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ABSTRACT

Hydrogen, methane, ethane, ethylene, acetylene, C_3 and C_4 hydrocarbons, methylene iodide and ethyl iodide have been observed as products in the radiolysis of liquid methyl iodide. The yields are directly proportional to the total irradiation of the sample and independent of the presence of small amounts of free iodine. The relative yields for irradiation with Co^{60} gamma radiation are identical to those for irradiation with X-radiation and the absolute yields are in approximate agreement. The relatively high yield of ethane, together with other complications evidenced by the formation of minor products, indicates the importance of ionic processes in the overall decomposition.

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(Contribution from the Department of Chemistry,
Canisius College)

THE RADIOLYSIS OF LIQUID METHYL IODIDE[1,2]

Robert C. Petry and Robert H. Schuler

(Abstract)

Hydrogen, methane, ethane, ethylene, and acetylene have been observed as gaseous products in the 100 kev. X-ray decomposition of liquid methyl iodide. The respective yields are found to be, relative to the yield of iodine as unity, equal to 0.067, 0.47, 0.90, 0.067, and 0.026 and are directly proportional to the total irradiation dose given the sample. The formation of trace amounts of higher hydrocarbons is indicated in the mass spectrometer analysis of the less volatile fractions. Methylene iodide and ethyl iodide are shown to be minor products of the radiolysis. In the presence of large amounts of iodine (1-20 mole percent), the yield of gaseous products decreases, with the effectivity of the iodine in quenching the reactions varying for the different products. The relative yields observed for decomposition produced by very low intensity Co^{60} gamma radiation are found to be identical to those given above for the more intense X-radiation. The absolute decomposition yields are in approximate agreement with

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(1) This work was supported, in part, under Contract AT (30-1)-1084 with the U.S. Atomic Energy Commission.

(2) From the M.S. Dissertation of R.C. Petry, Canisius College, June 1953.

the values obtained in fast-electron bombardment. The relatively high yield of ethane and iodine, together with other complications evidenced by the formation of ethylene, acetylene and higher hydrocarbons, indicates very strongly the importance of ionic processes in the overall decomposition.

* * *

Lefort, Bonet-Maury, and Frilley[3] have studied iodine production in the decomposition of air saturated liquid ethyl iodide by X-radiation and by radon alpha particles. Sue and Saeland[4] have studied the same process in various alkyl iodides using the mixed fast neutron-gamma radiation from a 300 mc. radium-beryllium source, and Schuler and Hamill[5] have observed the fast-electron and X-radiation induced processes using a 1-2 mev. Van de Graaf generator as the source of radiation. It was evidenced in this previous work[5] that the yield of iodine in the radiolysis of methyl iodide is much greater than anticipated from the low quantum yield for iodine production observed in the photodecomposition. The purpose of this investigation was to obtain

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(3) M. Lefort, P. Bonet-Maury, and M. Frilley, Compt. rend., 226, 1904 (1948)

(4) P. Sue and E. Saeland, Bull. soc. chim. France, 437, (1949)

(5) R.H. Schuler and W.H. Hamill, THIS JOURNAL, 74, 6171 (1952)

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information on the gaseous products of the radiolysis and to compare the yields to those observed in the photolysis of the same system[6].

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(6) R.H. Schuler and C.T. Chmiel, THIS JOURNAL, cf. previous communication

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EXPERIMENTAL

Methyl iodide. - The methyl iodide samples were from the same preparations used in the photolytic work[6]. The boiling point was 42.4°C and the refractive index (n_D^{25}) 1.5271-1.5272.

Irradiation. - The unfiltered radiation from a line operated, industrial X-ray unit with a tungsten target was used as the major source of activation. The instrument was operated at a constant intensity characterized by a current of 5 ma. at 120 pkv., the effective wavelength of the radiation being in the region of 0.2-0.4Å. The current was maintained at a constant value electronically and was monitored on a recording milliammeter. Variations in line voltage could be compensated for by a manual adjustment of the transformer setting.

The samples (10 ml.) were contained in a 50 ml. florence flask to which a high-vacuum stopcock and ground joint had been affixed for ease of attachment to the vacuum line. These were irradiated in the position

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of maximum X-ray dosage by placing the cell in the well of the tube with the radiation entering vertically through the bottom of the cell. During irradiation the sample temperature rose slightly due to heat transferred from the X-ray tube. A blower circulated air over the cell to keep this temperature rise to a minimum. No other temperature control was attempted. Utilizing this arrangement the reproducibility in positioning the sample was very good. The limiting factor in these investigations is the constancy in the intensity out-put of the X-ray tube. Our measurements indicate that this is controlled to within about ± 2%.

In the case of Expt. 31, the radiation from 300 millicuries of Co^{60} was used for activation. The irradiation vessel consisted of a cylindrical tube with an attached break-off seal through which the sample could be attached to the vacuum line after irradiation, and a square pyrex absorption cell which was used for measurement of the iodine concentration during the course of irradiation.

In reporting the results, the reaction yields are given in terms of moles of reaction product per unit of irradiation at the constant intensities described above. Both experimental arrangements were monitored through the radiation induced oxidation of ferrous sulfate in 0.8N sulfuric acid solution.

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Gas measurement. - The methods employed in degassing the samples and in measuring the gaseous products are essentially the same as those described in the previous contribution[6]. The hydrogen-methane fraction was taken as that volatile at liquid nitrogen temperature (-196°C) and the higher hydrocarbons were degassed and distilled at ethyl bromide mush temperature (∼-115°C). The hydrogen was found to be almost entirely recovered in the first degassing with the methane coming off somewhat more slowly than in the photolytic case, probably due to the increased area of the sample tube in the arrangement used here. The higher yield of ethane relative to methane makes it possible to obtain a somewhat greater accuracy in the present measurement than is possible in the case of photolysis.

Gas analysis. - The combustion analyses were performed essentially as previously described[6]. Since hydrogen is a product in this radiolysis, it was necessary to perform combustion analyses on each of the various samples volatile at liquid nitrogen temperature.

A measure of the unsaturation of the fraction volatile at -115°C was obtained by hydrogenation on nickel catalyst at room temperature in a tube attached to the Saunders-Taylor apparatus. The catalyst was prepared by the method of McMillan, Cole, and Ritchie[7]

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(7) W.A. McMillan, H.A. Cole, and A.J. Ritchie, Ind. End. Chem., Anal. Ed., 8, 105 (1936)

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and activated by heating in a hydrogen atmosphere at 300°C. A measured amount of hydrogen was compressed into the catalyst chamber, the sample measured, mixed with the hydrogen and the mixture placed over the catalyst where hydrogenation of the unsaturated portion occurred within 10 minutes at room temperature. The decrease in the pressure at constant volume was determined. After hydrogenation, the excess hydrogen was burned over copper oxide at 275°C and the remaining sample subjected to combustion analysis. As both ethylene and acetylene are products of the radiolysis, the results are expressed in terms of the total unsaturation, i.e. as extra bonds per molecule for the fraction volatile at ethyl bromide mush temperature. Preliminary tests with ethylene and ethane-ethylene mixtures indicate that the results of the hydrogenation analyses are reliable to within a few percent of the total sample (e.g. sample 100% ethylene, observed 1.00, 0.98, 1.00 C=C/molecule; sample 46.5% ethylene, 53.5% ethane, observed 0.455 C=C/molecule; sample 17.6% ethylene, 82.4% ethane, observed 0.182 C=C/molecule).

In two cases, one in which the sample initially contained no added iodine and one in which 10 mole % iodine was dissolved before irradiation, samples of the material volatile at -115°C were sealed in tubes and submitted for mass spectrometer analysis[8].

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

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Radiochemical analysis for methylene iodide and ethyl iodide. - McKenney[9] and Schuler and Hamill[5, 10] have shown that exchange between methyl iodide and iodine is induced by irradiation with X-rays and fast electrons. The former work was done under conditions similar to those used here. In the present experiments, methyl iodide was exchanged with radio-iodine[11], carrier methylene iodide was added, and the active methyl iodide was washed out of the sample[12]. The formation of methyl iodide is characterized in terms of the fraction of the total activity retained in the methylene iodide.

In one experiment, ethyl iodide carrier was also added and the activity retained in the ethyl iodide after thorough washing with methyl iodide, was attributed to the formation of this as product. A 30 cm. Podbielniak column was employed in the separations required in this particular case.

Iodine analysis. - Iodine was determined colorimetrically from observations of the optical density at 480, 500, and 520 $m\mu$. In the case of longer irradiations, were the concentrations of iodine produced

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(9) D.H. McKenney, M.S. Dissertation, Canisius College 1951

(10) R.H. Schuler, D.H. McKenney, and W.H. Hamill, to be published.

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

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

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were too high for accurate determinations at these wavelengths, the sample were diluted with known amounts of methyl iodide and the optical densities determined as above. The production of iodine was also determined during the initial phases of the irradiation utilizing a 1 cm. square pyrex absorption cell sealed to the reaction vessel. A Beckman quartz spectrophotometer was used for all determinations of optical density.

RESULTS

Gas analysis. - Combustion analysis of the fraction volatile at liquid nitrogen temperature shows that about 13% of this is hydrogen. The gas remaining after the hydrogen is burned off is methane (i.e. nC of this residue is 0.99-1.01 for all experiments reported in Table III). The hydrogen and methane yields are reported in Table III for the individual experiments in terms of the analysis for each particular experiment.

Measurement of the unsaturation of the fraction volatile at -115°C shows the presence of about 0.1 extra bonds per molecule of gas as indicated in Table I. Combustion analysis shows the entire fraction to be mainly C_2.

In Table II are reported the results obtained in the mass spectrometer analysis of the ~~same~~ Less volatile fraction together with the analysis of a similar

TABLE I

ANALYSIS OF PRODUCT VOLATILE AT -115°C

Experiment	23	24[a]	31[b]
Sample: moles x 10^6	15.0	8.0	17.4
Pressure: mm.[c]			
initial	75	115.5	64
hydrogen added	147	160	99
after hydrogenation	215	259	156
after oxidation at 275°C	77	117	63.5
after oxidation at 575°C	150	226	125
after absorption	3	4	1
Unsaturation	0.09	0.14	0.10
nC	2.04	1.99	1.97
Combustion: %	96	97	98

[a] Sample contained 2 mole percent iodine.
[b] Sample irradiated with Co^{60} gamma radiation.
[c] All pressures are corrected to the original volume.

TABLE II

MASS SPECTROMETER ANALYSIS OF PRODUCT VOLATILE AT -115°C

Experiment	27	28[a]	P[b]
Sample: moles x 10^6	42	8.5	5.1
Product: %			
Ethane	88.6	88.6	92.4
Ethylene	6.8	0.9	2.3
Acetylene	2.6	5.2	---
Propane	0.4	0.1	---
Propylene	0.1	0.03	---
C_4+	0.04	0.1	---
Oxygen	0.04	0.1	0.3
Carbon dioxide	1.4	4.9	4.6
Chloromethane	---	0.1	---
Methane	---	---	0.2

[a] Sample contained 10 mole percent iodine.
[b] Sample from similar photolytic experiment.

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fraction from the photolysis of methyl iodide which is included for comparison purposes. The major component is seen to be ethane. Ethylene and acetylene are produced in relatively high yields together with traces of higher hydrocarbons which are characteristically absent in the photolysis. The radiation yields of ethylene and acetylene are reported in terms of the mass spectrometer analysis for these products from Experiment 27. The unsaturation indicated here is in approximate agreement with the results obtained from hydrogenation experiments, the mass spectrometer and hydrogenation analysis giving respectively values of 0.09 and 0.12 extra bonds per molecule for iodine free samples. The marked decrease in the ethylene yield for the sample containing iodine may possibly be due to the formation of undissociated ethylene diiodide. The carbon dioxide is probably due to a residue remaining after the original degassings. The chloromethane is presumably real and probably originates as an impurity in the iodine added to the system (the amount present corresponds to 10^{-8} moles or 0.00001% of the iodine added).

<u>Gas production</u>. - The total yields of hydrogen, methane, and ethane, are given in Figure I for the radiolysis of methyl iodide samples initially containing no added iodine. In Table III are summarized the yields observed in each experiment. These are seen to

TABLE III

DECOMPOSITION YIELDS

Expt. #	Period min.	Yield moles x 10^8/min.			
		H_2	CH_4	C_2	I_2
X-irradiation: (Fe^{++} oxidation = 18.0×10^{-8} equil./min.)					
12	15	1.0	6.8	19.0	22.0
8	25	1.0	5.7	16.8	18.3
11	50	1.3	6.6	15.9	16.7
10	100	1.4	7.6	--	17.4
13	100	1.1	7.6	16.5	17.5
23	100	1.1	7.9	16.3	17.5
14	150	1.1	7.9	16.1	17.8
9	200	1.1	6.5	14.8	16.1
15	200	1.2	8.1	16.1	18.1
27	300	1.1	7.4	15.2	16.0
(graphical mean)		1.1	7.8	16.3	17.5[a]
Gamma-irradiation: (Fe^{++} oxidation ≅ 0.24×10^{-8} equil./min.)					
31	58,800	0.0019	0.0134	0.0301	0.0297

[a] Irradiation #33 indicates 16.5×10^{-8} moles I_2/min.

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be directly proportional to the irradiation dose with very little, if any, induction effect being observed. The presence of small amounts of iodine produced as a result of the decomposition does not apparently inhibit the formation of products to any appreciable extent. It is estimated, from the further experiments on the effect of high iodine concentrations, that at an iodine concentration of 0.004 M (the amount of iodine present after 250 minutes of irradiation) the gas yield is 98% of that for a sample containing only traces of iodine.

It will be noted that, in comparison to the photolysis where the methane yield is the greater, in the radiolysis the methane yield is less than that for ethane.

Effect of added iodine. - In the presence of iodine added to the sample before the irradiation (all experiments are of 100 minutes duration except Expt. 28 which is 300 minutes) the yields are found to decrease as shown in Fig. 2. It is seen that the iodine affects the products of the decomposition to an appreciable extent only when present at relatively high concentration (0.1 - 4 M in iodine). The effect of iodine on the various products is somewhat different, the yields being respectively for hydrogen, methane, and ethane production 64%, 36%, and 24% of normal in an irradiated

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sample containing 10 mole % iodine. Previously[5] a slight decrease in the iodine yield was observed at high iodine concentration.

Iodine production. - In Fig. 3, the results are given for iodine production in the X-ray decomposition of air free and air saturated methyl iodide together with data for the decomposition of air free methyl iodide induced by radiation from 300 mc. of Co^{60}. The iodine yield in ethyl iodide radiolysis is given here for comparison purposes. The data given in Fig. 3 were obtained during the course of decomposition of samples irradiated particularly for this purpose. The results listed in Table III were obtained from the individual samples after they had stood some time in the degassing operations. These are slightly ($\sim$10%) higher. In Fig. 3 the constancy of the iodine production yield over the course of the radiolysis is illustrated. The yields of iodine, on a mole basis, and of total C_2 gas are equivalent within experimental error.

Formation of methylene iodide and ethyl iodide. - The results of the radio-iodine carrier experiments are given in Table IV. It is seen that 2.8% of the active organic fraction carries with methylene iodide and 0.7% carries with ethyl iodide. The identification of the latter activity is given additional weight by the fact that, in the final distillation, the methyl iodide fraction

TABLE IV

FORMATION OF METHYLENE IODIDE

Expt. #	Carrier[a] iodine molesx10^6	Exch. %	Org. activity c/m	Activity as CH_2I_2 %	Activity as C_2H_5I %
29	40	61.0	4238	2.7	---
30	20	71.0	2308	2.9	---
32	19	73.8	2739	2.8	0.7

[a] In 10 ml. of sample.

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preceding the active ethyl iodide contained little activity.

If the fraction of the activity appearing in the above products is multiplied by the total exchange yield of 0.98 x 10^{-6} iodine atoms exchanged per minute[10], a radio methylene iodide yield of 0.028 x 10^{-6} moles/min. is obtained together with a radio ethyl iodide yield of 0.007 moles/min.. Thus, although largely masked by the exchange process, these products do account for a significant part of the net chemical reactions.

It will be noted that there is considerable discrepancy between our results and the 19% of the activity reported as methylene iodide and 15% reported as ethyl iodide by Gevantman and Williams[13]. It is difficult to reconcile this large discrepancy since we seem to be comparing similar systems. The present results represent the lower value and are presumably less liable to error by contamination. Also, if the yield of methylene iodide is compared to that of methane, a maximum of 8% of the activity would be expected to appear in the methylene iodide. The analogous yield in the photochemical case is likewise lower than anticipated.

The present results indicate even more strongly the general conclusion of Gevantman and Williams, that

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(13) L.H. Gevantman and R.R. Williams, Jr., J. Phys. Chem., <u>56</u>, 569 (1952)

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in the radiation decomposition of the alkyl iodides the C-I bond is preferentially broken. Methyl iodide, which seemed to be anomalous in their pattern, is seen to be in complete agreement with this principle.

Decomposition by gamma radiation. - Experiment 31, was undertaken utilizing gamma radiation in order to provide data for comparison to ferrous oxidation and to check any possible effects of radiation intensity and energy on the relative yields of products. Degassed methyl iodide was subjected to a five week irradiation over 300 millicuries of Co^{60} at a rate of energy absorption approximately one six hundredth that used in the X-ray experiments. The relative yields of the various products ($I_2:H_2:CH_4:C_2H_6:C\equiv C$ :: 1:0.065:0.45:0.89:0.13) are in excellent agreement with the relative yields observed in the X-ray decomposition. Since it is not likely that any intensity controlled process should affect all the products in so similar a manner over such a large intensity range, these results indicate that the absolute yields are not intensity dependent to any appreciable extent in this region.

DISCUSSION

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It is known from studies of the radiation induced exchange[9,10] that, in the region of iodine concentration of 10^{-4} to 10^{-2} molar, the iodine is reacting with the products of the decomposition. However in spite of the effectivity of the iodine in removing the major fraction of the radicals formed in the decomposition, the yields of the various products observed in the radiolysis of methyl iodide are not appreciably affected by the increase in the iodine concentration which occurs during the course of irradiation. Presumably the iodine serves as a sink, efficiently removing the thermal radicals formed.

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (1)$$

As in the photolysis, iodine cannot be involved in the present case in processes which are rate controlling with respect to the formation of net products. Reactions other than those of normal thermal radicals must be included in the overall mechanism in order to account for the observed decomposition.

In the photochemical analog it was found necessary to postulate reactions of extra-thermal radicals, the so called "hot Radical" reactions, in order to explain the production of methane, ethane, and iodine as products[6,14]. In the present case even greater energy is available. This energy is present as kinetic

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

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energy of the fragments and also in modes of electronic excitation and ionization. It has already been indicated[5], from the high yield of iodine production in the radiolysis of methyl relative to ethyl iodide (1:1.5) as compared to the same relative yields for the photolysis (1:25), that processes involving considerably greater energies are extremely important.

In addition to the methane, ethane, and iodine which are formed as products in the photolysis, hydrogen, ethylene, acetylene, and small amounts of propane, propylene, and higher hydrocarbons are observed as minor products in the radiolysis. A comparison of the yields is made in Table V based on the fractional yields for the radiolysis being calculated on the assumption that the total primary yield is equal to the sum of iodine molecule production and iodine atom exchange. It is assumed that in this respect the processes approximate the photochemical behavior. Should other, non-measurable, processes result from the absorption of energy, the relative yields will be as given in Table V.

A number of marked differences are observed in the yields for the various products. With perhaps the exception of a trace of ethylene, there is no evidence for the formation of the minor products in the photolysis, while these are formed in measurable yields in the radiolysis. The yields of iodine and ethane are very

TABLE V

RELATIVE YIELDS

	Photolysis	Radiolysis
	ϕ	G/G_t [a]
H_2	<0.0001	0.010
CH_4	0.023	0.068
C_2H_6	0.007	0.129
C_2H_4	<0.0002	0.010
C_2H_2	---	0.004
I_2	0.008	0.144
Exchange	~ 1.0	~ 0.85
$CH_2I_2^*$	0.014	0.024
$C_2H_5I^*$	---	0.006

[a] G_t corresponds to exchange plus iodine production.

considerably greater while the yields of methane and methylene iodide are only slightly greater. Corresponding to the increased iodine yield previously noted[5], an ~~corresponding~~ increased ethane yield is observed here. It is seen, however, that while the ethane and iodine yields increase by a factor of approximately 30, that the methane yield increases only by a factor of 2.5.

The net decomposition reactions are seen to represent the resultant products of an appreciable portions of the primary dissociation processes. The above indicates that reactions involving hot radicals, highly excited states, and ionic species are extremely important in the processes that control the overall reactions. Because of the complexities of the system it is difficult to describe a detailed mechanism for the decomposition. We shall attempt here to only suggest various processes of varying importance which may be operative in the formation of products.

Absorption of energy. - The primary physical process is the absorption of all or part of the energy of the quantum and the ensuant production of fast electrons which in turn produce ionization and excitation as secondary effects.

$$CH_3I \rightsquigarrow CH_3I^{\ddagger} \qquad (2a)$$

$$\rightsquigarrow CH_3I^{+} + e^{-} \qquad (2b)$$

With the presence of large amounts of iodine in the

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system, the absorption of the X-radiation is almost entirely due to the photoelectric effect and results in primary electrons which have an energy distribution (due to the heterogeneity of the radiation) in the region of 30-120 kev., As the photoelectric absorption coefficient of iodine is very high at the wavelengths employed here, the radiation is almost completely absorbed in the 0,7 cm. thickness of sample. Transmission studies, employing air saturated ethyl iodide for the relative intensity measurements, indicate that 96% of the incident energy is absorbed by the sample.

In the case of gamma radiation in the mev. region, the absorption is predominantly of the Compton type with only a fraction of the energy of each quantum being transferred to the electron. The energy distribution of the primary electrons in this case is continuous from 0 to approximately 1 mev.. A small photoelectric contribution contribution is also made here due to the presence of the iodine.

Because of the much greater number of processes induced by the secondary effects, the species resulting from the primary absorption of energy may be neglected in regard to the major products although these may conceivably be involved in the formation of minor products produced in fractional percentages.

<u>Electron attachment</u>. - The electron liberated in

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the ionization process may return to one of the positive ions with the neutralization resulting in the liberation of considerable energy, part of which may be retained in the form of electronic excitation.

$$CH_3I^+ + e^- \longrightarrow CH_3I^{\neq} + q; \ (q \leq 9.5 \text{ ev.}) \qquad (3)$$

The free electron, after it has been thermalized, may also attach itself to the solvent methyl iodide leading to the formation of a negative ion[15].

$$CH_3I + e^- \longrightarrow CH_3I^- + 3.6 \text{ ev.} \qquad (4)$$

This reaction is exothermic by the value of the electron affinity of methyl iodide (assumed in reaction 4 to be approximately that of iodine[15]). This energy is sufficient to rupture the C-I bond

$$CH_3I^- \longrightarrow CH_3\cdot + I^- \qquad (5)$$

although the negative ion may be stabilized sufficiently due to a redistribution of the energy in order to permit its existence long enough to be involved as an intermediate in the overall decomposition. The main result of reaction 5, if it occurs, should be radiochemical exchange.

Primary effects. - The energy dissipated in the excitation and ionization can give rise to a considerable number of primary processes. In the case where the

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(15) J.L. Magee and M. Burton, THIS JOURNAL, 72,1965 (1950); 73, 523 (1951), have discussed some of the theoretical appects of negative ion formation.

P energy appears as electronic excitation, the excited species may dissociate along a number of different reaction paths.

$$CH_3I^{\ddagger} \longrightarrow \underline{CH_3\cdot} + I\cdot \qquad (6a)$$

$$\longrightarrow CH_2 + HI \qquad (6b)$$

For reaction 6a, representing dissociation of the lowest excited state of methyl iodide, we have some knowledge of the chemical characteristics from studies of the photolysis at 2537Å. Since considerable amounts of energy are available, it seems likely that the methyl radical will have a sufficiently high kinetic energy as to be able to produce hot radical reactions analogous to those postulated in the photochemical case. Reactions 6a and 6b represent possible modes of dissociation of the more highly excited states which are expected to complicate the observed results.

Reactions of the positive ions must be considered in the overall mechanism. Dissociation of the positive ion presumably leads to the formation of ionic fragments.

$$CH_3I^{+} \longrightarrow CH_3^{+} + I\cdot \qquad (7)$$

Because this reaction is endothermic by about 3 ev., dissociation will occur only if the transfer of energy in ionization exceeds 12.4ev.[16]

For ionizing energies between 9.5 ev. (the ionization potential of methyl iodide) and 12.4 ev., stable CH_3I^+

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(16) C.A. McDowell and B.G. Cox, J. Chem. Phys., **20**, 1496 (1952)

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ions will be formed.

Charge Neutralization. - Neutralization of the negative ions appears to be extremely important in the production of the observed products. Possible reactions include:

$$CH_3I^+ + CH_3I^- \longrightarrow CH_3I + CH_3I \qquad (8a)$$

$$\longrightarrow CH_3\text{-}CH_3 + I_2 \qquad (8b)$$

$$CH_3^+ + CH_3I^- \longrightarrow CH_3\text{-}CH_3 + I\cdot \qquad (9a)$$

$$\longrightarrow \underline{CH_3\cdot} + CH_3I \qquad (9b)$$

$$CH_3I^+ + I^- \longrightarrow \underline{CH_3\cdot} + I_2 \qquad (10)$$

The charge neutralization reactions are highly exothermic (~6 ev. for reaction 8a) and are affected only slightly by the small chemical energies involved. The initial products may or may not be stable depending upon the distribution of the energy within the resulting species.

The charges present in these neutralization reactions represent a large driving force. A positive entropy change is involved and provided the ions have at least a momentary existence, these reactions should have a very high probability especially within the path of ionization.

Hydrogen production. - Hydrogen is produced in a small, constant yield which is affected only slightly by the addition of large amounts of iodine. The lack

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of effect of iodine indicates the absence of processes involving hydrogen atoms as intermediates. Hydrogen presumably is formed directly by the dissociation of the highly excited states and ionic species and possibly indirectly through the formation of hydrogen iodide as product. Hydrogen is also expected as a product of the charge neutralization reactions which ultimately produce unsaturated products (reactions 9d and 12). It will be noted that the hydrogen yield is only about 1/50 of that observed in hydrocarbon decomposition. The presence of a group more easily affected by the radiation reactions tends to lessen hydrogen production.

<u>Methane production</u>. - Methane is produced in a yield only slightly greater than observed in the photolysis. Since extrathermal methyl radicals are produced, at least in the dissociation of the lowest excited state and as a result of certain of the charge neutralization processes (in reactions 9b and 10 the energy of the methyl radical recoiling from the heavier molecule is of the order of 5 ev.), it seems likely that hot radical reactions are responsible for the major fraction of methane production.

$$\underline{CH_3}\cdot + CH_3I \longrightarrow CH_4 + CH_2I\cdot \qquad (11)$$

The slightly increased yield over that observed for photolysis at 2537Å presumably reflects the increased efficiency of the process at the higher available

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energies. Reactions such as

$$CH_3^{+} + CH_3I^{-} \longrightarrow CH_4 + CH_2I^{\cdot} \qquad (9c)$$

may have a minor importance here.

Methylene iodide production. - Presumably the methylene iodide is formed by the same processes which result in methane production. Although the two yields are not equal, as the stoichiometry of the system would indicate, the former is low to about the same extent as observed in the photolysis.

Ethane production. - The high yield of ethane indicated very strongly the importance of ionic processes in its formation. Reactions 8b and 9a are postulated and appear to depend only on the stability of the ionic species.

Hot radical production of ethane, as inferred from the low methane yield, probably accounts for only a small fraction of the total yield. It is not expected that the relative cross sections for methane and ethane production, in the hot radical processes, should differ very much from the photolysis to the radiolysis.

Radiochemical exchange. - Exchange results from the quench of thermal radicals by the molecular iodine present, according to reaction 1. The results of the exchange experiments are somewhat complicated and will

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be reported elsewhere[10]. Because of the low mole fraction of iodine in these systems, the exchange must result predominantly from radicals which have survived numerous collisions. These results show that a major fraction (~85%) of the primary decomposition results in species which are eventually thermalized and react with free iodine giving no net observed chemical yield. The reactions producing net chemical products correspond, therefore, to only a minor, but significant, part of the primary decomposition. This part is considerably more important in the radiolysis than in the photolysis (i.e. 15% as compared to 3%).

Ethylene and acetylene. - Ethylene and acetylene are produced in a total yield which approximates the yield of hydrogen. The lack of formation of these products, in any appreciable extent, in the photolysis indicates that they probably do not form from radical intermediates. Since two molecules must be involved in the formation of these products, it seems unlikely that excited species will be directly involved. Ionic processes which can account for these products are represented in reactions 9d and 12.

$$CH_3^+ + CH_3I^- \longrightarrow \cdot CH_2-CH_2I + H_2 \qquad (9d)$$
$$\hookrightarrow CH_2=CH_2 + I\cdot$$

$$CH^+ + CH_3I^{-\cdot} \longrightarrow \cdot CH=CHI + H_2 \qquad (12)$$
$$\hookrightarrow CH\equiv CH + I\cdot$$

Ethyl iodide production.- A low, but apparently real, yield of radio-ethyl iodide is produced in the radiolysis of methyl iodide containing radio-iodine. Ethyl radicals must be precursors to this product which involves the ultimate reaction of two carbon ato,s and an iodine molecule. Reaction 9e represents a possible reaction path which can account for this.

$$CH_3^{+} + CH_3I^{-} \longrightarrow CH_3\text{-}CH_2^{\circ} + HI$$

$$\xrightarrow{I_2^{*}} CH_3\text{-}CH_2I^{*} + I^{\circ}$$

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If reactions 9d and 9e accurately represent the mechanisms for the formation of these products, the ratio of the radio-ethyl iodide yield (assuming complete quenching of the ethyl radicals by radio-iodine) to ethylene yield represents the branching of these reactions (i.e. the relative probability of eliminating H_2 and HI in reaction 9). This ratio is seen to be of the order of unity.

Minor products. - The propane, propylene, and minute traces of C_4 hydrocarbons which are observed as products apparently result from ~~processes~~ reactions which occur in the ionization paths and reflect processes occurring either when the ionizing electron still has considerable energy or in regions of very high ionization density.

The effect of added iodine. - Iodine present as a large fraction of the irradiation system results in a decrease in the yield of products. This decrease may involve one or more of the following possibilities: (a) an effect of purely chemical nature; (b) an interference in the hot radical processes; (c) absorption of the energy by the iodine rather than methyl iodide; (d) electron capture by iodine rather than by methyl iodide; and (e) changes in the reacting system which result from charge transfer reactions. Possibility (a) seems unlikely since any effect of iodine is expected to occur at lower concentrations and (b) must

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await further clarification of the situation in the photolysis. Since the fractional absorption of the energy by iodine should be equal to the electron fraction of the iodine in the system, (c) is not sufficiently important to explain the observed quenching of ethane and methane production. This effect probably accounts for a large portion of the quench observed in the case of hydrogen production. The bulk of the quenching processes are believed to be due to (d) and (e).

The empirical nature of the quenching reactions is seen in Fig. 4 where the ratio of quench (the difference between the yield at low iodine concentration and the observed yield) to yield is found to be a linear function of the ratio of iodine to methyl iodide concentrations.

$$\frac{G_0 - G}{G} = Q \frac{I_2}{CH_3I} \qquad \text{I}$$

In Equation I, Q has the value of 28 in the case of ethane production, 13 for methane production, and approximately 6 for hydrogen production. In the region of 0.5 - 1.0% there is an initial decrease in yield somewhat greater than indicated by the above values. An effect of the type illustrated by Equation I would be expected if there is competition of iodine and methyl iodide for some important intermediate. Reaction 13 suggests itself as having the possibility of competing

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favorably with reaction 4.

$$I_2 + e^- \longrightarrow I_2^- \longrightarrow I^{\cdot} + I^- \qquad (13)$$

Absolute yields. - The absolute yields for the decomposition of methyl iodide by Co^{60} gamma radiation can be estimated by comparison with ferrous oxidation. In making such a comparison the relative absorption of the two systems must be taken into account. If the absorption is totally due to the Compton effect and it is assumed that the cross section for absorption per electron is the same in both the case of methyl iodide and water, then the ratio of the absorption of methyl iodide to water may be taken as the relative electron densities of the two samples (1.78:1). It is estimated from absorption coefficient data[17] that an additional contribution of about 15% is due to photoelectric absorption in iodine. The absorption of methyl iodide relative to water (for mev. gamma radiation) is taken here to be 2.03.

Unfortunately, at the present time, the absolute yield for ferrous oxidation is somewhat in question[18]. The measured yields vary from 15.5[19] to 20.4[20] and

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(17) "The Science and Engineering of Nuclear Power", Addison - Wesley Press, Inc., Cambridge, Mass., 1949, Chapter 1.

(18) N. Miller and J. Wilkinson, Discussion Far. Soc. #12, 50 (1952)

(19) C.J. Hochanadel, J. Phys. Chem., 56, 587 (1952) private communication

(20) T.J. Hardwick, Can. J. Chem., 30, 17 (1952); 30, 23 (1952)

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slightly higher. Basing our calculations on the higher value ($G_{Fe^{++}}$=20.4) which is presently given the greater emphasis and correcting for absorption as indicated above we obtain the following G values for the decomposition of methyl iodide induced by Co^{60} gamma radiation.

(Fe^{++} oxid. = 20.4)
I_2 = 1.26
C_2 = 1.28
CH_4 = 0.57
H_2 = 0.082

It is seen that the G for iodine production compares very favorably with the value (G_{I_2} = 1.38) obtained in electron bombardment studies where the energy input was measured directly in terms of the electron current and particle energy.[5]

The gamma radiation and fast electron yields are apparently very similar. One must, however, be careful in identifying these yields, at least in principle, since effects of intensity may be present in the fast electron studies. These effects are apparently minimized in this particular system. It is indeed surprising that for the large difference in the rates of energy absorption, 4 x 10^{18} ev./cc/min in the fast electron experiments and 6 x 10^{14} ev./cc/min in the gamma radiation experiments, that the decomposition yields are found to be so similar.

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Accurate yield calculations for the X-ray experiments are more difficult since in the region of 0.2-0.4Å the absorption of the water is due to both the photoelectric and Compton effects. Because of the inhomogeneity of the radiation the precise fractional absorption of the water is not known although the calculation is aided somewhat by the fact of complete absorption of the energy in methyl iodide. If an absorption of 5.5% of the incident energy is assumed for the water (corresponding to an effective wave length of 0.3Å) then the yield of iodine corresponds to a G_{I_2} of 1.20. This latter value, which because of the uncertainty in the absorption is somewhat in question, indicates that there is no extreme dependency upon energy or intensity.

ACKNOWLEDGEMENT

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Fig.1.- Production of C_2 hydrocarbon, methane, and hydrogen in the X-ray decomposition of methyl iodide.

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Fig. 2.- Effect of iodine on the gas production yields.

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Fig. 3.- Iodine production.in the X-ray decomposition of methyl iodide, ○ ; air saturated methyl iodide, ⊗ ; ethyl iodide, -o- ; and in the gamma radiation decomposition of methyl iodide, x . The relative irradiation is given in minutes for the X-ray decomposition and minutes x1/560 for the gamma ray decomposition.

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Fig. 4.- Effect of iodine on gas production. Relative quench as a function of the iodine to methyl iodide mole ratio. Circles refer to C_2 production, triangles to methane production, ahd crosses to hydrogen production.

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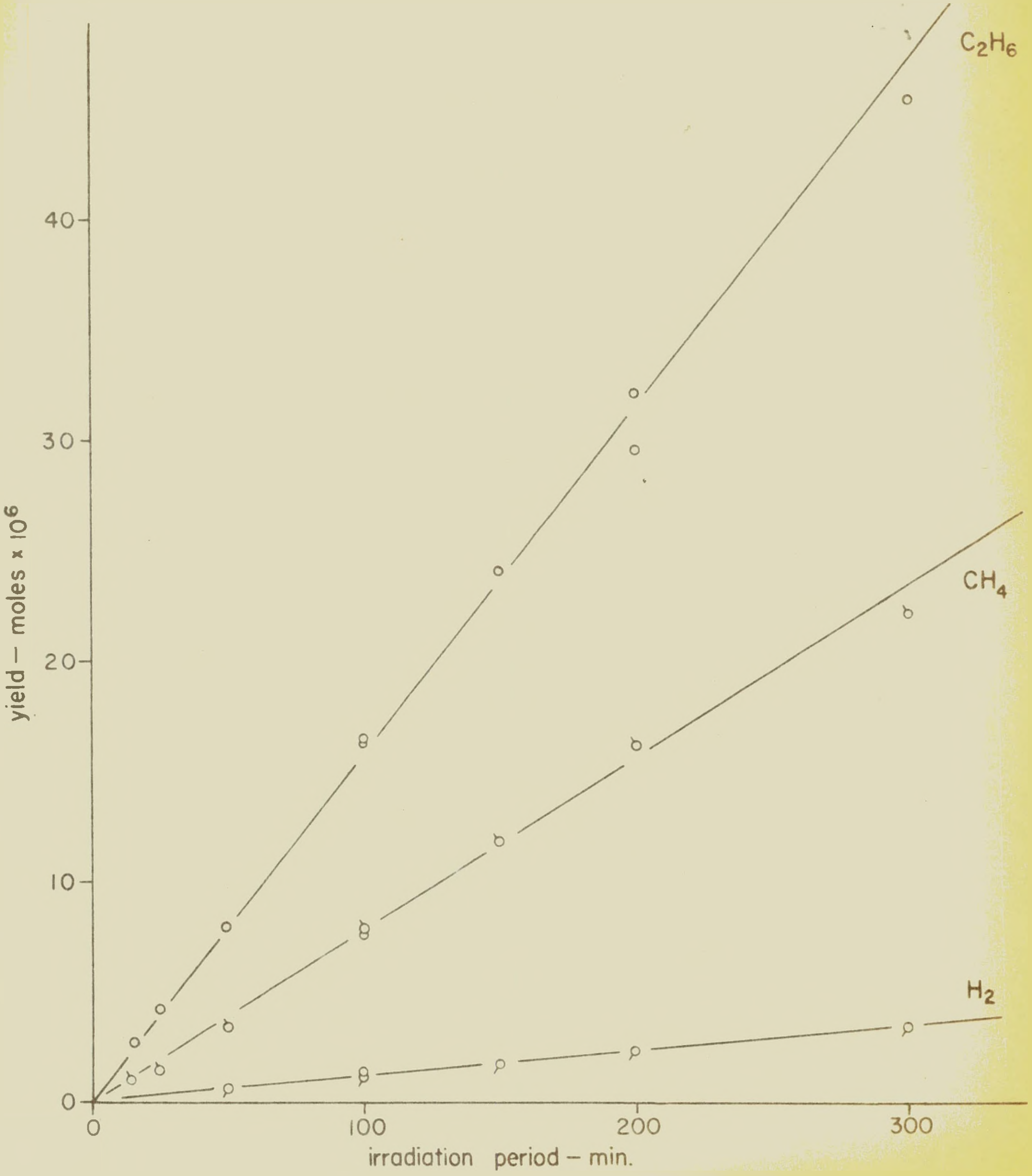
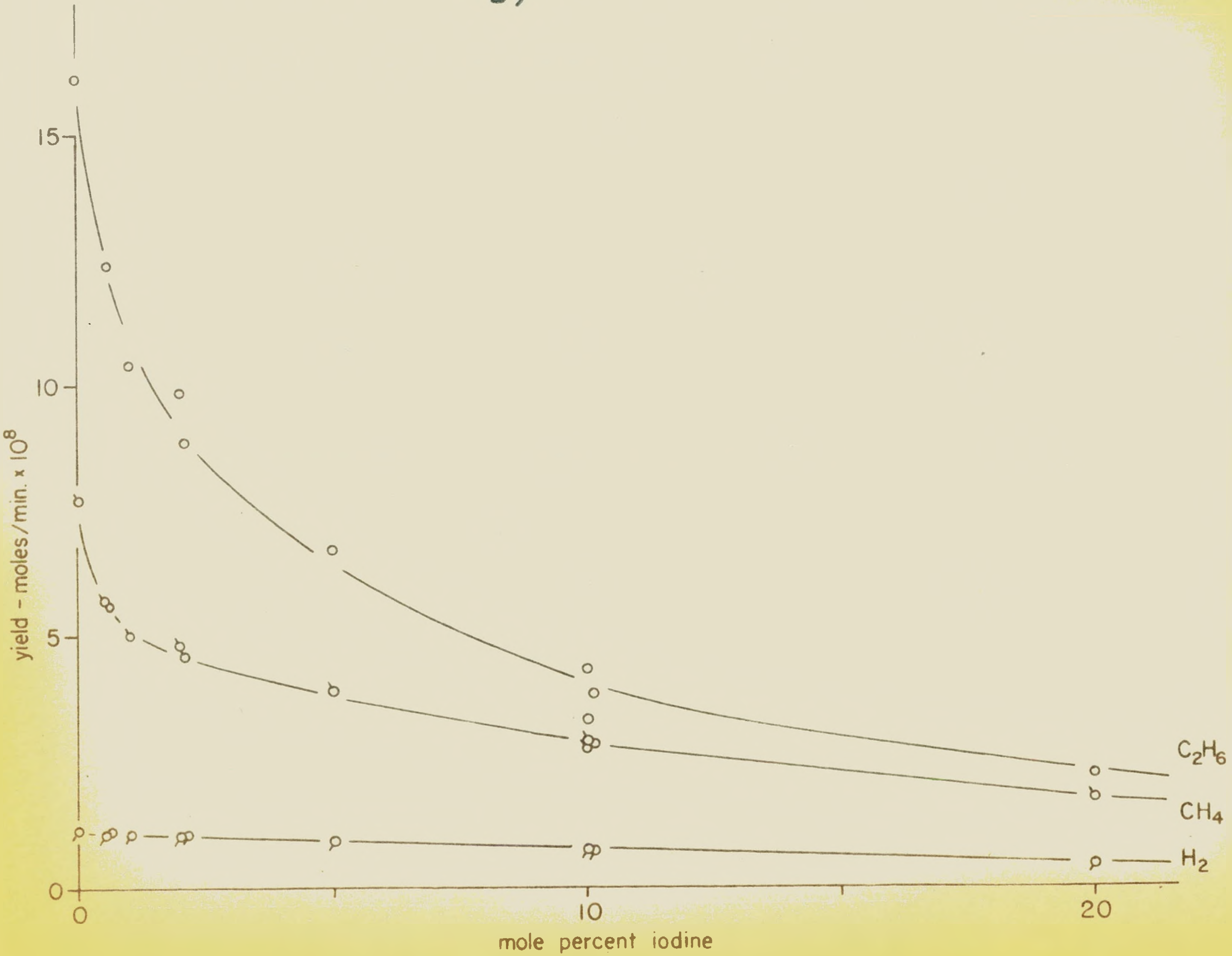
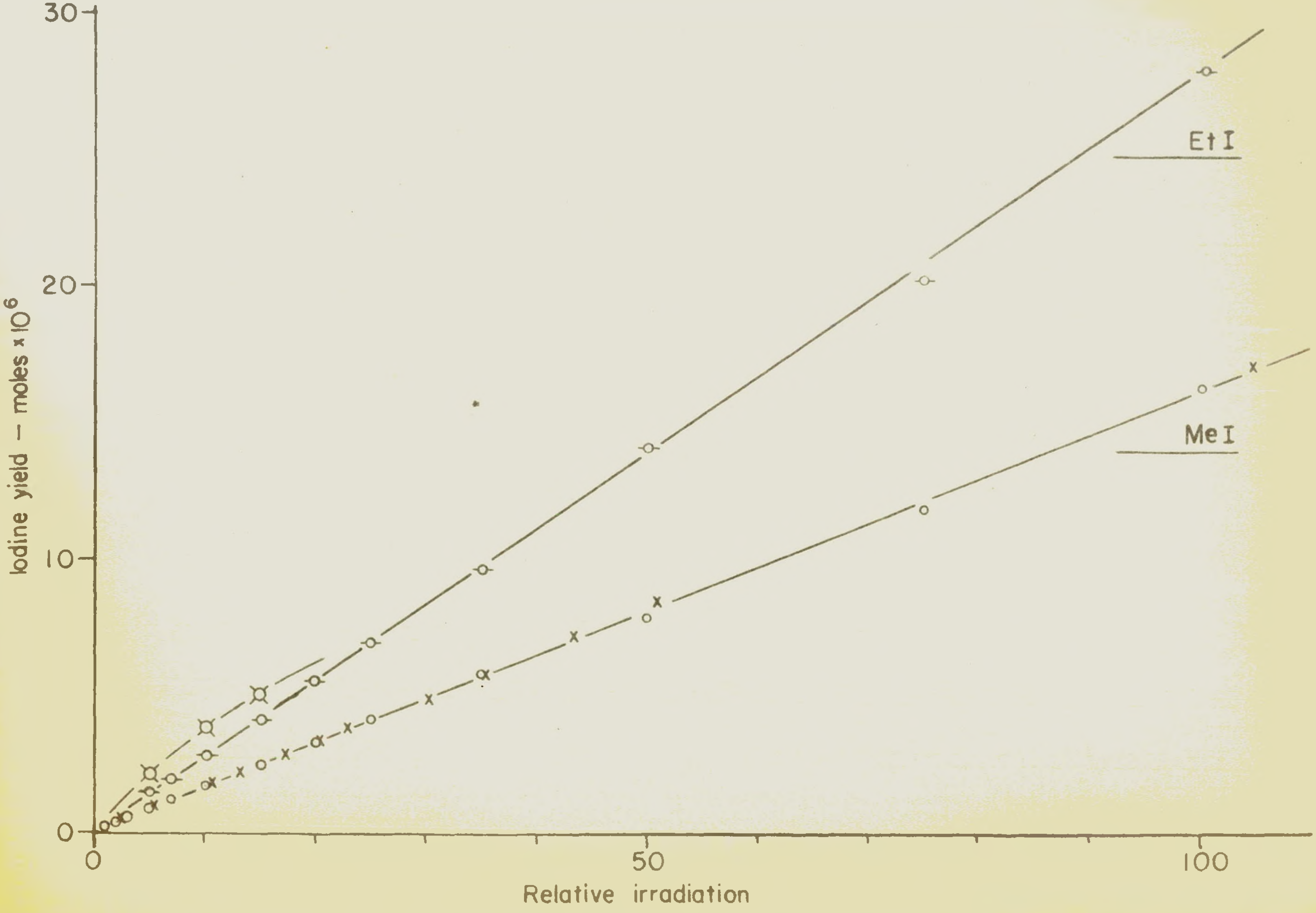
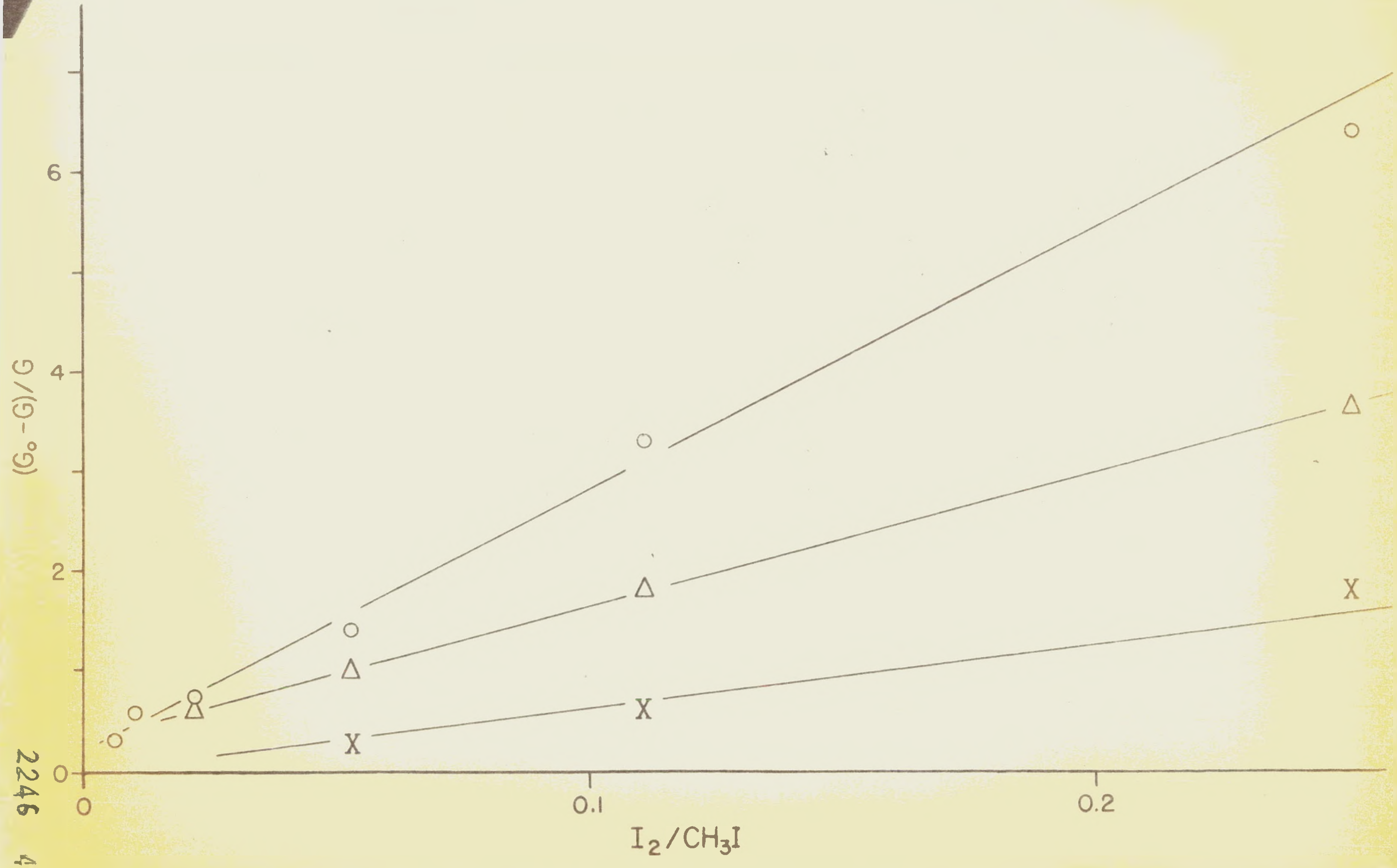

C$_2$H$_6$
CH$_4$
H$_2$
yield – moles x 10^6
0
10
20
30
40
0
100
200
300
irradiation period – min.


15
10
5
0
yield - moles/min. x 10^8
0
10
20
mole percent iodine
C_2H_6
CH_4
H_2


30
20
10
0
Iodine yield – moles × 10^6
0
50
100
Relative irradiation
Et I
Me I



(G₀ - G)/G
0
2
4
6
0
0.1
0.2
I₂/CH₃I