One deduces from (7), (31) and (33) the following equation in $\bar{E}(s)$

$$\frac{\bar{i}_t}{s} = -c_1 sE(s) - \frac{nF}{RT} i_0 \left[\bar{E}(s) - \frac{a\bar{E}(s)}{s^{1/2} + a}\right] \quad (34)$$

from which the Laplace transform of the potential can be easily obtained. Thus

$$\bar{E}(s) = -\frac{i_t}{c_1} \frac{s^{1/2} + a}{s^{3/2}(s + as^{1/2} + b)} \quad (35)$$

with

$$b = \frac{nF}{RT} \frac{i_0}{c_1} \quad (36)$$

By factorization of the denominator in (35) and application of the theory of partial fractions, one can write equation 35 in the form

$$\bar{E}(s) = -\frac{i_t}{c_1} \frac{1}{\gamma - \beta} \left[\frac{1}{s(s^{1/2} + \beta)} - \frac{1}{s(s^{1/2} + \gamma)} + \frac{a}{s^{3/2}(s^{1/2} + \beta)} - \frac{a}{s^{3/2}(s^{1/2} + \gamma)}\right] \quad (37)$$

where β is defined by equation 19 and γ is defined by the same equation as (19) but with a minus sign in front of the bracket in the right-hand member.

The inverse transform of (37) is derived by application of the convolution integral.[14] Thus, by noting that the inverse transform of $1/s$ and $1/s^{3/2}$ are 1 and $2(t/\pi)^{1/2}$, respectively, and that the inverse transform of $(s^{1/2} + \beta)^{-1}$ is

$$\frac{1}{(\pi t)^{1/2}} - \beta \exp(\beta^2 t) \operatorname{erfc}(\beta t^{1/2})$$

one has

$$E - E_e = -\frac{i_t}{c_1(\gamma - \beta)} \left[\begin{array}{c} \gamma \int_0^t \exp(\beta^2\theta) \operatorname{erfc}(\beta\theta^{1/2})\, d\theta \\ - \beta \int_0^t \exp(\gamma^2\theta) \operatorname{erfc}(\gamma\theta^{1/2})\, d\theta \end{array}\right] \quad (38)$$

The integrals in (38) can be readily evaluated by integration by parts, and equation 18 is thus obtained.

Acknowledgment.—The authors are indebted to the Office of Naval Research for the support of this investigation. They wish to thank Dr. W. Vielstich for his coöperation in some of the experimental work.

(14) (a) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, Oxford, 1947; (b) R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., New York, N. Y., 1944.

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

The Mechanism of the Thermal Decomposition of Methyl Ethyl Ketone

BY CHAS. E. WARING AND MARSHALL SPECTOR[1]

RECEIVED AUGUST 4, 1955

The thermal decomposition of gaseous methyl ethyl ketone has been investigated in the presence of various inhibitors. Nitric oxide was found to catalyze the decomposition while propylene reduced the rate to a limiting value. The amount of inhibition in the presence of propylene was found to be dependent upon the partial pressure of ketone, indicating that the chain propagating step must be bimolecular. A chain mechanism is proposed that is in accord with the experimental facts.

Introduction

A previous paper[2] has reported that the rate of the thermal decomposition of methyl ethyl ketone, like that of acetone,[3] was markedly catalyzed, rather than inhibited, by the addition of nitric oxide. At low partial pressures of NO (*ca.* 5 mm.) a slight inhibition was detectable in the initial stage of the MeEtCO reaction, indicating that free radicals were, perhaps, produced to some extent. However, since the magnitude of the inhibition was so small or, at least, masked by the strong catalytic effects, it seemed reasonable to assume that chain processes did not play an important role in the reaction. Consequently, the authors postulated a rearrangement mechanism for the decomposition that was in agreement with the reaction products.

More recently[4] it has been shown that the rate of diethyl ketone, unlike that of acetone and methyl ethyl ketone, is reduced to a limiting value by the addition of small amounts of NO. This limiting rate was reproducible and no catalytic effect was observed out to 20 mm. partial pressure of inhibitor. This unexpected result raised the question as to the difference between the mechanism of decomposition of diethyl ketone and the two lower members of the series. In view of their behavior toward nitric oxide, one is tempted to postulate that the decomposition of acetone and methyl ethyl ketone proceed through a rearrangement rather than a free radical mechanism. However, Smith and Hinshelwood[5] have shown that propylene inhibits the acetone decomposition, thus indicating the presence of free radicals.

As a first step in resolving these differences, it was thought worthwhile to reinvestigate the decomposition of methyl ethyl ketone in the presence of various inhibitors and to evaluate the decomposition mechanism proposed by the previous authors[2] in the light of our results.

Experimental

A. Material.—Technical grade methyl ethyl ketone was fractionated through a four-foot vacuum-jacketed, helices-packed column having a ten-to-one reflux ratio. The fraction distilling over at a constant temperature of 78.9° was collected and stored in a cool, dark place over anhydrous potassium carbonate, a drying agent found by Lochte[6] to have no tendency to cause internal condensation. The measured index of refraction at 23° was 1.3762, which compared favorably with the literature value of 1.3765 at the

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[1] Presented in partial fulfillment of the requirements for the Master of Science Degree at the University of Connecticut.

[2] C. E. Waring and W. E. Mutter, THIS JOURNAL, **70**, 4073 (1948).

[3] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A149**, 340 (1935).

[4] C. E. Waring and C. S. Barlow, THIS JOURNAL, **71**, 1519 (1949).

[5] R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A183**, 33 (1944).

[6] H. L. Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).

same temperature. During the course of the investigation the index of refraction was checked regularly and no variation was detected.

Nitric oxide was generated in the absence of oxygen by the action of concentrated nitric acid on C.P. mercury in the presence of a few cc. of concentrated sulfuric acid. The NO was stored under positive pressure in its original reaction chamber and before use was passed through anhydrous $CaSO_4$ and a trap surrounded by a solid CO_2–acetone mush.

Chemically pure propylene from a cylinder was first liquefied in a trap in the reaction system and then subjected to vacuum distillation. The distillate was stored in a previously evacuated flask until used.

The nitrogen employed was a commercial product which had been previously treated by standard methods to remove traces of oxygen and water vapor.

B. **Apparatus.**—The course of reactions was followed by a static manometric method in a reaction system previously described.[2] No run was made if the pressure was greater than 10^{-5} mm.

The reaction flask was maintained at constant temperature to within ±0.05° by a thyratron control system.[7,8]

A calibrated platinum–platinum-rhodium thermocouple was placed in contact with the reaction bulb at its largest diameter and temperatures were measured with a Type K_2 potentiometer in conjunction with a sensitive optical lever galvanometer.

Data and Results

1. **Nature of the Decomposition.**—Methyl ethyl ketone was found to decompose thermally at a conveniently measurable rate between 540 and 630°. For the purposes of this investigation the temperature of 550° was selected since at higher temperatures propylene undergoes appreciable decomposition. The reaction, as previously reported,[2] was found to be homogeneous and of the first order down to about 50 mm. initial pressure; below this the order approached that of second. This effect is shown in Fig. 1 where the reciprocals of the times for a 50% initial pressure increase are plotted against the initial ketone pressures. The times for 25, 50, 75 and 100% initial pressure increases at 550° all agreed well with those found by the previous authors[2] at the same temperature. In view of this and the fact that the average ratio of the final to the initial pressure, P_f/P_i, above 50 mm. initial pressure, was found to be 2.71, as compared to the previously determined value of 2.75, it was assumed that the same experimental conditions were being reproduced.

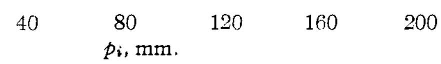

Fig. 1.—p_i *vs.* $1/t_{50\%}$ (T = 550°).

2. **Effect of Nitric Oxide.**—Figure 2 confirms the fact that NO strongly catalyses the decomposition of methyl ethyl ketone. The fact that none of the curves pass through the origin suggests that some slight inhibition may occur below 1.0 mm. pressure of NO. Since ketenes are produced in appreciable quantities in this decomposition, the catalytic effect is most likely due to the interaction of NO with the highly reactive ketenes to form oxidation products.

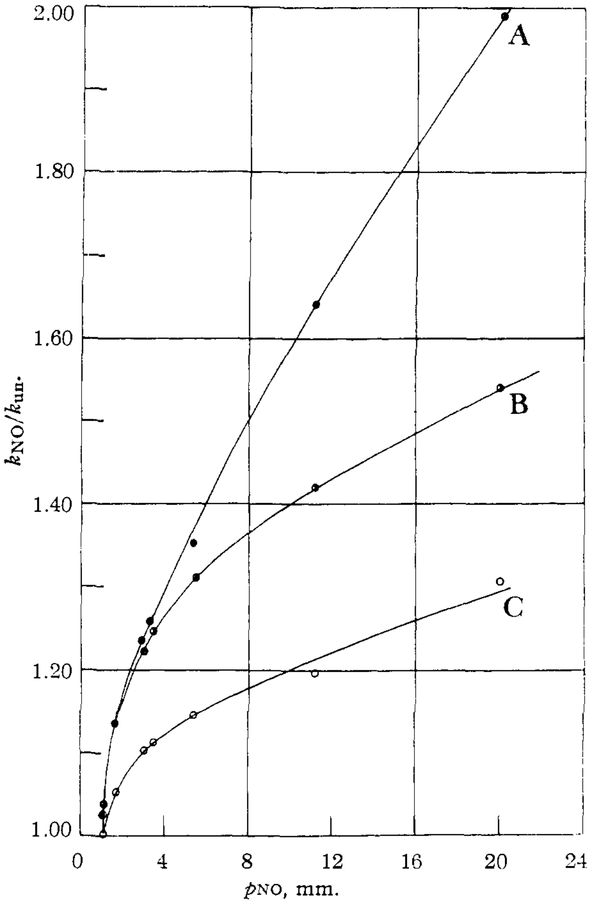

Fig. 2.—p_{NO} *vs.* k_{NO}/k_{un} (p_{ketone} = 100 mm.; T = 550°): ●, (A)$t_{100\%}$; ◑, (B) $t_{50\%}$; ○, (C) $t_{25\%}$.

3. **Effect of Propylene.**—The effect of propylene as an inhibitor was studied at three different initial pressures of methyl ethyl ketone and the results are presented in Fig. 3. It is seen that propylene reduces the rate to a definite, limiting value, and that the amount of inhibition at any given partial pressure of propylene is dependent upon the ketone pressure. This inhibition is evidence that free radicals are, indeed, produced in the decomposition of methyl ethyl ketone. The curves also indicate that above 50 mm. initial pressure of ketone the limiting rate is approximately 50% that of the uninhibited reaction. Since propylene reduces the rate to a limiting value, and not to zero, it is concluded that the reaction remaining after the chain processes have been removed proceeds through a rearrangement process.

Much more propylene is required to inhibit completely the decomposition than is normally required in nitric oxide inhibited reactions. Thus propylene may be less efficient than NO as an inhibitor. It

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[7] C. E. Waring and G. Robison, *Rev. Sci. Inst.*, **14**, 143 (1943).

[8] S. Steingiser, G. J. Rosenblitt and C. E. Waring, *ibid.*, **19**, 815 (1948).

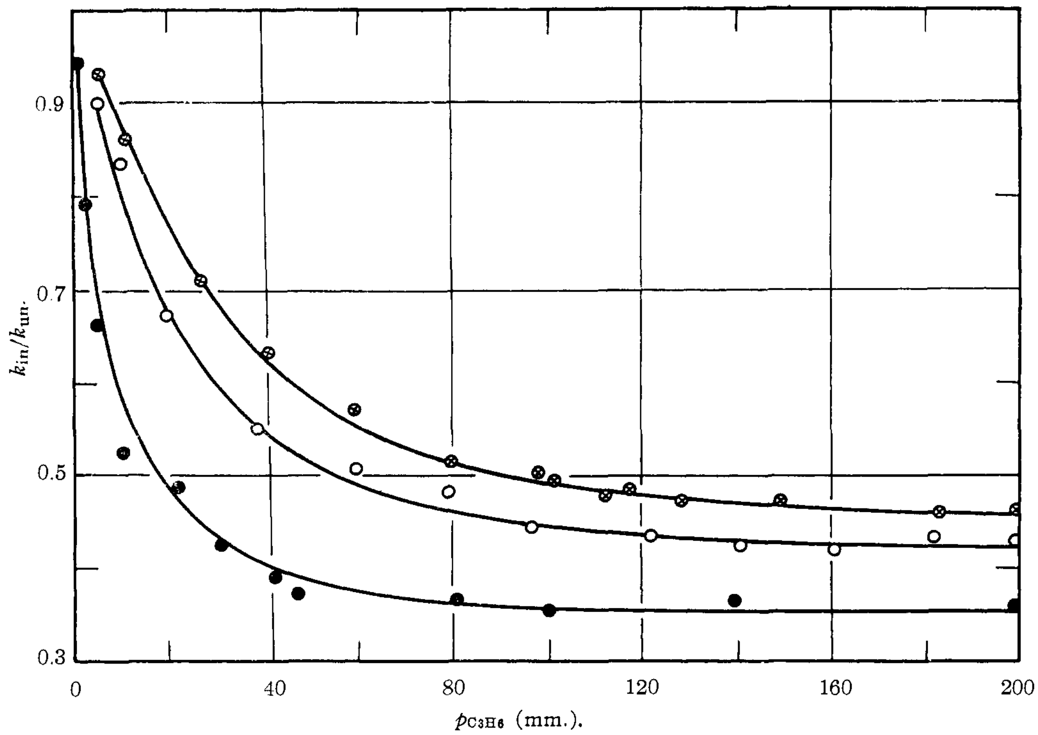

Fig. 3.—$p_{C_3H_6}$ *vs.* k_{in}/k_{un} (T = 550°); ⊕, 50 mm. ketone; ○, 100 mm. ketone; ●, 150 mm. ketone.

is interesting to note that propylene shows no tendency to catalyze the reaction out to 200 mm. partial pressure of inhibitor.

At 550° propylene itself undergoes no appreciable decomposition during the first 15 minutes reaction time. Since this is greater than the time for a 100% initial pressure increase, no correction was made. On the other hand, propylene gives a 27.6% increase in initial pressure at this temperature after 12 hours, by which time, however, the decomposition of methyl ethyl ketone is practically complete. In this case, appropriate corrections were made in computing the P_f/P_i values for the inhibited reaction.

The mean chain lengths at various initial pressures of methyl ethyl ketone were computed by dividing the relative rate constants of the uninhibited reaction by those of the fully inhibited. These values are presented in Table I together with those for acetone with propylene as an inhibitor.

TABLE I

MEAN CHAIN LENGTHS (k_{un}/k_{in})

Pressure (mm.)	Acetone	Methyl ethyl ketone
50	3.2	2.8
100	3.4	2.3
150	3.4	2.2

$\left(k \propto \frac{1}{t_{50\%}}\right)$

4. **Effect of Nitrogen.**—Since large amounts of propylene are required to reduce the decomposition to a limiting rate—as compared to nitric oxide inhibited reactions—there existed the possibility that propylene might be producing a simple mass action effect. To test this, purified nitrogen was added in varying amounts and the rates determined. The rates in all cases remained unchanged up to 200 mm. partial pressure of nitrogen, indicating that the effect of propylene was due to the removal of free radicals rather than to a pressure effect.

It was thought worthwhile to see if the ratio of the final to the initial pressure was affected by the addition of foreign gases. Consequently, the P_f/P_i ratio was determined at various initial pressures of ketone in the presence of nitric oxide and propylene. Figure 4 shows that this ratio remains unchanged. This suggests that the same products are formed in the presence of these foreign gases as in the uninhibited decomposition. More significant, perhaps, is the inference that the chain and rearrangement processes produce the same quantity of products.

5. **Effect of Surface.**—To test the effect of surface, experiments were conducted in a reaction bulb packed with quartz beads of uniform diameter. The surface/volume ratio of the packed to unpacked bulb was 16:4. After the packed bulb became conditioned, no significant difference in rate between the packed and unpacked bulbs could be observed.

6. **Discussion.**—The fact that the limiting rate of the inhibited decomposition is dependent upon the initial pressure of methyl ethyl ketone indicates that the chain propagator is being produced by a reaction of the type

$$R + M \longrightarrow R' + M'$$

Such a process would necessarily be pressure dependent since the inhibitor would be competing on equal terms with the ketone, M, for the free radical, R. If one assumes that free methyl radicals are produced initially from the decomposition of methyl ethyl ketone, these radicals would be expected to remove a hydrogen atom from the

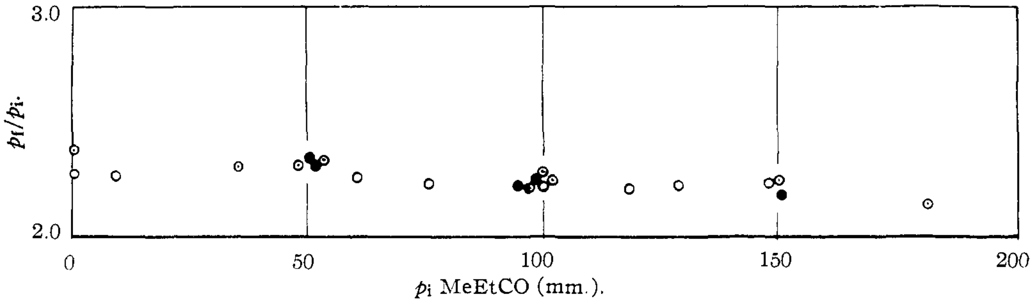

Fig. 4.—p_i MeEtCO *vs.* p_t/p_i (T = 550°): ⊙, uninhibited: ●, propylene inhibited; ◑, NO inhibited; ○, uninhibited—Waring and Mutter.

ketone to produce methane and a large free radical. This latter, of course, undoubtedly would decompose almost instantly to give a methyl radical and stable molecules.

Methyl ethyl ketone possesses eight hydrogens which the methyl radical may remove. According to Rice,[9] there are three different kinds of carbon–hydrogen bonds in this molecule and each has a different reaction probability. If one assigns a probability of three to the primary C–H bonds beta to the carbonyl, six to the primary C–H bonds alpha to the carbonyl, and eight to the secondary C–H bonds alpha to the carbonyl, the following chain mechanism can be written for the thermal decomposition of methyl ethyl ketone

P-3 Reaction

$$CH_3COCH_2CH_3 \longrightarrow CH_3 + CH_3CH_2CO \quad (1)$$

$$CH_3CH_2CO \longrightarrow C_2H_5 + CO \longrightarrow CO + C_2H_4 + H \quad (2)$$

$$CH_3 + CH_3COCH_2CH_3 \longrightarrow CH_4 + CH_3COCH_2CH_2 \longrightarrow CH_4 + C_2H_4 + CO + CH_3 \quad (3)$$

On the assumption that the chains are short and that all methyl and hydrogen radicals produced eventually end up as methane and hydrogen molecules, the over-all P-3 reaction becomes

$$2CH_3COCH_2CH_3 \longrightarrow 2C_2H_4 + 2CH_4 + 2CO + {}^1/_2H_2$$

Assuming steps (1) and (2) to be identical for all cases, step (3) for the P-6 reaction becomes

$$CH_3 + CH_3COCH_2CH_3 \longrightarrow CH_4 + CH_2COCH_2CH_3 \longrightarrow CH_4 + CH_2CO + C_2H_5 \quad (3a)$$

$$C_2H_5 \longrightarrow C_2H_4 + H \quad (3b)$$

The over-all P-6 reaction then is

$$2CH_3COCH_2CH_3 \longrightarrow 2C_2H_4 + CO + CH_2CO + H_2 + CH_4$$

For step (3) in the P-8 reaction

$$CH_3 + CH_3COCH_2CH_3 \longrightarrow CH_4 + CH_3COCHCH_3 \longrightarrow CH_4 + CH_3CHO + CH_3$$

whence the over-all P-8 is

$$2CH_3COCH_2CH_3 \longrightarrow 2CH_4 + CH_3CHCO + CO + C_2H_4 + {}^1/_2H_2$$

From the number of moles of products formed in each of the above three over-all reactions, one can calculate the mole percentage of each product present. If one now adjusts the percentages of products from the P-3, P-6 and P-8 reactions in accordance with their respective reaction probabilities of 17.6, 35.3 and 47.1, then one obtains the contribution of each of these reactions to the total products. Table II compares the experimental products of reactions after 30 seconds reaction time with those calculated in the manner described.

TABLE II

Mole %	Exptl.	Theo.
CH_4	29.1	28.4
CO	26.6	19.9
C_2H_4	27.8	25.7
H_2	4.1	11.5
Ketene	11.0	14.5
CO_2	1.6	0.0
	100.2	100.0

Table II reveals a remarkably good agreement between the experimental values and those obtained theoretically.

It is seen immediately that the greatest discrepancy lies in the amount of hydrogen predicted and that actually found at 30 seconds reaction time. This difference is most probably due to the fact that initially an appreciable amount of the hydrogen produced may be absorbed on the walls of the reaction flask which, when "conditioned," are coated with carbon. In support of this, it is interesting to note that at three minutes reaction time previous investigators[2] report that the concentration of hydrogen increased to a maximum of 10%. While this close concordance is by no means "proof" that the postulated mechanism is the correct one, it indicates, nevertheless, that a reasonable mechanism for the decomposition of methyl ethyl ketone can be devised which is not in disagreement with the experimental facts. All attempts to write alternate mechanisms such as

$$CH_3COCH_2CH_3 \longrightarrow CH_3 + CH_3COCH_2$$

for example, lead to large variations between the experimentally and theoretically determined products of reaction. In view of the almost identical activation energies for methyl ethyl ketone (67.2 kcal.) and acetone (68.0 kcal.) it does not seem unreasonable to conclude that the initial bond rupture is the same in both cases, namely, at the methyl–carbonyl bond.

In any theoretical reaction mechanism, marked differences in the products will result depending upon whether long or short chains are assumed. The question naturally arises as to whether the assumption here of short chains is justified. This is important since without this assumption the

[9] F. O. Rice, THIS JOURNAL, 56, 488 (1934).

products from step (2) would not ordinarily be expected to make a significant contribution to the total reaction products. This, of course, results from the fact that if the chains are long, step (1) and hence (2), would represent only a small per cent. of all the reactions occurring. That the chains in this reaction are short may be deduced from the experiments conducted in a packed reaction flask. The fact that no reduction in rate was observed is good evidence that the thermal decomposition of methyl ethyl ketone proceeds through a short chain mechanism.

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STORRS, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Kinetics of Hot Deuterium Atoms in the Photolysis of Deuterium Iodide[1,2]

BY ROBERT J. CARTER,[3] WILLIAM H. HAMILL AND RUSSELL R. WILLIAMS, JR.

RECEIVED AUGUST 5, 1955

Deuterium atoms with large kinetic energy have been produced by photolysis of gaseous deuterium iodide. The reaction of these hot deuterium atoms with hydrogen, methane, ethane and neopentane has been studied as a function of composition, wave length, temperature and added rare gas. With hydrogenous substrates the ratio of hot atom reaction producing HD to moderation producing thermal D atoms has been measured. The variation of the ratio D_2/HD with experimental conditions is described by a simple mechanism. Efficiencies of moderators are correlated with their molecular properties.

Introduction

The role of hot hydrogen atoms in the photolysis of hydrogen iodide at 2537 Å. has been described by Schwarz, Williams and Hamill[4] who found that the yield of hydrogen was significantly and systematically influenced by dilution with rare gases. In that study the products of hot atom reactions were chemically indistinguishable from the products of thermal atom reactions. That limitation has been removed in the present work by using deuterium iodide as the source of hot deuterium atoms which act upon various substrates containing protium. In this way, the product of hot atom reaction with the substrate (HD) can easily be distinguished from the product of reaction (hot or thermal) with deuterium iodide (D_2).

The results are examined in the framework of a mechanism analogous to that proposed in the previous study, with the addition of steps taking account of the hot atom reaction with and moderation by the substrate, designated in general by RH.

$$\mathrm{DI} + h\nu \longrightarrow \mathbf{D} + \mathrm{I} \qquad (1)$$

$$\mathbf{D} + \mathrm{DI} \longrightarrow \mathrm{D_2} + \mathrm{I} \quad \kappa_3 \qquad (2)$$

$$\mathbf{D} + \mathrm{RH} \longrightarrow \mathrm{HD} + \mathrm{R}\cdot \quad \kappa_3 \qquad (3)$$

$$\mathrm{R}\cdot + \mathrm{DI} \longrightarrow \mathrm{RD} + \mathrm{I} \qquad (4)$$

$$\mathbf{D} + \mathrm{DI} \longrightarrow \mathrm{D} + \mathrm{DI} \quad \kappa_5 \qquad (5)$$

$$\mathbf{D} + \mathrm{RH} \longrightarrow \mathrm{D} + \mathrm{RH} \quad \kappa_6 \qquad (6)$$

$$\mathbf{D} + \mathrm{M} \longrightarrow \mathrm{D} + \mathrm{M} \quad \kappa_7 \qquad (7)$$

$$\mathrm{D} + \mathrm{DI} \longrightarrow \mathrm{D_2} + \mathrm{I} \qquad (8)$$

$$\mathrm{D} + \mathrm{RH} \longrightarrow \mathrm{HD} + \mathrm{R} \qquad (9)$$

$$\mathrm{I} + \mathrm{I} + \mathrm{M} \longrightarrow \mathrm{I_2} + \mathrm{M} \qquad (10)$$

The **D** designates a hot deuterium atom. Processes 2 and 3 are the hot atom reactions with DI and substrate, respectively, and similarly κ implies that the quantity measured is the net probability of reaction before thermalization. Processes 5, 6 and 7 are those of moderation (thermalization). RH represents hydrogen, methane, ethane or neopentane while M in process 7 represents a rare gas. Processes 8 and 9 are the reactions of thermal atoms but in most of this work the ratio DI/RH is such that process 9 may be neglected. Further it seems reasonable to neglect process 5, since the heavy DI molecule should be a very poor moderator for D atoms.

Applying the ordinary steady-state treatment to D and for the present neglecting the production of HD by process 9, the following expression of the ratio of rates of production of isotopic hydrogen molecules is obtained

$$\frac{\mathrm{D_2}}{\mathrm{HD}} = \frac{\kappa_2}{\kappa_3} \times \frac{(\mathrm{DI})}{(\mathrm{RH})} + \frac{\kappa_6}{\kappa_3} + \frac{\kappa_7}{\kappa_3} \times \frac{(\mathrm{M})}{(\mathrm{RH})} \qquad (11)$$

This relation has been applied to the treatment of the results described below.

Experimental

Materials.—Deuterium iodide was prepared from the elements[5] on platinized asbestos at 300°. After several preparations to purge the system, it was possible to obtain DI containing as little as 2.0 mole % HI. Methane, ethane and neopentane were Phillip's Research Grade materials. Hydrogen, neon and helium were obtained from Matheson and were tested for absence of oxygen.

Apparatus.—Most of the photolyses were carried out at room temperature (25°) using the 2537 Å. mercury resonance radiation from a Hanovia SC 2537 lamp. The photolysis cells were cylindrical Vycor tubes having a volume of about 40 ml. The Vycor (Corning 7910) glass served as a filter for 1849 Å. radiation.

In some experiments quartz cells were used in order to admit 1849 Å. radiation. In still another series of runs a quartz cell was irradiated with a General Electric A-H6 capillary mercury arc through a benzene filter. In this case measurement of the spectral intensity combined with the measured absorption coefficients of hydrogen iodide and benzene permitted the estimate of energy absorption *versus* wave length shown in Fig. 1. It is estimated that the average wave length of light absorbed was 2950 Å.

Some experiments were conducted at 100° by enclosing the reaction cell in a quartz steam jacket.

Procedures.—Reaction mixtures were prepared by measuring pressures of reagents in a known volume, followed by condensation into the previously evacuated reaction cell.

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[1] From the doctoral dissertation of R. J. Carter, June, 1955.

[2] Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955.

[3] Eastman Kodak Fellow, 1954–1955.

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

[5] Deuterium gas, 99.66 mole % obtained from Stuart Oxygen Co., on authorization by the U.S.A.E.C.