[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

A Kinetic Study of the Addition of Bromine to Crotonic Acid in Ethylene Chloride[1]

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The rate of the reaction of crotonic acid with a mixture of bromine and tetramethylammonium tribromide in ethylene chloride was found to depend on the first power of the concentration of each of the three reagents. Three types of mechanism will explain these results: An electrophilic attack by bromine followed by a rate-determining reaction of the resulting intermediate with tribromide, a nucleophilic attack by tribromide followed by a rate-determining step involving the intermediate formed and bromine, or a concerted rate-determining attack of both bromine and tribromide on crotonic acid. If the usual electrophilic attack by bromine is the initial step it need not involve very much ionization of the intermediate to form the bromonium ion which is usually written. This may well be the main course of the reaction in the absence of the tribromide, however. With tribromide alone as the source of bromine the reaction is approximately first order with respect to the crotonic acid and the tribromide, and it appears to go by way of an initial nucleophilic attack of tribromide on the double bond. The average specific rate constant for the reaction of crotonic acid with bromine and tetramethylammonium tribromide at 30° was (9.7 ± 0.6) $\times 10^{-2}$ liter^2 per mole^2 per sec., and that for the reaction of crotonic acid with the tribromide at 30° was (2.29 ± 0.22) $\times 10^{-4}$ liter per mole per sec. Both tetramethylammonium tribromide and tetrabutylammonium tribromide showed very little tendency to dissociate to the monobromide and bromine in ethylene chloride. In each case at 25° the pK value for dissociation was 5.9 ± 0.1. Spectrophotometric evidence for a complex between bromine and crotonic acid in ethylene chloride was also found.

The stepwise, polar addition of halogen to olefinic compounds has been studied quite extensively from the standpoint of kinetics, stereochemistry and the effect of substituents on the double bond carbon atoms.[2] Not only has the usual electrophilic attack of the halogen on the double bond been considered as the initial, rate-determining step, but also in the case of double bonds substituted with electronegative groups an alternative initial nucleophilic attack by trihalide ion has been suggested as a possibility under suitable conditions.[2a] Also with the latter type of olefins substituted with electronegative groups, reactions in which the rate depends on both the electrophilic halogen molecule and the nucleophilic halide ion have been observed.[2a,3]

The present work is concerned with the kinetics of the addition of bromine to crotonic acid in the non-hydroxylic solvent, ethylene chloride, especially in the presence of tetramethylammonium tribromide.

Experimental

Quaternary Ammonium Tribromides.—To a hot solution of 2.70 g. (0.0174 mole) of tetramethylammonium bromide and 3.2 g. (0.020 mole) of bromine in 100 ml. of glacial acetic acid, approximately 20 ml. of carbon tetrachloride was added, and the mixture was cooled. A 5.1-g. (93%) yield of the crystalline tetramethylammonium tribromide was obtained after the product was filtered, washed with carbon tetrachloride containing a little bromine, and dried in a vacuum desiccator. The product had m.p. 118.0–118.5° which checks that reported.[4]

Tetrabutylammonium tribromide, m.p. 70–72°, from acetic acid–carbon tetrachloride, was prepared from tetrabutylammonium bromide and bromine as already reported.[5]

Tetrabutylammonium Triiodide.—When a solution of 3.7 g. (0.010 mole) of tetrabutylammonium iodide and 2.54 g. (0.010 mole) of iodine in 25 ml. of hot methanol was prepared, an oily layer immediately separated. This oil crystallized when the mixture was cooled. The solid was recrystallized from 95% ethanol to give 5.4 g. (87%) of tetrabutylammonium triiodide of m.p. 70.0–70.5°.

Anal. Calcd. for $C_{16}H_{36}NI_3$: I (reducible), 40.7. Found[5]: I (reducible), 40.8.

Quaternary Ammonium Bromides.—Tetrabutylammonium bromide was prepared from the reaction of tri-*n*-butylamine and *n*-butyl bromide in ethyl acetate. The salt was recrystallized from ethyl acetate to give a m.p. of 114–116.5°. Commercial tetramethylammonium bromide was crystallized from 95% ethanol.

Unsaturated Acids.—All of the substituted acrylic acids used were purified by crystallization from either ligroin or water. Water gave better results in each case: crotonic acid, m.p. 72.0–72.8°; tiglic acid,[6] m.p. 66.0–66.5°; *β,β*-dimethylacrylic acid,[7] m.p. 68–69°.

Ethylene Chloride and Bromine.—Ethylene chloride of sufficient purity for the kinetic measurements was obtained by the method outlined before.[8] For the spectrophotometric measurements of bromine and the quaternary ammonium tribromides in dilute solution it was necessary to use ethylene chloride which had been further purified by a final distillation from tetrabutylammonium tribromide (1.0 g. per 3 l.). Solutions of bromine or of a quaternary ammonium tribromide in this solvent were relatively stable even in light. This result is in marked contrast to the instability reported[5] for such solutions even in the dark. It was found by a number of quantitative experiments on solutions prepared from various samples of ethylene chloride that this instability was caused by small amounts of impurities. These impurities were evidently not removed by the purification procedure described[5] before. Solvent from which these impurities had not been removed was brominated quite rapidly and extensively with the evolution of hydrogen bromide.

Bromine was purified by treatment with potassium bromide and barium oxide as described by Bauer and Daniels,[9] except that the product of the final distillation was not recrystallized.

Product Isolation.—Two samples of 0.86 g. (0.01 mole) of crotonic acid were added to 20 ml. of ethylene chloride containing 3.14 g. (0.01 mole) of tetramethylammonium tribromide in one case and 3.20 g. (0.02 mole) of bromine and 1.54 g. (0.01 mole) of tetramethylammonium bromide in the other. The mixtures were allowed to stand two weeks in the dark. The solvent was mostly removed by evaporation after the reaction mixtures were shaken with aqueous sodium sulfite. Crystallization of the products from carbon

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[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Abstracted from the Ph.D. Thesis of James P. Yuk. Presented before the Organic Division of the American Chemical Society, Los Angeles, Calif., March, 1953.

[2] For detailed references and discussion see: (a) P. B. D. de la Mare, *Quart. Revs.*, **3**, 126 (1949); (b) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 137–141; (c) C. C. Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, Chap. 2.

[3] (a) K. Nozaki and R. A. Ogg, THIS JOURNAL, **64**, 697, 794, 709 (1942); (b) B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 131 (1945); 630 (1947).

[4] F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

[5] R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, THIS JOURNAL, **73**, 4525 (1951).

[6] R. E. Buckles and G. V. Mock, *J. Org. Chem.*, **15**, 680 (1950).

[7] L. I. Smith, W. W. Pritchard and L. J. Spillane, *Org. Syntheses*, **23**, 27 (1943).

[8] R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953).

[9] W. H. Bauer and F. Daniels, *ibid.*, **56**, 378 (1934).

tetrachloride gave 2.04 g. (83%) of α,β-dibromobutyric acid, m.p. 87–88°, for the first reaction and 2.14 g. (87%) of an identical product for the second.

Analytical Procedures.—Solutions of bromine or tetramethylammonium tribromide in ethylene chloride were analyzed iodometrically. A magnetic stirrer was used during the titrations in order to maintain equilibrium between the two liquid phases. It was found that the presence of the dibromides resulting from the addition of bromine to the unsaturated acids had no effect on the accuracy of the determinations.

Solutions of tetrabutylammonium tribromide in ethylene chloride could not be analyzed by this procedure. The complexes of iodine with the tetrabutylammonium iodide or bromide were so soluble in ethylene chloride compared to water that no effective titration could be carried out. This result was verified by an experiment in which tetrabutylammonium triiodide was shaken with a mixture of aqueous potassium iodide and ethylene chloride. The addition of starch solution led to no characteristic starch-iodine color in the water layer. Thus, the concentration of triiodide ion in the water must have been less than 10^{-7} *M*.

Direct treatment of the tribromide solution with excess standard aqueous thiosulfate solution followed by titration of the water layer with standard iodine solution was also unsatisfactory in that less thiosulfate reacted with tribromide than would be expected on the basis of its oxidation to tetrathionate. Similar low results in the tribromide analysis were obtained when excess standard sodium arsenite solution was used followed by titration with standard iodine solution. In fact the error was so great in this case that one is led to suspect that the arsenite catalyzed the addition of bromine to the double bond.

Kinetic Measurements.—The reactions were carried out in volumetric flasks which were immersed in a thermostatically controlled water-bath at 30.00 ± 0.05°. All the runs were made in complete darkness. For reactions involving both bromine and tribromide, tetramethylammonium bromide was weighed into the flask and dissolved in a measured amount of standard bromine in ethylene chloride. When tribromide was used alone the standard solution of bromine was saturated with tetramethylammonium bromide, which is, itself, virtually insoluble in ethylene chloride. The validity of this method of preparing solutions was shown by the fact that the results obtained were the same when solid tetramethylammonium tribromide was used in making up the solutions. Known volumes of these solutions were mixed as rapidly as possible with known volumes of standard solutions of the unsaturated acids. At appropriate intervals 10-ml. samples were withdrawn from the reaction solutions under illumination by a small ruby safe light. The presence of crystalline tetramethylammonium bromide which precipitated during reactions involving the tribromide had no appreciable effect on the results.

Absorption Spectra.—Absorption spectra measurements were carried out in silica cells of path length 1.00 ± 0.01 cm. with a Cary Model 11 recording spectrophotometer and a Beckman Model DU spectrophotometer. The uniform symbology and nomenclature suggested by the National Bureau of Standards have been used.[10]

Results and Discussion

Rate Laws and Mechanisms.—A preliminary comparison of rates of addition of bromine to crotonic acid in ethylene chloride showed that in general the reaction with bromine alone was slower than that with tetramethylammonium tribromide which in turn was slower than that with both bromine and tribromide present. Such a comparison is shown in Fig. 1. Furthermore, variations in concentration showed that the rate varied approximately as the first power of each of the concentrations of crotonic acid, bromine and tribromide when all three were present (see Table I). When tribromide only was present with the crotonic acid the reaction was approximately first order with respect to each of the two reagents (see Table II).

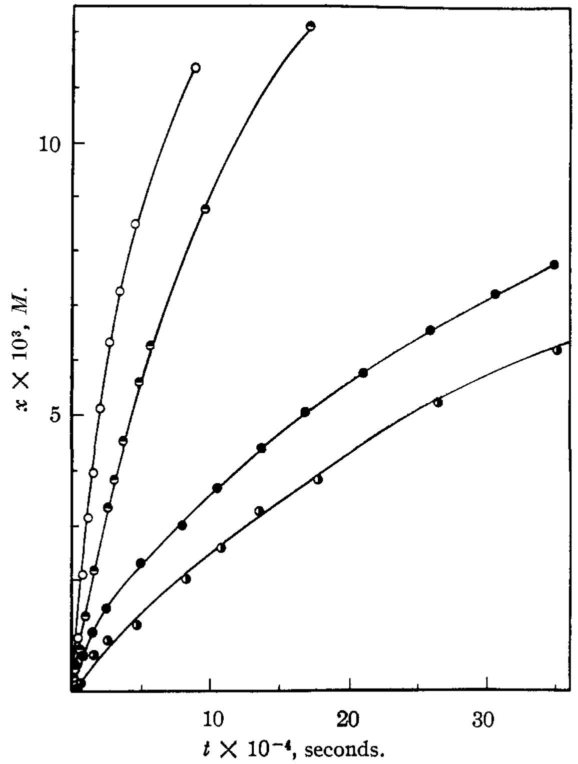

Fig. 1.—Representative titration curves for the reactions at 30° of 0.0250 *M* crotonic acid in ethylene chloride with: ○, a mixture of 0.0125 *M* bromine and 0.0125 *M* tetramethylammonium tribromide (run 6, Table I); ◐, 0.0250 *M* tetramethylammonium tribromide (run 24, Table II); ◑ and ●, 0.0250 *M* bromine.

TABLE I

SUMMARY OF THE KINETIC DATA FOR THE REACTION OF CROTONIC ACID WITH MIXTURES OF BROMINE AND TETRAMETHYLAMMONIUM TRIBROMIDE IN ETHYLENE CHLORIDE AT 30°

Run	Concn., *M* × 10^2 Acid	Bromine	Tribromide	$k_1 \times 10^2$, l.^{2}/mol^2 sec.
1	1.00	2.50	2.50	7.8
2	1.00	2.50	2.50	7.4
3	1.00	4.75	0.25	11.6
4	2.50	1.00	1.50	11.3
5	2.50	1.25	1.25	9.4
6	2.50	1.25	1.25	10.3
7	2.50	1.75	0.75	10.4
8	2.50	2.00	.50	9.6
9	2.50	2.00	.50	10.0
10	2.50	2.25	.25	10.7
11	2.50	2.40	.12	11.6
12	2.50	2.50	.10	11.9
13	2.50	2.50	.25	10.0
14	2.50	2.50	.50	9.4
15	2.50	2.50	.75	9.2
16	2.50	2.50	1.25	9.1
17	2.50	2.50	1.50	8.6
18	2.50	2.50	2.50	8.0
19	2.50	2.50	2.50	7.4
20	5.00	1.25	1.25	10.0
21	5.00	2.50	2.50	9.4
			Average	9.7 ± 0.6[a]

[a] The measure of the precision, ±0.6, sets the 95% confidence limits of the average.

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(10) National Bureau of Standards, Letter Circular, LC-857 (1947).

TABLE II

SUMMARY OF THE KINETIC DATA FOR THE REACTION OF CROTONIC ACID WITH TETRAMETHYLAMMONIUM TRIBROMIDE IN ETHYLENE CHLORIDE AT 30°

Run	Concentration, $M \times 10^2$ Acid	Tribromide	$k_{11} \times 10^4$, l./mole sec.
22	1.00	5.00	2.30
23	1.00	5.00	2.42
24	2.50	2.50	2.20
25	2.50	2.50	2.03
26	2.50	5.00	2.63
27	2.50	5.00	2.70
28	5.00	2.50	1.83
29	5.00	2.50	1.72
30	5.00	5.00	2.41
31	5.00	5.00	2.68
32	5.00	5.00	2.32
		Average	2.29 ± 0.22[a]
33	2.50[b]	2.50	5.38
34	2.50[b]	2.50	4.81
35	2.50[c]	2.50	6.54
36	2.50[c]	2.50	6.49

[a] The measure of the precision, ±0.22, sets the 95% confidence limits of the average. [b] Tiglic acid was used in place of crotonic acid. [c] β,β-Dimethylacrylic acid was used in place of crotonic acid.

The results with bromine alone were too erratic for accurate analysis.

The kinetic results of the reaction of mixtures of bromine and tetramethylammonium tribromide, which are given in Table I, can be explained by the rate law given in equation 1. This rate law was derived either from a mechanism involving an initial electrophilic attack by bromine followed by a rate-determining reaction with tribromide as given by equations 2 and 3, from a mechanism involving an initial nucleophilic attack by tribromide followed by a rate-determining reaction with bromine as given by equations 4 and 5, or from a mechanism involving a concerted attack by both the electrophilic and nucleophilic reagents as given by equation 6. The k's represent specific rate constants and the K's equilibrium constants of the equations designated by subscripts.

$$dx/dt = k_1(\mathrm{E})(\mathrm{Br_2})(\mathrm{Br_3^-});\ k_1 = k_3K_2,\ k_5K_4 \text{ or } k_6 \quad (1)$$

$$\mathrm{E + Br_2 \rightleftharpoons E\cdot Br_2\ (complex)} \quad (2)$$

$$\mathrm{E\cdot Br_2\ (complex) + Br_3^- \longrightarrow EBr_2 + Br_3^-} \quad (3)$$

$$\mathrm{E + Br_3^- \rightleftharpoons E\cdot Br_3^-} \quad (4)$$

$$\mathrm{E\cdot Br_3^- + Br_2 \longrightarrow EBr_2 + Br_3^-} \quad (5)$$

$$\mathrm{E + Br_2 + Br_3^- \longrightarrow EBr_2 + Br_3^-} \quad (6)$$

Ionization of the olefin–bromine complex formed by equation 2 would give the positive ion usually written as an intermediate in the polar mechanism of bromine addition. As has already been shown it is not necessary that this positive ion be considered an intermediate in the addition of bromine in the presence of tribromide. In the complete absence of tribromide, however, the ionization of the complex by equation 8 would give rise to bromide ion which would in turn form tribromide ion by equation 9, and a mechanism given by equations 2, 8, 9 and 10 would be expected to take place. With equation 10 representing the rate-determining step the rate law given by equation 7 can be derived.

$$dx/dt = k_7(\mathrm{E})(\mathrm{Br_2})^2;\ k_7 = k_{10}K_2K_8/K_9 \quad (7)$$

$$\mathrm{E\cdot Br_2\ (complex) \rightleftharpoons EBr^+ + Br^-} \quad (8)$$

$$\mathrm{Br_3^- \rightleftharpoons Br_2 + Br^-} \quad (9)$$

$$\mathrm{EBr^+ + Br_3^- \longrightarrow EBr_2 + Br_2} \quad (10)$$

At low concentrations of tribromide the ionization by way of equation 8 would effectively increase the concentration of tribromide ion so that the specific rate constant calculated by equation 1 on the basis of the initial concentration of tribromide would be higher than it would be if the true concentration were used. A slight trend in this direction is shown in Table I. This trend may indicate that the ionization step 8 is important in the mechanism when both bromine and tribromide are present.

The rate law given by equation 7 has often been reported[2a] for the addition of bromine to olefins, but the runs carried out in the present work in the absence of tribromide ion the kinetic results do not warrant choosing between equation 7 as a rate law and the usual rate law, first order with respect to both bromine and olefin, which can be derived from a mechanism in which the formation of the olefin–bromine complex is rate-determining. In fact, the results with this reaction were more erratic than the titration curves given in Fig. 1 would indicate. Induction periods of various lengths were sometimes observed and sometimes not. On other occasions the reaction stopped after starting in what appeared to be a normal fashion. Evidence of inhibition of the reaction by the product, α,β-dibromobutyric acid, also was obtained. A similar result has been reported before in addition of bromine to tetrachloroethylene.[11]

Dissociation of bromine from the olefin–tribromide complex of equation 4 would lead to an addition product of the olefin with bromide ion. The formation of such an intermediate would not be necessary with both bromine and tribromide present, but in the absence of bromine it seems quite likely. The rate law given by equation 11 can be derived from a mechanism given by equations 4, 12 and 13 which includes this dissociation step.

$$\frac{dx}{dt} = k_{11}(\mathrm{E})(\mathrm{Br_3^-});\ k_{11} = \frac{k_4k_{12}k_{13}}{k_{-2}k_{-12} + k_{-4}k_{13} + k_{12}k_{13}} \quad (11)$$

$$\mathrm{EBr_3^- \rightleftharpoons EBr^- + Br_2} \quad (12)$$

$$\mathrm{EBr^- + Br_2 \longrightarrow EBr_2 + Br^-} \quad (13)$$

Equation 11 does explain approximately the kinetic data obtained when only the tribromide was present as a source of bromine for addition to crotonic acid (Table II). The trend of k_{11} to lower values when the concentration of tribromide was lowered indicates that a small amount of addition might have taken place by way of a mechanism involving equations 2, 3 and 9 from which the rate law, equation 14 can be derived when equation 3 is considered to be rate-determining. The data for the runs involving tribromide fit equation 11 much more closely than equation 14, however.

$$dx/dt = k_{14}(\mathrm{E})(\mathrm{Br_3^-})^2;\ k_{14} = k_3K_2K_9/(\mathrm{Br^-}) \quad (14)^{12}$$

With the methyl-substituted crotonic acids, tiglic acid and β,β-dimethylacrylic acid, the kinetic data

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(11) J. Willard and F. Daniels, THIS JOURNAL, **57**, 2240 (1935).

(12) The concentration of tetramethylammonium bromide is constant since the solution would be saturated with it.

for additions by tribromide followed equation 11 less closely than with crotonic acid, but the fit was better with this rate law than with equation 14. The comparative rates (Table II) of the three acids reacting with tribromide show that the methyl groups on the double bond enhanced the reactivity. This result favors a mechanism involving the initial electrophilic attack on the double bond, which would lead to equation 14 as a rate law, rather than one involving the initial nucleophilic attack which leads to equation 11. It will be necessary to study the addition reactions of these and other methyl-substituted acrylic acids further to clear up this point.

Calculation of Rate Constants.—Values of *kt* calculated from the integrated forms of the rate laws were plotted against time. The values of the specific rate constants were obtained by statistical estimation of the slopes of the straight lines obtained. The rate constants are given in Tables I and II.

Dissociation of Quaternary Ammonium Tribromides.—The absorption spectrum of a 10^{-5} *M* solution of tetrabutylammonium tribromide in ethylene chloride showed a peak at 273 mμ with a molar absorbancy index of 4.0 × 10^4. This peak checks fairly well with that previously reported[5] at 272 mμ with a molar absorbancy index of 3.8 × 10^4 for solutions in ethylene chloride of doubtful purity. The measurements in the earlier work had been made very rapidly on fresh solutions.

The addition of excess bromine served to suppress the dissociation of either tetrabutylammonium tribromide or tetramethylammonium tribromide. In either case a concentration of bromine ten times that of the tribromide was more than enough to suppress the dissociation completely. For both tribromides the molar absorbancy index for the virtually undissociated complex at the peak wave length of 273 mμ was 5.8 × 10^4. Equilibrium constants for the dissociation of the tribromides were calculated.[13]

The *pK* values are listed in Table III. The *pK* values are considerably higher than those reported for the more polar solvent, water: 1.25 at 21.5°,[14] 1.27 at 16.5°[14] and 1.46 at 16°.[15] A similar trend to higher *pK*'s of dissociation in ethylene chloride has been observed for the triiodides.[16] The value of the *pK* of dissociation, 4.2 at 25°, reported[5] for bromotrichloromethane as a solvent is lower than would be expected since this solvent is less polar than ethylene chloride. The spectrophotometric measurements used for the calculation of this latter value had to be made at wave lengths quite far from the absorption peak characteristic of the tribromide, however. In any event, the quaternary ammonium tribromides are dissociated only slightly in such relatively non-polar solvents as ethylene chloride, and there seems to be no essential difference arising from the nature of the alkyl group.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF QUATERNARY AMMONIUM TRIBROMIDES IN ETHYLENE CHLORIDE AT 25°

$$R_4N^+Br_3^- \rightleftarrows R_4N^+Br^- + Br_2$$

R	Initial concn., *M* × 10^5 R$_4$N-Br$_3$	Br$_2$	λ, mμ	α	*pK*
C_4H_9	1.0	0	270–340	0.30 ± 0.02[a]	5.89 ± 0.07[a]
C_4H_9	2.0	0	273	0.30	6.0
CH_3	1.0	0.5	273	0.17	5.9

[a] Measurements made at 14 wave lengths. The measure of the precision sets the 95% confidence limits of the average.

Complexing of Crotonic Acid with Bromine.—In Fig. 2 are shown absorption spectra of bromine, crotonic acid, and combinations of the two in ethylene chloride. There is definite evidence of complex formation, especially in the region 300–350 mμ. The spectrophotometric changes noted cannot be explained by addition of bromine to the double bond because they take place much more rapidly than addition. Also the product of addition, α,β-dibromobutyric acid, does not absorb in the region in which the increased absorbance was observed.

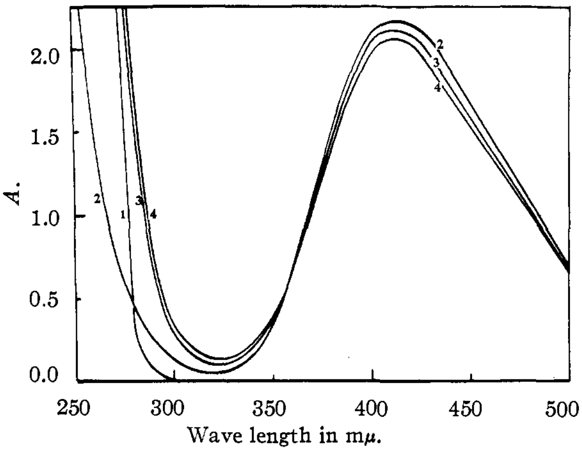

Fig. 2.—Absorption spectra in ethylene chloride, absorbance (optical density) of the following solutions plotted against wave length: (1) 0.1 *M* crotonic acid, (2) 0.01 *M* bromine, (3) 0.3 *M* crotonic acid and 0.01 *M* bromine, (4) 0.5 *M* crotonic acid and 0.01 *M* bromine.

In the presence of excess of crotonic acid (as high as 100 times that of bromine) the absorbance characteristic of the complex increases. Application of equation 15, which can be derived from the expression for the equilibrium constant for the formation of a 1:1 complex between crotonic acid and bromine and the expression for the total absorbance of the solution, as described before[8] makes possible the estimation of the equilibrium constant of complex formation

$$A_s - C_t a_c b = 1/K \left[\frac{C_t a_x b - A_s}{C_E}\right] \qquad (15)^{17}$$

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[13] A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, THIS JOURNAL, **73**, 514 (1951).

[14] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932).

[15] P. Job, *Compt. rend.*, **182**, 632 (1926.)

[16] R. E. Buckles, J. P. Yuk and A. I. Popov, THIS JOURNAL, **74**, 4379 (1952).

[17] A_s is the total absorbance of the solution. a_c and a_x are the respective molar absorbancy indices of the complex and the bromine b is the thickness of the solution in the cell. C_t is the total bromine concentration, C_E is the concentration of crotonic acid and K is the equilibrium constant.

Measurements were made at 300, 310 and 320 mμ. The average value for the equilibrium constant was 0.08 ± 0.08 where the standard deviation is the measure of the precision.

Complexes of this sort between an olefin and bromine would certainly be expected on the basis of recent work[18] on the 1:1 complexes of halogens acting as electron acceptors with various types of electron donors including olefinic compounds.[19] Ionization of some donor–acceptor halogen complexes also had been observed,[20] but as it has already been pointed out[2a] ionization of olefin–bromine complex is not necessary to explain most of the kinetic results obtained for bromine addition. In fact, in the present work the evidence shows that ionization is not a necessary step if the bromine–crotonic acid complex is an intermediate in the bromine addition in the presence of tribromide.

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[18] See footnote 8, and R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952), for references.

[19] (a) R. J. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952); (b) S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952).

[20] (a) L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933); (b) R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951); (c) R. E. Buckles and N. A. Meinhardt, *ibid.*, **74**, 1171 (1952).

IOWA CITY, IOWA

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Thermal Initiation of Styrene Polymerization

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When styrene polymerization is initiated by moderate concentrations of active monoradical-producing catalysts, the rate of initiation of polymer chains can be measured by the rate of consumption of the inhibitors, 2,2-diphenylpicrylhydrazyl and benzoquinone. However, the rate of consumption of these inhibitors during *thermal* polymerization of highly purified styrene is very much greater than the rate of initiation of polymer chains. It is suggested that diradicals are formed at a rapid rate in the thermal polymerization of styrene and that a high proportion, perhaps all, of these diradicals undergo self-termination to form small rings. While the rate of production of diradicals is very much greater than the rate of initiation of polymer chains, the actual weight fraction of the rings formed should be very small. A relation between the production of diradicals and the formation of high molecular weight polymer has not been established.

The relationship[1]

$$R_p^2 - R_{p.th}^2 = \frac{k_p^2[M]^2}{2k_t} R_i = 3 \times 10^{-2} R_i \qquad (1)$$

holds for the polymerization of styrene in bulk at 60°, initiated by monoradical-producing catalysts such as benzoyl peroxide and 2-azobisisobutyronitrile. In equation 1 R_p is the total rate of polymerization at 60°, $R_{p.th}$ is the rate of thermal polymerization and R_i is the rate of initiation of the polymer chains which started frrom catalyst fragments. The quantities k_p and $2k_t$ are the specific rate constants for propagation and termination, respectively, and [M] is the monomer concentration.[1] In this paper concentrations are expressed in moles/liter and time in seconds.

For moderate concentrations of active monoradical-producing initiators, the second term on the left-hand side of (1) can be neglected, giving

$$R_p^2 = 3 \times 10^{-2} R_i \qquad (2)$$

The constant in equation 2 has been determined by experimental measurements of R_p and R_i. The measurement of R_i was carried out by three independent methods, the results of which were all in close agreement.[1] The best value of the constant in equation 1 was evaluated from data from various sources.[2,3] It is highly improbable that the numerical value 3×10^{-2} is in error by more than 50%.

One of the most successful methods for measuring R_i in monoradical-initiated polymerization involves the use of the inhibitor 2,2-diphenylpicrylhydrazyl.[1,4,5] In the presence of this substance, there is an induction period in the polymerization during which the inhibitor is consumed. The rate of consumption of inhibitor R_{DPPH} is taken to be equal to the rate of initiation R_i which prevails with inhibitor absent. It is assumed that one molecule of inhibitor stops one radical chain. This assumption has been proved for the case where the initiation occurs *via* a fragment from an active monoradical-producing catalyst, by comparison of R_{DPPH} with R_i determined by two independent methods.[1]

If thermal polymerization proceeds with the same mechanisms of propagation and termination as does polymerization initiated by monoradical-producing catalysts, the following equation should apply

$$R_{p.th}^2 = 3 \times 10^{-2} R_{i.th} \qquad (3)$$

where $R_{i,th}$ represents the rate of initiation of growing polymer radicals produced thermally (a growing polymer diradical, if present, is considered as two growing polymer radicals). Equation 3 may be regarded as a definition of $R_{i,th}$ at 60°. $R_{p,th}$ at 60° has the value 2.0×10^{-6} mole/liter/sec.[6] so that $R_{i.th} = 1.3 \times 10^{-10}$ mole/liter/sec.

It is interesting to compare the value of $R_{i,th}$ defined by equation 3 with some other measured value of the rate of thermal initiation. To this end we determined R_{DPPH} in pure styrene at 60°. We found R_{DPPH} to be 1.1×10^{-8} mole/liter/sec. and

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