mixture of 91% **2** (methyl absorption at δ 2.09), 5% **3** (methyl absorption at δ 1.97), and 4% **1** (methyl absorption at δ 1.73).

Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.80; H, 5.22; N, 18.03.

In subsequent preparations, samples containing no more than 2-4% **1** and **3** were obtained.

If the pyrolysis of dicyanodiazomethane in toluene was allowed to proceed at reflux for extended periods, the product was almost entirely a mixture of the tolylmalononitriles. Hydrolysis and decarboxylation was effected by heating with 60% aqueous sulfuric acid for 6 hr at 120–150°. Dilution with water, extraction with ether, and concentration gave a mixture of tolylacetic acids. The nmr spectrum in carbon tetrachloride showed a carboxyl proton (δ 11.2, 1 H), aromatic protons (δ 6.95, 4 H), methylene protons (δ 3.35, 2 H), and methyl protons (δ 2.15, 3 H). A small amount of impurity was present as evidenced by a weak absorption (δ 1.1, <1 H). Esterification with diazomethane gave a mixture of the three methyl tolylacetates, identified by comparisons of retention times with those of authentic samples on a Ucon Polar vpc column, 6 mm × 4.4 m, at 175°.

The ultraviolet spectra of mixtures of the tolylmalononitriles were concentration dependent. In 95% ethanol the spectra showed sharply detailed bands at 263 and 270 mμ and a broad band at 290 mμ. The extinction coefficient of the 290-mμ band increased with decreasing concentration and was completely eliminated by addition of a trace of hydrochloric acid. The long-wavelength band thus seems to be attributable to ionization of the malononitrile to the corresponding anion. The data reported in Table II for the tolylmalononitriles and for the samples of norcaradienes containing varying amounts of aromatics were therefore taken on solutions containing *ca.* 0.01 *M* hydrochloric acid, which was more than sufficient to suppress the ionization, and the extinction coefficients for the norcaradienes are corrected for the weak tolylmalononitrile absorption. The spectra of the norcaradienes closely resemble those reported[5,8b] for other norcaradienes. Table II shows that there is no significant change in spectral properties of mixtures of the three norcaradiene isomers **1**, **2**, and **3** as the proportions change.

The rearrangements were followed by nmr spectroscopy. Initial concentrations were about 1-3%. In runs 1 and 5 (Table I), the composition was determined after evaporation of the solvent (dioxane or toluene) *in vacuo* and dissolution of the residue in deuteriochloroform at a convenient concentration. In runs 6 and 7, samples were sealed under nitrogen in nmr tubes and immersed in an oil bath at 100 ± 4°.

Reactions of dicyanodiazomethane with *o*- and *p*-deuteriotoluenes were carried out as in the undeuterated series. The deuterated toluenes were prepared by quenching solutions of *o*- and *p*-tolylmagnesium bromides, respectively, with 99.77% isotopically pure deuterium oxide. The *o*- and *p*-bromotoluenes used in the preparations of the Grignard reagents were obtained from Aldrich Chemical Co. and were at least 99% isomerically pure as established by vpc on a 6 mm × 2 m 20% didecyl phthalate-on-Chromosorb P column. Carbonation of the Grignard reagents gave *o*- and *p*-toluic acids, respectively.

Photochemical Interchange of Halogens in Aromatic Compounds. III[1a]

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Abstract: Measurements of the rate of the photochemical reaction, $PhBr + Cl_2 \longrightarrow PhCl + Br_2$, in carbon tetrachloride solution have been made. The rate is proportional to the square root of light intensity, the halogen concentration, and the bromobenzene concentration over a limited range, but different proportionalities apply at large and at small bromobenzene concentrations. Quantum yields vary from small numbers to as high as 1300 depending upon conditions, and they generally pass through a maximum during the course of the reaction. Substituent effects in the same reaction, as measured by competition experiments, depend upon whether the reagent providing the chlorine is molecular chlorine or bromine chloride. These results are interpreted as contradicting previously postulated mechanisms and as supporting a concerted displacement. The heat of reaction has been found to be 12.2 ± 1 kcal/mole.

In previous papers[3] we have set forth evidence bearing upon the general scope of the photochemical reactions represented by

$$ArX + X' \longrightarrow ArX' + X$$

and upon the implication of π complexes in the mechanism (or mechanisms) through which reaction takes place. The exact relationships between these reactions and the formally similar thermal reactions observed at high temperatures by Levine and Noyes[4] and by Engelsma and Kooyman[5] are not yet clear, but certain differences are becoming apparent.

The results reported previously have been concerned in the main with relative measurements of substituent effects, which were obtained in nonchain reactions, such as the reactions of bromine with iodobenzenes or iodine chloride with bromobenzenes, as well as in the chain reactions of chlorine with bromobenzenes. In this report we turn our attention to measurement of the absolute rate of the reaction of bromobenzene with chlorine in moderately dilute carbon tetrachloride solution, a system which we have shown previously[3] to give quantitative yields at room temperature under ir-

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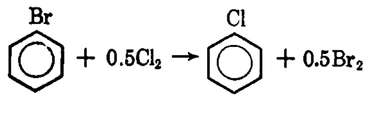
[2] Author to whom inquiries may be addressed: Houdry Laboratories, P. O. Box 427, Marius Hook, Pa. 19061.

[3] B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Am. Chem. Soc.*, **84**, 158 (1962); B. Milligan and R. L. Bradow, *J. Phys. Chem.*, **66**, 2118 (1962).

[4] S. Levine and R. M. Noyes, *J. Am. Chem. Soc.*, **80**, 2401 (1958).

[5] J. W. Engelsma and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 537 (1961).



radiation with visible light. We also report additional substituent effect data which taken with the kinetic results require extensive revision of our ideas about the mechanism of the chlorine–aryl bromide reaction. Furthermore, the mechanistic relationship to related displacements (bromine from aryl bromide by sulfuryl chloride–peroxide,[6] other displacements reported by Miller and Walling,[6] and the disproportionation of arylsilanes reported by Nelson, Angelotti, and Weyenberg[7]) becomes unclear.

Experimental Section

Kinetic Measurements. The apparatus is shown schematically in Figure 1. The entire apparatus was mounted on an optical bench fashioned from an old lathe bed.

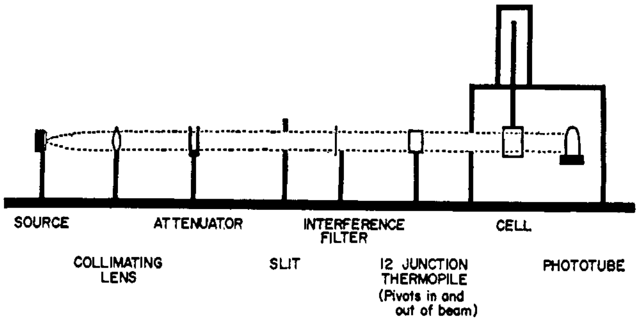


Figure 1. Experimental apparatus (schematic).

The source was an Osram HBO 100W/2 super pressure mercury arc lamp operated with a Gates P109 power supply connected to a constant-voltage transformer. Collimation was achieved by locating the source at the focus of an Aero-Ektar lens with 6-in. focal length and *f*/2.5 aperture. One of three wavelengths, 405, 436, or 546 mμ, was selected from the mercury spectrum by means of an interference filter with appropriate band pass. That for the last wavelength was a Schott "band double" type filter and had immeasurably small (by Beckman Model DU) transmission at all shorter wavelengths at which mercury arc lines occur.

An Eppley Laboratories 12 junction thermopile, with Pyrex glass, window, was mounted on a pivot which permitted it to be inserted into the beam when necessary. The vacuum phototube and the associated circuitry[8] were calibrated at each wavelength against the thermopile.

The sample cell, fabricated of Pyrex glass by the Pyrocell Manufacturing Co., N. Y., was a cylinder 39 mm i.d. × 20 mm long with optically plane windows. The cell was filled by means of two 0.5-mm i.d. precision bore capillary tubes leading into the top and bottom of the cell, respectively. The small diameter and length (60 cm) of these tubes prevented measurable loss of either solvent or halogen without stoppers over a period several hours longer than required for a run.

The housing in which the cell and phototube were mounted consisted of two concentric aluminum cylinders surrounded on all sides by a layer of extended polyurethan foam insulation. The capillary tubes of the cell extended into a polyurethan foam housing having a narrow glass window. Water from a thermostat bath mantained at 25.0° with a precision of ±0.002° was circulated through the annular space between the metal cylinders. Despite these precautions a small amount of temperature drift would occur during runs. The amount of drift was measured by a carbon tetrachloride filled thermometer having approximately the same sensitivity as the sample cell. Raw data consisted of observations of the height of liquid in the capillary tubes of the cell and the comparison thermometer with a cathetometer.

Materials. Carbon tetrachloride solvent was purified with a silica gel column as described previously.[3] Distillation of reagent grade bromobenzene through a column of approximately 25 plates was not sufficient purification. Bromobenzene was treated with a small amount of chlorine under irradiation. Following washing with thiosulfate, sodium hydroxide, sulfuric acid, and water, the bromobenzene was dried and distilled through the 25-plate column. Chlorine was prepared by careful oxidation of reagent grade hydrochloric acid with reagent grade potassium peroxydisulfate.[9] The chlorine was swept from the reaction vessel with a stream of helium and was dried before being passed into carbon tetrachloride which had been previously "blown" with helium. The chlorine solution so obtained, as well as bromobenzene and carbon tetrachloride used for dilution, was maintained under a helium atmosphere in an apparatus which permitted transfer to the reaction vessel without exposure to air. All stopcocks had Teflon plugs.

Treatment of Data. The general principle upon which the measurement of the amount of product chlorobenzene was based on the increase in volume of the reacting system as a result of the temperature rise caused by evolution of the heat of reaction. The actual rise observed was usually in the range of 0.2 to 0.5°. In view of the small activation energies which must obtain if the reaction is to occur by a chain mechanism, such a rise was not considered sufficient to cause measurable distortion of observed rates. A small but measurable decrease in volume at constant temperature also accompanied the reaction. A correction for this decrease was included in the calculations.

Because of the opposing directions of two effects upon the volume of the system and because of the loss of heat from the cell to its surroundings, the simple calculations normally applicable to dilatometry could not be used, and the following treatment was derived.

At time t the cathetometer reading of the height of the meniscus, h, should be given by

$$h = h_0 - x(h_0 - h_\infty) + x\Delta H\alpha/C - (\alpha\beta/C)\int_0^t (T - T_0)\mathrm{d}t + (\alpha/C)\int_0^t I_a\mathrm{d}t \quad (1)$$

where h_0 = height at time zero, x = fraction of reaction completed at time t, h_∞ = height at time infinity (complete reaction), ΔH = heat evolved by reaction, α = thermometric constant of the cell with contents (cm/deg), C = heat capacity of cell and contents (cal/deg), β = heat transfer coefficient of cell to surroundings (cal/deg sec), $T - T_0$ = temperature difference between cell and surroundings, and I_a = absorbed light flux (cal/sec). The second term on the right side, $x(h_0 - h_\infty)$, allows for the decrease in height resulting from the decrease in volume accompanying the reaction itself. The third term represents the increase in height resulting from the heat evolved. The fourth term allows for the heat lost from the cell to the surroundings up to time t, and the last term corrects for the small increase in height resulting from heating by the light source. The thermometric constant of the cell and contents, α, was directly determined by immersing it in various baths of precisely known temperature. The ratio of the heat transfer coefficient to the heat capacity of the cell and contents, β/C, was measured by observing the decrease in height of the liquid meniscus when the cell and its contents had been warmed slightly before placement in the apparatus, the ratio being equal to the slope of log height *vs.* time. The precisely exponential decay of the height during these measurements confirms the assumption of Newton's law which was made in the derivation of eq 1. The heat capacity, C, was calculated from the known specific heats of the contents and Pyrex glass. The absorbed light flux, I_a, was measured directly during each experiment and its integral over time was obtained graphically. Because the quantity $(h_0 - h_\infty)$ is relatively small, we chose to approximate $x(h_0 - h_\infty)$ by linear interpolation within the time span of the reaction. So doing permitted graphical integration of the heat loss term, which means that every factor in eq 1 is either known or directly measurable except the fraction of reaction, x, and the heat of reaction, ΔH. That ΔH can be measured if x is known with certainty at some point is immediately

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[6] B. Miller and C. Walling, *J. Am. Chem. Soc.*, 79, 4187 (1957).

[7] L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *ibid.*, 85, 2662 (1963).

[8] RCA Phototubes, Form PT-20R1, 6/53. A bridge-type circuit described in this publication was modified to give greater stability. Copies of the circuit will be provided upon request.

[9] F. Brown, R. Gillies, and W. H. Stevens, *Can. J. Chem.*, 31, 768 (1953).

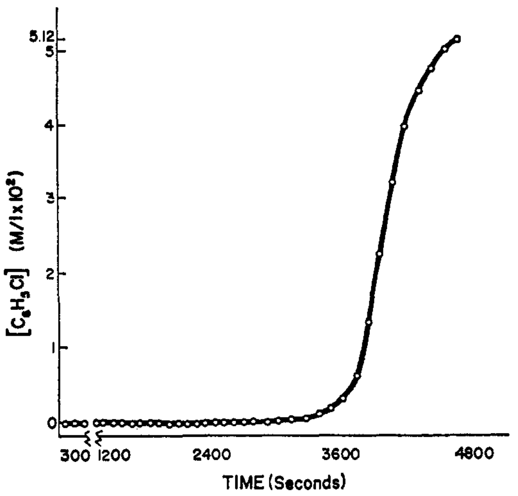

Figure 2. Photochemical reaction of bromobenzene with chlorine. Chlorobenzene concentration *vs.* time; initial bromobenzene 2.56 *M;* initial chlorine, 0.0256 *M;* wavelength 546 mμ, CCl_4 solvent, incident intensity 6.58 × 10^{-9} einstein/sec.

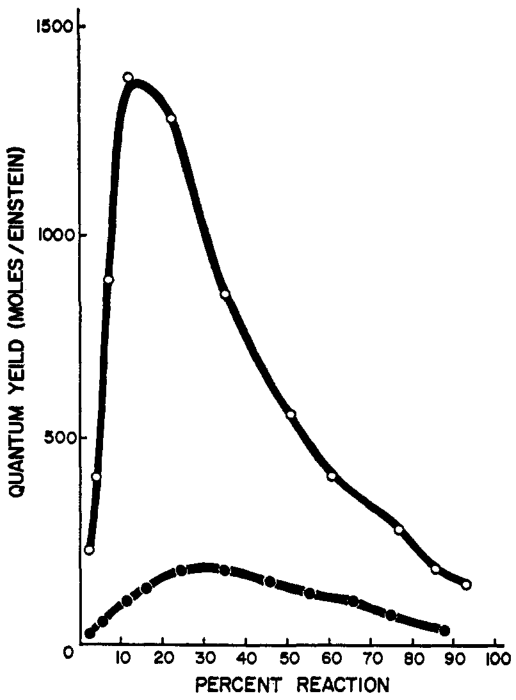

Figure 3. Quantum yield *vs.* per cent reaction: ○, 2.56 *M* bromobenzene + 0.0256 *M* chlorine, incident intensity 4.04 × 10^{-9} einstein/sec; ●, 0.0256 *M* bromobenzene + 0.0256 *M* chlorine, incident intensity 6.71 × 10^{-9} einstein/sec.

apparent. We chose to evaluate ΔH from certain runs in which the time of complete reaction could be ascertained with confidence. In such cases x is equal to unity, and one should note that in principle choosing a time beyond the moment of completion should not affect the result according to eq 1. In practice inaccuracies in the evaluation of the heat loss term accumulate, so we chose as the point of completion that reading whose successor did not lead to further increase in the calculated value of ΔH.

Relative Rate Measurements. The general techniques employed were those described earlier.[3] Measured quantities of aryl bromides were diluted with carbon tetrachloride in a volumetric flask; an appropriate quantity of halogen solution was added, and the mixture was diluted to volume while being protected from light. After equilibration with the thermostat in the dark, each reaction mixture was irradiated with a mercury arc lamp (filtered to remove radiation at 405 mμ and below) for an appropriate period. Analysis of products was by gas chromatography.

In runs involving bromine chloride, bromine solution amounting to a five- to tenfold excess over the amount of chlorine to be used was added.[10] The reaction was allowed to procede to complete conversion of bromine chloride to bromine. In runs involving chlorine, the amount of chlorine used was equivalent to the aryl halides (all 0.1 *M*), but irradiation was continued only long enough (20–45 sec) to effect 1% or less of reaction. In runs involving mixed chlorine–bromine chloride, our past practice[4a,b] of using an amount of chlorine representing 5–20% of combined aryl halides and irradiating until reaction was complete was followed.

Results

The rather unusual character of the reaction of bromobenzene with chlorine is shown in Figure 2 in which concentration of chlorobenzene is plotted against time for a typical run with insolation at 546 mμ. Although the induction period was much longer at this wavelength than at the shorter ones used, the relatively long induction period followed by a rapid rise in chlorobenzene concentration was a feature of virtually all runs. Formation of chlorobenzene was accompanied by an increase in the absorbance of the system as a result of the bromine generated. We consider the induction period to be a genuine characteristic of the reaction rather than the influence of impurities for the following reasons. (1) Although oxygen definitely increases the induction period when intentionally added, our efforts to exclude it were rewarded by gradual reduction of the induction period to a fairly reproducible minimum. (2) Some reduction of the induction period accompanied purification by the method described in the Experimental Section, but *increase* of bromobenzene concentration in a set of runs identical in all other respects led to a progressive *decrease* in the induction period. This result is a direct contradiction of expectation if the induction period were *solely* the result of impurities in the bromobenzene. Furthermore, the introduction of a small amount of bromine as well as chlorine in the reaction mixture virtually eliminated the induction period. The absence of any measurable dark reaction was demonstrated by interrupting illumination of several runs at various stages. In every instance the optical density of the partially reacted system remained unchanged during the dark period of several hours. One should note that the lack of scatter in the points is a consequence of the graphical integration procedures involved in their determination rather than a claim of great precision of measurement.

The rate of reaction at each experimental point was determined by fitting the concentration–time data to high order polynomials (usually eighth to tenth order) by least squares and computing the derivative of the polynomial. The rates so obtained agreed within a few per cent to those obtained by careful graphical differentiation in selected cases. Furthermore, the rates obtained from the polynomials appeared to be more reliable than those obtained by Newton's method.[12]

The ratio of the rate of reaction to the light flux being absorbed by the system is the instantaneous quantum

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(10) Since the equilibrium constant for the formation of bromine chloride is 6.09 ± 0.24,[11] 95% or more of the chlorine is in the form of the interhalogen. The observations of Popov and Mannion[11] would indicate that equilibrium was reached by the time our irradiation had begun.

(11) A. I. Popov and J. J. Mannion, *J. Am. Chem. Soc.*, **74**, 222 (1952).

(12) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1956, p 472.

Table I. Substituent Effects and Differential Activation Parameters (Substituted/Unsubstituted) for the Photochemical Reaction $C_6H_5Br + Cl \rightarrow C_6H_5Cl + Br$ with Various Sources of Chlorine

	Source of chlorine								
	Cl_2			Mixed Cl_2–BrCl			BrCl		
Substit	W_{25}	$\Delta\Delta H^{\ddagger}$, kcal	$\Delta\Delta S^{\ddagger}$, cal/deg	W_{25}	$\Delta\Delta H^{\ddagger}$, kcal	$\Delta\Delta S^{\ddagger}$, cal/deg	W_{25}	$\Delta\Delta H^{\ddagger}$, kcal	$\Delta\Delta S^{\ddagger}$, cal/deg
2-F				0.809[a,b]	0.55	1.4	0.774	1.53	4.6
2-Cl	0.820	0.51	1.3	0.783[c]	0.87	2.4	1.12	−1.42	−4.6
2-CH_3O	39.4	−0.79	4.6	59.7	−4.15	−5.8	127.2	−3.93	−3.6
3-F	0.300	−7.3	−27.0	0.153[a,d]	−4.24	−18	0.132	2.63	4.8
3-Cl	0.163	−0.53	−5.4	0.161[c]	1.05	−0.2	0.137	0.82	−1.2
3-CF_3				0.0509	2.83	2.4	0.0537		
4-F	1.06			1.28[a]	−2.67	−8.5	1.56	−1.40	−3.8
4-Cl	1.28	1.48	5.4	1.24	0.30	1.4	1.21	−0.77	−2.2
4-CF_3				0.0461[e]	2.48	2.4	0.0342		
4-CH_3O	56.1	−2.87	−1.6	*f*			59.6[g]	(−7.0)	(−13.0)

[a] From paper II. [b] 23°. [c] 27°. [d] 25.8°. [e] 28°. [f] The values reported in paper II for the 4-methoxy substituent effect are, by comparison with the data presented here, incorrect. [g] 39°, activation parameters based on two points.

yield, which we feel is a more significant quantity for description of this system than the customary integrated quantum yield, the total amount of product formed divided by the total quantity of light absorbed. Typical results are shown in Figure 3. The most noteworthy feature of these curves is the maximum through which the quantum yield passes. This behavior is observed regardless of whether chlorine or bromobenzene is present in excess. The magnitude of the quantum yield is of some interest and ranges from immeasurably small (by our method) values during the induction period to a maximum of 1300 (in the most favorable cases) and drops off to ill-defined values as the reaction nears completion.

These quantum yields represent a lower limit on chain length. Since the primary quantum yield of iodine atoms in carbon tetrachloride solution is on the order of 10^{-1},[13] and since complexation effects in the presence of aromatic molecules would probably more than offset any increases resulting from the smaller size and greater energy of lighter halogen atoms, the actual chain lengths may be 10^2 or more times the measured quantum yields.

From experiments conducted at varying initial concentrations of bromobenzene and chlorine and at varying incident light intensities, we conclude that when bromobenzene is in large excess (0.4–2.5 *M* bromobenzene and 0.01–0.05 *M* initial chlorine), the rate of formation of chlorobenzene is accurately proportional to the square root of absorbed light flux and to the concentrations of bromobenzene and halogen. That is, if the rate divided by the product of bromobenzene concentration, initial chlorine concentration, and the square root of absorbed light flux is plotted against per cent reaction, the points for all runs fall on the same curve. This curve rises sharply to a maximum at about 25% reaction and falls thereafter with near linearity. On the other hand, when the bromobenzene concentration is reduced to the 0.02–0.05 *M* region and allowed to react with a twofold excess of chlorine, plots of rate divided by the product of bromobenzene concentration, initial halogen concentration, and the square root of absorbed light flux are again coincidental, but they are not identical with those from experiments employing higher concentrations of aromatic. In sum, a 100-fold reduction in the concentration of bromobenzene results in a roughly tenfold reduction in the rate if other factors are held constant. A single run employing a fivefold excess of bromobenzene displayed intermediate behavior.

No significant effects attributable to change of the wavelength of irradiation were discernible. Nonetheless, the results obtained with 546-mμ illumination are considered the most reliable, primarily because of the more favorable extinction coefficients which obtain at that wavelength. At the two shorter wavelengths, the reaction mixture in most cases was nearing opacity (absorbance >2) before reaction was 50% complete. Thus, extraction of numerical constants from the data would require allowance for the fact that reactive centers are not generated uniformly throughout the reaction mixture. The enthalpy change accompanying the reaction

$$C_6H_5Br + 0.5Cl_2 \longrightarrow C_6H_5Cl + 0.5\,Br_2$$

was measured to be 12.2 ± 1.0 kcal/mole.

The results of a number of relative rate experiments are given in Table I. Some of the results are taken from an earlier paper as shown. The relative reactivity, *W*, is defined as either the ratio of products corrected for reactant ratio when conversion was low (or when the ratio was near unity) or the result of the integrated relative rate expression

$$W = \log[(A - x)/A]/\log[(B - y)/B]$$

when conversion was high. Except in the one case so denoted the differential activation parameters are based on measurements of the relative reactivity at at least three temperatures and are taken from plots of log *W* *vs.* $1/T$.

Isokinetic plots ($\Delta\Delta H^{\ddagger}$ *vs.* $\Delta\Delta S^{\ddagger}$) of the data in Table I show no discernible tendency to lie upon a line. Therefore, we conclude that the apparent relationship mentioned by Milligan and Bradow[3] was merely fortuitous as was suspected. Linear free energy plots are somewhat more successful in that most of the points for a given reagent fall near a line with negative slope when log *W* is plotted *vs.* σ^+. However, the 4-chloro substituent, which has a positive σ^+, consistently activates substitution. Unless there is some reason which escapes us to consider the 4-chloro substituent different from all others investigated so far, there seems to be

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[13] R. L. Strong and J. E. Willard, *J. Am. Chem. Soc.*, 79, 2099 (1957), and references therein.

little reason to claim that the data adhere to a linear free energy relationship.

Some substituent effects were measured at several reactant ratios, and the reactivity ratio was found to be insensitive to the ratio of reactants. This finding confirms a first-order dependence of the rate upon aryl bromide. The addition of nitrobenzene or *m*-dinitrobenzene was not observed to have much, if any, effect upon relative reactivities and did not cause noticeable inhibition of the over-all reaction under our conditions, although Miller and Walling did report inhibition by the former compound[6] under different conditions. In a number of cases, reaction mixtures which were not irradiated contained no detectable amounts of products establishing that the results are not complicated by concurrent thermal reactions.

Discussion

The measured heat of reaction should in principle be corrected for the heat effects on π-complex formation between halogen and aromatic halides. Although the data required for such a correction are not known, one can quickly estimate from available data[14] that the contribution would be no greater than 100 cal and is probably much less. Therefore, with an experimental uncertainty of 1 kcal, the correction is meaningless. If one can make certain assumptions about heats of solution, one can compute from standard thermochemical data the enthalpy change of the gas-phase process

$$C_6H_5Br + Cl \longrightarrow C_6H_5Cl + Br$$

This enthalpy change is of interest because it represents the difference between the bond dissociation energies of bromo- and chlorobenzenes into halogen atoms and phenyl. The summation[15] to achieve the result desired is as follows (m indicating solution in the reaction medium)

$$\begin{aligned}
&0.5Cl_2(m) + C_6H_5Br(m) \longrightarrow \\
&\qquad Br_2(m) + C_6H_5Cl(m) && \Delta H = -12.2 \pm 1 \text{ kcal} \\
&0.5Cl_2(g) \longrightarrow 0.5Cl_2(CCl_4 \text{ soln}) && \Delta H = -2.3 \text{ kcal} \\
&0.5\,Cl_2(CCl_4 \text{ soln}) \longrightarrow 0.5Cl_2(m) && \Delta H = Q_1 \\
&Cl(g) \longrightarrow 0.5Cl_2(g) && \Delta H = -29.0 \text{ kcal} \\
&0.5Br_2(CCl_4 \text{ soln}) \longrightarrow 0.5\,Br_2(l) && \Delta H = -0.35 \text{ kcal} \\
&0.5Br_2(m) \longrightarrow 0.5Br_2(CCl_4 \text{ soln}) && \Delta H = Q_2 \\
&0.5Br_2(l) \longrightarrow Br_2(g) && \Delta H = 3.6 \text{ kcal} \\
&0.5Br_2(g) \longrightarrow Br(g) && \Delta H = 23.05 \text{ kcal} \\
&C_6H_5Br(l) \longrightarrow C_6H_5Br(m) && \Delta H = Q_3 \\
&C_6H_5Br(g) \longrightarrow C_6H_5Br(l) && \Delta H = -9.05 \text{ kcal} \\
&C_6H_5Cl(m) \longrightarrow C_6H_5Cl(l) && \Delta H = Q_4 \\
&C_6H_5Cl(l) \longrightarrow C_6H_5Cl(g) && \Delta H = 8.7 \text{ kcal}
\end{aligned}$$

$$C_6H_5Br(g) + Cl(g) \longrightarrow C_6H_5Cl(g) + Br(g)$$

$$\Delta H = -17.6 \pm 1 \text{ kcal} + Q_1 + Q_2 + Q_3 + Q_4$$

A priori the sum of Q_1 to Q_4 is not zero, and the observation that the volume of the system decreases as the reaction occurs testifies to that fact. However, the extremely small value of the volume change and the usual chemical considerations enable one to predict that the sum would be negligibly small and certainly well within the 1-kcal experimental uncertainty. Our value is somewhat higher than the one calculated from dissociation energies obtained by the toluene carrier method (14.6 kcal),[16] but further study will be required to ascertain which is the more reliable.

The formation of bromine chloride creates a considerable problem, for the equilibrium constant is too large to be ignored and is too small to be assumed infinite. In all calculations we have used the equilibrium constant reported by Popov and Mannion[11] and have assumed no loss of halogen by side reaction or volatilization, an assumption which is justified by past experience and control experiments. The concentrations of bromine, bromine chloride, and chlorine can then be found by solution of the simultaneous equations

$$K = [BrCl]^2/[Br_2][Cl_2]$$

$$[PhCl] = 2[Br_2] + [BrCl]$$

$$[Cl_2]_0 = [Cl_2] + [Br_2] + [BrCl]$$

We interpret the maximum observed in the instantaneous quantum yield when either bromobenzene or halogen is in excess as clear evidence for the kinetic involvement and greater reactivity of bromine chloride. Furthermore, the difference between chlorine and bromine chloride as reagents in relative rate studies (Table I) is also clear evidence for a kinetic difference between these two reagents.

Christie, Roy, and Thrush[17] have investigated the chlorine–bromine system by flash photolysis and report the following results

$$Br\cdot + Cl_2 \rightleftarrows BrCl + Cl\cdot \qquad (2)$$

$$E_a(\text{forward}) = 6.9 \text{ kcal}$$

$$E_a(\text{reverse}) = 1.1 \text{ kcal}$$

$$Br\cdot + BrCl \rightleftarrows Br_2 + Cl\cdot \qquad (3)$$

$$E_a(\text{forward}) = 8.0 \text{ kcal}$$

$$E_a(\text{reverse}) = 1.7 \text{ kcal}$$

The low activation energies for the reverse reactions assure that bromine chloride will be present in effectively equilibrium concentration at all times under our conditions. In addition, these low activation energies enable one to predict that bromine atoms will be present in quasi-equilibrium concentration at all times except during the earliest portions of the reaction. Because equilibrium favors bromine atoms over chlorine atoms by a factor of 10^4 or more, chlorine atoms cannot play a significant kinetic role in any of our experiments save those restricted to extremely low conversion, *i.e.*, those giving relative rates for chlorine as a reagent.

A kinetic formulation consistent with the considerations just given and the experimental observations outlined earlier is

$$d[PhCl]/dt = [Br\cdot][PhBr]\{k_1[Cl_2] + k_2[BrCl]\} \qquad (4)$$

Furthermore, a steady-state approximation for bromine atoms, assuming bimolecular recombination would lead to

$$[Br\cdot] = \left[\frac{\Sigma\phi_i I_i}{k_3}\right]^{1/2}$$

where $\phi_i I_i$ is the product of the light flux absorbed by

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(14) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 106.

(15) Thermochemical data taken from "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, p 20401.

(16) M. Szwarz and D. Williams, *J. Chem. Phys.*, **20**, 1171 (1952).

(17) M. I. Christie, R. S. Roy, and B. A. Thrush, *Trans. Faraday Soc.*, **55**, 1139 (1959).

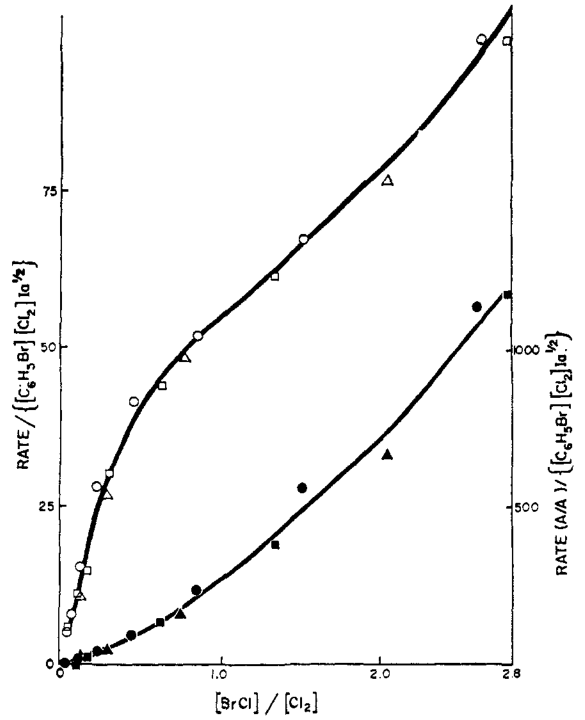

Figure 4. Kinetic plots: left ordinate, open figures; right ordinate, closed figures; 0.0256 *M* chlorine, 546 mμ; circles, 1.28 *M* PhBr, 6.22 × 10^{-9} einstein/sec; triangles, 2.56 *M* PhBr, 6.28 × 10^{-9} einstein/sec; squares, 2.56 *M* PhBr, 3.85 × 10^{-9} einstein/sec.

the *i*th absorbing species and the primary quantum yield of halogen atoms for that species. The total rate of generation of atoms, which we are assuming to be all bromine, is then the sum over all absorbing species in the medium. If all the ϕ's are nearly equal or if one is much greater than all others, the quantum yield can be factored out of the sum, and

$$[\mathrm{Br}\cdot] = \left[\frac{\phi I_a}{k_3}\right]^{1/2}$$

where I_a is the total absorbed light flux. Substitution into eq 3 yields an expression consistent with our observation of half-order dependence upon absorbed light intensity.

If ϕ were a constant throughout reaction or some considerable fraction, eq 4 predicts that a plot of

$$\frac{d[\mathrm{PhCl}]/dt}{[\mathrm{Cl_2}][\mathrm{PhBr}]I_a^{1/2}} \ vs.\ \frac{[\mathrm{BrCl}]}{[\mathrm{Cl_2}]}$$

would be linear for that portion of the reaction for which uniform generation of bromine atoms throughout the reaction mixture could be assumed. Unfortunately, that assumption can be applied only to a small segment of each run at 546 mμ and to none of the runs at shorter wavelengths. To circumvent this difficulty we propose that an approximate correction can be made by applying the concept of effective thickness.

The uniform generation of atoms becomes strictly true only as the absorbance of the reacting system approaches zero. Under this condition the entire thickness of the sample cell would be "effective." As the absorbance of the system increases, the rearmost layers of the cell receive less and less illumination, or to put it another way the proportion of the cell which receives effectively the same intensity of illumination as the entire cell at the outset would become progressively smaller. Since this proportion would be unity at zero absorbance and zero at infinite absorbance, we suggest that the observed rate of the photochemical reaction can be multiplied by the ratio of the absorbance of the reacting system to its initial absorbance to allow approximately for changes of the nonuniform generation of active centers.

Indeed, multiplication by the factor A/A_0 converts plots of the quantity $(d[\mathrm{PhCl}]/dt)/\{[\mathrm{PhBr}][\mathrm{Cl_2}]I_a^{1/2}\}$ *vs.* $[\mathrm{BrCl}]/[\mathrm{Cl_2}]$ from a complex shape to near linearity as shown in Figure 4 for the first half of each of three runs made at 546 mμ. These runs were made at constant halogen concentration, but the bromobenzene concentrations and light intensities were varied. The slight upward curvature of the lower plot could be a result of lack of accuracy in the measurement of absorbance, which is magnified, of course, by using the ratio of two such values. At this juncture, we wish to suggest that this formulation (of the large number we have investigated) offers the most consistent explanation of the data.

The extremely long induction periods of the runs made at 546 mμ (*cf.* Figure 1) are perhaps as much a result of a low quantum efficiency of dissociation of chlorine at this wavelength, which is longer than the so-called threshold wavelength (about 490 mμ) required for dissociation of an isolated ground-state chlorine molecule, as a result of low absorbance. The considerations discussed by Innes,[18] as well as specific solution interactions, make the dissociation of chlorine perfectly plausible at this wavelength, but one would expect the efficiency to be low.

Application of the rate eq 4 to competitive rate experiments yields

$$\frac{d[\mathrm{Ph'Cl}]}{d[\mathrm{PhCl}]} = \frac{[\mathrm{Ph'Br}]\{k_1'[\mathrm{Cl_2}] + k_2'[\mathrm{BrCl}]\}}{[\mathrm{PhBr}]\{k_1[\mathrm{Cl_2}] + k_2[\mathrm{BrCl}]\}} \qquad (5)$$

That the relative rate of product formation is determined by k_2'/k_2 when the concentration of chlorine is small is immediately apparent. However, the results in Table I for chlorine may well not be simply k_1'/k_1 in the sense of eq 4 and 5 because the experimental conditions were necessarily such that the assumption of propagation of chains solely by bromine atoms is not entirely justified. In fact, there are indications that the assumption does fail as developed in the following paragraphs.

The results for mixed chlorine–bromine chloride given in Table I were obtained by adding a small quantity of chlorine and permitting the reaction to proceed to completion, *i.e.*, until all chlorine was converted to bromine. Thus, these results represent, by eq 5, an integrated average of k_1'/k_1 and k_2'/k_2. Substitution of the function relating chlorine, bromine chloride, and products into eq 5 results in an intractable equation. Therefore, the mixed $\mathrm{Cl_2}$–BrCl data, obtained by such a bequilingly simple technique, are of empirical interest only.

If one uses separately determined ratios of k_1's and k_2's and assumes a ratio of k_1/k_2, numerical integration of eq 5 is possible. The ratio k_1/k_2 is of chlorine and bromine chloride rate constants for unsubstituted

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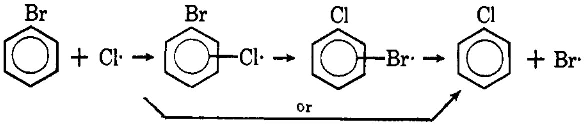
[18] K. Innes, *J. Chem. Educ.*, **42**, 190 (1965).

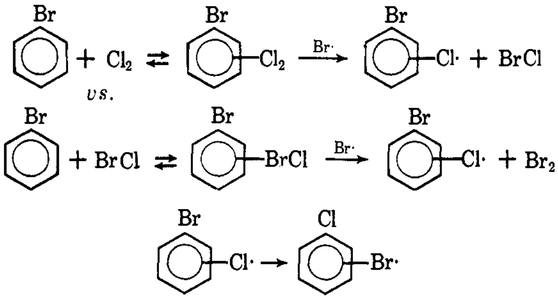
bromobenzene, and the same value should apply to all results. Thus, the correct k_1/k_2 value together with k_1'/k_1 and k_2'/k_2 for a given substituent should lead under numerical integration to the mixed Cl_2–BrCl result, or, if a series of k_1/k_2 values is used, the same value should give the observed result for every substituent. However, no tendency toward such behavior was observed. We conclude that the data obtained using chlorine as the reagent probably embody a substantial contribution from propagation by chlorine atoms. An alternative interpretation is that $k_1/k_2 << 1$, which would mean that our techniques did not completely eliminate contributions from bromine chloride. However, the kinetic data suggest that k_1/k_2 is on the order of 10^1–10^2, and we favor the former interpretation.

Results reported in the past[3] showed that substituent effects for displacement of bromine by chlorine depend upon whether chlorine or iodine chloride is the initial reagent, but these results are complicated by the fact that the iodine chloride reaction is a nonchain process. The present results do not include such a complication and point clearly to the conclusion that a simple displacement mechanism involving only chlorine atoms (whether with or without the intermediacy of a π complex) as shown in eq 6 is not applicable.



(6)

An alternative involving formation of an atom–molecule complex through the intermediacy of a molecule–molecule complex (7) is untenable on two grounds despite the fact that it offers kinetic differentiation of Cl_2 and BrCl.



(7a)

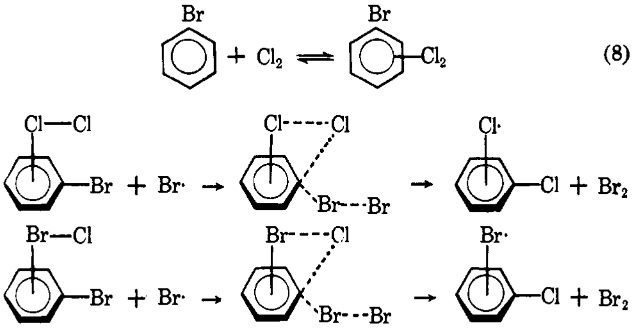
(7b)

(7c)

First, the positive or bromine end of the bromine–chlorine dipole should be the more closely bound to the aromatic donor in a π complex, making eq 7b most improbable. Second, such a mechanism is unable to explain the fact that bromine chloride is more reactive than chlorine. The data of Christie, Roy, and Thrush[17] show that the reaction of eq 2 is faster than that of eq 3 in the gas phase. In solution, the greater acidity of bromine chloride and the resultant tendency toward complex formation would *accentuate* the corresponding rate differential. Thus, the propagation step of eq 7a is predicted to be faster than that of eq 7b, contrary to observation.

Rate-determining formation of the molecular complexes between chlorine or bromine chloride and the aryl bromide is not only inconsistent with general knowledge of complex formation but is also contradicted by our observation of dependence upon light intensity.

We now postulate that reaction occurs by bromine atom attack upon the carbon-bound bromine atom of a complex of aryl bromide with halogen in a concerted displacement as shown in eq 8.



(8)

One immediately notes that propagation through attack on a chlorine molecule complex leads to formation of a chlorine atom while attack upon a bromine chloride complex leads to formation of a bromine atom. Although both processes are exothermic, a higher activation energy for the chlorine atom forming process does not seem out of reason.

Our formulation of the complexes in the manner shown is intended to be merely indicative, for the geometry of the complex could be quite different without altering the kinetic consequences. Therefore, this mechanism should be placed in Kowsower's classification C (or chaperon)[19] unless further evidence upon the nature of the complexes themselves should reveal that their geometries are especially favorable to the reactions. The constants of eq 4 and 5 now become products of rate constants for propagation and equilibrium constants for complex formation. As previously stated[3] such a formulation is necessary but is also sufficient to explain the character of the differential activation parameters derived from the variation of relative rates with temperature.

An additional question which arises is the possibility that chains are propagated by complexed rather than by free halogen atoms. According to the model provided by the work of Russell and co-workers[20] on complexed chlorine atoms, the addition of strong donors to the reaction medium should alter relative reactivities. However, relative reactivities are nearly insensitive to the addition of such donors as benzene and carbon disulfide.[21] However, there is some evidence that bromine atom–aromatic complexes are appreciably dissociated,[22] and since the free atoms in equilibrium with the complex would naturally be more reactive, the greater selectivity of the complex would not manifest itself.

In the section on results, the fact was mentioned that different proportionalities between concentration and rate apply at high and at low bromobenzene concentrations. That is, low concentrations (chlorine and bromobenzene both in the range of 0.02 *M*) yield plots similar to those in Figure 4, but the slopes are greater by a factor of about 10. Such behavior can be ra-

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(19) E. M. Kowsower, *Progr. Phys. Org. Chem.*, **3**, 81 (1966).

(20) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4998, 5992 (1958); *Tetrahedron*, **8**, 101 (1960); G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963).

(21) H. W. G. Seay, unpublished results.

(22) J. S. Bartlett, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1962.

tionalized by means of a kinetic law such as

$$\frac{d[PhCl]}{dt} = \left[\frac{\phi I_a}{k_3}\right]^{1/2}\left[\frac{a + b[PhBr]^n}{c + e[PhBr]^n}\right]^m \times [PhBr]\{k_1[Cl_2] + k_2[BrCl]\}$$

Thus, when the concentration of bromobenzene is small the rate would be proportional to a/c, and when bromobenzene concentration is large the rate would be proportional to b/e. Any number of schemes leading to such a law suggest themselves, but their consideration without additional data does not seem appropriate.

Acknowledgment. We wish to thank Brown University for computer time when B. M. was visiting there on sabbatical leave.

Anodic Oxidations. IV. The Electrochemical Oxidation of the Side Chain of Mesitylene and Toluene in Acetic Acid

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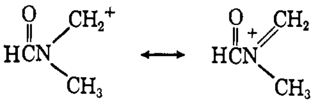
Contribution from the Research and Development Center, Sprague Electric Company, North Adams, Massachusetts 01247. *Received March 28, 1967*

Abstract: The electrochemical oxidation of mesitylene and toluene in acetic acid containing tetramethylammonium nitrate results almost exclusively in substitution of the side chain rather than the ring. These products include the benzyl nitrates, the benzyl acetates, and the bibenzyls as well as further oxidation products, benzaldehydes, and benzal diacetates. Evidence is presented in support of a mechanism in which the first two steps are: (1) discharge of a nitrate ion to give a nitrate radical, and (2) hydrogen abstraction by the nitrate radical on the aromatic substrate to give a benzyl radical.

When N,N-dimethylformamide is oxidized anodically in acetic acid containing acetate ion, it is the amide rather than acetate ion which is oxidized at the electrode in the primary step.[1,2] When the anodic acetoxylation is carried out in acetic acid containing ammonium nitrate, nitrate ion is oxidized in the primary anodic process.[3] Both reactions lead to the same product, N-acetoxymethyl-N-methylformamide, since in both reactions the product-forming intermediate is almost certainly the cation, I. The essential difference between the two systems is not in the nature of the product but in the manner in which I is generated.



I

In the electrochemical acetoxylation of alkyl-substituted aromatic hydrocarbons, *e.g.*, ethylbenzene and mesitylene, the primary anodic process is again the oxidation of the hydrocarbon rather than acetate ion.[2,4] The reaction is a complex one, since discharge of acetate ion accompanies the anodic oxidation of the hydrocarbon. The total product contains both ring- and side-chain-substituted acetoxylation products as well as ring- and side-chain-substituted methylation products. Nevertheless, the predominant reaction mode is acetoxylation, with substitution on the ring.

If such substrates could be electrochemically reacted in a system such that an anion, *e.g.*, nitrate ion, is oxidized at the anode in the primary step in preference to the hydrocarbon, one might hope to find the product composition significantly altered. In particular one might hope to eliminate the methylation products and find that the major site of attack is now the side chain rather than the ring. The present study was designed to explore this possibility by investigating the anodic oxidation of mesitylene and toluene in acetic acid containing tetramethylammonium nitrate.

Results

When a solution of mesitylene (10 ml) and tetramethylammonium nitrate (0.05 mole) in glacial acetic acid (50 ml) is electrolyzed at a current of 400 ma, the only gaseous product produced is hydrogen, and it is formed at almost exactly the theoretical rate of 1 mole of hydrogen per 2 faradays of charge passed through the solution.[5] To determine the nongaseous products formed in this reaction the electrolysis was run in the larger apparatus described in the Experimental Section. In this experiment a solution of mesitylene (0.144 mole) and tetramethylammonium nitrate (0.20 mole) in glacial acetic acid (160 ml) was electrolyzed at 2.0 amps until 2.02 equiv of charge per mole of mesitylene was passed through the solution. The products, determined by vpc, are listed in Table I.

The products listed in Table I account for more than 55% of the starting mesitylene. In addition it was possible to isolate, by a combination of molecular distillation and column chromatography, a sufficient amount of 3,3′,5,5′-tetramethylbibenzyl to unequivocally establish its presence in the reaction mixture.

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

[2] L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

[3] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **88**, 4657 (1966).

[4] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 4139 (1964).

[5] For a description of the apparatus and procedure used in this determination see ref 4.