for 20 min in the constant-temperature bath before starting measurements.

The Rate of Hydrolysis of *p*-Methoxybenzenediazonium Fluoroborate. This rate was measured at 90.5°, and confirmed the first-order rate constant measured at this temperature by Insole.[9] The method of measurement was identical with that described above for *p*-chlorobenzenediazonium fluoroborate.

The Determination of *m*, the Fraction of Primary Nitrogen. The fraction of primary nitrogen, *m*, was determined by measuring the volumes of primary and secondary nitrogen formed in the azide reaction.

p-Chlorobenzenediazonium fluoroborate (160 mg) was dissolved in a solution of aqueous ethanol (50 ml of 0.01 *N* sulfuric acid, 39 ml of ethanol) and cooled to −27°. Carbon dioxide was bubbled through the well-stirred solution until all of the dissolved air was removed from the system. A threefold excess of sodium azide in 10 ml of 5 to 1 aqueous ethanol was added to the diazonium salt solution through a rubber septum in the top of reactor. (The azide solution had been degassed previously.) The primary nitrogen, which was evolved over a 1-hr period, was swept from the reactor with carbon dioxide and collected in a nitrometer containing 50% potassium hydroxide solution. After the primary nitrogen was collected, the pentazole solution was warmed to room temperature, and the secondary nitrogen was collected in a similar manner. Corrections were made for impurities present in the carbon dioxide by running a blank. The fraction of primary nitrogen, *m*, was calculated by simply dividing the volume of primary nitrogen collected by the total volume of nitrogen collected. The values of *m* measured were: *m*-toluenediazonium ion, *m* = 0.71; *p*-chlorobenzenediazonium ion, *m* = 0.78; *p*-methoxybenzenediazonium ion, *m* = 0.64.

Relation between Thermal and Photochemical Hydrolyses of Diazonium Salts[1]

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Abstract: In the presence of chloride ion, aryl chlorides as well as phenols result from the photolysis of aranediazonium salts in aqueous solution, as in the thermal reaction. Benzenediazonium ion in aqueous sodium chloride yields just as much chlorobenzene in the photolysis as it does thermally at the same temperature, but others (*p*-CH$_3$C$_6$H$_4$N$_2^+$, *p*-ClC$_6$H$_4$N$_2^+$) give a significantly higher yield of the chloride photochemically than thermally. A similarity but not identity of product-determining steps is indicated. When *p*-CH$_3$C$_6$H$_4$^{15}N$^+$≡N and *p*-CH$_3$OC$_6$-H$_4$^{15}N$^+$≡N are exposed to light insufficient to complete the photolysis, the residual diazonium salt is in part rearranged to Ar$^+$N^{15}≡N, and the relative extents of rearrangement to hydrolysis are significantly more than in the corresponding dark hydrolysis. There are major uncertainties in the photochemical mechanism, but it can be unequivocally concluded that there is no single intermediate common to the photochemical and thermal reactions.

The photosensitivity of diazonium salts has long been known and has been the subject of much published work[5,6] and probably a great deal of unpublished work also, since destruction of diazonium salts by light is the basis of "diazotype" processes. Very little modern photochemistry has been done on solutions of diazonium salts; a paper on *p*-nitrobenzenediazonium ion in ethanol disclosed the contribution of both radical and ionic processes,[7] but uncovered more questions than were answered. It was established that a phenol-forming reaction is important in photolysis of aqueous solutions, suggesting that the photolysis of diazonium salts constituted an alternative synthesis of the aryl cat-ion, the proposed[8] intermediate in the thermal hydrolysis. Although the intermediate was believed to be highly reactive, it might be characterized by the result of competition for it between chloride ion and water, *i.e.*, relative the yields of chlorobenzene and phenol.[9] If the thermal and photochemical reactions passed through a common intermediate (the aryl cation or some other), then the yield of chlorobenzene in the reaction of benzenediazonium ion in a given solution of sodium chloride in water should be independent of whether the necessary energy is provided thermally or photochemically.

The intermediacy of an irreversibly formed aryl cation in the thermal reaction is now eliminated,[10] but the existence of a high-energy nitrogen containing intermediate was rejected only because no satisfactory structure could be proposed. The possibility of a common intermediate therefore remained a remote possibility and was worth investigating.

When the two nitrogens of a diazonium salt are rendered distinguishable by nitrogen labeling, a rearrangement accompanies thermal hydrolysis,[11] and the mech-

(1) Reactions of Diazonium Salts with Nucleophiles. XV. From portions of the Ph.D. theses of Robert E. Holliday and Levoy D. Hartung, 1966.

(2) John Simon Guggenheim Fellow at the Physical Chemistry Laboratory, Oxford, 1968.

(3) National Aeronautics and Space Administration Trainee, 1964–1966.

(4) Robert A. Welch Foundation predoctoral fellow, 1963–1966.

(5) Older work is summarized by K. H. Saunders, "The Aromatic Diazo Compounds," 2nd ed, E. Arnold and Co., London, 1949.

(6) Some newer work is summarized by J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 473.

(7) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Amer. Chem. Soc.*, **83**, 1928 (1961).

(8) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(9) E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 1371 (1958).

(10) E. S. Lewis, L. D. Hartung, and B. M. McKay, *ibid.*, **91**, 419 (1969).

anism of the rearrangement closely resembles that of the hydrolysis.[12] It appeared to be of interest to see if a photochemical rearrangement reaction can occur.

Results and Discussion

The determination of yields of chlorobenzene from the photolysis of benzenediazonium ion suffers from a difficulty not present in the thermal reaction: chlorobenzene itself is destroyed by illumination. Two methods were used to overcome this difficulty. First, and simplest, is to interpose a Pyrex filter between the light source and the solution. This eliminates the wavelengths to which chlorobenzene is sensitive and therefore prevents the product photolysis. It also cuts out a great deal of the light absorbed by the diazonium salts, but these have a low intensity tail in the absorption spectrum going into the region of Pyrex transparency, and thus are sensitive to the filtered light. The alternative method was to operate the photoreaction vessel as one part of a continuous extractor and remove the chlorobenzene into petroleum ether (bp 30–60°) rapidly, thus reducing the time of exposure to the unfiltered source. The chlorobenzene yields were the same by either method, suggesting that the product is insensitive to wavelength, at least between the region of Pyrex cutoff and the major output of the medium-pressure mercury arc. When the unfiltered light was used without the extraction apparatus, control runs suggested that about 10% of the chlorobenzene might have been lost.

The yields of aryl chlorides from a number of runs on three different diazonium salts are presented in Table I, along with the corresponding results of thermal experi-

Table I. Yields of Aryl Chloride from Diazonium Salts in Aqueous Sodium Chloride

Diazonium salt	(NaCl), M	Y_{ArCl}^{photo}, % at 4 ± 4°	$Y_{ArCl}^{thermal}$, % (t, °C)
$C_6H_5N_2^+$	0.2	2.5	2.5 (3)[a]
	0.5	5.0	4.9 (3)[a]
	1.0	8.5	
	2.0	14.2	
	3.0	19.3	
p-$CH_3C_6H_4N_2^+$	0.2	3.2	2.1[b] (49)
	0.5	6.8	4.4[b] (49)
	1.0	11.0	6.8[b] (49)
	1.0		7.5 (49)
	1.0		7.5 (36)
	1.0		7.3 (62)
	2.0	17.9	11.9[b] (49)
	3.0	24.1	16.6[b] (49)
	1.0[c]	9.9[c]	
	1.0[d]	11.5[d]	
p-$ClC_6H_4N_2^+$	0.2	3.8	2.5 (80)
	0.5	7.7	4.5 (80)
	1.0	11.9	7.7 (80)
	2.0	17.5	13.7 (80)
	3.0	24.2	18.7 (80)

[a] Interpolated from more extensive data shown in Figure 1. [b] Yields measured in open system as in ref 9. These values in general run about 10% low. [c] In pH 7 phosphate buffer. [d] 1 M hydrochloric acid instead of sodium chloride.

ments. Many experiments were run several times under identical conditions. All yields fell within 3%

(11) J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32 (1964).

(12) E. S. Lewis and R. E. Holliday, *ibid.*, **88**, 5043 (1966); E. S. Lewis and R. E. Holliday, *ibid.*, **91**, 426 (1969).
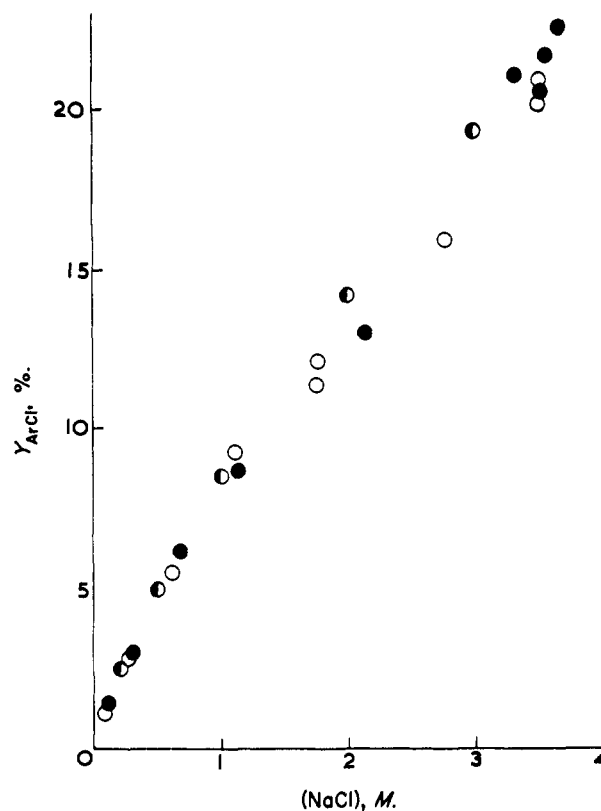

Figure 1. Relation between thermal and photochemical yields of chlorobenzene in sodium chloride solutions of benzenediazonium ion: O, thermal reaction, 3°; ●, photochemical reaction, 4 ± 4°, unfiltered light on continuously extracted solution; ◐, photochemical reaction, 4 ± 4°, with Pyrex filter.

(relative) of the means given, with the exception of those marked *b*. In these thermal reactions the vessel was not sealed, and as described before[10] and illustrated in one case here with 1 M sodium chloride, there is a loss of about 10% of the aryl halide by vaporization. The similarity between the photochemical and thermal yields from benzenediazonium ion, shown only briefly in the table, is illustrated forcibly in Figure 1, in which the results of an extensive series of thermal runs at 3° (previously presented in Figure 2 of ref 10) and those of a number of photochemical runs (including those of Table I) are shown. The differences in yields between thermal and photochemical processes are within the scatter of either, which is somewhat greater than the 3% mentioned above, probably because it represents the independent work of two men using different techniques. A slight case could be made for somewhat greater photochemical yields.

With p-toluenediazonium ion the photochemical yields are distinctly larger. Thermal yields at three different temperatures from 36 to 62° show that these are insensitive to, if not even independent of temperature, in agreement with results on benzenediazonium ion.[10] It therefore is unlikely that the thermal yields would increase to the photochemical ones at 4°. The last two entries show that the yields are insensitive to the nature of the cation or the pH. The somewhat lower yield at pH 7 doubtless reflects loss of diazonium salt by coupling with p-cresol.

High photochemical yields also characterize p-chlorobenzenediazonium ion, although still further evidence

of temperature independence of the thermal yields is lacking.

An obvious trivial explanation of the similarities, if not the differences, is that there is in fact no photochemical reaction at all, and the effect of the source is merely to warm the solution. Since the solution was cooled on both the lamp side and the outside by ice water, and the lamp was only 200 W total, this explanation is highly improbable. The temperature given, $4 \pm 4°$, is believed to cover all such uncertainties. The diazonium ion was entirely gone in 2–3 hr of illumination; the half-life of the thermal reaction at these temperatures was several days to many weeks. The existence of a real photochemical reaction is established.

The fact that the yields differ in the two processes indicates that they do not pass exclusively through a common intermediate. The conclusion is rigorous unless there is a very peculiar temperature dependence, not shared by the unsubstituted compound, of the thermal yields. In view of the probability that the photochemical reaction is a reaction of an excited state of the diazonium ion, whereas the thermal reaction appears to be a one-step bimolecular reaction,[10] the similarity of yields is more surprising than the difference. It is a little surprising that the photochemical reaction, which must involve the higher energy transition state, is somewhat more selective.

The close similarity brings up the question of whether the isotopic rearrangement of ^{15}N-labeled diazonium salts can also occur photochemically. For quantitative comparison it was desirable to compare the rates of rearrangement to those of hydrolysis, and this could be done, as in the thermal reaction, by recovering diazonium salt after partial hydrolysis. In order to have a meaningful result, it is necessary that the recovered diazonium ion should have been exposed to the reaction conditions, and not merely be a sample which had escaped illumination. This was achieved by putting the diazonium salt in a very thin annular cell around the light, so that when the solutions were sufficiently dilute, the absorbance was small and the entire sample was exposed to essentially the same intensity of light. The criterion that this situation was achieved was that at constant light intensity, the disappearance of diazonium salt (as measured by coupling) followed a first-order course. When the cell was too thick or the solution too concentrated, the rate was limited by light output, and a zero-order course was approached.

Two diazonium salts, the p-toluenediazonium and p-methoxybenzenediazonium salts were used, and with the first, we were able to achieve the desired conditions. However, the most dilute practical solutions of p-methoxybenzenediazonium fluoroborate still gave some initial downward concavity in a plot of log (ArN_2^+) vs. time. The first-order plot was nevertheless better than a zero-order plot. We attribute this to the higher extinction coefficient of this salt at the wavelengths used (medium-pressure mercury arc, Pyrex filter), but recognize the possibility that the deviation from a first-order course could also be caused by a product-sensitized reaction. This is not completely unlikely, for perceptible amounts of parabenzoquinone are formed in the thermal reaction.[13] The behavior was nevertheless very similar to that of p-toluenediazonium ion at too

(13) J. M. Insole, unpublished observations.

high a concentration, so the excessive absorption explanation is reasonable. Table II presents the results of these experiments, using the notation of the earlier papers.[11,12]
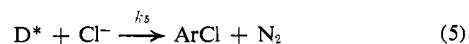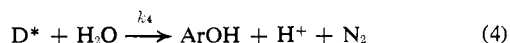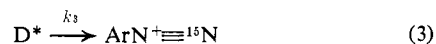
Table II. Extent of Photochemical Rearrangement of Isotopically Labeled Benzenediazonium Salts

para substituent	Extent of photolysis, %	P_{sec}, %	P_{ars}, %	R_{sec}	R_{ars}	$R_{thermal}$
CH$_3$	40.5	6.91	5.56	0.19	0.15	
CH$_3$	44.2	5.65	5.56	0.10	0.10	
CH$_3$	47.5	7.25	7.17	0.12	0.12	
CH$_3$	...	...	Av	0.13		0.03[12]
OCH$_3$	56^a	4.45	...	0.056^a		
OCH$_3$	55^a	5.57	...	0.075^a		
OCH$_3$	...	...	Av	0.066^a		0.038[12]

^{a} The reaction did not follow an exact first-order course.

Table II shows that there is a photochemical rearrangement which is more extensive than in the thermal hydrolysis, in the case of p-toluenediazonium ion by a factor of about 4. The value of relative rate of rearrangement to hydrolysis (R) for the p-methoxy compound is a lower limit, if the explanation for deviation from a first-order course is correct, but even this lower limit for R is almost twice the value for the thermal reaction.
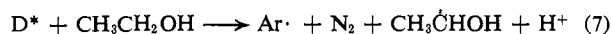
The presence of the photochemical rearrangement allows us to reject the intermediacy of the aryl cation as the only intermediate leading to products, and the slightly greater selectivity of the photochemical reaction suggests that it is not an intermediate on the route to phenols or aryl chlorides. A simple mechanism adequate to describe all results is given below, and the similarity but nonidentity of the thermal and photochemical processes is an obvious consequence.

$$Ar^{15}N^+ \!\!\equiv\!\! N \xrightarrow{h\nu} D^* \qquad (1)$$

$$D^* \xrightarrow{k_2} Ar^{15}N^+ \!\!\equiv\!\! N \qquad (2)$$

$$D^* \xrightarrow{k_3} ArN^+ \!\!\equiv\!\! ^{15}N \qquad (3)$$

$$D^* + H_2O \xrightarrow{k_4} ArOH + H^+ + N_2 \qquad (4)$$

$$D^* + Cl^- \xrightarrow{k_5} ArCl + N_2 \qquad (5)$$

Reaction 1 conceals the complex process following the absorption of light and leading to a state (of unestablished multiplicity) stable enough to undergo the bimolecular reactions 4 and 5. Reaction 2 is included simply because it seems unreasonable that (3) would occur without (2). It is of course undetectable by our product studies. It is reasonable that the transition states of the bimolecular reactions 4 and 5, which are presumably highly exothermic, could resemble the transition states for the high activition energy thermal substitution reactions.

It is attractive to identify D^* with the intermediate in the photolysis of p-nitrobenzenediazonium ion,[7] which shows in water reactions 4 and 5 and in ethanol two reac-

tions which may rewrite as (6) and (7), to account for all

$$D^* + CH_3CH_2OH \longrightarrow ArOCH_2CH_3 + N_2 + H^+ \quad (6)$$

$$D^* + CH_3CH_2OH \longrightarrow Ar\cdot + N_2 + CH_3\dot{C}HOH + H^+ \quad (7)$$

the observed products.

Equation 8 expresses the quantum yield of nitrogen (ϕ_{N_2}) which arises from this mechanism. It is assumed

$$\phi_{N_2} = \frac{\alpha k_4}{k_2 + k_3 + k_4} \quad (8)$$

that water is the only nucleophile, *i.e.*, that only reaction 4 gives nitrogen, and α is the quantum yield of D*. Writing for convenience $k_2 = ck_3$, in which it is unreasonable to assume $c < 1$, we get eq 9, where R, as before,

$$\phi_{N_2} = \alpha k_4/[k_4 + (1 + c)k_3] = \alpha/[1 + (1 + c)R] \quad (9)$$

is k_3/k_4. We can then put an upper limit on ϕ_{N_2}, by assuming $\alpha = 1$ and $c = 1$, which is then expressed by (10).

$$\phi_{N_2} \leqslant 1/(1 + 2R) \quad (10)$$

The observed value of $R = 0.12$ for p-toluenediazonium ion gives an upper limit of $\phi_{N_2} = 0.79$. The quantum yield in this reaction has not been measured, but several others have been measured,[6] with values ranging from 0.2 to 0.74 in solution for various diazonium salts. It thus appears that c can not in general have very high values, for it would lead to quantum yields below those measured, even if α were unity.

One may speculate that D* corresponds to the species observed by Lee, Calvert, and Malmberg[7] from the low-temperature irradiations of p-dimethylaminobenzene-diazonium hexachlorostannate, for which the symmetric structure I was tentatively suggested by Calvert and Pitts,[6] reminiscent of the similar structure proposed[14]

(14) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **86**, 34 (1964).

for the thermal reaction but rejected because the evidence for it was shown to be largely due to coincidence.[10,12] This structure necessarily requires that $k_3 = k_4$ and hence that $c = 1$, so values of ϕ_{N_2} less than the largest value calculated by eq 10 can only be due to less than unit values of α. This speculation is subject to experimental test, certainly in part by determining ϕ_{N_2} and R in the same system.
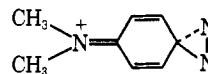
Experimental Section

Materials. All diazonium salts were prepared as the fluoroborates as before,[10,12] and mostly are the same samples.

Methods. Irradiation was carried out using a Hanovia 654A medium-pressure source in a water-cooled Pyrex immersion well. For the yield studies a commercial vessel, of 500-ml capacity surrounding the immersion well was used. It was stirred magnetically to remove solution from any dark region. The apparatus using continuous extraction and a quartz immersion well offers no special advantages, it is described in detail in the thesis of Hartung.[1] For the rate and isomerization studies, a much thinner vessel, with a thickness of 0.35 cm was used. It had a capacity of about 100 ml, and the products of irradiation of several fillings with 10^{-3} M diazonium salt solution were combined in order to get enough remaining diazonium salt for analysis. The dilute solutions of p-toluenediazonium salt were worked up by an ion-exchange procedure.[12] The dilute solutions of the more stable p-methoxybenzenediazonium salt were concentrated on a rotary evaporator. The degradation and isotopic analyses have been described before.[12] In each case the extent of reaction was determined by a coupling analysis of the solution[10,12] after about 2–3 min of irradiation.

Yields. Photochemical and thermal reaction yields of aryl chlorides were determined as before,[10] using p-chloroanisole as an internal standard for p-dichlorobenzene. Except for a few runs on the p-tolyl compound, all thermal runs were sealed to prevent loss.

Rates. The rates of photolysis were measured by the coupling analysis; the rates are not given since they depend on light intensity and distribution. With the same source, the p-methoxy compound reacted about six times as fast as the p-methyl compound in the thin cell.