[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MANCHESTER]

The Reactions of Methyl Radicals with Acetone

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The kinetics of the radical reaction (2) have been investigated, methyl radicals being generated by the thermal decomposition of di-*t*-butyl peroxide. The activation energy of (2) has been estimated at 9.5 ± 1.5 kcal./mole. This value and the value for $k_2/k_3^{1/2}$ (k_3 being the rate constant for the bimolecular recombination of methyl radicals) are in fair agreement with those reported recently by Trotman-Dickenson and Steacie, who used a photochemical method for the generation of methyl radicals.

An extensive study of reactions of the type

$$RH + \cdot CH_3 \longrightarrow R\cdot + CH_4 \qquad (1)$$

has recently been carried out by Trotman-Dickenson and Steacie.[1] These authors have determined the activation energies and pre-exponential factors corresponding to various substrates, RH, by comparing the rate of reaction (1) with the rate of reaction (2)

$$CH_3COCH_3 + \cdot CH_3 \longrightarrow CH_3COCH_2\cdot + CH_4 \quad (2)$$

Reaction 2 was investigated by many workers. Most of the studies being carried out by photolytic technique, and in view of the great importance of this reaction, we consider it useful to reinvestigate it by using a different technique and a different source of methyl radicals. The thermal decomposition of di-*t*-butyl peroxide seems to be a convenient generator of methyl radicals, and thus we investigated this decomposition in the presence of acetone. We have applied the technique described previously by Murawski, Roberts and Szwarc,[2] and we refer the reader to this paper for all the details of experimental procedure.

The Kinetics of the Decomposition of Di-*t*-butyl Peroxide.—The system di-*t*-butyl peroxide/acetone seems to be relatively simple. The decomposition of di-*t*-butyl peroxide takes place according to the well established scheme, proved by the work of Rust, Vaughan and their colleagues,[3] namely

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (4)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (5)$$

Methyl radicals, generated in reaction (5), either dimerize

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (3)$$

or react with acetone[4] producing methane according to reaction (2)

$$CH_3COCH_3 + \cdot CH_3 \longrightarrow CH_3COCH_2\cdot + CH_4 \quad (2)$$

It has been demonstrated by Raley, Rust and Vaughan[3] that the $CH_3CO{\cdot}CH_2\cdot$ radicals produced in reaction (2) recombine with methyl radicals to form methyl ethyl ketone

$$CH_3COCH_2\cdot + CH_3\cdot \longrightarrow CH_3COCH_2CH_3 \quad (6)$$

According to the above scheme, the rate of decomposition of di-*t*-butyl peroxide is measured by the rate of formation of $C_2H_6 + CH_4$.

$$-d(\text{peroxide})/dt = d(CH_4 + C_2H_6)/dt$$

On this basis we calculated from our present results the unimolecular rate constants of the thermal decomposition of di-*t*-butyl peroxide which are listed in Table I.

TABLE I

Expt.	Temp., °C.	Di-*t*-butyl peroxide 10^3 mole/l.	Acetone 10^3 mole/l.	Reaction time, min.	Decomp. of peroxide, %	$k \times 10^5$, sec.$^{-1}$
20	126.5	2.0	14	120	5.2	0.74
26	127	2.5	6.6	120	4.9	.70
27	127	1.4	13	240	9.9	.72
23	127.5	2.4	12	120	5.2	.74
25	127.5	1.6	14	240	10.3	.75
24	129	2.5	13	180	9.4	.91
21	131	1.7	14	200	12.7	1.13
22	131	1.2	7.2	200	12.3	1.10
18	146	0.54	15	100	30	6.0
19	147	.49	3.4	100	29	5.7
5	148	.77	4.2	75	26	6.7
7	148	.88	1.5	30	13.0	7.7
6	149	1.5	7.7	35	15.3	7.9
3	150	0.60	9.7	75	35	9.5
4	150	.68	9.4	75	33	9.0
30	151.5	.77	14	50	26	10.3
8	152	.48	15	60	33	11.5
10	152	.31	21	90	49	12.3
28	152	.53	14	64	36	11.8
9	153	.27	21	110	61	14.4
29	154	.86	5.6	30	22	13.9
16	162	.49	18	18	32	36
17	164.5	.51	18	18	35	41
34	165	.39	8.6	23	44	42
13	165	.29	16	18	38	45
14	165.5	.50	17	16	36	47
15	167	.52	9.4	16	41	55
31	167	.46	16	17	41	52
33	168.5	.33	7.8	18	45	55
12	169	.33	7.7	16	45	62
32	169	.37	9.5	16	44	60
11	175	.15	3.9	18	74	125

These unimolecular rate constants are independent of the initial concentration of peroxide, of the initial concentration of acetone and of the time of heating. Moreover, the present results compare well with those reported previously by Roberts and Szwarc,[2,5] who investigated this decomposition in the presence of toluene. The agreement between these two investigations is excellent within the higher temperature range. At lower temperatures, the rate constants obtained in the experiments in which acetone was present are slightly lower than those obtained in the experiments carried out in the presence of toluene.

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[1] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950); **19**, 163, 169, 329 (1951).

[2] J. Murawski, J. S. Roberts and M. Szwarc, *ibid.*, **19**, 698 (1951).

[3] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 88 (1948).

[4] In our experiments acetone was always in excess.

[5] M. Szwarc and J. S. Roberts, *J. Chem. Phys.*, **18**, 561 (1950).

The plot of the logarithm of the unimolecular rate constant against $1/T$ is given in Fig. 1. The "best" straight line corresponds to an activation energy of 37 kcal./mole. The activation energy reported by Roberts and Szwarc[2,5] (the result of an investigation carried out in a static system in the presence of toluene) is 34 ± 2 kcal./mole, the results of Murawski, Roberts and Szwarc[2] (obtained by a flow technique) lead to an activation energy of 36 ± 1 kcal./mole, and the value reported by Raley, Rust and Vaughan[3] is 39 kcal./mole. In spite of these small differences in the observed activation energies, we infer that in all these decompositions the rate of the same initial process generating methyl radicals has been measured, since the absolute rate constants reported in all these studies agree very well.[5a]

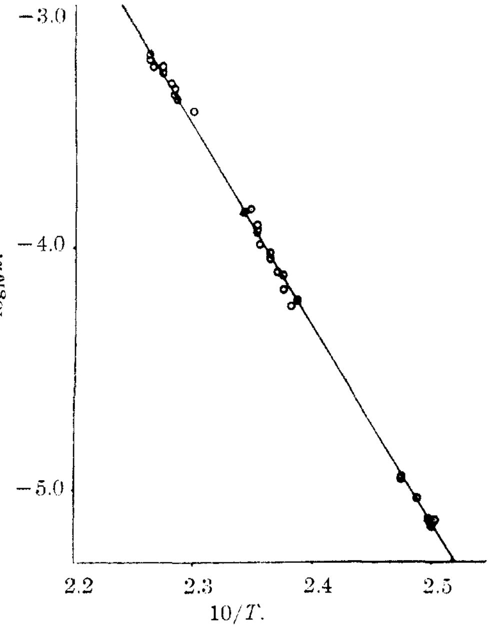

Fig. 1.—$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$.

The Rate of the Reaction (2).—Since all the evidence indicates that methane is produced by reaction (2) and that ethane is formed in the bimolecular recombination (3) we may calculate the ratio $k_2/k_3^{1/2}$ from the equation

$$k_2/k_3^{1/2} = (\text{rate of formation of } CH_4)/(\text{rate of formation of } C_2H_6)^{1/2}\,[\text{acetone}] =$$

$$(\text{amount of } CH_4 \text{ formed})/\{(\text{amount of } C_2H_6 \text{ formed}) \times t^{1/2} \times [\text{acetone}]\}$$

t denoting the time of reaction. This derivation neglects the correction for the slight time dependence of the stationary concentration of methyl radicals,[6] this correction being quite small. The values of $k_2/k_3^{1/2}$ are listed in Table II. For a given temperature, $k_2/k_3^{1/2}$ remains constant even if the conditions of experiments are changed in such a manner that the ratio of CH_4/C_2H_6 which are produced in the decomposition varies by a factor of 5.

Table II

Expt.	Temp., °C.	Molar ratio, acetone/peroxide	CH_4, mmoles	C_2H_6, mmoles	$k_2/k_3^{1/2}$, cc.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$
20	126.5	7.0	1.33	0.97	0.25
26	127	2.7	0.93	1.71	.27
27	127	9.4	1.87	1.11	.24
23	127.5	5.1	1.46	1.30	.26
25	127.5	8.6	2.34	1.33	.26
24	129	5.4	2.85	2.27	.29
21	131	8.0	2.88	1.89	.29
22	131	5.8	1.53	1.84	.30
18	146	28	2.46	1.19	.42
19	147	7.0	0.91	2.23	.49
5	148	5.5	1.21	3.2	.51
6	149	5.0	1.52	3.5	.49
3	150	16	2.25	2.33	.48
4	150	14	2.35	2.65	.49
30	151.5	18	2.48	1.98	.48
8	152	31	2.18	1.29	.46
28	152	27	2.60	1.63	.49
29	154	6.5	1.09	3.1	.56
16	162	36	2.02	1.43	.62
17	164.5	35	2.32	1.66	.66
34	165	22	1.55	2.24	.69
13	165	55	1.55	0.92	.66
14	165.5	34	2.24	1.77	.68
15	167	18	1.79	2.94	.76
31	167	34	2.27	1.92	.70
33	168.5	22	1.40	2.13	.80
12	169	23	1.28	2.02	.81
32	169	25	1.52	2.06	.78
11	175	25	0.78	1.73	.99

The plot of log $(k_2/k_3^{1/2})$ against $1/T$ is given in Fig. 2. The "best" straight line corresponds to

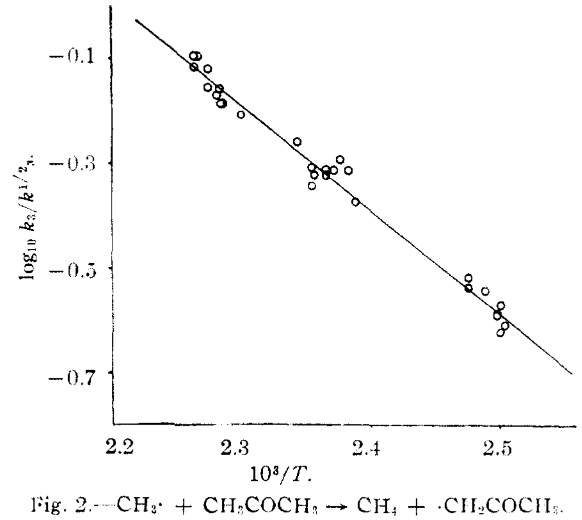

Fig. 2.—$CH_3\cdot + CH_3COCH_3 \rightarrow CH_4 + \cdot CH_2COCH_3$.

Table III

T, °C.	Steacie and Trotman-Dickenson[a] $k_2/k_3^{1/2}$, cc.$^{1/2}$ sec.$^{-1/2}$ moles$^{-1/2}$	Jaquiss, Roberts and Szwarc $k_2/k_3^{1/2}$, cc.$^{1/2}$ sec.$^{-1/2}$ moles$^{-1/2}$
121	0.27	0.20
131	.37	.30
150	.63	.50
167	.99	.75

[a] The values listed in the second column of this table were obtained from the graph reported by Trotman-Dickenson and Steacie for acetone pressure of 100 mm.

[5a] A paper by Lossing and Tickner, *J. Chem. Phys.*, **20**, 907 (1952), appeared after the present communication was sent for publication. These authors extended the temperature range of the decomposition of di-*t*-butyl peroxide up to 350°, and they found that their results, Murawski, Roberts and Szwarc results, and Raley, Rust and Vaughan results give a set of mutually consistent data.

[6] M. Szwarc, *ibid.*, **19**, 296 (1951).

$E_2 - {}^1/_2E_3 = 9.5$ kcal./mole and we consider this value to be correct within 1.5 kcal./mole. We note the very good agreement between this value and that reported by Trotman-Dickenson and Steacie[1] (9.7 ± 0.1 kcal./mole). The values of $k_2/k_3^{1/2}$ obtained by us are lower by about 25% than those recorded by Trotman-Dickenson and Steacie (see Table III).

The agreement in the estimated activation energy and the observed rates for the processes producing methane in the photolytic system investigated by Trotman-Dickenson and Steacie and in the pyrolytic system investigated by us is particularly gratifying. It assures us that we do indeed measure the activation energy for the radical reaction (2).

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The Kinetics of Hot Hydrogen Atoms in the Photolysis of the Hydrogen Halides[1-3]

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The photolyses of hydrogen iodide, deuterium iodide and hydrogen bromide were studied in the presence of added inert gases. The inhibiting effect of the free halogens was found to be a function of the concentration of inert gas, the effect being independent of its nature at large pressure of inert gas. The results are interpreted in terms of hot atom mechanisms. The moderating effect of the inert gas is accounted for semi-quantitatively and the difference of activation energies between the thermal reactions, $E_1 - E_2$: [$H + HI \rightarrow H_2 + I$, k_1; $H + I_2 \rightarrow HI + I$, k_2] is found to be 4.5 ± 0.8 kcal. mole^{-1}.

Introduction

The photodissociation of the hydrogen halides with light of λ 2537 Å. yields hydrogen atoms with considerable kinetic energy, since the bond strength is much less than the quantum energy and this energy difference will be divided in the inverse ratio of the atomic masses. In the case of hydrogen iodide, spectral investigations[5,6] indicate the production of the $^2P_{3/2}$ state of the iodine atom and, therefore, hydrogen atoms of *ca.* 42 kcal. mole^{-1} excess energy should be produced. The inhibitory effect of iodine in this photolysis, represented by the ratio $k_2/k_1 = 3.8$ (independent of temperature) in pure hydrogen iodide[7] increases to a value of 7.0

$$H + HI \longrightarrow H_2 + I \quad k_1$$
$$H + I_2 \longrightarrow HI + I \quad k_2$$

at pressures of cyclohexane greater than 300 mm.[8] This effect was attributed to the moderation of the hot hydrogen atoms by cyclohexane and appropriate reactions were added to the classical mechanism

$$\mathbf{H} + HI \longrightarrow H_2 + I \quad k_3$$
$$\mathbf{H} + I_2 \longrightarrow HI + I \quad k_4$$
$$\mathbf{H} + M \longrightarrow H + M \quad k_5$$

where **H** is a hot hydrogen atom and M the moderating substance.

In a similar fashion, the photolysis of hydrogen bromide should yield hydrogen atoms of *ca.* 26 kcal. mole^{-1} excess energy. In this case, the inhibition constant k_7/k_6 has not been measured

$$H + HBr \longrightarrow H_2 + Br \quad k_6$$
$$H + Br_2 \longrightarrow HBr + Br \quad k_7$$

directly, but is expected to have a value of 8.6, independent of temperature, from experiments on the photobromination of hydrogen.[9]

It is the purpose of the present work to investigate more extensively the effect of inert diluents on these photolyses in the light of the hot atom mechanism previously proposed.

Experimental

The extent of photolysis was measured through titration of the halogen produced. The high degree of precision required in the analyses did not permit initial additions of halogen to the reaction mixture, which consisted of the hydrogen halide with various amounts of inert gas. Four photolyses were conducted simultaneously in four quartz cells held in rigid positions with respect to each other and rotated past a light source. In each group one cell, containing only the hydrogen halide, was used as an actinometer for the other three, which contained added moderator. The relative extents of photolysis in the various cells could be repeated with a reproducibility of 1%, but since the quantity of interest, the inhibition constant, is obtained by a difference calculation (see equation 2), the reproducibility of this quantity is approximately 10%.

Apparatus.—Each quartz cell (35 × 75 mm.) was provided with a fused, quartz window (Fig. 1). The other end was constricted to 8–10 mm. and led to a graded seal. A side-arm was provided for freezing the hydrogen iodide while adding the inert gas. The cells were secured permanently in copper tubes soldered to a brass sleeve which could be fastened to a rotating steel shaft. The cells were rotated in a furnace at 140 r.p.m. No attempt was made to stabilize the speed of rotation since only the average value of the product (intensity) × (time) for each cell is significant. The cells passed the light source about 17,000 times during an experiment and even transient variations due to rotation or illumination were effectively averaged out.

The furnace consisted of an aluminum box about 150 mm. on each edge with two nichrome heating elements in opposite sides. A 35-mm. square window in the bottom of the furnace was covered with a quartz plate. Temperature was measured with a 360° thermometer in an aluminum sheath and was regulated within ±1° by manually adjusting a Variac.

The Hanovia Sc2537 lamp employed in this work is stated by the manufacturer to give about 85% of its light as the 2537 Å. resonance line.

Materials.—All reagents, including those used in preparations, were C.P. or analytical grade. Hydrogen iodide

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(1) From the doctoral dissertation of H. A. Schwarz.

(2) Presented at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952.

(3) Work supported in part under A.E.C. contract At(11-1)-38.

(4) A.E.C. Predoctoral Fellow, 1949–1951.

(5) C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc., London*, **154**, 181 (1936).

(6) J. Romand, *Compt. rend.*, **227**, 117 (1948).

(7) R. R. Williams, Jr., and R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 691 (1947).

(8) R. A. Ogg, Jr., and R. R. Williams, *ibid.*, **13**, 586 (1945).

(9) M. Bodenstein and G. Z. Jung, *Z. physik. Chem.*, **121**, 127 (1926).