4.6.2. Yields of Methane.—Employing approximations similar to those already described it may be shown that

$$\frac{\Delta C_2H_4}{\Delta CH_2D_2} \simeq \frac{k_5}{k_{21}} \frac{(CH_2CO)}{(CD_4)} \qquad (11)$$

Values of $[\Delta C_2H_4 \times (CD_4)]/[\Delta CH_2D_2 \times (CH_2CO)]$, equal in each case to k_5/k_{21}, may be calculated directly from Table I; they are

Temp., °C.	k_5/k_{21}
27	5.99, 5.94, 5.92
99	4.56
200	3.61, 3.64, 3.46
298	2.88
412	2.11, 2.14, 2.30

The usual $1/T$ plot (omitting the 412° values) yields values for $E_5 - E_{21}$ and a_{21}/a_5 the same as those given in section 4.6.1.

Another interesting point relates to the relative yields of CH_2D_2 and CH_2CD_2. If we assume that significantly all CH_2D_2 is formed by reaction 21 even at the highest temperatures, it follows (employing the usual approximations) that

$$\frac{\Delta CH_2D_2}{\Delta CH_2CD_2} = \frac{2k_4 + k_5 + k_{12}}{k_5} \qquad (12)$$

Values for the right-hand term are derived from the data of Table I in section 4.6.1. Comparisons of the two sets of values give

	Left-hand term	Right-hand term
27°	1.18	1.18
99°	1.29	1.27
200°	1.49	1.53
298°	1.87	1.91
412°	2.30	2.55

Too much credence must not be given to the 412° values, (a) because too much ketene has decomposed, and (b) because other reactions for production of mixed methanes become increasingly important. Otherwise, the data reveal a high degree of internal consistency.

4.6.3. Excitation of Methylene.—In some previous work on ketene (*cf.* section 4.1), distinction has been made between methylene radicals produced in excited and unexcited condition. In the treatment of sections 4.6.2 and 4.6.3 rate constants for reactions involving CD_2 have been treated as being practically the same as those involving CH_2 with generally self-consistent results. Three different conclusions are admissible. Either we may write that in the steady-state $(CH_2)/(CH_2') = (CD_2)/(CD_2')$ or that $(CH_2') = (CD_2') = 0$ or that there are no perceptible differences in the rate constants for reactions involving CH_2, CH_2', CD_2 or CD_2'. If the latter view is accepted, there would appear to be no reason for hypothesizing the existence of excited methylene radicals in photolysis of ketene.

The view that in the steady-state $(CH_2)/(CH_2') = (CD_2)/(CD_2')$ entails some consideration of the nature of the excited radicals and the manner of the formation of CD_2'. The simplest concept is that CH_2' is triplet; for maintenance of equality of ratios it is required in reaction 21 not only that multiplicity be conserved (which would be normally expected) but also that the rate constants k_{21} and k_{21}' for the reactions of CH_2 and CH_2' be the same. Thus, once again whatever view we adopt we require that, if the excited radicals exist in this case, they behave the same as the unexcited.

Without specific evidence to the contrary, it appears most satisfactory to conclude that $(CH_2') = 0$ in the photolysis of ketene.

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NOTRE DAME, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Diffusion Kinetics: The Photolysis of Azo-bis-isobutyronitrile[1]

BY J.-C. ROY,[2] J. R. NASH, R. R. WILLIAMS, JR., AND W. H. HAMILL

RECEIVED AUGUST 5, 1955

The photolysis of 2,2'-azo-bis-isobutyronitrile in benzene solution with iodine as scavenger gives evidence of diffusion controlled combination of isobutyronitrile radicals. The thermal decomposition does not exhibit this effect.

It has been shown by Lewis and Matheson[3] that 2,2'-azo-bis-isobutyronitrile (AIBN) is an efficient photosensitizer and thermal initiator of free radical polymerization. The thermal decomposition gives a quantitative yield of nitrogen and a somewhat smaller yield of tetramethylsuccinonitrile.[3,4] The rate of decomposition is nearly the same in a variety of solvent types.[3,5,6] The rate of thermal decomposition, measured by nitrogen evolved, is unimolecular[3,5] and is uninfluenced by addition of tetrachloroquinone[3] or diphenylpicrylhydrazyl.[6] We also find no change in rate upon adding iodine, in the presence of which the iodoisobutyronitrile is known to form.[7] The efficiency of iodine as scavenger in this case is much less than unity[8] at *ca.* 10^{-3} mole/l.

After considering the facts available at the time this work was started it was anticipated that photolysis and/or thermal decomposition of AIBN in solution in the presence of appropriate concentrations of iodine as free radical scavenger might pro-

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[1] This work was supported in part under AEC contract At(11-1)-38 and Navy Department loan contract Nonr-06900.

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vide additional evidence of diffusion recombination.[9,10]

Experimental

Photochemical Measurements (J.-C.R.).—The light source was a Pyrex-jacketed, General Electric AH-6 high pressure mercury arc. From the measurements of Back and Sivertz[11] of the extinction coefficients of AIBN it appears that the total output of this lamp would be effective chiefly in the region 3300–3600 Å. The nitrogen evolved served as an internal actinometer.

Ten-ml. portions of 0.03 *M* AIBN in benzene with appropriate amounts of iodine were deaerated and sealed in a 50-ml. Pyrex cell. A jet of air directed at the cell kept its temperature near 35°. An upright 2 mm. capillary, 30 cm. long was an integral part of the reaction vessel. To measure the amount of nitrogen produced the cell was thermostated and slowly rotated. The nitrogen in the capillary was trapped by the solution above it, the capillary preventing the bubble at the lower tip of the gage from rising. The pressure P of nitrogen in the cell can be determined from the volumes V and v of the capillary and of the compressed bubble, and from the length h of the column of liquid of density d. Then

$$P = h'dv(V - v)^{-1}$$

where h' is the observed value corrected for capillary rise.

Thermal Decomposition (J.R.N.).—Rates of thermal decomposition at 80° of 0.1 *M* AIBN in chlorobenzene, with and without added iodine, were followed manometrically. The reaction vessel was cooled intermittently to 0° to facilitate the pressure measurements.

The measurements of efficiency of the reaction between iodine and the free radicals resulting from decomposition were measured in toluene solutions. Duplicate samples, 0.02 *M* in AIBN and with different amounts of iodine were heated at 80° for 45 min. The reaction vessels, provided with magnetic stirrers, were brought to −92° and the gas collected, through breakoff seals, with a Saunders–Taylor apparatus. Gas samples were occasionally subjected to mass spectrometric analysis (Consolidated 21-103A) and found to consist of nearly pure nitrogen.

Chemical Analysis.—Solutions of reaction products from each of the procedures just described were analyzed by a common method. The reaction mixture was rapidly extracted with dilute aqueous sodium sulfite and washed with water. An excess of sodium biphenyl was added to the organic layer and the acidulated aqueous extract titrated potentiometrically with standard silver nitrate by methods previously described.[12]

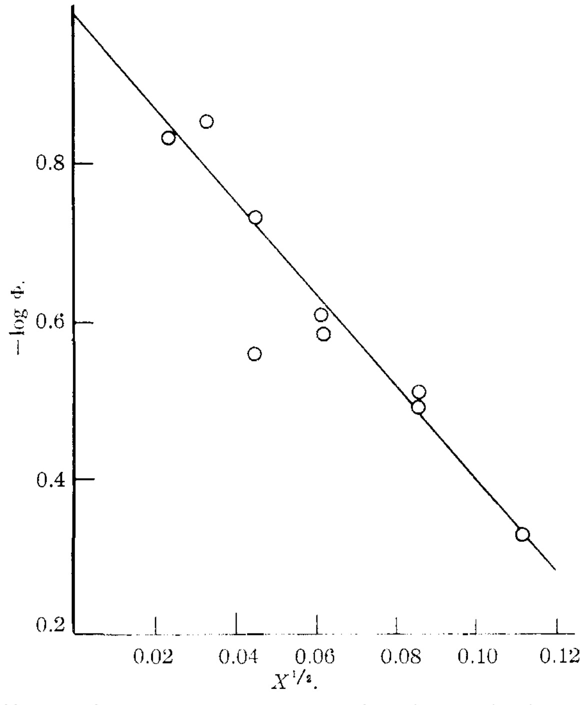

Fig. 1.—The quantum efficiency for the production of organic iodide as a function of mole fraction X of iodine.

Results

We find for the thermal decomposition that log (AIBN) *vs.* time at 80° is quite linear both in the absence of iodine and also with 0.10 *M* iodine present. The rate constants are 1.50×10^{-4} and 1.55×10^{-4} sec.$^{-1}$, respectively. These results agree with those of Lewis and Matheson[8] who found a rate constant equal to 1.53×10^{-4} at 80°.

The efficiency ϵ of all reactions producing organic iodides, which would be measured by our analytical method, is defined by $\epsilon = 0.5\ (RI/N_2)$. Measured efficiencies are reported in Table I and are comparable to values ranging from 0.4–0.7 at 62° in other solvents[8] at much lower concentrations of iodine.

Table I

Efficiency of Iodine as Scavenger in AIBN Decomposition in Toluene at 80°

Iodine, moles/l.	0.151	0.0807	0.0371	0.0218
AIBN, moles/l.	.0200	.0199	.0201	.0199
Efficiency, av.	.58	.64	.58	.59

The efficiency of the photoreaction is defined as in the thermal decomposition and the quantum yield for one-half the organic iodide produced presumably corresponds to $\Phi = \epsilon$. Figure 1 summarizes all photolytic measurements in benzene solution at 35°. It is to be noted that the efficiency of formation of organic iodides from free radicals produced by photolysis is definitely a function of the iodine concentration. No such dependence was found for the thermal decomposition.

Discussion

Let us suppose that the photodecomposition of AIBN obeys the following mechanism where brackets enclose particles subject to diffusion encounters

$$\mathrm{R{-}N{=}N{-}R} = [\mathrm{R}\cdot + \mathrm{N_2} + \mathrm{R}\cdot] \qquad (1)$$

$$[\mathrm{R}\cdot + \mathrm{R}\cdot] = \mathrm{R}\cdot + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{I_2} = \mathrm{RI} + \mathrm{I}\cdot \qquad (3)$$

$$[\mathrm{R}\cdot + \mathrm{R}\cdot] = \mathrm{R} - \mathrm{R} \qquad (4)$$

$$[\mathrm{R}\cdot + \mathrm{R}\cdot] + \mathrm{I_2} = [\mathrm{RI} + \mathrm{R}\cdot + \mathrm{I}\cdot] \qquad (5)$$

We have previously considered analogous diffusion-controlled processes[9,10] and Noyes[13] has treated diffusion kinetics in detail. The present situation differs in one respect from others previously considered because, if the primary process yields a pair of radicals with an intervening molecule of nitrogen, primary recombination (or true "cage effect") should be impossible. Step (2) will always be succeeded by (3) when even a very small concentration of an efficient scavenger is present. Step (4) will not be affected by small concentrations of

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even quite efficient scavengers. It is commonly, though erroneously, assumed that even appreciable concentrations of scavenger cannot intervene in the "cage effect." This present work is consistent with our previous observations[9,10] that iodine at moderate concentrations intervenes in step (5) to react with free radicals still capable of "geminate recombination"[13] (step 4)).

Employing methods previously described[9,10] let the probability of non-recombination be identified with one-half the yield of organic iodide (steps (3) plus (5)). Then

$$\log \Phi = 0.31 P_1 P_2^{1/2} \gamma^{-2} X^{1/2} - 0.17 P_1 \gamma^{-1} \rho_0^{-1}$$

where P_1 and P_2 are probabilities of reaction upon encounter for steps (4), (5); γ and ρ_0 are relative mean free path and initial separation of radicals R· in units of collision diameters. From the diffusion equation and Fig. 1 we find $P_1\gamma^{-1}\rho_0^{-1} = 6$ and $P_1 \cdot P_2^{1/2}\gamma^{-2} = 19$. For the ratio $P_2^{1/2}\gamma^{-1}\rho_0 = 3$. No great error can arise from taking $P_2 = 0.25$, for which the initial separation R . . . . R is six mean free paths. If the initial process for photodecomposition is that postulated in step (1), then the mean free path for diffusion is rather small but is consistent with our previous work.[9,10] It is also consistent with very recent considerations of Noyes.[14]

Since it appears from the photochemical measurements that steps (4) and (5) compete effectively it follows that absence of similar diffusion effects for thermal decomposition of AIBN (Table I) indicates different primary products for the two modes of decomposition. Whatever free radicals are produced by thermal decomposition, they appear to be incapable of recombination upon one or two encounters. There appear to be two mechanisms for thermal decomposition, one of which corresponds to the constant ratio $RI/N_2 = 2$, whose relative contributions do not vary up to appreciable iodine concentrations. The second mechanism, applying to 40% of the reaction under our experimental conditions but somewhat dependent upon the solvent,[8] produces nitrogen but apparently produces no free radicals. It has been proposed that this mechanism consists of rearrangement to tetramethylsuccinodinitrile with elimination of nitrogen.[8]

Other recent work[15] demonstrates that thermal decomposition of AIBN at 80° in toluene produces an unstable intermediate amounting to about one-third of the whole reaction and eventually yielding tetramethylsuccinodinitrile. Under the same conditions but with added iodine we find an efficiency of 60% which indicates that free radicals are not involved in the formation of the intermediate or in its decomposition as postulated.[15]

Acknowledgment.—We are indebted to Professor R. M. Noyes for the opportunity to read an unpublished manuscript.

NOTRE DAME, INDIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate Measurements on Fast Reactions in the Stirred Flow Reactor; the Alkaline Hydrolysis of Methyl and Ethyl Formate[1]

BY HARRIE M. HUMPHREYS AND LOUIS P. HAMMETT

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The stirred flow reactor technique for measuring reaction rates in solution gains considerably in convenience and in generality of application without losing in precision when one of the reactants is injected into the reactor as a pure liquid or as a concentrated solution by a hypodermic syringe driven by a screw rotating at constant speed. The technique is found to be applicable to reactions with half times as short as 0.6 sec. Measurements by this method on the alkaline hydrolysis of ethyl formate in 85% ethanol and of methyl formate in water show that compared with acetate the several hundred-fold higher rate of reaction of the formate is essentially the result of a more positive entropy of activation, the enthalpies of activation for acetate and formate differing by unimportant amounts. This result, taken with available data on the acid-catalyzed esterification and on the ionization of acetic and formic acids appears to justify the generalization that the conversion of an electrically neutral acetic acid derivative to an electrically charged entity involves a considerably greater decrease in entropy than does the analogous process in the case of a formic acid derivative.

Thanks to the excellent work of H. A. Smith and his students[2] precise data are available on the temperature coefficients of the alkaline hydrolysis rates of a wide range of ethyl esters in 85% ethanol. But this list does not include the outstandingly important case of the formate ester, presumably because of the inconveniently high rate of reaction. Leimu, *et al.*,[3] have obtained data on several formates in water solution by a highly refined adaptation of the usual batch technique and find that the 200-fold difference in reaction rate between methyl formate and methyl acetate results almost exactly from a difference in entropy of activation, the activation energies being identical within experimental error. If their results are essentially correct, the matter is of very considerable theoretical interest, but the danger of systematic error in measurements of this sort on a reaction with a half-time measured in seconds is so large that a verification by a different technique is clearly desirable. It

[1] Based on a dissertation submitted by Harrie M. Humphreys in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The work was carried out as project NR 056-062, under contract N6-onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

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