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The Photolysis of Acetone in Presence of Hydrogen

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The photodecomposition of acetone in presence and absence of hydrogen with light of wave-length >2500A has been studied at temperatures from 70 to 300°C. Up to 160°C acetone alone yields negligible amounts of methane and ethane is the hydrocarbon predominantly produced. The proportion of methane increases rapidly with temperature, the activation energy of its formation in acetone being 8.6 kcal. In presence of hydrogen methane formation is negligible at 70°C, is marked at 160°C and increases rapidly with temperature with an activation energy of this increase equal to 6.4 kcal. At 300°C it represents 75 percent of the ethane-methane product, which shows that photodissociation to methyl radicals is the major, if not exclusive primary process. Analysis of the data indicates that ethane formation is either a wall reaction with zero activation energy or a bimolecular association process of small activation energy. A decrease in ethane formation with increase of temperature is ascribed to a decrease in the stationary state concentration of methyl radicals. An activation energy of the reaction $CH_3+H_2=CH_4+H$ equal to 11 ± 2 kcal. has been deduced. A mechanism to account for quantum yields less than unity in the low temperature range, consistent with primary dissociation into radicals, has been suggested.

RECENT investigations of the photolysis of acetone vapor by ultraviolet light have revealed the decomposition of the molecule into radical fragments and the reorganization of these to yield the observed reaction products. Free methyl radicals are the intermediates postulated in the production of ethane.[3] Spence and Wild[4] have shown that below 60°C the free radical, acetyl, must have a definite lifetime since diacetyl is found in isolable amounts among the reaction products below, but not above, this temperature. We have employed the photolysis of acetone, in the range 70–300°C, as a source of free methyl radicals with which to study the kinetics of the reaction with hydrogen, $CH_3+H_2=CH_4+H$. We have compared the yields of ethane and methane at these temperatures from the photolysis of acetone in presence and absence of hydrogen.

EXPERIMENTAL PROCEDURE

Acetone at approximately 35 mm pressure alone or admixed with hydrogen at 175 mm pressure measured at room temperature could be introduced from reservoirs of the carefully purified materials into a cylindrical quartz vessel, 20 cm long and 2.8 cm in diameter, mounted vertically. This vessel, the volume of which, with dead space, amounted to 131.4 cc, could be enclosed in an aluminum block electric furnace with an even temperature distribution, illumination entering through a quartz tube placed snugly in a cut-away section of the furnace the length of the reaction vessel. Ultraviolet light from a hot mercury arc of the Heraeus type, operated vertically (arc length = 12 cm) at 85 volts and 3.9 amp. hand controlled to constant wattage, entered the reaction vessel through a cylindrical quartz vessel containing a continuously renewed stream of 25 percent acetic acid solution by volume to reduce the intensity of the short wave ultraviolet light. The interposition of two quartz tubes between light source and reaction vessel resulted in a separation of these two latter by about 10 cm.

The reaction vessel was suitably connected to an oil pump-mercury vapor pump high vacuum line, to the reservoirs of reactants, to a mercury manometer and to a gas analysis unit for the analysis of gaseous reaction products, with Töpler pumps for transfer of gases from the reaction zone and to constituent units of the analytical system.

Analytical procedure

The reaction products were separated into two fractions by fractional condensation in liquid air. The noncondensible fraction contained the hydrogen, carbon monoxide and methane. This also comprised all gases removed from the condensible fraction by repeated pumping at liquid-air tem-

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[3] Norrish, Crone and Saltmarsh, J. Chem. Soc. 1456 (1934).

[4] Spence and Wild, J. Chem. Soc. 352 (1937).

peratures. The residual condensate contained undecomposed acetone, any condensible polymeric products and the C_2 hydrocarbons.

An aliquot portion of the measured volume of the noncondensible fraction was introduced into a copper oxide chamber maintained at 310°C, an adjoining U-tube being kept immersed in liquid air. Circulation was maintained by raising and lowering the mercury reservoirs in the Töpler pump system. On completion of the combustion the residual methane was pumped into a Ramsay measuring burette and its volume determined. The liquid air around the U-tube was then replaced by acetone-carbon dioxide mixture. The carbon dioxide in the products of combustion thus vaporized were then transferred to the measuring burette and determined. Special tests on the water vapor obtained in the acetone experiments showed that only negligible amounts of carbon dioxide and methane were not recovered by the procedure used. In the experiments in presence of hydrogen, the final amount of hydrogen and the amount consumed were obtained by difference.

In the condensed fraction, the C_2 gases were obtained by pumping the condensate cooled in an acetone-carbon dioxide mixture. Here also the last fractions of the gas were recovered after vaporisation and condensation. The analysis of this fraction involved a catalytic hydrogenation of unsaturated hydrocarbons on an active copper catalyst. The results obtained by this test indicated negligibly small quantities of unsaturated hydrocarbon, within the error of the determination which was rather high, due to the use of an extremely active copper catalyst,[5] which also possessed a high adsorptive capacity for hydrogen. For this analytical work the less active copper catalyst, used by Morikawa,[6] from copper oxide granules, is to be preferred.

TABLE I. *Photolysis of acetone with and without hydrogen.*

	Moles Reactant ×10⁴		Moles Products ×10⁴					
			"Me_2CO"					
t°C	Me_2CO	H_2	By Diff.	Meas.	CH_4	CO	H_2	C–C
71	2.52	—	0.81	0.72	0.109	1.305	—	1.524
71	2.57	12.85	0.87	0.82	0.101	1.383	12.79	1.512
160	2.52	—	1.07	1.01	0.079	1.377	—	1.352
160	2.55	12.74	0.90	0.86	0.423	1.582	12.61	1.353
200	2.49	12.44	0.88	0.83	0.933	1.592	12.11	0.949
250	2.52	—	0.76	0.71	0.463	1.753	—	1.213
250	2.50	12.49	0.95	0.89	1.57	1.51	11.96	0.482
300	2.49	—	0.86	0.71	0.802	1.513	—	0.863[a]
300	2.54	12.69	0.77	0.72	2.327	1.728	11.69	0.378

[a] This value may be high by ~8 percent which would yield for the final acetone values ~0.92 by difference and ~0.77 by measurement.

The composition of the saturated fraction resulting after the hydrogenation was determined by the method of catalytic hydrogenation to methane, used in the work of Morikawa on these hydrocarbons. A measured quantity of hydrogen was added to a measured portion of the C_2 fraction ($H_2 : C_2 > 2$) and the mixture transferred to a nickel catalyst at 230–240°. The gases were circulated 10–20 times during an average reaction time of two hours, and then returned to the gas burette to test for gas retention by the nickel. The excess hydrogen was then removed by copper oxide at 270–280° with an adjoining tube in liquid air. The measure of the residual methane, giving by difference the hydrogen unused in the reaction on nickel gave a double check on the composition of the saturated hydrocarbon sample. For pure C_2H_6, the hydrogen consumed on nickel and half the methane formed should and, within experimental error, did coincide. We have therefore recorded the condensible hydrocarbon as C–C.

EXPERIMENTAL RESULTS

The analytical results for the experiments at five temperatures from 70 to 300°C are presented in Table I. Columns 2 and 3 record the initial reactants in moles and the following six columns the moles of products. In each experiment the illumination period was 35±5 minutes, except at 71° where the exposure was 2.5 hours.

An analysis of this table indicates that there is no material increase in the acetone decomposed (CO produced) per unit of illumination over the range of temperature 160–300°C, whether hydrogen is present or absent. The random variations are entirely accounted for by variations in the position of the arc and its intensity. The ethane formed in absence of hydrogen progressively decreases with increase in temperature. The decrease in presence of hydrogen is much more

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[5] Taylor and Joris, Bull. Soc. Chim. Belg. **46**, 241 (1937).

[6] Morikawa, Trenner, Taylor, J. Am. Chem. Soc. **59**, 1104 (1937).

TABLE II. C_2H_6 : CO *and* CH_4 : CO *in presence and absence of hydrogen.*

t°C	C_2H_6 : CO RATIO		CH_4 : CO RATIO			$(C_2H_6+\frac{1}{2}CH_4)$: CO RATIO	
	H_2 ABSENT	H_2 PRESENT	H_2 ABSENT	H_2 PRESENT	$\frac{2(-\Delta H_2)}{CO}$	H_2 ABSENT	H_2 PRESENT
71	1.17	1.09	0.083	0.073	0.087	1.21	1.13
160	0.982	0.855	0.057	0.268	0.164	1.01	0.99
200	(0.86)[a]	0.595	(0.11)[a]	0.585	0.414	(0.91)[a]	0.89
250	0.692	0.319	0.264	1.04	0.702	0.82	0.84
300	0.570	0.219	0.530	1.35	1.16	0.83	0.89

[a] Interpolated values.

pronounced. *Vice versa*, methane production increases with temperature with acetone alone and much more rapidly in presence of hydrogen, from 160° upwards. At 70°C the methane production is within experimental error the same in the two conditions. These observations are exhibited by the data in Table II.

In the last two columns are given the ratios $(C_2H_6+\frac{1}{2}CH_4)$: CO, which indicates the relation between total hydrocarbon produced (reckoned as C_2) per unit of carbon monoxide formed. These columns reveal that at low temperatures a carbon monoxide deficiency obtains, whereas, at temperatures above 160°, a hydrocarbon deficiency is observed. We interpret these results most readily on the assumption that at temperatures of 70° and lower there occurs the formation of more complex molecules, as for example, $CH_3COCOCH_3$.[4] At high temperatures these do not form, but polymers of the hydrocarbons are formed as well as ethane and methane. The recent work of Taylor and Jungers[7] has revealed that in presence of free radicals any unsaturated hydrocarbons are rapidly polymerized in the temperature range here under study.

Since methane is formed in the absence of hydrogen it is to be expected that the methane formation in presence of hydrogen should be greater than that calculated from measurements of hydrogen consumed, expressed as a ratio to CO produced in the column of Table II headed $2(-\Delta H_2)/CO$. Comparison of this column with the adjoining column CH_4 : CO indicates that this is consistently the case. The agreement between the two sets of data cannot be very close. The hydrogen consumption involves the small difference of two large quantities. The methane value depends on the efficiency of the fractionation process and on the extent to which methane formation from acetone alone is suppressed in presence of hydrogen.

DISCUSSION OF RESULTS

Activation energies

The influence of temperature on methane formation can be deduced from the data on hydrogen consumption and from the actual measurements of methane production. The result in the latter case will be less certain than in the former for the reason just discussed. A plot of the logarithms of the $(-\Delta H_2/CO)$ values, which represent rates of reaction, against the reciprocal of the absolute temperature gives a straight line with slope corresponding to an activation energy of 6.4 kcal. This line passes through the points for $t=250$ and 300°C which are the most accurate and passes below and above the points at 200 and 160°C. The value at 71° is off the line entirely, due to the large experimental error in the determination, consequent, in all probability, on extraneous secondary processes, during the long period of exposure required at this temperature. A straight line through the data from 160–300° for observed methane production (CH_4/CO) in presence of hydrogen is not so satisfactory, tending to curve over at the high temperatures. Such curvature undoubtedly arises from diminishing methane production from acetone due to the competition of the hydrogen reaction. The best straight line through the four points gives a slope with an activation energy of 5.9 kcal.

The activation energy of methane formation from acetone in the absence of hydrogen (CH_4/CO) has a value of 8.6 kcal. in the range 160–300°C, a value which accounts for the increasing effectiveness of the interaction with hydrogen when this is present.

The data on ethane and methane formation can also be represented on a plot log (CH_4/C_2H_6) against $1/T$ giving a good straight line with a slope corresponding to an activation energy of 11.4 kcal. The increase of slope over that of methane formation arises from the decrease in the yield (C_2H_6/CO) with rise in temperature as

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[7] Taylor and Jungers, Trans. Faraday Soc. **33**, 1353 (1937).

set forth in Table II. The straight line obtained implies, however, that the ethane producing process, if represented by a kinetic expression of the form $+dC_2H_6/dt=Ze^{-E/RT}$, must yield values of Z in the equation *decreasing* exponentially with temperature. The obvious method of interpreting this is in terms of a decreasing stationary state concentration of methyl radicals with increase of temperature, due to the competition, with the reaction which produces ethane, of the reaction of the radicals with hydrogen, or with acetone, producing methane.

We may represent the reaction producing methane in presence of hydrogen by means of the equation

$$+d[CH_4]/dt=k_1[H_2][CH_3]e^{-E_M/RT}.$$

The process producing ethane may be unimolecular at the wall, a bimolecular association of methyl radicals or a three-body combination of two radicals, representable by an equation

$$+d[C_2H_6]/dt=k_2[CH_3]^xe^{-E_E/RT},$$

where x may be either 1 or 2 and k_2 in the case of a termolecular reaction would include a concentration of a third body.

Taking the unimolecular case first with $x=1$, $[H_2]$ constant, and the activation energy $E_E=0$ we obtain

$$+\frac{d[CH_4]}{d[C_2H_6]}=\frac{k_1[H_2][CH_3]e^{-E_M/RT}}{k_2[CH_3]}=k_3e^{-11.4/RT},$$

from the slope of the curve log $([CH_4]/[C_2H_6])$ *vs*. $1/T$. On this assumption $E_M=11.4$ kcal. The difference between this value and the observed slope log $[CH_4]/[CO]$ *vs*. $1/T=6.4$ kcal., must represent the variation of stationary state concentration of methane with temperature, $[CH_3]=ke^{5.0/RT}$. In the interval from 160 to 300°C the quantity $e^{5.0/RT}$ changes by the factor $e^{-1.42}$ or approximately 0.24. This is almost exactly the ratio in which ethane production in presence of hydrogen decreases in the same interval. This concordance therefore strongly suggests a unimolecular reaction at the wall with negligible activation energy.

In the bimolecular case, $x=2$ we have

$$+\frac{d[CH_4]}{d[C_2H_6]}=\frac{k_1[H_2][CH_3]e^{-E_M/RT}}{k_2[CH_3]^2e^{-E_E/RT}}=k_3e^{-11.4/RT}.$$

From this equation we deduce

$$E_{[CH_3]}-E_M=-11.4-E_E+2E_{[CH_3]}.$$

As before, from the observed slope log $[CH_4]/[CO]$ *vs*. $1/T$,

$$E_{[CH_3]}-E_M=-6.4.$$

By addition,

$$2E_M-E_E=17.8 \text{ kcal.}$$

This gives a minimum value for E_M when $E_E=0$, in which case $E_M=8.9$ kcal., and $E_{[CH_3]}$ becomes 2.5 kcal. This also will give the correct variation of ethane formation in presence of hydrogen with temperature. A positive value of E_E would increase E_M by $\frac{1}{2}E_E$; for $E_E=5$ kcal., the value of E_M would be $8.9+2.5=11.4$ kcal., and for $E_E=8$ kcal., $E_M=12.9$ kcal. Recent researches have assigned to E_E a value of zero or at most a few kilocalories.[8]

The analysis therefore does not lead to an unequivocal value for the activation energy of the reaction $CH_3+H_2=CH_4+H$. The data just cited would indicate that it should lie within the range $E_M=11\pm2$ kcal.

A further observation is possible from an analysis of the data in Table II. At 300°C it is seen that, with hydrogen present, at least 75 percent of the decomposed acetone found in the form of the two hydrocarbons is present as methane, and the percentage is increasing rapidly with rise in temperature. Under our experimental conditions ethane once formed would not be markedly converted to methane. This signifies that, in the photochemical decomposition, under these conditions, the primary absorption process in the diffuse region leads mainly, if not exclusively, to radical fragments and that an intramolecular rearrangement of an activated molecule to yield ethane and carbon monoxide is a minor, if not entirely negligible, mode of decomposition. In processes of thermal decomposition of organic molecules both modes of decomposition appear to be possible, with the relative extent of each still a matter for experimental decision.

Our data on the photolysis of acetone alone overlap those previously obtained by

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[8] See, for example, Bawn, Trans. Faraday Soc. **31**, 1542 (1935).

Leermakers.[9] They check these latter in the invariance of quantum yield with temperature over the range 160–300°. At 71° the quantum yield is much smaller since the illumination for 2.5 hours produced approximately the same decomposition as 35 minutes at the higher temperatures. This points to a quantum yield of approximately 0.2 at 70°C a value comparable with those of Damon and Daniels[10] at 56°C. We suggest that the increase in quantum yield from 70 to 160° is to be associated with the suppression in the higher temperature range of diacetyl formation. From room temperatures to 70° the formation of diacetyl might permit, in addition to processes of recombination of the radicals CH_3 and $COCH_3$, a reaction, regenerative of acetone, of the form,

$$CH_3CO\cdot CO\cdot CH_3+CH_3 = CH_3COCH_3+CH_3CO.$$

This would decrease the quantum yield below the value of unity which might be anticipated from the spectroscopic evidence concerning the primary process. This suggestion is analogous to that put forward by Mund and van Tiggelen[11] to account for the low quantum yield in ammonia photodecomposition by the regenerative reaction,

$$N_2H_4+H=NH_3+H_2.$$

The occurrence of diacetyl formation in the low temperature range is probably also responsible for methane formation which is abnormal when compared with that in the higher temperature range, due to secondary reactions during the longer period of illuminations involved.

The value of 11±2 kcal. which we obtain for the activation energy of the reaction $CH_3+H_2 = CH_4+H$ is to be compared with the experimental data of Hartel and Polanyi[12] for the same reaction with the methyl radicals from sodium vapor and methyl halides. Their observations are generally quoted as leading to a value of 8 kcal. Examination of their data shows two series of determinations, one of which, at 9 mm hydrogen pressure, leads to the value of 8 kcal., the other at 10 mm hydrogen pressure leading to a "best" value of 5.5 kcal., and 6.3 kcal. as the largest value which can be obtained from the data. Our value is beyond their upper limit and is coincident with the value of 11 kcal. estimated by Morikawa, Trenner and Taylor[6] from their studies of interaction between atomic hydrogen and hydrocarbons.

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[9] Leermakers, J. Am. Chem. Soc. **56**, 1899 (1934).

[10] Damon and Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

[11] Mund and van Tiggelen, Bull. Soc. Chim. Belg. **46**, 104 (1937).

[12] Hartel and Polanyi, Zeits. f. physik. Chemie **11B**, 97 (1930).