

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

## Kinetics of the Reaction of Methyl Iodide with Toluene

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The kinetics of the reaction of methyl iodide with toluene have been studied at 326, 354 and 374° in a static system at total pressures from 180–780 mm. The ratio of methyl iodide (M) to toluene (T) was varied from 0.021–0.63. It was found that methane was the sole end-product of the methyl iodide carbon, so that the methane production could be used as a measure of the extent of reaction. Molecular iodine accounted for only a fraction (0.25–0.70) of the iodine from the reacted M, due to the formation of HI and benzyl iodide. Analysis of the kinetic data (with emphasis on the measurements at low extent of reaction of M) yielded the expression:  $-d(M)/dt = k_1(M)(T) + k_2(M)^{1/2}(T)^{1/2}$ , with activation energies  $E_1 = 51.6$  and  $E_2 = 45.2$  kcal./mole. Auxiliary experiments showed that the reaction was accelerated by added iodine. No evidence for an inert gas pressure effect or a surface reaction was found. The C<sup>12</sup>/C<sup>13</sup> kinetic isotope effect was  $1.019 \pm 0.002$  over the range studied, compared to  $1.026 \pm 0.001$  for the reaction of M with HI. Experiments on the pyrolysis of M alone were carried out using a high speed flow system with He carrier at 475–575°. Product analyses indicated the relationship:  $CH_3I \rightarrow 0.64 CH_4 + 0.072 C_2H_6 + 0.22 C + 0.50 I_2$ .

## Introduction

The kinetics of the thermal decomposition of methyl iodide are rather complex and not well understood. The early work has been summarized by Steacie.<sup>2a</sup> Szwarc,<sup>2b</sup> employing the toluene carrier technique, investigated the reaction at temperatures near 500°; more recent similar work has been reported by Horrex.<sup>3</sup> Unfortunately, in the case of iodides at least, the applicability of the toluene carrier technique is dubious, due to various complications. Here, for example, (a) iodine reacts with toluene readily to produce HI, which in turn reacts with methyl iodide yielding methane, and (b) the possibility of a direct bimolecular reaction ( $CH_3I + C_6H_5CH_3$ ) may not be excluded. The present paper reports an investigation of the kinetics of the reaction of methyl iodide with toluene using a conventional static method at lower temperatures (326–374°), where complexities would presumably be less important. It was found that the kinetic data were quite reproducible and that the observations could be represented by the simple empirical rate expression

$$-d(M)/dt = k_1(M)(T) + k_2(M)^{1/2}(T)^{1/2} \quad (1)$$

where M and T refer to methyl iodide and toluene, respectively.

Experimental<sup>4</sup>

Kinetic experiments were carried out in a conventional vacuum apparatus. The Vycor reaction vessel was identical with the one used in a previous study<sup>5</sup> and had been conditioned by the deposition of a carbonaceous coating. Good reproducibility of results for given initial conditions over the duration of the investigation indicated the negligible influence of the condition of the surface.

Methyl iodide (Eastman Org. Chem. No. 164) was further purified,<sup>6</sup> distilled *in vacuo* and stored in the dark at  $-78^\circ$ . Vapor pressure, boiling point measurements and the infrared spectrum of the vapor agreed with the literature.<sup>4</sup> Toluene

(Mallinckrodt A.R.) was further purified<sup>6</sup> and then treated by the procedure of Szwarc.<sup>7</sup> Blank runs of the toluene alone at the highest reaction temperature yielded no methane.

By allowing the reaction of methyl iodide with excess toluene to proceed longer than the time for complete decomposition ( $> 99.9\%$ ), it was found that the number of moles of methane formed was equal to the initial number of moles of methyl iodide taken, within the experimental uncertainty of  $\pm 2\%$ . Moreover, the C<sup>12</sup>/C<sup>13</sup> ratio of the CO<sub>2</sub> derived from the above methane corresponded (within  $\pm 1$  part per mil) with that for CO<sub>2</sub> from quantitative combustion of the methyl iodide. Since the C<sup>13</sup>/C<sup>12</sup> ratio in the CH<sub>3</sub>I happened to be smaller than the ratio in tank CO<sub>2</sub> (and in most hydrocarbons) by the factor 0.926, the above result constitutes a tracer determination implying that  $< 2\%$  of the CH<sub>4</sub> is derived from the toluene.

Consideration of these important observations indicates that the methane production may be used as the measure of the extent of reaction of the methyl iodide, *i.e.*,  $-d(CH_3I)/dt = d(CH_4)/dt$ .

The standard kinetic experiment consisted of evaporating premixed amounts of CH<sub>3</sub>I and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (the latter usually in excess) into the thermostated reactor. Total pressures ranged from 180–780 mm. After times ranging from 5 min. to 6 hr. the contents of the reactor were passed through traps at  $-196^\circ$  and the volatile product (essentially pure CH<sub>4</sub>, as determined by gas chromatography and by quantitative combustion to CO<sub>2</sub>) was transferred to a measuring volume. When isotopic assays were also desired, the CH<sub>4</sub> was oxidized to CO<sub>2</sub> by cycling through CuO (850°, then 300°), water being removed at  $-78^\circ$ . The iodine (originally condensed at  $-196^\circ$ ) was titrated with thiosulfate; typical analyses were in the range  $7 \times 10^{-6}$  to  $5 \times 10^{-4}$  g. at. of iodine. Gas chromatographic analysis showed that no ethane ( $< 1.5\%$ ) was formed under the present experimental conditions.

Auxiliary experiments showed the presence of small quantities of HI and benzyl iodide in the products. Separate studies on the reaction of I<sub>2</sub> with toluene at 326° indicated extensive formation of HI.

A number of high temperature experiments were also carried out with a flow system using He carrier gas; the CH<sub>3</sub>I was present at a level of 0.02–0.2 of the total pressure. A cyclone "stirred flow" reactor<sup>8</sup> was used, followed by a conventional vacuum system to separate CH<sub>3</sub>I and I<sub>2</sub> from more volatile products. A silica gel adsorption trap at  $-196^\circ$  isolated the product CH<sub>4</sub>. Alternatively, the total mixture issuing from the reactor was sampled by gas chromatography. Results are presented in Appendix I.

For both static and flow experiments the carbon in the CH<sub>3</sub>I was converted to CO<sub>2</sub> by a modified Wilzbach-Sykes<sup>9</sup> combustion. The mass spectrometric technique for C<sup>12</sup>/C<sup>13</sup> assay was standard.<sup>10</sup> Isotopic fractionation results are presented in Appendix II.

(7) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).(8) T. J. Houser and R. B. Bernstein, *THIS JOURNAL*, **80**, 4439 (1958).(9) K. E. Wilzbach and W. Y. Sykes, *Science*, **120**, 494 (1954).(10) M. E. Russell and R. B. Bernstein, *J. Chem. Phys.*, **30**, 613 (1959).

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(2) (a) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1954. (b) M. Szwarc, Thesis, Manchester Univ., 1947.

(3) C. Horrex and R. La Page, *Discussions Faraday Soc.*, **10**, 233 (1951).

(4) For further details see Ph.D. dissertation of R. F. Klemm, University of Michigan (1959), available from University Microfilms, Ann Arbor, Michigan.

(5) M. E. Russell and R. B. Bernstein, *J. Chem. Phys.*, **30**, 607 (1959).(6) A. Weissberger, *et al.*, "Techniques of Organic Chemistry," Vol. VII, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957.

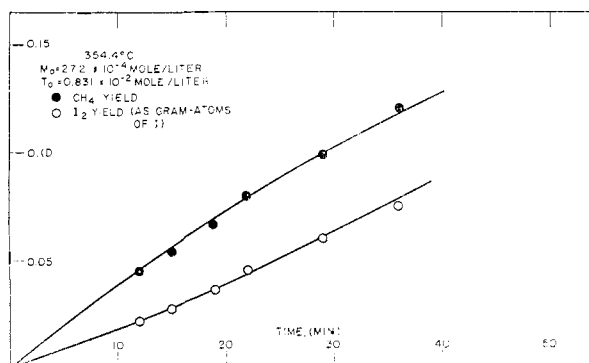
Fig. 1.—Typical dependence of  $x/a_0$  upon  $t$ .Results<sup>4,11,12</sup>

Fig. 1 is a typical graph of the time dependence of the fraction of methyl iodide reacted, based on  $\text{CH}_4$  formation. For comparison the data for  $\text{I}_2$  production is also shown. It is clear that molecular  $\text{I}_2$  does not constitute the sole end-product of I atoms from the reacted  $\text{CH}_3\text{I}$ . For a number of reasons the kinetic data for  $\text{I}_2$  formation are less reliable (and less extensive) than the comparable data for  $\text{CH}_4$ . However, in every case the ratio of the  $\text{I}_2$  recovered (in g. at. of I)/ $\text{CH}_3\text{I}$  reacted (in moles) was  $< 1$ . This ratio varied rather systematically over a range from 0.25 to 0.70, generally increasing with increasing extent of reaction. The distribution of the remainder of the iodine between the HI and  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$  products was not measured, however.

Figs. 2 and 3 show semilogarithmic plots of the methane data for typical sets of experiments. Ranges of initial concentrations used in the present study were as follows:  $10^4 M_0$  from 3.80–27.2;  $10^2 T_0$  from 0.42–1.78. Initial slopes, designated  $k_{\text{exp}}$  ( $\text{min.}^{-1}$ ), of such lines were helpful in deducing the empirical rate expression.

Additional hitherto unreported observations are briefly summarized.

A. In the reaction of M with T in the range 326–374°:

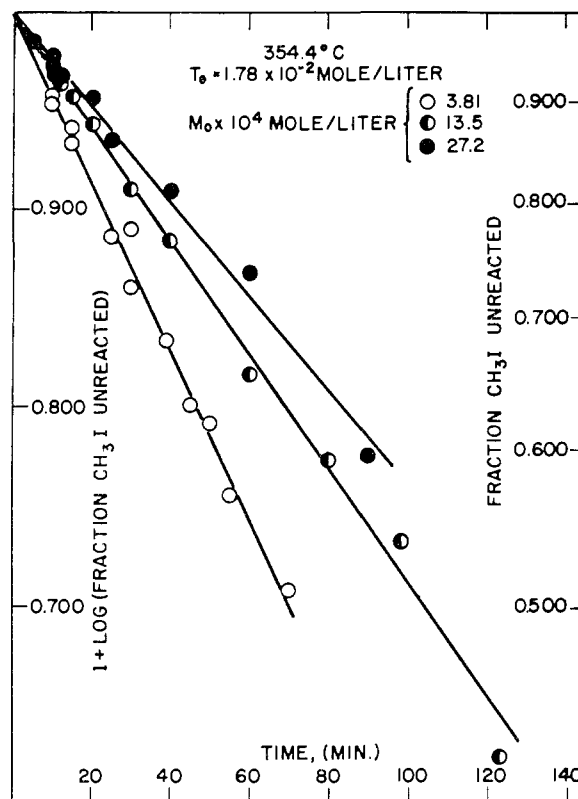
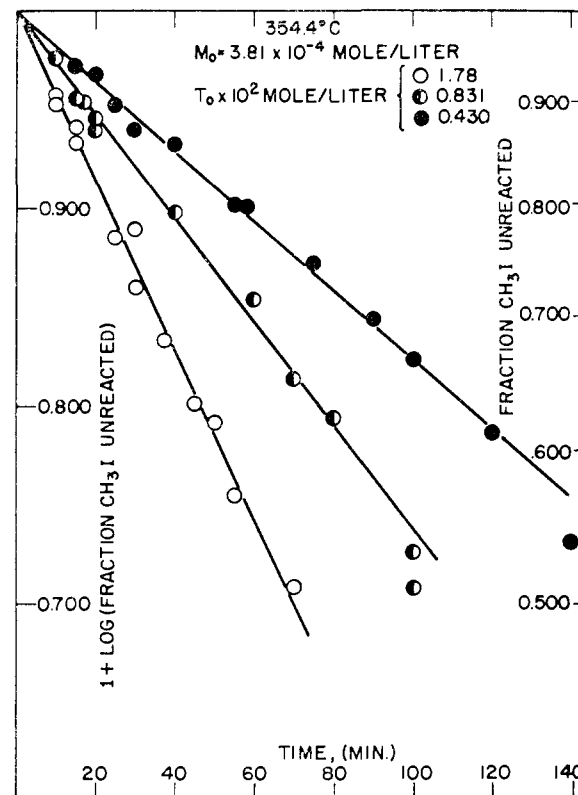
(a) Addition of  $\text{I}_2$  (in concentration ratios relative to  $M_0$  ranging from 0.25 to 3.0) caused an increase in the  $\text{CH}_4$  production. Quantitative evaluation of the  $\text{I}_2$  dependence was not feasible using the present experimental technique.

(b) The reaction is unaffected by inert gas ( $\text{SF}_6$ ) pressure in the range 180–760 mm. and is increased by only 50% upon 100-fold increase in the  $S/V$  ratio.

(c) Pyrolysis of M alone (in clean Pyrex reaction vessels) was accompanied by extensive carbon deposition, whereas in the presence of T

(11) A compilation of original data has been deposited as Document number 6336 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints or \$1.25 for 35mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(12) The abbreviated notations employed are:  $M_0$ , initial concentration of  $\text{CH}_3\text{I}$  (mole/l.);  $T_0$ , initial concentration of  $\text{C}_6\text{H}_5\text{CH}_3$  (mole/l.);  $Q_0$ , initial molar ratio of methyl iodide to toluene;  $x/a_0$ , molar concentration of product/ $M_0$ ;  $f$ , fraction of methyl iodide reacted, assumed equal to  $x/a_0$  for methane.

Fig. 2.—Dependence of rate on  $M_0$ .Fig. 3.—Dependence of rate on  $T_0$ .

the reaction was clean, yielding no visible surface film or deposit.

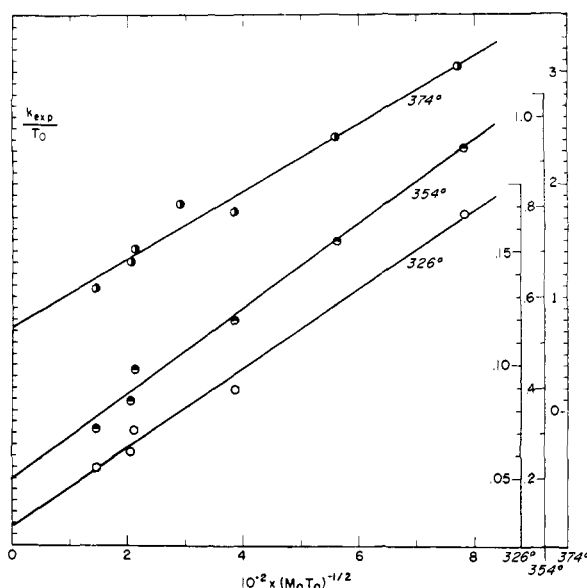


Fig. 4.—Plot for evaluation of rate constants.

(d) The average  $C^{12}/C^{13}$  kinetic isotope effect over the temperature range studied is  $1.019 \pm 0.002$  compared to  $1.026 \pm 0.001$  for the reaction of M with HI (see Appendix II).

B. In the high temperature pyrolysis of M in the range  $475\text{--}575^\circ$  (Appendixes I and II):

(a)  $C_2H_6$  is identified as a significant product.

(b) The rate of  $CH_4$  production increases upon addition of toluene.

(c) The  $C^{12}/C^{13}$  kinetic isotope effect is 1.010 (at  $486^\circ$ ).

**Empirical Rate Expression.**—Inspection of the dependence of  $k_{exp}$  upon the initial concentrations of M and T in the absence of added  $I_2$  suggested the relation

$$k_{exp} = k_1 T_0 + k_2 (T_0/M_0)^{1/2} \quad (2)$$

leading to the form of the rate expression, eq. 1. In Fig. 4 are shown least-square lines of  $k_{exp}/T_0$  vs.  $(M_0 T_0)^{-1/2}$  at the three temperatures of the measurements, from which the rate constants  $k_1$  and  $k_2$  were evaluated; the results are listed in Table I.

TABLE I  
SUMMARY OF RATE CONSTANTS

T (°C.)	$k_1$ (l. mole <sup>-1</sup> min. <sup>-1</sup> )	$10^3 \times k_2$ (min. <sup>-1</sup> )
326.0	0.0287	0.175
354.4	.197	0.938
374.4	.736	3.00

Since for the present experiments  $(T) \cong T_0$ , eq. 1 becomes

$$-d(M)/dt = k_1(M)T_0 + k_2(M)^{1/2}T_0^{1/2} \quad (3)$$

which is integrated to yield the equation

$$t = \frac{2}{k_1 T_0} \ln \left[ \frac{1+b}{(M/M_0)^{1/2} + b} \right] = \frac{-2}{k_1 T_0} \ln \left[ 1 - \frac{\alpha}{1+b} \right] \quad (4)$$

where  $b = k_2/k_1(M_0 T_0)^{1/2}$ ,  $\alpha = 1 - (1-f)^{1/2}$  and  $f = 1 - (M)/M_0$ , the fraction reacted. For  $\alpha/(1+b) \ll 1$

$$t \cong 2\alpha/k_1 T_0 (1+b) \quad (5)$$

For small extent of reaction ( $f < 0.1$ ),  $\alpha \cong f/2$  so that

$$t \cong f/k_1 T_0 (1+b) \quad (6)$$

(pseudo-first order behavior); thus  $k_{exp}$  is identified with  $k_1 T_0 (1+b)$ , consistent with eq. 2, of course.

The fit of the time-dependent solution (eq. 4) to the experimental points is shown in Fig. 5, where  $t_c$  (the time calculated using eq. 4–6 with rate constants of Table I) is plotted vs.  $t_{obsd.}$  for each experiment for which  $f \leq 0.7$  and  $t \leq 180$  min. More than 80% of the points lie within the designated band corresponding to an error of  $\pm 10\%$ . At each temperature, however, there appears to be a systematic deviation for the points at relatively large  $t$  (and/or high extent of reaction). Thus eq. 1 must be regarded as an approximation best describing the observations at low extent of reaction.<sup>13</sup>

Over the limited temperature range studied, linear Arrhenius plots of  $k_1$  and  $k_2$  were obtained. Least-square treatments yielded

$$k_1 (\text{l. mole}^{-1} \text{ min.}^{-1}) = 1.9 \times 10^{17} \exp(-51,600/RT) \quad (7)$$

$$\text{and } k_2 (\text{min.}^{-1}) = 5.2 \times 10^{12} \exp(-45,200/RT) \quad (8)$$

A detailed discussion of various plausible steps in the reaction mechanism and the question of the isotope effects is presented elsewhere.<sup>4</sup> However, no mechanism has been found which satisfactorily encompasses all the present experimental results, yielding the empirical rate equation (eq. 1). Speculation of mechanism therefore does not appear warranted at the present time.

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## Appendix I

**High Temperature Experiments.**—The thermal decomposition of methyl iodide alone and in the presence of toluene was investigated<sup>4</sup> using a high speed flow technique in the range  $475\text{--}575^\circ$  and 2–5% decomposition. From product analyses for experiments made over a fair range of initial conditions the stoichiometry for the pyrolysis of methyl iodide alone could be approximated by<sup>14</sup>  $CH_3I \rightarrow 0.64CH_4 + 0.072C_2H_6 + 0.22C + 0.50I_2$ . This may be compared to Horrex's<sup>15</sup> stoichiometry in the lower pressure region over the same temperature range:  $CH_3I \rightarrow 0.75CH_4 + 0.25C + 0.50I_2$ . From the present results it is seen that ethane production accounts for an appreciable fraction of the decomposed methyl iodide.

Addition of toluene in excess gave rise to a significant increase in the over-all rate of methane formation, as would be expected from the results of the static experiments at lower temperatures.

## Appendix II

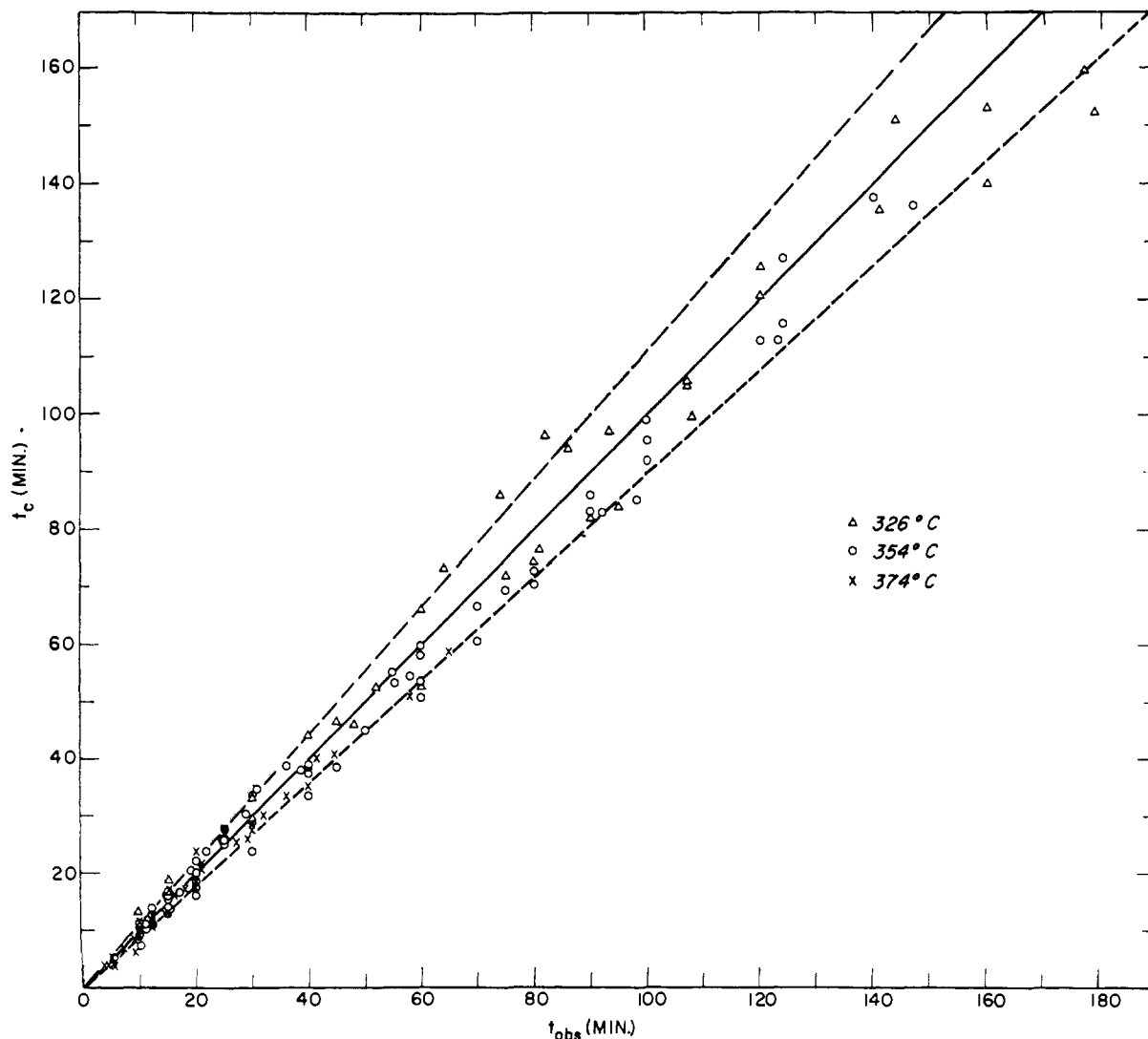
**$C^{12}C^{13}$  Isotope Effect.**—The isotope fractionation factor  $S$  is defined in the usual way:

$$S = \frac{[(C^{12}H_4)/(C^{13}H_4)]}{[(C^{12}H_3I)/(C^{13}H_3I)]_0}$$

(13) It must be pointed out that the empirical rate equation is necessarily incomplete, since it does not show explicitly the catalysis by added  $I_2$ . One difficulty, as mentioned in the introduction, is associated with the ability of  $I_2$  and/or I to react with T to form HI, which then reacts with M yielding  $CH_4$  and  $I_2$ .  $I_2$  is thus only a precursor to the real accelerator, HI.

(14) This result assumes that at these elevated temperatures all iodine atoms from the decomposed  $CH_3I$  appear as molecular iodine. The experimental results of Horrex<sup>3</sup> seem to confirm this postulate.

(15) C. Horrex, private communication, Nov. 5, 1957.

Fig. 5.—Calculated *vs.* observed time.

where the isotope ratio in the methane is that of the  $\text{CO}_2$  from its (quantitative) combustion and that in the original  $\text{CH}_3\text{I}$  is similarly obtained. A very small correction to zero extent of reaction was made using the simplified equation<sup>16</sup>  $S^0 - 1 = (S - 1)(1 + f/2)$ . The experimental uncertainty in  $S^0$  is less than  $\pm 0.001$  (95% confidence limit).

The data are presented in Table II. The slight negative trend with temperature is normal for all isotope effects. At a given temperature  $S^0$  showed no apparent dependence on  $T_0$ ; however, a slight dependence on  $M_0$  was observed<sup>4</sup> at  $326^\circ$ .

For comparison, the  $\text{C}^{12}/\text{C}^{13}$  isotope effect associated with the reaction of  $\text{HI}$  and  $\text{CH}_3\text{I}$  (in the absence of  $\text{C}_6\text{H}_5\text{CH}_3$ ) was measured; the average of four experiments at  $314^\circ$  was  $S^0 =$

TABLE II  
 $\text{C}^{12}/\text{C}^{13}$  ISOTOPE EFFECT

$T$ ( $^\circ\text{C}.$ )	$S^0_{\text{av}}$
326.0	1.0204
354.4	1.0185
374.4	1.0181

$1.026 \pm 0.001$ . The isotope effect in the pyrolysis of  $M$  alone under flow conditions was  $1.010 \pm 0.002$  at  $486^\circ$ .<sup>16</sup>

(16) H. Friedman, R. Bernstein and H. Gunning, *J. Chem. Phys.*, **23**, 109 (1955).