over a potassium film in a glass bulb which had been sealed off under high-vacuum conditions. They were degassed by alternate solidification and melting in a 10^{-7}-torr pressure. Finally all substances were collected in sample tubes equipped with break-seal valves and were then sealed off from the high-vacuum apparatus.

Procedures and Measurements.—Reactions of the solid phenylmethanes with potassium were carried out in a 1-l. glass bulb. A potassium film was formed by distilling the metal out of a sample tube into the bulb, under good high-vacuum conditions (10^{-7} torr). Subsequently the bulb was sealed off from the high-vacuum apparatus, and the hydrocarbon was sublimed onto the metal film. After the reaction had taken place the bulb was attached to a mass spectrometer (CH4, Atlas, Bremen) in order to analyze the volatile reaction compounds. The mass spectrometer was equipped with a capacitance manometre for partial pressure determination. The bulb was then evacuated to 10^{-5} torr and an attached sample tube containing carbon dioxide was opened. The additional release of any gaseous compounds was determined mass spectrometrically.

Solutions of the solid potassium compounds were prepared in a glass apparatus which consisted of a sample tube with the solvent, a glass bulb with the solid potassium compound, and several optical and conductivity cells. The apparatus was sealed off after it had been baked out at 400° for about 10 hr in a 10^{-7} torr vacuum. The break-seal valves above the sample tube and the bulb were opened and a small amount of the solid potassium compound was dissolved. The solution (about 50 ml) was then poured through a sealed-in glass frit into measurement cells which were subsequently sealed off.

The concentration of the solutions was determined by potentiometric titration of the potassium hydroxide, formed by hydrolizing the solutions. The ultraviolet spectra were measured by means of a spectrophotometer (H 700 308, Hilger and Watts, London). A picoamperemeter (Knick, Berlin) was used for determining low electric conductivity data of solutions in 1,4-dioxane. Higher conductivity data of solutions in tetrahydrofuran were measured by means of a Wheatstone bridge.

Registry No.—Diphenylmethylpotassium, 10060-17-0; diphenylmethane, 101-81-5; triphenylmethylpotassium, 1528-27-4; triphenylmethane, 517-16-8; potassium tetraphenylmethane, 10036-54-1; tetraphenylmethane, 630-76-2.

Perchloric Acid Catalyzed Aromatic Mercuration in Acetic Acid Solution. I. Electrophilic Reagents[1,2]

A. J. KRESGE,[3] M. DUBECK,[4] AND HERBERT C. BROWN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616,
and the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 49707

Received November 14, 1966

The rate of the perchloric acid catalyzed mercuration of benzene by mercuric acetate or mercuric perchlorate in acetic acid solution at 25° is directly proportional to benzene concentration but is a complicated function of the concentration of the mercurating agent. The reaction is catalyzed strongly by perchloric acid, retarded weakly by water, and affected by sodium perchlorate in a way which depends on the acidity and water content of the reaction medium. These observations can be understood in terms of an acid-base reaction between perchloric acid and mercuric acetate which forms appreciable quantities of acetatomercury(II) perchlorate ion pairs; these, in turn, are protonated further to give small amounts of mercuric perchlorate ion triplets. Since water is weakly basic in acetic acid solution, it supresses these equilibria; sodium perchlorate affects the activity of water and also produces a small amount of perchloric acid through solvolysis. All three mercury-containing species, $Hg(OAc)_2$, $HgOAc^+ClO_4^-$, and $Hg^{2+}(ClO_4^-)_2$, are active mercurating agents which account for sizable portions of the mercuration reaction under different conditions; the relative reactivities of the first two toward benzene at 25° stand in the ratio 1:10^4.

Aromatic mercuration in acetic acid solution has been of considerable value in providing data to test proposed quantitative treatments of aromatic substitution: rates and isomer distributions for mercuration by mercuric acetate are now available for benzene and toluene,[5] the monoalkylbenzenes and polymethylbenzenes,[6] anisole,[7] biphenyl and fluorene,[8] and the halobenzenes.[9] Unfortunately, it is difficult to extend these studies to aromatic substrates containing appreciably deactivating substituents, for here the reaction of mercuric acetate with aromatic substrate is very slow and, at the high temperatures which must be used, mercuric acetate is not stable in acetic acid solution.[5,9]

Perchloric acid is known to accelerate the rate of aromatic mercuration in acetic acid solution very strongly.[5,10] This catalyzed reaction would therefore seem to provide a good system in which to obtain rate and isomer distribution data for aromatic substrates with deactivating substituents. In contrast to the situation for aromatic mercuration in aqueous solution,[11] however, comparatively little research seems to have been done on the kinetics and mechanism of perchloric acid catalyzed mercuration in acetic acid solution, and there appear, moreover, to be points of disagreement even in the little information which is available. Before attempting to provide quantitative data for deactivated aromatics, we therefore decided to undertake a detailed mechanistic study of aromatic mercuration in acetic acid solution with special emphasis on catalysis by perchloric acid.

We soon discovered that the perchloric acid catalyzed reaction is relatively complex: it involves the

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(1) Directive Effects in Aromatic Substitution. LIX.

(2) Based in part upon a thesis submitted by M. Dubeck to Purdue University in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(3) Postdoctoral Research Associate at Purdue University, 1954–1955, on projects supported by grants from the National Science Foundation (No. G-2752) and the Atomic Energy Commission [No. At(11-1)-170].

(4) Monsanto Chemical Co. Fellow at Purdue University, 1956–1957.

(5) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2306 (1955).

(6) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955).

(7) H. C. Brown and M. Dubeck, *ibid.*, **82**, 1939 (1960).

(8) H. C. Brown, M. Dubeck, and G. Goldman, *ibid.*, **84**, 1229 (1962).

(9) H. C. Brown and G. Goldman, *ibid.*, **84**, 1650 (1962).

(10) R. M. Schramm, W. J. Klapproth, and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(11) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2733 (1963).

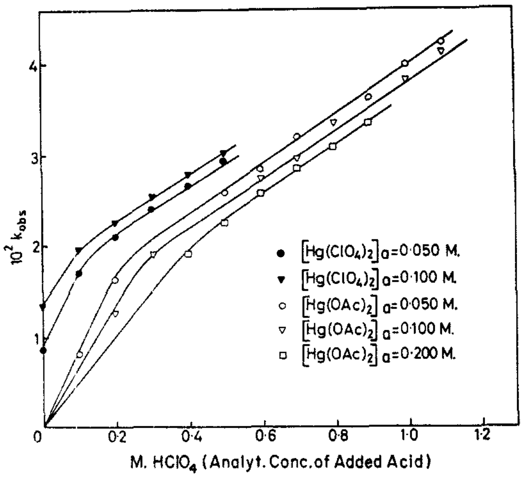

Figure 1.—Relationship between observed rate constants for the mercuration of benzene in acetic acid solution at 25° and the analytical concentration of added perchloric acid at an analytical water concentration of 0.25 *M*.

possibility of substitution by no less than three different mercury(II)-containing species. This rendered the reaction undesirable for the original objective of our study, and alternative solutions to the problem have been developed,[12] but the chemistry of perchloric acid catalyzed mercuration itself proved to have a number of points of intrinsic interest, and the purpose of our study was consequently altered so that primary attention could be devoted to understanding the mechanism of aromatic mercuration in acetic acid solution. The results of this investigation are presented in the present series of papers. In the first paper, we report results which identify the electrophilic species taking part in the reaction; in the second,[13] we shall discuss the substitution itself; and in the third,[14] we shall describe the effect of changing the aromatic substrate.

Results

Rates of aromatic mercuration were measured by determining the amount of unreacted mercury(II) present in a reaction mixture as a function of time. Titration with thiocyanate was employed for this purpose: inorganic mercuric salts react with 2 equiv of thiocyanate whereas aryl mercuric salts consume only 1 equiv. The analytical concentration of perchloric acid in the reaction mixtures was measured by titration with sodium acetate in anhydrous acetic acid; the water content of acetic acid solutions was determined by Karl Fischer titration. Benzene was the representative aromatic substrate used for most of this mechanistic study. Mercury(II) was supplied either as mercuric acetate or mercuric perchlorate.

The polymercuration of benzene occurs at a rate which is comparable to that of monomercuration.[11,14,15] In order, therefore, to ensure that the rates measured were representative of monomercuration, the aromatic substrate was generally supplied in considerable excess over mercury(II). Even with this precaution, however, the reported[5,10,15] compliance with second-order kinetics was not always observed: second-order rate constants sometimes increased with time. These deviations, however, were only minor disturbances to a basically second-order process, and the rate data were therefore always treated in a standard second-order manner. Rate constants were estimated graphically from plots of log [HAr]/[Hg^{II}] against time. Where such plots gave curved lines, rate constants were obtained from their initial straight portions; where the lines were straight, data to about 75% reaction were normally used.

Reaction Order in Benzene.—Observed second-order rate constants for the mercuration of benzene by mercuric acetate in the presence of perchloric acid and by mercuric perchlorate, measured at a number of different benzene concentrations, are presented in Table I. These rate constants, calculated on the basis of disappearance of both benzene and mercury(II), are essentially constant over a considerable concentration range, and the reaction is therefore first order in benzene.

TABLE I

EFFECT OF BENZENE CONCENTRATION ON THE RATE OF MERCURATION OF BENZENE IN ACETIC ACID SOLUTION AT 25°

Initial concn (*M*) of C_6H_6	10^2k_{obsd} (M^{-1} min^{-1})
Hg^{II} Supplied as 0.050 *M* $Hg(OAc)_2$[a]	
0.100	2.74
0.200	2.57
0.500	2.53 ± 0.04[b]
1.00	2.63
2.00	2.79
Hg^{II} Supplied as 0.100 *M* $Hg(ClO_4)_2$[c]	
0.56	1.32[d]
1.13	1.35

[a] $[H_2O]_{analyt}$ = 0.20 *M*, $[HClO_4]_{analyt}$ = 0.50 *M*. [b] Standard deviation of five determinations. [c] $[H_2O]_{analyt}$ = 0.25 *M*; no added $HClO_4$. [d] Identical values were obtained in two determinations.

The data of Table I do show small systematic deviations from strict proportionality between benzene concentration and rate: the rate constants near the middle of the range of benzene concentrations are about 10% lower than those at either extreme. But these deviations can be understood in terms of phenomena which do not effect reaction molecularity: polymercuration at the low concentration end and a medium effect of large amounts of benzene (18 vol. % at 2.0 *M*) at the high concentration end. This medium effect, an increase in rate with decreasing polarity, is consistent with the small, negative, primary salt effect of sodium perchlorate described below.

Reaction Order in Mercuric Salt.—Observed second-order rate constants for the mercuration of benzene by mercuric acetate and by mercuric perchlorate in the presence of varying amounts of added perchloric acid are presented in Table II and are shown in Figure 1. These rate constants do change with the initial concentration of the mercuric salt, and the direction of the change is not the same for the two mercurating agents: with mercuric acetate, an increase in initial mercury(II) concentration produces a decrease in rate constant, whereas, with mercuric perchlorate, an increase in initial mercury(II) concentration results in

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(12) H. C. Brown and R. A. Wirkkala, *J. Am. Chem. Soc.*, **88**, 1447, 1453, 1456 (1966).

(13) A. J. Kresge and J. F. Brennan, *J. Org. Chem.*, **32**, 752 (1967).

(14) A. J. Kresge and H. C. Brown, *ibid.*, **32**, 756 (1967).

(15) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2300 (1955).

an increase in rate constant. These effects are pronounced at low concentrations of added perchloric acid; at higher acidities, they diminish to only a few per cent of the observed rate constants. In the case of mercuric perchlorate, the effect is still present in the absence of added perchloric acid; in the case of mercuric acetate, the data suggest that the effect disappears when no perchloric acid is added.

Table II

Effect of Mercuric Salt Concentration on the Rate of Mercuration of Benzene in Acetic Acid Solution at 25°[a]

Concn (M)		10^2k_{obsd}
$HClO_4$[b]	Hg^{II}[c]	(M^{-1} min^{-1})
	Hg^{II} Supplied as $Hg(OAc)_2$	
0.20	0.050	1.63
0.20	0.100	1.27
0.50	0.050	2.58
0.50	0.200	2.26
0.60	0.050	2.85
0.60	0.100	2.76
0.60	0.200	2.59
0.70	0.050	3.20
0.70	0.100	2.96
0.70	0.200	2.87
	Hg^{II} Supplied as $Hg(ClO_4)_2$	
0.00	0.050	0.88
0.00	0.100	1.32
0.20	0.050	2.10
0.20	0.100	2.26
0.40	0.050	2.67
0.40	0.100	2.76

[a] Initial concentration of C_6H_6 = 0.50 M; $[H_2O]_{analyt}$ = 0.25 M. [b] Analytical concentration of added perchloric acid. [c] Initial concentration.

Significant deviations from bimolecular behavior within a kinetic run were observed in the experiments of Table II performed at lower acidities. These deviations were in the same direction, increasing second-order rate constant with increasing reaction time, for mercuration by both salts.

Effect of Perchloric Acid.—The data of Figure 1 show that small quantities of added perchloric acid accelerate the rate of aromatic mercuration strongly, but this acceleration is diminished somewhat at higher acidities. In the region of weaker catalysis, the catalytic effect is independent of initial mercuric salt concentration: the upper portions of all the lines of Figure 1 have the same slope. In the region of strong catalysis, however, the catalytic effect does depend on the initial concentration of mercuric salt, being greater at lower concentrations of mercury(II); this is true for both salts.

Effect of Sodium Perchlorate.—Observed second-order rate constants for the mercuration of benzene by mercuric perchlorate in the presence of sodium perchlorate in acetic acid containing a small amount of water are presented in Table III. These data show that the rate of mercuration is not greatly affected by this neutral salt under these conditions. What small effect there is amounts to a mild retardation which might be ascribed to a weak primary salt effect.

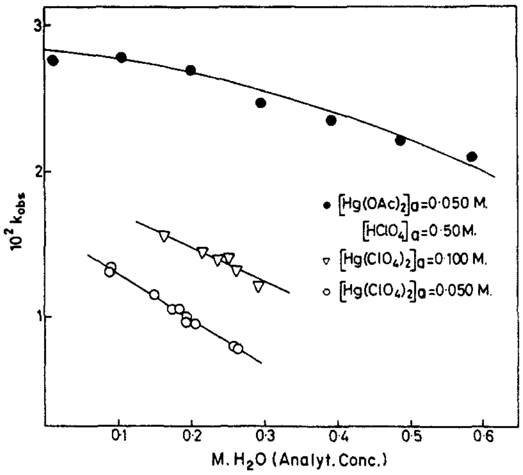

Figure 2.—Relationship between observed rate constants for the mercuration of benzene in acetic acid solution at 25° and the analytical concentration of water.

Table III

Effect of Sodium Perchlorate on the Rate of Mercuration of Benzene in Acetic Acid Solution at 25°[a]

Concn (M) of $NaClO_4$	10^2k_{obsd} (M^{-1} min^{-1})
0.000	1.00 ± 0.01[b]
0.100	0.98
0.200	0.94

[a] Initial concentration of benzene = 0.56 M; $[H_2O]_{analyt}$ = 0.20 M; Hg^{II} supplied as 0.050 M $Hg(ClO_4)_2$. [b] Standard deviation of two determinations.

It should be pointed out that in two previous studies sodium perchlorate was found to increase the rate of aromatic mercuration in acetic acid solution. In one of these,[10] a moderate acceleration was found for mercuration by mercuric perchlorate in 97% acetic acid; in the other,[5] a somewhat stronger acceleration was found for mercuration by mercuric acetate in glacial acetic acid. It will be shown below that neither of these effects is inconsistent with the data of Table III.

Effect of Water.—Observed second-order rate constants for the mercuration of benzene in the presence of varying analytical concentrations of water are shown in Figure 2. Water is seen to retard the reaction, and this retardation is greater for mercuration by 0.100 and 0.050 M mercuric perchlorate in the absence of added perchloric acid than for mercuration by 0.050 M mercuric acetate in the presence of 0.50 M added acid. In the case of mercuric perchlorate, a given amount of water is more effective at the lower concentration of the mercuric salt.

Discussion

The mercuration of benzene in acetic acid solution is first order in aromatic substrate and approximately first order in mercuric salt. The reaction is catalyzed by perchloric acid and retarded by water, and mercuric perchlorate is generally a more rapid mercurating agent than mercuric acetate. Sodium perchlorate has an effect which depends on the form in which the mercurating agent is supplied and on the water content of the solvent. Observed rate constants for perchloric acid catalyzed mercuration by both mercuric salts, as well as the rate constants of uncatalyzed mercuration by mercuric perchlorate, are sensitive to changes in the initial mercuric salt concentration. These are the major facts which must fit any mechanism for this reaction.

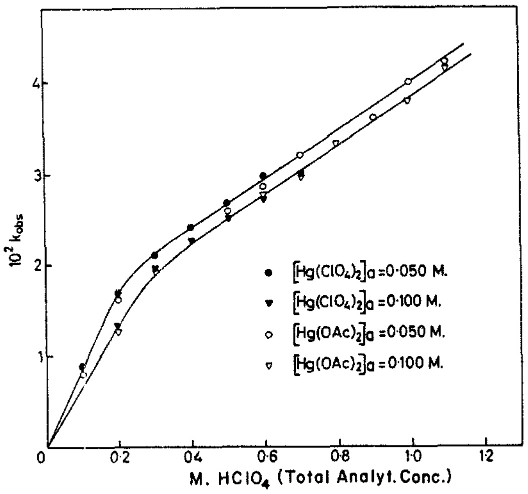

Figure 3.—Relationship between observed rate constants for the mercuration of benzene in acetic acid solution at 25° and total analytical concentration of perchloric acid at an analytical water concentration of 0.25 *M*.

Comparison of Mercuric Acetate and Mercuric Perchlorate as Mercurating Agents.

—Mercuration by mercuric perchlorate appears to be a reaction which, in its general features, is different from mercuration by mercuric acetate. These two reactions, however, can be shown to be fundamentally the same by considering the species present in an acetic acid solution of mercuric perchlorate.

Mercuric perchlorate is an ionic salt.[16] In acetic acid solution, it will be partially solvolyzed to perchloric acid and the weak electrolyte mercuric acetate.[17,18]

$$Hg^{2+}(ClO_4^-)_2 + 2HOAc \rightleftarrows Hg(OAc)_2 + 2HClO_4 \quad (1)$$

Evidence for this reaction comes from an indicator study of the acidity of acetic acid solutions of mercuric acetate and perchloric acid.[19] Mercuric acetate was found to be weakly basic in this solvent; it combines with perchloric acid in a reaction which is the reverse of that presented in eq 1. The reaction occurs in states, and the equilibrium constant for the first stage, formation of acetatomercury(II) perchlorate ion pairs from perchloric acid and mercuric acetate, is 70.[20]

$$HClO_4 + Hg(OAc)_2 \rightleftarrows HgOAc^+ClO_4^- + HOAc \quad (2)$$

$$K_f^{HgOAc^+ClO_4^-} = \frac{[HgOAc^+ClO_4^-]}{C_{HClO_4}[Hg(OAc)_2]} = 70 \quad (3)$$

This means that an acetic acid solution of mercuric perchlorate at an analytical concentration of 0.10 *M* does in fact contain very little of the species mercuric perchlorate: about 90% of the mercury(II) is present in the form of acetatomercury(II) perchlorate ion pairs and 10% as mercuric acetate.

This solution is also 0.11 *M* in free perchloric acid. Perchloric acid has a catalytic effect on the mercuration of benzene, and rates of mercuration by mercuric perchlorate will therefore be greater than rates of mercuration by an equivalent amount of mercuric acetate. Moreover, the amount of perchloric acid produced by solvolysis will depend on the quantity of mercuric perchlorate supplied, and observed rate constants for mercuration by mercuric perchlorate will increase with increasing initial concentration of mercury(II). This, of course, will not be the case for mercuration by mercuric acetate where solvolysis is not possible, and, with this source of mercury(II), observed rate constants will be independent of initial mercuric salt concentration.

The equilibrium reaction of eq 1 implies that an acetic acid solution prepared from a given amount of mercuric perchlorate is identical with a solution prepared from an equivalent amount of mercuric acetate plus a twice molar amount of perchloric acid. These solutions should therefore give the same rates of mercuration. Figure 3 shows that this is indeed the case, and this demonstrates that there is no fundamental difference between mercuration by these two mercuric salts.

Catalysis by Perchloric Acid and Retardation by Water.

—The reaction between mercuric acetate and perchloric acid (eq 2) provides a ready explanation for the catalytic effect of perchloric acid on aromatic mercuration in acetic acid solution. Perchloric acid converts neutral mercury(II) into a positively charged form, and positively charged electrophiles are generally more effective in aromatic substitution than the corresponding neutral species.[21]

Water is known to be weakly basic in acetic acid solution;[22] the equilibrium constant for the formation of hydronium perchlorate ion pairs from water and perchloric acid is 34.[22b] Since this is only a factor of

$$H_2O + HClO_4 \rightleftarrows H_3O^+ClO^{4-} \quad (4)$$

$$K_f^{H_3O^+ClO_4^-} = \frac{[H_3O^+ClO_4^-]}{C_{HClO_4}[H_2O]} = 34 \quad (5)$$

2 smaller than the formation constant for positively charged mercury(II) (eq 3), water can compete successfully with uncharged mercury(II) for the available perchloric acid and can therefore be expected to lower the rate of mercuration.

At the concentrations of mercury(II) and water used in this study, the positions of the relevant equilibria are such that, at an analytical perchloric acid concentration of 0.1 *M*, about half of the mercury(II) exists in

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[16] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 485; N. V. Sidgewick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p 325.

[17] Perchloric acid exists half as the un-ionized acid and half as acetoxonium perchlorate ion pairs in acetic acid solution; only a very small fraction of the ion pairs is dissociated into free ions.[18a] In the discussion which follows, the symbol $HClO_4$ will be used to designate free perchloric acid (that not combined with any base) in all its forms: un-ionized, ionized, and dissociated; C_{HClO_4} will mean the total concentration of free perchloric acid.

[18] S. Bruckenstein in "Treatise on Analytical Chemistry," Vol. I, Part I, I. M. Kolthoff and P. J. Elving, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p 499, *et seq.*; (b) p 514; (c) p 492; (d) p 504; (e) p 501; (f) p 502.

[19] H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **77**, 939 (1955).

[20] It has been observed[10] that, in potentiometric titrations of perchloric acid with acetate salts in acetic acid solution, the sharp change in potential which occurs at the equivalence point when potassium and barium acetates are the titrants is absent in the case of mercuric acetate. This is not inconsistent with the value of 70 for the equilibrium constant of eq 3, for this equation describes an ion-pair-formation constant and potentiometric titrations are based on the activity of free ions. It can be shown by standard methods[18a] that, using 70 for the constant of eq 3 and assuming a reasonable value (5×10^{-6}) for the dissociation constant of acetatomercury(II) perchlorate ion pairs, the titration with mercuric acetate should produce a potential change of only 30 mv in completely anhydrous acetic acid and 5 mv in a solvent containing 3% water (the solvent actually used). A similar titration using the much stronger base potassium acetate would produce a potential change of several tenths of a volt in either solvent.

[21] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959.

[22] (a) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5198 (1951); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956).

the positively charged form; at an analytical perchloric acid concentration of 0.5 M, however, nearly all of the mercury is positively charged and the catalytic effect by this mechanism is saturated. Water, therefore, should have a stronger anticatalytic effect in the former situation than in the latter, and this is what is observed (Figure 2).

Water also influences the rate of aromatic mercuration in wholly aqueous solutions; here the rate of reaction increases markedly as ionic solutes, which decrease the activity of water, are added.[10,11] This has been attributed[11] to desolvation and concomitant increase in the electrophilicity of the mercuric ion, the only electrophile effective under these conditions. In the case of mercuration by acetatomercury(II) perchlorate ion pairs in acetic acid solutions containing water only as a low concentration solute, such an effect, in addition to the influence of water on the equilibrium of eq 4, might be expected to be absent; this can be demonstrated to be the case by comparing rates of mercuration in acetic acid solutions of different water concentration but similar acidity. A rate constant of $1.07 \times 10^{-2}\ M^{-1}\ \text{min}^{-1}$ is reported[10] for the mercuration of benzene at 25° in the presence of 0.60 M perchloric acid (analytical concentration) in 97% acetic acid; under these conditions, 49.6% of the mercury(II) is converted to acetatomercury(II) perchlorate ion pairs, and the concentration of free water is 1.13 M (calculated on the basis of the equilibria of eq 3 and 5). This rate constant is *greater* than that measured in this study, $0.85 \times 10^{-2}\ M^{-1}\ \text{min}^{-1}$, for mercuration in 99.5% acetic acid at an acidity ($[\text{HClO}_4]_{\text{analyt}} = 0.10$ M) sufficient to effect a similar conversion of mercury(II) to acetatomercury(II) perchlorate ion pairs (44.7%) in spite of the fact that the concentration of free water is in this case much lower (0.18 M). When these two observed rate constants are compared at the same extent of conversion of mercury(II) to acetatomercury(II) perchlorate ion pairs, they are found to agree within about 10%; this leaves little room for a solvation effect by water, and the difference is, in any case, in the wrong direction.

Effects of Sodium Perchlorate.—Sodium perchlorate is solvolyzed very slightly in acetic acid solution to give sodium acetate and perchloric acid.[18b]

$$\text{Na}^+\text{ClO}_4^- + \text{HOAc} \rightleftharpoons \text{Na}^+\text{OAc}^- + \text{HClO}_4 \qquad (6)$$

Although the amount of perchloric acid so produced is very small (*ca.* 6×10^{-5} M by 0.1 M salt), it is sufficient, in the absence of any additional perchloric acid, to convert enough mercuric acetate to acetatomercury(II) perchlorate ion pairs to produce a significant increase in the rate of mercuration. Both the direction and the magnitude of the effect of sodium perchlorate on the rate of mercuration of toluene in glacial acetic acid by mercuric acetate in the absence of added perchloric acid[5] can be accounted for in this way. In solutions containing analytical concentrations of perchloric acid of the order of a few tenths molar, however, the solvolysis of sodium perchlorate cannot change the acidity to any significant extent. Consequently, the rate of mercuration by 0.050 M mercuric perchlorate (equivalent to $[\text{HClO}_4]_{\text{analyt}} = 0.100$ M) is not affected by adding sodium perchlorate (Table III).

Sodium perchlorate, however, does have a mild accelerative effect on the rate of aromatic mercuration by 0.100 M mercuric perchlorate in an acetic acid solvent containing 3% water.[10] In this medium, the mole fraction of water is nearly 0.1, and water can be expected to solvate a considerable portion of any dissolved ionic salt. Dissolved salts will therefore lower the activity of free water in this medium, and this will shift the equilibrium formation of hydronium perchlorate ion pairs from water and perchloric acid (eq 4) back to the perchloric acid side. Thus, ionic salts will have the secondary effect of increasing the acidity of the solution; this will accelerate the rate of mercuration.

Mercuration by the Mercuric Ion.—Many features of the mercuration of benzene in acetic acid solution in the presence of perchloric acid can be accounted for by a bimolecular reaction between the aromatic substrate and acetatomercury(II) perchlorate ion pairs. Mercury(II), however, may be present in these solutions in other forms, specifically as mercuric perchlorate ion triplets, and it is of some significance, therefore, to inquire whether all of the catalyzed mercuration reaction does in fact occur through direct substitution by acetatomercury(II) perchlorate ion pairs.

Since the equilibria which govern the formation of acetatomercury(II) perchlorate ion pairs have been identified and the relevant equilibrium constants are known, this question may be answered by calculating the concentrations of acetatomercury(II) perchlorate ion pairs in each of the mercurating solutions and comparing these concentrations with the observed rate constants. If no other mercurating agent plays a significant role in the substitution reaction, observed rate constants will increase in direct proportion to the fraction of mercury(II) present as acetatomercury(II) perchlorate ion pairs, and the quantity $k_{\text{obsd}}[\text{Hg}^{\text{II}}]/[\text{HgOAc}^+\text{ClO}_4^-]$ will be constant. The data of Table IV show that this is not the case: $k_{\text{obsd}}[\text{Hg}^{\text{II}}]/[\text{HgOAc}^+\text{ClO}_4^-]$ increases by more than a factor of 2 over the range of acidity studied.

The rate law for mercuration by mercuric perchlorate ion triplets in addition to acetatomercury(II) perchlorate ion pairs by two parallel reactions is

$$v = k^+[\text{HgOAc}^+\text{ClO}_4^-][\text{C}_6\text{H}_6] + k^{2+}[\text{Hg}^{2+}(\text{ClO}_4^-)_2][\text{C}_6\text{H}_6] \qquad (7)$$

On this basis, observed rate constants calculated from decreasing concentrations of benzene and total mercury(II) are sums of two terms.

$$\frac{v}{[\text{C}_6\text{H}_6][\text{Hg}^{\text{II}}]} = k_{\text{obsd}} = \frac{k^+[\text{HgOAc}^+\text{ClO}_4^-]}{[\text{Hg}^{\text{II}}]} + \frac{k^{2+}[\text{Hg}^{2+}(\text{ClO}_4^-)_2]}{[\text{Hg}^{\text{II}}]} \qquad (8)$$

Mercuric perchlorate ion triplets can be expected to be formed by further protonation of acetatomercury(II) ion pairs in a reaction whose equilibrium constant is K^{2+}.

$$\text{HgOAc}^+\text{ClO}_4^- + \text{HClO}_4 \rightleftharpoons \text{Hg}^{2+}(\text{ClO}_4^-)_2 + \text{HOAc} \qquad (9)$$

$$K^{2+} = \frac{[\text{Hg}^{2+}(\text{ClO}_4^-)]}{[\text{HgOAc}^+\text{ClO}_4^-]C_{\text{HClO}_4}} \qquad (10)$$

It then follows that this situation predicts a linear relationship between $k_{\text{obsd}}[\text{Hg}^{\text{II}}]/[\text{HgOAc}^+\text{ClO}_4^-]$ and C_{HClO_4}.

$$\frac{k_{\text{obsd}}[\text{Hg}^{\text{II}}]}{[\text{HgOAc}^+\text{ClO}_4^-]} = k^+ + k^{2+}K^{2+}C_{\text{HClO}_4} \qquad (11)$$

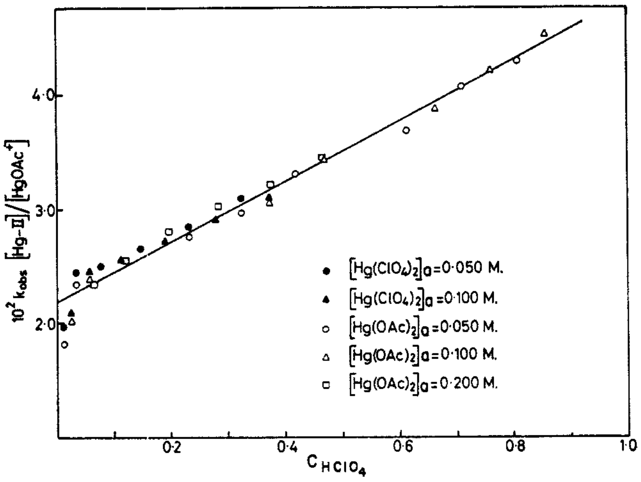

Figure 4. Plot of mercuration data according to eq 11.

TABLE IV

ANALYSIS OF RATES OF MERCURATION OF BENZENE IN ACETIC ACID SOLUTION AT 25° IN TERMS OF THE COMPOSITION OF THE SOLUTIONS[a]

Concn (M)			% Hg^{II} present as HgOAc$^+$-ClO$_4^-$ [b]	$10^2 k_{obsd}$ × [Hg^{II}]/[HgOAc$^+$-ClO$_4^-$]
[HClO$_4$]$_{analyt}$	[Hg^{II}]$_{analyt}$	C_{HClO_4} [b]		
0.100	0.050	0.011	44.7	1.89
0.200	0.050	0.033	69.9	2.38
0.200	0.100	0.024	63.1	2.05
0.400	0.050	0.146	91.2	2.64
0.400	0.100	0.112	88.8	2.55
0.400	0.200	0.064	82.0	2.33
0.600	0.050	0.323	95.8	3.03
0.600	0.100	0.278	95.2	2.90
0.600	0.200	0.196	93.3	2.78
0.800	0.100	0.467	97.1	3.44
0.800	0.200	0.376	96.4	3.21
1.00	0.050	0.710	98.1	4.07
1.00	0.100	0.662	97.9	3.88
1.20	0.100	0.859	98.4	4.53

[a] $[H_2O]_{analyt} = 0.25\ M$. [b] Calculated using the equilibrium expressions of eq 3 and 5 plus the following stoichiometric relationships.

$$[HClO_4]_{analyt} = C_{HClO_4} + [HgOAc^+ClO_4^-] + [H_3O^+ClO_4^-]$$

$$[Hg^{II}]_{analyt} = [Hg(OAc)_2] + [HgOAc^+ClO^{4-}]$$

$$[H_2O]_{analyt} = [H_2O] + [H_3O^+ClO_4^-]$$

This set of five equations was reduced to a single cubic expression in one unknown whose roots for each condition of analytical concentrations were obtained by electronic computation (IBM 650).

Figure 4 shows that the mercuration data collected in this study do obey eq 11 quite well.[23] The intercept of the best line through the points provides a value of $2.2 \times 10^{-2}\ M^{-1}\ \text{min}^{-1}$ for k^+, the bimolecular rate constant for the mercuration of benzene by acetatomercury(II) perchlorate ion pairs at 25°. The slope of this line, $2.6 \times 10^{-2}\ M^{-2}\ \text{min}^{-1}$, is the product of K^{2+} and k^{2+}, the latter being the rate constant for the reaction of benzene with mercuric perchlorate ion triplets. Since K^{2+} is not known, k^{2+} cannot be evaluated. It seems likely, however, that K^{2+} is small;[18c] this would give k^{2+} a large value consistent with the fact that it represents mercuration by a dipositive and therefore highly electrophilic species.

Effects of Changing Mercuric Salt Concentration.—In this study, deviations from second-order kinetics were observed as the mercuration reaction proceeded and changes in the initial concentration of mercurating agent were found to produce changes in observed bimolecular rate constants. These effects are of course related and are a direct consequence of a mercuration reaction which proceeds through substitution by both acetatomercury(II) perchlorate ion pairs and mercury perchlorate ion triplets.

At low acidities, the conversion of mercury(II) to acetatomercury(II) perchlorate ion pairs is not complete. When mercury(II) and perchloric acid are supplied in comparable amounts, as was the case here, a change in the concentration of either one of these substances will alter the fraction of mercury(II) which is converted to a positively charged form. Specifically, a decrease in the concentration on mercury(II) at constant analytical perchloric acid concentration will decrease the concentration of both un-ionized mercuric acetate and acetatomercury(II) perchlorate ion pairs. But the decrease in the concentration of the latter will free some perchloric acid, and this will increase the acidity of the solution and have the secondary effect of raising the fraction of mercury(II) which is positively charged. This will appear as a positive deviation from second-order kinetics (increasing rate constant) for mercuration by both mercuric acetate and mercuric perchlorate. It will also appear as an increase in observed rate constant with decreasing initial concentration of mercurating agent at a constant amount of *added* perchloric acid for mercuration by mercuric acetate but not for mercuration by mercuric perchlorate, for, in the latter case, a decrease in mercuric salt concentration is necessarily accompanied by a decrease in analytical perchloric acid concentration as well. This decrease in analytical perchloric acid concentration with decreasing initial concentration of mercuric perchlorate will be particularly marked because solvolysis produces 2 equiv of acid, and a decrease in observed rate constant will result. The quantitative effects of these changes can be seen by comparing suitable entries of Table IV.

At higher acidities, essentially all of the mercury(II) is converted to a singly positively charged form, and moderate changes in the mercury(II) or perchloric acid concentrations cannot appreciably alter the extent of this conversion and its contribution to the observed rate constant, but here, however, mercuration by doubly charged mercury(II) is important, and its contribution to the observed rate constant depends on the concentration of free perchloric acid (eq 11). When the mercurating agent is supplied as mercuric acetate, 1 full equiv of perchloric acid is used up in forming acetatomercury(II) perchlorate ion pairs. The concentration of free perchloric acid at a constant amount of *added* acid will therefore increase with decreasing initial mercury(II) concentration, and observed rate constants will increase accordingly. When the mercurating agent is supplied as mercuric perchlorate, on the other hand, 1 equiv of perchloric acid is liberated by solvolysis of the mercuric salt to acetatomercury(II) perchlorate ion pairs. The concentration

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[23] The deviations seen in Figure 4 at low acidities seem to be real. In this region, however, the calculated concentrations of HgOAc$^+$ClO$_4^-$ and HClO$_4$ are unusually sensitive to the values used for the equilibrium constants of eq 3 and 5; one or both of the published values could have been slightly in error.

of free perchloric acid at a constant amount of *added* acid will therefore decrease with decreasing initial mercury(II) concentration, and observed rate constants will decrease accordingly. Since the conversion of singly to doubly charged mercury(II) is presumably low at the acidities employed here, no perchloric acid will be consumed in this conversion, the fraction of mercury(II) present as mercuric perchlorate ion triplets will therefore not change during a kinetic experiment, and deviations from second-order kinetics within a run will not be observed. The quantitative effects of these changes can again be seen in Table IV.

Mercuration by Un-ionized Mercuric Acetate.—Uncatalyzed mercuration by mercuric acetate in acetic acid solution may occur through direct substitution by un-ionized mercuric acetate. Alternatively, it could take place through substitution by positively charged mercury(II) expected to be present in these solutions as acetatomercury(II) acetate ion pairs formed in the ionization of mercuric acetate. If the concentration of

$$\mathrm{Hg(OAc)_2} \rightleftarrows \mathrm{HgOAc^+OAc^-} \qquad (12)$$

acetatomercury(II) acetate ion pairs in an acetic acid solution of mercuric acetate were known, a choice of these two reaction mechanisms might be possible.

The equilibrium constant for the reaction of eq 12, $K_i^{\mathrm{Hg(OAc)_2}}$, has not been measured, but it can be estimated with the aid of a reasonable assumption concerning ion-pair dissociation constants. It is generally true of acetic acid solutions that the formation constant of the perchlorate salt of any base, $K_f^{\mathrm{BHClO_4}}$, is a function of K_s, the autoprotolysis constant of acetic acid, and $K_{\mathrm{HClO_4}}$, K_{B}, and $K_{\mathrm{BHClO_4}}$, the over-all dissociation constants of perchloric acid, the base, and the base

$$K_f^{\mathrm{BHClO_4}} = \frac{K_{\mathrm{HClO_4}}K_{\mathrm{B}}}{K_sK_{\mathrm{BHClO_4}}} \qquad (13)$$

perchlorate.[18d] For the case of mercuric acetate, this relationship gives

$$K_f^{\mathrm{HgOAc^+ClO_4^-}} = \frac{K_{\mathrm{HClO_4}}K_{\mathrm{Hg(OAc)_2}}}{K_sK_{\mathrm{HgOAc^+ClO_4^-}}} \qquad (14)$$

The formation constant, $K_f^{\mathrm{HgOAc^+ClO_4^-}}$, is of course the constant defined above in eq 3 whose value is known to be 70.[19] In acetic acid solution, over-all dissociation constants of weak bases are equal to the products of their ionization and ion-pair dissociation constants,[18e] so that for mercuric acetate

$$K_{\mathrm{Hg(OAc)_2}} = K_i^{\mathrm{Hg(OAc)_2}}K_d^{\mathrm{HgOAc^+OAc^-}} \qquad (15)$$

Over-all dissociation constants of strong electrolytes, on the other hand, are equal to their dissociation constants alone,[18e] so that for acetatomercury(II) perchlorate

$$K_{\mathrm{HgOAc^+ClO_4^-}} = K_d^{\mathrm{HgOAc^+ClO_4^-}} \qquad (16)$$

Combining eq 14, 15, and 16 gives

$$K_f^{\mathrm{HgOAc^+ClO_4^-}} = \frac{K_{\mathrm{HClO_4}}K_i^{\mathrm{Hg(OAc)_2}}K_d^{\mathrm{HgOAc^+OAc^-}}}{K_sK_d^{\mathrm{HgOAc^+ClO_4^-}}} \qquad (17)$$

Of the quantities in eq 17, $K_f^{\mathrm{HgOAc^+ClO_4^-}}$, $K_{\mathrm{HClO_4}}$, and K_s are known;[18f, 19] $K_i^{\mathrm{Hg(OAc)_2}}$ is the desired equilibrium constant for eq 12, and $K_d^{\mathrm{HgOAc^+OAc^-}}$ and $K_d^{\mathrm{HgOAc^+ClO_4^-}}$ are not known. The latter two constants, however, can be expected to be approximately equal, certainly within an order of magnitude, for they refer to dissociation of ion pairs with the same cation and with anions of the same charge and similar size: ion-pair dissociation constants of salts of the same charge type in a given solvent are known to depend primarily on ion size.[24] This permits $K_i^{\mathrm{Hg(OAc)_2}}$ to be evaluated as 2×10^{-8}.

It is not unreasonable to assume that the rate constant for the reaction of benzene with acetatomercury(II) acetate ion pairs is of the same magnitude as that for the reaction of benzene with acetatomercury(II) perchlorate ion pairs (k^+ of eq 11 evaluated as $2.2 \times 10^{-2}\ M^{-1}\ \mathrm{min}^{-1}$). The observed rate constant for the uncatalyzed mercuration of benzene through substitution by acetatomercury(II) acetate ion pairs can therefore be estimated as $(2.2 \times 10^{-2})(2 \times 10^{-8}) = 4 \times 10^{-10}\ M^{-1}\ \mathrm{min}^{-1}$. Since this is several orders of magnitude less than the measured[5,10] value, $2.5 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$, it can be safely concluded that uncatalyzed mercuration does not occur through positively charged mercury(II). The mercurating agent responsible for this reaction is therefore un-ionized mercuric acetate.

Conclusions

Aromatic mercuration in acetic acid solution containing perchloric acid may occur by reaction of the aromatic substrate with either one of two electrophiles, acetatomercury(II) perchlorate ion pairs or mercuric perchlorate ion triplets; there is, in addition, an uncatalyzed reaction in which the electrophile is un-ionized mercuric acetate. The complete rate law is

$$v = k^0[\mathrm{Hg(OAc)_2}][\mathrm{HAr}] + k^+[\mathrm{HgOAc^+ClO_4^-}][\mathrm{HAr}] + k^{2+}[\mathrm{Hg^{2+}(ClO_4^-)_2}][\mathrm{HAr}] \qquad (18)$$

For the mercuration of benzene at 25°, the values of k^0 and k^+ are $2.5 \times 10^{-6}\ M^{-1}\ \mathrm{min}^{-1}$ and $2.2 \times 10^{-2}\ M^{-1}\ \mathrm{min}^{-1}$, respectively. The fact that perchloric acid catalyzed aromatic mercuration involves reaction of the aromatic substrate with two different electrophiles of different reactivity suggests that this reaction is not suitable for the original objective of this study, the determination of partial rate factors for aromatics containing deactivating substituents. This matter is explored in greater detail in the third paper of this series.[14]

Experimental Section

A. **Materials. Benzene.**—Thiophene-free benzene was dried over calcium hydride (Metal Hydrides, commercial grade) and was then fractionally distilled through a 50-plate Fenske column. A center cut of constant refractive index ($n^{20}\mathrm{D}$ 1.5003) was used.

Acetic Acid.—Glacial acetic acid (B and A, reagent grade) was analyzed for water by Karl Fischer titration, the necessary quantity of purified acetic anhydride[25] was added, and the solution was heated under reflux for 1 day. The material was then distilled rapidly. Karl Fischer analysis of the distillate usually showed a water content of less than 0.005 *M*.

Mercuric Acetate.—Mercuric acetate (B and A, reagent grade) was recrystallized once from acetic acid and once from anhydrous methanol. The crystals were dried *in vacuo* over phosphorus pentoxide. *Anal.* Calcd: $\mathrm{Hg^{II}}$, 62.946. Found: $\mathrm{Hg^{II}}$, 62.71, 62.86, 62.86.

Mercuric Perchlorate Hexahydrate.—Two hundred seventy grams (1.25 moles) of yellow mercuric oxide (J. T. Baker,

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[24] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. (Publishers) Ltd., London, 1959, p 392, *et seq.*

[25] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p 380.

U.S.P. grade) was added to a solution of 365 g (2.60 moles) of 71% perchloric acid (J. T. Baker, Analyzed reagent grade) in 1.0 l. of water. The oxide dissolved quickly as the mixture was swirled. The slightly warm reaction mixture was then filtered through a sintered-glass funnel, and the filtrate was concentrated to 250 ml by gentle warming on a water bath (bath temperature kept below 60°) and application of vacuum. The residue was permitted to cool to room temperature whereupon it solidified almost completely to a crystalline mass. The crystals were separated from the adhering mother liquor by filtration on a sintered-glass funnel; approximately 500 g of material was obtained in this way. This was recrystallized from about 50 ml water, and the product, colorless, regular hexagonal rods, was dried by centrifuging (weight, 300 g). *Anal.* Calcd for $Hg(ClO_4)_2 \cdot 6H_2O$: Hg^{II}, 39.52; ClO_4^-, 39.18; H_2O, 21.30. Found: Hg^{II}, 39.78; ClO_4^-, 39.27; H_2O, 21.72.

B. Analytical Methods. **Water Analysis.**—The Karl Fischer method using a methanol-based reagent was employed.[26] Titrations were done to a visual end point in 250-ml, glass-stoppered erlenmeyer flasks. No special precautions were taken to exclude atmospheric moisture during a titration since it was found that no appreciable error was introduced from this source during a reasonably rapid determination. Empty stoppered flasks did pick up moisture when allowed to stand in a normal laboratory atmosphere for 1 day or longer, and titration flasks were therefore dried in an oven at 110° just before use. The reagent was standardized daily against sodium acetate trihydrate (J. T. Baker, Analyzed reagent grade) which was stored in a hygrostat whose humidity was controlled by a saturated solution of potassium carbonate.[27]

It was found that acetic acid solutions of water, especially those containing dissolved acids or salts, gave high results and fading end points when analyzed with methanol-based Karl Fischer reagent. It is likely that this was the result of a water-producing esterification reaction between acetic acid and methanol; the error was corrected by dissolving these acetic acid solutions in at least two volumes of anhydrous pyridine and cooling the resultant solutions in ice just before titration.

Perchloric Acid Analysis.—Acetic acid solutions of perchloric acid were analyzed for strong acid by nonaqueous titration with sodium acetate in anhydrous acetic acid.[28] End points were determined visually using bromothymol blue indicator.

Mercury Analysis.—Mercury analyses were conducted by titration with standard aqueous potassium thiocyanate (J. T. Baker, Analyzed reagent grade) solution using ferric alum as an indicator.[29]

C. Kinetic Method.—Reaction mixtures were prepared by combining appropriate quantities of three different acetic acid solutions, one containing mercury(II) either as mercuric acetate or mercuric perchlorate, one containing perchloric acid, and the third containing benzene; all three solutions were allowed to equilibrate with the thermostated water bath (25.00 ± 0.02°) before they were mixed. Reactions were conducted in glass-stoppered flasks; 10-ml samples were removed at appropriate intervals of time and were quenched in equal volumes of water. Two to five milliliters of indicator solution (the quantity was adjusted to the mercury content of the sample) was added to the quenched samples, and the mixture was cooled to 10° in ice water. (Sharper end points were observed when titrations were conducted below 15°.) Titrations were carried out by adding 0.1 *N* thiocyanate solution as the sample was swirled in ice water; the first faint appearance of color was taken as the end point and blank corrections were found to be unneccessary. It was found that the color change could be discerned more clearly by playing a strong tungsten light at an oblique angle to the surface of the solution being titrated. Washings were kept to a minimum in order to avoid unnecessary dilution.

Registry No.—Perchloric acid, 7616-81-1; benzene, 71-43-2; sodium perchlorate, 7601-89-0; mercuric acetate, 1600-27-7; mercuric perchlorate, 7616-83-3.

Acknowledgment.—The authors wish to thank Mr. George Barry who performed the numerical calculations on the IBM 650 computer, Mr. Gerald Koeppl for clarifying discussions, and the Chemistry Department of Bedford College, London, and the Physical Chemistry Laboratory, Oxford University, for their hospitality while this manuscript was being written during the tenure of a National Science Foundation Senior Postdoctoral Fellowship by A. J. K.

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Perchloric Acid Catalyzed Aromatic Mercuration in Acetic Acid Solution. II. The Substitution Process[1,2]

A. J. KRESGE AND J. F. BRENNAN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

Received November 14, 1966

The mercuration of benzene by acetatomercury(II) perchlorate ion pairs in acetic acid solution shows a large primary hydrogen isotope effect and the reaction is first order in the excess reactant. This indicates that aromatic substrate and electrophile combine rapidly and reversibly to form a σ-complex intermediate in low concentration, and that proton transfer from this intermediate is rate determining. The acetate group originally present in the electrophile is lost during the reaction to give phenylatomercury(II) perchlorate ion pairs as the final product. Acetate group loss may be concerted with proton transfer, the acetate group serving as the proton transfer agent in a cyclic transition state, or proton transfer may occur externally to a solvent molecule.

It is usually convenient to divide an electrophilic aromatic substitution reaction into two parts: generation of the electrophilic reagent and reaction of the electrophile with the aromatic substrate. In the first paper of this series,[3] we showed that mercuric acetate is the electrophilic reagent for uncatalyzed aromatic mercuration in acetic acid solution and that acetatomercury(II) perchlorate ion pairs and mercuric perchlorate ion triplets are the electrophiles in the perchloric acid catalyzed reaction. In this paper, we shall discuss the details of the reaction of these mercurating

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(1) Based in part upon a thesis submitted by J. F. Brennan to the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) This investigation was supported by Public Health Service Research Grant GM 09369-03 from the National Institute of General Medical Sciences.

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