$\nu$ and $\lambda$ were calculated from the standard gas-kinetic expressions.

The loss found in this way must be multiplied by the probability of a tritium atom reaching thermal energies. This probability is approximately equal to $1 - A_0/A_s$, values of which can be found from Fig. 4.

**Acknowledgments.**—The authors wish to thank Professor L. Onsager for stimulating discussions of the mechanisms of hot reaction and for help with the calculations of the recoil loss. Suggestions of Professor F. S. Rowland regarding recoil ranges are gratefully acknowledged. Comparisons with the work of T. Pratt on radiation induced exchange reactions was very useful. Mr. Pratt also provided much help on problems of technique. This work was performed under the auspices of the United States Atomic Energy Commission.

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[CONTRIBUTION NO. 1565, STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

# Kinetic Theory of Hot Atom Reactions: Application to the System H + $CH_4$

BY PEDER J. ESTRUP[1] AND RICHARD WOLFGANG

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A model has been developed for the kinetics of hot atom reactions in the gas phase. An expression is derived giving the total probability that a hot atom will react before losing its excess energy, in terms of the average collisional energy loss and the efficiency of reaction upon collision. The model predicts the relative effect of inert moderating compounds and provides a measure of the relative energy at which various products are formed in reactions with a given substance. The theory is tested using experimental data on the action of moderators on the reactions of hot hydrogen with methane and is found to provide a good representation of this system.

## Introduction

Atoms having much higher kinetic energy than provided by the thermal motion of their surroundings are usually termed "hot" atoms. If such atoms take part in reactions before they have lost their excess energy, the processes are called "hot" reactions.

In recent years several systems have been found in which hot atoms, produced by photochemical or nuclear processes, could be unambiguously shown to undergo hot reactions.[2-5] These hot reactions were identified by one or more of several characteristic features which serve to distinguish them from thermal reactions:

(1) Since the energy required for the reaction is almost exclusively supplied by the hot atom rather than by the environment, the hot reactions are to a first approximation temperature independent.

(2) The hot species rapidly loses its excess energy to the surroundings. Thus, any reaction must take place in one of the relatively few collisions that it makes before it is thermalized. Hot reaction yields are therefore independent of minor constituents, in particular scavengers (such as $I_2$) which may be added to remove reactive thermal species.

(3) Hot reactions are sensitive to moderators (*e.g.*, helium) which, though chemically inert, will efficiently remove energy from the hot species.

The detailed experimental investigation of the effect of moderators on the hot reactions of hydrogen atoms with methane[5] has provided a stimulus for attempting to develop a quantitative model of hot atom kinetics. Evidently models involving an equilibrium distribution of thermal energies, such as that leading to the Arrhenius equation $k = pZe^{-\Delta E/RT}$ and its variants[6] will not be applicable to hot species since, by definition, these are outside such an equilibrium distribution. Furthermore, hot species may in general be expected to react well above the "activation energy" $\Delta E$, and it seems quite likely that $p$, the "steric factor" cannot be considered constant when the available energy exceeds $\Delta E$. Indeed the variation of $p$ with energy is a central problem in high-energy kinetics.

Using a rather simple model of hot atom reactions this study attempts to describe their kinetics and develops an equation which might be considered a hot atom analog of conventional rate expressions for thermal systems.

## Model

Consider a system which is comprised of hot atoms of initial energy $E_0$, in a thermal environment consisting of one or more components. The hot atoms lose energy in successive collisions but may react to enter combinations over a certain energy range $E_2$ to $E_1$. Above $E_2$ the collisions are too energetic to result in stable combinations, while $E_1$ is the minimum energy required for reaction.

The reaction probability per collision between the hot atom and a molecule of component $j$ is denoted by $p_j(E)$ where this quantity is finite in the interval $E_2 > E > E_1$ and zero elsewhere. ($p_j(E)$ corresponds to the collision efficiency $pe^{-\Delta E/RT}$ in normal kinetic terminology. However, since for hot atoms $E > \Delta E$ and $e^{-\Delta E/RT} \sim 1$, $p_j(E)$ becomes a high energy equivalent to the "steric factor," $p$.) Then if $N_s$ is the total number of hot atoms available for reaction and if $f_j$ is the relative probability of collision with compound $j$, the number of hot combination products is

$$N_{\text{hot}} = N_s \sum_j \int_{E_2}^{E_1} f_j p_j(E) n(E)\, \mathrm{d}E \tag{1}$$

where $n(E)\mathrm{d}E$ is the number of collisions suffered between $E + \mathrm{d}E$ and $E$.

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[1] CERN, Geneva, Switzerland. Work performed in partial fulfilment of the requirements for the Ph.D. degree at Yale University.

[2] H. A. Schwarz, R. R. Williams and W. H. Hamill, THIS JOURNAL, **74**, 6007 (1952).

[3] R. J. Carter, W. H. Hamill and R. R. Williams, *ibid.*, **77**, 6457 (1955).

[4] M. Amr El-Sayed, P. J. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

[5] P. J. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2661 (1960).

[6] A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955.

To obtain an expression for $n(E)$ three assumptions are made.

(1) The energy loss occurs by collisions in which the collision partners can be treated as elastic spheres. As will be seen later, the applicability of the model is not very sensitive to the exact validity of this assumption.

(2) The initial energy of the atom, $E_0$, is sufficiently high so that the atom has made a number of collisions before reaching the upper limit of the reaction zone $E_2$, thus providing a statistically well-defined distribution of energies for the hot atoms in the region of interest. This assumption will be justified for most hot atoms produced by nuclear recoil (*e.g.*, the reaction $He^3(n,p)H^3$ yields $H^3$ particles of energy 0.2 mev.) but will generally not be valid in photochemical systems. For the latter the distribution function $n(E)$ must be computed somewhat differently from this treatment.

(3) The minimum energy required for reaction, $E_1$, is still large compared to thermal energies.

If the probability for reaction $p(E) = \sum_j p_j(E)$ were zero we could write[7,8]:

$$n(E) = -\frac{1}{\alpha E} \qquad (2)$$

where $\alpha$ is the average logarithmic energy loss per collision

$$\alpha = \sum_j f_j \alpha_j \qquad (3)$$

$$\alpha_j = 1 - \frac{(M_j - m)^2}{2M_j m} \ln \left| \frac{M_j + m}{M_j - m} \right| \qquad (4)$$

$m$ is the mass of the hot atom and $M_j$ that of the molecule struck. Since $p(E)$ is finite in the energy range of interest, equation 2 must be multiplied by the probability that the hot atom has escaped reaction in the energy interval $E_2$ to $E$

$$n(E) = -\frac{1}{\alpha E} \left[ 1 - \sum_j \int_{E_2(j)}^{E} f_j p_j(E)\, n(E)\, \mathrm{d}E \right] \qquad (5)$$

Differentiation with respect to $E$ and separation of the variables gives

$$\frac{\mathrm{d}n(E)}{n(E)} = \frac{\sum_j f_j p_j(E)}{\alpha} \frac{\mathrm{d}E}{E} - \frac{\mathrm{d}E}{E} \qquad (6)$$

Since equation 2 is valid for $E = E_2$, integration of equation 6 between $E$ and $E_2$ leads to

$$n(E) = -\frac{1}{\alpha E} \exp\left[ -\sum_j \int_E^{E_2} \frac{f_j p_j(E)}{\alpha E}\, \mathrm{d}E \right] \qquad (7)$$

Substituting this into equation 1

$$\frac{N_{\text{hot}}}{N_s} = \sum_j \int_{E_1}^{E_2} \frac{f_j p_j(E)}{\alpha E} \exp\left[ -\sum_j \int_E^{E_2} \frac{f_j p_j(E)}{\alpha E}\, \mathrm{d}E \right] \mathrm{d}E \qquad (8)$$

Equation 8 is a rather general expression giving the total probability that a hot atom will undergo high energy reaction in a mixture of $j$ components. The quantity $N_{\text{hot}}/N_s$ may be termed the "Relative Yield of Hot Products," or the "Total Probability of Hot Reaction."

**System of Single Reactant: Yield of All Hot Products.**—It is now of interest to consider a system in which hot reactions can occur with only one of the components, *i.e.*, where the values of $f_j p_j$ for all other components are negligible. The subscripts are then omitted and $f$ and $p$ are understood to refer to the reactive compound. The relative yield of hot products now becomes

$$\frac{N_{\text{hot}}}{N_s} = \int_{E_1}^{E_2} \frac{f p(E)}{\alpha E} \exp\left[ -\int_E^{E_2} \frac{f p(E)}{\alpha E}\, \mathrm{d}E \right] \mathrm{d}E \qquad (9)$$

$$\frac{N_{\text{hot}}}{N_s} = 1 - \exp\left[ -\frac{f}{\alpha} I \right] \qquad (10)$$

where

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E}\, \mathrm{d}E$$

and $f$ has been assumed to be independent of $E$.

**System of Single Reactant: Yield of Individual Hot Product.**—It should be noted that equation 10 treats the sum of *all* hot reactions which may occur with the reactive component. $N_{\text{hot}}/N_s$, $I$ and $p(E)$ as given are applicable *only* to a situation in which there is a single hot product or where the sum of all hot products is considered. In such a case the data may be interpreted using (10), plotting ln $(1 - N_{\text{hot}}/N_s)$ *vs.* $f/\alpha$.

In general, however, there may be several hot products (*e.g.*, $CH_3T$, HT and $CH_2T\cdot$ from $CH_4 + T$). The sum of these products is expressed by equation 10 but when they are considered individually the treatment must be modified somewhat. Let $p_i$ be the partial probability for formation of product $i$, so that $p(E) = \sum_i p_i(E)$. Equation 1 for the number of hot products $N_i$ of a single species $i$ is then

$$N_i = N_s \int_{E_2}^{E_1} f p_i(E)\, n(E)\, \mathrm{d}E \qquad (1a)$$

(Again only one reactive component $j$ is considered.) Substituting equation 7 (for one reactive component) we have in analogy to (9)

$$\frac{N_i}{N_s} = \int_{E_1}^{E_2} \frac{f\, p_i(E)}{\alpha E} \exp\left[ -\int_E^{E_2} \frac{f\, p(E)}{\alpha E}\, \mathrm{d}E \right] \mathrm{d}E \qquad (11)$$

Note that while the pre-exponential contains $p_i$, the exponent, being the factor which determines the number of hot atoms reaching energy $E$, involves $p$, the probability for all hot combination reactions.

Equation 11 is more useful when expanded as a series

$$\frac{N_i}{N_s} = \frac{f}{\alpha} I_i - \frac{f^2}{\alpha^2} K_i + \frac{f^3}{\alpha^3} L_i - \ldots \qquad (12)$$

where the constants in the expansion are given by

$$I_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E}\, \mathrm{d}E$$

$$K_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[ \int_E^{E_2} \frac{p(E)}{E}\, \mathrm{d}E \right] \mathrm{d}E,$$

$$L_i = {}^1/_2 \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[ \int_E^{E_2} \frac{p(E)}{E}\, \mathrm{d}E \right]^2 \mathrm{d}E, \text{ etc.}$$

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[7] See, for example, S. Glasstone, "Principles of Nuclear Reactor Engineering," Van Nostrand, Inc., New York, N. Y., 1955, p. 147 ff.

[8] G. Placzek, *Phys. Rev.*, **69**, 423 (1946).

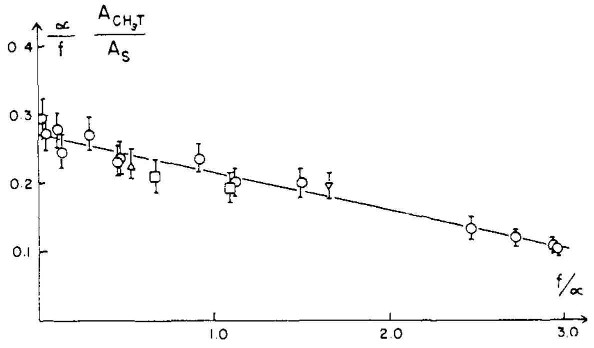

Fig. 1.—Plot corresponding to equation 15 for the yield of labeled methane, $CH_3T$: intercept, 0.27; slope, $-0.055$; moderators: helium, ○; neon, □; argon, ▽; xenon, △.

In general the series should converge rapidly, requiring the use of only the first two or three terms. It is evident by comparing (12) with a series expansion of (10), that

$$I = \sum_i I_i \qquad (13)$$

$$\sum_i K_i = {}^1/_2 I^2 \qquad (14)$$

Equations 10 and 12 provide a statement of the model in a form that can be compared with experimental data on total and individual product yields respectively. When only one product is formed, equation 12 will of course reduce to equation 10.

At this point it is useful to examine the physical significance of the terms in equation 12. The first term, $I_i$, is the integral of the inherent probability that the hot atom will react at energy $E$ to form product $i$. The sum of the succeeding terms $K_i$, $L_i$, etc., correct the first term by taking into account the probability that the hot atom will already have reacted above energy $E$ to form *any* product. Thus for a product formed primarily near the top of the energy range for reaction, this sum will be small; while for a product formed at relatively low energy it will be comparatively large since this product is highly dependent on the number of hot atoms which manage to pass through the higher energy region without combining. The magnitude of the ratio $L_i/K_i$ will thus be a measure of the relative mean energy at which the products are formed.

## Test of Model: The System H + $CH_4$

The model, as expressed in equation 12 may be tested by investigating the variation in the relative yield of hot products with $f/\alpha$. By adding inert gas moderators to the system the collision probability with the reative component $f$ and the average logarithmic energy loss per collision $\alpha$ may be varied over wide limits.

The accompanying paper[5] gives data for such experiments carried out on the system of methane reacting with recoiling tritium produced by the process $He^3(n,p)T$. In this system thermal reactions which might also give the products of interest were eliminated by the use of halogens as scavengers. $CH_3T$. HT and $CH_2T\cdot$ were identified as hot products by the criteria listed in the introduction. (Subsequent to its hot formation $CH_2T\cdot$ reacts with halogen and thus appears as $CH_2TX$.) The effect on the probability of forming these products of the addition of He, Ne, Ar and Xe moderators was studied.

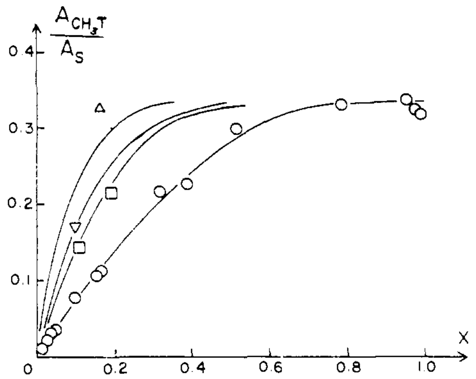

Fig. 2.—Plot of the relative yield of $CH_3T$ as function of the mole fraction of methane. The curves represent calculated values; moderators: helium, ○; neon, □; argon, ▽; xenon, △.

Since the amount of added scavenger in these systems was very small the assumption that $(fp)_{\text{scavenger}} << (fp)_{\text{methane}}$ should be valid and equations 10 and 12 can therefore be used. The relative experimental yields are given by $A_i/A_s$ where $A_i$ is the observed activity of product $i$ and $A_s$ the total activity stopped in the gas phase. Only retaining the first two terms in the expansion and substituting $A_i/A_s$ for $N_i/N_s$ (12) can then be written

$$\frac{\alpha}{f}\frac{A_i}{A_s} \simeq I_i - \frac{f}{\alpha}K_i \qquad (15)$$

A plot of $\alpha/f \cdot A_i/A_s$ *versus* $f/\alpha$ should consequently approximate to a straight line (at least for small values of $f$) and give $I_i$ as intercept. Furthermore all points should fall on the same line, regardless of the moderator used.

$f$ was calculated from the expression

$$f = \frac{X_{CH_4}S_{T,\,CH_4}}{\sum_j X_j S_{T,\,j}}$$

where $X_j$ denotes the mole fraction of component $j$ in the mixture and $S_{T,j}$ the cross-section for a T-$j$ collision. To find $S$ these values for the diameters were used[9]: T, 1.1; $CH_4$, 4.2; He, 2.2; Ne, 2.6; Ar, 3.6; Xe, 4.9 Å. $\alpha$ was computed from equations 3 and 4.

Figure 1 shows the plot corresponding to equation 15 for the yield of $CH_3T$. As seen the points do fall on a straight line regardless of the differences in moderators. A least square analysis gives $I_{CH_3T} = 0.27$ and $K_{CH_3T} = 0.055$. $L_{CH_3T}$ is negligible. Using these values the probability of hot reaction to form $CH_3T$, $A_{CH_3T}/A_s$ can now be plotted directly against $X$, the mole fraction of methane (Fig. 2). The coincidence of the experimental points with the calculated curve is an alternative indication of the validity of the model.

Figures 3 and 4 show the analogous plots for the yield of labeled methyl halide, $CH_2TX$.

It is noteworthy that the ratio $I_i/K_i$ has the same order of magnitude for $CH_3T$ and $CH_2TX$. This may be taken to imply that similar energies are

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(9) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge, 1953, p. 229.

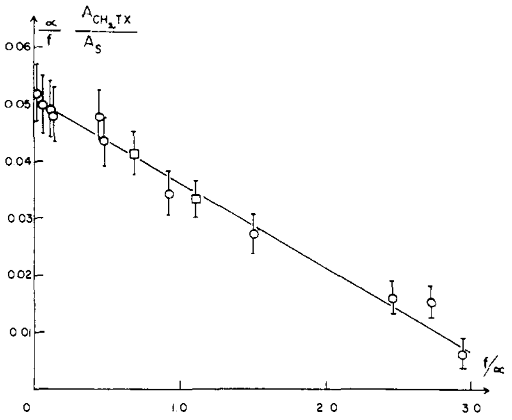

Fig. 3.—Plot corresponding to equation 15 for the yield of labeled methyl halide, $CH_2TX$: intercept, 0.051; slope, −0.012; moderators: helium, O; neon, □.

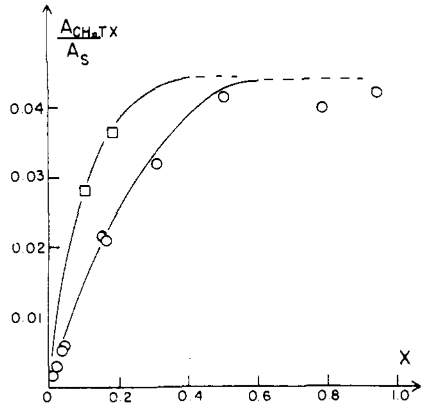

Fig. 4.—Plot of the relative yield of $CH_2TX$ as function of the mole fraction of methane. The curves represent calculated values; moderators: helium, O; neon, □.

required for formation of these two products and would indicate that in the reaction leading to $CH_2T\cdot$, $H_2$ rather than 2H is ejected.

Figure 5 shows the plot for HT. Obviously the experimental data could only be fitted with difficulty—even with employment of extreme values of $I_i$, $K_i$, $L_i$ etc., which would clearly be inconsistent with equations 10, 13 and 14. As discussed in the accompanying paper, this effect probably is caused by the spurious formation of HT in a thermal side reaction which becomes relatively important in highly moderated systems. Figure 5 is thus at least useful in demonstrating that this model cannot be "adjusted" to provide a fit for thermal reactions.

Although $I_{HT}$ thus cannot be determined directly, an upper limit can be calculated using the data for the total observed activity in combination with equations 10 and 13. This gives $I_{HT} \leq 0.14$ and the corresponding value for $K_{HT}$ (equation 14) is 0.035.

**Reaction Probabilities.**—From the values of $I_i$ an estimate can be made of the average reaction probabilities, using the expression (derived from the definition of $I_i$ in (12))

$$\overline{p_i(E)} = \frac{I_i}{\ln E_2/E_1} \qquad (16)$$

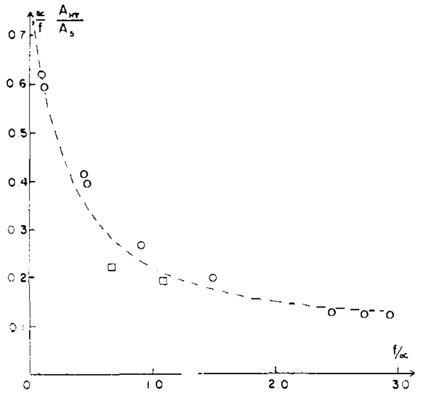

Fig. 5.—Plot corresponding to equation 15 for the yield of labeled hydrogen, HT.

An appropriate value for $\frac{E_2}{E_1}$ must be chosen. In the choice of $E_1$ there is some pertinent information regarding the formation of labeled methane. Thus no formation of $CH_3D$ was reported in the work on the reactions of 1–2 ev. deuterium atoms with methane.[3] Similarly, a theoretical treatment (assuming inversion) gave an activation energy of 1.6 ev. for this process.[10] We may therefore expect an $E_1$ of comparable magnitude. It is more difficult to estimate $E_2$. Obviously, at very high energies an inelastic collision between a tritium atom and a methane molecule will merely result in breaking one or more C–H bonds with no possibility for formation of labeled products. Simple considerations of the collision dynamics may therefore be of some help, and in the case of $CH_3T$ production they indicate a value of 10–20 ev. for the energy at which $p_i(E)$ becomes negligible. Although it is unlikely that $p_i(E)$ becomes exactly zero at this or any other energy, we may use it as an effective value of $E_2$ for the purpose of estimating $\overline{p_i(E)}$. Fortunately $\overline{p_i(E)}$ varies very slowly with $E_2/E_1$ for $E_2/E_1 > \sim 10$, and the value chosen is therefore not critical. Table I gives the values for $\overline{p_i(E)}$ with $E_2/E_1 = 10$ for all three reactions. The corresponding order of magnitude for the average energy of the hot reactions is ~5 ev.

TABLE I

| Product | $I_i$ | $I_i/K_i$ | $\overline{p_i(E)}$ | $P_{thermal}$ |
|---|---|---|---|---|
| $CH_3T$ | 0.27 | 5 | 0.12 | . . . |
| $CH_2T$ | .051 | 4 | .02 | . . . |
| HT | $\leq .14$ | ~5 | $\leq .06$ | 0.025[11] |

The model as applied here thus cannot give $p_i(E)$ as a continuous function of the energy. It does however provide average values for reaction probabilities at high energies. Information can thus be obtained about reactions which are not observed at ordinary temperatures; and where data are available for the thermal reactions a comparison may give an indication of the energy dependence of the reaction probabilities.

[10] E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

[11] R. Klein, J. R. McNesby, M. D. Scheer and L. J. Schoen, *ibid.*, **30**, 58 (1959).

## 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE VIRGINIA POLYTECHNIC INSTITUTE, BLACKSBURG, VIRGINIA]

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

BY L. K. BRICE AND R. D. KATSTRA

RECEIVED AUGUST 20, 1959

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.

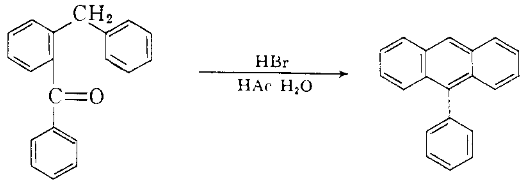
## Introduction

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 $1.25 \times 10^{-3}$ *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.