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Bromination of Hydrocarbons. VI. Photochemical and Thermal Bromination of Toluene. Bond Dissociation Energies

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Let
$$a=6\alpha+1$$
, $b=4\alpha+1$, $c=2\alpha+1$, $d=1$. We obtain

$$\langle n^{4\alpha+1} \rangle^3 \leq \langle n \rangle \langle n^{6\alpha+1} \rangle^2, \tag{1}$$

$$\langle n^{2\alpha+1} \rangle^3 \leq \langle n \rangle^2 \langle n^{6\alpha+1} \rangle, \tag{2}$$

$$\langle n^{2\alpha+1} \rangle^2 \leq \langle n \rangle \langle n^{4\alpha+1} \rangle. \tag{3}$$

$$\langle n^{4\alpha+1} \rangle^2 \leq \langle n^{2\alpha+1} \rangle \langle n^{6\alpha+1} \rangle. \tag{4}$$

Equations (3) and (4) are also special cases of Schwarz's inequality. If we take the product of (1) and (2), we obtain

$$\langle n^{4\alpha+1} \rangle \langle n^{2\alpha+1} \rangle \leq \langle n \rangle \langle n^{6\alpha+1} \rangle.$$
 (5)

If in $\langle n^b \rangle^{a-c} \leq \langle n^c \rangle^{a-b} \langle n^a \rangle^{b-c}$ we let c=0, we obtain

$$\langle n^b \rangle^a \leq \langle n^a \rangle^b$$
 (6a)

$$\langle n^b \rangle^{1/b} \leq \langle n^a \rangle^{1/a}.$$
 (6b)

Similarly

or

 $\langle n^c \rangle^a \leq \langle n^a \rangle^c$.

Multiplying this by (6a) and letting a=b+c, we obtain

$$\langle n^a \rangle \ge \langle n^b \rangle \langle n^c \rangle. \tag{7}$$

Note added in proof.-Benoit⁹ has shown that for Gaussian coils the ratio of the asymptotic slope of a $P^{-1}(\theta)$ plot to the initial slope is smaller the greater the polydispersity. An analogous

⁹ H. Benoit, J. Polymer Sci. (to be published).

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relation holds for rods. From this, and the greater initial downward curvature in polydisperse systems, he was led to the conjecture that polydisperse curves should lie under the monodisperse curve under very broad conditions.

The nature of these conditions may be found as follows: the function $nf(n)/\langle n \rangle$ has the properties of a normalized distribution function. Without loss in generality this function may be expressed in terms of l^2 as a variable, l being the characteristic dimension of the molecule. This new function, $h(l^2)$, has the property that $\langle l^2 \rangle$, defined as $\int l^2 h(l^2) d(l^2)$, is the average dimension obtained from the initial slope of a $P^{-1}(\theta)$ plot. Expressing $P(\theta)$ also as a function of l^2 , we obtain for polydisperse systems $P_z = \int P(l^2)h(l^2)d(l^2)$. The scattering function for the monodisperse system having the same initial slope is $P(\langle l^2 \rangle)$.

The necessary and sufficient condition for the inequality $P(\langle l^2 \rangle) \leq P_z$ is that $P(l^2)$ be a convex function of l^2 .¹⁰ From the Debye expression for $P(\theta)$ as a power series, we see that all scattering functions are initially convex. How long they remain convex has to be determined in each case; the rod and Gaussian coil functions are convex everywhere, proving the inequality $P(\langle l^2 \rangle) \leq P_z$ for all polydisperse systems (the equality sign holding only for $\theta = 0$). In other words, in a $P^{-1}(\theta)$ plot, the polydisperse curve must always lie below the monodisperse curve for rods and coils.

For molecules such as spheres, whose scattering functions are not convex everywhere, the inequality holds for any distribution in which the largest molecule present is not so large that $P(l^2)$ has ceased to be convex.

¹⁰ Hardy, Littlewood, and Polya, Inequalities (Cambridge University Press, Cambridge, 1934), Theorem 86.

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Bromination of Hydrocarbons. VI. Photochemical and Thermal Bromination of Toluene. **Bond Dissociation Energies***

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(Received March 9, 1953)

With the aid of a high temperature, high vacuum, corrosionresistant valve and photometers operating with high sensitivity at low light intensities, it has been possible to study the homogeneous gas-phase kinetics of the photochemical and thermal bromination of toluene. Infrared analyses indicated that the reaction is predominantly a side-chain substitution, the products being benzyl bromide and hydrogen bromide. The photochemical reaction, studied in the temperature range 82° to 132°C, was strongly inhibited by hydrogen bromide. The thermal reaction was studied in the absence of added hydrogen bromide at 166°C. Except for the step involving the dissociation of bromine molecules, both the photochemical and thermal mechanisms involve the same type of atom and radical chain, as found previously for the bromination of simple alkanes. The corrected activation

INTRODUCTION

PREVIOUS studies of the kinetics of the gas phase bromination of aliphatic hydrocarbons have provided information about the carbon-hydrogen and carbon-carbon bond dissociation energies in these and

* In part from the thesis submitted by Herbert R. Anderson, Jr., for the Ph.D. degree at Cornell University, February, 1953. † U. S. Rubber Company Fellow, 1951–1952.

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energy of the over-all reaction, as determined from the temperature coefficient of the photochemical reaction, was found to be 7.2 kcal/mole. This value was assigned to the rate determining step Br+RH=R+HBr. From the temperature dependence of the hydrogen bromide inhibition, the activation energy for the reverse of this step was assigned the value 5.0 kcal/mole permitting the C-H bond dissociation energy in the alkyl side chain of toluene to be estimated as 89.5 kcal/mole at room temperature. The discrepancy between this value and Szwarc's value of 77.5 kcal/mole from pyrolysis studies has been pointed out. The efficiency of toluene as a third body in the homogeneous recombination of bromine atoms, and also problems relating to steric effects in atom and radical reactions have been discussed.

related compounds.¹⁻⁴ It was of interest to consider the effect of the substitution of an aromatic nucleus on the bond dissociation energy in methane, thereby requiring

¹G. B. Kistiakowsky and E. R. VanArtsdalen, J. Chem. Phys. 12, 469 (1944).

² H. C. Andersen and E. R. VanArtsdalen, J. Chem. Phys. 12, 479 (1944).

³ E. I. Hormats and E. R. VanArtsdalen, J. Chem. Phys. 19, 778 (1951).

⁴ E. R. VanArtsdalen, J. Chem. Phys. 10, 653 (1942).

a kinetic study of the bromination of toluene. A preliminary report⁵ indicated that the kinetics of this reaction were similar to those found for aliphatic compounds. Also, as might be expected, and as borne out by the results here, the bromination of toluene in the gas phase is a radical reaction involving the alkyl side chain with no attack on the aromatic nucleus.

During the course of this investigation, considerable work by Szwarc has appeared in which bond dissociation energies were determined from pyrolysis studies involving a toluene carrier gas technique.⁶ It thus becomes of considerable interest to compare the bond dissociation energies obtained from pyrolysis experiments with those obtained from bromination kinetics.

MATERIALS

In the purification of materials, cognizance was taken of the fact that reactions of this type are extremely sensitive to traces of oxygen and water. All purification operations were carried out in grease-free, high vacuum systems. The toluene used in this investigation was Bureau of Standards sample 211a-8S which had been purified by fractional distillation from petroleum, outgassed under high vacuum, and supplied in ampoules with breakseals. Freezing point measurements made by the Bureau of Standards indicated that the mole percent of impurities was 0.04 ± 0.02 . After sealing these ampoules to the high vacuum reaction system, the pressure of noncondensable gases was found to be less than 10⁻⁶ mm of mercury ("stick" vacuum on a Mac-Leod gauge). The contents of several ampoules were combined by distillation under high vacuum.

Analytical reagent grade bromine was allowed to stand in vacuum over reagent grade potassium bromide for several weeks to remove traces of chlorine, after which it was distilled in a grease-free high vacuum system through a large tube of phosphorus pentoxide. Several trap-to-trap distillations under conditions of a "stick" vacuum were carried out, followed by fractional distillation, the middle fraction being sealed off in ampoules behind breakseals.

FIG. 1. High temperature, high vacuum, corrosion-resistant valve.



⁵ Swegler, Scheraga, and VanArtsdalen, J. Chem. Phys. 19, 135 (1951). ⁶ M. Szwarc, J. Chem. Phys. 16, 128 (1948), and later papers.



FIG. 2. Thermostatted reaction vessel and related portion of high vacuum system.

Tanked hydrogen bromide (Matheson Company) of a stated purity of 99.5 percent was passed over copper turnings to remove bromine, over phosphorus pentoxide to remove water, then outgassed (stick vacuum) by trap-to-trap distillation under high vacuum, and finally stored as a gas at slightly under 1 atmos pressure in a 1-liter flask behind a breakseal.

Tanked oxygen (Air Reduction Company) of a stated purity of 99.5 percent was introduced into the reaction vessel in several runs to obtain qualitative information about oxygen inhibition.

EXPERIMENTAL

It will be demonstrated below that the gas phase bromination of toluene (herein designated as RH) is a side chain substitution with the production of benzyl bromide (RBr) and hydrogen bromide. Since the products of the reaction are known, the course of the reaction could be studied by observation of the rate of disappearance of bromine. However, the method used in previous investigations of this type¹⁻³ was not easily applicable to this problem since toluene, unlike the hydrocarbons previously studied, is much higher boiling. Because of this property, consideration had to be given to the problem of avoiding condensation of toluene in the reaction system. This was accomplished by thermostatting the leads and stopcocks of the high vacuum system at a temperature slightly in excess of the normal boiling point of toluene.

Ordinary stopcocks are not suitable at the temperature used here (115°C). Accordingly, the high temperature, high vacuum, corrosion-resistant valve illustrated in Fig. 1 was designed. The glass insert A consists of an envelope, a central capillary tube, and two capillary sidearms. The envelope was constructed from a section of Pyrex pipe which has a conical end designed to withstand large axial stresses. The upper end of the central capillary tube and the rim of the glass envelope



FIG. 3 (a). Photometer circuit used for photochemical runs. C₁, C₂—4 μ f; R₁, R₁₅—50k Ω ; R₂—25k Ω ; R₃—25 Ω ; R₄—2 Ω ; R₅—540k Ω ; R₆—150k Ω ; R₇—20k Ω ; R₈—100k Ω ; R₉, R₁₀—37 meg Ω ; R₁₁, R₁₂—240k Ω ; R₁₃—15 Ω ; R₁₄—250k Ω .



FIG. 3 (b). Typical curve for the rate of disappearance of bromine.

were ground flat so that both surfaces were in the same plane. The rim features a centrally located concentric recess enabling a vacuum-tight seal to be made with the aid of a gasket, C. The lower end of the central capillary tube was ground flat and parallel to the rim of the glass envelope. The glass insert fits into a brass housing and is cushioned from the metal by means of an asbestos insert, B. A ring-type gasket C is placed on the rim of the glass envelope. A thin diaphragm D fits on top of the gasket. Both the gasket and the diaphragm were made from Kel-F, kindly supplied to us by Dr. W. E. Hanford of the M. W. Kellogg Company, New York, New York. The whole assembly is held in place by a brass cover-piece E which is secured to the brass housing by set-screws. The cover-piece features an air-lock F and standard fitting G which can be readily connected to copper tubing. When the assembly has been made vacuum-tight, the set-screw H is adjusted with very slight manual pressure to provide support for the central glass capillary.

In operation, the diaphragm D is forced against the central glass capillary to close the valve by admitting air up to a pressure of one atmos in the air-lock. The valve is opened by evacuating the air-lock. This valve, which was found to be very satisfactory, may be operated in a high vacuum system over a range of temperatures and with a variety of corrosive materials, both liquid and gaseous.

The reaction vessel was made from a 35-mm length of 45-mm i.d. Pyrex tubing whose ends were sealed with parallel, planar windows (Fisher and Porter Company, Hatboro, Pennsylvania). The inlet tube on the cylindrical wall was of 1-mm i.d. capillary tubing to minimize dead space in the 60-cc absorption cell.

A quartz-spiral manometer, attached to the absorption cell by means of a 1-mm i.d. capillary tube, was used as a null instrument against a mercury manometer to measure the gas pressure. In order to prevent condensation of toluene and benzyl bromide in the essential parts of the reaction system (enclosed by the dashed lines in Fig. 2), the high temperature valves a and b, the vaporizing chamber V, and the quartz-spiral manometer Q were maintained at high temperature. The reaction cell R, was also maintained at elevated temperatures by means of an air thermostat ($\pm 0.1^{\circ}$ C). Temperatures were measured with a 3-junction copper-constant thermocouple.

The reactants were stored at low temperature $(-78^{\circ}C)$ behind stopcocks on a high vacuum line leading to the reaction system at H in Fig. 2. These stopcocks were lubricated with perfluorolube oil FCX-334 (we are indebted to Dr. S. W. McCune, III, of the du Pont Company, Wilmington, Delaware for giving us this material).

In filling the reaction cell, bromine was introduced first and its pressure determined by means of the photometer described below. Valve b (Fig. 2) was then closed, and the excess bromine in the high-vacuum line was pumped out. With the aid of a pycnometer attached to the high vacuum line, and a liquid nitrogen bath around the cold finger C, a roughly measured quantity of toluene was distilled into the vaporizing chamber V. Valve a was then closed, the liquid nitrogen bath removed from C, and the cold finger brought to temperature equilibrium with the rest of the reaction system. The vaporized toluene was then introduced into the reaction cell by virtue of the pressure differential existing between V and R when valve b was opened. The total pressure was measured with the quartz-spiral manometer and the toluene pressure was obtained by subtraction of the bromine pressure. In runs involving inhibition studies by HBr, this gas was introduced in a similar manner just before the toluene.

The same light source was used for photoactivation and also for photometric determination of the bromine pressure. The source was a 1000-watt projection lamp, used in conjunction with a suitable optical system to obtain parallel and uniform illumination over the face of the reaction cell, a water filter and a Farrand interference filter being used to obtain light with a peak wavelength of 4890A and half-band width of about 150A. Bromine is the only substance in the reaction mixture which absorbs in this region; it dissociates in the continuum to give one normal and one excited



FIG. 4. Infrared spectra of bromotoluenes.

atom.⁷ The lamp was operated below its rated capacity, and the light intensity was maintained constant by adjustment of the lamp voltage using an *independent* photronic-cell circuit for monitoring purposes. The photronic cell was activated by a by-pass portion of the high light intensity available close to the lamp.

The temperature range in which the photochemical reaction could be studied had to be high enough to volatilize enough toluene but low enough to avoid any thermal bromination. These requirements essentially fixed the allowable temperature range for the photochemical reaction between 80° and 135° C. In order to obtain a conveniently measurable rate of bromination at these temperatures, the light intensity had to be very low so that the usual photronic cell circuits were not sufficiently sensitive. In the photochemical studies, bromine absorption was measured by means of 929 photoelectric cells (with suitable response in the blue region) used in the circuit shown in Fig. 3(a). We are indebted to Mr. Leonard Walker of the Newman Laboratory for Nuclear Studies for the design of this circuit.

⁷ W. A. Noyes, Jr., and P. A. Leighton, *Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), p. 133.



FIG. 5. Infrared spectra of benzyl bromide and reaction products.

The circuit, consisting essentially of a power supply, an amplifier, and a sensitive galvanometer (Leeds and Northrup 2500a, type R, sens. 0.2 $\mu v/mm$) is relatively insensitive to line voltage fluctuations because of a combination of a stabilizer on the ac input (not shown), the 5651 voltage-regulating tubes, and the circuit symmetry; also, it is capable of a high degree of precision and rapid response. The signal from the two 929 photocells controlled the grids of the 6SU-7 twin triode tube. Any difference in potential existing between the two cathodes of the 6SU-7 gave rise to a flow of current through the galvanometer. One of the 929 tubes was in a path directly behind the reaction cell to detect changes in bromine absorption; the other was in a path illuminated independently by the same lamp and served as a compensating tube. Electromagnetically activated shutters were available to cut off either path from the photolamp.

In operation, the galvanometer was removed from the circuit and its zero point determined. It was then reinserted in the circuit and, with no light falling on the 929 tubes, it was reset to this zero point by adjusting the plate potentiometers R_7 and R_8 . With the circuit thus balanced, the shutters were opened so that light might fall on both photocells (with no reactants in the absorption cell). The zero point was again matched by adjusting the light falling on the compensating photocell by means of an iris diaphragm. Then the shutter for the measuring photocell was closed, and full-scale deflection of the galvanometer (50 cm) was attained by adjusting R_{14} and R_{15} . The circuit was then ready for measuring the concentration of bromine subsequently placed in the absorption cell.

Reactants were introduced into the absorption cell and the shutter opened to start the reaction. As the latter proceeded, the decrease in bromine concentration caused the galvanometer reading to approach that obtained for the zero point of the galvanometer. The photronic cell monitoring circuit indicated that the light intensity remained constant within 0.2 percent over the period required for a run, usually not more than $\frac{1}{2}$ hr. The galvanometer readings were calibrated against known pressures of bromine in the absorption cell, the pressures having been measured by the quartzspiral manometer. An exceptionally high degree of precision was achieved using this photometer and circuit as shown by a typical rate curve in Fig. 3b. Particularly noteworthy was the ease with which closely spaced measurements could be made by recording time with a Signal Corps Tape Recorder (BC-1016, Waters

Conley Company, Rochester, Minnesota). This operation merely required one to depress a telegraph key as the galvanometer passed closely spaced, predetermined intervals. In this way a very large number of points was obtained during the critical, initial stages of bromination.

In the thermal runs at a higher temperature (166°C) the light intensity had to be reduced to such a low value to eliminate photochemical reaction that this circuit was no longer sufficiently sensitive without considerable modification. The modifications were not made, however, because of the availability of a photometer normally used in light scattering investigations. This Photovolt Electronic Photometer (Model 512, Photovolt Corporation, New York, New York) provided the required sensitivity for the thermal runs which were followed photometrically at an extremely low level of light intensity.

The thermal reaction is negligible in practically the whole temperature range over which the photochemical reaction was studied. It has a small detectable rate (0.3 percent of the photochemical one) at 133°C, the highest temperature used in the photochemical runs.

Szwarc⁶ has shown that none of the reactants or products are pyrolyzed at the temperatures used in the photochemical or thermal runs.

The initial rate of disappearance of bromine was determined from the initial slope of the experimental rate curves. These initial rates were used in all computations of rate constants, inhibition constants, and temperature coefficients in order to minimize the effects of accumulating products of reaction.

The reaction products were analyzed by means of their infrared absorption spectra, obtained with a Perkin-Elmer spectrophotometer, Model 21, using a 0.1-mm sodium chloride absorption cell. The spectra of 1-mole percent solutions of o-, m-, p-bromotoluene, and benzyl bromide in toluene are shown in Figs. 4 and 5. Each diagram represents the absorption spectrum of the given solution superimposed upon that of pure toluene. The shaded areas indicated by arrows represent those peaks not present in toluene but arising only from the respective brominated product. The limit of detectability of these additional peaks was found to correspond to 0.04-mole percent of ring substituted bromotoluenes in the presence of 1-mole percent of benzyl bromide in toluene. This would correspond to 4 percent ring substitution compared to the 96 percent production of benzyl bromide by side chain bromination.

The products obtained from 27 experiments were combined to give a 1-mole percent solution of brominated toluene in toluene as determined from the amount of bromine reacting in each run. The organic material was washed with 10 percent aqueous sodium bisulfite to remove bromine and then with water. It was then dried with anhydrous magnesium sulfate and a portion taken for determination of the infrared absorption spectrum.

TABLE I. Photobromination of toluene at constant light intensity (wavelength 4890A).

t°C	Initial pressure Br2	es (mm at l°C) RH	$k(\sec^{-1}) \times 10^4$
	Series A, L	ight intensity, I ₀ '	
82.5	10.64	107.1	4 20
	10.90	112.2	3 77
	11 40	112.8	3.86
	19.67	97.4	3.96
	20.40	93.7	3.81
			3.92 ± 0.13
		· ,	0.72.20.10
97.1	9.25	113.3	6.95
	9.72	79.1	6.88
	9.95	90.2	0.34
	9.97	07.1	5.70
	10.11	159.3	0.40
	10.33	114.9	5.81
	10.39	192.5	5.93
	10.55	18.2	5.80
	10.00	150.2	0.08
	10.95	192.8	0.09
	11.03	98.7	0.3/
	18.93	104.9	5.98
	19.17	102.4	5.53
	24.50	95.1	0.91
	25.00	102.8	0.40
	31.10	108.2	0.01
	32.30	90.0	
			6.25 ± 0.35
132.7	10.35	121.1	15.1
	10.42	186.6	15.4
	10.63	112.0	15.1
	19.80	110.4	17.4
	20.78	107.7	16.7
			15.9 ± 0.9
	Series B, L	ight intensity, I_0	
82.5	10.17	105.8	7.37
	10.70	118.4	6.70
			7.03 ± 0.33
89.8	10.30	118.1	8.55
	10.63	117.6	9.00
	10.67	94.8	8.59
	10.67	117.8	8.27
	11.02	113.4	9.66
			8.81 ± 0.41
115.0	9.15	115.8	17.1
	10.20	119.6	17.5
	10.20	125.4	18.1
	10.44	109.4	17.4
	10.67	114.5	17.3
	10.81	108.8	18.2
	10.89	120.1	18.0
	19.80	113.7	16.4
	20.30	107.8	18.0
			17.6 ± 0.4
132 3	0.05	117 0	23 7
104.0	10.20	115.4	25.5
	10.20	118 1	23.2
	10.72	121.5	24.4
			24.2 + 0.8



FIG. 6. Temperature dependence of photobromination of toluene for two series of measurements.

The spectrum obtained with these reaction products, bottom of Fig. 5, shows unambiguously that every absorption peak that occurred could be identified with those of toluene or benzyl bromide with no indication of any bromotoluenes. Therefore, it may be concluded that the amount of ring substitution was negligible, and the kinetic study may be based on the correct premise that the reaction is predominantly a side-chain bromination with the formation of benzyl bromide and hydrogen bromide. We are indebted to Professor D. F. DeTar and Mr. T. Wentink for aid with the infrared experiments.

RESULTS

The rate law, which corresponds to the initial rate of disappearance of bromine at constant light intensity, was determined from an extensive series of runs at 97.1°C over approximately a threefold range of pressures of reactants. The specific reaction rate constants k were calculated from the initial rate by means of the expression

$$-d(\mathrm{Br}_2)/dt = k(\mathrm{Br}_2)^{\frac{1}{2}}(\mathrm{RH})^{\frac{1}{2}}.$$
 (I)

Experimental values of k at several temperatures are given in Table I. It is evident that there are no significant trends in k with changing pressure of either reactant, nor is there any dependence of the reaction rate constant on the sequence in which the runs were carried out. The two series of measurements, A and B, correspond to somewhat different apparatus constants (involving a change in light intensity) which appear in k.

Equation (I) fits the data better than the rate law

$$-d(\operatorname{Br}_2)/dt = k'(\operatorname{Br}_2)^{\frac{1}{2}}(\operatorname{RH})(1/P)^{\frac{1}{2}}, \qquad (\mathrm{II})$$

which has been found for the photobromination of methane,¹ where P represents the total pressure. A similar situation was encountered in the photobromination of neopentane.³ The better precision obtained with Eq. (I) is probably the result of toluene, like neo-

TABLE II. Photobromination of toluene at reduced light intensity, $0.511I_0$ (wavelength 4890A).

Initial pressures (mm at $t^{\circ}C$)			
t°C	Br2	RH	$k(\text{sec}^{-1}) \times 10^{-1}$
115.0	10.91	115.6	12.3
	11.10	110.9	12.4
			12.4 ± 0.1

pentane, having an efficiency for aiding in the recombination of bromine atoms very much greater than that of any of the other substances present. It can be seen that Eq. (II) approximates Eq. (I) when the toluene pressure is much greater than the bromine pressure.

TABLE III. Photobromination of toluene at constant light intensity, I_0 (wavelength 4890A). Inhibition by HBr.

100	Initial pressure	RH	HBr	51
90.0	10.50	130.0	19.2	0.49
	11.70	124.6	18.5	0.71
	19.60	121.5	21.8	0.61
	20.10	115.1	23.6	0.60
	20.30	100.9	20.7	0.57
				0.60 ± 0.05
115.1	10.57	139.6	19.4	0.89
	10.60	130.9	18.7	0.91
	11.60	134.6	16.4	0.96
				0.92 ± 0.03
132.6	9.7	128.9	21.2	1.21
	19.7	124.8	14.9	1.31
	19.8	124.6	16.2	1.43
				1.32 ± 0.08

The effect of change of incident light intensity on the rate of the reaction was investigated by inserting a calibrated screen between the light source and the reaction cell. This screen had a transmission of 51.1 percent. Table II shows the data obtained at 115.0° C at the reduced light intensity $(0.511I_0)$. The average value of k is 70.4 ± 1.8 percent of its value at this temperature (Table I, Series B) at the higher light intensity, I_0 . If the reaction is one-half order in light intensity, then this screen should reduce the value of k to $(0.511)^{\frac{1}{2}}$ or 71.5 percent of its value without the screen. The ex-

(III)

cellent agreement between the calculated reduction and the observed reduction in k supports the view that the rate of reaction is proportional to the square root of the light intensity.

The effect of temperature on the initial rate of photobromination of toluene was investigated over a 50 degree temperature range, and the results are given in Table I and plotted in Fig. 6 for both series of data. While the magnitudes of the specific rate constants in series A and B differ (for the reason stated above), the temperature coefficients for the two series are in reasonable agreement. The best straight lines, obtained by the method of least squares, for each series, are represented by the equations

and

$$\log k_{\rm A} = 1.497 - 1742/T$$
 (III)

$$\log k_{\rm B} = 1.270 - 1570/T.$$
 (IV)

Considering that the reaction is half-order in light intensity, it can be shown that the effect of the slight temperature dependence of the absorption coefficient of

TABLE IV. Thermal bromination of toluene.

	Initial pressure	es (mm at $t^{\circ}C$)	k
t°C	Br ₂	RH	(cc moles ⁻¹) ⁹ sec ⁻¹ ×10 ⁴
166.2	10.75	113.6	9.56
	15.30	107.8	8.51
	19.65	195.6	9.23
	20.80	195.2	9.06
	23.30	127.7	10.03
	27.10	105.4	9.00
			9.23 ± 0.38

bromine^{8,9} is negligible, and its neglect corresponds to an error no greater than 1.5 percent in the activation energy. It is thus possible to obtain the experimental activation energy from Eqs. (III) and (IV). These are 7.97 kcal/mole for Series A and 7.18 kcal/mole for Series B, the average of the two series being 7.58 ± 0.6 kcal/mole. When corrected for the temperature dependence of the frequency factor in the Arrhenius equation by subtraction of RT/2, the activation energy for photobromination becomes 7.2 ± 0.6 kcal.

Hydrogen bromide, produced during bromination, greatly inhibits this reaction. This inhibition was investigated in the presence of added hydrogen bromide by keeping the hydrogen bromide and toluene pressures approximately constant while the bromine pressure was varied over a twofold range. The complete rate law, taking the inhibition into account, was found to be similar to that obtained in previous bromination studies. Equation (I), therefore, may be modified to

$$-d(Br_2)/dt = \frac{k(Br_2)^{\frac{1}{2}}(RH)^{\frac{1}{2}}}{1+n(HBr)/(Br_2)},$$
 (V)

⁸ M. Bodenstein and H. Luetkemeyer, Z. physik. Chem. 114, 208 (1924).

since the light intensity was the same as for the data shown in Table I. Series B. Here n is the inhibition constant, k is the value of the rate constant for the uninhibited reaction at the same temperature, and $-d(Br_2)/dt$ is the experimentally observed initial rate of the inhibited reaction in the presence of excess HBr. The values of k used in computing n from experimental rates were calculated from Eq. (IV). It should be pointed out that the value for n is very sensitive to errors in the value of k.

The values of *n* are quite large compared to those for the bromination of hydrogen^{8,10} in the range up to 300°C and methane¹ between 120 and 180°C. They are, however, of similar size to those obtained for neopentane³ in agreement with the notion that the larger and more complicated the molecule being brominated, the greater appears to be the degree of inhibition by HBr.

The inhibition constant is also temperature dependent, as shown in Table III and Fig. 7. The equation for the best straight line, obtained by the method of least squares, is

$$\log n = 3.007 - 1176/T.$$
 (VI)

From this equation, one can calculate an apparent activation energy of inhibition of 5.38 ± 1.2 kcal/mole. Upon correction for the small temperature dependence of the frequency factor, by subtraction of RT/2, the apparent activation energy of inhibition becomes 5.0 ± 1.2 kcal/mole.

As with other hydrocarbons, photobromination of toluene is also inhibited by oxygen. It was found that the introduction of 8 mm of oxygen to a mixture containing 20 mm of bromine and 103 mm of toluene caused a fourfold decrease in the normal rate. No extensive study was made of oxygen inhibition.



FIG. 7. Temperature dependence of inhibition by hydrogen bromide of photobromination of toluene.

¹⁰ M. Bodenstein and S. C. Lind, Z. physik. Chem. 57, 168 (1906).

Acton, Aickin, and Bayliss, J. Chem. Phys. 4, 474 (1936).

It was also desirable to investigate the mechanism of the thermal reaction in order to obtain more detailed information about the rate determining step in the bromination reaction. Since the amount of thermal reaction in the photochemical studies was negligible, it was necessary to raise the temperature to 166.2°C in order to obtain a conveniently measurable rate of reaction between bromine and toluene. Also, in order to follow the reaction photometrically, it was necessary to decrease the incident light intensity to a level which would not produce a photochemical reaction. The data for the thermal runs were calculated from the rate law

$$-d(\mathrm{Br}_2)/dt = k(\mathrm{Br}_2)^{\frac{1}{2}}(\mathrm{RH}) \qquad (\mathrm{VII})$$

and are shown in Table IV. Pressures were converted to concentration units by use of the ideal gas law. There is no dependence of the reaction rate constant on the sequence in which the runs were carried out.

DISCUSSION

From a consideration of the observed rate laws for the photochemical and thermal reactions, the inhibition by hydrogen bromide, and the half-order in light intensity, the following mechanism, which was also deduced from similar studies of other hydrocarbons, is postulated:

$$Br_2 + h\nu = 2 Br \tag{1}$$

or
$$\operatorname{Br}_2 + M = 2 \operatorname{Br} + M$$
 (1a)

$$Br+RH=R+HBr$$
 (2)

$$R+Br_2=RBr+Br \tag{3}$$

$$\mathbf{R} + \mathbf{H}\mathbf{B}\mathbf{r} = \mathbf{R}\mathbf{H} + \mathbf{B}\mathbf{r} \tag{4}$$

$$\mathbf{Br} + \mathbf{Br} + M = \mathbf{Br}_2 + M, \tag{5}$$

where M represents any molecule present. Steps (1) and (1a) represent the photochemical or thermal dissociation of bromine molecules, respectively. The subsequent steps 2-5 are identical for both the photochemical and thermal reactions. Since this mechanism is postulated for the initial part of the bromination reaction only, no consideration need be given to the bromination of benzyl bromide.

By application of steady-state considerations to the postulated mechanism, the following rate law can be derived for the photochemical reaction

$$-\frac{d(\mathrm{Br}_2)}{dt} = \frac{k_2(\mathrm{RH})\{\Phi I_a/k_5(M)\}^{\frac{1}{2}}}{1+k_4(\mathrm{HBr})/k_3(\mathrm{Br}_2)}, \quad (\mathrm{VIII})$$

where Φ represents absorbed effective light quanta and I_a is the intensity of absorbed light. As pointed out in previous papers of this series, $\Phi I_a = k_{app} \alpha I_0(Br_2)$, where k_{app} is a temperature-independent apparatus constant and α the absorption coefficient of Br₂ for the wavelength of light of incident intensity I_0 .

In deriving Eq. (VIII) from the photobromination

mechanism it has been assumed that all molecules are equally effective third bodies in the homogeneous recombination of Br atoms. This is not the case, as has been demonstrated for instance by Jost,¹¹ Rabinowitch,¹² and Kistiakowsky and VanArtsdalen.¹ Actually, the term $k_5(M)$ in Eq. (VIII) should be replaced by a summation of k_5 's and (M)'s for each molecular species present. Thus, at the start of the reaction it is possible to write

$$k_5(M) = k_5'(Br_2) + k_5''(RH).$$
 (IX)

If $k_5'' \gg k_5'$, i.e., if toluene is a much more effective third body than bromine, and the concentration of toluene is greater than that of bromine, then Eq. (VIII) reduces to the experimentally obtained Eq. (V) at constant incident light intensity I_0 , with

$$k = k_2 [k_{app} \alpha I_0 / k_5]^{\frac{1}{2}}$$
 and $n = k_4 / k_3$.

The rate law for the thermal reaction may be derived in a similar manner, the result being

$$-\frac{d(Br_2)}{dt} = \frac{k_2 K^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(BH)}{1 + k_4 (HBr)/k_3 (Br_2)},$$
 (X)

where K is the equilibrium constant for the thermal dissociation of bromine and equals k_{1a}/k_5 . Relative efficiencies of the various molecules as third bodies are of no consequence since any given molecule must be equally effective in promoting dissociation of bromine molecules and recombination of bromine atoms (principle of microscopic reversibility). If we set the concentration of HBr equal to zero, then a comparison of Eq. (X) with the experimentally obtained rate law for the thermal reaction (Eq. (VII)) indicates that $k = k_2 K^{\frac{1}{2}}$.

Reactions involving H atoms have been omitted from consideration on energetic grounds.¹ Other chain termination steps, including heterogeneous reactions at the wall, have been eliminated since they are not consistent with the observed rate law and dependence on light intensity.

The thermal rate law provides data for calculation of k_2 and, thereby, the frequency factor for this rate determining step, since the experimental thermal rate constant is $k_2 K^{\frac{1}{2}}$, where K is the equilibrium constant for the reaction: $Br_2(g) = 2Br(g)$. The value of $K^{\frac{1}{2}} = 1.06$ $\times 10^{-11}$ (mole cc⁻¹)¹ at 439.4°K was obtained by interpolation of the standard free energy data of Gordon and Barnes.¹³ Thus $k_2 = 9.23 \times 10^{-2} / 1.06 \times 10^{-11} = 8.71$ $\times 10^9$ (cc mole⁻¹ sec⁻¹). Writing the Arrhenius equation as

$$k_2 = s_2 Z_2 e^{-E_2/RT}$$

where Z_2 is the collision number and s_2 is a steric factor for the reaction Br+RH=R+HBr, the frequency factor is found to be $A_2 = s_2 Z_2 = k_2 / \exp((-E_2/RT))$

- ¹¹ W. Jost, Z. physik. Chem. **B3**, 95 (1929). ¹² E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 907 (1936); E. Rabinowitch and H. L. Lehman, Trans. Faraday Soc. **31**, 689 (1935).
 - ¹³ A. R. Gordon and C. Barnes, J. Chem. Phys. 1, 694 (1933).

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=3.3×10¹³ (cc mole⁻¹ sec⁻¹), using the value E_2 =7.2 kcal/mole. The collision number Z_2 was evaluated at 439.4°K using Nasini's value¹⁴ of 5.3A for the diameter of toluene and 3.0A for the diameter of the bromine atom.³ The value of Z_2 at this temperature is 1.5×10^{14} (cc mole⁻¹ sec⁻¹). Thus the value of the steric factor is s_2 =3.3×10¹³/1.5×10¹⁴=0.22. This means that about one-fifth of the collisions, which are energetically adequate for reaction, leads to reaction. The steric factor for the corresponding reaction with methane¹ was of the order of 0.1 to 0.2. Because of inherent imprecision in steric factor calculations, it is not possible to conclude that there is any significant difference between methane and toluene in this respect.

A comparison of steric factors of reactions competing for benzyl radicals may be made with the aid of Eq. (VI) for the temperature coefficient of the inhibition constant n, which is equal to k_4/k_3 . Eq. (VI) may be written in the form

$$\log(k_4/k_3) = \log(A_4/A_3) - (E_4 - E_3)/2.3RT, \quad (XI)$$

and by comparison with Eq. (VI) it is seen that $\log(A_4/A_3) = 3.01$. Since A = sZ and the collision numbers for the competing reactions are about the same, the steric factor for the reaction

$$R + Br_2 = RBr + Br \tag{3}$$

is smaller than the steric factor of the reaction

$$R + HBr = RH + Br \tag{4}$$

by a factor of approximately 10^3 . This difference in steric factors is thought to arise from the ease of approach to within bonding distance of the side-chain carbon of the benzyl radical by the relatively smaller hydrogen end of hydrogen bromide compared to the large bromine atoms in the bromine molecule. This question has been discussed previously in the case of neopentane.³

BOND DISSOCIATION ENERGIES

It is possible to determine $D(C_6H_5CH_2-H)$ for toluene from the experimental activation energies reported here. The bond dissociation energy referred to is the enthalpy change of the reaction RH=R+H at $T^{\circ}K$ and a pressure of 1 atmos. The average activation energy, determined from Eqs. (III) and (IV) may be assigned to k_2 , because $k_{app}\alpha I_0$ is practically temperature independent, and k_5 would also be temperature independent since the activation energy for the recombination of bromine atoms is considered to be zero. For the reaction

$$Br + RH = R + HBr, \qquad (2)$$

 $E_2=7.2$ kcal/mole. From a comparison of Eqs. (VI) and (XI), $(E_4-E_3)=5.0$ kcal/mole. Since reaction (3) is a quite exothermic radical reaction, we assume that

TABLE V. Heats of formation and dissociation.

Т°К	$\Delta H_f(R)$ kcal/mole	D(R-H) kcal/mole
0	53.9 ± 1.4	88.1 ± 1.4
298	49.4 ± 1.4	89.5 ± 1.4
381	48.4 ± 1.4	89.9 ± 1.4

it proceeds with practically zero activation energy. Therefore, $E_4 = 5.0$ kcal/mole for the reaction

$$R + HBr = RH + Br.$$
(4)

Clearly, this is a minimum value for E_4 , the value being higher if E_3 has a small positive value.

Activation energies of reactions 2 and 4 may be combined to obtain the enthalpy change for the reaction

$$Br+RH=R+HBr$$

at the mean temperature of the experiments, 381°K. Because there is no volume change in the reaction, we may write

$$\Delta H_{381} = \Delta E_{381} = E_2 - E_4 = 7.2 - 5.0 = 2.2 \text{ kcal/mole}$$

with an estimated probable error of ± 1.3 kcal. Using the value of the Bureau of Standards¹⁵ for the heat of dissociation of hydrogen bromide, one obtains $D(C_6H_5CH_2-H)$ in toluene at 381°K in the following manner:

$$\frac{\text{Br+RH=R+HBr}}{\text{HBr=H+Br}} \xrightarrow{\Delta H_{381}=2.2 \text{ kcal}}{\frac{\Delta H_{381}=87.7 \text{ kcal}}{\frac{\Delta H_{381}=89.9 \text{ kcal}}}$$

or $D(C_6H_5CH_2-H) = 89.9 \text{ kcal/mole}$.

The heat of formation of the benzyl radical may be computed from the value of the C-H bond dissociation energy and the heats of formation of toluene¹⁵ and the hydrogen atom¹⁵ by means of the equation

$$\Delta H_f(\mathbf{R}) = \Delta H_f(\mathbf{R}\mathbf{H}) - \Delta H_f(\mathbf{H}) + D(\mathbf{R} - \mathbf{H}).$$

The values thus determined are listed in Table V together with the bond dissociation energies at several temperatures, the temperature dependence having been evaluated as was done previously.^{1,3}

The values of D(R-H) reported here are significantly different from the value 77.5 obtained by Szwarc⁶ from pyrolysis studies. This point has been discussed in considerable detail with Szwarc. Thus far it has not been possible to make any unimpeachable criticism of either the reliability of the data or the interpretation of them in both the pyrolytic method and the method of bromination kinetics. It may remain the task of still another independent technique to resolve this discrepancy.

¹⁵ Selected Values of Chemical Thermodynamic Properties, Circ. 500, Natl. Bur. Standards (U. S. Government Printing Office, Washington, 1952).

¹⁴ A. G. Nasini, Proc. Roy. Soc. (London) A123, 703 (1929).