perature. On working up in the usual way 44.7 g. (98%) of *n*-butyl methanesulfonate was recovered.

Repetition of this experiment using ethyl benzenesulfonate and stirring with silver nitrite for 20 hours at 0° and 72 hours at room temperature resulted in 95% recovery of the ester. Again, with ethyl *p*-toluenesulfonate in ether solution, after stirring with silver nitrite for 10 hours at 0° and 112 hours at room temperature, a 94% recovery of the ester was obtained.[57]

It should be noted that the above reaction times are much in excess of the time needed for complete reaction of primary alkyl halides.

The Solubility of Silver Nitrite in Ether.[12]—A preliminary experiment established that 50 g. of silver nitrite, shaken with 500 ml. of ether for 2 days, loses very little weight. The solvent contained no detectable solid material but gave an oil as main residue. Under identical conditions silver nitrite from another batch lost 0.14 g. The solvent left 0.13 g. of residue which was separated with ether into 0.04 g. of oil and 0.09 g. of colorless solid. The solid (0.0930 g.) was dissolved in water and made up to 50 ml. A portion of this solution failed to give any precipitate with 1:5 hydrochloric acid.

LAFAYETTE, INDIANA

---

[57] Our thanks are due Miss Mary E. Chalmers for this experiment.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

Aromatic Substitution. II. The Acid Cleavage of Diphenylmercury[1]

BY FREDERICK KAUFMAN[2] AND ALSOPH H. CORWIN

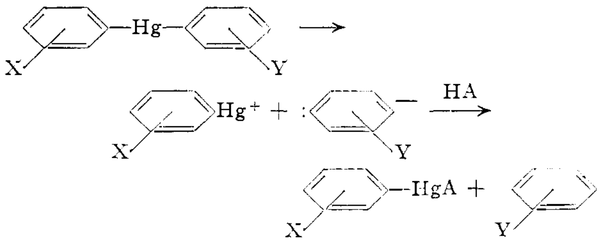
RECEIVED MAY 2, 1955

Independent and sensitive methods to determine rate constants of acid cleavage of diphenylmercury are described. The reaction with large excess of acetic and formic acid was found to be first order in diphenylmercury, the rate constant independent of initial mercurial concentration, and varying as the 3.37th power of acetic acid concentration. The reaction with dilute perchloric acid was found to be strictly second order in accordance with the proposed mechanism of acid attack on the ring carbon atom adjacent to the mercury. Protonated ethanol or dioxane give higher rates than hydronium ion. There is no salt effect for added perchlorate, but a definite rise in *k* for added chloride. Explanations for this behavior are discussed. The temperature dependence in three solvents shows large increases of the frequency factor overbalance the retarding effect of increased activation energy.

Introduction

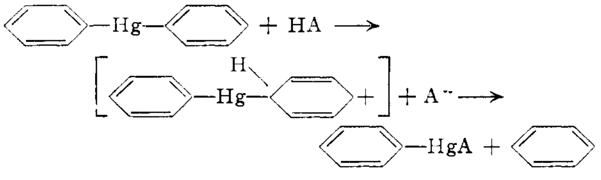
The acid cleavage of aromatic mercurials was recognized by Kharasch[3] as a valuable tool in the general problem of aromatic substitution. Unsymmetrically substituted diaryl mercury compounds were prepared, reacted with acid, and the resulting hydrocarbon and arylmercuric salt isolated. In most cases, only one of the two possible sets of products was formed, independent of the choice of acid or solvent, and this was attributed to the different electronegativities of the groups bonded to the mercury atom.

It was later shown by Corwin and Naylor[4] that Kharasch's proposed ionization mechanism



failed to account for the experimental results. The cleavage rate of diphenylmercury was found to be strongly dependent on the strength of the acid used, it was not strongly affected by increasing the dielectric constant of the solvent, and, above all, it led to an electronegativity series which was in inverted order to all findings of the English school, Hammett, and other investigators.

Corwin and Naylor studied the kinetics of the reaction of diphenylmercury with large excess of acetic and formic acid in dioxane using a tapless dilatometer. They concluded that a mechanism of acid attack leading to a protonated intermediate was in agreement with experiment. This can be formulated as



and explains the rate dependence on acid strength as well as the products obtained by Kharasch in the cleavage of unsymmetrical mercurials in terms of an electrophilic attack by acid on the ring carbon atom.

A free radical mechanism was ruled out by the absence of products such as diphenyl or phenol, and by the independence of the observed rate of peroxide concentration.

Before the general problem of aromatic substitution could be studied, as was the aim of the earlier paper, it was necessary to examine in greater detail the cleavage of diphenylmercury using more accurate methods. The alleged puzzling dependence of the rate constants on initial mercurial concentration had to be clarified, and the temperature dependence, the reaction with strong acids in dilute solution, solvent- and salt effects required further study.

Experimental

Apparatus.—Reactions were carried out in small round-bottom flasks immersed in a 15-gallon constant tempera-

---

[1] From the doctoral dissertation of Frederick Kaufman at the Johns Hopkins University. Presented at the Symposium on Aromatic Substitution of the San Francisco Meeting of the American Chemical Society, March, 1949.

[2] Ballistic Research Laboratories, Aberdeen Proving Ground, Md.

[3] (a) M. S. Kharasch, H. Pines and J. H. Levine, *J. Org. Chem.*, **3**, 347 (1938); (b) M. S. Kharasch and S. Swartz, *ibid.*, **3**, 405 (1938); (c) M. S. Kharasch, R. R. Legault and W. R. Sprowl, *ibid.*, **3**, 409 (1938).

[4] A. H. Corwin and M. A. Naylor, Jr., THIS JOURNAL, **69**, 1004 (1947).

ture water-bath equipped with an efficient stirrer and a sensitive thermoregulator. The regulator was a copper coil filled with toluene, fitted with a needle valve at one end, and expanding against a mercury column which made contact with a tungsten wire in a capillary tube.

The needle valve greatly simplified the attainment of any desired temperature. The temperature rise from the time of closing the valve to full regulation amounted to 0.2° and was quite reproducible. Temperature control of ±0.005° or better over periods of 4 to 24 hours was obtained.

Concentration changes were followed by removing small volumes at accurately known times using the simple sampler shown in Fig. 1. Its main volume, A, is sealed to two small capillaries so that inlet and outlet are at an equal level. One of the capillaries is sealed into a larger bulb, E, connected through a threeway stopcock to approximately 10 p.s.i. pressure, B, and aspirator vacuum, C.

The sample was introduced by turning the stopcock to suction and closing the open tube, D, by fingertip. Excess sample overflows and with the stopcock in the off position, the liquid does not run out at either capillary. Moreover, the bulk of the sample is still in the thermostat, immersed in the bath liquid.

The sampler was rigidly clamped to a brass block which was restrained to ride smoothly up or down on a ring stand. A pin on the brass block and two vertical grooves in the ring stand, connected at their highest point, allowed only vertical motion in two paths with a horizontal connection at the top. In this way, the full sampler was pulled up, across, and down into a flask, the stopcock turned to pressure, and the contents blown out into the flask by pressing a fingertip on sidearm D. Thus, the aliquot to be analyzed is both taken up and removed from the same orifice.

From the time the sampler leaves the thermostat until complete delivery of the sample, about 3 to 5 seconds elapse. Since this operation is quite reproducible, the reaction time can be controlled to about one second. Two such samplers were made and calibrated. Their volumes were 0.7450 ± 0.0002 and 2.303 ± 0.002 cc.

Materials.—Diphenylmercury was sublimed, then recrystallized twice from ethanol; m.p. 125.5-126°. Dioxane was purified according to the procedure recommended by Weissberger and Proskauer.[5] 90% aqueous formic acid was used without purification. Glacial acetic acid was refluxed over solid $KMnO_4$, fractionally distilled, and the middle fraction used. Dilute solutions of C.P. $HClO_4$ in water and in 95% ethanol were made up and standardized against borax prepared according to Hurley.[6]

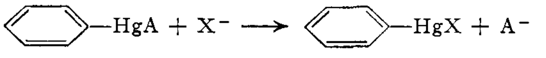
0.3 to 0.4 *M* $HClO_4$ in purified dioxane was not entirely stable, its normality increasing *ca.* 1% in 48 hours. This slow increase made the possibility of side reactions seem unlikely at perchloric acid concentrations of 0.02 to 0.03 *M* in 0.5 to 3 hours under conditions of kinetic runs.

Methods and Procedures.—Samples were removed from the reaction vessel at regular intervals using the above sampler. The reaction was stopped by dilution, excess base, temperature decrease, or combinations of the three. The extent of reaction was determined by one of two different methods.

In method A, the sample was diluted with ethanol containing excess ammonia and the absorption spectrum determined in the range of 240 to 270 mμ on a Beckman spectrophotometer model DU. Phenylmercuric salts are far more transparent than diphenylmercury in this wave length region. Beer's law is well obeyed by diphenylmercury solutions and the optical density therefore measures the extent of reaction. Rate constants were obtained from data at four different wave lengths and the average used.

In method B, the reaction mixture was added to a solution containing a known excess of X^- ($X^- = Br^-, CNS^-, I^-$) the solution filtered (unnecessary for $X^- = I^-$) and the excess X^- backtitrated with Ag^+ or Hg^{++} solution.

This method depends on the rapid reaction



where A^- is acetate, formate, perchlorate or chloride. Titrations were carried out using adsorption indicator or potentiometric analyses. A Beckman *p*H meter model G, a bright platinum and a saturated calomel electrode gave accurate electrometric analyses.

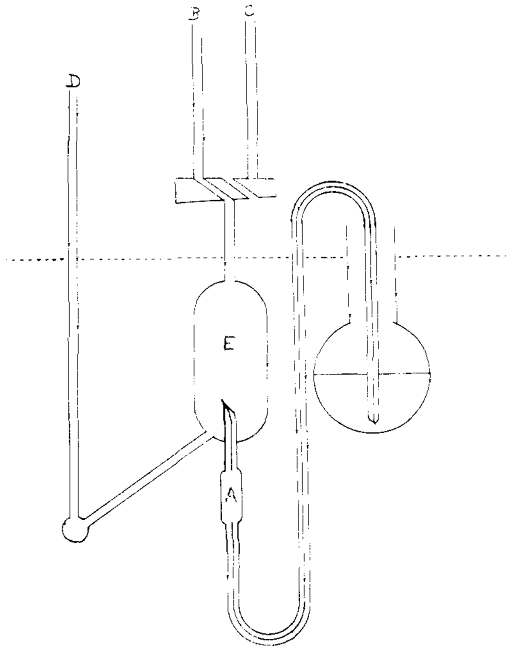


Fig. 1.—Sampler.

The general method is most accurate when $X^- = I^-$ and when mercuric chloride solution is used in the back titration. (The silver iodide titration is too slow because of strong adsorption.) The iodide solution also contained excess 0.1 *f* Na_2CO_3 to neutralize the reacting acid.

It is worth pointing out that method A essentially measures the rate of disappearance of diphenylmercury, while method B measures the rate of formation of phenylmercuric salt, the reaction product. The observed agreement of rate constants obtained by both methods is therefore significant. Under equal reaction conditions in acetic acid runs, method A gave $k = 1.97 \times 10^{-4}$ and 2.05×10^{-4} sec.$^{-1}$, while method B gave 2.00×10^{-4} sec.$^{-1}$.

In all cases, the reaction was found to be quite clean and free of side reactions. While points covering the first 50 to 55% of reaction were usually used, frequent checks showed that no further change of physical properties could be observed after the time necessary for virtual completion of the reaction. Moreover, rate constants were calculated from points covering only the last half of reaction and agreed well with those obtained for the first half. Example, expt. 8: 0 to 50% reaction, $k = 2.05 \times 10^{-4}$ sec.$^{-1}$; 55 to 90% reaction, $k = 2.02 \times 10^{-4}$ sec.$^{-1}$.

Several first- and second-order rate runs are shown in Figs. 2 and 3.

Calculations.—Rate constants were calculated in the usual manner from the linear relation of log $(d_t - d_\infty)$ or log $(v_t - v_\infty)$ *vs.* time in those runs which appeared first order because of large excess of weak acid. The *d*'s and *v*'s are optical densities and titration volumes at times *t* and at completion of the reaction.

Second-order rate constants were obtained from the linear dependence of log c_A/c_B on time where the *c*'s are concentrations of reactants at time *t*.

Sampling times were always equally spaced and the method of least squares utilized to calculate the best slope in each case. This turned out to be a good deal more accurate and also less laborious than graphical plotting.

Results and Discussion

Diphenylmercury Concentration Dependence.—Because of the alleged puzzling increase of the first-order rate constant, k_u, with decreasing initial mercurial concentration observed in the dilatometer experiments, the cleavage with large excess of

---

[5] A. Weissberger and E. Proskauer, "Organic Solvents," The Clarendon Press, Oxford, England, 1935.

[6] F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.*, **8**, 220 (1936); **9**, 237 (1937).

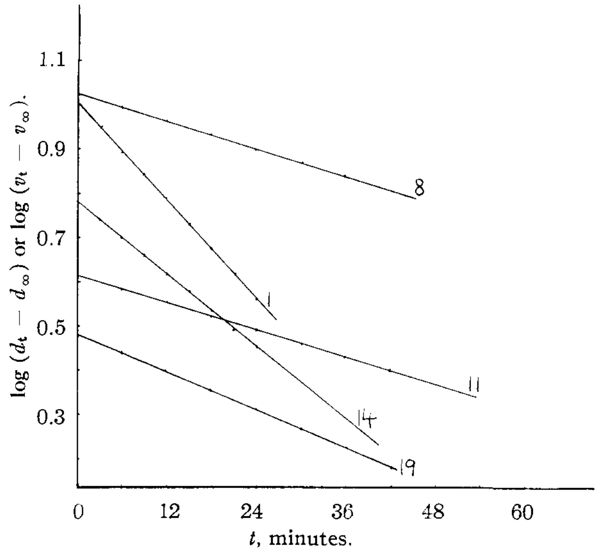


Fig. 2.—First-order runs.

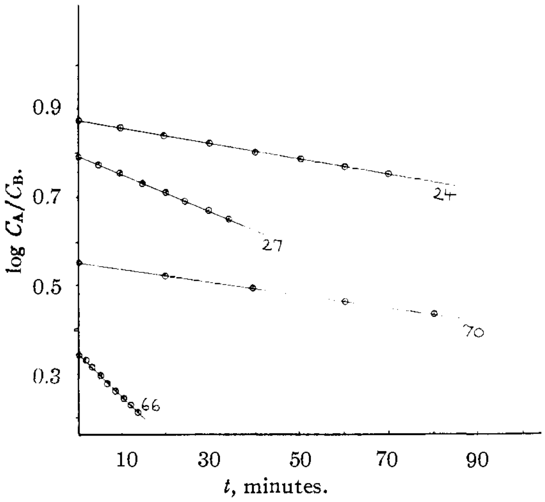


Fig. 3.—Second order runs.

acetic and formic acid was reinvestigated using both methods of following the reaction.

The data presented in Table I yield three results. k_u was reproducible to ±1–2%. The rate constants were much smaller than those found by the dilatometer method. k_u did not seem to depend on initial mercurial concentration. Since this is the normally expected behavior, further work with the dilatometer appears desirable.

TABLE I

CLEAVAGE OF DIPHENYLMERCURY WITH EXCESS FORMIC OR ACETIC ACID IN DIOXANE

Expt.	[HCOOH], moles/liter	[$(C_6H_5)_2Hg$], mole/liter	Temp., °C.	$k_u \times 10^4$, sec.$^{-1}$
1	8.80	0.0987	29.39	7.05
2	8.80	.0987	29.39	6.99
3	8.80	.0987	29 39	7.07
4	8.80	.0822	29.39	6.99
6	8.80	.0493	29.39	7.07
8[a]	8.80	.0972	30.2	10.8[a]
	[CH_3COOH]			
8	8.80	.0989	41.96	2.05
10	8.80	.0989	41.90	1.95
11	8.80	.0989	41.96	2.00
1[a]	8.80	.0972	42.2	5.20[a]

[a] Taken from reference 4.

Acetic Acid Concentration Dependence.—Similar to Corwin and Naylor's observations in formic acid runs, the increase of k_u with increasing acetic acid concentration is much greater than linear. Using the interpretation of a reaction polymolecular in acetic acid

$$-dc/dt = k_1[CH_3COOH]^n[(C_6H_5)_2Hg] = k_u[(C_6H_5)_2Hg]$$

and determining n from a plot of log k_u *vs.* log CH_3COOH, n is found to be 3.37, in approximate agreement with the reported value of 2.83 for formic acid.

TABLE II

ACID CONCENTRATION DEPENDENCE

[$(C_6H_5)_2Hg$] = 0.0995 M, T = 41.96°, solvent: dioxane

Expt.	[CH_3COOH], moles/l.	$k_u \times 10^4$, sec.$^{-1}$
11	8.80	2.00
19	9.81	2.75
18	10.24	3.17
15	10.70	3.71
16	11.22	4.37
14	11.77	5.08
13	11.77	5.12

It must be pointed out, however, that at such high acid concentrations, *i.e.*, dioxane:acetic acid volume ratios ranging from 1:1 to 1:2, the solvent medium also changes considerably. As it can be assumed that the reaction intermediate carries a positive charge, the effect of an increased dielectric constant of the solvent would be to speed the reaction. A clear decision about the number of acetic acid molecules involved in the reaction cannot be reached on the basis of these experiments.

The Cleavage with Strong Acids.—With the accurate and sensitive analytical methods available, the reaction between diphenylmercury and a strong acid at small and comparable concentrations could now be studied. Thus, it was shown that the reaction is strictly second order under these conditions, its rate being proportional to the concentrations of mercurial and of acid. The integrated second-order rate equation gave an excellent fit for the experimental points in all cases.

Additional proof is given in Table III which summarizes experiments with dilute perchloric acid in 95% ethanol.

TABLE III

CLEAVAGE OF DIPHENYLMERCURY WITH DILUTE PERCHLORIC ACID IN 95% ETHANOL

Expt.	[$HClO_4$], mole/l.	[$(C_6H_5)_2Hg$], mole/l.	Temp., °C.	$k_b \times 10^3$, l. mole^{-1}, sec.$^{-1}$	$k_u \times 10^4$, sec.$^{-1}$
22	0.01482	0.03223	47.34	11.6	3.3
23	.01482	.01611	47.34	11.3	1.3
24	.01900	.02506	47.34	11.4	2.2
25	.02420	.03221	42.75	7.24	1.7
26	.01594	.02596	42.75	7.22	1.5

As is seen from these experiments, an approximate first-order rate constant, k_u, calculated on the basis of mercurial concentration alone, varies by a factor of 2.5, while the second-order constant, k_b, varies only 2 to 3%.

This, again, supports the view that the cleavage reaction is a simple, bimolecular attack of the solvated proton on the ring carbon atom.

Solvent Effects.—The search for reaction conditions which could be used with a series of substituted diphenylmercury compounds yielded some information on solvent effects as a by-product of other investigations. Only scattered results are presented in Table IV.

TABLE IV

SOLVENT EFFECT ON CLEAVAGE WITH PERCHLORIC ACID

Expt.	T = 50.13° Solvent, vol. %	$k_b \times 10^3$, l. mole^{-1} sec.$^{-1}$
24, 26, 27[a]	Ethanol, 95	15.1
45, 46, 66[a]	Dioxane, 97.23 Water, 2.77	39.1
34, 37[a]	Dioxane, 96.77 Water, 3.23	29.7
69	Dioxane, 69.50 Water, 30.50	4.84

[a] k_b calculated from known temperature dependence.

Since perchloric acid was used and protonated solvent was therefore the attacking agent, the solvent effect is determined mainly by the base strength of the solvent. From the results in Table IV it seems that protonated ethanol or dioxane are stronger attacking agents than hydronium ion. At low water concentration, the rate decreases sharply with increasing water content.

Braude[7] studied the acid strength of HCl in various organic solvents and solvent–water mixtures by the indicator method and observed that small amounts of water strongly decreased the acidity of HCl solutions in ethanol and dioxane.

Similar observations in equilibrium and rate studies by other investigators are also quoted in Braude's papers. This effect can be explained as due to the greater base strength of the isolated solute water at small concentration in another solvent compared with that of the solvent water in its extensively associated and hydrogen bonded form.

From Braude's graph of the acidity function, H, *vs.* mole per cent. water in ethanol and dioxane, the values of H for the four solvent compositions in the order of Table IV are -1.88, -1.62, -1.65 and -2.33. The rate constants are in proper order, highest in the solvent of most positive H and decreasing with decreasing H. The agreement is semi-quantitative since log k_b varies approximately linearly with H. The fact that the cleavage rate constant is a linear function of H is further evidence for the proposed acid attack mechanism.

Salt Effect.—A limited number of experiments were run to determine the effect of anions on the rate, and results are listed in Table V.

The rate constant is independent of added perchlorate ion, it increases with added chloride ion, but there is no reaction at all with chloride in the absence of acid. While these observations are insufficient for a general understanding of the effect, they do serve to rule out several explanations.

An independent reaction with chloride ion is ruled out by expt. 75, since there is no cleavage of diphenylmercury in the absence of acid.

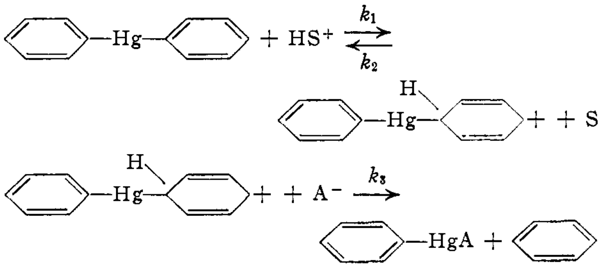
TABLE V

SALT EFFECT

Solvent: 69.5 vol. % dioxane, 30.5 vol. % water; T = 50.13°

Expt.	[$(C_6H_5)_2$-Hg], mole/l.	[$HClO_4$], mole/l.	Salt concn., mole/l.	$K_b \times 10^3$, l. mole^{-1} sec.$^{-1}$
69	0.01566	0.02741	None	4.84
70	.01561	.02741	0.0125 $KClO_4$	4.71
73	.01565	.02741	.01397 KCl	5.94
74	.01567	.02741	.02794 KCl	7.49
75	.01570	None	.02794 KCl	No reacn.

If it were supposed that the reaction occurred in two successive steps



and that the over-all rate were increased because k_3 is greater for chloride than for perchlorate, this leads to a contradiction. The reaction would be accurately second order only if $k_3[A^-] >> k_2[S]$. Since the reaction was shown to be second order and since the rate is insensitive to added perchlorate ion (expt. 69, 70), the above inequality holds for $A^- = ClO_4^-$. This means that the forward rate of the first step, k_1, is rate determining. The over-all rate which is independent of A^- when $A^- = ClO_4^-$ should then certainly be independent of A^- when $A^- = Cl^-$, contrary to experiment. This scheme must therefore be discarded.

To ascribe the chloride effect to complex formation with the mercury atom with resulting higher electron density at the ring carbon is at variance with Strobel's[8] findings that the slight solubility of mercury substituted benzoic acids is not increased by the presence of a large excess of chloride, iodide or cyanide ion.

Braude[7] found HCl to be a weak acid in dioxane. There may exist a small concentration of free HCl in equilibrium with protonated dioxane and hydronium ion in aqueous dioxane. The salt effect of chloride ion may then be due to the high specific cleavage rate of undissociated HCl.

The possibility of concerted attack of acid and chloride must also be considered, though it is rendered doubtful by the clean second-order nature during the course of reaction when chloride is present in approximately stoichiometric amount. More work is need to clarify this problem.

Temperature Dependence.—Rate constants were determined as functions of temperature in three different solvents. Rates were measured over temperature ranges of 10 to 15° and interpreted by the simple Arrhenius expression which was found to fit the data to within experimental error.

---

[7] (a) E. A. Braude, *J. Chem. Soc.*, 1971 (1948); (b) E. A. Braude and E. S. Stern, *ibid.*, 1976 (1948).

[8] A. F. Strobel, Dissertation, Johns Hopkins University, 1943.

TABLE VI

TEMPERATURE DEPENDENCE

Expt.	Solvent	Acid	E, kcal. mole^{-1}	log A
11, 17, 20	Dioxane	CH_3COOH (Excess)	18.5 ± 0.2	9.11 ± 0.15
24, 26, 27	95% EtOH	$HClO_4$	20.6 ± .3	12.08 ± .2
45, 46, 66	Dioxane 2.77% H_2O	$HClO_4$	23.7 ± .2	14.61 ± .15

Since the reaction is fastest in dioxane with perchloric acid and slowest in dioxane with excess acetic acid, it is apparent that the activation energies vary in just the opposite order. The activation energy is highest in the fastest solvent, but the large increase in the frequency factor outweighs the unfavorable energy effect by far.

Similar behavior with such reactions as the alkaline hydrolysis of ethyl benzoate, methylation of pyridine, etc., was studied by Fairclough and Hinshelwood.[9] It does seem qualitatively plausible that, in a reaction with a charged intermediate, increased solvation will lower the energy of the intermediate, but will magnify steric requirements and thus lead to lower values of A.

The bimolecular reaction with perchloric acid is seen to be quite fast, A ranging from 10^{12} to 10^{14} l. mole^{-1} sec.$^{-1}$, in agreement with the simple mechanism originally proposed. This facilitates the application to the wider problem of aromatic substitution which is discussed in a subsequent publication.

Acknowledgment.—F. K. is happy to acknowledge a generous grant-in-aid from the Hynson, Westcott, and Dunning Fund.

[9] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538, 1573 (1937); 236 (1938); 598 (1939).

ABERDEEN, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

A Kinetic Study of the Diels–Alder Reaction of Various Anthracene and Maleic Anhydride Derivatives

BY L. J. ANDREWS AND R. M. KEEFER

RECEIVED MAY 31, 1955

The rates of reaction of anthracene and dimethylanthracene with maleic anhydride and several of its substitution products have been followed by colorimetric procedures. In the presence of a large excess of dienophile the reactions in chloroform are first order with respect to diene, but the first-order rate constants are not directly proportional to dienophile concentration. This kinetic behavior can be explained quantitatively through consideration of the fact that a substantial fraction of the diene in the reaction mixtures is bound in a molecular complex with the dienophile. The mechanism of the reaction is discussed in the light of these observations and in terms of the effects of changes in temperature, solvent and substituents in the reactant molecules on the reaction rates. The possibility that Diels–Alder adduct may form by reaction of the diene–dienophile complex with a second dienophile molecule has been ruled out on the basis of rate studies.

The results of previous kinetic studies indicate that the Diels–Alder reaction is first order with respect to both the diene and dienophile.[1] The reaction often is accompanied by the transitory formation of highly colored molecular complexes of the two reactants, and it has been suggested that these complexes are necessary precursors of the adducts.[2] In view of what is known concerning the rate laws of other reactions in which molecular complex formation is an adjunct to the formation of stable products,[3] it seems likely that the kinetics of the Diels–Alder reaction may, in some cases, be more complex than earlier investigations have revealed.

This matter has now been explored through a study of the rates of reaction of anthracene and dimethylanthracene with maleic anhydride and some of its derivatives in chloroform and other solvents at several temperatures. These compounds have been chosen for study since, in the vicinity of room temperature, they display a marked tendency to form complexes[4] and undergo essentially irreversible Diels–Alder reaction at measurable rates. The mechanistic significance of the effects of changes in structure of diene and dienophile components on these reaction rates has been considered.

The Reactions in Chloroform.—In all rate runs the concentration of the dienophile was in large excess over that of the diene. The rate of disappearance of the diene to form the Diels–Alder adduct was followed by measuring (on the Beckman spectrophotometer) the changes in solution color with time. This color, which results from a composite of the absorptions of the diene and diene–dienophile complex, initially was reddish-orange in the runs with dimethylanthracene and yellow in those with anthracene. Primary attention was given to the reactions of dimethylanthracene with maleic anhydride and chloromaleic anhydride, both of which occur rapidly in chloroform to yield the colorless substituted succinic anhydride derivatives.

Rate constants, k (see Table I), were evaluated for individual runs on the assumption that equation 1 accounted for the change in optical density, d, of the reaction mixtures with time.

$$2.303 \log \frac{[(\mathrm{ArH})_\mathrm{T}]_\mathrm{i}}{[(\mathrm{ArH})_\mathrm{T}]_\mathrm{t}} = 2.303 \log \frac{d_\mathrm{i}}{d_\mathrm{t}} = k(\mathrm{D})t \quad (1)$$

The term $(\mathrm{ArH})_\mathrm{T}$ represents the total concentration (both free and complexed) of the diene, and (D) is

---

(1) See, for example (a) A. Wassermann, *J. Chem. Soc.*, 828 (1935); (b) W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948).

(2) See M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., pp. 8 and 9, for a summary.

(3) (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953); **76**, 253 (1954); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3557 (1953); (c) R. M. Keefer, J. H. Blake and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3776 (1953).