ADDITION OF BROMOTRICHLOROMETHANE TO VINYL ACETATE

PART 2.—KINETICS OF THE PHOTOCHEMICAL REACTION

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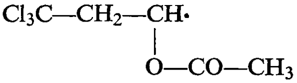
Attempts have been made to measure the velocity coefficients involved in the photochemical addition of bromotrichloromethane to vinyl acetate. The system was studied using concentrations of bromotrichloromethane ranging from 0·26-9·58 mole l.$^{-1}$, and of vinyl acetate from 0·55-10·5 mole l.$^{-1}$. Conditions could not be found such that the chain-transfer reaction between a bromotrichloromethane molecule and the radical produced by the addition of a trichloromethyl radical to a vinyl acetate molecule became rate-controlling, and hence we could not measure its velocity coefficient. Rates of initiation were measured using DPPH, and the values obtained were found to be influenced to some extent by the solvent employed, and also by the technique used. These effects are reflected in the values of the velocity coefficients, which at 25°C were found to be: $k_2 = 795$, 2410 and 1590 l. mole^{-1} sec^{-1}, and $k_4 = 0{\cdot}53 \times 10^8$, $1{\cdot}61 \times 10^8$ and $1{\cdot}06 \times 10^8$ l. mole^{-1} sec^{-1}, when the rate of initiation was determined absorptiometrically in monomer, in solvent, and dilatometrically respectively. The last value in each case, is in good agreement with the results of previous workers [1] who evaluated these coefficients by substantially the same method.

In a study of the photochemical reaction between vinyl acetate (VA) and bromotrichloromethane (BTCM), Melville, Robb, and Tutton [1] proposed the following kinetic scheme:

$$\begin{array}{rlcr}
\mathrm{TBr} \rightarrow & \mathrm{T\cdot} + \mathrm{Br\cdot} & k_1 & (1) \\
\mathrm{T\cdot} + \mathrm{VA} \rightarrow & \mathrm{T(VA)\cdot} & k_2 & (2) \\
\mathrm{T(VA)\cdot} + \mathrm{TBr} \rightarrow & \mathrm{T(VA)Br} + \mathrm{T\cdot} & k_3 & (3) \\
\mathrm{2T\cdot} \rightarrow & \left\{\begin{array}{l} \text{non-} \\ \text{radical} \\ \text{products} \end{array}\right\} & \begin{array}{c} k_4 \\ k_5 \\ k_6 \end{array} & \begin{array}{r} (4) \\ (5) \\ (6) \end{array} \\
\mathrm{T\cdot} + \mathrm{T(VA)\cdot} \rightarrow & & & \\
\mathrm{2T(VA)\cdot} \rightarrow & & &
\end{array}$$

where T· represents the trichloromethyl radical, VA a molecule of vinyl acetate and T(VA)· the free radical



$$\mathrm{Cl_3C{-}CH_2{-}CH\cdot(O{-}CO{-}CH_3)}$$

They deduced that if in excess BTCM, reaction (2) is the slow step in the propagation process, and termination occurs principally via reaction (4), then the rate of reaction is given by

$$-\frac{\mathrm{d[VA]}}{\mathrm{d}t} = k_2\left(\frac{I}{k_4}\right)^{\frac{1}{2}}[\mathrm{VA}], \qquad (a)$$

where I is the rate of initiation.

They also deduced that in excess VA, if reaction (3) is rate-controlling and termination occurs mainly by reaction (6), then the rate is given by

$$-\frac{\mathrm{d}[\mathrm{VA}]}{\mathrm{d}t} = k_3\left(\frac{I}{k_6}\right)^{\frac{1}{2}}[\mathrm{BTCM}]. \qquad (b)$$

In their work they found that the rate-dependences predicted by (*a*) and (*b*) were obeyed. In particular, they obtained the predicted 3/2 rate-dependence on BTCM concentration in the presence of excess vinyl acetate expected from (*b*), since I is proportional to the BTCM concentration. They were thus able to evaluate k_2, k_3, k_4, k_6, and by a suitable kinetic analysis, an average value for k_5. For k_2, k_3 and k_4, they obtained values of 1120, 2740, and 10^8 l. mole^{-1} sec^{-1} at 30°C respectively. The value of k_3 is of the same order of magnitude as that for the propagation reaction in vinyl acetate polymerization.[2, 3] Polymerization might therefore be expected to occur when the reaction mixture contains a large excess of vinyl acetate. No polymer formation was observed by Melville *et al.*,[1] nor did their observed rate-dependencies indicate that polymerization was occurring. In part 1 of this series [4] it was shown that under the conditions used by the above-mentioned authors no polymerization occurs, which presumably means that either the velocity coefficient for reaction (7),

$$\mathrm{T(VA)\bullet + VA \rightarrow T(VA)_2^{\bullet}} \qquad (7)$$

is considerably lower than for polymerization, or else the value obtained for k_3 by Melville *et al.*[1] is inaccurate. It was decided therefore to re-evaluate the velocity coefficients involved in the reaction.

EXPERIMENTAL

Vinyl acetate and bromotrichloromethane were purified by the treatment described in part 1 of this series [4] and A.R. chloroform, cyclohexane and benzene (molecular-weight-determination grade) were redistilled before use. 1 : 1′-di-phenyl-2-picrylhydrazyl (DPPH) was prepared by the method of Goldschmidt and Renn [5] and recrystallized from a mixture of ligroin and benzene. This gave the 1 : 1 crystalline complex [6] of DPPH and benzene (cryoscopic molecular weight in benzene 476±6). This complex was used without any further treatment, the weights used being corrected for the benzene content of the complex.

Dilatometers were usually of 10-20 ml capacity and consisted of a Pyrex glass bulb joined to a Veridia precision bore stem. Those used in the kinetic chain life-time experiments have been described in a previous paper.[7] Pyrex glass tubes were used in the absorptiometric experiments. The usual filling techniques were employed for filling the dilatometers in the absence of air. The reactions were carried out at 25°C in a water-thermostat and initiated with light from a 125 W mercury-vapour lamp, filtered through a Chance 0X1 filter.

Reaction rates were measured dilatometrically either by following the rate of contraction during the thermal steady state [7] (i.e., when the rate of self-heating due to reaction is equal to the rate of loss of heat to the surroundings), or by following the rate of expansion immediately on the commencement of irradiation. In the experiments involving the use of benzene or cyclohexane as a diluent, the former method was always used.

Intensity exponents were determined by measuring the rate of contraction due to reaction under full light intensity and then under a known reduced light intensity. As a precaution, the rate was re-measured under full intensity to ensure that no permanent retardation had occurred during the intervening period.

The rate of formation of trichloromethyl radicals was obtained by measuring the rate of removal of DPPH [8] spectrophotometrically at 5240 Å from inhibition period measurements.

The kinetic chain life-time was obtained by (*a*) the dilatometric non-stationary state method,[9] and (*b*) a modified rotating sector method.[10] In (*b*), the initial expansion rate immediately on the commencement of irradiation was measured under steady and intermittent illumination of various frequencies. The intermittent illumination was obtained by interposing a rotating sector (divided into four equal segments, two of which had been removed) in the path of the beam of light. The sector was driven through a 25 : 1 reduction gear by a variable speed electric motor. Flash-times were measured using a photo-electric cell, the light input also being chopped by the sector. The output of this cell was amplified and the pulses were recorded by an Elliott d.c. pen-recording voltmeter when they were of low frequency, and when high, they were balanced against the output of a signal generator using a cathode-ray oscilloscope.

RESULTS AND DISCUSSION

INTENSITY EXPONENTS

The results in table 1 show that the intensity exponent is approximately 0·5 over the concentration used. This indicates that the chain termination reaction proceeds by the mutual interaction of the chain carrier radicals, in agreement with the kinetic scheme suggested previously.[1]

TABLE 1.—INTENSITY EXPONENTS

[BTCM]/[VA] (mole ratio)	(relative light intensity)$^{\frac{1}{2}}$	relative rate	intensity exponent
10 : 1	1 0·56	1 0·56	0·50
6 : 1	1 0·56	1 0·57	0·49
1 : 5	1 0·56	1 0·56	0·50

RATE-DEPENDENCIES ON CONCENTRATIONS OF REACTANTS

Experiments were carried out both in the presence and in the absence of diluents. The results for the latter case are given in table 2. These indicate that when vinyl acetate is in excess the rate is proportional to $[\mathrm{BTCM}]^{0\cdot65}$, whereas it was expected from previous work[1] to be proportional to $[\mathrm{BTCM}]^{1\cdot5}$. When the excess reactant was BTCM, the rate was found to be proportional to $[\mathrm{VA}]^1$ in agreement with previous workers.[1] The above results are, however, not entirely satisfactory since in a liquid-phase system consisting of two components, it is impossible at constant pressure to vary each component independently. Diluents were therefore employed. Cyclohexane and benzene were found to be suitable as they gave rise to no apparent contraction when irradiated in the presence of BTCM for periods of up to 2 h, although prolonged irradiation gave rise to a very slight contraction with benzene.

TABLE 2.—DEPENDENCE OF THE REACTION RATE ON THE CONCENTRATION OF THE REACTANT OF LOWEST CONCENTRATION IN THE ABSENCE OF A DILUENT

[BTCM] mole l.$^{-1}$	[VA] mole l.$^{-1}$	rate dependence
0·26-1·04	10·50-9·66	$[\mathrm{BTCM}]^{0\cdot65}$
5·20-9·58	5·22-0·55	$[\mathrm{VA}]^1$

The dependence of the rate of reaction on the vinyl acetate concentration in the presence of excess BTCM is shown in fig. 1, curve A, both in the presence and in the absence of benzene. It will be apparent that under these conditions the rate is first order with respect to the vinyl acetate concentration.

The rate-dependence on BTCM concentration in the presence of excess vinyl acetate for three different concentration ranges using benzene as diluent are also shown in fig. 1, curves B, C and D. It will be seen from the slopes of the lines that the reaction rate is proportional to the BTCM concentration to the power of from 0·67 to 0·77. In the absence of diluent, the rate dependence was found to be 0·65, and in the presence of cyclohexane as diluent 0·61. All these values differ profoundly from the 3/2 dependence obtained by previous workers.[1]

The determination of the rate-dependence on the concentration of the reactant which is in excess is much less accurate since it is only possible to make relatively small percentage changes in the reactant concentration which results in a relatively small change in rate. However, an indication of the dependence of the rate on the concentration of vinyl acetate when in excess is given by curve A, and of BTCM when in excess by curve B of fig. 2. It is clear from this figure that in the former case, the rate is not independent of the vinyl acetate concentration as predicted by previous workers.[1] From the slope of curve A the rate appears to be proportional to the vinyl acetate concentration to the power of *ca.* 1·5. In view of the possible errors involved in such a determination, the rate-dependence may be greater than first order with respect to vinyl acetate concentration when the latter is present in excess. From the gradient of curve B (i.e., when BTCM is present in excess) the rate appears to be proportional to the BTCM concentration to the power of 0·5. Such a rate dependence would be expected if under these conditions reaction (2) were rate-controlling, and is also in keeping with the value of 0·5 obtained for the intensity exponents under these conditions.

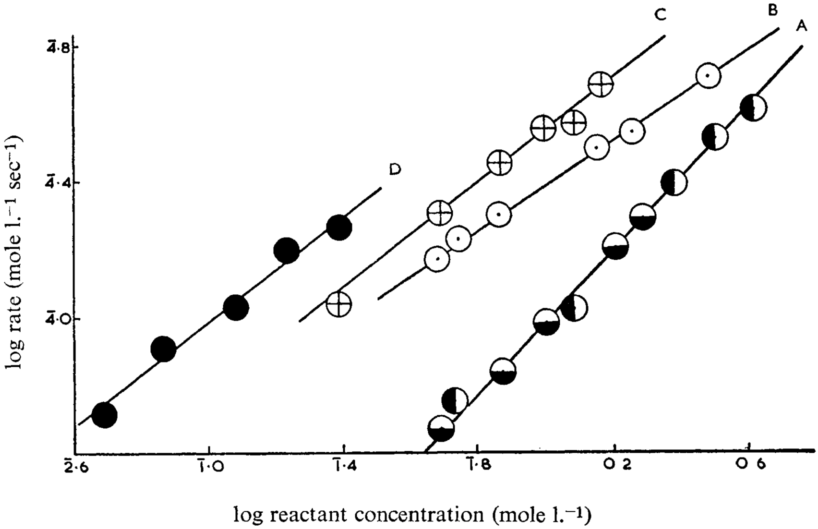


FIG. 1.—Dependence of the reaction rate on the concentration of (i) vinyl acetate in the presence of excess BTCM, curve A, and (ii) BTCM in the presence of benzene as diluent and of excess vinyl acetate, curves B, C and D.

Curve A { ◒ benzene as diluent, [BTCM] = 7·82 mole l.$^{-1}$,
{ ◐ no diluent, [BTCM] ~ 6·10 mole l.$^{-1}$,
,, B○ [VA] = 6·25 mole l.$^{-1}$,
,, C⊕ [VA] = 8·33 mole l.$^{-1}$,
,, D● [VA] = 10·42 mole l.$^{-1}$.

The rate-concentration relationships can therefore be summarized as follows:

in excess BTCM, rate $\propto[\mathrm{BTCM}]^{0\cdot5}\,]\mathrm{VA}]^{1\cdot0}$,
in excess VA, rate $\propto[\mathrm{BTCM}]^{0\cdot6-0\cdot5}\,[\mathrm{VA}]^{1-1\cdot5}$

It follows therefore that in excess BTCM, reaction (2) is rate-controlling and consequently termination proceeds mainly by reaction (4). Thus, it is possible to evaluate both k_2 and k_4. When vinyl acetate is used in excess, however, it is clear that reaction (3) is not rate-controlling since if this were so, the rate would be independent of the vinyl acetate concentration and would be proportional to the 3/2 power of the BTCM concentration. From the observed rate-dependencies it appears that the rate is determined bv contributions from both reactions (2) and (3), and hence under these conditions neither of the propagation reactions is rate-controlling. It is thus not possible to measure k_3 and k_6. If a much greater excess of vinyl acetate were used, reaction (3) might conceivably become rate-controlling. However, this would lead to experimental difficulties since the very low concentrations of BTCM would result in extremely low rates which would be difficult to measure. Furthermore, the BTCM concentration would fall relatively quickly as the reaction proceeded, giving rise to a lowering of the rate.

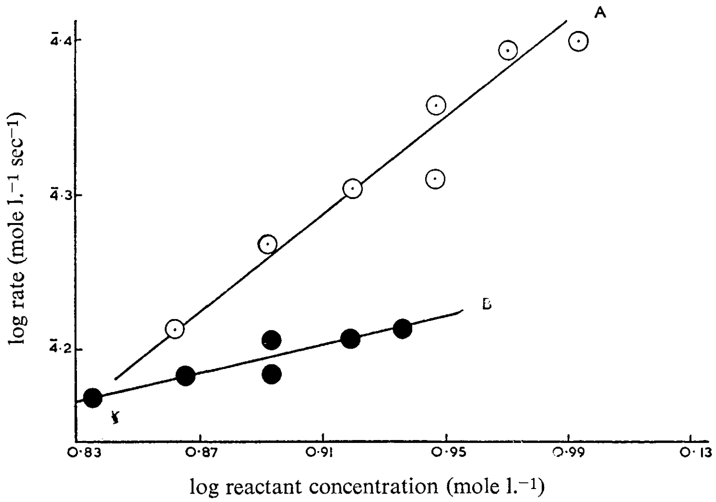


FIG. 2.—Dependence of the reaction rate on the concentration of the reactant which is in excess.

○ VA; ● BTCM.

Again, from the results given in part 1,[4] it would appear that reaction (7) and subsequent polymerization propagation reactions might contribute to the overall contraction rate and hence be indistinguishable from the reaction resulting in the formation of 1 : 1 adduct. No obvious explanation can be given for the 3/2 power dependence of the rate on the BTCM concentration obtained by previous workers [1] under conditions of excess vinyl acetate. It may be that too narrow a concentration range was used leading to relatively large experimental errors.

DETERMINATION OF ABSOLUTE RATE

Under the conditions used in this study, the reaction leads solely to the formation of the 1 : 1 adduct of VA and BTCM. Thus the rates of removal of VA and BTCM, and the rate of formation of the adduct are numerically equal.

The reaction rate has been determined mainly from the measured steady rate of expansion which occurs following the commencement of irradiation. This rate of expansion $(\varepsilon - z)$ (under adiabatic conditions) can be related to the rate of contraction z (under isothermal conditions) by

$$(\varepsilon - z) = \left[\frac{\alpha\rho'\Delta H}{SM(\rho-\rho^1)} - 1\right] z,$$

where ΔH is the heat of reaction; s, M, ρ and α are the specific heat, molecular weight, specific gravity and coefficient of expansion of the reactant mixture, and ρ^1 is the specific gravity of the reaction product. The methods employed in the calculation of the combined heat capacity, expansion coefficient and specific gravity of the initial reaction mixture are given in a previous paper [11] together with the required data. Thus, the rate of contraction can readily be calculated from the expansion measurements.

The molar volumes at 25°C of BTCM, VA, and the reaction product were found to be 99, 93 and 171 ml, respectively. Thus, the photochemical addition at 25°C of 1 mole of VA to 1 mole of BTCM to form 1 mole of adduct results in a volume contraction of 21 ml. Hence, the absolute rate is given by

$$\text{absolute rate} = 1000z/21 \text{ mole l.}^{-1} \text{ sec}^{-1},$$

where z is calculated as the fractional contraction per second.

RATE OF INITIATION

In evaluating the rate of initiation, two assumptions are made: each DPPH radical is assumed to react with one bromine atom or a chain-carrying radical, and the efficiency of the initiation process is assumed to be 100 %. Up to the present, it has not been possible to verify these assumptions, but even if they are subsequently proved to be incorrect (e.g., if several atoms or radicals are found to react with one DPPH radical, or if the efficiency of initiation is found to be less than 100 %) it will still be a relatively simple task to recalculate the present results.

The rate of removal of DPPH from solutions of BTCM and DPPH in VA and chloroform respectively was determined spectrophotometrically in the usual manner. The rate of removal of DPPH was different and that the optical densities of the end products also differed slightly in the two solutions. The latter observation is readily explained since in the presence of vinyl acetate a greater number of end products are possible.

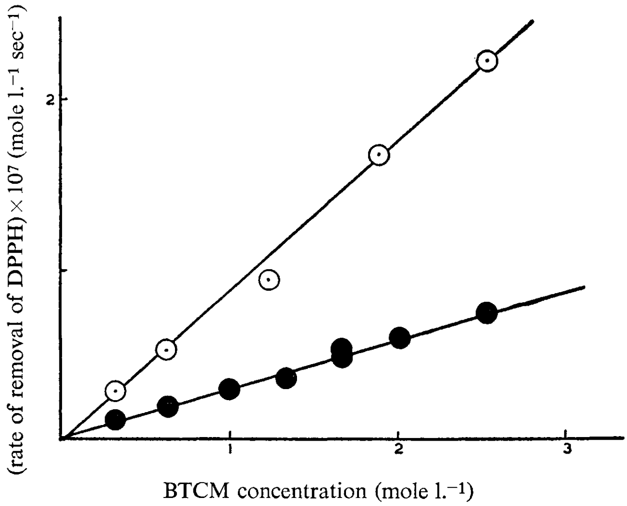


FIG. 3.—Dependence of the rate of removal of DPPH on the BTCM concentration. ⊙ VA; ● chloroform.

The plot of the rate of removal of DPPH against the concentration of BTCM is shown in fig. 3 for VA and chloroform solutions. It will be observed that both systems give linear plots, and that the rate of removal of DPPH is greater in VA solution than in chloroform solution. Two values for the rate of formation of radicals from BTCM (i.e., rate of initiation on the basis of our assumptions) will be obtained for each BTCM concentration.

The rate of initiation has also been determined dilatometrically using the inhibition period method. In this method, however, in order to obtain inhibition periods of convenient length, it was necessary to use rather smaller concentrations of BTCM than normally used in the kinetic experiments. The alternative method of increasing the inhibition periods, namely, increasing the DPPH concentration, could not be used since this would increase the optical density of the system and cause "skin effects". For a BTCM concentration of 0·661 mole l.$^{-1}$ the relationship between the inhibition period and the DPPH concentration is given by the equation

$$[\mathrm{DPPH}] = 2{\cdot}2\times 10^{-6}\,(\text{inhibition period}),$$

where the inhibition period is measured in minutes. Thus, the rate of initiation for the above BTCM concentration is $2{\cdot}2\times 10^{-6}$ mole l.$^{-1}$ min^{-1}. A linear relationship of the type shown in fig. 3 has been assumed in order to calculate the rate of initiation corresponding to higher BTCM concentrations.

The values of the ratio $k_2/k_4^{\frac{1}{2}}$ given in table 3 have been calculated from rate measurements and the rate of initiation measurements given above. It will be seen that they vary depending upon the method of determining the rate of initiation, but that the variation is a little less than a factor of two in the value of the ratio. The reason for these differences is not clear. The simplest explanation might be that the efficiency of DPPH as a radical scavenger varies with the radical involved, being less efficient in removing T· radicals than T(VA)· radicals. If this is the explanation, then the lower value of the ratio $k_2/k_4^{\frac{1}{2}}$ in table 3 would be the more accurate. The difference in this value and the one obtained using the inhibition period method may be due to some reaction between the propagating radicals and the products of these radicals after reaction with DPPH,[13] or to the absorption of initiating irradiation by these products.

TABLE 3.—EVALUATION OF VELOCITY COEFFICIENTS FOR PHOTOCHEMICAL REACTION BETWEEN VA AND BTCM AT 25°C

medium of rate of initiation determination	VA		CHCl$_3$	Melville *et al.*[1]
method	(absorptiometric)	(dilatometric)	(absorptiometric)	
$k_2/k_4^{\frac{1}{2}}$	$1{\cdot}09\times 10^{-1}$	$1{\cdot}55\times 10^{-1}$	$1{\cdot}90\times 10^{-1}$	
k_2/k_4	$1{\cdot}50\times 10^{-5}$	$1{\cdot}50\times 10^{-5}$	$1{\cdot}50\times 10^{-5}$	
k_2	795	1590	2410	1120
k_4	$0{\cdot}53\times 10^{8}$	$1{\cdot}06\times 10^{8}$	$1{\cdot}61\times 10^{8}$	$1{\cdot}0\times 10^{8}$

(k in units of l. mole^{-1} sec^{-1})

LIFETIME OF THE KINETIC CHAIN

Preliminary measurements of the lifetime of the kinetic chain were carried out using the dilatometric method of following the non-stationary state of the reaction.[9] Plots of expansion against time for the first 10 sec or so of the reaction were obtained. The linear portions of these curves intersect the time axis at times equal to $\tau \ln 2$, where τ is the lifetime of the kinetic chain. The value of τ was found to be in the region of a $\frac{1}{10}$th sec, and could clearly not be determined accurately by this method. A modification[10] of the rotating sector method[12] was therefore used. The usual sector plot of the ratio of the sectored to unsectored rate against the logarithm of the flash time is shown in fig. 4. The theoretical curve has been drawn through the experimental points obtained for the shorter flash times, since at flash times of about a second or greater, it is difficult, if not impossible, to obtain accurate rate data from the expansion-time curves. The deviations from the theoretical curve at low sector speeds are therefore not unexpected. The value of the ratio k_2/k_4 obtained from these measurements was $1{\cdot}5\times 10^{-5}$ at 25°C, which together with the values of $k_2/k_4^{\frac{1}{2}}$ obtained from rate of initiation measurements gave the values for the individual velocity coefficients shown in table 3. It will be seen that our values of k_2 and k_4 are in fairly good agreement with those of Melville *et al.*[1] which are also included in table 3. They used the dilatometric inhibition method of determining the rate of initiation and so it would seem more reasonable to compare their values for k_2 and k_4 with our determinations using this method. Using this method of comparison, the agreement will be seen to be very good. It is clear that the methods of determining rates of initiation available at present are not very satisfactory, and are probably the main cause of error in the evaluation of velocity coefficients involved in chain processes at the present time.

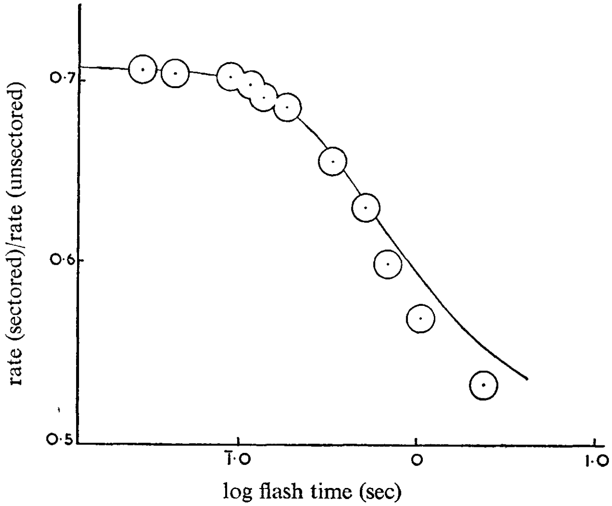


FIG. 4.—A typical rotating sector curve for the photochemical addition of BTCM to VA.

As mentioned earlier in this paper, the values of k_3 and k_6 could not be obtained since the required rate dependencies were not observed. In fact, even when the VA/BTCM ratio was 10 : 1 the rate dependence on the BTCM concentration was in the region of 0·75. Thus, under these conditions, the rate of reaction (3) is still of a similar order of magnitude as that of reaction (2). This means that the value of k_3 must be very much greater than that of k_2, which is in keeping with the rather high values obtained for the chain transfer constant in part 1. It is also possible that the value of the velocity coefficient for the propagation reaction in the polymerization of vinyl acetate may vary with the degree of polymerization of the propagating radical. This would also contribute to the high values of the chain transfer constant if, for example, k_7 were less than k_p for long-chain radicals.

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