MnO_2 (298–780°K.):

(1) $H_T - H_{298.16} = 16.60\ T + 1.22 \times 10^{-3}\ T^2 + (3.88 \times 10^5/T) - 6359$

(2) $C_p = 16.60 + 2.44 \times 10^{-3}\ T - (3.88 \times 10^5/T^2)$

(3) $S_T - S_{298.16} = 38.223 \log T + 2.44 \times 10^{-3}\ T + (1.94 \times 10^5/T^2) - 97.491$

$MnCO_3$ (298–660°K.):

(4) $H_T - H_{298.16} = 23.36\ T + 3.76 \times 10^{-3}\ T^2 + (5.69 \times 10^5/T) - 9208$

(5) $C_p = 23.36 + 7.52 \times 10^{-3}\ T - (5.69 \times 10^5/T^2)$

(6) $S_T - S_{298.16} = 53.789 \log T + 7.52 \times 10^{-3}\ T + (2.845 \times 10^5/T^2) - 138.540$

Equation (2) gives $C_p = 12.96$ at 298.16°K., in excellent agreement with the value obtained by Kelley and Moore, 12.92.[3] Equation (5) gives $C_p = 19.2$ at 298.16°K., whereas Anderson[4] obtained 19.5 at this temperature; this is satisfactory agreement, in view of the fact that the uncertainty in both methods of measurement is the greatest in this temperature region.

There appear to be no previous pertinent measurements on either of these substances in the temperature range investigated.

Summary

The heat contents of manganese dioxide and manganese carbonate above room temperature have been determined up to 505 and 320°, respectively.

The data have been summarized by means of tables and algebraic equations.

BERKELEY, CALIFORNIA RECEIVED APRIL 2, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Versatile Apparatus for Photolysis Studies in the Gas Phase. I. Acetone and Iodine Mixtures

BY SIDNEY W. BENSON AND GEORGE S. FORBES

The work of Gorin[1,2] and more recently Blacet and co-workers[3,4] on the photolysis of aldehydes and ketones in the presence of iodine vapor have yielded what is perhaps the most direct evidence available on the nature of the primary process in these reactions. Since the activation energy for the reaction of free radicals with iodine molecules is usually zero or close to zero, by working with a sufficient concentration of iodine vapor, all free radicals can be converted to iodides and secondary reactions reduced to a negligible factor. Identification of the iodides will then reveal the identity of the free radicals formed in the primary process.

In this manner Gorin[2] has established that at 3130 Å. the primary process in the photolysis of acetone is the formation of methyl and acetyl radicals. By a further comparison of the products with those formed in the absence of iodine he was able to arrive at a value for the quantum yield of this reaction of about 0.95.

It has been the aim of the present investigation to repeat Gorin's work at other wave lengths and under more favorable experimental conditions, and then extend it to further reactions. Unfortunately the present emergency has necessitated a halt in the work so that results of a preliminary nature only have been obtained for the photolysis of acetone at a wave length of 2537 Å.

To reduce secondary reactions as much as possible, it was decided to perform the photolysis in a flow system. This is especially desirable since both methyl iodide and acetyl iodide absorb slightly in the region around 2537 Å. Under the conditions of flow used the concentration of products in the light path never exceeded 1% of the reactants. In static systems this may frequently run as high as 20%. Because of the novelty of the flow system the experimental procedures are given in detail.

Experimental Procedures

Light Source.—Approximately monochromatic light (2537 Å.) was obtained from a specially constructed mercury resonance lamp (Fig. 1). Melville[5] has shown that it is possible to get an efficiency of 10% from a resonance lamp filled with neon or argon. About 90% of this output will be in the 2537 Å. resonance line,[6] obviating the necessity of filters or monochromators. The circular portion of the lamp (Fig. 1) was used as the emittor and was constructed by Macalaster-Bicknell Co., from fused quartz. The electrodes were mounted by the Hanovia Chem. Co., who also filled the lamp with mercury and argon at a pressure of 6 mm. The auxiliary lamp (Fig. 1) was designed after Thomas's[7] resonance lamp. This

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[1] Gorin, *Acta Physicochim.*, U. S. S. R., **9**, 681 (1938).

[2] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[3] Blacet and Heldman, THIS JOURNAL, **64**, 889 (1942).

[4] Blacet and Loeffler, *ibid.*, **64**, 893 (1942).

[5] Melville, *Trans Faraday Soc.*, **32**, 1525 (1936).

[6] Taylor, *J. Chem. Phys.*, **2**, 377 (1934).

[7] Thomas, *Rev. Sci. Instruments*, **12**, 309 (1941).

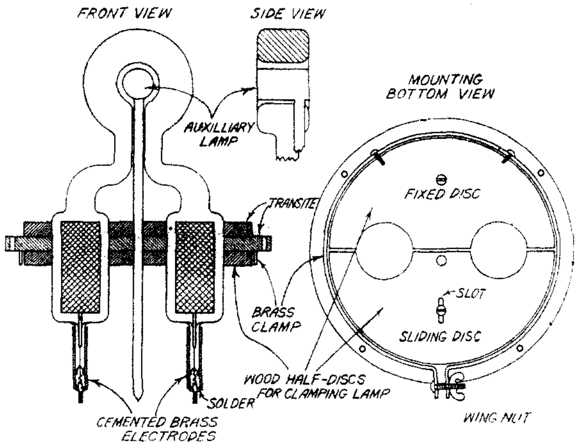

Fig. 1.—Resonance lamp and mounting.

auxiliary lamp will absorb resonance radiation from the large lamp and emit only the 2537 Å. line of purity exceeding 99.5%[7]. Measurements made with a Hilger thermopile showed it increased the intensity of the large lamp by about 13%.

The lamp and auxiliary lamp were housed in a closely fitted, polished aluminum reflector with 40-mm. holes adjacent to the circular section of the lamp. This eliminated stray reflection. The lamp and reflector were mounted in the reaction oven (Fig. 2) so that the electrodes remained outside and could be kept at room temperature by passing a stream of cold air over them. By splitting the reaction tube into two parts (Fig. 2) and mounting the lamp between them it was possible to use the radiation from both faces of the lamp.

The lamp was operated from a special 5000-volt transformer drawing a secondary current of 120 milliamperes. A Varitran autotransformer in the primary was used to vary the input. Measurements made with the Hilger thermopile showed the light output to be very nearly proportional to the current. The intensity within the reaction tubes along the axis perpendicular to the center of the lamp was nearly constant, owing to internal reflections. Outside the tubes, the intensity at 12 cm. was found to be about 5000 ergs/sq. cm.-sec. Measurements made with crystal quartz, fused quartz, and Pyrex filters showed that there was negligible intensity at 1849 Å., even over an air path of 2 cm. They also showed that about 93% of the light was below 3660 Å. and 90% below 3130 Å. Pictures taken at different exposures and light paths with a Hilger quartz spectrograph confirmed this.

Simple calculations then show that the intensity of 2537 Å. passing through a quartz plate 3.5 cm. in diameter and 1 cm. from the face of the lamp is about 5.2×10^{17} quanta/sec. For two faces this would be 1.0×10^{18} quanta/sec. The amount of radiation that would be absorbed in a cell 61 cm. long, containing acetone ($c = 7.05 \times 10^{-4}$ mole/liter; $\epsilon = 8.92$) is then about 2.0×10^{16} quanta/sec. This agrees quite well with the absorption computed from the total decomposition (*ca.* 1.5×10^{16} quanta/sec.).

Reaction Vessel and Oven.—The reaction vessel (Fig. 2) consisted of 2 pieces of 35-mm. i. d. Pyrex tubing, each 61 cm. long, connected by an 18 mm. by-pass. Fused quartz windows, 2 mm. thick were sealed on the ends with silver chloride.[8] The two tubes were mounted in a rigid frame (not shown) and fixed in the oven with respect to the lamp. A piece of 2-mm. capillary connected the reaction chamber with the outside of a thermostated Bodenstein quartz spiral (Fig. 2). This jacket was connected to a gold leaf trap, then to a trap containing mercury and finally to a mercury manometer where the absolute pressure of the reaction chamber could be read to ±0.1 mm. The inside

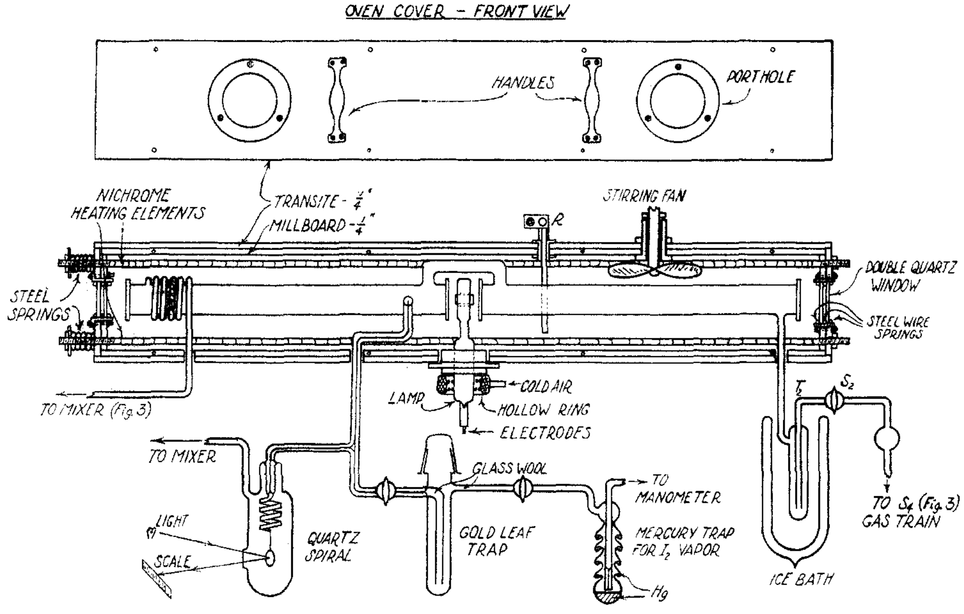

Fig. 2.—Reaction tube and oven: R, de Khotinsky bimetallic thermoregulator; S, stopcocks; T, trap; S_2, capillary leak stopcock.

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[8] Benson, *Rev. Sci. Instruments*, **13**, 267 (1942).

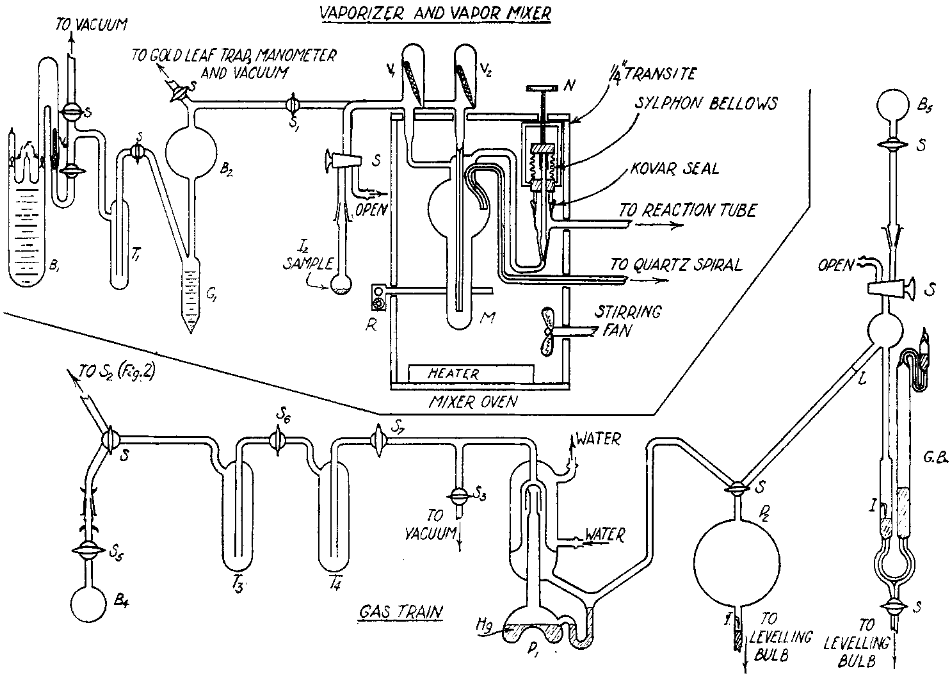

Fig. 3.—Flow System.

G_1—Graduated tube
B_1—100-cc. graduated bulb for storing acetone
B_2—500-cc. ballast flask
B_4—Weighed container for condensable liquids
B_5—50-cc. bulb for transferring gases
F_1—Magnetic break-off valves
V_0, V_1, V_2—Magnetic ground-glass valves
N—Needle valve
M—Vapor mixer
R—de Khotinsky bimetallic regulator
S_1—Capillary leak stopcock
S—Stopcocks
L—Constant level scratch
I—Constant level markers
P_2—200-cc. Toepler pump
G. B.—Gas buret and Toepler pump
P_1—Micro mercury diffusion pump
T—Traps

of the quartz spiral was connected to the mixing chamber (Fig. 3). The spiral's sensitivity was 1.3 mm./mm. Hg at 2 meters (using a light beam as lever). The difference in reading between the spiral and manometer gave the pressure in the mixing chamber.

The products passing from the reaction zone through a trap, T_2 (Fig. 2) (immersed in ice to remove most of the iodine vapor), passed through a capillary leak stopcock S_2 (Fig. 2) to the gas collection system (Fig. 3).

The oven current was regulated by a Varitran together with a shielded bimetallic de Khotinsky regulator R (Fig. 2) and electronic relay which could cut an external load (15% of the oven load) in or out of the circuit. The regulator kept the oven at constant temperature (±0.3°) for days. There were gradients from the ends to the center of 2° at 150°, and 5° at 220°. Radial gradients were 1.5° at 220°; 0.5° at 150°.

Flow System.—The flow system is shown in Fig. 3. All stopcocks were greased with Apiezon "N" grease. It will slowly dissolve iodine and acetone but this does not seem to have any appreciable effect on the results. All parts of the system containing mercury were connected to the flow system through either liquid air or gold leaf traps to eliminate sensitization.

The purified ketone (acetone) was stored in the graduated storage bulb (Fig. 3) sealed to the system through a magnetic break-off. This was connected in turn to a magnetic ground glass valve which prevented acetone from distilling into the stopcocks. Before each run the system was thoroughly pumped out and about 8 cc. of acetone distilled under vacuum into Trap T_1 (Fig. 3) and then into the graduated tube (Fig. 3) with Trap T_1 at −10°. This graduated tube was then allowed to come to equilibrium at 0°. This maintained a constant vapor pressure of acetone in Bulb 1 (Fig. 3) which fed the flow system. This bulb was connected through a capillary leak stopcock to the vapor mixing bulb (Fig. 3). This vapor mixing bulb was placed in a small transite oven where the temperature could be regulated to 0.05°. The regulating system was similar to that used for the reaction oven. For the runs with iodine present, a weighed sample of sublimed iodine was distilled under vacuum from the side tube (Fig. 3) through the magnetic valve V_1 (Fig. 3) into the mixing bulb. It was kept there at −30° and the system thoroughly pumped out. The magnetic valves V_1 and V_2 were closed to prevent back diffusion of iodine and the iodine allowed to come to equilibrium at a temperature of about 35.0°. The vapor pressure of I_2 at this temperature is about 0.75 mm.

The capillary leak stopcock and the valve V_1 were then opened and the leak regulated so that the rate of pressure increase in this mixing bulb corresponded to the desired rate of flow. This method of controlling the flow proved very effective and obviated flow calibrations. With this method the flow could be reproduced to within 10%.

The flow of the mixed vapors from the mixing bulb to the reaction vessel was regulated by a needle valve, V_3 (Fig. 3). This was a homemade ground glass needle valve controlled by a sylphon bellows. When the pressure in the mixing bulb had reached the proper value, this valve was opened and the vapors admitted to the system. It was adjusted to keep the pressure in the mixing bulb constant. When the pressure in the reaction vessel reached the proper value, the final leak stopcock S_2 (Fig. 2) was adjusted to maintain this constant pressure. The entire operation took about fifteen minutes and despite the use of two greased stopcocks S_1 and S_2 it was found that the flow would remain constant for hours, once adjusted in this manner. P_1 (Fig. 3) is a micro mercury diffusion pump resembling the one described by Prescott and Morrison.[9] It kept the gaseous products of the reaction from diffusing back into the reaction zone and facilitated their collection and measurement. P_2 is a Toepler pump used for final collection of the permanent gases. Only permanent gases were collected in the Toepler pump. At the end of a run stopcock S_4 (Fig. 3) (120°—3-way cock) was turned and the condensable products collected in Bulb B_4 (Fig. 3). This bulb had been previously weighed (±1 mg.) and evacuated with a drop of mercury in it.

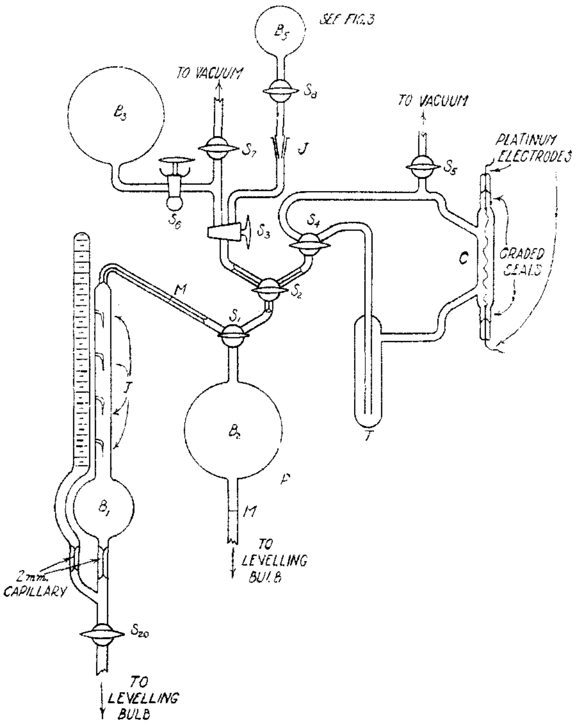

Fig. 4.—Micro gas analysis system: B_1, 35-cc. bulb; P, B_2, 225-cc. bulb and Toepler pump; B_3, 500-cc. oxygen bulb; B_5, 50-cc. gas transfer bulb; I, constant level markers; M, constant level scratches; C, combustion pipet; T, trap; J, ground-glass joint; S, stopcocks.

Stopcock S_5 (Fig. 3) was closed, the bulb B_4 disconnected from the line and allowed to come to room temperature so that the mercury would remove any traces of iodine in the products. It was then weighed to obtain the weight of acetone collected and thus measure the rate of flow. It was finally connected to the liquid analytical system.

The permanent gases collected in the Toepler pump were forced into the gas buret G. B. (Fig. 3) where the mercury was brought to a constant level and the pressure measured (±0.1 mm.). The gases measured in this way were forced into the gas bulb B_5 which was disconnected and attached to the gas analytical system.

Analytical Methods

Permanent Gases.—The gas analysis system is shown in Fig. 4. It was used for analysis of permanent gases and ethane. Since it is a low pressure system it can be used to analyze any substances which have vapor pressures of over 40 mm. at room temperatures.

The left-hand side of the buret is a graduated Pyrex tube from which pressures are read. The right-hand side is a Pyrex tube with constant level indicators sealed inside. It is connected to the Toepler pump by 2-mm. capillary. The volumes indicated by the levels were obtained by weighing drops of mercury prior to making the buret. Since the absolute volume is not needed, the ratio of the four volumes can be determined by measuring the pressure of the same amount of gas at each level. Measurements by these two methods checked to within 0.15%. The level indicators allow the volumes to be fixed to within 0.05 mm. and kept there during a reading by closing stopcock S_2. The four volumes are about 2.3, 4.8, 7.1, and 9.2 cc., respectively. At a pressure of 30 mm. it can analyze 80 cu. mm. at N. T. P. to ±1%. This compares favorably with other micromethods. In the present analyses the volume used was about 250 cu. mm.

Gas samples are analyzed by slow combustion with excess of oxygen. Dry-ice and liquid air on Trap T (Fig. 4) are used to remove water vapor and carbon dioxide, respectively. Mixtures of carbon monoxide, carbon dioxide, oxygen, hydrogen, methane, and nitrogen can be analyzed; also mixtures of hydrocarbons as high as pentane. No others were tested. Using 250 cu. mm. the precision was ±0.5%. As the carbon value of the gas increased the precision also increased. On butanes the precision was ±0.2%.

The combustion pipet was made from 10-mm. o. d. Pyrex tubing with graded seals (Pyrex–uranium glass–nonex-705 A J) at each end. A piece of #32 Pt wire was spot-welded at each end to two pieces of #28 Pt wire. The #28 wires were sealed through the 705 A J glass and served as electrodes.

Liquids.—It was found impossible to separate methyl iodide from acetyl iodide by Gorin's[1,2] method, so analysis was restricted to total volatile iodides. All iodides distilled over with the first four-fifths of the acetone fraction and none could be found in the last fifth. This may indicate the absence of acetyl iodide or more likely the presence of small amounts. The iodides were hydrolyzed with freshly prepared sodium ethylate in absolute alcohol and titrated electrometrically against a silver electrode using 0.01 *N* silver nitrate solution. The end-points were very sharp (0.01 cc.) and blanks run on methyl iodide–acetone mixtures showed an accuracy of better than 0.1%.

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(9) Prescott and Morrison, *Ind. Eng. Chem., Anal. Ed.*, **11**, 230 (1939).

TABLE I

PHOTOLYSIS OF ACETONE, ACETONE–IODINE MIXTURES AT λ 2537 Å.

Col. →	1	2	3	4	5	6	7	8	9	10
Run	Temp., °C.	Flow, cm./sec.	CO, cc. N. T. P.	CH_4, cc. N. T. P.	C_2H_6, cc. N. T. P.	$(CH_3CO)_2$, cc. N. T. P.	Iodides	CH_4/CO	C_2H_6/CO	$(CH_3CO)_2/CO$
4	60.1	1.05	2.34	0.18	2.81	0.90	..	0.078	1.20	0.38
5[a]	60.0	?	2.11	.061	..	..	?	.029	..	..
6	59.9	0.79	2.48	.21	3.06	.73	..	.083	1.23	.29
7[a]	59.9	.53	2.09	.036	..	..	5.42	.017	..	..
8	100.3	.97	3.45	.23	3.49	.10	..	.067	1.01	.029
9[a]	100.5	.88	1.38(?)	.021	..	..	3.60	.015	..	..
10	142	.62	3.68	.37	3.35	.00	..	.100	0.911	.00
11[a]	142	.67	2.03	.029	..	..	4.26	.014	..	..
12	60.2	.54	2.00	.14	2.20	.22	..	.068	1.10	.11
13[a]	60.2	.65	1.68	.022	..	..	4.46	.013	..	..
14[a]	102.0	.63	1.84	.038	..	..	4.16	.020	..	..
15	60.5	.96	2.02	.13	2.37	.44	..	.066	1.17	.22

Time of runs = ninety minutes. [a] Runs made with I_2 present. $P_{\text{acetone}} = 12.0 \pm 0.2$ mm. (corrected to 0°) $P_{\text{acetone}}/P_{\text{iodine}} = 54 \pm 2$.

Bulb B_4 (Fig. 3) after having been weighed was connected to a distillation train on a high vacuum line and all the ethane collected by isothermal distillation over a series of traps immersed in baths at different temperatures. This scheme allowed complete recovery of ethane from acetone–biacetyl. No other gases were present so the acetone–biacetyl residue was distilled into a trap, taken off the line and weighed into a spectrocolorimeter tube. Additional purified acetone was weighed in to make up a volume of 3 cc. and an identical tube with pure acetone was used as a blank. The Klett Spectrocolorimeter was used with a condensing lens and yellow filter. With this system quantities of biacetyl as small as 0.3 mg./gram of solution could be measured to within 8%. Quantities this small gave a noticeably yellow color to the solution. Known solutions of biacetyl in acetone prepared from redistilled Eastman Kodak Co. biacetyl (b. p. 88°) followed Beer's law very closely up to concentrations of 4 mg./gram of solution. A final check on the biacetyl was obtained by preparing the oxime and precipitating the red nickel dimethylglyoxime.

No way was found for demonstrating the presence of methyl ethyl ketone, which is probably present in very small amounts (see discussion).

Acetone.—The acetone in these runs was Mallinckrodt, C. P. grade, distilled in a 100-cm. column packed with a spiral gage (60 × 80 mesh, $^1/_8''$ pitch) made of stainless steel with an estimated 50 plates at a reflux ratio of 50:1. A middle fraction of 150 g. taken at a ratio of 30:1 (b. p. 55.9–56.0° at 760.0. mm.) was put through two isothermal bulb-to-bulb distillations under vacuum and sealed into the storage bulb (B_1, Fig. 3). The vapor pressure of each sample at 0° was checked before each run.

Experimental Results

The experimental results are tabulated in Table I. The products are recorded as cc. of gas at N. T. P. The iodides are methyl iodide and possibly some acetyl iodide if it is formed. The small amount of methane and biacetyl formed made a reliable estimate of the CH_4/CO and $(CH_3CO)_2/CO$ ratios difficult to obtain. However, it may be said that the $(CH_3CO)_2/CO$ ratio decreases as the temperature increases whereas the CH_4/CO ratio increases as the temperature increases.

A significant deviation from the results of Gorin[2] is to be observed in the fact that considerable quantities of carbon monoxide are formed at all temperatures in the presence of iodine whereas no biacetyl is formed at any temperatures in the presence of iodine.

The material balance in the runs without iodine checks to within 4% with an average unbalance of about 1.5% basing the calculations on equations 1′, 2′ and 3′.

$$CH_3COCH_3 \longrightarrow C_2H_6 + CO \qquad (1')$$

$$CH_3COCH_3 \longrightarrow {}^1/_2(CH_3CO)_2 + {}^1/_2C_2H_6 \qquad (2')$$

$$2CH_3COCH_3 \longrightarrow CH_4 + CO + CH_3CH_2COCH_3 \qquad (3')$$

Lack of information on the composition of the iodides prevents a check on the material balance in the runs with iodine.

An error in turning stopcocks makes the carbon monoxide value in Run 9* low.

Repeated analyses on the permanent gases failed to show the presence of hydrogen in any of the runs.

Because of the newness of the lamp comparisons of quantum yields must be restricted to consecutive runs. Rough estimates show a drop of 25% in the lamp intensity over twenty hours of use.

A few preliminary runs on the photolysis of acetone in the presence of oxygen show that carbon dioxide and ethane are the main gaseous products with little methane formed. In the absence of oxygen no carbon dioxide could be found in the products.

Discussion

The absence of ethane in the products of the photolysis of acetone in the presence of iodine vapor is conclusive evidence that the primary process is a splitting of acetone into free radicals, and the formation of ethane in absence of iodine must come about through a recombination of methyl radicals.

$$h\nu + CH_3COCH_3 \longrightarrow CH_3CO^* + CH_3^* \quad (1)$$

The large yield of carbon monoxide in the presence of iodine indicates that this primary step (1) is accompanied by a spontaneous decomposition of the activated acetyl radicals into methyl radicals and carbon monoxide. If α is the fraction of acetyl radicals that undergo this spontaneous decomposition, then α will be a function of the wave length and temperature only. The influence of wave length on quantum yield is compatible with this spontaneous decomposition. This is verified by the work of Herr and Noyes[10] and Howe and Noyes[11] who found that the increase of quantum yield with ν can be satisfactorily explained by giving α a value of 0.07 at 3130 Å., 0.22 at 2537 Å. and about 0.50 at 1900 Å. Gorin[2] found only very slight amounts of carbon monoxide at 3130 Å. in the presence of iodine vapor, which is in rough agreement with the value of α at this wave length. He further found that pressure had no effect on the amount of carbon monoxide formed in the presence of iodine, which would not be true if the decisive factor were the homogeneous or heterogeneous decomposition of acetyl radicals by collision or at the walls

$$CH_3CO + M \longrightarrow CH_3 + CO \quad (2)$$

There is ample evidence to indicate that this reaction is heterogeneous[12,13] and the probability is that both homogeneous and heterogeneous reactions go on together.

The formation of biacetyl reported by Gorin[2] in the presence of iodine at 3130 Å. is in direct contrast to its complete absence at 2537 Å. This may be a consequence of the large value of α at 2537 Å. or of the increase in heterogeneous decomposition of CH_3CO at the low pressures which obtained in the present work. However, a plot of log (biacetyl/CO) against $1/T$ gives a straight line with an activation energy of 15 ± 2 kcal./mole. If the activation energies of formation of biacetyl homogeneously or heterogeneously are negligible then this value of 15 kcal. will represent the activation energy for the disappearance of acetyl radicals and if it is corrected for the small increase in carbon monoxide we get a value of 16 kcal. for the activation energy of reaction (2). This is in good agreement with the values of 17 and 18 kcal. obtained by Gorin[2] and Noyes,[10] respectively.

Comparisons of consecutive runs show that the efficiency of the primary process in the presence and absence of iodine is close to unity, a result in agreement with the work of Herr and Noyes.[10] These calculations of the quantum yield are made on the consistent assumption that the iodides are mixtures of acetyl and methyl iodides using the values of Herr and Noyes[10] for pure acetone. In the absence of iodine it is assumed that two methyl radicals are consumed for every molecule of methane formed according to the following scheme.

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + \text{-}CH_2COCH_3 \quad (3)$$
$$CH_3 + \text{-}CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3 \quad (4)$$

Allen[12] has shown that methyl ethyl ketone is formed in the photolysis of acetone at temperatures as high as 450°. If reactions (3) and (4) are added to the scheme of Herr and Noyes,[10] then the following relations will hold independently of the nature of the secondary reactions

$$CO + 2[(CH_3CO)_2]\,(1 - \beta)I_{\text{abs.}} \quad (5)$$
$$2[CH_4 + C_2H_6] - CO = (1 - \beta)I_{\text{abs.}} \quad (6)$$

in which (1-β) is the efficiency of the primary process and the quantities are expressed in moles of products. These relations satisfy the work of Herr and Noyes,[10] Taylor and Rosenblum,[14] Spence and Wild,[15] and the present work.

The failure of iodine to reduce Φ of methane to zero may be due to the retention of excess energy by the methyl radicals comparable to that of the acetyl. If this is true, then Φ of methane should depend on wave length. Spence and Wild[15] report an increase in Φ of methane as the wave length decreases but unfortunately there are no other data on the formation of methane. Gorin[2] failed to report it in his experiments but he did not say whether he found it or merely ignored it.

The ratios of CH_4/CO and C_2H_6/CO (Table I) are in good agreement with those reported by

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(10) Herr and Noyes, THIS JOURNAL, **62**, 2052 (1940).

(11) Howe and Noyes, *ibid.*, **58**, 1404 (1936).

(12) Allen, *ibid.*, **63**, 708 (1941).

(13) Anderson and Rollefson, *ibid.*, **63**, 816 (1941).

(14) Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

(15) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

Taylor and Rosenblum[14] and Herr and Noyes[10] and their changes with temperature are consistent with equations (5) and (6). Because of the experimental difficulties, nothing in the nature of direct evidence can be applied to the formation of acetyl iodide. However, if we assume its presence and calculate it by difference, then we find that the log [CH_3CO] against $1/T$ gives a straight line with an activation energy of 6 kcal./mole. If there is a rapid equilibrium between acetyl iodide and iodide atoms as suggested by Gorin[2]

$$CH_3CO + I_2 \rightleftarrows CH_3COI + I \qquad (7)$$

then this value represents the difference in activation energy between (2) and the forward reacton in (7) which gives a value of 9 kcal. for the latter. This value is quite reasonable and can be compared with the value of 12 kcal./mole found for the reaction of $ICH_2\text{-}CH_2\text{-}$ with iodine[16] and a similar value found for the reaction of $ICH_2\text{-}CH_2CH_2\text{-}$ and iodine.[17] It is this relatively high value, in our opinion, that explains the small amounts of acetyl iodide found by Gorin[2] and by us, and also the large quantities of biacetyl found by the former at 3130 Å., in the presence of iodine.

Acknowledgment.—We are indebted to Dr. J. J. Lingane for the use of his apparatus in the electrometric titrations for iodine.

Summary

1a. A description has been given of a versatile apparatus especially designed for the study of the flow photolysis of mixed vapors.

1b. A low pressure system for the microanalysis of hydrocarbon vapors is described.

2. The photolysis of acetone by λ 2537 Å. in the presence and absence of iodine has been investigated over the range 60–140°.

3. In the absence of iodine the main products are ethane and carbon monoxide with small amounts of methane and biacetyl, and relative yields are in good agreement with the values found by other investigators.

4. In the presence of iodine the products are carbon monoxide and methyl iodide with small amounts of acetyl iodide and traces of methane formed.

5. The primary process at 2537 Å. is exclusively a splitting of the acetone into methyl and acetyl radicals accompanied by a spontaneous decomposition of at least 22% of the acetyl radicals formed. The efficiency of the primary process is close to unity.

6. The formation of methane is probably accompanied by the disappearance of two methyl radicals and the formation of methyl ethyl ketone.

7. Minimum activation energies are found of 16 kcal./mole for the decomposition of acetyl radicals and 9 kcal./mole for the formation of acetyl iodide from acetyl radicals and iodine.

CAMBRIDGE, MASS. RECEIVED MARCH 3, 1943

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(16) Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(17) Ogg and Priest, *ibid.*, **7**, 77 (1939).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Sterical Course and the Mechanism of the Diene Reaction

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Since the discovery of the Diels–Alder reaction, there have been found in numerous cases two isomeric addition compounds,[1] which are usually explained as stereoisomers. During a study of the adducts of dicyclohexenyl, we have made some observations, which we believe make it possible to draw several general conclusions about the sterical course of the diene reaction.

From the interaction of dicyclohexenyl with cinnamic acid, we isolated, in addition to the one already known adduct (Ia),[2] a second isomer Ib. The possibility of *cis–trans* isomerism with regard to the phenyl and carboxyl groups could be excluded by the fact that both acids could be recovered unchanged after saponification of their methyl esters with sodium butylate. This procedure is known to isomerize *cis*-esters bearing an α-hydrogen atom.[3] Both isomers, therefore, are derived from the *trans*-cinnamic acid. Condensation of dicyclohexenyl with benzalacetone yielded only one form of II, which corresponds to acid

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(1) (a) Fieser and Fieser, THIS JOURNAL, **57**, 1679 (1935); (b) Adams and Geissman, *ibid.*, **61**, 2083 (1939); (c) Goldberg and Müller, *Helv.*, **23**, 831 (1940).

(2) Ch. Weizmann, E. Bergmann and T. Berlin, THIS JOURNAL, **60**, 1331 (1938).

(3) Hückel and Goth, *Ber.*, **58**, 447 (1925); Bickel, THIS JOURNAL, **60**, 927 (1938).