3 N nitric acid solution previously reported, but tends in time to approach the same level of activity.

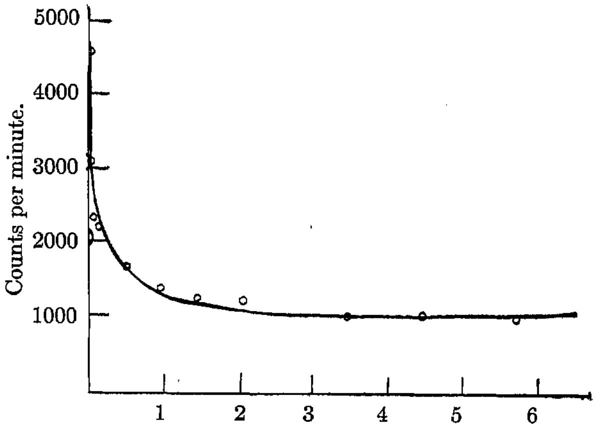

Fig. 8.—Desorption of radium E in 2 molar NH_4Cl.

Radio-bismuth (Radium E).—The colloidal behavior of bismuth salts in water (both in trace and macroscopic concentrations) has been investigated by Haissinsky.[8] The extent of colloidal aggregation, measured by centrifugation experiments, is markedly affected by the pH of the solution. For example, Haissinsky reported that much more colloid was formed at pH 2.5 than at pH 5. The results which were obtained with a coated dipping counter are at least qualitatively comparable. They are illustrated in Fig. 6. A nitric acid solution of radium E was adjusted to pH 6.3 by ammonia. There was virtually no increase in counting rate for an hour. At this point, the counter was removed, and nitric acid was added to pH 2.1. The same counter was re-introduced; the marked increase in counting rate is obvious.

Another aspect of the chemistry of bismuth is described below. It will precipitate from bismuth nitrate solutions upon the addition of small quantities of chloride ion. However, the resulting precipitate will redissolve in 4 M sodium chloride solution.[8] Figure 7 illustrates several experiments performed with radium E at pH 3 (where a considerable proportion of the bismuth is in the colloidal form). In the presence of 2 M sodium or ammonium nitrate there is a decided increase in counting rate with time. A low concentration of ammonium chloride (0.05 M) produces little change. However, in 2 M sodium chloride or 2 M ammonium chloride, at approximately the same pH, there is no increase in counting rate, and no adsorption.

Figure 8 shows the action of a concentrated ammonium chloride solution in complexing radio-bismuth. Radium E was cumulatively adsorbed from solution (having a pH of 3) on a coated counter for some hours. The tube was removed, and washed. The initial count in air was 4700 counts per minute. On immersion in a 2 M ammonium chloride solution (pH 3), the Radium E desorbed very rapidly to reach a constant count of about 1400 counts per minute.

Acknowledgment.—We wish to thank Professor F. C. Collins and Dr. Joseph Greenspan for many helpful discussions.

THE PHOTOLYSIS OF CADMIUM DIMETHYL[1]

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The photolysis of cadmium dimethyl vapor both alone and in the presence of a four-fold excess of hydrogen has been studied in a temperature range up to 250°. In the presence of hydrogen, methane and ethane are the sole gaseous products. From the alkyl alone small amounts of ethylene, propane and butane in addition to ethane and methane are produced. An appraisal of the relative light intensity as a result of metal deposition during a run has been made by observing acetone photolysis in the air-poisoned vessel. The simplest mechanism consistent with the data leads, on the assumption of zero activation energy of the recombination of two methyl radicals, to a value of 13 ± 2 kcal. for the energy of activation of the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ consistent with the strength of the C–H bond in methane and the energy of activation of the reverse reaction. The energy of activation of hydrogen abstraction by a methyl radical from cadmium dimethyl is found to be 14 ± 2 kcal.

The photolysis of mercury dimethyl has been studied by a number of workers[2] and each effort seems to have shown a greater complexity in the reaction than was suspected in earlier work. The interpretation of the effect of temperature on the reaction depends in large measure on the steps postulated in the mechanism. It is in this way that energies of activation of intermediate step, radical reactions are frequently arrived at.[3] By varying the source of the radicals some confirmation of the energy of activation may be possible.[4] The present paper is concerned with a study of the photolysis of cadmium dimethyl vapor both in the presence and absence of hydrogen in the expectation that from the similarities and dissimilarities of the mercury and cadmium compounds information significant to both mechanisms might be forthcoming.

Experimental

Apparatus.—Preliminary experiments carried out at temperatures below 50° showed ethane to be the sole gaseous product of the photolysis of cadmium dimethyl. The presence of ethane and absence of methane were demonstrated

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(1) Abstract from a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, February, 1951.

(2) R. D. Anderson and H. A. Taylor, THIS JOURNAL, **55**, 161 (1952).

(3) J. H. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

(4) H. S. Taylor and C. Rosenblum, *ibid.*, **6**, 119 (1938).

by infrared analysis.[5] The rate of production of ethane leveled off after about one minute due to the sharp decrease in light intensity penetrating the cadmium mirror deposited on the illuminated side of the reaction flask. Experiments made at 17, 32 and 47° showed no appreciable differences suggesting zero energy of activation of ethane production and recombination of methyl radicals as the source of ethane. It was from this experience that the apparatus used in the bulk of the experiments was developed.

The reaction vessel was a heavy-walled cylinder of transparent quartz about 6 cm. in length carrying two circular plane windows, 10 cm. in diameter, attached by a special sinter seal achieved at a temperature below that at which any significant strain could be introduced into the windows. A side-arm was joined to the curved part of the cell.

The furnace for the reaction cell was a narrow metal box thoroughly insulated and equipped with variable heating elements controlled in part by a bimetallic thermoregulator. Double quartz windows with an air space between them for insulation were fitted on both sides of the box and aligned with the windows of the reaction cell. Metal shutters sliding vertically served to screen these windows from the incident radiation. A fan circulated the air in the furnace preventing any temperature gradients. The temperature was measured by means of a chromel–alumel thermocouple. The variation in temperature during a run amounted to less than 0.1°.

The furnace for the reaction cell was installed inside a much larger oven designed to maintain two ultraviolet lamps, one for each window of the cell at a temperature of 45°. The lamps were flat spiral low-pressure mercury resonance lamps, Hanovia Type SC2537, operated on separate 120 milliamp. 5000 volt transformers which at 120 volts drew about 5.8 amp. The air in the oven was circulated rapidly over the lamp by two fans and heaters in series with a metallic thermoregulator maintained constant temperature. Separate thermometers recorded the temperature in the vicinity of the electrodes of each lamp.

The quartz reaction cell was connected by a quartz-to-Pyrex seal to a manifold through a Crist valve[6] which permits only platinum, silver and silver chloride to come in contact with a vapor stream passing through it. Provision was made for the handling of cadmium dimethyl vapor without contamination by mercury vapor, a second Crist valve confining the storage reservoir. When hydrogen was used it was passed through two traps in liquid nitrogen before entering a storage bulb, the pressure in which was registered on a mechanical vacuum gage sensitive to pressure changes of about 5 mm. and covering a range up to 760 mm. A helium storage bulb with vacuum gage was attached to the manifold as was also a storage flask for acetone. This manifold was never in direct contact with mercury and the reaction cell and its contents before and during a run were thus also free from mercury. A quartz spiral manometer was used as the pressure-measuring instrument. Readings were made through a forty magnification microscope with superimposed scale. In the range 0 to 35 mm. of mercury the manometer served as an absolute gage giving pressures reproducible to 0.1 mm. For pressures greater than 35 mm. the manometer was used as a null instrument.

A second manifold carried Toepler pumps, McLeod gage, mercury diffusion pump and Cenco Megavac oil pump. The two manifolds were connected through a two-way stopcock to the Crist valve attached to the reaction vessel, two liquid nitrogen traps in series standing between this stopcock and the portion of the second manifold exposed to mercury. The McLeod gage and the diffusion pump in addition were isolated through liquid nitrogen traps. All stopcocks with which cadmium dimethyl vapor or acetone came in contact were lubricated with a perfluorocarbon. Gas samples after photolysis were withdrawn by a Toepler pump through a trap in solid carbon dioxide and trichloroethylene and delivered to a sample flask with stopcock connected by a ball joint for easy detachment for analysis.

Materials.—Cadmium dimethyl was made by the reaction of anhydrous cadmium chloride with methylmagnesium iodide in ether solution. Details of the method and critical tests of purity showing that previously reported physical constants were in error have already been described.[2]

Acetone was prepared by distillation from the sodium iodide compound and stored at the temperature of solid carbon dioxide.

Tank helium described as 99.8% was found to contain traces of nitrogen and hydrogen. For rinsing purposes it was first passed over copper oxide at about 400° to remove hydrogen, through a drying tower containing potassium hydroxide pellets and through a trap in liquid nitrogen to its storage bulb on the main manifold.

Electrolytic tank hydrogen was passed over platinized asbestos at about 400°, dried over potassium hydroxide and through a trap in liquid nitrogen. Mass spectrometer analysis showed hydrogen, 99.7%, nitrogen 0.3%.

Procedure.—In all runs the initial pressure of cadmium dimethyl vapor in the reaction vessel was approximately 17.5 mm. at 27.0°. In the runs with hydrogen a fourfold dilution of cadmium dimethyl vapor with hydrogen was employed.

Preceding a run, the lamps were allowed to warm up to full intensity for half an hour. The cadmium dimethyl vapor was allowed to warm up for 15 minutes in the reaction cell before exposure. When hydrogen was present an additional 15 minutes was allowed. Special pyrolysis runs were made to correct the photolysis results for the decomposition of cadmium dimethyl during the warm-up periods.

Since even traces of oxygen react readily with cadmium dimethyl vapor the pumping procedure on all parts of the apparatus included a rinsing with helium prior to the final pumping. The control mechanism of the Crist valve permitted its use as a throttle to control the input of cadmium dimethyl vapor to the reaction cell. The pressure of the vapor was registered by the quartz spiral manometer. In taking the metal alkyl vapor from its reservoir in Dry Ice, the latter was partially removed and about one-third of the cadmium dimethyl melted. The Dry Ice was replaced freezing the liquid again and the system was pumped out to remove any ethane which might have formed. The alkyl was again melted and the vapor drawn into the reaction vessel. In runs using hydrogen a storage bulb was first filled to such a pressure of hydrogen that on opening it to the reaction cell with its desired quota of cadmium dimethyl and establishing pressure equilibrium the correct fourfold dilution was achieved almost instantaneously. This was accomplished by a volume calibration of the various parts of the whole apparatus. By such a procedure the Crist valve on the reaction cell was opened to a relatively high pressure of hydrogen which swept rapidly into the cell and minimized the possibility of a change in the amount of cadmium dimethyl in the cell. After the warm-up period for the hydrogen had elapsed, irradiation of the system was begun by raising the shutters. Since only a fraction of a second was required for this operation the timing of the run was quite accurate.

On completion of a run the reaction cell was opened so that residual cadmium dimethyl would move over into a trap in Dry Ice. Although experiment showed this would take less than one minute, 15 minutes were allowed for its completion. During this period the furnace around the reaction cell was adjusted to 100° which was the temperature used for all the acetone photolysis runs made for the purpose of measuring the density of the cadmium deposit. The remaining gases were transferred by a Toepler pump to the portion of the manifold in contact with the spiral manometer, their pressure was measured and by a second Toepler they were transferred to the sample tube for analysis by the mass spectrometer. The residual cadmium dimethyl was then vaporized and its pressure measured. Knowledge of the volumes of the different parts of the system permitted conversion of these pressures into quantities of material.

In runs at different temperatures in order to maintain constant concentration of the cadmium dimethyl and of the hydrogen for all runs the loading pressures had to be adjusted which for the former could not exceed the vapor pressure at room temperature. A pressure of 20 mm. was used for runs at 50° increasing to 30 mm. for runs at 250°. Similarly the hydrogen pressure was varied from about 80 to 120 mm.

Acetone Photolysis.—Light intensity within the reaction cell was appraised by means of a standardized acetone vapor photolysis carried out in the reaction cell after each cadmium dimethyl photolysis. Diminution of the light intensity

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[5] These analyses were made on the Baird Model B Infrared Spectrometer by Dr. R. D. Schultz through the courtesy of the Brookhaven National Labs., Upton, N. Y.

[6] R. H. Crist and F. B. Brown, *Ind. Eng. Chem., Anal. Ed.*, **11**, 396 (1939).

within the cell was proportional to the density of the cadmium deposit.

When all measurements after a cadmium dimethyl run had been completed the evacuated reaction cell was opened to the air and the cadmium deposit left in contact with air for 15 minutes at 100°. This treatment did not alter the appearance or apparent transparency of the cadmium deposit. Glazebrook and Pearson[7] have shown, however, that a trace of oxygen will remove the capacity of a metallic deposit to react with free radicals. The reaction cell was evacuated, the lamps again warmed up and acetone, first pumped out while frozen in liquid nitrogen, was warmed up to 0° and a pressure of 69.8 mm. loaded into the cell. After a 15-minute warm-up period, irradiation for 15 minutes was made and subsequently the total pressure of products and residual acetone was measured. A number of runs similarly made but using a freshly-cleaned cell containing a strip of cadmium metal which was not in the light path gave an average pressure increase of 17.4 mm. Using the reaction cell with the cadmium deposit from a cadmium dimethyl run a smaller pressure increase would be observed. The ratio of this latter to 17.4 mm. gave a relative measure of light intensity within the cell at the end of the cadmium dimethyl run as compared with that at the beginning.

After the acetone run the reaction cell was filled with helium and cut from the system. Cold nitric acid removed all visible cadmium and the cell was rinsed with water, washed out with acetone and then heated to about 80° and rinsed three times with hot concentrated nitric acid. At least six washings with distilled water completed the cleaning. The outer surface was washed in dilute soap solution and rinsed thoroughly before the cell was re-sealed to the apparatus.

Analysis.—Analysis of the product gases from the photolysis and pyrolysis runs was carried out on Consolidated Engineering Corporation mass spectrometers.[8]

Results

Photolysis of Cadmium Dimethyl Vapor.—The cadmium deposits in the photolysis runs were not mirror-like in the range 150 to 275° as they were at lower temperatures. At first glance the cell windows appeared almost clean but slight magnification showed bright silvery particles of cadmium, uniform in size covering about one quarter of the irradiated area.

The analytical results of the photolysis and several pyrolyses are shown in Table I. All measurements are reported in mm. of mercury at 27°. The quantities of products refer to the amounts produced by the photolysis alone, that is, the total amounts observed corrected for the amounts produced by pyrolysis. The acetone run results are reported as the light flux as described above. Zero light then indicates pyrolysis.

In the runs in presence of hydrogen the cadmium deposits were mirror-like at 50° and somewhat less so at 100°. At the higher temperatures the deposits were much more transparent. The deposits covered the entire surface of the cell although most of it was confined to the windows. On magnification many very small black particles could be seen interspersed among the cadmium beads. The results of the product analyses are given in Table II. Two pyrolysis times were necessary for the runs with hydrogen due to the preliminary heat treatment of 15 minutes for the cadmium dimethyl alone and 15 minutes more after the addition of the hydrogen.

The variation of the light flux with time at each temperature was found to be exponential in form expressible by an equation of the form $I = ae^{-bt} + c$ where I is the fractional light intensity at time t in minutes. The values of a, b and c for each type of run are listed in Table III.

Discussion of Results

The equations from data in Table III indicate that the light variation with time was comparable for all runs carried out above 100°. It thus became possible to estimate rates of formation of the products at zero time with fair certainty. These were obtained from plots of the ethane and methane produced as a function of time. The ethane plots were practically straight lines indicating ethane production to be independent of cadmium dimethyl concentration. The methane plots showed more curvature especially at the highest temperatures. In order to ensure comparability large scale plots of methane production were made and the initial slope was taken to include that portion of the curve from zero time to one quarter of a minute. The curve was linear in this range. The rate data thus measured are listed in Table IV.

TABLE I

PHOTOLYSIS OF CADMIUM DIMETHYL VAPOR

Time, min.	$CdMe_2$ res.	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4	Light flux
Temperature 150°							
0	17.50	..	...	..	..	..	1.00
.5	15.33	0.02	2.30	..	..	..	0.88
1.5	11.03	.06	6.53	..	..	..	.83
3.0	4.54	.06	12.50	..	..	..	.83
15.5	17.12	.06	0.01	..	..	..	.00
Temperature 200°							
0	17.18	..	...	..	..	..	1.00
.5	15.20	0.04	2.31	..	..	..	0.83
1.5	10.42	.10	6.60	0.06	..	..	.80
2.5	6.58	.06	10.62	.05	..	..	.80
3.0	4.26	.18	12.86	..	..	..	.82
16.0	17.17	.11	0.01	..	..	..	.00
Temperature 225°							
0	17.16	..	...	..	..	..	1.00
.5	14.62	0.05	2.51	0.02	..	..	0.82
1.5	10.26	.16	6.75	.08	..	..	.78
2.5	6.09	.20	10.64	.11	..	..	.77
15.0	17.22	.12	0.01	..	..	..	.00
15.5	16.83	.11	.01	..	..	..	.00
Temperature 250°							
0	17.16	..	...	..	..	..	1.00
.5	14.50	0.18	2.44	0.19	0.04	..	0.83
1.5	9.09	.28	7.31	.06	.06	0.02	.77
2.5	5.62	.43	10.88	.12	.11	.03	.79
15.0	17.22	.20	0.03	..	..	..	.00
Temperature 275°							
0	17.26	..	...	..	..	..	1.00
.5	13.92	0.24	3.19	0.07	0.03	0.01	0.84
1.5	7.53	.67	8.85	.16	.12	.04	.83
2.5	4.35	.85	12.37	.07	.23	.06	.78
15.5	16.83	.10	0.01	..	..	..	.00

The photolysis of cadmium dimethyl vapor alone produced ethane with smaller amounts of methane, ethylene, propane and butane. The analysis was reliable above 150° for all products except ethylene. Thermochemical data indicate[9] that the energy of removal of both methyl radicals from the cadmium in the cadmium dimethyl molecule amounts to about 63 kcal. per mole. Since absorption of light of 2537 Å. wave length corresponds to an energy of 112 kcal. per mole, it is energetically possible for both methyl radicals to be freed by the initial absorption. The following mechanism is suggested

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[7] H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 567 (1937).

[8] Two-thirds of the analyses were obtained through the courtesy of the M. W. Kellogg Company of New Jersey; one-third through the Mass Spectrometer Analytical Service of the Consolidated Engineering Corporation, Pasadena, Calif.

[9] L. H. Long and R. W. G. Norrish, *Phil. Trans.*, **A241**, 587 (1948).

TABLE II

PHOTOLYSIS OF CADMIUM DIMETHYL AND HYDROGEN

Time, min.	$CdMe_2$ res.	H_2	CH_4	C_2H_6	Light flux
		Temperature 50°			
0	17.56	73.2	..	...	1.00
.5	16.06	69.2	0.15	1.56	0.78
1.5	14.06	72.6	.14	3.26	.51
3.0	11.17	73.0	.14	6.25	.31
6.0	8.10	73.2	.07	9.34	.20
15.0	.17	71.2	.14	17.10	.22
		Temperature 100°			
0	17.53	73.6	..	...	1.00
.5	15.71	73.8	0.07	1.80	0.76
1.5	12.52	73.7	.08	4.47	.66
3.0	9.26	74.2	.14	7.77	.53
6.0	2.56	71.0	.53	15.47	.47
		Temperature 150°			
0	17.50	74.1	..	...	1.00
.5	15.23	73.7	0.07	2.21	0.83
1.5	11.68	73.9	.14	5.09	.78
3.0	5.74	73.0	.39	11.50	.74
4.5	1.04	73.1	.64	16.78	.77
15–15	17.16	73.6	.16	...	.00
		Temperature 200°			
0	17.18	73.1	..	...	1.00
.5	14.90	72.3	.72	2.20	.83
1.5	10.43	71.5	1.28	6.44	.81
3.0	4.40	71.0	2.21	11.96	.75
4.0	.19	70.1	3.06	16.55	.80
15–15	16.47	73.5	.36	.03	.00
15–20	17.12	71.6	.51	.03	.00
		Temperature 225°			
0	17.16	73.3	..	...	1.00
.5	13.55	71.8	1.06	2.43	.87
1.5	9.10	71.5	1.93	6.39	.80
2.5	4.52	70.7	4.12	10.24	.80
22–15	16.66	73.5	1.00	.11	.00
		Temperature 250°			
0	17.16	73.3	..	...	1.00
.5	12.13	71.4	1.94	2.90	.88
1.0	8.64	69.5	4.69	4.92	.85
1.5	6.78	69.3	4.73	6.47	.83
2.5	1.61	66.2	8.98	10.59	.78
16.5–15.5	15.46	71.8	2.65	.42	.00
16.5–18	14.90	72.6	3.13	.45	.00

TABLE III

FRACTIONAL LIGHT INTENSITY $I = ae^{-bt} + c$

Temp., °C.	a	b	c
	Cadmium Dimethyl		
150	0.17	2.5	0.83
200	.20	2.8	.80
225	.23	2.9	.77
250	.22	3.0	.78
275	.22	2.6	.78
	Cadmium Dimethyl and Hydrogen		
50	0.80	0.66	0.20
100	.54	0.70	.46
150	.25	1.6	.75
200	.22	2.8	.78
225	.20	2.1	.80
250	.20	1.4	.80

TABLE IV[a]

RATE DATA AND ACTIVATION ENERGIES

Temp., °C.	$CdMe_2$		$CdMe_2 + H_2$	
	R_M	R_E	R_M	R_E
50	..	..	..	3.2
100	..	..	..	3.8
150	..	4.8	.15	4.3
200	0.085	4.9	1.2	4.4
225	.14	5.7	1.8	5.0
250	.39	6.2	4.0	6.1
275	.76	7.8	..	..
	$E_M - 1/2E_E =$ 14 ± 2 kcal.		$E_M - 1/2E_E =$ 13 ± 2 kcal.	

[a] R_M and R_E represent rates of production of methane and ethane, respectively, in mm. (at 27°) per min. E_M and E_E represent similarly the activation energies.

as the simplest for the photolysis as here observed

$$Cd(CH_3)_2 + h\nu = 2CH_3 + Cd \qquad (1)$$

$$2CH_3 = C_2H_6 \qquad (2)$$

$$CH_3 + Cd(CH_3)_2 = CH_4 + CH_2 + Cd + CH_3 \qquad (3)$$

The small amounts of ethylene, propane and butane may result from the methylene radicals by association with themselves or with methyl radicals to give ethyl radicals.

The Arrhenius plot of ethane production at temperatures above 150° from both cadmium dimethyl alone as also in presence of hydrogen is not linear, suggesting a constantly increasing energy of activation with increase in temperature. Since ethane production is relatively high at low temperatures and appears to be temperature independent the variation at higher temperatures must be due to variation in the concentration of methyl radicals, increasing with increase in temperature. Evidence has recently been presented[10] that reaction (2) has zero energy of activation. An alternative reaction producing ethane might be

$$CH_3 + Cd(CH_3)_2 = C_2H_6 + Cd + CH_3 \qquad (4)$$

It was pointed out above, however, that ethane production is independent of the concentration of cadmium dimethyl and the contribution of reaction (4), if any, cannot be large.

This variation in methyl radical concentration with temperature must be taken into account in calculating the energy of activation of methane formation. Since the rate of ethane production is given by $R_E = k_2[CH_3]^2$ and of methane by $R_M = k_3[CH_3][Cd(CH_3)_2]$, eliminating the radical concentration gives $R_M/R_E^{1/2}$ proportional at a given cadmium dimethyl concentration to $k_3/k_2^{1/2}$ and the slope of an Arrhenius plot of $R_M/R_E^{1/2}$ should give the value of $E_3 - {}^1/_2\,E_2$. As shown in Table IV the value found is 14 ± 2 kcal.

The fourfold dilution with hydrogen results in about a twelve-fold increase in the rate of methane production although the rate of ethane production remains virtually unchanged from that with the cadmium alkyl alone. The presence of hydrogen reduces the number of gaseous products to two, methane and ethane. The methane analysis was reliable for the runs above 150° where the dilution of the products by the hydrogen had less effect. The consumption of hydrogen necessarily lacks

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(10) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, 19, 85 (1951).

precision, being the difference of two large quantities. At the highest temperature with the largest amounts of methane produced it would seem that the total methane produced is approximately twice the hydrogen consumed. This suggests the following additional reactions when hydrogen is present in excess, to those occurring in its absence

$$\mathrm{CH_3 + H_2 = CH_4 + H} \qquad (5)$$
$$\mathrm{H + Cd(CH_3)_2 = CH_4 + Cd + CH_3} \qquad (6)$$

Application of the usual steady state consideration shows that at a given hydrogen concentration $R_{\mathrm{M}}/R_{\mathrm{E}}^{1/2}$ is proportional to $k_5/k_2^{1/2}$ and the slope of an Arrhenius plot should give the value of $E_5 - {}^1/_2\,E_2$. The value found is 13 ± 2 kcal.

If the value of E_2 is taken as zero, the energy of activation of (5) is 13 ± 2 kcal. This agrees well with that calculated from the reverse reaction

$$\mathrm{H + CH_4 = CH_3 + H_2} \qquad E = 11 \pm 2$$ [11,12]

which reaction is 2 ± 1 kcal. exothermal since

$$\mathrm{CH_4 = CH_3 + H} \qquad H = 101 \pm 1$$ [13]

and

$$\mathrm{H_2 = 2H} \qquad H = 103.3$$ [14]

Therefore reaction (5) should be endothermal by 2 ± 1 and the energy of activation equal to 13 ± 3 kcal.

Since the energy of removal of two methyl radicals from cadmium dimethyl is about 63 kcal., whereas the comparable value for mercury dimethyl is 31 kcal.,[9] the "hot" radical effect should be less than that observed in mercury dimethyl.[15] The data of the latter research indicate no hot methyl effect above 150°. In the present research no such effect was observed above 100°.

A further significant difference exists between the photolyses of cadmium dimethyl and mercury dimethyl. In the former case the cadmium set free is deposited on the walls of the reaction vessel at all temperatures. Any back reaction with products must be of a heterogeneous nature. With mercury dimethyl at low temperatures most of the mercury from the decomposition is deposited on the walls but at higher temperatures the mercury exists almost exclusively as a vapor and any back reactions with products may proceed homogeneously. This may in part account for the lower activation energy value 9 ± 2 found from the photolysis of mercury dimethyl in presence of excess hydrogen (3) which has been assigned to reaction (5) and has caused conflict between the activation energies of (5) and its reverse and the strength of the C–H bond in methane. The above value of 13 ± 2 is consistent.

On the same assumption that E_2 is zero, the value of E_3 becomes 14 ± 2 kcal. Although the average deviation of ±2 appears to be the same from the treatment of the data as for E_5 it should be observed that the rates of methane production in the absence of hydrogen are much slower and the precision of the result cannot be as high. In comparison with hydrogen abstraction reactions, from paraffins,[16] the value seems high. However Cunningham and Taylor[3] found a value of 13 kcal. and Gomer and Noyes[17] a value of 11 kcal. for methane formation from mercury dimethyl. A somewhat higher value from cadmium dimethyl is not unreasonable.

(11) E. W. R. Steacie, B. de B. Darwent and W. R. Trost, *Discussion Faraday Soc.*, **2**, 80 (1947).

(12) M. G. Evans and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).

(13) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(14) A. G. Gaydon, *Proc. Phys. Soc.*, **58**, 525 (1946).

(15) M. K. Phibbs and B. de B. Darwent, *Trans. Faraday Soc.*, **45**, 541 (1949).

(16) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

(17) R. Gomer and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **71**, 3390 (1949).

THE HYDROGEN BOND IN ORGANIC CRYSTALS[1]

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The results of crystal structure investigations on organic crystals containing various types of hydrogen bonds have been collected together. These types are N–H· · ·N, N–H· · ·Cl, N–H· · ·O, O–H· · ·N, and O–H· · ·O. The lengths and strengths of these bonds are found to vary in a reasonable way with the departure of the angle C–XH· · ·X from the expected near-tetrahedral value, and with the situation of the donor and acceptor atoms. In general, strong hydrogen bonding occurs only when the hydrogen atom is collinear with the bonded atoms. Several proposed structures of the polypeptide chain in proteins, presumed to contain N–H· · ·O bonds, are examined on the basis of the characteristics found for this bond.

Introduction

The purpose of this review is to gather together the information which has thus far (*i.e.*, to about Feb., 1951) been obtained concerning hydrogen bonds in organic crystals. Inasmuch as deductions and generalizations about hydrogen bonds require that the crystallographic data be as accurate as possible, no attempt has been made to include the results on all crystals in which hydrogen bonds are presumed to be present; rather only the results of those X-ray investigations which in the opinion of the original authors, or others, yield interatomic distances accurate to 0.1 Å. or better. It is an unfortunate truth that many X-ray crystallographers have a tendency to overestimate the accuracy of their work, and it is still more unfortunate that there are in the literature a host of crystal structure investigations which are essentially incomplete because the authors neglected to refine the parameters defining the atomic positions to a degree warranted by their data. As will be seen, such inac-

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