ditions similar to those used in this study. The slope of the plots of log K *vs.* $1/T$ seem to be slightly greater for the activity constants. If this relationship is assumed to be general, the ΔF values can be interpreted as maximum values and the ΔH values as minimum values. This interpretation of the limits of the ΔH and ΔF values would indicate that the correct ΔS values are probably no more positive than those given in Table III.

There are rather large differences in the thermodynamic quantities reported by various workers[13,14,17] for nickel with ethylenediamine. The conditions used by Hares[18] in this Laboratory are very nearly the same as those used in this investigation and the constants obtained by Hares are in closer agreement with the activity constants obtained by McIntyre[17] than any other values which have been reported. The thermodynamic data of McIntyre are used for comparisons rather than those of Basolo[13] because of the close agreement between the results of Hares and McIntyre and the wide discrepancies between the results of Basolo and McIntyre. Basolo[19] has since reported that the ΔH values obtained by calorimetric measurement are in much closer agreement with those of McIntyre.

The lower ΔF values indicate clearly that the sulfur-containing amines give much less stable complexes than the corresponding polyamines without sulfur. However, the decreased stability is not due entirely to a decrease in bond strength, although the ΔH values are generally lower for the complexes of the sulfur-containing amines. The stability is decreased appreciably by the less favorable entropy changes accompanying the formation of the complexes of the sulfur-containing amines.

The irregularities in the formation curves of zinc and copper with bis-(2-aminoethyl) sulfide are probably due to other equilibria which apparently are not important in the formation of the cobalt and nickel complexes. In the case of zinc there might be an intermediate complex with a ratio of three ligands to two zinc ions, or perhaps the second molecule of amine is not coördinated through all three points of attachment initially. In the adjustment from a tetrahedral to an octahedral arrangement accompanying the change in the coördination number some alteration in the shape of the formation curve might be more likely in the case of the sulfur-containing amines because of the greater variety in the means of attachment of a second molecule of amine to the zinc ion with a tetrahedral configuration. The formation curve for copper might be drawn out because not all of the sulfur and nitrogen atoms are active in coördination and perhaps there is a change in the ratio of the number of copper–nitrogen to copper–sulfur bonds. No formation constants are given for zinc or copper with bis-(2-aminoethyl) sulfide because of the irregularities. More information is needed for an understanding of these cases.

The slope of the formation curve of copper with 1,8-diamino-3,6-dithiaoctane differs from the expected theoretical slope. However, the deviation is slight and the formation constant presented in Table II is probably not appreciably less reliable than the other constants given. The slope of the formation curve of nickel with 1,8-diamino-3,6-dithiaoctane shows no appreciable deviation from the theoretical slope for a one to one complex. However, the curve is somewhat unusual in that it levels off slightly above an $\bar{n}$ value of 1. In each of these cases the slight irregularities are probably due to equilibria of minor importance as compared to the simple addition reaction to form the one to one complex.

PITTSBURGH, PENNA.

---

[18] G. Hares, Ph.D. Thesis, Pennsylvania State University, 1952.

[19] F. Basolo and R. K. Murman, THIS JOURNAL, **76**, 313 (1954).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

An Investigation of the Low Pressure Photolysis of Acetone by Means of the Mass Spectrometer

BY THOR RUBIN AND ROBERT O. LEACH

RECEIVED NOVEMBER 19, 1954

The photolysis of acetone in the wave length region 2800 to 3100 Å. has been studied by means of mass spectrometric technique. The pressure includes those in the range from 5 to 100 μ. Additional steps in the mechanism proposed by Dorfman and Noyes and Herr and Noyes appear to be demanded by the data.

In the photolysis of acetone, the formation of ethane, methane, carbon monoxide and biacetyl as major products has been substantiated by many authors.[1-7] The quantum yields of carbon monoxide and ethane under varying conditions of light intensity and pressure have been studied in great detail.[4-7] However, the direct measurement of the quantum yield for biacetyl has been made infrequently and the measured quantum yield of acetone decomposition has been determined only from the total amounts of the major products.[4]

Indirect estimates of the number of molecules of acetone decomposed per quantum and yield of biacetyl per quantum have been in general based upon the two net reactions[5,7]

$$(CH_3)_2CO \longrightarrow C_2H_6 + CO$$
$$2(CH_3)_2CO \longrightarrow (CH_3CO)_2 + C_2H_6$$

It has been found[5,6] too in the most successful mechanism explaining the results that both a het-

---

[1] G. H. Damon and F. Daniels, THIS JOURNAL, **55**, 2363 (1933).

[2] M. Burak and D. W. G. Style, *Nature*, **135**, 307 (1935).

[3] R. Spence and W. Wild, *ibid.*, **138**, 206 (1936).

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

[5] D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

[6] H. W. Anderson and G. K. Rollefson, *ibid.*, **63**, 816 (1941).

[7] J. J. Howland and W. A. Noyes, Jr., *ibid.*, **66**, 974 (1944).

erogeneous process and parallel homogeneous process appear to be necessary for formation of biacetyl and ethane.

At pressures at which reaction has been studied in the present work (all lower than 0.1 mm.) the heterogeneous process only is expected to be of importance. There has been some disagreement as to the effect of light intensity on the amount of acetone decomposed per quantum,[4,5,7] therefore, a direct determination of this quantity (or a quantity proportional to it) was believed desirable also.

Experimental

Reagents.—The acetone, Baker and Adamson, reagent quality, was degassed under vacuum and distilled once into thermally insulated storage flasks protected from light. The ethane used to determine the spectrometer sensitivity was research grade gas manufactured by the Phillips Petroleum Company. Reagent grade methane gas was obtained from the Matheson Chemical Company. Carbon monoxide was prepared by the dehydration of formic acid with sulfuric acid. The biacetyl was obtained from the Eastern Chemical Company. This sample was dried, degassed and distilled once before use.

Apparatus.—The flow system consisted of a cylindrical irradiation chamber 48 cm. long fitted with a 43-mm. quartz window. The chamber was attached to the mass spectrometer *via* a high speed fractionating leak and connected to glass storage tanks through non-fractionating glass capillary leaks. A Clark micromanometer[8] together with a McLeod gage were used for the pressure measurements.

The mass spectrometer was a Nier type machine with a 60° deflection and a 15 cm. radius of curvature. The gas from the leak was led into the ion source *via* a Pyrex thimble. It was ionized by 75 volt electrons from the filament.

Since all of the gas introduced into the irradiation chamber was pumped through the mass spectrometer the pumping system of the machine was quite large having a total speed of about 40 l./sec. at 10^{-6} mm. The spectrometer had good long time stability provided that the filament ribbon was carbonized occasionally with butene-1.

Light Source.—A General Electric AH-6 high pressure mercury vapor lamp provided the source of ultraviolet radiation. Two quartz lenses having a resultant focal length of 1.8 inches, served to collimate the light obtained from the lamp. A filter cell, a shutter or a wire screen were interposed in the light beam as the occasion demanded. The light intensity was determined by means of a monitoring system attached to the lamp housing. The system consisted of another shutter, a filter cell and an Eppley air type thermopile fitted with a quartz window. A Leeds and Northrup H.S. galvanometer sensitive to 4×10^{-10} amp./mm. at one meter completed the system. The galvanometer deflections in centimeters were recorded as the relative values of the incident light intensity, I_0.

The solution used in both filter cells isolating the portion of mercury arc spectrum from 2200 to 3600 Å. was 0.49 molar with respect to nickel sulfate and 0.32 molar with respect to cobalt sulfate. Solution was continuously circulated through the filter cell interposed in the main light beam.

Measurements.—The residuals from the irradiation chamber were determined first. Acetone was introduced and after the steady flow conditions were obtained, the mass spectrum for acetone was measured for mass numbers from 14 to 18 and from 25 to 58. The light shutter was opened and irradiation of the gas was maintained for one hour. The mass spectrum of the resulting steady state gas mixture was obtained and a relative I_0 value recorded. To average out the depletion in the storage bulbs the mass spectrum of the gas in the reservoir (acetone) was then rerun after an hour.

Products.—The amounts of ethane, methane and carbon monoxide were determined by standard methods of mass spectrometry using calibrating gases and synthetic mixtures. Since the mass range of the instrument was restricted, the fragment at mass 43 served to determine biacetyl.[9]

Other compounds corresponding to mass 42 and of mass 15 were found also. Traces of polymeric materials deposited on the glass walls of the irradiation chamber were detected. Effects of its presence on the reactions were negligible.

The temperature of all experiments listed in Table I was 31 ± 0.1°. P_1 was the steady state partial pressure of acetone during photolysis, P_0 was the steady state acetone pressure before and after photolysis expressed in microns. P_E, P_{co}, P_d and P_M were the partial pressures, respectively, of ethane, carbon monoxide, biacetyl and methane. I_0 was the incident light intensity containing for runs 48, 50, 54, 57, 58 and 60 the factor $^1/_3$ corresponding to the fraction of light passed through the intensity modulating screen.

TABLE I

Run	P_1	$P_0 - P_1$	P_E	P_{CO}	P_d	P_M	I_0	I_0'	$(P_0 - P_1)$ calcd.
22	17.6	3.7	1.7	1.08	1.00	0.14	1.67	1.48	3.43
24	15.3	4.7	2.3	1.5	1.10	.16	1.87	1.87	4.54
26	27.6	7.9	3.5	2.1	3.06	.19	1.82	2.22	7.08
27	27.2	7.7	3.76	1.8	2.65	.31	1.79	1.82	8.6
29	69.8	19.6	8.0	3.3	7.56	.81	1.85	1.93	18.9
31	4.3	1.3	0.66	0.49	0.19	.11	1.70	2.23	1.3
33	42.5	10.5	3.1	1.8	4.41	.34	1.72	1.97	6.69
35	85.2	19.6	(5.7)	(3.4)	7.13	.51	1.65	1.60	(11.8)
37	34.9	7.1	2.4	1.5	3.00	.19	1.59	1.51	5.1
40	65.5	15.7	7.2	3.0	5.83	.41	1.45	1.59	16.5
42	2.9	0.60	0.36	0.3	0.66	.05	1.47	1.48	0.66
48	50.5	3.4	1.34	0.41	1.53	.08	0.41	0.495	3.28
50	17.5	0.94	0.35	0.15	0.24	.03	0.40	0.409	0.71
51	78.4	14.1	6.3	2.4	4.77	.27	1.28	1.17	14.3
53	60.5	9.9	4.6	1.6	4.18	.19	1.26	1.16	10.9
54	84.4	4.0	1.6	0.52	1.86	.08	0.39	0.382	3.88
56	50.0	10.4	4.2	2.2	3.49	.26	1.55	1.46	9.08
57	98.2	4.1	1.8	0.63	1.86	.08	0.43	0.280	4.26
58	42.6	2.3	0.80	0.25	0.86	.01	0.43	0.413	1.90
60	91.4	3.1	1.2	0.40	1.55	.03	0.40	0.250	2.82
61	84.5	9.3	4.0	1.7	4.05	.21	1.28	0.778	8.92

The results for runs 36 and 39 were not given because of instrumental failures. For the same reason ethane and carbon monoxide data of run 35 were approximate values. All the partial pressures given were partial pressure throughout the entire irradiation chamber since diffusion mixing is very rapid for these pressures as compared to the mass flow rate of gas through the system.

Errors.—The sources of error in these results were considered to arise from uncertainties in the various peak height measurements, errors in instrument sensitivity and from variation of residuals.

The ethane results were the most precise of those taken for any product. The probable errors in the higher light intensity ethane data were between 6 and 12%. These estimates include those for runs 22 to 42. The probable errors in ethane pressure determinations for the rest of the results (runs 48 to 61) were between 11 and 15%.

The biacetyl pressure determinations had probable errors between 11 and 18% for all runs from 22 to 40 and had probable errors between 14 and 30% for runs 48, 51, 53, 54, 56, 57 and 60. The probable error for the very low biacetyl pressures measured in run 42 is 30%. The probable errors of the results of experiments 50 and 58 which were determined at the lowest light intensities used, were about 60%.

The carbon monoxide determinations corresponding to runs 22 to 37 had probable errors between 11 and 15%. Those designated by run numbers 37 to 50 and 51 to 61 except run 58 had probable errors between 14 and 28%, the probable errors of experiments numbered 50 and 58 had probable errors of 50%. The probable errors in the methane data were less than 10% except for the results given by runs 50 and 58 where practically no yield of methane was found.

The probable errors in the determinations of the pressure loss of acetone, $P_0 - P_1$, were about 5% for all runs.

Before discussing these data in terms of reaction mechanism, possible reactions occurring in the mass spectrometer must be discussed. Significant reactions occur within the mass spectrometer if appreciable amounts of radicals flow into it. The net peak at mass fifteen was essentially zero for all runs except number 29. Also the pressure changes in the irradiation chamber measured by the micromanome-

---

(8) Clark Instrument Co., Silver Springs, Maryland.

(9) D. K. Brewer and V. H. Diabele, *J. Research Natl. Bur. Standards*, **35**, 125 (1945).

ter agreed with the algebraic sum of mass spectrometrically measured product partial pressures and pressure loss of acetone, for all cases except for run 29. Thus, inappreciable steady state partial pressures of radicals existed in the irradiation chamber. Furthermore for run 29 where the manometrically determined pressure change was at least several microns greater than the algebraic sum pressures, a measurable net peak at mass fifteen was found. Therefore the apparatus was assumed capable of detecting methyl radicals if they were present. A spectrometer sensitivity calculated for mass fifteen based on run 29 alone was about 75% of the instrument sensitivity for methane. It might be mentioned too that the mass balance ratio between the acetone lost and products found excluding mass 42 and possible polymer was such that 90% of the carbon can be accounted for in all but two of the runs, numbers 33 and 58.

Mechanism.—Correlations of these data with mechanism were made by a steady-state treatment of the proposed equations together with mass balance relations. For acetone the rate at which gas entered the irradiation chamber during a run whether the gas was illuminated or not is given by RP_0 where R is the molecular flow rate constant of the spectrometer leak for acetone. During illumination acetone disappeared from the irradiation chamber by photochemical decomposition as well as by flow into the spectrometer. Designating the quantity k_1 as the acetone absorption coefficient the amount of light absorbed was assumed to be directly proportional to the incident light intensity times the pressure of acetone since the light absorption is less than a few hundredths of a per cent.[10] Thus

$$0 = \frac{dP_1}{dt} = RP_0 - RP_1 - I_0k_1P_1 \qquad (1)$$

Recombination of fragments from the primary process to give acetone gave additional terms through which pressure dependence could be related to the process by which the recombination occurs. It follows that the quantity $(P_0 - P_1)$ will be a linear function of I_0P_1 with a zero intercept if recombination processes were unimportant.

The results were shown in Fig. 1. The solid circles designate runs made at low light intensities. The results from runs 57, 60 and 61 are not included on this graph since a new lamp was installed after run 56. This second lamp lost intensity quite rapidly at first, which was interpreted by us to indicate that a rapid change in spectral distribution of the second lamp had occurred during its initial operation. After this lamp was stabilized somewhat the second series of runs were taken. The results with the second lamp after stabilization fell on a different straight line from the first, also intersecting the origin.

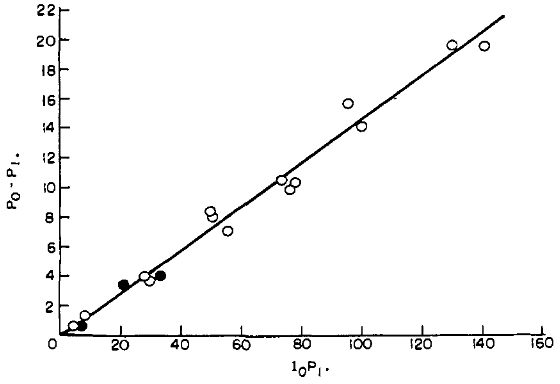

Fig. 1.—Acetone decomposed.

It can be concluded then that recombination of the primary products was small for acetone photolysis at pressures less than 100 μ and incident light intensities less than about 5 × 10^{17} quanta per second cm.[3] used in these experiments.

Since the limits of error for $P_0 - P_1$ and P_1 were less than the scatter of the points from each of the two lines mentioned it appeared that the plot of $P_0 - P_1$ *versus* I_0P_1 was a good basis for placing I_0 values from all of the data on a single arbitrary scale of intensity. This was done by assuming that all P_0 and P_1 measurements are correct and assigning new values denoted by $I_{0,1}$ to the intensity data. In this way correlations of all the steady state pressure data for the products were made with one arbitrary light intensity scale.

The pressure drop $(P_0 - P_1)$ of acetone was proportional to the light absorbed. In terms of this work it was expected using the mechanism of Herr and Noyes[5] that the ratio $(P_0 - P_1)/P_d$ be proportional to the function $1 + (k_2/k_3)\,P$. k_2 was a rate constant of the monomolecular decomposition of acetyl radical into methyl radical and carbon monoxide. k_3 was a rate constant for the diffusion of the acetyl radical to the wall. P was the pressure. The value of the ratio k_2/k_3 is very small[5] (of the order of $3 \times 10^{-5}\ \mu^{-1}$). On this basis then, $(P_0 - P_1)/P_d$ was expected to be almost independent of pressure.

Such was not found in the present data $(P_0 - P_1)/P_d$ increases quite rapidly with decreasing pressure at constant light intensity. The total variation of this function over the pressure range covered by this work was found to be four times larger than the probable errors assigned to this function.

On this basis it would appear that at least two pressure dependent competing reactions existed. Biacetyl was formed at least indirectly by one of these processes and in the other, carbon monoxide and ethane. The pressure dependence must be such as to favor biacetyl formation at the higher pressures.

The simplest mechanism to explain the formation of the main products using the idea of excited acetyl radicals[6,11] is as follows

$$CH_3COCH_3 + h\nu \xrightarrow{bI_0k_1} 2CH_3 + CO \qquad (2)$$

$$CH_3COCH_3 + h\nu \xrightarrow{(1-b)I_0k_1} CH_3CO^* + CH_3 \qquad (3)$$

$$CH_3CO^* \xrightarrow{k_2^*} CH_3 + CO \qquad (4)$$

$$CH_3CO^* + CH_3COCH_3 \xrightarrow{k_{13}} CH_3CO + CH_3COCH_3^* \qquad (5)$$

$$CH_3CO \xrightarrow{k_9/P_1} {}^1/_2(CH_3CO)_2 \text{ wall} \qquad (6)$$

$$CH_3CO \xrightarrow{k_2} CH_3 + CO \qquad (7)$$

$$CH_3 \xrightarrow{k_3/P_1} {}^1/_2C_2H_6 \text{ wall} \qquad (8)$$

This mechanism and the designation of the rate

---

(10) C. W. Porter and C. J. Iddings, THIS JOURNAL, **48**, 40 (1926).

(11) L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

constants was essentially that of Herr and Noyes[5] with the addition of two reactions 4 and 5.

Although the measured yield of acetone loss was not dependent upon the light intensity (Fig. 1) the relative yield of biacetyl to acetone was. A better correlation of the present data with the mechanism was obtained if a photochemical decomposition of biacetyl was supposed. This correction removed a small discrepancy between the high and low intensity biacetyl results. As far as these data are concerned, formation of products of molecular weight greater than sixty or formation of excited acetyl radical were equally satisfactory explanations of this effect of light intensity. The first case was not detectable in this machine and the second was not distinguishable from the intermediates formed from the acetone photolysis. Anderson and Rollefson[6] have discussed the chemistry of the acetyl radical from biacetyl photolysis in the same way given here. Blacet and Bell[12] have considered also possible formation of high molecular weight products.

The primary process of biacetyl photolysis considered in this work was expressed as

$$(CH_3CO)_2 \xrightarrow{k_{11}I_0} \begin{array}{l}\text{excited acetyl or}\\ \text{high molecular weight products}\end{array}$$

The contribution of excited acetyl to equation 5 and of acetyl to equation 6 if the mechanism of Anderson and Rollefson were valid under these experimental conditions, was ignored. Such terms introduced effects of the same magnitude as the experimental error.

The steady-state conditions applied to the mechanism showed the biacetyl steady-state pressure, P_d, was governed by the relation

$$\frac{(1 - b)R(P_0 - P_1)}{(I_0'k_{11} + R_d\ )P_d} = \frac{2k_2}{k_9} P_1 + \frac{2k_2{}^*k_2}{k_{13}k_9} + 2 + 2\frac{k_2{}^*}{k_{13}} P_1{}^{-1}$$

The value of $I_0'k_{11}/R$ was assumed to be approximately equal to $I_0'k_1/R$. The value of k_1/R which was used to establish the scale of I_0' was the slope of the corrected line from the acetone plot. This value was 0.142.

The ratio of the flow rate ratio, R_d/R, for biacetyl and acetone equaled 0.822.

The plot of the function $(P_0 - P_1)/[(0.142I_0' + 0.822)P_d]$ *vs.* $P_1{}^{-1}$ was given in Fig. 2. A straight line with a slope different from zero was drawn representing the data within the experimental errors quoted. The solid circles represent the low intensity data. A "best" line determined by least squares yields an intercept of 2.2 and a slope of 2.6 corresponding to a value for b of 0.09 and 9.4 μ for $k_2{}^*/k_{13}$. Since the value of b depended also on the correctness of the approximation $k_{11} = k_1$ it was of low accuracy.

Herr and Noyes determined values of b at various wave lengths for acetone photolysis at high pressures ranging from 1 to 16 cm. At 3130 Å. they find b = 0.11; at 2537 Å. b has risen to 0.25. Those results are to be regarded as satisfactory agreement with those of the present work. Of course $k_2{}^*/k_{13}$ cannot be determined from the data of Herr and Noyes[11] as the $k_2{}^*/k_{13}P_1$ term was negligible at high pressure conditions.

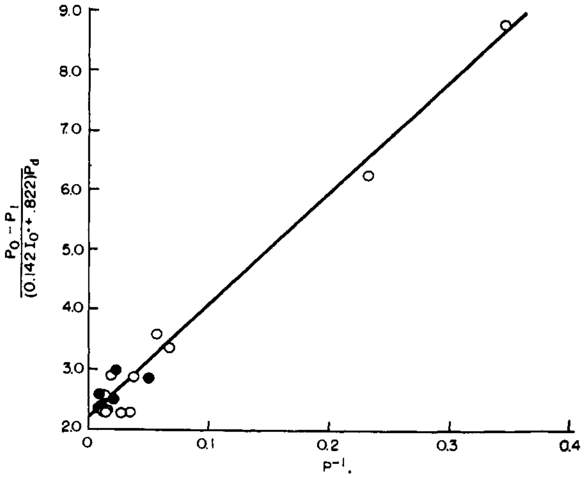

Fig. 2.—Relative biacetyl yield.

Formation of methane was postulated to occur by

$$CH_3 \xrightarrow{k_{14}/P_1} CH_4 \text{ at wall} \qquad (11)$$

The relations 2 to 8 together with flow equation for effusive flow[13] of gas through a hole of diameter smaller than the mean free path of the molecules determined the steady-state partial pressures of both the acetone and the products.

Designating the molecular flow rate constants of ethane, methane, carbon monoxide and biacetyl by R_E, R_M, R_{CO} and R_4 the formation of methane and ethane together within the irradiation chamber were related by

$$(k_{14} + k_3)/P_1 = R_MP_M + 2R_EP_E \qquad (12)$$

This is done since the coefficient $(k_{14} + k_3)$ was independent of the total pressure but the separate rate process coefficients varied with different conditions on the wall from experiment to experiment.

The steady-state pressures of ethane, methane and carbon monoxide were related to the steady-state pressure decrease in acetone by

$$(P_0 - P_1) = 2\frac{P_E}{R} P_E + \frac{R_M}{R} P_M - \frac{R_{CO}}{R} P_{CO} \qquad (13)$$

This equation was derived directly from the mechanism. Using R_E/R = 1.386, R_M/R = 1.902, R_{CO}/R_M = 1.430 for the ratios of the flow constants, values of $(P_0 - P_1)$ calcd. were determined and listed in the last column of Table I. The observed values agree with the calculated values within the experimental errors except for runs 33, 35 and 37. The results of run 35 were estimated values only since there was an instrument failure during this run. In run 33 the filament current had been inadvertently varied at some time during the photolysis period. We were unable to account for the large deviation in the case of experiment 37.

$$\frac{2P_ER_E + R_MP_M}{R(P_0 - P_1)} = (1 + b) + \left(1 + \frac{\dfrac{k_2k_{13}P_1{}^2}{k_2{}^*}}{k_9 + k_2P_1}\right)\frac{1 - b}{1 + \dfrac{k_{13}}{k_2{}^*}P_1} \qquad (15)$$

---

(12) F. E. Blacet and W. E. Bell, *Disc. Faraday Soc.*, **14**, 703 (1953).

(13) E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, N. Y., 1938, p. 61.

in terms of the mechanism. The values $b = 0.09$, $k_2^*/k_{13} = 9.4$ from the biacetyl data inserted in 15 gave

$$\frac{2R_EP_E + R_MP_M}{R(P_0 - P_1)} = 1.09 + 0.91\,(1 + 0.11P_1)^{-1} \quad (16)$$

The solid line drawn in Fig. 3 was based entirely on the right-hand side of equation 16. The points fitted this line within experimental error, except runs 33, 35 and 37.

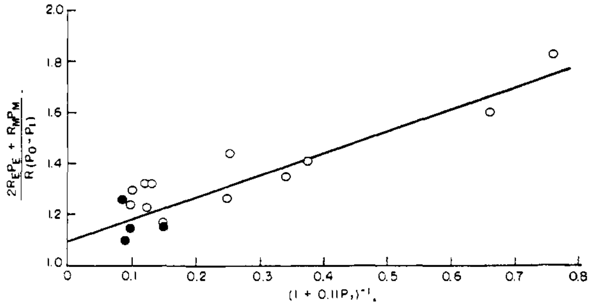

Fig. 3.—Relative ethane-methane yield.

Discussion

In this work as in the classical results of Herr and Noyes it was postulated that a fraction b of the acetone molecules absorbing radiation, spontaneously dissociate into methyl and acetyl radicals. The value of b for heterochromatic light found from this work fell within the range of the more precise values given by Herr and Noyes.

The fraction $(1 - b)$ of the acetone molecules which have absorbed light decomposed into methyl radicals and acetyl radicals, the latter in some excited energy state. In order to explain the increased biacetyl yield at higher pressure a collision reaction between excited acetyl radicals and acetone, equation 4 was proposed. The energy transferred in the deactivation collision either was distributed among the many vibrational modes of the acetone molecule or was dissipated possibly by acetone fluorescence. Follow dissociation processes from reaction 4 forming methyl radical and carbon monoxide appear to be ruled out, for the formation of such intermediates would call for considerable different kinetic interpretation than was consistent with these data.

It is easily shown that the modifications of mechanism proposed in this work introduced no effect which could be detected in the high pressure studies of Herr and Noyes or of Howland and Noyes. However, our experimentally determined quantum yields for acetone decomposition did not depend on the light absorbed whereas the calculated results of Howland and Noyes showed dependence. The reasons for this were not certain. However, possible traces of methane in the samples of carbon monoxide analyzed by Howland and Noyes could account for part of the variation of their calculated acetone quantum yield.

Acknowledgment.—The authors are grateful for aid received from the Graduate School of The Ohio State University, and from the du Pont Fund, in support of this work.

COLUMBUS, OHIO

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

Photochemical Reactions in the System Methyl Iodide–Iodine–Methane; The Reaction $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$

BY G. M. HARRIS[1] AND J. E. WILLARD

RECEIVED JANUARY 11, 1954

The work reported includes studies of: (1) exchange of iodine between CH_3I and I_2, using I^{131} as tracer; (2) photolysis of CH_3I to produce CH_4, CH_2I_2, CHI_3 and I_2; (3) reaction of $C^{14}H_3$ radicals with CH_4 to form $C^{14}H_4 + CH_3$; and (4) formation of CH_3I and HI as the result of absorption of 1849 Å. light by I_2 in CH_4–I_2 mixtures. It has been found that: (1) Gaseous CH_3I and I_2 undergo a slow surface catalyzed exchange reaction in Pyrex in the dark at 25°, and that exchange is also induced by light from a tungsten filament lamp transmitted by Pyrex and absorbed by CH_3I. (2) The quantum yield for the gas phase exchange between CH_3I and I_2 in 2537 Å. light absorbed by CH_3I is unity. (3) "Hot" methyl radicals formed by the dissociation of gaseous CH_3I by 2537 Å. light undergo the reaction $CH_3 + CH_3I \rightarrow CH_4 + CH_2I$ with a quantum yield of about 0.0027, in agreement with the earlier result of Schultz and Taylor. For radicals formed by 1849 Å. light the yield is twelve-fold higher. (4) For hot radicals formed by 2537 Å. light the relative probability per collision that they will abstract hydrogen from CH_3I, CH_2I_2 and CH_4 is $1: \geqq 16:0.3$. (5) The rate of the photolysis of CH_3I to form CH_4 and CH_2I_2 is independent of temperature up to at least 300°. It is inhibited by the presence of A or CH_4. (6) Secondary products from the photolysis of gaseous CH_3I include CHI_3, C_2H_4 and probably C_2H_2 but not H_2. (7) By coupling spectrophotometric and mass spectra analyses a satisfactory material balance for I, C and H in the products of the photolysis of CH_3I has been obtained. (8) 1849 Å. is absorbed by I_2 to produce excited molecules which react with CH_4 to produce CH_3I and HI with a quantum yield of 0.1. (9) Thermal $C^{14}H_3$ radicals from the photolysis of $C^{14}H_3I$ undergo the reaction $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$ with an activation energy which is about 6.5 kcal./mole higher and a frequency factor about 3×10^{-4} lower than the $C^{14}H_3 + I_2 \rightarrow C^{14}H_3I + I$ reaction.

Introduction

The purpose of this research was to investigate the feasibility of using the photodissociation of $C^{14}H_3I$ as a means of producing labeled methyl radicals for use in studying their reactions.

The first step in the photolysis of CH_3I is its dissociation by the reaction $CH_3I \xrightarrow{h\nu} CH_3 + I$. This conclusion is supported by the presence of a continuum in its absorption spectrum,[2] by the fact that

---

[1] Department of Chemistry, University of Buffalo, Buffalo, New York.

[2] (a) G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 300 (1930); (b) C. F. Goodeve and D. Porret, *Proc. Roy. Soc. (London)*, **A165**, 31 (1938).