[Contribution from the Department of Chemistry, University of California, Davis]

# The Dark Reaction of Bromine with Mesitylene in Carbon Tetrachloride Solution

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In the dark the reaction of mesitylene with bromine in carbon tetrachloride at 25° to form ring brominated product is subject to catalysis by both water and hydrogen bromide. The rate of consumption of bromine in carbon tetrachloride solutions containing water shows a first order dependence on the concentration of bromine and is proportional to the square root of the hydrogen bromide concentration of the medium. At low concentrations of mesitylene the rate of the reaction shows a first-order dependence on mesitylene but at higher concentrations of mesitylene the order with respect to mesitylene appears to decrease. The temperature coefficient of the rate of reaction is less than one. A mechanism is proposed in which hydronium ion attacks a 1:1 mesitylene–bromine addition complex in the rate-determining step.

Bruner's investigation[1] of the iodine-catalyzed bromination of benzene represents the first attempt to elucidate through kinetic studies the mechanism of non-radical type halogenations of aromatic substances in non-aqueous solvents. The data reported by Bruner have been interpreted by several different workers,[2] all of whom concur in the opinion that the reaction rate is of higher order than first with respect to halogen concentration. There is, however, disagreement among these investigators concerning the expression of the exact rate law. The rates of halogen substitution in other aromatic compounds in carbon tetrachloride or acetic acid solution also show higher order dependence on halogen concentration.[2b,3] Two mechanistic interpretations of this high order contribution of halogen have been offered. In one of these the active halogenating agent which attacks the aromatic nucleus is pictured as a complex polyhalogen molecule[3e] and in the other the rate-determining step is formulated as one in which a 1:1 aromatic halogen complex is subject to attack by one or more halogen molecules.[2b,c,3b]

In reviewing the kinetic evidence for the function of an aromatic–halogen complex as an intermediate in these reactions, one observes that many of the experiments to establish the rate laws are based on a determination of the time required to effect consumption of 10% of the total halogen in the reaction mixture.[2b,3b,c,d] This procedure which has merit since it avoids the complication of hydrogen halide catalysis in later phases of the reaction, can lead to erroneous conclusions concerning the halogenation rate law if the aromatic reagent is not free of halogen consuming impurities. Because mesitylene is a notable example of an aromatic substance which may contain such impurities,[4] it has seemed worthwhile to examine in more detail the kinetics of its bromination in acetic acid[3b] and also in carbon tetrachloride, both in the presence and absence of an iodine catalyst.[2b] This report presents the results of that phase of this investigation which deals with the reaction of highly purified mesitylene in iodine-free carbon tetrachloride solution.

**The Effects of Changes in Reaction Conditions on the Reaction Rates and Products.**—Samples of commercial mesitylene, which had been subjected to no further purification procedure than ordinary distillation, were found to decolorize dilute solutions of bromine in carbon tetrachloride within a few minutes even when the reacting solutions were contained in black bottles. Solutions of comparable concentrations of reactants prepared from carefully purified[5] mesitylene showed a comparatively slow decrease in bromine concentration, and this reaction was preceded by a long induction period. The mesitylene sample employed by Robertson[2b] consumed bromine in carbon tetrachloride much more readily than did the purified sample used in the present series of experiments.

The induction period was not evident in solutions which had been gassed with hydrogen bromide. The catalytic effect of hydrogen bromide was greater for solutions in which water saturated carbon tetrachloride was used as the solvent than for those in which carbon tetrachloride dried over Drierite was employed. The disappearance of bromine from solutions which were prepared from water-saturated carbon tetrachloride but which were not gassed with hydrogen bromide again was subject to an induction period. Thus the role of water as a reaction catalyst appears to be dependent on the concomitant function of hydrogen bromide. These observations are summarized in part in Fig. 1.

The extreme photosensitivity of the reaction of bromine and toluene has been demonstrated previously.[6] In the present work it was observed that the consumption of bromine in dilute mesitylene solutions in the dark at 25° proceeded at a sufficiently low rate to permit kinetic measurements. If the solutions were exposed to daylight, the bromine disappeared completely within very short time intervals. In mixtures prepared from solutions of hydrogen bromide in carbon tetrachloride that had been dried for several weeks over Drierite the rate of the reaction in the dark sometimes accelerated suddenly. This rate increase, which occurred erratically and which probably resulted from a competition of a radical type reaction with the normal dark reaction, was effectively inhibited by the addition of one drop of isoamyl nitrite to the reaction

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(1) L. Bruner, *Z. physik. Chem.*, **41**, 415 (1902).

(2) (a) C. C. Price, This Journal, **58**, 2101 (1936); (b) P. W. Robertson, J. E. Allen, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949); (c) T. Tsuruta, K. Sasaki and J. Furukawa, This Journal, **74**, 5995 (1952).

(3) (a) C. C. Price and C. E. Arntzen, *ibid.*, **60**, 2835 (1938); (b) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); (c) L. J. Lambourne and P. W. Robertson, *ibid.*, 1167 (1947); (d) P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948); (e) A. E. Bradfield, G. I. Davies and E. Long, *ibid.*, 1389 (1949).

(4) (a) N. S. Ham, A. L. G. Rees and A. Walsh, *J. Chem. Phys.*, **20**, 1336 (1952); (b) H. A. Benesi, This Journal, **75**, 2250 (1953).

(5) L. I. Smith and O. W. Cass, *ibid.*, **54**, 1606 (1932).

(6) J. R. Sampey, F. S. Fawcett and B. A. Morehead, *ibid.*, **62**, 1839 (1940).

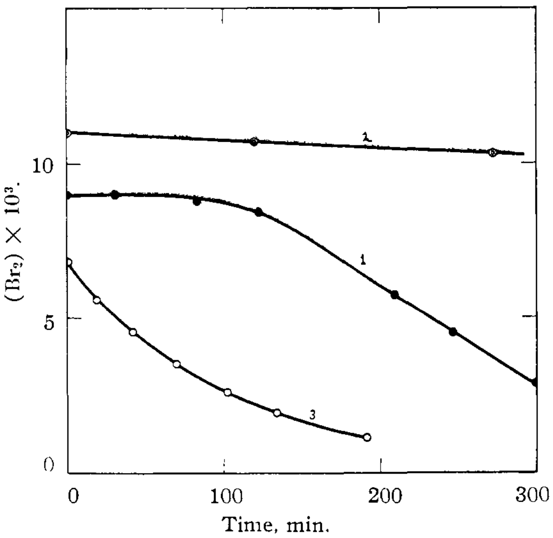

Fig. 1.—The effect of hydrogen bromide and water on the rate of reaction of bromine with mesitylene in carbon tetrachloride solutions. The initial mesitylene concentration in all runs was 0.10 *M:* 1, water saturated, $(HBr)_i = 0$; 2, solution dried with Drierite, $(HBr)_i = 0.120$ *M;* 3, water saturated, $(HBr)_i = 0.260$ *M.*

mixtures. This device has been used previously in studying the bromination of toluene to prevent side chain substitution.[7]

The rate of the reaction was not influenced by changes in the surface of the reaction vessel (quartz, corex, Pyrex, Desicote) nor by addition of powdered quartz to the reaction mixture; therefore the reaction is probably a homogeneous reaction.

It was observed that those reactions which proceeded normally in the dark led to the formation of ring halogenated material. Those dark reactions which were subject to erratic acceleration, like the reactions carried out in daylight, yielded primarily side-chain bromination product. These facts were established through analysis of the reaction products by a procedure[6] which is based on the precipitation of side chain substituted bromine as silver bromide. Analyses of the products of several of the rate runs which had proceeded to completion showed that hydrogen bromide was produced in quantity equivalent to the bromine in the initial reaction mixture. It has been shown[8] that monobromomesitylene can be recovered in 80% yield from the reaction of bromine with mesitylene in carbon tetrachloride solutions under conditions similar to those in the rate runs reported below. In view of the above facts it seems likely that the organic product in the rate runs is monobromomesitylene.

**Kinetic Studies.**—In a series of runs made to determine reaction orders with respect to the concentrations of reagents other than water, each reaction mixture was prepared from the same set of solutions so that the water concentration remained constant. In this set of runs carbon tetrachloride solutions of bromine and mesitylene were mixed and the bromine concentration of the reaction mixture was determined spectrophotometrically, in the wave length region 520 to 580 m$\mu$, at various times. In all runs reported the mesitylene concentration was at least ten times that of bromine so that the mesitylene concentration remained nearly constant throughout the reaction. Under these conditions the individual runs were found to be in agreement with the rate law[9]

$$-\,d(Br_2)_T/dt = k(Br_2)_T(HBr)^{1/2} \qquad (1)$$

The integrated form of equation 1 may be expressed as

$$kt = \text{constant} + \frac{2.303}{(HBr)_f^{1/2}} \log_{10} \frac{(HBr)_f^{1/2} + (HBr)^{1/2}}{(HBr)_f^{1/2} - (HBr)^{1/2}} \qquad (2)$$

where $(HBr)_f = (HBr) + (Br_2)_T$ = the concentration of hydrogen bromide at the completion of the reaction. Thus a plot of the logarithmic term of equation 2 against time should give a straight line from the slope of which the value of *k* may be calculated. Such plots show a straight-line relationship, after the initial induction period, until about 90% of the initial bromine has been consumed. A typical plot of the experimental data is shown in Fig. 2. Values of *k* calculated from the straight lines obtained in plots similar to Fig. 2 are summarized in Table I for various initial concentrations of bromine, $(Br_2)_i$, and of mesitylene, $(M)_i$. The first-order dependence of the rate of reaction on the bromine concentration is demonstrated by the insensitivity of the calculated *k* values to an eightfold variation in initial bromine concentration (first

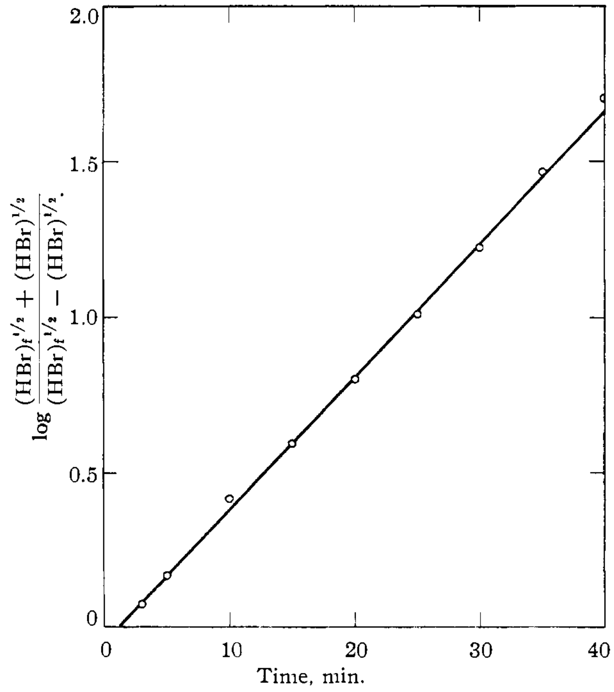

Fig. 2.—Evaluation of the rate constant, *k*. Initial concentrations of reagents in carbon tetrachloride solution were: mesitylene = 2.85 *M*, bromine = 0.0174 *M*, hydrogen bromide = 0.

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[7] M. S. Kharasch, P. C. White and F. R. Mayo, *J. Org. Chem.*, **3**, 33 (1938).

[8] L. I. Smith, *Org. Syntheses*, **11**, 24 (1931).

[9] The term $(Br_2)_T$ refers to the sum of the concentrations of the free bromine and of that complexed with mesitylene (see equation 3).

four runs of Table I). At low mesitylene concentrations (0.1 to 0.7 *M*) the reaction rate appears to be nearly first order in mesitylene as demonstrated by the constancy of the values of $k/(M)_i$ reported in the last column of Table I. However, at higher concentrations of mesitylene the values of $k/(M)_i$ drop off rapidly.

TABLE I

RATE CONSTANTS[a] AT 25.2° FOR THE HYDROGEN BROMIDE CATALYZED REACTION OF BROMINE WITH MESITYLENE IN CARBON TETRACHLORIDE SOLUTION $(HBr)_i = 0$

| $(Br_2)_i$, mole/l. $\times 10^3$ | $(M)_i$, mole/l. | $k$, min.$^{-1}$ mole$^{-1/2}$ l.$^{1/2}$ | $k/(M)_i$, min.$^{-1}$ mole$^{-3/2}$ l.$^{3/2}$ |
|---|---|---|---|
| 8.72 | 0.712 | 0.31 | 0.46 |
| 17.4 | .712 | .35 | |
| 34.9 | .712 | .34 | |
| 69.8 | .712 | .32 | |
| 15.9 | .103 | .049 | 0.47 |
| 17.4 | .285 | .13 | .46 |
| 17.4 | 1.42 | .46 | .32 |
| 17.4 | 2.85 | .76 | .27 |

[a] Average values for two or more runs. The rate constants for individual runs did not deviate by more than 2% from the average value.

In order to test further the validity of the postulated rate equation (eq. 1) with respect to the dependence of the reaction rate on the hydrogen bromide concentration a series of runs was made in which hydrogen bromine was present initially. When hydrogen bromide was introduced into the carbon tetrachloride solution containing bromine, it was observed that a finely divided aqueous phase formed slowly. The solutions were allowed to stand for two weeks at 25° to permit condensation of the finely divided aqueous phase on the walls of the reaction vessel before the reaction was started by introduction of the mesitylene. The kinetic data for this series of runs is presented in Table II. The calculated values of $k/(M)_i$ in the last column of Table II indicate that the postulated dependence of the rate of reaction on the one-half power of the hydrogen bromide concentration (eq. 1) holds over a fivefold change in initial hydrogen bromide concentration (0.012–0.060 *M*). The observed decreases in the values of $k/(M)_i$ for solutions of higher initial hydrogen bromide concentrations probably reflects the decreases in the water content of these solutions through salting out by the hydrogen bromide. It should be noted that in these runs the hydrogen bromide content of the dispersed aqueous phase must have been relatively high (>11 *M*), since this phase eventually settled to the bottom of the carbon tetrachloride phase. The vapor pressure of the water above such concentrated hydrogen bromide solutions, which constitutes a measure of the water activity in the carbon tetrachloride solutions, is not markedly influenced by changes in the hydrogen bromide concentration.[10] The close agreement of the values of $k/(M)_i$ reported in Table II for solutions of low hydrogen bromide concentrations with similar values reported in Table I must be regarded as fortuitous since the respective water concentrations in the two series of runs are not known.

TABLE II

RATE CONSTANTS[a] AT 25° FOR THE HYDROGEN BROMIDE CATALYZED REACTION OF BROMINE WITH MESITYLENE IN CARBON TETRACHLORIDE SOLUTIONS CONTAINING A FEW DROPS OF A CONDENSED AQUEOUS PHASE

| $(Br_2)_i$, mole/l. $\times 10^3$ | $(M)_i$, mole/l. $\times 10^3$ | $(HBr)_i$, mole/l. $\times 10^3$ | $k/(M)_i$, min.$^{-1}$ moles$^{-3/2}$ l.$^{3/2}$ |
|---|---|---|---|
| 6.8 | 96 | 12.5 | 0.43 |
| 3.7 | 102 | 30.1 | .40 |
| 3.7 | 107 | 59.9 | .41 |
| 6.9 | 67 | 260 | .27 |
| 6.6 | 107 | 301 | .22 |

[a] Average values for two or more runs. Values of $k/(M)_i$ for individual runs did not deviate by more than 5% from the average value.

The effect of water on the rate of the reaction was investigated using reaction mixtures prepared by mixing carbon tetrachloride solutions that had been dried over Drierite with water saturated carbon tetrachloride.

The bromine concentration of these solutions was determined at various times using the same methods employed in the runs reported in Table I. Values of $k/(M)_i$ determined for these runs are summarized in Table III. For the last three runs reported in Table III it was observed that $k/(M)_i$ increased by a factor of a little over four as the water concentration was doubled. This would indicate that the rate of reaction is second order with respect to the water concentration. This should, however, be regarded as tentative since it is difficult to prepare solutions of such low water content with any accuracy. The possibility must also be considered that solutions of water in a non-polar solvent such as carbon tetrachloride would show serious deviations from Henry's law.

TABLE III

THE EFFECT OF WATER ON THE HYDROGEN BROMIDE CATALYZED REACTION OF BROMINE WITH MESITYLENE IN CARBON TETRACHLORIDE SOLUTIONS AT 25°

| $(Br_2)_i$, mole/l. $\times 10^3$ | $(M)_i$, mole/l. | Water satd. $CCl_4$ in reacn. mixt., % | $k/(M)_i$, min.$^{-1}$ moles$^{-3/2}$ l.$^{3/2}$ |
|---|---|---|---|
| 9.79 | 0.712 | 0 | 0.018 |
| 9.79 | .712 | 20 | .034 |
| 9.79 | .712 | 40 | .155 |
| 17.44 | .712 | 80 | .74 |

**Temperature Coefficient of the Reaction Rate.**—Reaction mixtures for runs at 33.6° and 17.6° were prepared in the same manner as the reaction mixtures for the runs reported in Table I. The values of the reaction rate constant, *k*, were determined (in the same manner as those reported in Table I) and are given in column 3 of Table IV. For convenience the average value of *k* at 25.2° from Table I is also recorded in Table IV. Since the values of *k* decrease with increasing temperature, it is obvious that the temperature coefficient of the rate of reaction is less than one. The negative value of the activation energy shown in column 5 of Table IV was calculated utilizing the value of *k* for the run and the value of *k* at 25.2°.

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[10] "Gmelin's Handbuch der Anorganischen Chemie," System Number 7, Verlag Chemie, Berlin, Germany, 1931, p. 217-218.

TABLE IV

THE EFFECT OF TEMPERATURE ON THE HYDROGEN BROMIDE CATALYZED REACTION OF BROMINE WITH MESITYLENE IN CARBON TETRACHLORIDE SOLUTIONS

| $(Br_2)_i$, mole/l. $\times 10^3$ | $(M)_i$, mole/l. | $k$, min.$^{-1}$ moles$^{-1/2}$ l.$^{1/2}$ | Temp., °C. | $-E$,[a] kcal./mole |
|---|---|---|---|---|
| 17.28 | 0.710 | 0.20 | 33.5 | 11.0 |
| 17.28 | .710 | .20 | 33.7 | 10.7 |
| 8.90 | .714 | .54 | 17.4 | 10.9 |
| 17.8 | .714 | .54 | 17.8 | 11.1 |
| 8.7–70 | .712 | .33 | 25.2 | |
| | | | Av. | 10.9 |

[a] Activation energies were calculated for each run by utilizing the value of $k$ for that run and the value of $k$ at 25.2°.

**The Reaction Mechanism.**—It is interesting to note that the dark reaction of bromine with ethylene in carbon tetrachloride is similar in several respects[11] to the reaction of bromine with mesitylene. Both reactions are subject to autocatalysis and are catalyzed by water and hydrogen bromide, and both reactions have negative values of the over-all activation energy. Unfortunately this comparison cannot be further extended since detailed kinetic data for the ethylene reaction are not available.

Since under the conditions of the kinetic experiments described in this paper, the mesitylene–bromine reaction leads to the production of ring substituted product it seems unlikely that the reaction proceeds through the formation of radical intermediates. It also seems unlikely that hypobromous acid serves as the effective bromination agent since the reaction rate is enhanced by hydrogen bromide.

The following proposed mechanism is in agreement with the results presented in this investigation.

$$(CH_3)_3C_6H_3 + Br_2 \underset{\text{fast}}{\overset{K_3}{\rightleftarrows}} (CH_3)_3C_6H_3{\cdot}Br_2 \qquad (3)$$

$$n\text{-}H_2O + HBr \underset{\text{fast}}{\overset{K_4}{\rightleftarrows}} H_3O^+ \text{ aq.} + Br^- \text{ aq.} \qquad (4)$$

$$(CH_3)_3C_6H_3{\cdot}Br_2 + H_3O^+ \xrightarrow[\text{slow}]{k_1} (CH_3)_3C_6H_3Br^+ + HBr + H_2O \qquad (5)$$

$$(CH_3)_3C_6H_3Br^+ \xrightarrow[\text{fast}]{} (CH_3)_3C_6H_2Br + H^+ \qquad (6)$$

Thus the effect of water and the one-half order dependence of the reaction rate on hydrogen bromide concentration is explained by the assumption that hydronium ion, present in the reaction mixtures through establishment of equilibrium 4, functions as a reactant in the rate determining step (eq. 5). The extent of hydration of the hydronium and bromide ions would be determined by the value of $n$ to which the value of two has tentatively been assigned. One must make the further assumption, which is most reasonable since the solvent for the reaction is carbon tetrachloride, that $K_4$ is very small.

NOTE ADDED IN PROOF.—The proposed mechanism (eqs. 3–6) appears objectionable since it requires the formation of ions ($H_3O^+$ and $Br^-$), although in minute quantities, in a non-polar medium. However the markedly greater electrical conductivity of carbon tetrachloride solutions containing hydrogen bromide and water compared to carbon tetrachloride containing water indicates that some ions are present in this medium. A possible alternative equilibrium for eq. 4 is

$$(HBr)_2 + nH_2O \rightleftarrows 2(H_3O^+Br^-)$$

The ion pair could then attack the 1:1 complex. However this would require hydrogen bromide to be present in carbon tetrachloride solutions principally as the dimer. From the results of freezing point depression measurements on 0.09–0.24 $M$ hydrogen bromide in moist carbon tetrachloride, it is evident that hydrogen bromide exists as the monomer rather than the dimer in such solutions.

The proposed mechanism would require a rate law of the form

$$-\frac{d(Br_2)_T}{dt} = k_1(M{\cdot}Br_2)(H_3O^+)_{aq} \qquad (7)$$

The following equation may be derived from eq. 7 by making the appropriate substitutions for $(M{\cdot}Br_2)$ and $(H_3O^+)_{aq}$ (eq. 3 and 4) and making the assumption that $(H_3O^+)_{aq} = (Br^-)_{aq}$

$$-\frac{d(Br_2)_T}{dt} = \frac{k_1'K_3(M)(Br_2)_T(HBr)^{1/2}}{1 + K_3(M)} \qquad (8)$$

where $k'_1 = k_1K_4^{1/2}(H_2O)^{n/2}$ and $(M) >> (Br_2)_i$. It may be shown by using equations 1 and 8 that $k'_1$ is related to the experimentally determined rate constant, $k$, by equation 9.

$$\frac{1}{k} = \frac{1}{k'_1} + \frac{1}{k'_1K_3(M)} \qquad (9)$$

If this interpretation of the experimental observations concerning the variation of $k$ with mesitylene concentration is correct, a plot of values of $1/k$ *vs.* corresponding values of $1/(M)$ should produce a straight line of intercept $1/k'_1$ and slope $1/k'_1K_3$. As indicated in Fig. 3 the data of Table I conform reasonably well to graphical analysis according to eq. 9. Values of $k'_1 = 1.61$ and $K_3 = 0.308$ were calculated from the ordinate intercept and the slope of the straight line of Fig. 3. However, it is possible to evaluate $K_3$ by using spectrophotometric procedures[12] to determine the concentration of the mesitylene–bromine complex as a function of the mesitylene concentration. The results of such an investigation, reported in the Experimental section, may be used to calculate a value of $K_3 = 0.381$ mole$^{-1}$ l. The good agreement between the values of $K_3$ calculated from rate runs and equilibrium measurements provides strong support for the postulated existence of the bromine–mesitylene complex in carbon tetrachloride solutions containing bromine and mesitylene. However, the same value of $K_3$ may be calculated from the experimental rate constants assuming a termolecular reaction of mesitylene, bromine and hydronium ion so that the agreement between the values of $K_3$ noted above does not constitute proof that the complex, $M{\cdot}Br_2$, is involved in the rate-determining step as postulated in eq. 5. In view of the demonstrated existence of the mesitylene–bromine complex the second-order reaction postulated in eq. 5 seems more likely than the possible termolecular reaction. Since it is generally held that the separation of a

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[11] (a) H. S. Davis, THIS JOURNAL, **50**, 2769 (1928); (b) D. M. Williams, *J. Chem. Soc.*, 2911 (1932).

[12] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **72**, 4677 (1950).

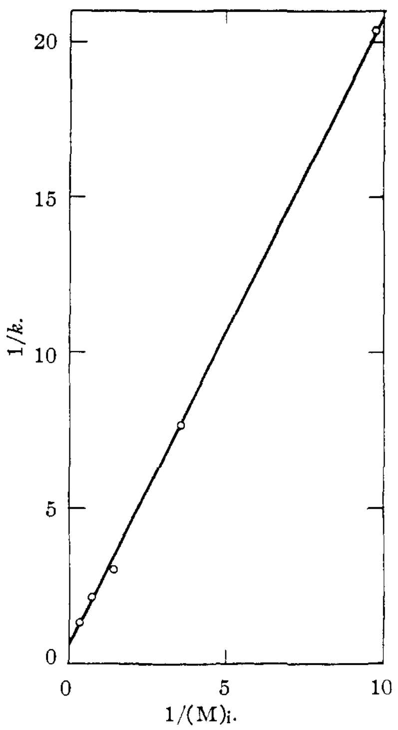

Fig. 3.—Evaluation of the equilibrium constant, $K_3$, for the mesitylene-bromine complex from the kinetic data.

proton from the aromatic nucleus does not occur in the rate-determining step,[13] it is postulated that $(CH_3)_3C_6H_3Br^+$ is formed in the rate-determining step. The rapid follow reaction in which the organic cation eliminates a proton to form bromomesitylene is shown as eq. 6.

If the postulated mechanism is correct and if $K_3 \cdot (M)$ is negligible compared to one, the observed activation energies ($\Delta E_0$) reported in Table IV may be expressed in terms of the activation energy of the rate-determining step ($\Delta E_1$) and the heats of reaction of eqs. 3 and 4 as shown by eqs. 10.

$$\Delta E_0 = \Delta E_1 + \Delta H_3 + 1/2\Delta H_4 \qquad (10)$$

The value of $\Delta H_3$ estimated from the temperature dependence of $K_3$ is $-1.5$ kcal./mole (Experimental section). The value of $\Delta H_4$ cannot be obtained readily but would probably not exceed the heat of solution of hydrogen bromide in water[10] which is about $-20$ kcal./mole at 25°. If these values of $\Delta H_3$ and $\Delta H_4$ are substituted in eq. 10, a probable maximum value of 0.6 kcal./mole is obtained for the activation energy, $\Delta E_1$, of the reaction of hydronium ion with the bromine-mesitylene complex.

**Acknowledgment.**—The authors are indebted to Research Corporation for a grant in support of this research.

## Experimental

**Materials.**—Eastman Kodak Co. mesitylene was purified through conversion to mesitylenesulfonic acid[5] to provide a product of b.p. 164.0°, $n^{20}_D$ 1.4979. Mallinckrodt bromine was used without further purification. Eastman Kodak sulfur free carbon tetrachloride was used without purification for the runs reported in Tables I, III and IV and was distilled before use in the runs reported in Table II. Matheson Chemical Company anhydrous hydrogen bromide was screened through Drierite and glass wool before use in the rate studies. Desicote was obtained from Beckman Instruments Company.

**The Rate Measurements.**—In the runs reported in Tables I, III and IV carbon tetrachloride solutions of mesitylene and bromine maintained at the temperature to be used were mixed in the dark, and a sample was removed and placed in a 1-cm. quartz cell. The bromine concentration of the reaction mixture was determined spectrophotometrically at various times using a Beckman Model DU spectrophotometer in the wave length region 520–580 mμ. The quartz cell was left in the cell housing which was maintained at the proper temperature by a water circulating system.

In the runs reported in Table II the bromine concentration of the reaction mixtures at various times was determined colorimetrically at 540 mμ using an Evelyn colorimeter. For this purpose a seven-eighths inch o.d. Pyrex tube provided, by means of a standard taper joint, with a glass cap was used as a reaction vessel. A 1 mm. capillary tube topped with a rubber policeman was sealed through the glass cap. This reaction tube was filled to at least two-thirds capacity with standardized solutions prepared at 25° of bromine in carbon tetrachloride saturated with water. Hydrogen bromide gas was added and the tube was then immersed in a constant temperature bath in a dark room. A small sample of a carbon tetrachloride solution of mesitylene was added through the rubber policeman and capillary tube by means of a calibrated hypodermic syringe, and the reaction vessel was shaken. The tube, which was constructed to fit the colorimeter cell holder, was removed occasionally for rapid colorimeter reading and was then returned to the bath. The colorimeter readings were converted to bromine concentrations by reference to a calibration curve developed for carbon tetrachloride solutions of known bromine concentration.

In spite of the photosensitivity of the reaction, brief exposure of the rate samples to the colorimeter light or the spectrophotometer light did not appear to induce photochemical reaction. A few of the runs which were carried out in complete darkness over the period during which measurements were made were followed by iodometric procedures. The results of such runs were in reasonable agreement with those followed by the optical procedure.

Analysis for hydrogen bromide in these solutions were performed on samples which had been freed of bromine by shaking with aqueous potassium iodide followed by titration with sodium thiosulfate solution. The product solution was then treated with potassium iodate solution, and the liberated iodine was titrated with sodium thiosulfate solution.

Water-saturated carbon tetrachloride was prepared for use in these runs by slow agitation at 25° over a three-day period of mixtures of water and carbon tetrachloride. For the runs reported in Table IV solutions were prepared by mixing a bromine solution in carbon tetrachloride and mesitylene, all of which had been dried for several weeks over Drierite, with water-saturated carbon tetrachloride. All equipment, including the spectrophotometer cell, had been treated with Desicote to reduce errors due to adsorption of water on the walls of the equipment.

**Analysis for Side-chain Bromination Product.**—Certain of the reaction mixtures from which bromine had completely disappeared were freed of hydrogen bromide by exposure for several hours to a slow stream of air. The solution was then heated with methanolic silver nitrate solution. The precipitated silver nitrate, corresponding to side-chain bromination product, was collected and weighed by the usual gravimetric procedures. For those reactions which proceeded normally in the dark the amounts of silver halide obtained indicated that less than 1% of the halogen had reacted to give side chain bromination.

**The Equilibrium Constant for the Mesitylene-Bromine Complex.**—Several solutions of mesitylene (0.08–5.8 $M$) and bromine ($0.86 \times 10^{-4}$ to $15.4 \times 10^{-4}$ $M$) in carbon tetrachloride were measured at 25° and 20° in 1 cm. absorption cells at 326 mμ on the Beckman spectrophotometer. Solutions of corresponding mesitylene concentration were used as blanks. Using methods of earlier investigations[13,14] the concentration equilibrium constant and the molecular

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[13] L. Melander, *Arkiv. Kemi*, **2**, 287 (1950).

[14] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

extinction coefficient of the complex were calculated. The value of the molecular extinction coefficient was found to be 9830 at both temperatures. The value of the equilibrium constant, $K_3$, was calculated to be 0.381 mole$^{-1}$ l. at 25° and 0.398 at 20°.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Intramolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid in Quinoline Solution

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The intramolecular carbon isotope effects for the decarboxylation of malonic acid in quinoline solution have been measured between 86 and 138°. Combination of the results with those obtained previously under similar conditions for the intermolecular carbon isotope effect permits a new test of simplified models which have been proposed for the decomposition. A modification of Bigeleisen's model results in improved agreement between the experimental results and the theoretical calculations. A suggestion is made as to the manner of carrying out a stringent test of the modified model.

## Introduction

In a recent paper[1] we presented the results of experiments on the decarboxylation of malonic acid in quinoline solution which were designed to yield the temperature coefficient of the *inter*molecular carbon isotope effect under conditions of homogeneous decomposition. The differences between the magnitudes of the isotope effects observed and those predicted by calculation based on the corrected[2] simple model suggested by Bigeleisen[3,4] were explained by postulation of the existence of one or more rapid solvation equilibria antecedent to the rate determining step, which is a bimolecular process involving a solvent molecule.

In the investigation to be reported here, the experiments with quinoline medium were extended to the determination of the *intra*molecular isotope effect in the temperature range 86–138°.

## Experimental

**Materials.**—The malonic acid used was Eastman Kodak Company white label grade. Preliminary tests indicated that it was of high purity and the material was used as received. The quinoline employed was Eastman Kodak Company white label grade (synthetic). It was found to have been dried thoroughly and was used as received.

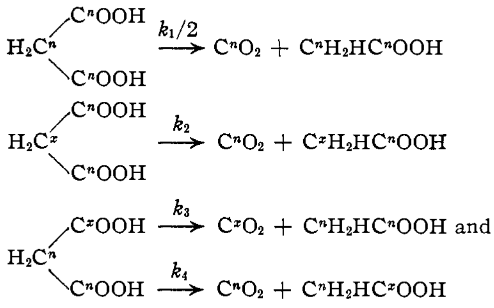
**Apparatus and Procedure.**—The apparatus and general procedure have been described in previous publications.[1,5] About 100 mg. of dried malonic acid and 25 ml. of quinoline were combined after being brought to the decarboxylation temperature; an exception to this procedure was required in the runs at 138°, in which the acid was heated to just below its melting point. The sweep rate of pre-heated, carbon dioxide-free helium was approximately 100 cc. per min. The time allowed for decarboxylation to reach essential completion varied from 40 minutes at 138° to 10 hours at 86°.

**Degradations.**—If accurate isotope effect calculations are to be made, one must have information as to the isotopic constitution of the carboxyl and methylene carbon atoms of the malonic acid starting material. Lindsay, Bourns and Thode[6] compared the carbon isotope ratios of carbon dioxide obtained from the combustion of a sample of Eastman Kodak Co. malonic acid and that obtained by the combustion of methane produced from the methylene carbon atom *via* soda lime–sodium acetate pyrolysis. They found these ratios to be insignificantly different.

In the course of another investigation,[7] it was found that the isotopic constitution of the carbon atoms of acetic acid depends upon the source of that material; accordingly, one would expect that different samples of malonic acid (which is produced by the sequence acetic acid–chloroacetic acid–cyanoacetic acid–malonic acid) might have carboxyl and methylene carbon atoms of differing isotope make-up. Samples of the malonic acid used in this investigation were decomposed in the absence of solvent and the resultant acetic acid degraded by a modification[7] of Phares' application[8] of the Schmidt reaction.[9]

**Isotope Analyses.**—The carbon isotope ratios of the various samples were obtained from measurements with a Consolidated-Nier Isotope-Ratio Mass Spectrometer. The ratio was determined once on each of at least three introductions of sample carbon dioxide into the manifold of the spectrometer. Frequent checks were made among the samples and two working standards. The mass spectrum of each gas sample was determined in the range m/q 27 to 48; the sample was rejected if this spectrum deviated appreciably from that of tank carbon dioxide which had been subjected to the same high vacuum manipulations. The observed carbon isotope ratios were corrected for the contribution to the ion current at m/q 45 of the species $C^{12}O^{16}O^{17}$ and for incomplete resolution.

**Calculations.**—Bigeleisen and Friedman's[4] notation for the description of the carbon isotope effects in malonic acid decarboxylation is



$$H_2C^n(C^nOOH)_2 \xrightarrow{k_1/2} C^nO_2 + C^nH_2HC^nOOH \tag{1}$$

$$H_2C^x(C^nOOH)_2 \xrightarrow{k_2} C^nO_2 + C^xH_2HC^nOOH \tag{2}$$

$$H_2C^n(C^xOOH)(C^nOOH) \xrightarrow{k_3} C^xO_2 + C^nH_2HC^nOOH \text{ and} \tag{3}$$

$$H_2C^n(C^xOOH)(C^nOOH) \xrightarrow{k_4} C^nO_2 + C^nH_2HC^xOOH \tag{4}$$

(where *n* and *x* denote different isotopes or concentrations of isotopes of carbon); the deviation from unity of the ratio $k_4/k_3$ is a measure of the *intra*molecular isotope effect, while that of $k_1/2k_3$ is one measure of an *inter*molecular effect. The former can be determined from analysis of the carbon dioxide obtained by complete decarboxylation to acetic acid, while the latter is gotten from analysis of the first carbon dioxide evolved. Other intermolecular isotope effects are related to the ratios $k_1/2k_4$ and $k_1/k_2$.

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