Summary

(1) A kinetic model for hot atom reactions has been developed.

(2) An expression derived from this model successfully describes and predicts the action of noble gas moderators on the reaction of hot H atoms with methane.

(3) The model provides a measure of the relative energy at which various products in a given hot reaction system are formed. For T + CH_4 it suggests that CH_3T and $CH_2T\cdot$ are formed at about the same average energy.

(4) The treatment cannot yield explicit values for the reaction probability $p(E)$. However an estimate of the average $\overline{p(E)}$ over the whole hot reaction region can be made.

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The Kinetics of an Acid Catalyzed Aromatic Cyclodehydration Reaction in Acetic Acid–Water Mixtures

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The rate of cyclization of *o*-benzylbenzophenone to 9-phenylanthracene catalyzed by HBr in acetic acid–water mixtures has been measured at 99.8° at two HBr concentrations as a function of the acetic acid–water solvent composition between 56.3 and 99.6 mole % acetic acid. The results indicate that (1) the rate of reaction at constant HBr concentration decreases rapidly as the mole fraction of water in the solvent increases and (2) the rate of reaction at constant solvent composition increases more rapidly than the first power of the HBr concentration.

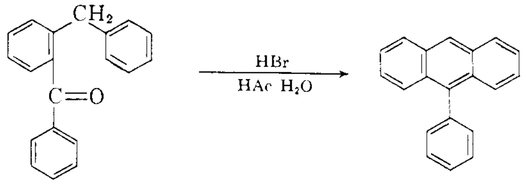
Introduction

The acid catalyzed cyclodehydration of certain aromatic aldehydes and ketones is an important method of synthesis for many polynuclear hydrocarbons.[1] A widely used medium for carrying out these cyclodehydration reactions, as well as a number of other acid catalyzed organic reactions[2] requiring strongly acidic media, is a mixture of hydrobromic acid, acetic acid and water, usually prepared by mixing appropriate quantities of 48% aqueous hydrobromic acid and glacial acetic acid. Hydrobromic acid is used since it is one of the strongest of the mineral acids. Acetic acid serves as a solvent for the organic compounds involved and also markedly enhances the strength of hydrobromic acid.

A number of studies have been made of the rates of various reactions in acetic acid–water mixtures catalyzed by mineral acids.[3] However, a limited amount of kinetic data is available for aromatic cyclodehydration reactions carried out in this medium.[4]

The present investigation is a kinetic study of the role of water in the acid catalyzed cyclodehydration of *o*-benzylbenzophenone to 9-phenylanthracene in hydrobromic acid–acetic acid–water mixtures.

This reaction was chosen for study because it proceeds at a convenient rate at 100° and is relatively free from interfering side reactions.



Experimental

Materials.—*o*-Benzylbenzophenone was prepared from reagent grade *o*-chlorobenzaldehyde and bromobenzene by the method employed by Bergmann.[5] The product was recrystallized from ethanol and melted at 55° (corrected). Baker reagent grade acetic acid was redistilled at 112–123°. Baker reagent grade 48% hydrobromic acid was redistilled at 114–116° and standardized against sodium carbonate and was found to have a concentration of 8.71 *M* (47.8%). Baker and Adamson reagent grade acetic anhydride was redistilled at 114–116°.

Kinetic Measurements.[6]—Reaction mixtures containing known amounts of *o*-benzylbenzophenone, hydrobromic acid, acetic acid and water were prepared by mixing appropriate quantities of these reagents with acetic anhydride.[7] The reaction mixtures then were placed in 10 ml. sealed tubes which were heated to 99.8 ± 0.1° in an oil-bath. The tubes were removed and analyzed spectrophotometrically after various time intervals for the hydrocarbon product at its four major absorption peaks using a Beckman DU spectrophotometer. Molar absorbancy indexes were determined by preparing 9-phenylanthracene[8] solutions of known concentrations up to 1.25×10^{-3} *M*, diluting these solutions to five times their original volumes with 95% ethanol and measuring the absorbances of the diluted solutions at the four wave length maxima. Table I gives the results of these measurements.[9]

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[1] For recent work, see: (a) C. K. Bradsher and H. Berger, THIS JOURNAL, **80**, 930 (1958); (b) F. A. Vingiello and A. Borkovec, *ibid.*, **78**, 1240 (1956).

[2] (a) D. M. Birosel, *ibid.*, **52**, 1944 (1930); (b) R. P. Ghaswalla and F. G. Donnan, *J. Chem. Soc.*, 1341 (1936); (c) C. K. Bradsher, THIS JOURNAL, **61**, 3131 (1939); (d) W. S. Johnson and W. E. Heinz, *ibid.*, **71**, 2913 (1949).

[3] See ref. 2a,b,d. For a recent review, see (a) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957). See also: (b) V. K. Krieble, F. C. Duennebier and E. Colton, THIS JOURNAL, **65**, 1479 (1943); (c) K. B. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958); (d) D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4033 (1958); (e) D. Bethell and V. Gold, *J. Chem. Soc.*, 1905 (1958).

[4] (a) C. K. Bradsher and F. A. Vingiello, THIS JOURNAL, **71**, 1434 (1949); (b) R. P. Moffett, Ph.D. Dissertation, Duke University, 1950.

[5] E. J. Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

[6] A procedure similar to that described here was devised by Moffett (ref. 4b).

[7] The water content of the glacial acetic acid was determined by Karl Fischer titration and was found to be 2.4 ± 0.1 mg. of water per ml. of acetic acid. The purity of the acetic anhydride, determined by diluting with water and titrating with sodium hydroxide, was 99.4%.

[8] We are indebted to Mr. Melvin Schlechter for supplying several grams of 9-phenylanthracene for these measurements.

[9] The absorbance, A_s, and the molar absorbancy index, a_s, are defined by the equations $A_s = \log \frac{I_0}{I} = a_s bc$ where I_0 and I are the intensities of the incident and transmitted light, *b* is the cell length (1 cm.) and *c* is the molar concentration of the absorbing species.

TABLE I

MOLAR ABSORBANCY INDEXES OF 9-PHENYLANTHRACENE

Wave length (Å.)	Molar absorb. index[a]
3300	0.600
3470	1.175
3630	1.767
3820	1.517

[a] In l. mole^{-1} cm.$^{-1}$ × 10^{-3}. Slit width = 0.3 mm.

The reaction mixtures were diluted similarly with ethanol before their absorbances were measured. It was found necessary to apply two corrections to the absorbances of the reaction mixtures. The first of these was for the ketone, which has a small absorbance in the range 3000 to 4000 Å., and was made in the following manner. The absorbance of 5.00×10^{-3} *M* ketone in the unheated reaction mixture was measured at each of the wave length maxima. The concentrations of 9-phenylanthracene in the reaction mixtures after various times of heating were roughly determined using the uncorrected absorbances and absorbancy indexes. The approximate percentage of unreacted ketone remaining in each solution was calculated. This percentage was then multiplied by the absorbance of the unheated reaction mixture containing 5.00×10^{-3} *M* ketone and the product was subtracted from the absorbance of the reaction mixture.

A second correction was made for the slow decrease that was found to occur in the absorbance of the hydrocarbon product when the latter is heated at 99.8°. This rate of decrease in absorbance was determined at the four wave length maxima and was found to be uniform and approximately independent of the concentration of the hydrocarbon. At 3630 Å., for example, the absorbance of the hydrocarbon decreases at the rate of 2.5×10^{-5} absorbance units per second. Thus, to make the correction for the decrease in hydrocarbon absorbance at 3630 Å., this value (2.5×10^{-5} sec.$^{-1}$) was multiplied by the time of heating and the product was added to the absorbance reading of the reaction mixture obtained at the same wave length.

The reactions were found to be first order with respect to the ketone, in agreement with results previously obtained.[4] The data for a typical kinetic run are given in Table II. The first order rate constants (see Table III) were calculated from the slope of the straight line obtained by plotting log c/c_0 *vs.* time, *t*, where *c* is the concentration of the unreacted ketone at time *t* and c_0 is its initial concentration (5.00×10^{-3} *M* at room temperature in all runs). Spectrophotometric data were obtained for each run at the four wave length maxima and the four rate constants calculated for a given run agreed to within 5% of each other. All of the absorbance measurements from which the kinetic data in Table III were calculated were made at 3630 Å.

Results and Discussion

Kinetic runs were carried out at two hydrobromic acid concentrations with varying relative amounts of acetic acid and water as the solvent. The results are summarized in Table III.

TABLE II

KINETIC DATA FOR THE HYDROBROMIC ACID CATALYZED CYCLIZATION OF *o*-BENZYLBENZOPHENONE TO 9-PHENYLANTHRACENE IN ACETIC ACID–WATER SOLVENT FOR RUN NUMBER EIGHT[a]

T. = 99.8°; (HBr) = 0.987 *M* at 99.8°; wave length = 3630 Å.; solvent composition, 0.865 mole fraction acetic acid, 0.135 mole fraction water

Time (hr.) A	Uncorr. absorb. B	Correction for Heating C	Correction for Ketone D	Corr. absorb. (B + C − D) E
0.00	0.102	0.000	0.102	0.000
1.58	0.976	.015	.090	0.901
2.75	1.562	.025	.083	1.504
3.58	2.012	.033	.077	1.968
4.92	2.632	.045	.069	2.608

[a] A = time of heating of reaction mixture; B = the uncorrected absorbance of the reaction mixture; C = the correction to the absorbance of the reaction mixture for the decrease in absorbance of the hydrocarbon product due to heating = (2.5×10^{-5} sec.$^{-1}$) × (the time of heating in seconds); D = the correction to the absorbance of the reaction mixture for the absorbance of the unreacted ketone = B at zero hours of heating times a rough estimate of the per cent. reaction; E = the corrected value of the absorbance = B + C − D.

TABLE III

RATES OF THE HYDROBROMIC ACID CATALYZED CYCLIZATION OF *o*-BENZYLBENZOPHENONE TO 9-PHENYLANTHRACENE IN ACETIC ACID–WATER MIXTURES AT 99.8°

HBr at 99.8° (*M*)[a]	Mole fract. HAc in solvent[b]	$k \times 10^6$ (sec.$^{-1}$)
0.987	0.996	33.6
.987	.866	11.7
.987	.748	2.86
.987	.650	1.04
.987	.566	0.636
1.223	.996	51.3
1.223	.865	19.5
1.223	.746	5.82
1.223	.647	1.98
1.223	.563	1.10

[a] Corrected for volume expansion of solvent from room temperature to 99.8°. The concentrations at room temperature were 1.056 and 1.320 *M*. [b] Mole fraction HAc + Mole fraction H_2O = 1.

It is evident that water greatly retards the rate of cyclodehydration of *o*-benzylbenzophenone catalyzed by hydrobromic acid in acetic acid. This result is consistent with effects observed for other acid catalyzed reactions in acetic acid–water mixtures.[2b,3a–c] In the non-aqueous solvent, HBr is only slightly ionized, so that the protonating species that are present are molecular HBr and small concentrations of H_2Ac^+, these ions being highly associated into ion pairs and quadruplets with Br^-.[10] Water, being a stronger base than HAc or Br^-, will accept protons from HBr and H_2Ac^+, forming H_3O^+. Since H_3O^+ is a weaker acid than HBr or H_2Ac^+, the rate of an acid catalyzed reaction will decrease upon the addition of water.

It is also observed that the rate of cyclodehydration increases more rapidly than the stoichiometric concentration of the acid catalyst at a given solvent composition. Other acid catalyzed reactions in acetic acid–water mixtures have been observed to behave in a similar manner and, in some cases, correlation of the rate with the Hammett acidity function, H_0, has been found.[3a,c–e] It will be of interest to determine H_0 for HBr in this solvent.

Acknowledgment.—The authors wish to thank the Research Corporation for support of this work.

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[10] S. S. Bruckenstein and I. M. Kolthoff, THIS JOURNAL, **78**, 10 (1956).