We now conclude that the band under discussion corresponds to a single electronic transition and that the presence of the long axis component (which represents 29% of the short axis intensity) is direct evidence for the break-down of selection rules based on Eq. 1.[6] A mathematical study[4] of this breakdown demonstrates that such anomalous absorption is not unexpected and in fact represents the "borrowing" of long axis intensity from the higher energy long axis absorption region through the perturbation of the pure electronic wave functions by suitably non-totally symmetric vibrations.

While these experiments have established the presence of mixed polarization, there is much that remains unexplained as far as the method of polarized photoöxidation is concerned. Although the parameter ϵ is useful for bringing different experiments into line, its origin is by no means understood nor therefore is it understood why it varies rather markedly from one experiment to the next (see also I in this connection). One of the mechanisms proposed in I for randomization involves the concept of local heating and momentary melting of the rigid environment about a molecule due to the degradation of electronic energy into heat. Unsuccessful attempts have been made to induce randomization of oriented WB molecules by illuminating with intense light for long periods of time. Apparently this mechanism is not important in this case. Other proposed mechanisms for randomization include energy transfer. It is hoped that some of these questions shall be answered through a more careful study of the problem now in progress.

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(6) The short axis component is considered to be the normal component because it is found in the zero–zero region and to the red. Here there can be little question of vibrational perturbation in the excited electronic state.

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

Reactions of Hydrogen and Hydrocarbons with Iodine Excited by 1849 Å. Radiation[1]

BY THOMAS A. GOVER AND JOHN E. WILLARD

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Previous work from this Laboratory has shown that iodine molecules excited by 1849 Å. radiation react with CH_4 to form CH_3I and HI. We have now found that similar reactions occur with C_2H_4, C_2H_6, C_4H_{10} and H_2. There is strong evidence that in the I_2–CH_4 system 1849 Å. radiation absorbed by the I_2 initiates steps which lead to carbon-carbon bond formation resulting in products such as C_2H_5I, C_3H_7I, C_4H_9I, C_2H_6 and C_3H_8. These products are formed with quantum yields in the range of 10^{-5} to 10^{-3} whereas the yields of the CH_3I and HI are about 5×10^{-2} (assuming a quantum yield of unity for the CH_3I–I_2 exchange activated by 1849 Å. light absorbed by CH_3I). The reactions of excited I_2 molecules with hydrocarbons to produce HI and the alkyl iodide appear to occur only on the first collision of an excited iodine molecule with the hydrocarbon. Evidence for this and information on the quenching cross sections has been obtained by studying the reaction yields as a function of total pressure. At low pressures the yields are low, increasing to a maximum at pressures where the average time between collisions is small compared to the fluorescence lifetime of the iodine molecule. Incidental to these investigations it has been found that the absorbancy index of I_2 at 1849 Å. is pressure sensitive, varying from about 10^4 at very low pressures to about 2×10^5 at atmospheric pressure.

Introduction

Iodine molecules activated by 1849 Å. radiation are able to react with CH_4[2] to form CH_3I and HI and with H_2[3] to form HI. These reactions are unique in that iodine atoms ($^2P_{1/2}$ and $^2P_{3/2}$) formed by the photodissociation of I_2 by radiation in the 5000 Å. region do not attack hydrogen or hydrocarbons at room temperature because of the endothermicity of the reactions. The observed reactions at 1849 Å. must result either from a step of the type $CH_4 + I \rightarrow CH_3 + HI$, made possible by electronic or kinetic excitation of the iodine atom, or from a step involving an excited I_2 molecule (*e.g.*, $CH_4 + I_2 \rightarrow CH_3I + HI$). The iodine atom has as its first two excited electronic levels $^2P_{1/2}$ at 7600 and $^4P_{5/2}$ at 54,600 cm.$^{-1}$ above the ground state.[4] 1849 Å. radiation (54,200 cm.$^{-1}$) is incapable of dissociating the iodine molecule (35 kcal./mole, 12,300 cm.$^{-1}$) and raising one of the atoms to the $^4P_{5/2}$ state. The $^2P_{1/2}$ state of I does not have enough energy to lead to reaction with CH_4. If an 1849 Å. photon absorbed by I_2 produced one atom in the ground state and one $^2P_{1/2}$ atom with the residual energy as kinetic energy each of the two atoms would have 49 kcal./mole as kinetic energy. This is somewhat greater than the endothermic heat of the reaction $I + CH_4 \rightarrow CH_3 + HI$ and is approximately equal to the heat of the reaction $I + CH_4 \rightarrow CH_3I + H$, but cannot be used for reaction because if momentum is to be conserved in the formation of the activated complex a maximum of 0.11 (*i.e.*, $M_{CH_4}/(M_I + M_{CH_4})$) of this energy can go into internal energy of the activated complex and so be available for causing bond rupture. These considerations plus spectroscopic evidence for an excited electronic state of iodine molecules in the 1850 Å. region[5] and the observation of fluorescence from iodine molecules following absorption of such radiation indicate that the observed chemical reactions require an electronically excited iodine molecule. Thus these systems offer the opportunity for further study of chemical processes initiated by a simple electron-

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(1) Further details of this work are given in the Ph.D. thesis of Thomas A. Gover, filed with the University of Wisconsin library in November, 1959, and available from University Microfilms, Ann Arbor, Michigan.

(2) G. M. Harris and J. E. Willard, THIS JOURNAL, **76**, 4678 (1954).

(3) J. Gailey and J. E. Willard, unpublished.

(4) "Landolt-Börnstein Zahlenwerte und Funktionen," Springer-Verlag (1950), 6-I-I.

(5) (a) J. C. McLennan, *Proc. Roy. Soc.* (*London*), **A91**, 23 (1914); (b) O. Oldenberg, *Z. Physik*, **18**, 1 (1923); (c) F. W. Loomis and A. J. Allen, *Phys. Rev.*, **33**, 639 (1929); (d) P. Hirschloff, *Z. Physik*, **75**, 325 (1932); (e) H. Cordes, *ibid.*, **97**, 603 (1935); (f) C. V. Narayana Rao and V. Ramakrishma Rao, *Ind. J. Phys.*, **28**, 403 (1954).

ically excited species which itself takes part in the chemical changes. In the present work we have investigated the competition between fluorescence and quenching, the relative reaction probability for different hydrocarbons and the production of compounds which require carbon–carbon bond formation.

Experimental

Apparatus, Reagents and Procedure.—A Hanovia SC 2537 low pressure mercury vapor lamp with a 2.5 cm. diameter end window furnished 1849 Å. radiation which passed into a fused silica reaction cell 2.8 cm. in diameter and 10 cm. long housed in an aluminum block furnace which was maintained within ±3° at the desired temperature within the range from 25 to 175°. A WL789 platinum-cathode phototube which was sensitive only to wave lengths below 2000 Å. was used for monitoring the intensity of the lamp and determining the absorbancy indices of the reactants and products studied. The reactions of iodine with hydrogen and with hydrocarbons were carried out with the full light of the mercury arc, it having been shown that when wave lengths below 2000 Å. were eliminated by the use of a Corning 791 filter, no reaction occurred. Unless otherwise noted the extent of reaction was always such that effects due to absorption of light by the product alkyl iodides were negligible. The light from the mercury lamp passed through 6 cm. of air before entering the reaction cell. This caused some loss in intensity since it was shown that the phototube response was changed by 50% when the 10 cm. path length of the reaction cell was filled with air, as compared to when it was evacuated. The spectrum of the mercury vapor lamp at wave lengths below 2000 Å. was determined with a Hilger quartz spectrograph. Lines at 1849 and 1942 Å. were observed. The 1849 line was at least ten times more intense than the 1942 Å. line.

For filling, the fused silica reaction cells were attached to a vacuum line through a graded seal. Known amounts of iodine were sublimed into the cell from another tube on the vacuum line where they were prepared by fusing $K_2Cr_2O_7$ with a known amount of potassium iodide obtained by evaporating a solution of standard potassium iodide. The iodine passed through a short P_2O_5 column between a preparation tube and the reaction cell. When radioactive iodine was needed, a predetermined volume of carrier-free NaI^{131} solution was added to the standard KI solution before evaporation. The radioiodide was "chemical synthesis grade with no additives" from Abbott Laboratories. Although this was presumed to be free from the benzyl alcohol and ascorbic acid present in the "Oriodide" solutions normally furnished for medical purposes, it liberated a gas, during the dichromate fusion, which was removed by pumping at −78°.

Following addition of the iodine the desired hydrocarbon gas was added to the desired pressure as measured on a mercury manometer, the cell was isolated from the vacuum system by a stopcock, cooled with liquid air and sealed off. When low pressures of hydrocarbon were used they were metered with a Saunders–Taylor apparatus and transferred to the reaction cell by Toepler pump action. Liquid air was used to condense methane and the sealing of the cell was done rapidly at a capillary constriction. Gas chromatography showed that no impurities were produced by this operation. All of the hydrocarbons were Phillips research grade. The hydrogen was Airco ("99.9% pure"). Matheson Co. argon was passed over reduced copper oxide at 250° to remove oxygen. Linde U.S.P. oxygen was used without further purification.

Some of the experiments required methyl iodide. For this purpose Eastman Kodak Co. white label reagent was further purified by passing through a 30 cm. column of anhydrous silica gel and then fractional distillation through a Todd glass helix column, the middle fraction being retained. Gas chromatographic analysis of this showed no impurities above the limit of detection, which was about 10^{-4} mole fraction. Methyl iodide-C^{14} from Nuclear-Chicago was diluted to 0.6 mc./mmole with inactive methyl iodide and was purified from the products of self irradiation by passing through a gas chromatographic column of silicone oil on firebrick. The methyl iodide peak was trapped in a 10 inch 4 mm. i.d. spiral trap packed with firebrick coated with silicone oil and held at 0°. This trap containing the pure methyl iodide was attached to the vacuum line by a ball joint, the helium was pumped off while the trap was cooled with liquid air, and the trap then was warmed to 50° which allowed the methyl iodide to escape into a Saunders–Taylor apparatus where it was measured and transferred to a reaction cell.

Those experiments using C^{14} labelled methane employed 0.5 mc. (Nuclear Chicago 1.1 mc./mmole) which filled the 55 ml. reaction vessel to a pressure of 150 mm. This same radiomethane was used repeatedly, the products of self-irradiation being removed prior to each use by Toepler pumping the methane from a container cooled with liquid nitrogen. Gas chromatograms showed that this procedure removed all detectable impurities.

Product Analysis.—The amounts of methyl iodide, methylene iodide and hydrogen iodide formed in the reactions and the amount of iodine consumed were determined from the absorbance of the cell at 2200, 2600, 2900 and 5000 Å. as measured with a Beckmann DU spectrophotometer maintained at 50° to keep the iodine vaporized. The molar absorbancy indexes of Table I were used.

TABLE I

MOLAR ABSORBANCY INDEXES USED IN PRODUCT ANALYSIS

	Å.: 2200	2600	2900	5000
CH_3I	20	350	22	..
CH_2I_2	810	330	1100	..
HI	175	40	..	..
I_2	..	..	..	578

The alkyl iodides also were determined by gas chromatography analysis, as were the hydrocarbons, employing a 12 ft. long 4 mm. i.d. spiral Pyrex column filled with 40–60 mesh acid-washed Johns–Manville C22 firebrick coated with GE SF96 (40) silicone oil. The samples for gas chromatographic analysis were obtained by attaching the reaction cell to the vacuum line with the aid of a break seal, cooling with liquid nitrogen, pumping off the methane and transferring the species non-volatile at liquid nitrogen temperatures to a thin walled small bulb which could be broken with a plunger in the inlet stream of the gas chromatography column. Analysis for non-radioactive products from the gas chromatographic columns was made by a Gow-Mac thermal conductivity detector coupled with a Brown chart recorder, the sensitivity of the system being about 10^{-1} μmole. Detection of alkyl iodides containing radioiodine was done by passing the effluent stream from the chromatographic column through a finger in the well of a sodium iodide scintillation crystal, the output being noted on a chart recorder. Helium was used as the flow gas through the chromatographic column except when it was desired to analyze for compounds labeled with C^{14} in which case the flow gas was methane which passed from the column through a flow proportional counter similar to that described by Wolfgang and Rowland.[6] In those runs using radioactive iodine no I_2 or HI was allowed to enter the chromatographic column because it was found that one or both of these compounds when adsorbed on such a column exchanges iodine with alkyl iodides. The iodine was removed by a small drop of mercury placed in the sample bulb and the HI was removed by a short tube of Amberlite IRA 400 anion exchange resin which preceded the column in the gas flow streams.

In those runs where alkyl iodides were being determined by thermal conductivity, the yields of those other than methyl iodide were determined by comparing their peak heights with the methyl iodide peak since the moles represented by the latter were known from the absorbancy measurements in the reaction cell. In the runs where the iodides were determined by I^{131} activity the ratio of peak height to moles was determined in a similar way. By making a known amount of $C^{14}H_3I$ by the photochemical reaction of I_2 with $C^{14}H_4$, as measured by its absorbance, and by using the specific activity of the $C^{14}H_4$ given by Nuclear-Chicago, it was possible to standardize the flow proportional counter in terms of counts/min.mc. It was found to be nearly 100% efficient for counting the C^{14} beta particles, from the $C^{14}H_3I$ at the concentrations used. In other work we have found that considerably higher concentrations of CH_3I interfere with the performance of the counter, as might be expected.

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[6] R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

Actinometry.—It is well established that the quantum yield is unity for the exchange of iodine between CH_3I and I_2 under the influence of 2537 Å. light absorbed by the CH_3I.[2] Using this exchange as an actinometer we have found a quantum yield of two molecules of HI decomposed per photon of 2537 Å. light absorbed by HI in agreement with earlier work.[7]

In the earlier work from this Laboratory,[2] it was assumed that the quantum yield of the CH_3I–I_2 exchange at 1849 Å. is unity. It is not feasible to use a thermopile to make an absolute determination of the 1849 Å. intensity entering our reaction systems because of absorption by air and by the reaction cell and thermopile windows and because no suitable filter is available for isolating the 1849 Å. line from those of higher wave length from the arc. Since the 1849 Å. line falls in a banded region of the CH_3I absorption spectrum,[8] there is no assurance that the quantum yield of exchange at 1849 Å. must be unity. If some of the molecules fluoresced it might be lower. We have sought to determine the absolute quantum yield with a high intensity monochromator using the light from an aluminum spark standardized against a Bureau of Standards thermopile and reference phototube. This gave values of 3.4 for the quantum yield of I_2 formation by the decomposition of HI and values several fold higher for the quantum yield of the CH_3I–I_2 exchange. Since these results seem unreasonably high, it can only be said at this time that absolute quantum yields in the 1849 Å. region should be investigated further and that the quantum yield for the exchange at 1849 Å. may be higher than unity. For the purpose of stating relative quantum yields in this paper, we have used an *assumed* yield of unity for the CH_3I–I_2 exchange activated by 1849 Å. light absorbed by CH_3I.

Molar Absorbancy Indexes of Alkyl Iodides and of Iodine at 1849 Å.—Using the platinum cathode phototube, sensitive only to radiation of wave length less than 2000 Å., and the low pressure mercury arc the approximate molar absorbancy indexes of iodine and some of the product alkyl iodides were determined at 1849 Å. so that estimates concerning secondary reactions could be made.

The alkyl iodides were measured with the Saunders–Taylor apparatus and then transferred to a 55 ml. fused silica cell with 10 cm. optical path length and a suitable ballast volume (sometimes as large as 600 ml.) to reduce the pressure of alkyl iodide to a value which would permit phototube current measurement. Each alkyl iodide was measured at a variety of pressures and in all cases Beer's law was obeyed. The molar absorbancy indices obtained were CH_3I, 220; C_2H_5I, 1200; n-C_3H_7I, 2300; i-C_3H_7I, 6000; n-C_4H_9I, 3000 and i-C_4H_9I, *ca.* 1×10^4.

Iodine was studied in a sealed cell with a side-arm containing solid iodine. The temperature of the side-arm was varied to obtain different known vapor pressures of iodine in the cell. The iodine concentration was calculated from the known vapor pressure data on iodine.[9] Iodine did not follow Beer's law but A_m appeared to depend strongly on pressure, it being found empirically that a plot of log A_m *vs.* 1/log P_{I_2} gave a straight line. The values ranged from 5700 at 0.20 mm. of I_2 to 30,000 at 3×10^{-3} mm. of I_2. The extrapolated value at vanishing pressures was 50,000.

The variation probably is due to a large difference in absorbancy for the 1849 and 1942 Å. lines, with most of the photocurrent at high iodine pressures being caused by the less strongly absorbed 1942 Å. line. When 600 mm. of argon was added to a cell and the measurement repeated, the same function gave a straight line but the absorbancy indices were increased at all iodine pressures. In the low pressure region the effect was largest and the extrapolated value at this pressure of argon was 200,000. The increase with pressure was thought to be due to the pressure broadening of the iodine absorption bands in the region of 1849 Å. thus increasing the overlap between the iodine band and the 1849 Å. mercury line.

The value of 11,000 for A_m reported previously[2] agrees well with the value obtained in this work for iodine for the pressure used (0.08 mm.). in the previous determination.

Results and Discussion

The present work has confirmed earlier observations[2,3] that excited iodine molecules activated by 1849 Å. radiation can react with methane to form CH_3I and HI and with hydrogen to form HI and has shown that similar reactions occur with ethylene, ethane and butane. In all cases the quantum yields are between 0.02 and 0.07 molecules of I_2 consumed per photon of 1849 Å. radiation absorbed by the iodine, as shown in Table IIA (calculated on the assumption that the quantum yield for the CH_3I–I_2 exchange using 1849 Å. light absorbed by CH_3I is unity). In the case of the iodine–methane system the reaction has been shown to be independent of temperature in the range from 50 to 175°. Two additional features of the excited iodine molecule reactions have been explored. The first is the production from methane of alkyl iodides and hydrocarbons requiring the formation of carbon–carbon bonds, and the second is the effect of pressure of the reactant gas on the competition between fluorescence and reaction.

Evidence for Carbon–Carbon Bond Formation.—Using I_2 labeled with I^{131} as the reactant in methane and analyzing for the products by gas chromatography with a sodium iodide scintillation detector, the limit of detection of alkyl iodide products is about 1×10^{-10} mole (*i.e.*, equivalent to about 10^{-5} mm. in the reaction cell, or a quantum yield of about 10^{-5}). Some 10 runs under our best conditions have been made on this system. These show reproducible peaks for ethyl iodide, n-propyl iodide, *sec*-butyl iodide and n-butyl iodide. From the peak areas the quantum yields recorded in Table IIB have been estimated. Trace amounts of isopropyl iodide (*i.e.*, a per cent. or so of the n-propyl iodide) were also observed; these may possibly have been formed by isomerization of the n-propyl iodide under the influence of the 2537 Å. light absorbed by it. Further evidence of carbon–carbon bond formation was obtained in experiments where the methane was tagged with C^{14} and the iodine was untagged. The gas chromatographic columns used for this work (silicone oil on firebrick) did not separate olefinic from saturated hydrocarbons but did give satisfactory separation between hydrocarbons of different chain lengths. The chromatograms obtained using the flow proportional counter indicated quantum yields of about 0.004 and 0.001 for the C_2 and C_3 hydrocarbons, respectively. The specific activity of methane-C^{14} was such that the limit of detection with it was about 5×10^{-9} mole and thus the alkyl iodides involving carbon–carbon bond formation were not detected since their quantum yields, as shown by the radioiodine experiments, are much lower than those of the hydrocarbons.

The formation of carbon–carbon bonds caused by 1849 Å. radiation absorbed only by the iodine in a system containing only iodine and methane is very surprising. We were at first inclined to attribute the observed products to reaction with im-

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[7] K. F. Bonhoeffer and P. Harteck, "Grundlagen der Photochemie," T. Steinkopf, Dresden, 1953.

[8] H. Sponer and E. Teller, *Revs. Mod. Phys.*, **13**, 76 (1941).

[9] (a) G. P. Baxter, C. H. Hickey and W. C. Holmes, THIS JOURNAL, **29**, 127 (1907); (b) G. P. Baxter and M. R. Grose, *ibid.*, **37**, 1061 (1915); (c) F. Haber and F. Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

TABLE II

A. Quantum yields[a] for the reaction $I_2 + RH \rightarrow RI + HI$ of excited I_2 molecules formed by 1849 Å. radiation

Reactant	CH_4	C_2H_4	C_2H_6	C_4H_{10}	H_2
Quantum yield	0.05	0.05	0.07	0.04	0.02

B. Quantum yields[a] of various products from the reaction of excited I_2 molecules in CH_4[b]

Product	CH_3I	HI	CH_2I_2	C_2H_5I	
Quantum yield	0.05	0.05	*ca.* 0.004	1×10^{-4}	
Product	*n*-C_3H_7I	*n*-C_4H_9I	*sec*-C_4H_9I	C_2 hydcarb.	C_3 hydcarb.
Quantum yield	5×10^{-5}	*ca.* 10^{-5}	*ca.* 10^{-5}	*ca.* 0.004	*ca.* 0.001

[a] Based on actinometry which assumes a quantum yield of unity for the exchange of iodine between I_2 and CH_3I caused by 1849 Å. light absorbed by CH_3I. [b] 250 mm. of CH_4, 0.68 mm. of I_2 and illuminated for 102 min. at 50°.

purities present in the reactants or formed in the reactants by the ionizing radiation from the radioactive tracers. Careful analyses for impurities and rather exhaustive purifications with no resultant change in the product spectra make it difficult to avoid the conclusion that the new carbon–carbon bonds result from an initial step in which an excited iodine molecule reacts with methane. Some of these tests are as follows. A mass spectrometric analysis of the Phillips research grade methane showed less than 3×10^{-4} mole fraction of ethane and no detectable propane. Variations in the source and method of preparing the radioiodine led to no change in the alkyl iodide peaks, although new peaks were introduced when the condensable gas which was evolved on dichromate oxidation of the commercial radioiodide solutions was not pumped off. Experiments with methyl iodide-C^{14} in which the 1849 Å. radiation was removed by a 7910 filter showed that the chain lengthened hydrocarbons were not produced by 2537 Å. radiation absorbed by the methyl iodide. (In this connection it may be noted that when methyl iodide-I^{131} (0.5 mm.) or methyl iodide-C^{14} (22 mm.) was added to the I_2–CH_4 system, the amounts of ethyl iodide and *n*-propyl iodide formed by 1849 Å. light were increased by factors of 3 and 300, respectively, indicating that in this pressure range the rate of formation of the chain lengthened products depends on the amount of methyl iodide present. We believe, however, that the methyl iodide formed in the usual I_2–CH_4 run is not a contributing reactant in chain lengthening since the maximum methyl iodide pressure in such runs was a factor of 10 lower than the 0.5 mm. cited here and since it was observed that the ethyl iodide and *n*-propyl iodide were formed at a constant rate in the I_2–CH_4 system without additives.) As mentioned in the Experimental section, methane labeled with C^{14} could be purified so that it showed no detectable impurities when passed through a gas chromatographic column the output of which was monitored with a proportional counter. Product peaks for C^{14} labeled ethane or ethene and propane or propene then reappeared after mixing with I_2 and irradiating with 1849 Å. light. It may be estimated that in the CH_4–I_2 systems containing a few hundred mm. of CH_4 and 0.7 mm. of I_2, about 10^{-4} of the 1849 Å. radiation was absorbed by the CH_4. If this absorption were responsible for the chain lengthened products, the quantum yields would be of the order of unity for C_2H_5I and ten-fold higher for the hydrocarbons. These values are too high to be rationalized readily and therefore support the conclusion that reaction is caused by light absorbed by the iodine rather than the methane. Mercury sensitization cannot have been a factor in these reactions since any residual mercury vapor in the system would have been removed by reaction with the iodine. If any mercury iodide was deposited on the walls, it absorbed a negligible part of the total radiation.

It is impossible on the basis of the information thus far available to suggest a probable mechanism for the carbon–carbon bond formation steps. They cannot be due to ion molecule reactions since the energy of the 1849 Å. radiation is less than the ionization potential of either methane or iodine. It is conceivable that methylene radical may be formed by a reaction of the excited iodine molecule with methane. If this reaction resulted in methylene and 2 molecules of HI, it would be endothermic by about 50 kcal./mole while 150 kcal./mole is available from the excitation energy of the iodine. Likewise the iodine photosensitized decomposition of the methane to form CH_2 and H_2 would be exothermic. There is evidence that methylene radical is able to react with saturated hydrocarbons to form carbon–carbon bonds.[10a] If such a step were involved, it would still be difficult to explain the formation of propane and of propyl and butyl compounds from the methane since each methylene formed would have many collisions with methane before encountering the small amount of product ethane or propane in the system. The fact that the ratio of ethyl iodide to propyl iodide is uniformly two seems to require that the freshly formed two carbon species has about a two thirds chance of being stabilized at the chain length, of two and one third chance of forming a longer chain by reaction with CH_4.

Because of the high molar absorbancy index of iodine vapor for 1849 Å. radiation, 90% of the radiation is absorbed in the first 2 mm. of a cell containing 0.7 mm. of iodine. Consequently the fraction of excited species formed very close to the window is higher than in most photochemical reactions and the possibility that heterogeneous processes may be involved in forming the observed products cannot be eliminated. It may be noted in this connection that no differences in results were observed for a cell annealed at 550° as compared to cells which were not annealed nor for cells cleaned

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(10a) See, for example, H. M. Frey and G. B. Kistiakowsky, THIS JOURNAL, **79**, 6373 (1957).

with hot concentrated nitric acid as compared to those merely rinsed with water before using.

Effect of Pressure on the Competition between Fluorescence and Reaction.—Harris and Willard[2] reasoned that the reaction of methane with iodine activated by 1849 Å. radiation was initiated by an electronically excited iodine molecule. From the f-value obtained for transitions in the 54,000 cm.$^{-1}$ region of iodine,[10b] one calculates a mean natural lifetime of 1.1 × 10^{-9} second for the iodine molecule excited by 1849 Å. radiation. The electronic state involved is probably state H proposed by Mathieson and Rees[11] and has been called a $^1\Sigma$ state. Immediately below state H are four triplet states not observed in absorption but from which fluorescence is observed when state H is excited in the presence of inert gas.

The present work has shown that the rate of consumption of iodine in methane, ethane and hydrogen increases with the pressure of the reactant gas and asymptotically approaches a maximum value at high pressures (Fig. 1). The data taken for the systems CH_4–I_2, C_2H_6–I_2 and H_2–I_2 are given in Table III.

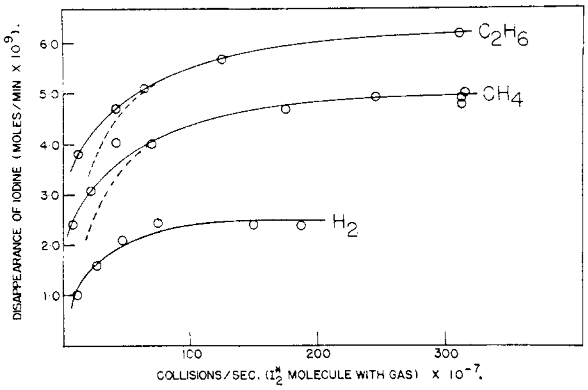

Fig. 1.—Effect of pressure on competition between fluorescence and the RH + I_2* → RI + HI reaction.

TABLE III

RATE OF REACTION OF I_2 AS A FUNCTION OF THE PRESSURE OF THE REACTANT GAS[a]

Initial I_2 pressure 0.68 mm. in all cases

CH_4, mm.	Coll./sec. of I atom with RH, × 10^{-7}	R_{HI} mole/min. × 10^9	R_{CH_3I} mole/min. × 10^9
248	315	4.5	5.0
246	312	5.8	4.8
248	315	4.2	4.7
194	246	3.3	4.9
139	176	4.2	4.7
62	79	3.4	4.3
33	42	3.6	4.0
18	23	3.0	3.1
6.3	8.0	2.2	2.4
3.1	3.9	2.0	2.1
C_2H_6, mm.		$-R_{I_2}$	
283	311	6.2	
115	126	5.7	
67	73	5.9	
57	63	5.1	
38	42	4.7	
22	24	5.9	
11	12	3.8	
H_2, mm.		R_{HI} mole/min. × 10^9	$-R_{I_2}$ mole/min. × 10^9
72	187	5.0	2.4
54	140	3.1	2.5
29	75	3.2	2.4
18	47	3.2	2.2
10	27	..	1.6
4.2	11	..	1.0

[a] The rates given in this table were determined from spectrophotometric analyses made at 15 min. intervals for experiments of 1 hr. duration, during which the conversion was in all cases linear with time. The fractional conversion of the iodine was about 0.1 and that of the hydrocarbon about 10^{-5}. The temperature in all cases was 50°.

The kinetic theory collision frequency of an iodine molecule with molecules of the reactant gas, B, was calculated from the expression $Z = n_B\sigma^2_{IB} \times [8\pi(kTm_A + m_B)/m_Am_B]^{1/2}$. The collision cross sections used were all determined from gas viscosity measurements.[12] In the pressure range of 1 to 250 mm. the time between collisions is the same order of magnitude as the mean lifetime for fluorescence. The plots of observed reaction rate *vs.* collision frequency (Fig. 1) can be accounted for if it is assumed that the drop in rate at low pressures is due to the greater number of excited iodine molecules which lose their energy by fluorescence before collision. Fluorescence is a first order decay and thus is described by the reaction

$$\log \frac{N_0}{N} = \frac{kt}{2.3} \tag{1}$$

The maximum rate, R_0, would be reached at high collision frequencies where all excited iodine molecules, N_0, were quenched before fluorescence. The experimental rate, R, would result because only N of the original N_0 were quenched before fluorescence. R_0 and R are thus proportional to N_0 and N. The decay constant, k, is equal to $1/\tau$ where τ is the mean lifetime for fluorescence. Thus

$$\log \frac{R_0}{R} = \frac{t}{2.3\tau} \tag{2}$$

If W is the probability that the excited iodine molecule will be quenched in any kinetic theory collision, $1/W$ is the average number of kinetic theory collisions required for quenching. If Z is the collision frequency of an excited iodine molecule, $1/WZ$ is the average time, t, at a given reactant pressure in which fluorescence can occur and is the time which allows $N_0 - N$ molecules to fluoresce rather than be quenched. Equation 2 becomes

$$\log \frac{R_0}{R} = \frac{1}{2.3W\tau Z} \tag{3}$$

From plots of log R *vs.* $1/\tau Z$ for the CH_4–I_2 and C_2H_6–I_2 systems the values 6.2 and 5.0, respectively, were obtained for W which implies that the quenching cross sections are larger than the momentum transfer cross sections by these factors. This gives a value of 120 Å.^{2} for the cross section of ethane. The value for W is inversely propor-

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tional to the value used for τ. If the 1.1×10^{-9} used in the above calculation is lower than the true value for the state excited by 1849 Å. radiation, the value of W should be lower than that obtained. Likewise, if there is a high probability of quenching a reaction on the first collision, the use of the factor Z introduces an error since the average time between the excitation of an I_2 molecule and its first collision would be one half of the average time per collision calculated for a series of successive collisions.

It should be noted that the cross sections obtained are quenching cross sections (total cross sections for all processes which made the molecule incapable of the observed reaction) and not necessarily reaction cross sections. If the iodine molecule can be quenched by a mechanism which does not result in reaction, the reaction cross section is less than the quenching cross section. The high quenching cross section determined suggests that the iodine molecule is quenched on every collision with methane. If so and if the reaction cross section were the same as the quenching cross section, then the reaction quantum yield would be unity. Because of the uncertainty in actinometry at 1849 Å., this point cannot be checked at present.

The values obtained for R_0 were 6.6×10^{-9} mole min.$^{-1}$ in ethane (ϕ = 0.07) and 5.2×10^{-9} mole/min.$^{-1}$ in methane (ϕ = 0.05). From the values for R_0 and W for the C_2H_6–I_2 and CH_4–I_2 systems calculated curves for the observed rates, R, *vs.* collision frequency Z were plotted (dotted lines of Fig. 1) and compared to the experimental curves. The reason that the experimental curves are higher than the calculated curves at low pressure is believed to be the fact that the reabsorption of fluorescence radiation increases the probability of reaction per initial photon.

The rate of consumption of iodine in the I_2–H_2 system was studied at various hydrogen pressures (Table I). Because of the scatter of the data the quenching cross section was not calculated. The maximum quantum yield for iodine consumption was about 0.02.

Single runs in which iodine (0.7 mm.) was illuminated in ethylene (290 mm.) and in butane (324 mm.) each gave a constant rate of iodine consumption, the quantum yields being 0.05 and 0.04, respectively. Thus the quantum yields in all of the systems studied were between 0.02 and 0.06.

When a mixture of O_2 (660 mm.), I_2 (0.7 mm.) and CH_4 (116 mm.) was illuminated, a substance began to deposit on the windows making absorptometry impossible. In a period of time when half of the iodine would, in the absence of oxygen, have been consumed, there was no visible decrease in the amount of iodine. After illumination the cell was scanned in the 2015 Å. region with a Cary spectrophotometer. The absorption band of methyl iodide at 2015 Å. was detected. This is further evidence that CH_3I can be formed in I_2–CH_4 mixtures by a process which does not involve thermal radicals, since all such radicals would be expected to react with oxygen in this system.

To determine the effect of inert gases a cell containing 710 mm. of Ar, 91 mm. of CH_4 and 0.7 mm. of I_2 was illuminated and the rate of iodine consumption determined. The rate observed was linear (ϕ = 0.03) but was 40% less than would have been expected for the same system in the absence of argon. It has been observed that inert gases cause the fluorescence from the singlet level H of iodine to fade and fluorescence from the triplet states D through G to appear.[11] Argon has two possible ways of quenching an iodine molecule in state H. It can induce predissociation or it can cause transfer to one of the adjacent triplet states. From the potential energy diagram drawn by Mathieson and Rees,[11] it appears that the repulsive state leading to two $^2P_{1/2}$ iodine atoms crosses state H several vibrational levels lower than the point where the excited iodine molecule is initially formed. Since there is reason to believe that no more than two vibrational quanta can be lost in one collision,[9,13] it should require several collisions before predissociation can become important. Since the triplet states are probably much longer lived than the singlet state H, there appear to be two possibilities which will account for the observed result: (1) all iodine molecules transferred to a triplet state eventually react, but there is competition between transfer and induced dissociation; (2) dissociation is not important but molecules transferred to triplet states are not reactive. The quenching cross section of argon is probably much less than that of methane which, if the triplet states are non-reactive, would explain why the rate was decreased only 40% in a system where iodine was colliding five times as frequently with argon as with methane.

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