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Kinetics of the Thermal and Photochemical Exchange between Benzyl Iodide and Iodine

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The exchange between benzyl iodide and iodine has been studied both thermally and photochemically in hexachlorobutadiene-1,3. The reaction proceeds by a radical chain mechanism initiated by dissociation of both species and involving alternately benzyl radicals and iodine atoms. A direct substitution by iodine atoms may also occur. All seven of the rate constants for the individual steps have been estimated at 36°. The data help to establish the benzyl–iodine bond strength. Oxygen inhibits the reaction by reacting reversibly with benzyl radicals, but it does not appear to affect iodine atoms. These results support previous proposals that the molecular and atomic exchange reactions of allyl iodide involve direct interaction with the double bond. They also suggest that allylperoxy radicals may react with other radicals by substitution reactions leading to stable products.

Introduction

Various organic iodine compounds undergo isotopic exchange with the element in non-polar solvents, and the mechanisms frequently involve iodine atoms and other radical species. Diiodoethylene[2] and allyl iodide[3] are the only compounds for which atomic exchange mechanisms have been studied in detail; both react by direct substitutions that apparently involve reversible interaction of an iodine atom with the π-electrons of a carbon–carbon double bond.

Benzyl iodide does not offer any obvious mechanism for atomic exchange following interaction with a π-electron system, but it does contain a very weak carbon–iodine bond which might break easily under attack by a radical. In this paper, we show that benzyl radicals are indeed intermediates in this exchange.

Experimental

Materials.—The high boiling (210–220°) solvent used in all experiments was hexachlorobutadiene-1,3 purchased from the Hooker Electrochemical Company and used without further purification. It apparently contained impurities capable of reacting with about 2.5×10^{-6} mole/liter of iodine but seemed inert after this reaction was completed. The amount of impurity was determined by illuminating solutions of iodine and measuring both the decrease in light absorption and the organically bound radioactivity obtained from solutions containing iodine-131.

The benzyl iodide was prepared in almost quantitative yield from benzyl alcohol and concentrated hydriodic acid by the method of Norris.[4] The crude material was washed with sodium sulfite solution and dried over magnesium sulfate. It was then distilled over silver wire in the dark under reduced pressure of nitrogen. The middle fraction, boiling 57–59.5° under 0.5–0.6 mm., was immediately made up to 0.30 *M* in solvent and stored in the dark in a refrigerator. The purified benzyl iodide had a faintly yellow color and crystallized and melted sharply at 24.0°. Refractive index of the liquid (not reported previously) was $n^{25.0}\text{D}$ 1.6334. Molar refraction calculated for $C_6H_5CH_2I$ is 44.0; found is 45.0.[5] A sample was hydrolyzed by alkali and the liberated iodide was titrated with silver nitrate with eosin as an adsorption indicator.[6] Percentage of iodine calculated is 58.2; found was 58.1. The solutions remained colorless during the period of this work.

trans-Diiodoethylene was prepared from acetylene and iodine and purified by recrystallization from alcohol.[2]

Resublimed reagent grade iodine was used without further purification. Solutions were activated with aqueous carrier-free solutions of iodine-131 obtained on allocation from the United States Atomic Energy Commission. No systematic differences in rate were observed whether these wet solutions were dried with magnesium sulfate, filtered through paper to remove water present as a second phase, or merely used without further treatment. Apparently water does not affect this exchange reaction.

Procedure for Thermal Experiments.—The molar ratio of iodine to benzyl iodide was varied from 1/4000 to 200/1. Unless the concentrations were approximately equal, most

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[1] Based on the Ph.D. Dissertation of Moshe Gazith. The more complete account and microfilms thereof are available from the Library of Columbia University.

[2] R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

[3] D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 763 (1953).

[4] J. F. Norris, *Am. Chem. J.*, **38**, 638 (1907).

[5] Data from A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Philadelphia, Pa., 1948, p. 898.

[6] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Edition, The Macmillan Co., New York, N. Y., 1943, pp. 571–572.

of the initial radioactivity was necessarily present in the species in smaller concentration. Solutions containing activity in the iodine were prepared by pipetting together solutions of activated iodine and inactive benzyl iodide. The other solutions were prepared by driving the exchange to completion in a degassed solution containing benzyl iodide and dilute iodine of high specific activity. The resulting stock solution was mixed with concentrated solutions of inactive iodine to prepare runs. When the concentrations of both reactants were comparable, the exchange rates agreed regardless of the initial distribution of radioactivity.

Some of the runs were made in glass-capped ampules in the presence of air. The other runs were degassed by cooling to Dry Ice temperatures, evacuating with a mercury diffusion pump, warming the solution to room temperature, and repeating the operation three to five times. The frozen ampule was then sealed off and warmed to room temperature. Photochemical exchange was avoided by performing all operations by the light of a ruby dark room lamp. During sealing, the contents of the ampule were shielded as much as possible from the light emitted. Blank experiments indicated that this preparatory procedure induced a little exchange in the lowest concentrations of iodine, but this could be corrected for.

The prepared ampules were heated in an oil thermostat regulated to ±0.05°, and checked against a Bureau of Standards thermometer. Times of heating ranged from 150 seconds to about 4 days. In the fastest runs, the uncertainty in zero time was eliminated by heating three or four identical ampules for different times, and calculating the rate from the time dependence of the amount of exchange.

At the end of a run, the ampule was chilled and opened. The iodine was extracted with aqueous sulfite, and the separated layers were washed and counted with a liquid jacketed Geiger counter. The mechanical error in the separation was shown to be less than 1 per cent. Standard equations were used for each run to calculate R, the rate of the net process

$$BI + I_2^* \longrightarrow BI^* + II^* \qquad (1)$$

where BI designates benzyl iodide.

In some runs, the concentration of iodine before and after a run was compared by measurements with a Beckman spectrophotometer. No significant changes were observed.

Procedure for Photochemical Experiments.—The optical cells were 1.9 cm. long and 3.2 cm. in diameter. Since cells containing liquid could not stand the strains associated with degassing and opening, each was fitted with a cylindrical ampule attached to the side arm. The solution was frozen in this ampule during the degassing procedure and was tipped back into the ampule before the seal was broken at the end of a run.

The degassed cell was mounted in a water thermostat at 25 or 36° and was illuminated with the 5461 Å. green line isolated with filters from a mercury AH4 arc. The absolute intensity of the lamp was measured with a calibrated thermopile–galvanometer system, and a photo tube was used for monitoring. The intensity incident on the solution was 1.17×10^{14} quanta/cm.^{2} sec. The system is described in more detail elsewhere.[1,7]

After a run, the iodine was extracted and the distribution of radioactivity was measured as in the thermal runs. Identical runs were thermostated at the same temperature as the illuminated runs, and the photochemical exchange was calculated by subtracting the small amount of parallel thermal exchange.

Any change in iodine concentration during a run was measured with a Beckman spectrophotometer before the cell was opened.

Thermal Results

Runs in Degassed Solutions.—The results of runs in carefully degassed solutions are presented in Tables I to IV. The data at each temperature cover a range of about 10^6 in the ratio of iodine to benzyl iodide concentrations. The runs at lower temperatures show more sensitivity to extraneous influences, but the rate of exchange is clearly first order in benzyl iodide and half order in iodine. The probable error of the mean rate constant is given at the bottom of each table.

TABLE I

THERMAL EXCHANGE OF IODINE AND BENZYL IODIDE AT 90°

$10^5[I_2]$, mole/l.	$10^5[BI]$, mole/l.	$[I_2]/[BI]$, Q	10^9R, mole/l. sec.	$\frac{10^4R}{[BI][I_2]^{1/2}}$
5.00	15000	0.000333	541	5.10
5.15	7500	.000682	286	5.31
47.2	15000	.00314	1710	5.25
49.5	7500	.00660	975	5.83
47.0	3750	.0125	466	5.72
125	3750	.0333	712	5.36
125	1875	.0667	375	5.65
50.0	469	.107	65.6	6.25
500	3750	.133	1270	4.78
125	937.5	.133	178	5.37
50.0	234	.213	30.5	5.81
500	1875	.267	658	5.03
125	469	.267	93.6	5.65
500	469	1.07	178	5.37
101	93.75	1.09	16.3	5.47
51.0	46.9	1.09	6.52	6.15
51.0	23.4	2.18	3.08	5.81
100	23.4	4.30	3.70	4.98
501	46.9	10.7	16.5	4.96
501	46.9	10.7	16.1	4.85
501	23.4	21.4	8.31	5.00
2500	93.75	26.6	76.7	5.17
1250	23.4	53.3	13.3	5.10
5000	46.9	107	60.0	5.72
5000	23.4	213	28.8	5.48
			Av.	5.41 ± 0.05

TABLE II

THERMAL EXCHANGE OF IODINE AND BENZYL IODIDE AT 80°

$10^5[I_2]$, mole/l.	$10^5[BI]$, mole/l.	$[I_2]/[BI]$, Q	10^9R, mole/l. sec.	$\frac{10^4R}{[BI][I_2]^{1/2}}$
3.36	15000	0.000224	165	1.90
46.2	15000	.00308	842	2.60
100	15000	.00667	834	1.76
125	3750	.0333	274	2.06
125	1875	.0667	135	2.03
50.0	469	.107	23.8	2.27
500	3750	.133	484	1.82
500	1875	.267	233	1.76
125	469	.267	29.2	1.76
500	469	1.07	77.5	2.34
500	469	1.07	57.1	1.72
500	469	1.07	57.1	1.72
51.0	46.9	1.09	2.73	2.58
101	93.75	1.09	6.18	2.08
51.0	23.4	2.18	1.20	2.25
50.5	11.7	4.30	0.705	2.68
501	46.9	10.7	5.97	1.80
625	46.9	13.3	6.28	1.68
500	23.4	21.3	3.66	2.20
1250	46.9	26.6	9.16	1.75
500	11.7	42.6	1.45	1.74
1250	23.4	53.3	4.48	1.71
1250	11.7	107	2.53	1.93
5000	46.9	107	20.1	1.92
5000	23.4	213	9.83	1.87
			Av.	2.00 ± 0.04

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(7) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

TABLE III

THERMAL EXCHANGE OF IODINE AND BENZYL IODIDE AT 70°

$10^5[I_2]$, mole/l.	$10^5[BI]$, mole/l.	$[I_2]/[BI]$, Q	10^9R, mole/l. sec.	$\frac{10^4R}{[BI][I_2]^{1/2}}$
50.0	15000	0.00333	130.0	0.388
125	3750	.0333	54.0	.407
125	1875	.0667	28.6	.430
50.0	469	.107	7.74	.739
50.0	469	.107	5.40	.515
500	3750	.133	159.0	.600
125	937.5	.133	19.8	.597
50.0	234	.213	4.63	.883
500	1875	.267	74.2	.559
125	469	.267	10.8	.651
625	1875	.333	89.3	.601
625	937.5	.667	42.6	.575
500	469	1.07	19.6	.592
100	93.75	1.09	2.80	.935
51.0	46.9	1.09	0.775	.731
100	46.9	2.18	.915	.617
500	46.9	10.7	2.02	.609
500	23.4	21.4	1.05	.621
500	23.4	21.4	1.07	.641
1250	23.4	53.3	1.62	.616
5000	46.9	107	7.49	.714
			Av.	0.620 ± 0.020

TABLE IV

THERMAL EXCHANGE OF IODINE AND BENZYL IODIDE AT 60°

$10^5[I_2]$, mole/l.	$10^5[BI]$, mole/l.	$[I_2]/[BI]$, Q	10^9R, mole/l. sec.	$\frac{10^4R}{[BI][I_2]^{1/2}}$
50.0	15000	0.00333	86.9	0.259
100	15000	.00667	121.0	.255
125	3750	.0333	22.0	.166
125	1875	.0667	11.2	.169
50.0	469	.107	2.80	.267
500	1875	.267	26.4	.198
500	469	1.07	6.19	.181
51.0	46.9	1.09	0.233	.220
100	23.4	4.30	.179	.241
500	46.9	10.7	.594	.179
500	23.4	21.4	.329	.193
1250	23.4	53.3	.470	.179
5000	46.9	107	3.02	.288
			Av.	0.215 ± 0.008

The temperature dependence of the rate can be fitted by an equation of the form

$$N = R/[BI][I_2]^{1/2} = 10^{12.42 \pm 0.15}\, e^{-(26{,}060 \pm 240)/RT} \quad (1./\text{mole})^{1/2}\ \text{sec.}^{-1} \qquad (2)$$

Effect of Oxygen.—The solutions were very sensitive to traces of oxygen. The sensitivity was greater at lower temperatures and especially at low ratios of iodine to benzyl iodide. Figure 1 shows a number of runs at 80° both in the presence of air at atmospheric pressure and with different extents of degassing. The runs in presence of air obey the kinetic expression $R = k[BI]^{1/2}[I_2]$ in contrast to the $R = N[BI][I_2]^{1/2}$ observed in degassed systems. As $[I_2]/[BI]$ varies from 0.000333 to 2.0, the factor of inhibition by air drops from 250 to 3. The inhibition should vanish when iodine is in about 10-fold excess, and for greater excesses of iodine the rate in air should be the same as when degassed. This last conclusion was not tested experimentally.

The data strongly suggest that oxygen inhibits by reacting with benzyl radicals but not with iodine atoms. The detailed mechanistic implications are discussed below.

Photochemical Results

Exchange of Benzyl Iodide.—Several runs were made at 25 and 36° in degassed solutions illuminated with 5461 Å. light. Extinction coefficients, defined by $E_i = (1/c_il)\log(I_0/I)$, were measured by a Beckman spectrophotometer as $E_{I_2} = 738 \pm 3$ and $E_{BI} = 0.110$ liter/mole cm. In all of the solutions, at least 80% of the light absorbed was absorbed by iodine and there was no evidence that light absorbed by benzyl iodide contributed to the exchange reaction.

Because iodine absorbed so strongly at this wave length, and because very dilute solutions were more sensitive to impurities, the concentrations were limited between 9×10^{-5} and 2.5×10^{-4} M. The benzyl iodide concentration was varied between 2.3×10^{-4} and 0.150 M.

Because a significant fraction of the incident light was absorbed in the cell, the rate of absorption by iodine was not directly proportional to $[I_2]$. The intensity of the beam at a distance L from the face is given by

$$I = I_0 e^{-(\alpha_{I_2}[I_2] + \alpha_{BI}[BI])L} \qquad (3)$$

where $\alpha_i = 2.303\ E_i$. Integration over a cell of length l gives

$$q_{I_2} = I_0\alpha_{I_2}[I_2]f \qquad (4)$$

where q_{I_2} is the rate per unit volume of absorption by iodine and

$$f = \frac{1 - e^{-(\alpha_{I_2}[I_2] + \alpha_{BI}[BI])l}}{(\alpha_{I_2}[I_2] + \alpha_{BI}[BI])l} \qquad (5)$$

In these experiments, $q_{I_2} = 3.30 \times 10^{-4}[I_2]f$ einstein liter^{-1} sec.$^{-1}$.

If chains were terminated only by recombination of iodine atoms, $R/[BI][I_2]^{1/2}f^{1/2}$ should be constant. Although a function of this type was constant in the thermal experiments, Fig. 2 shows that it varies considerably in the range studied in the photochemical experiments.

Exchange of Diiodoethylene.—*trans*-Diiodoethylene, $C_2H_2I_2$, was exchanged with iodine under the same conditions. Let $[DI] = 2[C_2H_2I_2]$ be the concentration of organically bound iodine. E_{DI} was negligibly small at this wave length, so the appropriate expression for f was somewhat simpler than equation 5. The data are also shown in Fig. 2 and exhibit the constancy of $R/[DI][I_2]^{1/2}f^{1/2}$ to be expected for a chain reaction in which almost all radical species are iodine atoms. Although this function does decrease about 15% if $[I_2]/[DI]$ is reduced to[8] 1×10^{-4}, the effect is much smaller than that exhibited by benzyl iodide in Fig. 2.

Decomposition of Benzyl Iodide.—If a significant fraction of chains are terminated by reaction between the two benzyl radicals, the mechanism discussed below indicates that additional iodine should be produced. The concentration of iodine did not change during thermal experiments or dur-

[8] R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

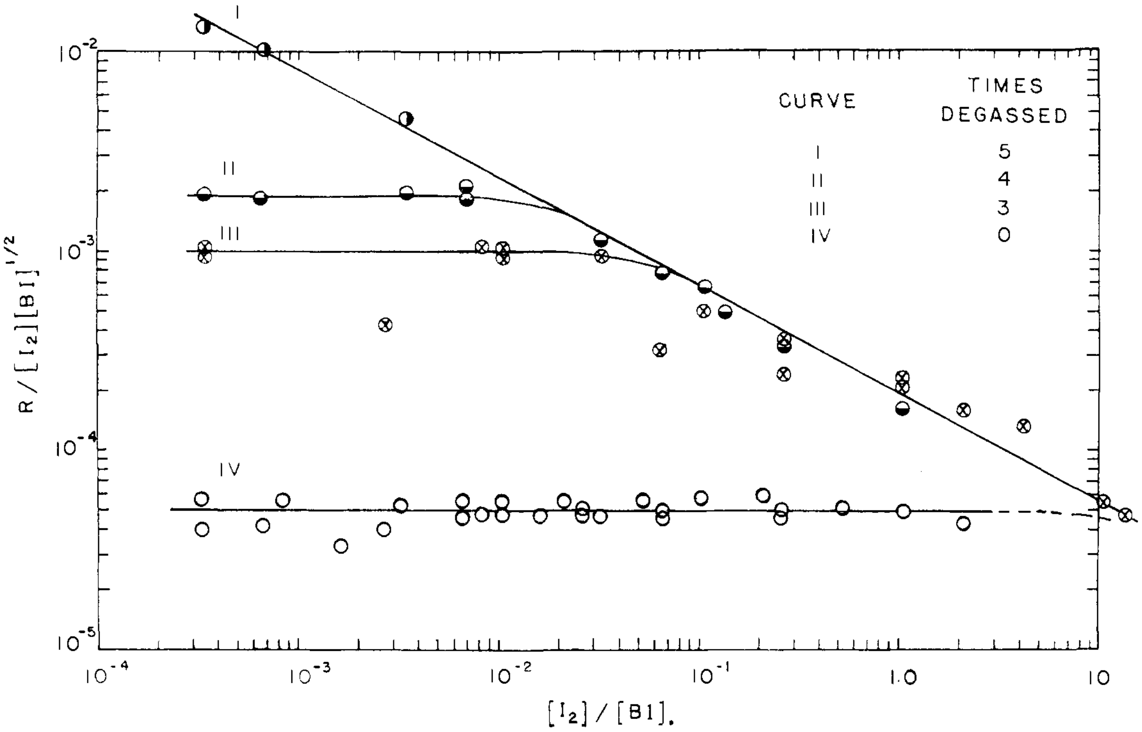

Fig. 1.—Effect of degassing on kinetics of exchange at 80° between benzyl iodide and iodine.

ing photochemical experiments containing initial iodine of 10^{-4} *M* or higher. In a photochemical experiment containing 0.15 *M* benzyl iodide but no iodine initially, iodine was produced at a constant rate of 2.66×10^{-10} mole/liter sec. At 2.6×10^{-5} *M* iodine (the highest concentration reached in this experiment), the calculated rate of exchange is 170 times the observed rate of formation of iodine.

Some rough experiments with unfiltered sunlight indicated that benzyl iodide decomposed rapidly at first but that the concentration of iodine reached a limiting value. This limiting concentration was much greater in a solution containing air than it was in a degassed solution.

Discussion

Thermal Mechanism in Degassed Solutions.—The data can be fitted by the following chain mechanism

Initiation:

$$BI \longrightarrow B + I \qquad (S1)$$
$$I_2 \longrightarrow 2I \qquad (S2)$$

Propagation:

$$I + BI \longrightarrow B + I_2 \qquad (S3)$$
$$B + I_2 \longrightarrow I + BI \qquad (S4)$$

Termination:

$$I + I \longrightarrow I_2 \qquad (S5)$$
$$B + I \longrightarrow BI \qquad (S6)$$
$$B + B \longrightarrow B_2 \qquad (S7)$$

The two initiation steps are needed to explain the kinetics in the presence of air and to account for the fact that $R/[BI][I_2]^{1/2}$ is independent of $[I_2]/[BI]$ in thermal experiments but varies greatly in photochemical experiments. Step (S7) is needed to explain the photochemical decomposition of benzyl iodide.

Since the rate of production of radicals equals the rate of destruction

$$k_1[BI] + k_2[I_2] = k_5[I]^2 + k_6[B][I] + k_7[B]^2 \qquad (6)$$

Since subsequent data indicate that the chain length is long, step (S6) contributes negligibly to the exchange and the rates of the two propagation steps are equal. Then

$$R = k_3[BI][I] = k_4[B][I_2] \qquad (7)$$

Algebraic combination of equations 6 and 7 gives

$$R = \frac{k_3\sqrt{\frac{k_2}{k_5}}\,[BI][I_2]^{1/2}\sqrt{1 + \frac{k_1[BI]}{k_2[I_2]}}}{\sqrt{1 + \frac{k_6k_3[BI]}{k_5k_4[I_2]} + \frac{k_7k_3^2[BI]^2}{k_5k_4^2[I_2]^2}}} \qquad (8)$$

Equation 8 appears to involve four independent parameters. The number can be reduced to three by an argument based on microscopic reversibility. If a system contained iodine, benzyl iodide and bibenzyl all in thermodynamic equilibrium, we could write

$$k_1[BI] = k_6[B][I] \qquad (9)$$
$$k_2[I_2] = k_5[I]^2 \qquad (10)$$

Combination with equation 7 gives

$$\frac{[B][I_2]}{[BI][I]} = \frac{k_1k_5}{k_2k_6} = \frac{k_3}{k_4} \qquad (11)$$

Although the first equality in equation 11 holds only in the equilibrium system, the second equality involving only rate constants must hold in all systems regardless of the concentration of bibenzyl.

The rate can then be defined in terms of three parameters

$$M = k_4\sqrt{k_1/k_7} \qquad (12)$$
$$N = k_3\sqrt{k_2/k_5} \qquad (13)$$
$$\phi = k_6/2\sqrt{k_5k_7} \qquad (14)$$

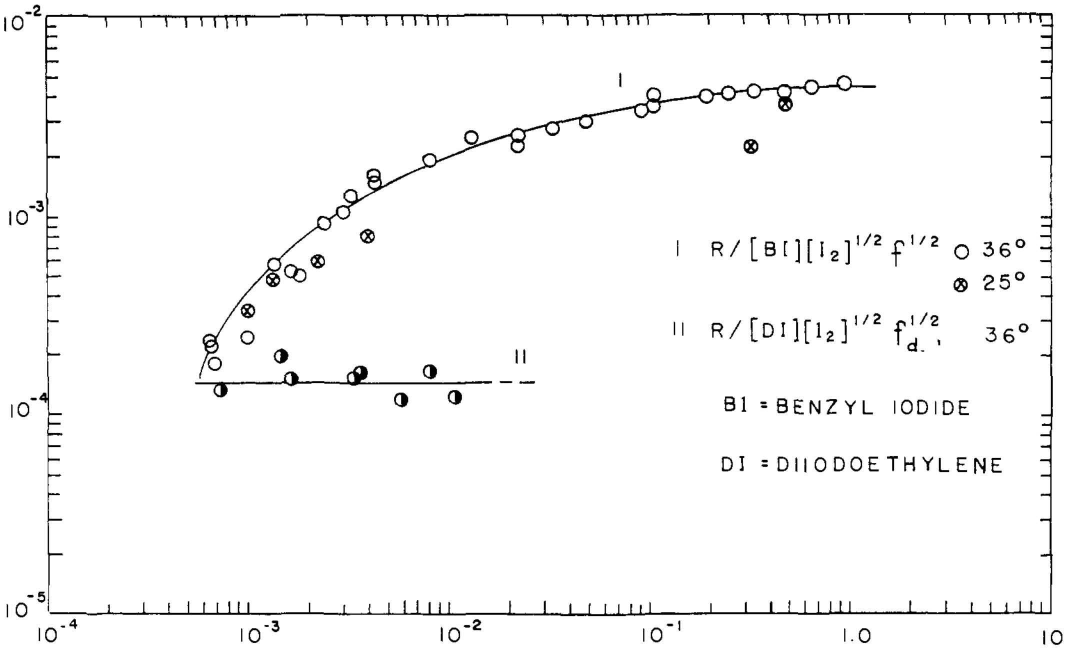

Fig. 2.—Photochemical exchange of benzyl iodide and diiodoethylene with iodine.

Here, M and N are limiting rate constants for exchange in sufficient excesses of benzyl iodide and iodine, respectively, and ϕ is a conventional parameter describing relative tendencies of termination reactions.[9] If we make the additional abbreviation

$$Q = [I_2]/[BI] \qquad (15)$$

equation 8 can be rearranged to

$$\frac{R}{[BI][I_2]^{1/2}} = \frac{N\sqrt{1 + 4\phi^2N^2/M^2Q}}{\sqrt{1 + 4\phi^2N^2/M^2Q + 4\phi^2N^4/M^4Q^2}} \qquad (16)$$

Since the terms in $1/Q$ in numerator and denominator are identical, the kinetics will obey the simple form of equation 2 until $4\phi^2N^4/M^4Q^2$ becomes significant compared to unity; as we shall see later, this requires a large excess of benzyl iodide over iodine.

Kinetics in Photochemical Runs.—In the photochemical experiments, steps (S1) and (S2) are omitted, and chains are initiated by the process

$$I_2 + h\nu \longrightarrow 2I \qquad (S2')$$

The rate of this process is $q_{\mathrm{I}2}\phi_{\mathrm{I}2}$, where $\phi_{\mathrm{I}2}$ (not to be confused with ϕ) is the quantum efficiency for producing atom pairs that escape their original partners and are able to start chains. A treatment identical with the thermal case gives

$$\frac{R}{[BI][I_2]^{1/2}f^{1/2}} = \frac{N_p}{\sqrt{1 + 2\phi N_p/M_pQ + N_p^2/M_p^2Q^2}} \qquad (17)$$

where

$$M_p = k_4(\phi_{I_2}\alpha_{I_2}I_0/k_7)^{1/2} \qquad (18)$$

$$N_p = k_3(\phi_{I_2}\alpha_{I_2}I_0/k_5)^{1/2} \qquad (19)$$

For computational purposes, equation 17 can be rewritten

$$\frac{[BI]^2[I_2]f}{R^2} = \frac{1}{N_p^2} + \frac{2\phi}{M_pN_pQ} + \frac{1}{M_p^2Q^2} \qquad (20)$$

Evaluation of Individual Rate Constants.—The proposed mechanisms involves seven individual steps. The four parameters N, M_p, N_p and ϕ are independently measurable and involve the rate constants. Equation 11 provides another independent relationship. The data on diiodoethylene exchange permit another parameter to be estimated, and one additional assumption is sufficient for the calculation of all seven rate constants. The results of such calculations at 36° are presented in Table V. The bases of the numerical values used are as follows.

TABLE V

INDIVIDUAL RATE CONSTANTS AT 36° FOR THE EXCHANGE BETWEEN IODINE AND BENZYL IODIDE

k_1	6.0×10^{-14} sec.$^{-1}$	k_5	7.0×10^9 l./mole sec.
k_2	1.4×10^{-12} sec.$^{-1}$	k_6	1.4×10^{10} l./mole sec.
k_3	7.1×10^4 l./mole sec.	k_7	1.6×10^9 l./mole sec.
k_4	3.3×10^6 l./mole sec.		

The photochemical parameters were $\alpha_{I_2} = 1700$ liter/mole cm., $I_0 = 1.94 \times 10^{-7}$ einstein/1000 cm.^{2} sec., and $\phi_{I_2} = 0.09$.

The value of N from equation 2 was 1.0×10^{-6} (l./mole)$^{1/2}$ sec.$^{-1}$.

Twenty-six photochemical runs were made at values of $[I_2]/[BI]$ ranging from 0.000665 to 0.972. The results were fitted to quadratic equation 20 by least squares, weighting the points on the basis of constant percentage uncertainty in R. The calculations gave $M_p = 0.368 \pm 0.016$, $N_p = 0.00414 \pm 0.00026$, $\phi = 1.01 \pm 0.24$, where the probable errors are based on the deviations of the experimental

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[9] Some British authors, including L. Bateman and H. W. Melville, omit the factor 2 in the definition. Their values of ϕ are identical with those computed by our method, but termination rate constants are defined differently. Rate constants in this paper are defined by dividing the *rate of the reaction as written* by the concentrations of reactants raised to appropriate powers. The convention used here is the same as in P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 200.

points from the curve. Observed values of R showed a standard deviation of 16.8% and a maximum deviation of 40.8% from calculated values, but the deviations were not random. The non-randomness clearly arose because rates in large excesses of benzyl iodide were more erratic and tended to be less than expected from the other points. This behavior is consistent with the extreme sensitivity of these solutions to oxygen and other impurities. The "best" values selected for these parameters were $M_p = 0.45$ (l./mole)$^{1/2}$ sec.$^{-1}$, $N_p = 0.0046$ (l./mole)$^{1/2}$ sec.$^{-1}$, $\phi = 2.1$.

If R_d is the rate of photochemical exchange of *trans*-diiodoethylene

$$\frac{R_d}{[\mathrm{DI}][\mathrm{I}_2]^{1/2}f^{1/2}} = N_d = k_{3d}(\phi_{\mathrm{I}_2}\alpha_{\mathrm{I}_2}I_0/k_5)^{1/2} \qquad (21)$$

where k_{3d} is half the rate constant for

$$\mathrm{C_2H_2I_2 + I^* \longrightarrow C_2H_2II^* + I} \qquad \text{(S3d)}$$

The data shown in Fig. 2 indicate $N_d = (1.43 \pm 0.05) \times 10^{-4}$. From the previously determined rate constant[8] at 25° and activation energy,[2] $k_{3d} = 2.2 \times 10^3$ l./mole sec. in hexane at 36°. If it is assumed that k_{3d} has the same value in hexachlorobutadiene, substitution into equation 21 yields $k_5 = 7.0 \times 10^9$ l./mole sec.

The final assumption is

$$k_6 = 2k_5 \qquad (22)$$

Critique.—The calculations for Table V involve three assumptions in addition to the validity of the proposed mechanism. The first assumption is that $\phi_{\mathrm{I}_2} = 0.09$. Lampe and Noyes[10] showed that the value is 0.15 for this solvent and temperature when the wave length is 4358 Å., and Zimmerman and Noyes[7] showed that $\phi_{5780}/\phi_{4358} = 0.62$ in hexane at 25°. The value of 0.09 is based on the assumption that the wave length dependence of quantum yield is the same in hexachlorobutadiene. The assumption could be checked by measuring quantum yield as a function of wave length for any chain reaction involving iodine atoms, but the value used here can hardly be badly off.

The second assumption, which permits the estimation of k_5, is that the rate of exchange of iodine atoms and diiodoethylene is the same in hexane and in hexachlorobutadiene. This assumption is probably reliable for an activation-controlled radical reaction in non-polar solvents. The value of k_5 calculated from this assumption is certainly consistent with values reported[10,11] for k_5 at 25° of 1-2 × 10^{10} in hexane and of 7-9 × 10^9 in carbon tetrachloride. Measurements now in progress will provide a direct measure of k_5 under these conditions. If the assumed value of k_5 is in error by some factor, the other termination rate constants (k_6 and k_7) will be in error by the same factor, and the propagation rate constants (k_3 and k_4) will be in error by the square root of that factor.

The third assumption, that $k_6 = 2k_5$, is equivalent to assuming that an iodine atom and benzyl radical behave toward each other as two iodine atoms do. The value of ϕ near unity means that $k_6/2$ is near the geometric mean of k_5 and k_7, and we would expect all of these reactions to take place with high efficiency during an encounter. The need for this assumption could be eliminated by lifetime measurements with intermittent light in solutions containing such an excess of benzyl iodide that most of the chains were terminated by step (S7). These measurements would be very difficult. If k_6 in Table V is in error by some factor, k_4 is in error by the same factor and k_7 is in error by the square of that factor; the other rate constants are unaffected.

The ratio $k_2/k_5 = 2.0 \times 10^{-22}$ mole/liter. If our interpretation is correct, this ratio is the equilibrium constant for the dissociation of molecular iodine. The gas phase equilibrium constant at 36° calculated from spectroscopic data is 2.5×10^{-22}. This close agreement between the equilibrium constant in gas phase and solution has also been observed in hexane[7] and supports our choice of k_5.

The ratio $k_1/k_2 = 0.043$ is $e^{-\Delta\Delta F^{\ddagger}/RT}$ where $\Delta\Delta F^{\ddagger}$ is the difference in free energies of activation for the two initiation reactions. Since the entropy requirements are probably very similar for these two dissociations, the result indicates that the C–I bond strength in benzyl iodide is about 1.9 kcal./mole more than in iodine and hence is about 37.4 kcal./mole. This value is in satisfactory agreement with several values from pyrolysis,[12] thermochemistry[13] and electron impact,[14] but is distinctly below a recent thermochemical value.[15]

The decomposition experiments with no iodine initially present presumably involved the step

$$\mathrm{BI} + h\nu \longrightarrow \mathrm{B + I} \qquad \text{(S1}')$$

followed by (S3) and (S7). Since no other steps occur significantly, one molecule of I_2 is produced for each occurrence of (S1′). The decomposition rate of 2.66×10^{-10} mole/liter sec. should be $\phi_{\mathrm{BI}}\alpha_{\mathrm{BI}}[\mathrm{BI}]I_0 = 7.4 \times 10^{-9}\ \phi_{\mathrm{BI}}$ and $\phi_{\mathrm{BI}} = 0.036$. The quantum yield is 0.052 for the dissociation of allyl iodide with 4358 Å. light in the same solvent and temperature.[10] Since allyl and benzyl iodides have nearly the same bond strengths, the quantum yields should be nearly equal under the same conditions. If they are indeed equal, the effect of wave length on quantum yield is about that used in estimating ϕ_{I_2} above.

We believe the data demonstrate that at least much of the exchange goes by the benzyl radical mechanism described. The data do not rule out the possibility that some of the exchange involves a direct substitution step.

$$\mathrm{BI + I^* \longrightarrow BI^* + I} \qquad \text{(S3s)}$$

If k_{3s} is the rate constant for this step, the value of k_3 reported in Table V is really $k_3 + k_{3s}$ and the value of k_4 is really $k_4(1 + k_{3s}/k_3)$. We hope the contribution (if any) of the step (S3s) can be estimated by experiments now being undertaken. If oxygen does not completely inhibit the photochemical exchange, the limiting quantum yield at infinite oxygen concentration should be independent of

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(15) W. S. Graham, R. J. Nichol and A. R. Ubbelohde, *J. Chem. Soc.*, 115 (1955).

the concentrations of other species and should permit an estimation of k_{3s}/k_3.

The thermal data indicate that $R/[BI][I_2]^{1/2}$ is independent of concentration for $[I_2]/[BI]$ as low as 0.00022. At 36°, we predict $M/N = 20.2$. However, $R/[BI][I_2]^{1/2}$ should fall off significantly at our lowest $[I_2]/[BI]$ unless M/N is about 80 or more. If M/N is this large at 36°, our value of M_p would have to be low by a factor of 16. We do not see how the photochemical experiments at 36° could be inhibited this much when thermal experiments at 60–90° show no inhibition in spite of a much longer chain length. An alternative explanation is that M/N increases with temperature (or ϕ decreases with temperature) enough to avoid a falling off in the range of our thermal experiments. We would expect the temperature coefficients would be small and that M/N would, if anything, decrease with increasing temperature. Although we cannot resolve the discrepancy, we do not believe it invalidates the major features of our mechanism.

Effect of Oxygen.—Air inhibits the reaction, and the effect is greatest in a large excess of benzyl iodide. The data can be explained by the following additional steps

$$B + O_2 \longrightarrow BO_2 \qquad (S8)$$

$$BO_2 \longrightarrow B + O_2 \qquad (S9)$$

$$BO_2 + I \longrightarrow \text{stable products} \qquad (S10)$$

$$BO_2 + B \longrightarrow \text{stable products} \qquad (S11)$$

$$BO_2 + BO_2 \longrightarrow \text{stable products} \qquad (S12)$$

If B and BO_2 can be regarded as in equilibrium (step (S9) equal in rate to (S8) and much more probable than the sum of steps (S10–S12)), and if equation 6 is modified to include the additional termination reactions, we can obtain

$$R = \frac{k_4\sqrt{\frac{k_1}{k_7}}\,[I_2][BI]^{1/2}\sqrt{1 + \frac{k_2[I_2]}{k_1[BI]}}}{\sqrt{1 + \frac{k_{11}k_8[O_2]}{k_7k_9} + \frac{k_{12}k_8{}^2[O_2]^2}{k_7k_9{}^2} + \left(\frac{k_6}{k_7} + \frac{k_{10}k_8[O_2]}{k_7k_9}\right)\frac{k_4[I_2]}{k_3[BI]} + \frac{k_5k_4{}^2[I_2]^2}{k_7k_3{}^2[BI]^2}}} \qquad (23)$$

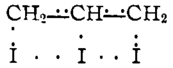
Even if equation 11 and the thermal parameters are introduced, this expression is too complex for detailed kinetic analysis. If k_{10} and k_{11} are of comparable magnitude, the data of Fig. 1 can be fitted if in air at 80° $k_8[O_2]/k_9 = 1.2(k_6/k_{10})\ (M^2/N^2)$. The degassed runs require that M^2/N^2 is of the order of 10^4 or greater, and the photochemical data at lower temperatures suggest that it is not much greater. Although k_{10} may be of the same magnitude as k_6, it can hardly be greater than 10^{10} liter/mole sec. Then $k_8[O_2]/k_9$ is at least 10^4 but may not be much greater.

The fit of the data requires that k_{10}/k_{12} cannot be much less than M^2/N^2 and hence is at least about 10^4. This means that step (S12) is very inefficient compared to most reactions between radicals.

Comparison with Diiodoethylene Exchange.—In this study, $N = 10^{12.42}e^{-26{,}100/RT}$ (l./mole)$^{1/2}$ sec.$^{-1}$. *trans*-Diiodoethylene shows the same thermal exchange kinetics, and the rate constant per iodine in the same units in decalin[2] is $10^{10.56}\cdot e^{-25{,}400/RT}$. The energies of activation are about the same, and the benzyl iodide exchange is about thirty times as fast as the other because of an entropy effect. This difference in entropy of activation is consistent with our interpretation that the benzyl iodide involves a loose transition state in which an iodine atom is pulled off, while the diiodoethylene involves a more crowded transition state in which an iodine atom adds to the double bond.

Comparison with Allyl Iodide Reactions.—Benzyl and allyl compounds usually have very similar bond strengths, and the resulting radicals seem to be stabilized about equally by resonance. Also, nucleophilic substitution reactions of benzyl and allyl compounds usually go at very similar rates, indicating that steric requirements are comparable and probably not severe. However, the iodine exchange reactions exhibit fundamentally different kinetics.

Allyl iodide exchanges with iodine thermally[16] between 0 and 40° by a mechanism involving *molecular* iodine. Benzyl iodide exchanges at a convenient rate between 60 and 90°, but the kinetics can be explained entirely by iodine *atom* initiation. The difference in behavior supports our previously unsubstantiated proposal that the allyl iodide reaction involves an interaction with the double bond (which is not available in benzyl iodide). The transition state might look like



$$\overset{\displaystyle CH_2\cdots CH\cdots CH_2}{\dot{I}\cdot\cdot I\cdot\cdot\dot{I}}$$

where we have no way of determining whether there is interaction between the middle carbon and iodine atoms.

Allyl iodide also exchanges readily with iodine atoms,[3] and the rate constant in hexane at 25° was estimated at 5 × 10^6 liter/mole sec. If we extrapolate the benzyl iodide data in hexachlorobutadiene to 25°, we find $k_3 = 4.0 \times 10^4$. Since allyl iodide is so much more susceptible to attack by iodine atoms, the double bond is probably involved in the transition state. The data support our previous proposal of $I\,..\,CH_2CHCH_2\,..\,I$.

The photochemical kinetics[3] also indicated that an iodine atom could remove the iodine from allyl iodide with formation of an allyl radical, and the interpretation was supported by the rate of formation of new iodine.[10] We proposed a rate constant of 3.3 × 10^3 l./mole sec. for this reaction. If allyl and benzyl iodides have equal bond strengths, the rate constants should be about equal for carbon radical formation, but we see that k_3 for benzyl iodide is about ten times the rate constant interpreted as allyl radical formation. The difference suggests that the benzyl iodide exchange studied here may contain a considerable contribution from direct substitution (step S3s). We hope to resolve this point by photochemical studies of the oxygen effect.

The kinetics in air also suggest some interesting differences between allyl and benzyl peroxy radicals. The allyl radical at 25° in illuminated systems[3] apparently reacted irreversibly with oxygen. The benzyl radical at 80° in the dark apparently reacted reversibly, and we needed to include the

[16] D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 761 (1953).

decomposition reaction (S9). The difference may be due solely to the fact that the allylperoxy radicals were formed at lower temperatures in the presence of a higher total concentration of radicals. The difference may also be associated with the reactivities of the peroxy radicals themselves. Although the conclusions were not certain, the allyl iodide exchange data indicated that allyl and allylperoxy radicals and iodine atoms all reacted with each other with comparable rate constants of the order of 10^{10} l./mole sec. The reactions of benzyl radicals and iodine atoms follow the same pattern. We have no information about the rate constants for reactions (S10) and (S11) of benzylperoxy radicals, but the data do suggest that reaction (S12) is slow for a radical–radical reaction. Here again, the incipient double bond in an allylperoxy radical permits radical reactions of a type not available to benzylperoxy. Examples might be

$$I\cdot + CH_2CHCH_2OO\cdot \longrightarrow ICH_2CH{=}CH_2 + O_2$$

$$2CH_2CHCH_2OO\cdot \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + 2O_2$$

or

$$CH_2{=}CHCH_2OOCH_2CH{=}CH_2 + O_2$$

The evidence for these radical–radical displacement reactions is still very tenuous.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Radical-sensitized Decomposition of Formaldehyde[1]

BY JAMES E. LONGFIELD[2] AND W. D. WALTERS

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The decomposition of formaldehyde has been sensitized by the addition of small percentages of ethylene oxide at 384–437°; the main products are hydrogen and carbon monoxide. The kinetics of the decomposition of formaldehyde sensitized by ethylene oxide have been investigated. Packing the vessel decreases the rate, and addition of an inert gas increases the rate. The mechanism of the decomposition is discussed. Mercury dimethyl at 381° and biacetyl at 477–489° also sensitize the decomposition.

The thermal decomposition of pure formaldehyde has been studied by Fletcher[3] in the region 510–607° at 30–400 mm. Fletcher observed that the principal primary reaction yields hydrogen and carbon monoxide and has an order of about two. A reaction which produces methanol and carbon monoxide was suggested also, but no direct evidence for the presence of methanol was given. The photolysis of formaldehyde has been studied by a number of investigators and it has been established that at temperatures above 160° and with light of 3130 Å. a chain reaction takes place with the formation of hydrogen and carbon monoxide as the chief products.[4]

Formaldehyde is formed as an intermediate in the thermal decomposition of dimethyl ether,[5] as well as other decompositions, which involve free radical processes. However, several investigators[6] have reached different conclusions regarding the possibility that free radicals promote a chain decomposition of the intermediate formaldehyde. The reaction of methyl radicals with formaldehyde at 310° has been studied by Kodama and Takezaki[7] who used the thermal decomposition of azomethane as a source of free radicals. The present work has been concerned mainly with the effect of radicals upon the decomposition of formaldehyde at 380–490° which is a temperature region not far below that used for the various thermal decompositions yielding formaldehyde as an intermediate.

Experimental

The formaldehyde, the ethylene oxide and the reaction system were the same as those reported earlier.[8] Nitrogen (99.99%) was purchased from the Linde Air Products Co. Carbon monoxide from the Matheson Co. was purified by passage through a trap at −78° or −196° (at reduced pressure). Hydrogen (Ohio, 99.5%) was passed through a Baker Deoxo purifier to remove oxygen. Carbon dioxide (Ohio, 99%) was repeatedly condensed at −196° and evacuated to 10^{-4} mm. to remove non-condensable gases.

Surface effects were studied in a bulb packed with small Pyrex tubes which provided a surface to volume ratio 35 times as great as the unpacked vessel. All parts of the vacuum system in contact with formaldehyde were heated electrically to about 90° to prevent its polymerization. Before introduction into the reaction vessel a mixture of formaldehyde and sensitizer was allowed to stand in a spherical bulb at 90° for at least 30 minutes to ensure complete mixing.

Mass spectrometric analyses[9] showed that the non-condensable gases formed in the sensitized decomposition consisted principally of hydrogen and carbon monoxide along with traces of methane. Consequently the gas mixture was analyzed by oxidizing the hydrogen and carbon monoxide over hot copper oxide and absorbing the carbon dioxide on moist potassium hydroxide pellets. The methane was determined by difference. Analyses of known mixtures agreed (±0.5%) with the compositions of the mixtures as prepared.

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[1] For two thirds of the period of this study financial support was received from the Office of Naval Research.

[2] E. I. du Pont de Nemours and Company Fellow, 1950–1951.

[3] C. J. M. Fletcher, *Proc. Roy. Soc.* (*London*), **A146**, 357 (1934). Other results have been reported by R. Klein, M. D. Sheer and L. J. Schoen, Abstracts, A.C.S. Meeting, Cincinnati, Ohio, Mar. 29–Apr. 7, 1955, p. 27Q.

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[8] J. E. Longfield and W. D. Walters, THIS JOURNAL, **77**, 810 (1955).

[9] Performed by Dr. F. L. Mohler and the staff of the National Bureau of Standards.