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The Kinetics of Bromination of Mesitylene in Acetic Acid

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The rate of bromination of mesitylene in acetic acid solution shows mixed first- and second-order dependence on bromine concentration. At low mesitylene concentrations ($<0.2\ M$) the measured rates of these two independent reactions are approximately first order in mesitylene, but in more concentrated solutions the rates do not increase in direct proportion to the hydrocarbon concentration. The rates are increased by the addition of water to the medium and are depressed by inert hydrocarbons. Both reactions are strongly accelerated by several different salts (with the exception of sodium acetate). The salt effect is more marked for the first-order (in bromine) than for the second-order reaction. Zinc chloride apparently is a true catalyst for the first-order reaction. Even in high dilution it accelerates the rate in direct proportion to its concentration and lowers the activation energy appreciably. These facts provide the basis for a discussion of the bromination mechanism.

The results of recent kinetic studies of the electrophilic bromination of mesitylene in carbon tetrachloride have been interpreted satisfactorily on the assumption that a mesitylene–bromine complex is a reactant in the rate determining step.[1,2] In this step the bromine–bromine bond of the complex presumably is severed on attack by an electrophilic reagent, E (equation 1)

$$C_6H_3(CH_3)_3 \cdot Br_2 + E \longrightarrow C_6H_3(CH_3)_3Br^+ + EBr^- \quad (1)$$

Subsequent loss of a proton by the cationic product leads to the formation of 2-bromomesitylene. Iodine bromide, which is an excellent catalyst for mesitylene bromination,[3] may serve as the reagent E.[2] In the absence of added catalyst, hydronium ion (formed from traces of water and hydrogen bromide in the medium) seems to fill this role. A similar picture has been presented to explain the kinetics of the iodine bromide catalyzed bromination of toluene in carbon tetrachloride.[4]

Experiments are now in progress to determine how this kinetic picture of electrophilic aromatic bromination is altered with increases in polarity of the medium. The present investigation has been concerned with the bromination of mesitylene in acetic acid. Robertson and co-workers[5] have reported extensively on the kinetics of aromatic halogenation in this solvent and find that in general the reactions are of higher than first order in halogen and that their rates are accelerated by salts and acids. In no case, however, has the rate law for any single reaction been proved in detail, nor has any extensive consideration been made of the modifications in the experimental rate law which are produced by added salts.

Experimental

Materials.—The acetic acid was purified through refluxing in the presence of chromic anhydride and acetic anhydride by the method of Orton and Bradfield.[6] The large majority of the rate measurements were made using a single batch of the purified material, of freezing point 16.2°, as the solvent. The observed rate constants varied slightly with changes in the batches of purified solvent. These variations presumably resulted from small differences in the acetic anhydride content of the different solvent preparations. Analytical Reagent grade bromine was used without further purification. Mesitylene was purified through preparation of its sulfonic acid.[7] Hydrated sodium perchlorate (G. Frederick Smith Chemical Co.) was dried for two days at 140°. Lithium chloride, lithium perchlorate

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[1] R. M. Keefer, J. H. Blake and L. J. Andrews, THIS JOURNAL, **76**, 3062 (1954).

[2] J. H. Blake and R. M. Keefer, *ibid.*, **77**, 3707 (1955).

[3] P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949).

[4] T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, **76**, 994 (1954).

[5] (a) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); (b) P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (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) P. W. Robertson, R. M. Dixon, W. G. M. Goodwin, I. R. McDonald and J. F. Scaife, *ibid.*, 294 (1949); (f) P. W. Robertson, *ibid.*, 1267 (1954).

[6] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

[7] L. I. Smith and O. W. Cass, THIS JOURNAL, **54**, 1606 (1932).

and lithium acetate were prepared by dissolving analytical grade lithium carbonate in the appropriate acid followed by evaporation of the solutions. The lithium chloride and lithium acetate were dried at 140°. The lithium perchlorate was fused at 350°. Analytical reagent grade sodium acetate trihydrate and zinc chloride were dried at 140°.

Kinetic Studies.—In general the disappearance of bromine from the reaction mixtures was followed by noting the changes in optical density of the solutions at 450 mμ with time. These measurements were made on the Beckman spectrophotometer with cell housing temperatures controlled[8] to ±0.1°. The reaction mixtures were contained in 2 cm. absorption cells and were measured against pure acetic acid as a blank. The bromine concentrations $(Br_2)_T$ were evaluated from measured optical densities using the independently measured molar extinction coefficient, 124.8, of bromine in acetic acid at 450 mμ. In solutions of mesitylene concentration in excess of 0.1 *M* the extinction coefficient of bromine showed noticeable increases with increasing mesitylene concentration. The halogen extinction coefficients in these media were deduced through extrapolation of optical densities measured in the initial phases of the rate runs to zero times at which the bromine concentrations were known.

For the runs at 25° rate samples were prepared by mixing aliquots of solutions in acetic acid of known concentrations of mesitylene, bromine and any added substances which had previously been stored at cell housing temperature. The bromine solutions were freshly prepared each day and were standardized through spectrophotometric measurement. In fast runs the aliquots of the various reagent solutions were mixed by dropping a small beaker containing one aliquot into a larger beaker containing the others, and a stopwatch was used to record time. In general reactions were followed to at least 75% completion.

In most runs the mesitylene concentration was in large excess over that of the bromine. The initial bromine concentrations were kept small (usually no greater than $4 \times 10^{-3} M$) to prevent the accumulation of large amounts of hydrogen bromide in the medium and to prevent the conversion of substantial amounts of bromine to hydrogen tribromide.[9] The kinetic complications of catalysis by hydrogen bromide or retardation through hydrogen tribromide formation reported previously[5f] for mesitylene brominations at higher halogen concentrations were not observed.

The use of a spectrophotometric method for rate study did not appear to induce a radical type bromination. The rates of bromine consumption were the same in two identical reaction mixtures one of which was exposed continuously and the other intermittently to the tungsten lamp of the instrument.

The validity of the colorimetric procedure for following the rates was further checked by repeating one of the slower runs (initial bromine and mesitylene concentrations were 2×10^{-3} and 2×10^{-2} *M*, respectively) and analyzing rate samples iodometrically. Rate constants obtained by the two procedures agreed with each other within experimental error.

The Equilibrium Constant for the Bromine–Mesitylene Complex.—A series of acetic acid solutions of mesitylene (varying from 1.0–0.2 *M*) and bromine (varying from $1 \times 10^{-3} - 0.25 \times 10^{-3}$ *M*) were placed in 2 cm. absorption cells immediately after preparation, and the optical densities of the solutions at 25.4° at 326 mμ were recorded against acetic acid as a blank as a function of time over a five-minute interval. The optical densities, d_0, of the freshly prepared solutions were then determined by extrapolation and were corrected for the slight absorption of mesitylene. From these d_0 values the extinction coefficients, ϵ_a, were calculated using the relation $d_0 = \epsilon_a l(Br_2)_T$ where l is the cell width in cm., and $(Br_2)_T$ is the molar concentration of total bromine both free and complexed in the solutions. The equilibrium constant, *K*, for complex formation was then calculated in the usual fashion by graphical analysis of the data by the equation[10]

$$1/(\epsilon_a - \epsilon_{Br_2}) = 1/K(\epsilon_0 - \epsilon_{Br_2})(M) + 1/(\epsilon_0 - \epsilon_{Br_2}) \quad (2)$$

where ϵ_{Br_2} and ϵ_0 are, respectively, the extinction coefficients of bromine and of the complex at 326 mμ, and (M) is the molar concentration of mesitylene in the medium. These measurements were repeated with freshly prepared solutions using a wave length of 350 mμ.

The Bromination Product.—To establish that no substantial amount of side chain bromination occurs in acetic acid a mixture of 6 ml. of acetic acid, 3 ml. of mesitylene and 0.25 ml. of bromine was allowed to stand overnight in a painted glass-stoppered bottle. By this time the bromine was completely consumed. The mixture was washed six times with a total of 180 ml. of water to remove hydrogen bromide and acetic acid. Two ml. of the organic phase was treated with alcoholic silver nitrate solution. Only about 0.6 mg. of silver bromide precipitated from this solution. This indicates that not more than 0.1% of the bromination reaction produced side chain substituted material.

Tests showed that 2-bromomesitylene (a commercial sample freed of side chain brominated material)[11] in acetic acid consumed bromine much more slowly than did solutions of equivalent mesitylene concentration. In reported rate runs the mesitylene concentration was always much greater than that of 2-bromomesitylene. Therefore no substantial quantity of dibromomesitylene, as compared to monobromomesitylene, could have formed during the runs.

Results

Runs without Added Salts.—The rate of disappearance of bromine from mesitylene solutions in acetic acid shows mixed first- and second-order dependence on total bromine concentration (equation 3)

$$R = -\frac{d(Br_2)_T}{dt} = k_1(M)(Br_2)_T + k_2(M)(Br_2)^2_T \quad (3)$$

The contribution of the first-order term is small except at very low bromine concentrations. To evaluate the rate constants for each mesitylene concentration at which runs were made plots of values of $(Br_2)_T$ against time were prepared. The slopes of these plots, *R*, at various bromine concentrations were measured, and plots of $R/(M)(Br_2)_T$ against corresponding $(Br_2)_T$ values were prepared. These are shown in Fig. 1. The intercepts and slopes of the resultant straight lines were recorded, respectively, as k_1 and k_2 values. In most cases several runs at each mesitylene concentration were made with at least a fourfold range in the initial bromine concentrations of the various reaction mixtures. Points for these several runs at varying initial bromine concentrations all conformed well to the same straight line plot of $R/(M)(Br_2)_T$ *versus* $(Br_2)_T$. This observation constitutes negative evidence for catalysis of the reaction by hydrogen bromide which is formed concurrently with bromomesitylene.

The observed values of k_1 and k_2 at 25.4° are listed as the first five entries in Table I, which summarizes all of the kinetic data taken in this investigation. The k_2 values are considerably less than those calculated from the results of another study on the assumption that the over-all reaction was second order in bromine.[5a] No great significance can be attached to the variations in k_1 with changing mesitylene concentration, since the evaluation of this constant is subject to considerable error because of the low contribution of the first-order reaction (with respect to the bromine) to the total reaction rate.

The variations of k_2 with mesitylene concentra-

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[8] Details of temperature control and measurement within the cell housing are recorded elsewhere: *cf.* R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955).

[9] K. Nozaki and R. A. Ogg, *ibid.*, **64**, 697 (1942).

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

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

tion might, as has been discussed in an earlier publication, result from the fact that some of the bromine in the reaction medium exists in the form of a 1:1 bromine–mesitylene complex (equation 4).

$$M + \mathrm{Br}_2 \rightleftarrows M\cdot\mathrm{Br}_2;\ K = \frac{(\mathrm{M}\cdot\mathrm{Br}_2)}{(\mathrm{M})(\mathrm{Br}_2)} \qquad (4)$$

It follows that if the rate-determining process in the formation of bromomesitylene requires the attack of the 1:1 complex either by solvent or by a bromine molecule, the correct rate expression for the reaction should be

$$R = k_x \frac{K(\mathrm{M})(\mathrm{Br}_2)_\mathrm{T}}{[1 + K(\mathrm{M})]} + k_y K(\mathrm{M}) \frac{(\mathrm{Br}_2)^2_\mathrm{T}}{[1 + K(\mathrm{M})]^2} \qquad (5)$$

Then the observed k_2 values should show variation with mesitylene concentration according to the expression

$$1/\sqrt{k_2} = 1/\sqrt{k_y K} + (\mathrm{M})\sqrt{K}/\sqrt{k_y} \qquad (6)$$

As is required by equation 6, a plot of observed values $1/\sqrt{k_2}$ *versus* mesitylene concentrations gives a straight line from the slope and intercept of which a value of $K = 0.95$ l. mole^{-1} may be calculated.[12] This value for the equilibrium constant is much higher than that, $K = 0.11$ mole^{-1} l., obtained by direct evaluation of the equilibrium concentration of the complex in solution at 25.4° (see the Experimental section).[13]

TABLE I

RATE CONSTANTS FOR THE REACTION OF BROMINE WITH MESITYLENE IN ACETIC ACID

(Mesitylene) 10^3 mole/l.	Added substance Substance	Added substance Concn., mole/l.	k_1, mole^{-1} min.$^{-1}$ l.	k_2, mole^{-2} min.$^{-1}$ l.^{2}
		Data taken at 25.4°		
9.5			0.029	221
47.5			.029	206
190			.029	167
380			.024	120
712			.021	79
190	CCl_4	10 vol. %	0	80
190	C_6H_6	10 vol. %	0	88
2.5	H_2O	7.4	40	11,000
1.25	H_2O	7.4		
47.6	$NaClO_4$	0.099	0.83	660
47.6	$NaClO_4$	.148	1.16	1,250
47.6	$NaClO_4$	.248	2.41	1,950
95.2	$NaClO_4$	.248		
47.6	NaOAc	.251	0.01	350
47.6	$LiClO_4$	.100	.35	800
47.6	$LiClO_4$	.250	.75	2,300
47.6	LiCl	.100	.06	700
47.6	LiCl	.250	.15	2,250
		10^3 *M*		
47.6	$ZnCl_2$	0.995	1.08	240
142.8	$ZnCl_2$	.995		
47.6	$ZnCl_2$	1.99	2.24	330
47.6	$ZnCl_2$	3.98	4.72	200
47.6	$ZnCl_2$	9.96	11.7	300
		Data taken at 16.2°		
190			0.013	116
47.6	$NaClO_4$	99	.34	470
47.6	$ZnCl_2$	0.995	.74	170

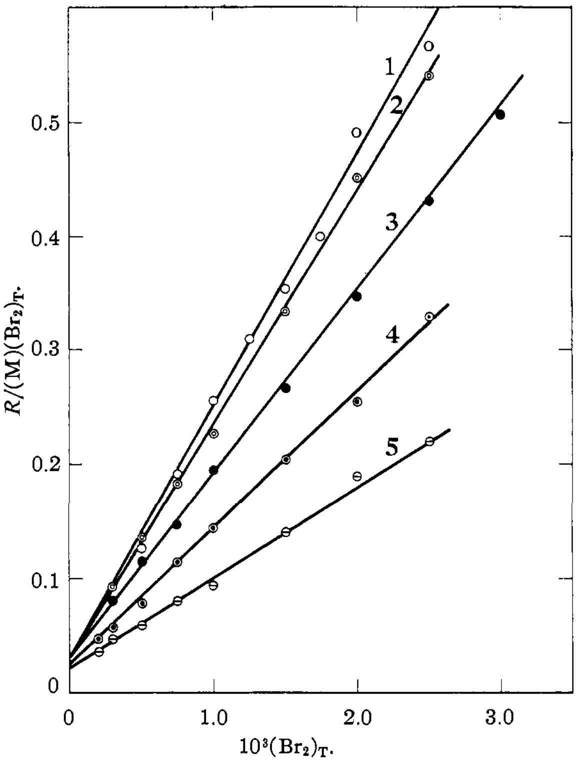

Fig. 1.—The effect of mesitylene concentration on the rate of bromination at 25.4°. The mesitylene concentrations for runs on which lines 1–5 are based are, respectively, 0.0095, 0.0475, 0.190, 0.380 and 0.712 *M*.

Thus the diminution in k_2 with increasing mesitylene concentration is by no means totally to be accounted for in terms of complex formation. A major portion of this reduction in rate constant must be classified as a solvent effect. In other words the reaction rate must be relatively sensitive to the change in polarity of the medium which results when a small amount of a material of low dielectric constant is added. This effect was also demonstrated kinetically by repeating runs at 0.190 *M* mesitylene with acetic acid containing 10 volume % carbon tetrachloride and also with 10 volume % benzene as the solvents. The k_2 values in these cases (see Table I—sixth and seventh entries) were approximately one-half those with pure acetic acid as the solvent and were about the same as those for runs at 0.7 *M* mesitylene in pure acetic acid (a medium which is about 10 volume % in mesitylene). The k_1 values for the runs with the added inert hydrocarbons were immeasurably small.

On the other hand the magnitudes of both k_1 and k_2 are increased as the polarity of the medium is increased by the addition of water (see the eighth and ninth entries of Table I). In solutions containing 7.4 *M* water (about 13 volume % water) k_1 and k_2 are, respectively, about 1400 and 50 times as great as when pure acetic acid is used as solvent.

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(12) This same value for *K* may be derived on the assumption that $M\cdot Br_2$ does not participate directly in rate-determining processes but rather that only bromine and mesitylene molecules which are not complexed with each other can react to give bromomesitylene.

(13) This figure for *K* is an average of two values, 0.10 and 0.12, obtained by measurements at 326 and 350 mμ, respectively. The complex extinction coefficients, ϵ_c, at these wave lengths are, respectively, about 14,000 and 8000.

These observed solvent effects are typical of reactions in which the transition state intermediates are more polar than the reactants. It is of significance in this regard that when pure carbon tetrachloride is used as solvent the rate of mesitylene bromination falls to zero in the absence of polar contaminants which can function as catalysts.[1,2]

Runs with Added Salts.—Rate constants for the runs with various added salts were also calculated assuming equation 3 as the rate law. The resultant k_1 and k_2 values are summarized in Table I, and typical plots of $R/(\mathrm{M})(\mathrm{Br}_2)_\mathrm{T}$ *vs.* $(\mathrm{Br}_2)_\mathrm{T}$ for runs with and without added salts are compared in Fig. 2.

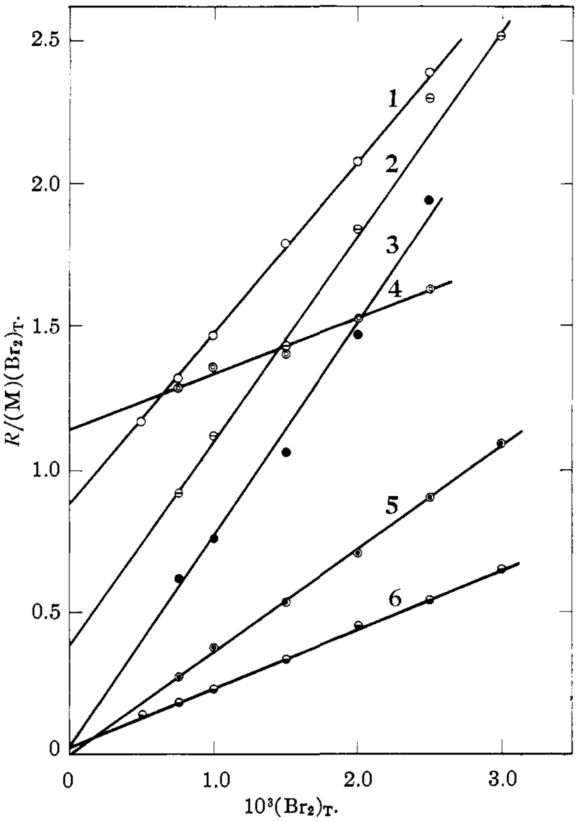

Fig. 2.—The effect of salts on the rate of bromination at 25.4°. In all runs the mesitylene concentration was 0.0476 *M*. The added salts and their concentrations for runs on which lines 1–5 are based are, respectively, 0.099 *M* sodium perchlorate, 0.100 *M* lithium perchlorate, 0.100 *M* lithium chloride, 1.0 × 10^{-3} *M* zinc chloride, 0.251 *M* sodium acetate. Line 6 was drawn from data taken in runs without added salts.

Of all added salts zinc chloride produced by far the most marked enhancement in reaction rate, and this enhancement appeared almost entirely in the increase in contribution of the first-order reaction (in bromine) to the total rate. With as little as 10^{-3} *M* zinc chloride the k_1 value was approximately forty times larger than in the absence of added salt. As shown by the data in Table I, the k_1 values for reactions in the region of 10^{-2} to 10^{-3} *M* zinc chloride concentration are directly proportional to the concentration of added salt.

Sodium perchlorate also enhances the over-all rate of the bromination reaction although its effect on k_1 is much less pronounced than that of zinc chloride. In solutions which are 0.248 *M* in sodium perchlorate, k_1 is about eighty times larger than it is in the absence of added salt. The increase in k_1 with increasing sodium perchlorate concentration of the medium is approximately linear. At 0.248 *M* sodium perchlorate k_2 is about ten times greater than it is in the absence of added salt. Lithium perchlorate and lithium chloride produce increases in k_2 of the same order of magnitude as was observed for reactions at equivalent concentrations of sodium perchlorate, but their effects on k_1 values are less marked than those observed in runs with sodium perchlorate. With added sodium acetate the k_2 value is enhanced slightly over that in runs with no added salt; but k_1 is, if anything, repressed by this salt.

The Activation Energies.—The rate constants at 16.4° (Table I) were used along with those for runs at equivalent mesitylene concentration at 25.4° to evaluate activation energies both for the first- and second-order (in bromine) reactions. The resultant values for runs without added salt and for runs with added sodium perchlorate and zinc chloride are given in Table II. The activation energies for the second-order reaction are apparently independent of the presence or absence of added salt. The precision of the activation energy for the first-order reaction in the absence of added salt is limited, since it is evaluated from small values of k_1 which cannot be accurately measured. It is safe to conclude, however, that E_1, for the reaction in the presence of zinc chloride is much less than that for reaction in the presence of sodium perchlorate or of no added salt.

Table II

Activation Energies for Mesitylene Bromination

(M),[a] mole/l.	Added salt	Salt concn.,[a] mole/l.	E_1, kcal./mole	E_2, kcal./mole
0.190	None	......	15	6.8
.0476	$\mathrm{NaClO_4}$	0.099	16.7	6.5
.0476	$\mathrm{ZnCl_2}$	0.000995	7.1	6.5

[a] These represent the concentrations of reagents in the particular runs which were made to evaluate the activation energies.

The Reaction Mechanism.—A termolecular collision involving a mesitylene molecule and two bromine molecules in the rate-determining step for that phase of the reaction which is second order in bromine is a less probable process than a bimolecular collision between a bromine molecule and a mesitylene–bromine complex (*cf.* equation 1) or between molecules of mesitylene and $\mathrm{Br_4}$. In view of the evidence for the existence of the mesitylene–bromine complex and the lack of evidence that there are significant amounts of $\mathrm{Br_4}$ in dilute solutions of bromine in acetic acid, the former of the alternate bimolecular processes (*cf.* equation 1) seems more probable.

Any proposed reaction mechanisms which require free (or solvated) Br^+ or acetyl hypobromite as the active brominating agents are not consistent with the observed rate law. Neither of these species can exist in the reaction mixtures in more than very small quantity, and their concentrations must be highly sensitive to the accumulation of bromide ion or hydrogen bromide in the medium during the course of the mesitylene bromination reaction. Acetyl hypobromite has previously[5f] been ruled out as the active halogenating species on the ground that its effectiveness should compare with that of acetyl hypochlorite, which does not appear to be the active chlorinating agent for aromatic substances in solutions of chlorine in acetic acid.[5b,14]

The effects of added salts on k_2 values are pronounced with the exception of those of sodium acetate and zinc chloride, the latter of which was used only in low concentration. This rate enhancement cannot safely be ascribed to direct participation of the salts in rate-determining processes in view of the high sensitivity of k_2 values to changes in solvent polarity. This conservative interpretation seems justified, since it is recognized[15] that salt effects in acetic acid solvent may be marked even though extensive dissociation of most salts to give free ions (with the notable exception of perchlorates) seems unlikely.[16–18] In this reaction salt addition apparently has a strong influence on the capacity of the medium to accommodate the transition state intermediate.

The first-order (in bromine) term of the rate law (equation 3) can be rationalized on the basis of either of two rate-determining processes. In one of these the mesitylene–bromine complex undergoes reaction to form products, probably through attack by solvent, and in the other product formation is accomplished through bimolecular reaction of mesitylene and bromine. If one adopts the mesitylene–bromine complex picture, he must conclude that acetic acid is a relatively feeble electrophilic reagent (E in equation 1), since the second-order term in bromine is of primary importance in governing the over-all reaction rate in the absence of added salts.[19]

The changes in k_1 values produced by salts, exclusive of those noted for zinc chloride and sodium acetate, may, as in the case of k_2 values, be ascribed to "salt effects." It is also possible that the concentration of an active species E, which is a proton donor in nature and which is a participant in the rate-determining step of the reaction which is first order in bromine, is enhanced by added salts. It is significant that the same salts which produce increases in k_1 also are reported[16] to increase the acidity of acetic acid. In further support of this argument is the fact that sodium acetate, which lowers the acidity of the solvent,[17] seems to repress k_1 values. It should be noted, however, that the rate of reaction is not highly sensitive to the hydrogen bromide concentration of the medium; but this acid may be extremely weak in acetic acid. Preliminary experiments indicate that in the presence of perchloric acid, which is a strong acid in acetic acid, the rate of mesitylene bromination is increased substantially over that in pure acetic acid but only to about the same extent as is observed in the presence of an equivalent concentration of sodium perchlorate. The lack of enhancement of k_1 values by sodium acetate is in accord with an earlier demonstration that removal of a proton from the aromatic nucleus does not occur in the rate determining step in aromatic bromination.[20]

Since zinc chloride, at the dilutions used in the rate runs, has little effect on k_2 values, its extremely pronounced influence on k_1 values is most easily interpreted on the assumption that the salt plays some direct part in the rate-determining step of the reaction which is first order in bromine. Either of the reactions given in equations 7 or 8 may be rate determining[21]

$$C_6H_3(CH_3)_3{\cdot}Br_2 + ZnCl_2 \longrightarrow C_6H_3(CH_3)_3Br^+ + BrZnCl_2^- \quad (7)$$

$$C_6H_3(CH_3)_3 + Br^+BrZnCl_2^- \longrightarrow C_6H_3(CH_3)_3Br^+ + BrZnCl_2^- \quad (8)$$

The marked difference in the activation energy for the k_1 term in the presence of zinc chloride as compared to that in the presence of sodium perchlorate or of no added salts may be cited as further evidence that zinc chloride plays a specific role in the rate-determining process.

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(14) P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *Research*, **6**, 12S (1953).

(15) J. Steigman and L. P. Hammett, THIS JOURNAL, **59**, 2536 (1937).

(16) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007, 1014 (1934).

(17) N. A. Izmailov and A. M. Aleksandrova, *Zhur. Obshcheĭ Khim.*, **20**, 217 (1950); *cf. C. A.*, **45**, 4581 (1951).

(18) M. M. Jones and E. Griswold, THIS JOURNAL, **76**, 3247 (1954).

(19) R. E. Buckles and J. F. Mills, *ibid.*, **75**, 552 (1953), have shown that in solvating bromine acetic acid in all probability functions as an electron donor, a role which is not compatible with its function as an electrophilic reagent in the present situation.

(20) L. Melander, *Arkiv. Kemi*, **2**, 211 (1950).

(21) In equation 7 and in 8 zinc chloride and its bromine complex must be represented in non-ionized form in order that the postulated reactions conform to the rate law. The products of these reactions, shown as ions, might be more correctly represented as ion pairs.