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GAS PRODUCTION IN THE PHOTOLYSIS OF LIQUID METHYL IODIDE

Robert H. Schuler and Chester T. Chmiel

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Canisius College, Buffalo, N.Y.

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GAS PRODUCTION IN THE PHOTOLYSIS OF LIQUID METHYL IODIDE

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ABSTRACT

Methane and ethane are observed in the photolysis, at 2537 Å, of liquid methyl iodide. The quantum yields are determined to be respectively 0.023 and 0.007 and are independent of the extent of irradiation, the temperature of irradiation, and the presence of small amounts of iodine. Little or no hydrogen, ethylene, or acetylene formation is observed.

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Canisius College)

GAS PRODUCTION IN THE PHOTOLYSIS OF LIQUID METHYL IODIDE^{1,2}

Robert H. Schuler and Chester T. Chmiel

(1) Presented at the 121st Meeting of the American
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Abstract

The importance of "Hot Radical" processes in the
photolysis of liquid methyl iodide is further evidenced
in the formation of methane and ethane as gaseous products.
For the reactions induced by light at 2537 Å the quantum
yield for the formation of methane is 0.023, while that of
ethane is 0.007. Although the iodine concentration is
increasing during the course of the reaction, the ethane
and methane yields are found to be independent of the
extent of irradiation. The gas yields are dependent upon
iodine concentration only at very high iodine concentrations.
At room temperature, these yields are independent of the
temperature of the sample. Methylene iodide is shown to
be a product of the photolysis, while little or no hydrogen,
ethylene, or acetylene formation is observed.

Previously Hamill and Schuler³ and Schultz and Taylor⁴

(3) W.H. Hamill and R.H. Schuler, THIS JOURNAL, 73,
3466 (1951)

(4) R.D. Schultz and H.A. Taylor, J. Chem. Phys., 18,
194 (1950)

have concluded from studies respectively of the liquid and vapor phase photolysis of methyl iodide that it is necessary to assume as part of the mechanism certain reactions which are independent of the iodine concentration and of the temperature of the system. This led to a proposed mechanism which bases the net observed products on reactions occurring as a result of the excess kinetic energy given to the methyl radicals in the photolytic step. These hot radical processes must take place before this excess energy has been entirely redistributed by collision with the surrounding molecules.

This investigation was undertaken in order to determine the effect of iodine on the production of methane and ethane in the liquid phase photolysis. Since iodine does not interfere with the required analyses, investigation of the gas production reactions allows a study of the iodine dependence of the processes over a much wider range of iodine concentrations than was possible in the iodine production measurements. This work also serves as the basis for a comparative study of gas production in the X-ray decomposition of methyl iodide⁵.

(5) R.C. Petry and R.H. Schuler, THIS JOURNAL, (See following contribution)

EXPERIMENTAL

Methyl iodide.— Both commercially obtained C.P. methyl iodide and a laboratory preparation (from methanol, phosphorus, and iodine) were used in this investigation. The samples were washed with thiosulfate and water, dried with silica gel, and carefully fractionated through a three foot helix packed column. The center cut boiling at 42.4°C was taken and, when kept in the dark, found to be without decomposition over periods of many months. All samples were found to have a refractive index (n_D^{25}) of 1.5271-1.5272. A total of 9 different fractions from 5 preparations were used with no apparent discrepancies being traceable to the individual samples.

Ultraviolet source.— A 50 watt Hanovia SC-2537 helical low pressure mercury discharge lamp was used. This was operated from the laboratory A.C. line through a variac and high voltage transformer. The intensity was monitored in terms of a constant lamp current of 50 ma.. The input to the transformer at this setting was 3.3 amperes at 97-98 volts. A small centrifugal blower was used to circulate air over the sample tube and lamp in order to keep these at room temperature and remove any ozone formed. There was very little increase in the temperature of the system with this arrangement.

Cells.— The cell used for a major part of the work consisted of a 12 mm. quartz tube with a graded seal to

pyrex and an attached high vacuum stopcock. Five ml. of methyl iodide was placed in this tube, the sample degassed, the vapor region masked to restrict the activation to the liquid phase, and the sample irradiated for the desired period in the center of the lamp helix.

A second cell, which permitted thermostating of the sample during the irradiation, consisted of a jacketed tube to which a quartz window was cemented with silver chloride and the seal made vacuum tight with glyptal. A side tube and stopcock, through which the tube could be evacuated, were arranged at angles of 120° to the cell axis. By rotating the assembly, the side arm could be employed in the freezing of the sample during the degassing and measuring operations. The sample was irradiated with the cell in a vertical position and with the window facing the end of the lamp helix. The transmission of the window of this cell was determined before the assembly of the cell to be 84% at 2537 Å.

The irradiation given a particular sample was determined from the period of irradiation at constant intensity, with the intensity defined in terms of the iodine produced in the photodecomposition of ethyl iodide. For actinometric purposes, the quantum yield of this latter reaction is taken as $\phi_I = 0.40$ (iodine atoms per quantum absorbed) on the basis of Norton's results⁶. As the absorption coefficients of the alkyl

(6) B.M. Norton, THIS JOURNAL, 56, 2294 (1934)

Iodides are very high at 2537 Å, all of the light transmitted through the window is absorbed in a relatively thin region adjacent to the window.

Gas measurement - methane. → The sample to be irradiated was degassed on the high vacuum line (Figure 1) by freezing in liquid nitrogen (-196°C) and pumping off the residual gas. The sample was then warmed to room temperature, bubbled, frozen and pumped again. This was repeated four times or until the residual gas amounted to 10^{-8} moles or less. Liquid nitrogen on trap (T) prevented mercury from condensing in the sample tube. After irradiation, the sample tube was attached to the line and the sample frozen in liquid nitrogen. With nitrogen on the trap and stopcock C closed, the methane was pumped to the McLeod gauge for measurement. The volume of the McLeod gauge had been previously calibrated and allowed measurement at 3.70, 0.166, 0.08, 0.06, 0.04, and 0.02 ml.. These volumes have proven to be very convenient for our studies up to total gas yields of 50 micromoles. The gas after measurement could then be allowed to expand into a modified Saunders-Taylor⁷ apparatus attached at F.

(7) K.W. Saunders and H.A. Taylor, J. Chem. Phys., 9, 616 (1941)

after closing stopcock A, and a suitable portion taken for combustion analysis. It was found that a single degassing of the sample in this manner recovered upwards of 90% of the methane formed in the photolysis with an additional 5-10% being obtained in subsequent degassings.

Gas measurement - ethane. - Ethane was obtained by degassing the sample at ethyl bromide mush temperature ($\sim -115^{\circ}\text{C}$). Higher temperatures must be avoided here because of the appreciable vapor pressure of methyl iodide. The fractionation was carried out in two steps, the first with the trap at liquid nitrogen temperature and the cell at -115°C , and then, after the ethane had been accumulated in the trap (with the fraction volatile at liquid nitrogen temperature being pumped off and added to the methane measurement), the trap was raised to -115°C and the ethane pumped to the McLeod and measured. The ethane was found to degas very slowly from the sample under these conditions. Because of this a total of at least 8-10 degassings were required to remove the major fraction of ethane which, together with the relatively low ethane yield, made the resultant accuracy of measurement rather poor.

Gas analysis. - Representative samples of the material volatile at -196°C were transferred to the Saunders-Taylor apparatus. Hydrogen was determined by burning the sample over copper oxide at 275°C , absorbing the water formed in dehydrite, and noting the decrease in pressure. The temperature of the furnace was then raised to 575°C and the methane burned. At this temperature the combustion was found to be complete within one hour. After absorbing the water, the carbon dioxide was measured and then absorbed in

ascarite. Any residual nitrogen (oxygen reacts with copper at this temperature) was noted. This ~~residual~~ ^{residue} serves as a check on any leakages in the system and was found to be negligible in almost all cases. From the corrected pressures before and after combustion, the ratio of carbon dioxide to hydrocarbon was calculated giving n_C , the average number of carbon atoms per molecule of the sample. No attempt was made to determine the hydrogen present in the hydrocarbon.

The fraction volatile at -115°C was subjected to a similar combustion analysis. One sample of this material was sealed into a tube and submitted for mass spectrometer analysis⁸.

(8) The analytical services of Consolidated Engineering Corp., Pasadena, Cal. were employed.

Methylene Iodide formation. - Methyl iodide was photochemically exchanged with radio-iodine⁹ and the

(9) I^{131} was obtained through the U.S. Atomic Energy Commission, Oak Ridge, Tenn.

formation of methylene iodide characterized in terms of the activity retained by methylene iodide carrier. It is believed not improper to identify this activity with the formation of methylene iodide, since this is a known product of the photolysis¹⁰, and since no other fraction

(10) W. West and L. Schlessinger, THIS JOURNAL, 60, 961 (1938)

probably present should distill with the methylene

iodide. Petry¹¹ has shown that methylene iodide and

(11) R.C. Petry, M.S. dissertation, Canisius College
1953

radio-methyl iodide do not exchange under the conditions
of these measurements.

After exchange, the iodine was extracted from the
sample, carrier methylene iodide was added in a volume
equal to that of the original sample, and the methyl
iodide distilled off. Activity due to contaminating
radio-methyl iodide was washed out¹² by addition of

(12) R.G. Badger, C.T. Chmiel, and R.H. Schuler, THIS
JOURNAL, in press

methyl iodide and subsequent distillation. This
operation was repeated until the distillate contained
no measurable radioactivity. The methylene iodide was
then distilled and a radiochemically pure cut character-
istic of this material obtained and counted. The activity
appearing in this fraction was compared to that of the
original after a correction was made for the difference
in the counting efficiency for the two sample densities.

Iodine. - Iodine was determined colorimetrically
by observing the optical density at 480, 500, and 520 m μ
with the aid of a Beckman DU Spectrophotometer.

RESULTS

Gas analysis. - Data on the combustion analysis of the gas fraction volatile at -196°C are given in Table IA. It is seen that very little or no hydrogen is produced in the photolysis and that this fraction represents, very nearly, pure methane.

Combustion analysis of the fraction volatile at -115°C gives the results of Table IB. It is seen that this sample corresponds to a sample which is predominantly C_2 .

Mass spectrometer analysis of the C_2 fraction (Experiment 14; 5.1×10^{-6} moles; analysis 913-3) gives the following mole percent composition; ethane - 92.4; ethylene - 2.3; acetylene - 0; propane - 0; propylene - 0; C_4 - 0; oxygen - 0.3; carbon dioxide - 4.6; methane - 0.2. It is seen that this fraction is predominantly ethane, with perhaps, a trace of ethylene. Since ethylene is difficult to determine in the presence of ethane, this may or may not be real. It is believed that the carbon dioxide (emphasized by the relatively small sample size) was retained by the sample in the initial degassing and released in the degassings at -115°C made for this measurement. Characteristically no acetylene, propane, propylene, or higher hydrocarbons are found although the latter three components could easily have been detected and are found in small amounts in analogous radiolytic experiments⁶.

Gas Production. - The total yields of methane, ethane and of iodine for samples initially containing no added iodine are summarized in Figure 2 as a function of the number of quanta absorbed by the sample. It is seen that the quantum yield for each of these products is constant over the course of the photolysis. The products of the decomposition apparently do not interfere with further decomposition, in spite of the fact that iodine does react, at the concentration levels present here, with the radicals produced in the photolysis³.

The quantum yield for methane production is constant at 0.023 over the entire region measured with no apparent induction effect or decrease for high irradiation periods. The yields of ethane and of iodine are considerably lower, and on a mole basis, are approximately equal, although that for ethane seems to be consistently about 10% lower than for iodine. This discrepancy may be at least partially due to the difficulty in completely degassing ethane from the sample¹³.

(13) It will be noted that G. Emschwiller, Compt. rend., 192, 799 (1931) claims that only methane is produced in the photolysis. Earlier A. Job and G. Emschwiller, Compt. rend., 179, 168 (1924) found that hydrogen, methane, ethane, and ethylene were formed. Since in the absence of other reactants capable of removing the radicals, such as oxygen, net iodine production can only result from processes producing carbon-carbon bonds. It is expected that molecular iodine and ethane should be formed in equal yields. Our experiments show no hydrogen and little ethylene.

Effect of temperature. - Methyl iodide was given identical 100 minute irradiations in the thermostated cell at 15, 25, and 40°C and the results are given in Table II. These results show that within the reproducibility of the measurements, the temperature coefficient for the production of all products is equal to unity.

Effect of added iodine. - A number of experiments were performed on samples to which quite high concentrations (up to 10 weight percent) of iodine were added before the irradiation with a decrease in the yields of methane and ethane being observed. The results for the yields relative to those in the absence of iodine are given in Figure 3 as a function of the mole ratio (I_2/CH_3I). The solid curve represents the functional relationship, $(\phi_0 - \phi)/\phi = 23 (I_2/CH_3I)$. The data indicate that the effectivity of the iodine in quenching the decomposition is about the same for both methane and ethane production.

Experimentally these results are somewhat difficult to obtain, as it is observed that the transmission of the cell window decreases during the course of the irradiation of solutions containing iodine. This decrease in transmission, due to a product being deposited on the cell window, has not been observed for solutions in which iodine has not been initially dissolved. The relative yields have been corrected to correspond to the average energy absorbed during the irradiation. It was found possible to restore the

irradiation cell to its original transparency by pumping while heating the quartz to red heat. Once the aforementioned deposit forms, it appears to behave autocatalytically, absorbing light itself and producing further discoloration.

The quenching of the gas production reactions is believed to be due to absorption of the energy by iodine rather than by the methyl iodide. The molar extinction coefficients of iodine and methyl iodide in n-heptane have been determined at 2537 μ to be 450 and 400 respectively and cannot account for the observed effectivity of the iodine. Iodine is, however, highly solvated in methyl iodide with a very intense absorption of the solvated complex being observed in the region around 300 μ ¹⁴. It is not impossible

(14) R.M. Keefer and L.J. Andrews, THIS JOURNAL, 74, 1891 (1952), estimate an extinction coefficient of 30,000 at 295 μ for the solvated complex.

that the extinction coefficient of the complex be greater than 10,000 at 254 μ , a value which would be in agreement with the required inner filter effect. Confirmation awaits the measurement of the absorption of the iodine-methyl iodide complex at 2537 μ .

Methylene iodide formation. - The results of the radio-methylene iodide carrier experiments are given in Table III. These results are considerable lower than given previously (~4-5%) and are believed to be much more accurate due to the greater care possible through

the use of iodine 131. If it is assumed that the quantum yield for total exchange is approximately unity³, then the fraction of the activity appearing as methylene iodide corresponds to the quantum yield for the formation of this product via the reactions



The yield of 0.013 is somewhat lower than anticipated from the higher methane quantum yield (0.023), since, if reaction 2 ~~is constant~~ ^{PKIVES} upon reaction 1, the two should be stoichiometrically equal.

DISCUSSION

The present investigation has carried the measurement of the photo-decomposition of methyl iodide into a region of iodine concentration far beyond ^{the point at} which iodine is known to react almost quantitatively with the radicals produced in the photolysis. The results show that the presence of iodine is not effective in quenching the reactions which result in the observed decomposition. Measurements of the effect of temperature on the processes involved show that the reactions producing methane, ethane, and iodine are not temperature dependent in the region around 25°C.

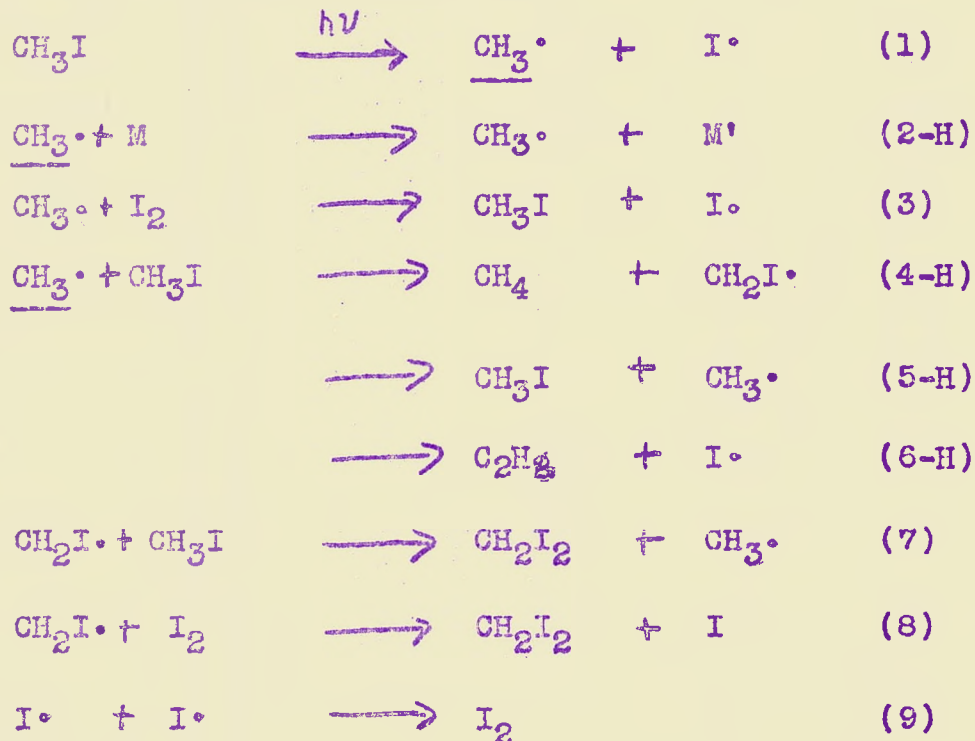
Any mechanism proposed as an explanation of the photodecomposition of methyl iodide must be consistent with the above facts and with the fact that the reactions

are wavelength dependent, in general increasing with decreasing wavelength. Also, the existence of decomposition reactions which are independent of iodine concentration, in spite of important iodine quenching reactions, must be resolved in terms of a mechanism which permits the formation of products along two different reaction paths. The relative importance of these different paths must then be given in terms of a "splitting ratio" *which is* determined by the probabilities of the different reactions.

It is believed that the hot radical reactions postulated for the photolysis of methyl iodide^{3,4} are not inconsistent with any of the known facts and offer a plausible explanation for the observed reactions. The hot radical mechanism proposed for the photodecomposition of methyl iodide attributes the reactions to processes which involve extrathermal methyl radicals before these radicals have had a chance to lose their excess kinetic energy. That such radicals (with an extrathermal energy of the order of 30 kcal/mole) are produced is seen in a consideration of the energy involved in the excitation process occurring at 2537Å (Figure 4). While this energy is certainly sufficient to give rise to the observed reactions, the question is whether or not the probability of the proposed reactions is sufficiently high to permit competition with the moderation process. In this respect the processes involved may be regarded as analogous to

side reactions encountered during the thermalization of high energy neutrons. Theoretical D calculations based on this analog suggest themselves as being capable of providing further information ^{concerning} ~~in regard to~~ the present problem. Since, in hot radical reactions, the distribution of energies in the reacting species is non-Boltzmanian, and therefore independent of temperature, it is expected (and found in the photolysis of methyl iodide) that the reactions should have a temperature coefficient not different from unity.

The following mechanism is proposed as being consistent with all of the known facts:



In this mechanism, the splitting ratios controlling the decomposition are the ratios of the relative probabilities of reaction 2 and reactions 4, 5, and 6.

Reaction 5, originally omitted from the mechanism, is included here in order to complete the possibilities of the hot radical reactions and to provide a basis for work in solutions. The net effect of this reaction is moderation, although the cross section may be considerably different than that of thermal moderation. Reaction 7 is included in order to account for the discrepancy between the formation of radio-methylene iodide and methane. There is some possibility that the $\text{CH}_2\text{I}\cdot$ radical decomposes before reacting with iodine. However if this occurs, this should result in a higher radio-methylene iodide yield or a quantum yield of ethylene greater than the observed value of less than 0.0002.

It will be observed that the above mechanism eliminates, except for the recombination of iodine atoms, all reactions which are second order in radicals. This is necessary since all radicals are quickly removed by reaction with the iodine and are therefore present only at very low concentration levels. This is one point of departure between our proposal for the liquid phase photolysis and that of Schultz and Taylor in studies of the vapor phase. We postulate that ethane results from a hot process (reaction 6-H) while Schultz and Taylor prefer to regard it as being formed by the combination of methyl radicals. This latter process can be of greater importance in the vapor phase because of a relatively low concentration of iodine.

Recent work on the flash photolysis of methyl iodide by Davidson and Carrington¹⁵ further indicates the importance

(15) N. Davidson and T. Carrington, THIS JOURNAL, 74,
6277 (1952)

of methyl radical combination in the vapor phase at very high light intensities.

It is pointed out that actually no new types of chemical reaction have been introduced in the usage of the idea of hot radical reactions. Ordinary thermal reactions involve molecules in the high energy ($E > E_a$) region of the normal energy distribution. Hot radical reactions, of the type postulated in the photolysis of methyl iodide, differ only in that the energy distribution is non-Boltzmannian, with a relatively large number of reacting species having extra-thermal energies. This is peculiar to the manner of formation of the radicals. The question in any particular case is whether or not that case illustrates such hot radical processes. In regard to the photolysis of methyl iodide, all evidences point in this direction. Since the proposed mechanism does explain the observed results and since all of the requisite conditions are present, it does not seem too extreme ^{to conclude} that hot radical processes significantly contribute to the reactions mentioned above.

ACKNOWLEDGEMENT

The authors wish to thank Professor William H. Hamill of the University of Notre Dame for numerous discussions on the subject. One of us (C.T.C.) is indebted to the Research Corporation for the grant of a fellowship.

TABLE IA
ANALYSIS OF METHANE FRACTION

Experiment	3	7	9	13
Sample: moles $\times 10^6$	24.4	52.0	10.6	10.8
Pressure: mm. ^a				
initial	392	828	170	58
after oxidation at 275°C	--	828	--	58
after oxidation at 575°C	395	832	170	61
after absorption	3	6	1	2
Combustion: %	99	99	99	98
Hydrogen: %	-- ^b	< 0.5	-- ^b	< 1.0
nC	1.01	1.01	1.00	1.05

^a All pressures corrected to initial volume.

^b Oxidation at 575°C indicates little or no hydrogen.

TABLE IB
ANALYSIS OF ETHANE FRACTION

Experiment	3	7	9	13
Sample: moles $\times 10^6$	8.1	11.8	2.4	2.8
Pressure: mm. ^a				
initial	130	191	35.6	39
after oxidation at 575°C	258	377	69	75
after absorption	2	3	0	2
Combustion: %	98	98	100	95
nC	1.99	1.99 ^{b,c}	1.94	1.97

^a All pressure are corrected to initial volume.

^b A duplicate analysis on a second portion of this fraction gives nC = 2.01

^c A second ethane fraction of 3.4 μ moles gives nC = 1.98

TABLE II

EFFECT OF TEMPERATURE

Temperature °C	Irradiation period min. ^a	Total yield moles x 10 ⁶		
		CH ₄	C ₂ H ₆	I ₂
13.5	100	7.55	2.9	2.7
25.0	100	6.95	2.6	2.8
40.0	100	7.04	2.5	2.5

^a 100 min. is equivalent to 283×10^{-6} Einsteins

TABLE III

FORMATION OF METHYLENE IODIDE

Carrier ^a iodine molesx10 ⁶	Irrad. Exch. period min. ^c	Exch. %	Activity ^b				Yield CH ₂ I ₂ /org.
			Org.	CH ₃ I	CH ₂ I ₂	resid. ^d	
36	100	97.5	4140	3975	63	58	0.015
66	50	81.5 ^e	4643	4382	62	61 ^f	0.013

^a In 5 ml. of sample.

^b Counts per min. corrected for dilution and self absorption (activity in CH₃I/ activity in CH₂I₂ = 1.26).

^c At 7.8 x 10⁻⁶ Einsteins/min.

^d Stillpot residue (2-3 ml.) diluted and counted; shows no concentration of activity over that in CH₂I₂.

^e Corresponds to a quantum yield of 0.6 (in the absence of stirring).

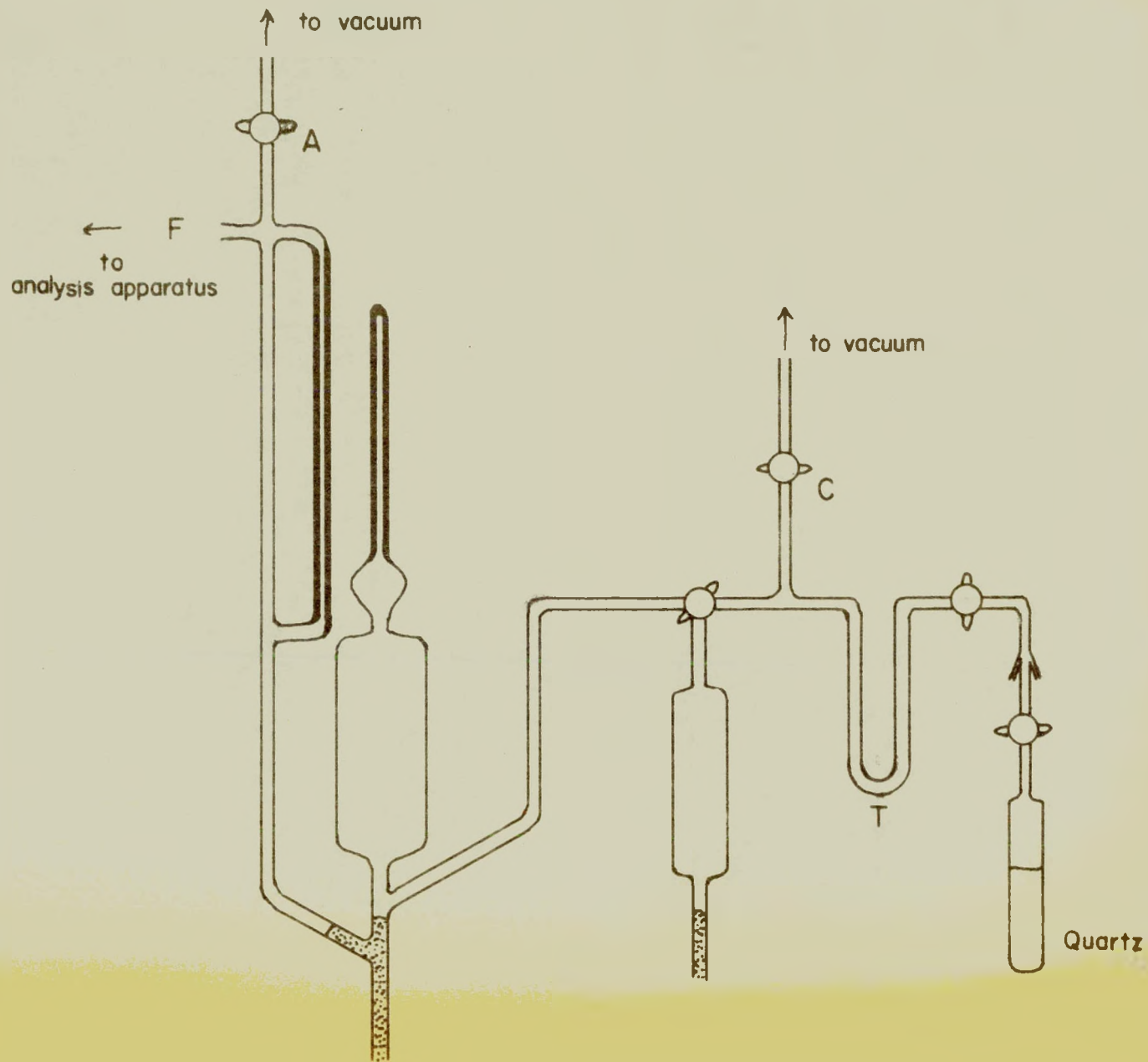
^f Stillpot rinsed with 5 ml. of acetone; negligible activity in this fraction.

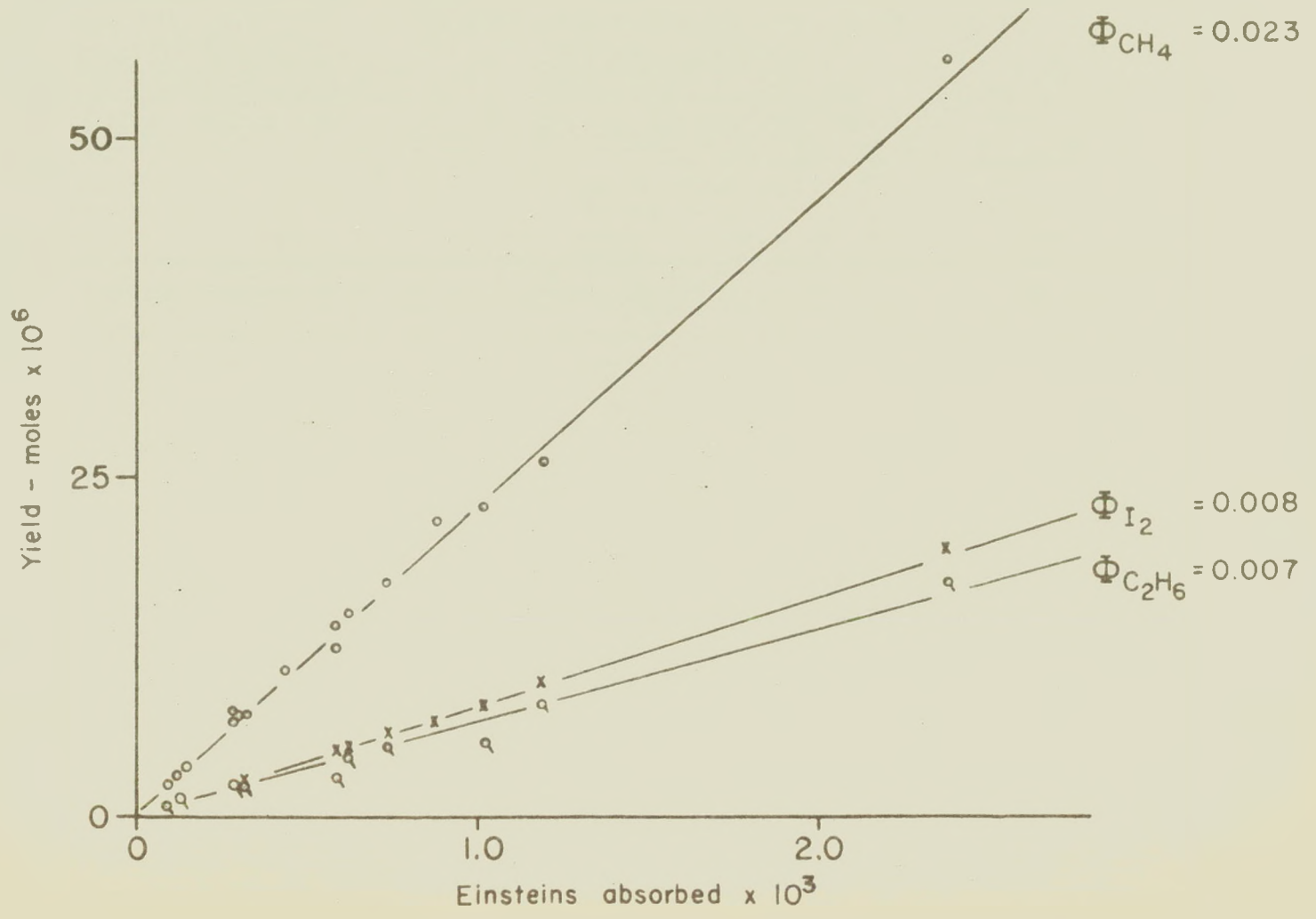
Fig. 1.- Gas measurement apparatus

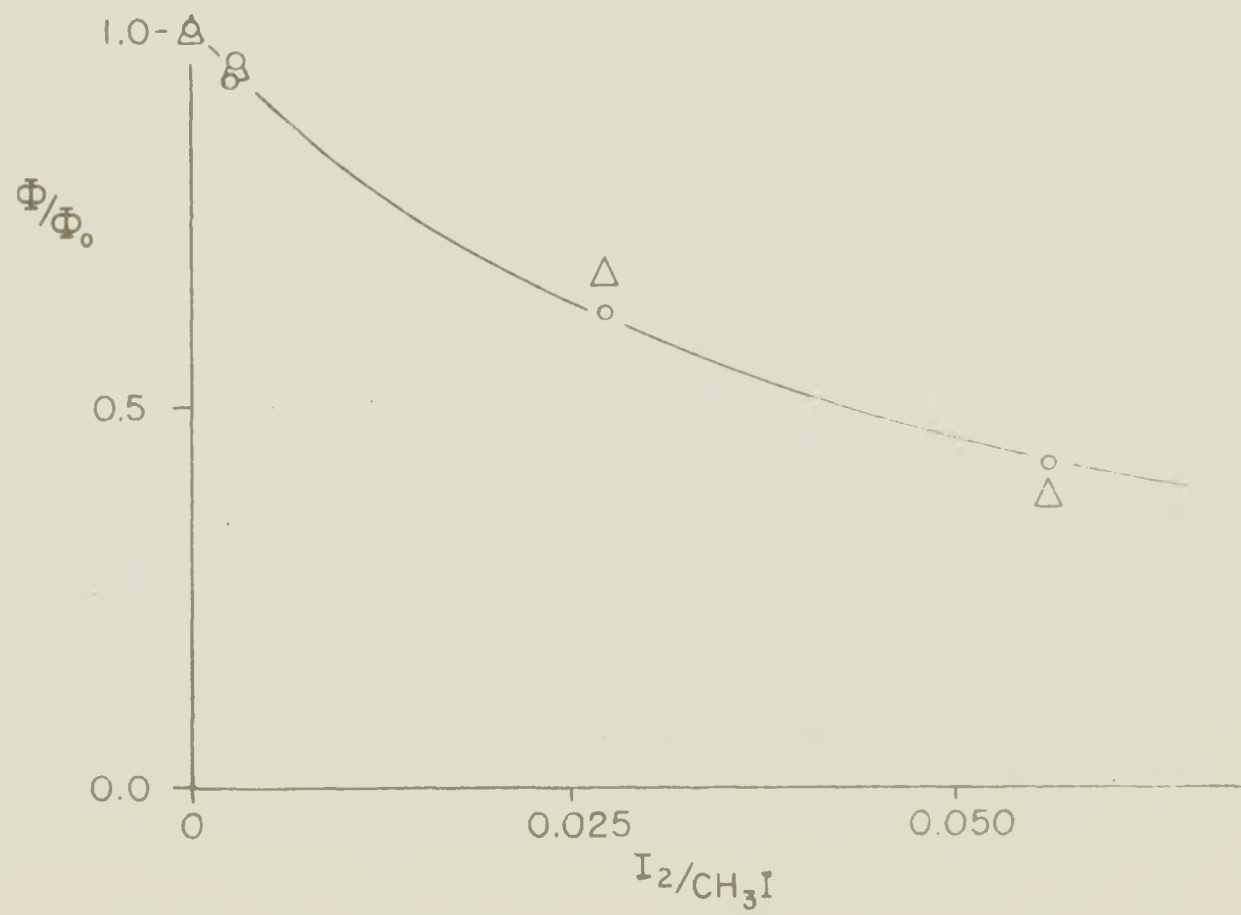
Fig. 2.- Production of methane, ethane, and iodine in the photolysis, at 2537 Å, of methyl iodide.

Fig. 3.- Effect of iodine on the gas production yields. Solid curve corresponds to $(\phi_0 - \phi)/\phi = 23 \text{ I}_2/\text{CH}_3\text{I}$. Circles refer to methane production; triangles to ethane production.

Fig. 4.- Potential energy functions for the ground and first excited states of methyl iodide illustrating the source of the kinetic energy of the methyl radical in the photolysis at 2537 Å.







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