to resolve the discrepancy in the literature, and this paper reports and discusses the results obtained.

Experimental

Vinyl Acetate.—Nozaki and Bartlett[8] have shown how difficult is the purification of vinyl acetate. In the present work, the preparation of pure vinyl acetate free of inhibiting impurities was found to be the major experimental problem encountered in the studies on this monomer. In the procedure finally adopted, 4 liters of commercial vinyl acetate (Eastman Kodak Co.) was distilled under purified nitrogen through a 60-plate glass column packed with glass helices. The automatic takeoff was set at 5% and the middle 2-liter fraction collected (b. p. 73.1° at 761 mm., uncor. $n^{20}\text{D}$ 1.3959) in one-liter round bottom flasks, 500 cc. to a flask. In ref. 8 b. p. 72.4° (760 mm.) and $n^{25}\text{D}$ 1.3934 reported.

Figure 1 shows a receiver flask F. During distillation F was attached to the distillation head by the joint J_1-J_1'. When a suitable fraction was received in F, the flask was removed and attached to a vacuum system by means of joint J_1 with D stoppered. The flask was degassed quickly and flushed with purified nitrogen, D being sealed off at B. Finally the flask, at −78°, was filled with purified dry nitrogen to 1 atm. and sealed off at A. The flasks were stored at −25° in the dark until used. For use the flask was opened by breaking the tubing at C and was then attached promptly by male joint J_2 to the vacuum system at J_2'. The vinyl acetate was then thoroughly degassed (to < 10^{-4} mm. permanent gas pressure), stopcock S was closed and the evacuated flask and attached stopcock were removed from the vacuum system by breaking the tube at E. Next the evacuated flask was irradiated in a water-bath at 30°, with an Hanovia Type A quartz arc about 3 inches away. After polymerization was estimated to be

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[1] In this paper a few of the final experiments and all of the preparation for publication were carried out with the assistance of the Office of Naval Research under Contract N8 onr-544.

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[4] (a) G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945); (b) *Proc. Roy. Soc.* (*London*), **A189**, 456 (1947).

[5] (a) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **67**, 2273 (1945); (b) C. G. Swain and P. D. Bartlett, *ibid.*, **68**, 2381 (1946).

[6] C. H. Bamford, The Labile Molecule, *Discussions of the Faraday Soc.*, No. 2, 317 (1947); G. Dixon-Lewis, *ibid.*, 319.

[7] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

[8] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946).

about 10%, the vinyl acetate was resealed to the vacuum system at E, and 80 cc. was distilled off *in vacuo* and discarded. Of the remainder, about two thirds was used to fill reaction cells[7] by distillation *in vacuo,* and the residue was discarded. During all these procedures great care was taken to exclude air or moisture, and it will be noted in Fig. 1 that no stopcock lubricant came in contact with the liquid monomer.

Initiator and Inhibitor.—Crude α-azo-bis-isobutyronitrile was recrystallized three times from redistilled C. P. toluene. This compound has an absorption maximum in the near ultraviolet at 3500 Å.,[9] and so is well suited for use as a sensitizer with 3660 Å. light from the mercury arc. The molar extinction coefficient, ϵ, is 9.2 (in ethanol) at 3660 Å.[9b] (see Fig. 3 for definition ϵ). Benzoquinone (Eastman Kodak Co.) was purified by sublimation. Benzoyl peroxide in 10-g. portions was recrystallized twice by dissolving in chloroform at room temp., filtering, pouring into methanol and cooling to 0°. The crystals were vacuum-dried.

Apparatus.—The apparatus was described in the first paper of this series,[7] the following minor changes being made for the experiments on vinyl acetate. The sectors for these experiments were made of 11 in. diameter aluminum discs divided into four equal sectors with one of the sectors cut out to a radial depth of 2 in. The use of these one-opening sectors reduced the transition time from 0 to full light intensity to about 1% of a light flash. By continuous circulation of bath water through the transparent Dewars surrounding the cell capillaries, the capillaries were maintained at the same temperature as the cells.

Procedure.—The cells (quartz for unsensitized and Pyrex for sensitized runs) were filled as previously described for methyl methacrylate, using the partially polymerized vinyl acetate as a source of monomer. In some experiments no sensitizer was used, while in the others α-azobisisobutyronitrile was weighed into bulb B, Fig. 3, ref. 7. As this compound is an efficient thermal initiator, appreciable dark rates were obtained in the sensitized runs and were accurately measured. The sensitizers used previously, biacetyl[7] and 2-azobispropane,[10] could not be used in vinyl acetate. Photosensitization by biacetyl at 3660 Å. was too low for experimental work. The 2-azobispropane effected an adequate polymerization rate at 3660 Å. but simultaneously functioned as an inhibitor: fast sector ratios (definition under sector experiments) were low and 0.04 cc. of the sensitizer in 30 cc. of vinyl acetate cut the rate induced by 0.105 *M* benzoyl peroxide by more than half.

Irradiation.—This procedure has also been reported elsewhere. The optical filters used for the various runs are given in the table below. One cm. of carbon tetrachloride eliminates all 2537 and transmits ~ 20% of the 2650 Å. line.

Run		Filters	Arc jacket
22		1 Corning 9863	Corex D
23 24	Unsensitized	1 Corning 9863 +1 cm. of CCl_4	Quartz
All sensitized runs		1 Corning 5970	Nonex

In order to evaluate the duration of growth of a kinetic chain from its initiation by light to its termination by interaction with another chain, the experimental data were taken and treated as described in ref. 7.

Densities.—To calculate rates of polymerization from observed volume contractions Table I was used. The densities used are mainly based on the data of Starkweather and Taylor.[11] By isolating the polymer formed, they showed that their densities at 82–111° correctly predicted the per cent. contraction corresponding to a given per cent. polymerization.

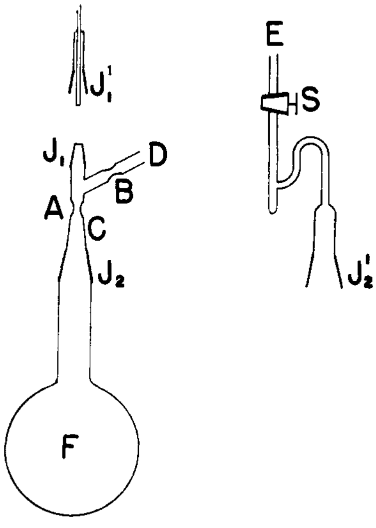

Fig. 1.—Receiver flask for vinyl acetate.

TABLE I

DENSITY VINYL ACETATE

Temp., °C.	Monomer[a]	Polymer[b]
5	0.952	1.203 (1.206)[c]
25	.925	1.187 (1.190)
50	.892	1.166 (1.169)

[a] From ref. 11 over range 82–111°, plus value at 20°, from P. O. Powers, "Synthetic Resins and Rubbers," John Wiley and Sons, Inc., New York, 1945, p. 14. Our measurement of density at 30° agrees with a plot of the monomer densities in this table. [b] From a plot of the data of ref. 11 in the range 82–111° extrapolated to lower temperatures. Values in parentheses from data obtained by us over range 30–60° using polymer prepared from purified vinyl acetate and fitting equation, density = 1.2098 − 8.068 × 10^{-4} t°C. [c] The polymer densities given for 5° are not the true values for pure polymer but result from extrapolation of the density-temperature results obtained above 24°, the second order transition point.

The finding of these authors that the density of the pure polymer and the apparent density of the polymer dissolved in monomer are nearly the same should be valid down to the second order transition temperature (24°).[12] However, solvent lowers the second order transition temperature, so that below 24° the apparent density of polymer in solution probably corresponds more closely to a value extrapolated from the plot of density *vs.* temperature which fits data above 24° than it does to the observed density of the pure polymer below the transition temperature.[12a]

Experiments on Rates of Initiation.—The U-shaped Pyrex cell used for measuring rates of initiation of chains is shown in Fig. 2. The section between the lines A and A′ consists of 3-mm. precision bore capillaries, while the U-shaped cell C was constructed of 15-mm. Pyrex tubing. The design of the cell facilitates removal of monomer-polymer mixtures and subsequent cleaning. For experi-

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[9] (a) A. Hantzsch and J. Lifschitz, *Ber.*, **45**, 3011 (1912); (b) work to be published from this Laboratory.

[10] Unpublished work on styrene from this Laboratory.

[11] H. W. Starkweather and G. B. Taylor, THIS JOURNAL, **52**, 4708 (1930).

[12] E. Jenckel, *Kolloid-Z.*, **100**, 163 (1942); R. H. Wiley, *J. Pol. Sci.*, **2**, 10 (1947).

[12a] The use of the measured density of the pure polymer at 5° instead of the density extrapolated from data above the second order transition temperature would affect calculations but slightly. In Table III the lifetime at 5° would be raised from 0.44 to 0.45 second, and the propagation rate constants calculated at 25 and 50° would be raised less than 1%.

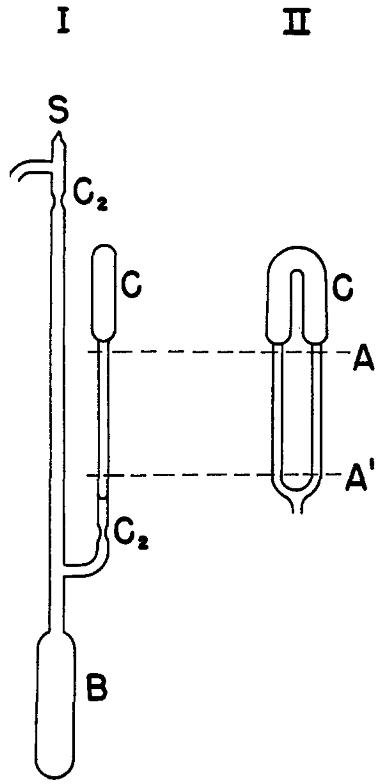

Fig. 2.—U-shaped cell and device for filling it: I, cell attached to filling device; II, cell only, side view; C_2, constrictions.

ments at 25°, α-azo-bis-isobutyronitrile crystals were weighed and transferred to B. At 50° such a small amount of initiator was required that it was added as 1 cc. of a 2.065 × 10^{-6} M solution in benzene. The benzene was removed by pumping three hours on the high vacuum system with B at −20°. (Prolonged evacuation at room temperature caused a small loss of the azo compound.) After the benzene (if any) was pumped off, benzoquinone was added to half of the cells as $^1/_2$ or 1 cc. of a solution of the quinone in optically pure normal hexane, by opening S and resealing. Since the hexane was not removed, 1 cc. of optically pure hexane was added to a pair of control cells. After initiator and inhibitor (if any) were added to B, the cell filling devices were evacuated to 10^{-4} mm. with B at −80° and subsequently a known amount of purified vinyl acetate was distilled in. The cell filling device was then sealed from the system and manipulated as with the cells used for rotating sector studies.[7] The reaction cells were placed in constant temperature baths (±0.01°) and the rates followed dilatometrically with cathetometers. No light fell on the cells except dim red illumination used on the capillaries.

Discussion

The accepted polymerization mechanism for such vinyl compounds as methyl methacrylate, styrene and vinyl acetate is represented herewith

Initiation Rate R_i

Propagation

$$M\cdot + M \xrightarrow{k_p} M\cdot \qquad k_p(M\cdot)(M)$$

Termination

$$M\cdot + M\cdot \xrightarrow{k_t} \text{Polymer} \qquad 2k_t(M\cdot)^2$$

Transfer with monomer

$$M\cdot + M \xrightarrow{k_{tr}} \text{Polymer} + \text{radical from monomer} \qquad k_{tr}(M\cdot)(M)$$

In the initiation step, heat or light activates the monomer or an initiator ("catalyst") to produce radicals which add to the monomer, M, to form growing polymer radicals, M·. With several assumptions previously justified,[7] this mechanism leads to equations (1) and (2)

$$(1) \quad \frac{R_p\tau_s}{(M)} = \frac{k_p}{2k_t}$$

$$(2) \quad \frac{R_p^2}{R_i(M)^2} = \frac{k_p^2}{2k_t}$$

where R_p = rate of polymerization and τ_s = lifetime of kinetic chain from initiation by a radical to its termination by another growing chain.

These two equations enable one to determine the rate constants of propagation and termination by means of two experiments. For a given rate of polymerization, the kinetic chain lifetime is measured by means of the rotating sector method in one experiment, the rate of initiation of chains in the second experiment. Where transfer with the monomer has a sufficiently small effect on the polymer molecular weight a correction can be made as in methyl methacrylate[13] or styrene,[14] and the rate of initiation may be calculated from polymer molecular weights and the rates of polymerization with changing initiator concentrations. On the other hand, the molecular weight of polyvinyl acetate is determined almost completely by transfer with the monomer, so that rates of initiation have been calculated from the rate of initiator decomposition and from the induction period caused by an inhibitor. Results of both methods agree closely.

The use of carefully purified vinyl acetate is essential to the correct evaluation of the rate constants. With insufficiently purified vinyl acetate in either the photochemical or initiator-induced polymerization, one obtains an induction period in which the rate of polymerization is initially low and gradually increases to a final steady value. The induction period is shorter, and the final steady rate higher, the more highly purified is the monomer. Further, the steady rate finally attained with impure monomer is not proportional to the square root of the rate of initiation as required by the assumed mechanism, presumably because of a trace of an inhibiting impurity. In our work monomer purity was judged by ultraviolet absorption and by the rate of polymerization induced by benzoyl peroxide, and by these tests our monomer appears to be the purest yet reported.

In succeeding sections the following topics are discussed: purity of vinyl acetate, sector experiments, rates of initiation experiments, rate constants of polymerization, and transfer with monomer.

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[13] G. V. Schulz and F. Blaschke, *Z. physik. Chem.*, **B51**, 75 (1942); G. V. Schulz and G. Harborth, *Die Makromolekulare Chemie*, 1, 106 (1947).

[14] G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

Purity of Vinyl Acetate.—The ultraviolet absorption of a sample of vinyl acetate is a test for the removal of light-absorbing impurities. Fig. 3 indicates the presence of more impurities in the vinyl acetate used by Burnett and Melville or by Dixon-Lewis, than in the other two samples. Further, the figure also indicates our monomer to be slightly more transparent in the 2650–2750 Å. range than the sample sent us by Prof. Bartlett. This sample, prepared like that used by Swain and Bartlett, was sent us in a Corning Lifetime Red Low Actinic flask sealed under nitrogen. The flask was attached to the vacuum system, degassed and handled by our usual procedures, omitting, however, the partial polymerization by irradiation.

Swain and Bartlett[5b] found that vinyl acetate polymerized at the rate of 8.4×10^{-5} m./l./sec. at 25° in the presence of 0.105 M benzoyl peroxide. All of our samples of vinyl acetate therefore were tested with 0.105 M benzoyl peroxide at 25°, using the experimental procedure described for rates of initiation. A rate of polymerization approximately equal to that reported above, together with a negligible induction period, was taken to indicate satisfactory purification. Table II summarizes the results on several samples. It was found in our distillation procedure that if the middle 2-liter fraction (see Experimental) was divided into four 500-cc. cuts, each succeeding cut reacted faster in peroxide initiated runs after a shorter induction period (first and second cuts in Table II). Redistillation of the monomer effected no appreciable improvement, possibly because of exposure of the once distilled vinyl acetate to air and moisture during assembly of the still. Table II shows that preirradiation affected the final constant rate but little (second cut before and after irradiation), but largely eliminated the induction period. This elimination of the induction period was important as several per cent. of monomer polymerized during an induction period of 120 minutes.

TABLE II

POLYMERIZATION OF VINYL ACETATE AT 25° WITH 0.105 M Bz_2O_2

Sample	Induction period, min.	Rate[a] m./l./sec. × 10^5
From Prof. Bartlett	120	7.5[b]
This paper Distilled First cut	162	7.7
This paper Distilled Second cut	95	8.2
Second cut—pre-irradiated	<15	8.1
Best sample (pre-irradiated)	< 5	8.6

[a] Constant rate following induction period. [b] Since Swain and Bartlett report 8.4×10^{-5} for similar sample, this sample may have deteriorated during our experiments.

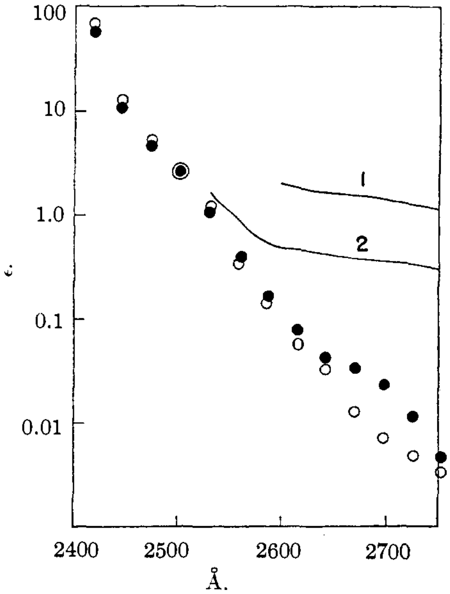

Fig. 3.—Ultraviolet absorption of vinyl acetate (in n-hexane): ○, our vinyl acetate; ●, Bartlett's vinyl acetate, our measurement; 1, Burnett and Melville (ref. 4b); 2, G. Dixon-Lewis (ref. 6); $\log_{10}(I_0/I) = \epsilon cl$ where ϵ = molar extinction coeff., c = concn. in moles/liter, l = cm. light path.

Sector Experiments.—In the rotating sector method[7] a reaction cell is irradiated with a beam of light of constant intensity. Provision is made, usually with a rotating disk from which a sector has been cut, to interrupt this light periodically, so that the cell undergoes repeated cycles of irradiation and darkness. The term "sector rate ratio" we define as the rate of polymerization under interrupted illumination divided by the rate under steady illumination. We have used a sector cycle of $^1/_4$ light to $^3/_4$ darkness and for such a cycle, in the absence of any dark reaction, the sector rate ratio varies between the limits 0.5 and 0.25 at high and low sector speeds, respectively, for systems in which the rate of reaction is proportional to the square root of the absorbed light intensity. For intermediate sector speeds the sector rate ratio is a function of b (the ratio of the duration of the light flash to the life of the kinetic chain) as shown by the curve in Fig. 4. This figure also shows the agreement obtained when the experimental rate ratios are plotted against time of flash, t_1, and the plot adjusted horizontally to the position of best fit with the theoretical curve. At this position the experimental abscissa t_1 at any point divided by the theoretical abscissa b at the same point yields the kinetic chain lifetime τ_s. In the remainder of this section these points are discussed: our lifetimes of the kinetic chains are presented and shown to agree with those of Swain and Bartlett; the importance of comparing rates in sectored light with that in steady light is discussed; non-uniform light absorption is shown to be a probable source of error in the work of Burnett and Melville; and $k_p/2k_t$ values are calculated from the kinetic chain lifetimes.

In Table III, lifetimes of kinetic chains in vinyl acetate as found by us and reported in the litera-

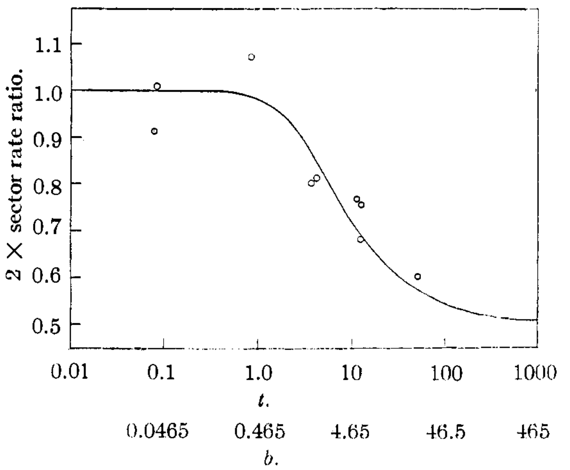

Fig. 4.—Rate of polymerization of vinyl acetate in intermittent light for different times of flash, t_1: curve, theory for zero dark rate, abscissa = b; points, run 23 at 50° at 0.85% contraction per hour, abscissa = t_1; b = (time of flash)/(life kinetic chain) = t_1/τ_s.

ture[4,5] are summarized. The third column gives the range of wave lengths in the light entering the reaction cell, and indicates whether the photoreaction was initiated by light alone or by the photodecomposition of α-azo-bis-isobutyronitrile. In the next to the last column the experimental fast sector rate ratios are listed. For our experimental conditions the ratio should approach a limit of 0.5 with increasing sector speeds. In all of our work the rate of polymerization for any given sector speed was compared with the rate in steady light. In the work in the literature[4,5] the rate for a given sector speed was compared with the limiting rate attained at high sector speeds. In case the experimental results deviate from theory either for high or else for low sector speeds the latter procedure will not show whether the limiting ratio at high or at low sector speeds is in error. In the presence of sufficient inhibitor, all kinetic chains in vinyl acetate will be terminated by inhibitor and the amount of reaction will be proportional to the total absorbed light without regard to flashing frequency.[5b] In such case the fast and slow sector ratios will both be 0.25 (for 1:3 light to dark cycle). For smaller amounts of inhibitor the fast sector ratio will be intermediate between 0.25 and 0.50. It was found that only the best monomer samples, as judged by the peroxide initiated rate test, gave fast sector ratios approximating 0.5. Even these samples at low rates of polymerization gave low fast sector ratios, presumably because a trace of impurity will terminate a greater fraction of the very long kinetic chains occurring in the slow polymerizations than will be the case for rapid polymerization where the chains are short. An example of this effect is given in Table III in the work at 25° run 24, where increasing the rate from 0.9 to 4.53% per hour brings the limiting ratio up from 0.4 to 0.48. Swain and Bartlett,[5b] using a 1:3 light to dark cycle, obtained a ratio of 0.6 instead of 0.5 between the limiting rate at low sector speed and the limiting rate at high sector speed. Our experience suggests that traces of inhibiting impurities were present, lowering the fast sector rate ratio. Burnett and Melville,[4b] with a flashing cycle in which the dark and light periods were equal, obtained agreement with the theoretical curve both for high and low flashing frequencies. As will be seen later the rate in the effective reaction zone was extremely high in their experiments, and at this high rate the very short chains usually terminated each other in spite of the impurities present.

Table III

Kinetic Chain Lifetimes in Vinyl Acetate Polymerization

Run	°C.	Irradiating[a] wave lengths	τ_s [b]	% polymerization per hr.	Fast sector[c] ratio	τ_s at 4.02%/hr.[d] polymerization
		Our Vinyl Acetate				
22	25	Small amount 2537 + all Hg lines to 4050 Å.	1.65	1.81	0.50	0.74
22	50		1.00	3.62	.47	.90
23	25	3660	0.72	9.05	0.57[e]	1.62
23	50	2650–4050 No 2537	2.15	3.62	.48	1.94
		Bartlett's Vinyl Acetate				
24	25	2650–4050 No 2537	..	0.9	0.4	
24	25	3660	0.64	4.53	0.48	0.72
24	5	3660	.92	1.91	.47	.44
		Literature				
S and B[5]	25	>3000	1.25	4.02	..	1.25
B and M[4]	15.9	?	0.023	3.7	..	0.021

[a] α-Azo-bis-isobutyronitrile used as sensitizer at 3660 Å. With other wave lengths no sensitizer used. [b] This τ_s is the experimentally measured kinetic chain lifetime found at the experimental rate in the following column. [c] Fast sector ratio = (rate in high frequency intermittent light)/(rate in steady light). [d] Kinetic chain life at the experimental rate of polymerization of ref. 5. [e] As α-azo-bis-isobutyronitrile is a thermal initiator as well as photosensitizer appreciable dark rates occurred. In this experiment the dark rate was 10% that in steady light and the theoretical ratio for such a dark rate is 0.508. Value given represents only one determination of limiting ratio.

The literature results in Table III are in distinct contradiction. Swain and Bartlett[5b] have suggested that in Burnett and Melville's work, the activating light was absorbed in a thin layer at the front of the reaction cell, so that the measured kinetic chain lifetime actually corresponds to a rate in this thin layer about 40-fold the rate averaged over the cell. Burnett and Melville measured the quantum yield of vinyl acetate polymerization for light 2800–3200 Å. If one assumes the same wave lengths were used by them in the sector studies, extrapolation of Fig. 3 would indicate high absorption for their monomer even above 2800 Å. Comparison of Runs 22 and 23 in Table III shows this effect of non-uniform absorption in a minor way. The small fraction of 2537 Å. in Run

22 was completely absorbed near the front of the reaction cell while the 2650 Å. mercury line is only 40% absorbed and longer wave lengths show much less absorption. Thus, in Run 22 the rate due to the 2537 Å. radiation near the front of the cell is appreciably higher than elsewhere and the lifetime measured for the average rate is short. In Run 23 at 50°, the unsensitized reaction is fairly uniform from front to back of cell (even with 2650 Å. radiation alone the relative variation in rate would be only 5 to 4). Where sensitizer was used the absorption of 3660 Å. was kept below 15%. Thus the lifetimes in the last column of Table III are somewhat longer for Run 23 than for Run 22. We attribute the slightly lower values in Run 24, using the sample of vinyl acetate from Professor Bartlett, as due to traces of retarding impurities. On the whole our work in Table III is in very good agreement with the results of Swain and Bartlett, and clearly at variance with the data of Burnett and Melville.

In the calculation of rate constants Table III was used as follows: Run 23 was taken as giving the correct absolute values of the kinetic chain lifetime. Assuming that the absorbed light intensity, but not diffusion or convection, regulates the distribution of reaction rates in the cell, Run 22 should yield the proper temperature coefficient for the lifetime even though the individual τ_s values are in error. Further, in view of the very mild retardation in Run 24 it might be assumed that a suitable temperature coefficient could be calculated from this run also. Therefore the temperature coefficients of Runs 22, 23, and 24 were averaged, and the τ_s values of Run 23 changed slightly to correspond to this temperature coefficient (Table IV). Since the average temperature coefficient derived as above differs but slightly from that in Run 23, the procedure followed simply confirms the temperature dependence found in Run 23. This confirmation is important because it shows the ratio (from which activation energies are calculated) between the τ_s values at different temperatures can be determined more precisely than can the individual absolute values of the lifetimes. This result might be expected, since the variation from one run to another depends upon the purification of the monomer or on the conditions of irradiation, whereas the relative values at two different temperatures measured in one experiment upon the same sample depend mainly on the precision of the method which previous work has shown to be rather good.[7]

In Table IV are the τ_s values of Run 23 corrected to the average temperature coefficient, and the $k_p/2k_t$ ratios calculated from the corrected lifetimes by eq. (1). The kinetic chain lifetimes given in Table IV are believed accurate to ±50%, which is about double the estimated error of the lifetime determinations on methyl methacrylate.[7] Since Swain and Bartlett estimate an error of not more than 100% for their lifetime result at 25°, and since our 25° value in Table IV differs from theirs by less than 25%, the agreement is well within experimental error. The chief error in $k_p/2k_t$ derives from τ_s.

TABLE IV

RATE CONSTANT RATIOS FROM SECTOR WORK

Temp., °C.	τ_s at 4.02% per hr.	$(k_p/2k_t) \times 10^5$
25	1.54	1.72
50	2.03	2.26

Rate of Initiation Experiments.—Since the molecular weight of polyvinyl acetate is determined mostly by the transfer reaction of the growing radical with the monomer, molecular weight studies do not enable one to calculate the rate of initiation. Two alternative methods suggest themselves: (1) the use of an inhibitor such as benzoquinone to count the chains started, or (2) the rate of initiation of chains can be assumed as twice the rate of decomposition of free radical initiator. Burnett and Melville[4b] showed that benzoquinone is an effective inhibitor for the photopolymerization of vinyl acetate, so this inhibitor was chosen for tests in our experiments.

TABLE V

RATES[a] OF INITIATION IN VINYL ACETATE

25°C.

Cell	25	23	26	16
% VA[b]	100	94.4	94.3	93.9
$R_p \times 10^4$ [c]	1.246	1.122	1.158	1.185
Initiator	0.1137	0.1163	0.1172	0.1279
$R_i \times 10^9$ from initiator[d]	8.3	8.49	8.56	9.34
$(k_p^2/2k_t) \times 10^2$ from initiator[e]	1.62	1.44	1.53	1.48
Quinone $\times 10^5$	....	....	5.11	11.19
Induction period (min.)	145	156	267(111)[f]	394(238)[f]
$R_i \times 10^9$ from quinone[h]	....	....	7.64	7.85
$(k_p^2/2k_t) \times 10^2$ from quinone[e]	....	....	1.71	1.76

50°C.

Cell	15	5	14	3
% VA[b]	100	97.3	97.0	97.2
$R_p \times 10^4$ [c]	1.344	1.249	1.355	1.050
Initiator $\times 10^4$	5.84	5.74	6.21	5.82
R_i from initiator[d]	2.69	2.64	2.80[g]	2.52[g]
$(k_p^2/2k_t) \times 10^2$ from initiator[e]	6.28	5.82	6.51	4.33
Quinone $\times 10^6$	....	....	2.73	5.10
Induction period, min.	<10	<10	153	435
$R_i \times 10^9$ from quinone[h]	....	....	2.93	1.91
$(k_p^2/2k_t) \times 10^2$ from quinone[e]	....	....	6.22	5.72

[a] All rates and concentrations in moles, liters, seconds. [b] Corrected for amount of n-hexane. [c] R_p = rate of polymerization. [d] R_i = rate of initiation calculated as $2k_d$ (Init.) where k_d is the unimolecular rate constant for decomposition of α-azo-bis-isobutyronitrile and is 3.65×10^{-8} sec.$^{-1}$ at 25° and 2.3×10^{-6} at 50° in xylene from ref. 17. [e] $k_p^2/2k_t$ calculated from equation (2). [f] Induction periods in parentheses have been corrected by subtracting the induction period of Cell 23 from measured period. [g] R_i for steady state reaction following induction period, and values have been corrected for initiator decrease during induction. [h] R_i calculated assuming 2 quinone molecules stop 2 chains.

In styrene at 100°, several molecules of quinone are consumed per growing chain,[15] but as this phenomenon is apparently absent at lower temperatures it has been suggested that the inhibitor method be used only at low temperatures.[16] Our experiments were done at 25 and 50°. Further, the use of an inhibitor should be more effective in vinyl acetate where a reactive polymer radical is adding to an unreactive monomer, in contrast to styrene where an unreactive radical is adding to a reactive monomer. The initiator used, α-azobisisobutyronitrile, has the advantage that its rate of decomposition varies little with solvent whether xylene, dodecyl mercaptan or dimethylaniline, and is not affected by inhibitors[17] and hence the rate of decomposition in vinyl acetate can be assumed equal to that in xylene.

Table V outlines the experiments on rates of initiation, and Fig. 5 illustrates the effect of the inhibitor on the reaction. It will be noted in Fig. 5 that at 50° no induction period is found in the absence of inhibitor and that the transition from almost zero reaction to the steady state reaction occurs abruptly at the end of the induction period.

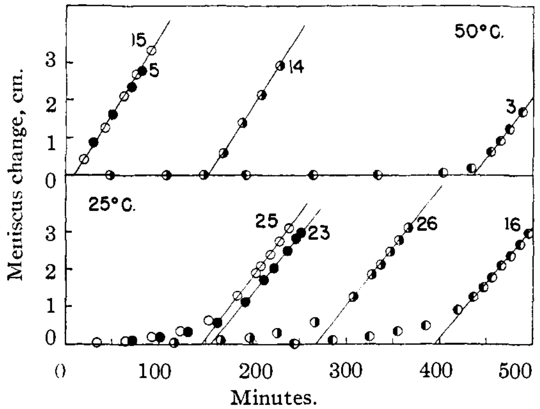

Fig. 5.—The inhibition of vinyl acetate polymerization by benzoquinone:

	Upper 50°		Lower 25°
Cell	15	○	25
	5	●	23
	14	◑	26
	3	◐	16

See Table V: apparent induction period in 15 and 5 due to lag in attaining temperature equilibrium.

At 25°, however, in the presence of inhibitor complete inhibition is followed by gradually increasing rate which attains a steady rate after a couple of hours. This period of gradual increase parallels very closely the behavior of the reaction at 25° in the absence of added inhibitor. Other than temperature the main experimental difference between the 25 and 50° cells is the relatively large amount of initiator used at 25°. We believe that a mild retarder (perhaps water)[5b] was associated with the azo initiator used. The measured induction periods in the presence of inhibitor at 25° were corrected by subtracting 156 min., the induction period in the absence of inhibitor. The resulting values in parentheses in Table V correspond exactly to the periods of complete inhibition (negligible reaction) observed in these cells.

The conclusions to be drawn from Table V are: (1) the induction period is proportional to the concentration of inhibitor, (2) the steady rate of polymerization after the induction period is not affected by inhibitor products, and (3) the assumption that twice the rate of initiator decomposition is the rate of chain initiation is consistent with the assumption that 2 quinone molecules stop 2 chains, the two inactive radicals formed presumably then interact.[15]

The average values of $k_p^2/2k_t$ are listed in Table VI.

TABLE VI

RATE CONSTANT RATIOS FROM INHIBITOR AND CATALYST CONSUMPTION

	25°	50°
$(k_p^2/2k_t) \times 10^2$ from catalyst	1.52	5.74
$(k_p^2/2k_t) \times 10^2$ from quinone	1.74	5.97

This agreement is considered good. If the assumption that two molecules stop two chains is correct, the quinone result depends largely on accuracy in measuring the amount of inhibitor; in the initiator calculation the rate constant for initiator decomposition offers additional error. In subsequent calculations the quinone values were used.

Rate Constants of Polymerization.—From Table VI and Table IV one can calculate values of the propagation and termination rate constants. These are compared with literature values in Table VII. The agreement with Swain and Bartlett at 25° and with Bamford and Dixon-Lewis at 60° is satisfactory. The factor of 6 disagreements with Bamford and Lewis at 0° may be attributable in part to impurities in their vinyl acetate if the absorption in Fig. 3 may be taken as

TABLE VII

RATE CONSTANTS OF POLYMERIZATION OF VINYL ACETATE

	0°	15.9°	25°	50°	60°
k_p	325	690	1012	2640	3700
	(1800)[a]	(770)[b]	(550)[c]		(2630)[a]
$2k_t \times 10^{-7}$	2.7	4.5	5.88	11.68	14.8
	(20)[a]	(310)[b]	(4)[c]		

$$k_p = 2.43 \times 10^8 e^{-7,320/RT}$$
$$2k_t = 4.16 \times 10^{11} e^{-5,240/RT}$$

[a] Ref. 6, Bamford, Dixon-Lewis. [b] Ref. 4b, Burnett and Melville. [c] Ref. 5b, Swain and Bartlett. Constants have been divided by 2. This factor of 2 derives from an analysis of their kinetic expressions. Professor Bartlett agrees with this change (private communication).

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(15) F. R. Mayo and R. A. Gregg, This Journal, **70**, 1284 (1948).

(16) P. D. Bartlett, G. S. Hammond and H. Qwart, "The Labile Molecule," *Discussion of the Faraday Soc.*, No. **2**, p. 342 (1947).

(17) F. M. Lewis and M. S. Matheson, This Journal, **71**, 747 (1949).

typical of their monomer samples.[18] The source of error in the termination constant of Burnett and Melville has already been discussed.

The propagation rate constant of vinyl acetate is higher than found for methyl methacrylate. A low frequency factor is again found for the propagation reaction and a normal one for the termination in agreement with results on methyl methacrylate. As molecular weights are governed by transfer with the monomer, a variation of the experimental rates does not enable one to study the effect of radical size on reactivity. Further, because of the low molecular weight of polymer formed one would not expect much acceleration of the reaction in the later stages of polymerization, and we have found no acceleration in polymerizations carried to 40% conversion.

Transfer with the Monomer.—A preliminary experiment was carried out at 50° to see if rates of initiation could be determined by molecular weight studies. Two cells of vinyl acetate, one containing benzoyl peroxide and the other α-azo-bis-isobutyronitrile were polymerized. The polymer was precipitated and isolated, and the measurement of the osmotic molecular weight of the polymer attempted (Table VIII). The rates of initiation were calculated assuming spontaneously decomposing initiator is 100% efficient in starting chains. The ratio of the rates of polymerization is 1.78 while the corresponding ratio of the square roots of the rates of initiation is 2.06. In view of the uncertainties in the rate constants of initiator decomposition the agreement is good. Thus, the radicals from benzoyl peroxide appear to be about 50 to 100% efficient in initiation, so that the 100% efficiency assumed by Swain and Bartlett[5b] is a good approximation. Osmotic measurements showed the polymers formed with both catalysts to have mol. wts. less than 50,000 as indicated in the table. Comparison with the kinetic chain length shows as many as 100 or more transfer reactions per kinetic chain. These transfers are mostly with the monomer, not with the initiator, since the unsensitized photoreactions also yield low viscosity polymers. The rate constant for transfer with monomer, k_{tr} is estimated to be ≥ 5 at 50°, in fair agreement with the value of 0.123 at 0° reported by Dixon-Lewis.[6] The transfer constant of vinyl acetate is thus about 0.002 at 50°, in comparison with 4.8×10^{-5} for methyl methacrylate.

TABLE VIII

MOLECULAR WEIGHTS IN POLYVINYL ACETATE

	Catalyst (m./l.) $\times 10^3$	$R_i \times 10^{9}$ [a]	$R_p \times 10^4$	$\bar{P}$ [b]	$\bar{\nu} \times 10^{-4}$ [c]
Benzoyl peroxide	1.618	7.13	1.89	<600	2.65
Azo initiator	0.362	1.67	1.06	<600	6.35

[a] Unimolecular rate constant for spontaneous decompn. 2.2×10^{-6} sec.$^{-1}$ at 50° estimated from Nozaki and Bartlett[8] for benzoyl peroxide. For α-azo-bis-isobutyronitrile 2.3×10^{-6} at 50° Table V. [b] Average degree of polymerization. [c] Kinetic chain length.

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Summary

The rotating sector method has been used to measure the lifetimes of kinetic chains in the polymerization of vinyl acetate. The results agree better with those of Swain and Bartlett[5b] than with those of Burnett and Melville.[4b] The rate of initiation for a given rate of vinyl acetate polymerization has been measured, (1) using α-azo-bis-isobutyronitrile as a thermal initiator and taking the rate of initiation as twice the rate of decomposition of initiator, and (2) by using benzoquinone as inhibitor and assuming that two quinone molecules stop two chains. The two methods agree. The lifetime and rate of initiation data have been combined to calculate the rate constants and activation energies for chain propagation and termination. Reasons are given for believing these rate constants to be the most precise yet reported for vinyl acetate. As with methyl methacrylate, a normal frequency factor is found for termination, and a somewhat lower factor for the propagation reaction which involves a double bond. The rate constant for transfer with the monomer is much higher than for methyl methacrylate.

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[18] The theory of Bamford and Dewar [*Proc. Roy. Soc.* (*London*), **A192**, 309 (1948)] assumes light absorbed by monomer initiates biradicals. However, light absorbed by an impurity might well initiate monoradicals.