[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

# CATALYTIC EFFECTS IN THE BROMINATION OF TOLUENE

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Numerous previous investigations of the bromination of toluene have dealt with the effects of light, temperature, concentrations, catalysts, and solvents. Of various interpretative hypotheses hitherto advanced, none accounts adequately for all the phenomena reported.

The observation in this laboratory that side-chain bromination of toluene is markedly facilitated by traces of organic peroxides and oxygen may be interpreted in a manner that permits the correlation of many hitherto unrelated, and some apparently discordant, data. In the light of the present and previous studies[1] the authors believe that hydrogen bromide is a source of bromine atoms in the presence of oxygen and sufficiently active oxygen-carriers. The working hypothesis proposed is that side-chain bromination of toluene is a chain reaction initiated by bromine atoms, whereas nuclear bromination is a slow bimolecular reaction in which bromine atoms do not participate. It is the purpose of the present communication to show that this hypothesis is consistent with the earlier experimental data, and to report certain supplementary studies that also tend to support it.

## REVIEW OF THE LITERATURE

It was early observed that nuclear and side-chain bromination of toluene are two separate and independent reactions and that their relative rates, and consequently the ratios of their respective products, vary widely with the experimental conditions.[2] Ordinarily *o*- and *p*-bromotoluenes (hereafter referred to as "bromotoluenes") are the only products of nuclear bromination. *m*-Bromotoluene is formed only in very high bromine concentrations, and in the presence of a catalyst.[3] Even then, the yield is only a fraction of one per cent. Likewise, polybromo compounds are not formed except in the presence of large amounts of catalyst, such as thirty mole per cent. of aluminum bromide,[2] or beryllium bromide.[4]

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[1] KHARASCH, MARGOLIS, WHITE, AND MAYO, *J. Am. Chem. Soc.*, **59**, 1405 (1937); KHARASCH, ENGELMANN, AND MAYO, J. ORG. CHEM., **2**, 298 (1937).

[2] VAN DER LAAN, *Rec. trav. chim.*, **26**, 1 (1907).

[3] HOLLEMAN, *ibid.*, **33**, 183 (1914).

[4] PAJEAU, *Compt. rend.*, **202**, 1795 (1936).

Catalysts exert a strong influence on the direction of bromine substitution in toluene. In general the catalytic effect may be divided into two classes. Metals, metal halides, and iodine increase the rate of nuclear substitution. Aluminum bromide seems to be the most effective of such catalysts. At 50° as little as 0.4 mole per cent of aluminum bromide (per mole of bromine) raises the yield of bromotoluenes from 46 per cent. to 99.5 per cent.[2] To produce such an effect with iodine at 25°, about 5 mole per cent. is required.[5] Photobromination, even in diffuse light yields 98 per cent. of benzyl bromide, and is complete in a few minutes, while reaction in the dark requires many days.[2] Ozone has an effect similar to light, greatly accelerating the side-chain reaction.[6] It appears to be a general rule that when benzyl bromide is the predominant product, the reaction is an extremely rapid one, while nuclear substitution is by comparison slow. Such a difference is to be expected between a bimolecular reaction and a chain reaction involving bromine atoms. The chain reaction involves unstable reactive intermediates; it must proceed rapidly or not at all.

TABLE I

EFFECT OF DILUTION UPON THE RATIO OF SUBSTITUTION PRODUCTS

| MOLE RATIO TOLUENE/BROMINE | BENZYL BROMIDE IN TOTAL BROMIDES (%) |
|---|---|
| 4.3 | 24 |
| 8.0 | 42 |
| 10.4 | 56 |
| 20.6 | 82 |
| 28.5 | 95 |

Temperature exerts a strong influence on the direction as well as the rate of the bromination reaction. Regardless of other factors, such as concentration and catalysts, it is uniformly true that the higher the temperature, the higher the yield of benzyl bromide.[2]

The effect of the bromine concentration upon the ratio of the two products in the absence of solvent and catalyst, was first observed by Bruner and Dluska,[5] and later studied by Holleman and Polak[7]. The more dilute the solution the higher is the relative yield of benzyl bromide. The effect appears at all temperatures studied. Table I records the results of reactions carried out by Holleman[7] at 50° in the dark, and allowed to run to com-

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[5] BRUNER AND DLUSKA, *Bull. intern. acad. sci. Cracovie*, **1907**, 691; *C. A.*, **2**, 1272 (1908).

[6] BRUNER AND LAHOCINSKI, *ibid.*, **1910**, 560; *C. A.*, **5**, 3045 (1911).

[7] HOLLEMAN AND POLAK, *Rec. trav. chim.* **27**, 435 (1908).

pletion. At very high dilution (100:1 or greater) and at elevated temperature the product is 100 per cent. benzyl bromide.

The dependence of the type of substitution upon concentration indicates that diminishing bromine concentration will change the direction of substitution during the course of the reaction. Hence the ratio of the products depends upon the point at which the reaction is stopped. Failure to recognize this is doubtless the cause of considerable disagreement among the observations of the early workers. Because Holleman's reaction went to completion his results do not show, as do those of Bruner, the interesting fact that while the rate of nuclear substitution falls off normally with increasing dilution, the rate of substitution in the side-chain is actually higher in more dilute solutions.[5] This would be expected if bromine molecules in some way hinder the side-chain substitution. We believe that bromine molecules act as "chain breakers" by combining with bromine atoms. Hence the rate of substitution in the methyl group decreases with increasing concentration of molecular bromine.

TABLE II

Effect of Solvents on the Bromination of Toluene[a]

| SOLVENT | TIME, DAYS | BROMINE REACTED (%) | BENZYL BROMIDE IN TOTAL BROMIDES (%) |
|---|---|---|---|
| Carbon disulfide | 33 | 38 | 82 |
| Carbon tetrachloride | 30 | 48 | 50 |
| Benzene | 30 | 73 | 38 |
| Acetic acid | 5.5 | 61 | 4 |
| Nitrobenzene | 1 | 92 | 3 |

[a] The toluene/bromine ratio was 10:1; solvents were added to give a volume equivalent to that of a 40:1 toluene-bromine mixture.

Bruner and his co-workers also studied the effect of various solvents on the bromination of toluene, both in the light and in the dark. For the dark reaction the results set forth in Table II are representative.[8] These investigators call attention to the direct relation between the ionizing power of the solvent and its effect in catalyzing nuclear and inhibiting side-chain substitution. Although carbon disulfide and carbon tetrachloride act merely as inert diluents, acetic acid and nitrobenzene have pronounced effects. Similar influences prevail in the photobromination, where acetic acid and nitrobenzene retard the rate of reaction and lower the yield of benzyl bromide to about 70 per cent.

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[8] Bruner and Vorbrodt, *Bull. intern. acad. sci. Cracovie*, **1909**, 221; *C. A.*, **4**, 3067 (1910).

A brief outline of the various theories proposed to account for the solvent effect will serve to show the general confusion existing in this field. Holleman explains these results on the basis of the relative solubility of hydrogen bromide in the various solvents,[7] but while his data for acetic acid solution demonstrate the inhibition of the side-chain substitution by hydrogen bromide, they do not establish any positive catalytic effect on nuclear substitution. LeBlanc and Andrich[9] attempt to interpret these data on the basis of differences in the degree of bromine solvation in associating solvents, such as toluene and ethyl acetate. Increased solvation, they suggest, decreases the photosensitivity of the bromine, and hence inhibits side-chain substitution. However, this interpretation fails to explain the effect of solvents on the yield of bromo-toluenes. Lauer and Oda[10] assume that the "ionoid character" of the ring is raised (with a corresponding increase in reactivity) because of the greater association of the toluene molecule in such solvents. It is argued that since association presumably takes place through the methyl group, substitution in the side-chain is thereby blocked. It might be predicted, therefore, that the more dilute the solution or toluene in the solvent, the less would be the degree of its association, and that higher rather than lower yields of benzyl bromide would be obtained. The results of experiments 26 and 27 (Table VI) do not fulfill this prediction.

The "after-effect" observed by Bruner and Lahocinski[6] is significant in the light of the present work on catalysis by peroxides. They report that photobromination is accompanied by the production of a catalyst which, upon addition of more bromine, causes very rapid reaction in the dark with the formation of 90–95 per cent. benzyl bromide. Oxygen is absorbed during the formation of the catalyst, and the solution takes on a yellow color. Replacement of the dissolved oxygen, before illumination, by carbon dioxide, hydrogen, or nitrogen prevents the occurrence of the "after effect," as does the addition of iodine or hydrogen bromide after the photobromination. Such a catalyst is not produced by illumination of a solution of toluene, benzyl bromide, and hydrogen bromide, so bromine is apparently necessary. The more dilute the bromine solution during the "after-effect," the greater is the influence of the catalyst. It is apparently destroyed or ineffective in very concentrated bromine solutions.

Further work on this "after-effect" shows that the catalyst formed liberates iodine from potassium iodide.[9] An attempt to isolate the catalyst yielded a small amount of material with a "phenol and cresol-like" odor. LeBlanc and Andrich assume the catalyst to be peroxidic. Since catalyst-formation takes place under the influence of light in the visible region of the

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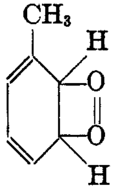
[9] ANDRICH AND LEBLANC, *Z. wiss. Photochem.*, **15**, 148, 183, 197, (1916).

[10] LAUER AND ODA, *Ber.*, **69B**, 978, 1061 (1936).

spectrum, which is not absorbed by either toluene or oxygen, it must be the bromine which renders the reaction light-sensitive. This property of bromine is cited as one established in other photochemical reactions.[11] The mode of action of the catalyst is not explained. They do suggest the formation of an intermediate:



In view of the findings of the present study it seems probable that this peroxide acts as do others to produce bromine atoms, thus initiating chain reactions resulting in substitution in the methyl group.

Oxygen itself is well-known to be involved in the photochemical reaction, but the fact seems to have received little attention. LeBlanc and Andrich found that in experiments conducted in an atmosphere of oxygen their yields of benzyl bromide were slightly higher and were more nearly reproducible than when the reaction was carried out in air.[9] Bruner and Czarnecki[12] observed that removal of oxygen by evacuation or replacement by an inert gas retarded the photobromination, *but they did not analyse the products to determine what effect this might have upon the direction of the reaction.* Furthermore, in the dark and in highly dilute solution, they observed an autocatalytic effect which depended upon the presence of oxygen for its existence. Here the reaction produced 100 per cent. of benzyl bromide, while the slower reaction, in the absence of oxygen, gave only 80–90 per cent. of benzyl bromide.

In summary it may be said that substitution in the side-chain is favored by dilution, high temperature, light, and the presence of oxygen, ozone, and some peroxide-like substance formed under the influence of light in the persence of bromine. Nuclear substitution, on the other hand, is catalysed by metal halides, iodine, and certain ionizing solvents, and is favored by high bromine concentrations.

## DISCUSSION OF MECHANISM

It was originally assumed that the metal halides catalyzed nuclear substitution through "active" complexes such as $MBr_3 \cdot Br_n$. However, Bancroft has pointed out that such an "active complex" might be ex-

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[11] BRUNER AND KROLIKOWSKI, *Bull. intern. acad. sci. Cracovie*, **1910**, 192; *C. A.*, **5**, 2248 (1911).

[12] BRUNER AND CZARNECKI, *ibid.*, **1910**, 516; *C. A.*, **5**, 3751 (1911).

pected to stimulate the side-chain as well as ring substitution.[13] It is now the consensus of opinion that the halogen carriers activate the hydrocarbon ring rather than the bromine molecule.

In the case of the uncatalyzed bromination of toluene it has been suggested that the mechanisms of nuclear and side-chain substitution differ with respect to the active agents involved in the respective substitutions. Holleman postulated that "$HBr_n$" attacks the nucleus, while bromine molecules cause substitution in the chain. This hypothesis is consistent with the results of his experiments in acetic acid solution, where hydrogen bromide decreases chain substitution. According to this hypothesis the temperature effect is due to the decomposition of the complex "$HBr_n$" by heat, which left the side-chain substitution the predominant reaction. However, Holleman himself recognized the failure of the theory to explain the dilution effect. At the beginning of the reaction no hydrogen bromide is present in the mixture, yet in concentrated bromine solution nuclear substitution proceeds very rapidly even in the absence of "$HBr_n$."

Bruner and co-workers suggested the bromine atom as the reagent for nuclear substitution, but offered no evidence in confirmation of this theory.

LeBlanc and Andrich ascribe the temperature effect to the decrease in solvation of the bromine molecule, but make no attempt to apply their theory to other factors affecting the reaction.

The hypothesis proposed by the present authors implies: (1) that factors favorable or inimical to the production of bromine atoms in the reaction system accelerate or retard side-chain substitution; (2) that factors operating to reduce the length of reaction chains, by the removal of bromine atoms or otherwise, inhibit side-chain substitution. Such factors are regarded as having only incidental effects upon the rate of nuclear substitution, and as affecting the ratio of products obtained primarily by altering the rate of one of two competing reactions.

Some bromine atoms doubtless exist in dilute toluene solutions of bromine by virtue of thermal dissociation, even at room temperature; increase in temperature would increase this dissociation. On the assumpgion that the heat of dissociation of bromine is in the neighborhood of 46,000 calories, the concentration of bromine atoms should be about a hundred times greater at 80° than at room temperature. Hence, a rather large positive temperature coefficient for side-chain substitution is implied. The work of Bruner and Diuska[5] shows that the temperature coefficient for substitution in the side-chain is over four times as large as that for nuclear substitution. To some extent a change in concentration would also affect the degree of dissociation of the bromine molecules by

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[13] BANCROFT, *J. Phys. Chem.*, **12**, 417 (1908).

operation of the mass law. While this effect is in qualitative agreement with the facts, it is doubtless too small to be of much significance.

If hydrogen bromide in the presence of oxygen is a source of bromine atoms as suggested,[1] then the results of Bruner *et al.* at high dilution, which revealed an autocatalytic reaction in the side-chain bromination in the presence of oxygen are explained, in part at least, by the increase in hydrogen bromide concentration as the reaction proceeds. This phenomenon would appear only at a dilution such that the formation of benzyl bromide is the principal reaction, and when the amount of available oxygen is relatively large. If interaction of oxygen and hydrogen bromide produces bromine atoms, it is obvious that peroxides and ozone should be still more effective in this respect. The very strong catalytic effect of these substances in the formation of benzyl bromide is thus explained.

It has long been recognized that visible light is effective in the direct photodissociation of bromine molecules. It now appears probable that, in the presence of bromine, visible light may be effective in the secondary production of bromine atoms, (1) by activating the interaction of oxygen and hydrogen bromide,[14] or (2) by activating the interaction of oxygen with hydrocarbons to form peroxidic catalysts,[6,9] or both.

Hence it appears that oxygen, peroxides, light, and heat all act on a reaction mixture of bromine and toluene in such a way as to increase the number of bromine atoms present; all increase the rate and extent of side-chain substitution. The effects of bromine concentration and solvents come under the category of factors influencing chain-length.

The chain presumably proceeds through one or both of the following pairs of reactions:

$$C_6H_5CH_3 + Br\cdot \rightarrow C_6H_5CH_2\cdot + HBr \tag{1a}$$

$$C_6H_5CH_2\cdot + Br_2 \rightarrow C_6H_5CH_2Br + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}\cdot \tag{1b}$$

$$C_6H_5CH_3 + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}\cdot \quad C_6H_5CH_2Br + H\cdot \tag{2a}$$

$$H\cdot + Br_2 \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}\cdot + HBr \tag{2b}$$

Once started, the chains continue until broken by some side-reaction. If, as seems probable, the bromine molecule acts as a chain-breaker by the formation of $Br_3$, it is to be expected that in concentrated bromine solutions the chain length will be relatively short, and the yields of benzyl bromide corresponding low. Likewise certain solvents (notably solvents rich in oxygen) act as inhibitors of the chain reaction.

[14] *Cf.* Kharasch and Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

## RESULTS

*Dilution.*—The addition of a small amount of an organic peroxide to a dilute toluene solution of bromine increases the rate of reaction greatly in the dark and raises the yield of benzyl bromide. This catalytic effect is greatest in dilute solutions of bromine, and vanishes in very concentrated solutions. Furthermore, the peroxide is more effective if added slowly during the course of the reaction, presumably because the catalyst is gradually destroyed in the course of the reaction. Benzoyl peroxide, ascaridole, and triacetone peroxide are all catalysts, but ascaridole was used in the recorded experiments. Table III records the results of a series of experiments at 25° in the presence of air, with and without peroxide, at various dilutions and reaction times. While a comparison of the various control experiments confirms the observations of earlier workers as to the dilution effect, the latter is much more strikingly evident in the case of the peroxide experiments. Here any variation in the initial

TABLE III

THE EFFECT OF ASCARIDOLE ON THE BROMINATION OF TOLUENE IN DARKNESS

| EXPT. NO. | MOLES TOLUENE[a] | MOLES ASCARIDOLE[a] | TIME, HOURS | YIELD OF BROMIDES ISOLATED (%) | ESTIMATED[b] YIELD, (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | Total Bromides | Benzyl Bromide | Bromo Toluenes |
| 1 | 2 | 0 | 23 | 72 | 89 | 1 | 88 |
| 2 | 2 | 0 | 0.75 | 38 | 47 | 0.3 | 47 |
| 3* | 2 | .03 | 23 | 64 | 82 | 4 | 78 |
| 4* | 2 | .03 | 0.75 | 37 | 47 | 4 | 43 |
| 5 | 5 | 0 | 23 | 48 | 58 | 2 | 56 |
| 6* | 5 | .03 | 23 | 53 | 65 | 17 | 48 |
| 7 | 10 | 0 | 96 | 61 | 75 | 7 | 68 |
| 8* | 10 | 0 | 23 | 14 | 22 | 1 | 21 |
| 9* | 10 | .03 | 23 | 67 | 94 | 85 | 9 |
| 10* | 10 | .03 | 5 | 79 | 94 | 89 | 4 |
| 11 | 10 | .03 | 0.06 | 73 | 90 | 87 | 3 |
| 12 | 20 | 0 | 91 | 25 | 33 | 11 | 22 |
| 13 | 20 | 0 | 48 | 15 | 22 | 8 | 14 |
| 14 | 20 | .03 | 0.5 | 85 | 100 | 95 | 5 |
| 15 | 20 | 0 (*in vacuo*) | 91 | 21 | 30 | 10 | 20 |

* Indicates average of two or more experiments.

[a] Per mole of bromine.

[b] The basis of estimation is explained in the experimental part.

concentration of the bromine atoms is overshadowed by the much greater atomic concentration from interaction of hydrogen bromide and peroxides. The wide variation in yield of benzyl bromide is due to the facts that the nuclear substitution is faster and the chain reaction is interrupted in concentrated solution.

Since the life of a bromine atom in such solutions must be extremely short, and the peroxide present is rapidly destroyed in forming atoms, one would expect the chain reaction to be extremely rapid. A comparison of the benzyl bromide yields in experiments 9 and 11 shows clearly that the reaction initiated by the peroxide has run its course within a few minutes. However, in the control experiments in dilute solution, where dissociation and the action of air on hydrogen bromide furnish a continuous supply of bromine atoms, the yield of benzyl bromide increases uniformly with time, as is shown by experiments 7, 8, 12, 13. The effect of oxygen in the production of bromine atoms in these control experiments is apparently insignificant at 20:1 dilution (*cf.* 12 and 15), although the work of Bruner indicates that it is appreciable at 200:1 dilution.

TABLE IV

EFFECT OF PEROXIDE ON THE BROMOTOLUENE ORTHO-PARA RATIO[c]

| EXPERIMENT | TIME | YIELD OF BROMIDES ISOLATED, (%) | BENZYL BROMIDE, (%) | FREEZING POINT, BROMO-TOLUENES | % *o*-BROMO TOLUENE |
|---|---|---|---|---|---|
| Control | 4 days | 61 | 90 | −8°C. | 54 |
| 3 Mole % Ascaridole | 1 day | 68 | 10 | −9°C. | 55 |

[c] The toluene/bromine ratio was 10:1 for both experiments.

The rate of nuclear substitution shows a uniform increase with increasing bromine concentration. The data do not warrant any kinetic interpretation which might throw light on the mechanism of ring bromination. It may be said only that the data are not inconsistent with the hypothesis of a bimolecular reaction for nuclear substitution, and that they do exclude the possibility that nuclear substitution takes place through a bromine-atom mechanism.

The bromotoluenes from one control and one peroxide-catalyzed experiment were analysed by the freezing-point method of van der Laan[2] (assuming the absence of *m*-bromotoluene) to determine whether the presence of peroxide during the reaction has any influence on the ortho/para ratio in the nuclear-substitution product. The data recorded in Table IV indicate that there is no such effect. The composition in each case was determined directly from the freezing-point curve given by van der Laan.

*Inhibitors.*—The complete inhibition of side-chain substitution by very small concentrations of certain substances supports the postulate that a chain mechanism is operative in the peroxide-catalyzed reaction. Several nitroso compounds have been found to have this effect, as, to a much lesser degree, has ethyl alcohol.[15] Table V records the results of several such experiments, with corresponding controls for comparison. Qualitative tests showed many similar substances, such as isoamyl nitrite, *p*-nitrosodimethylaniline, and even sodium nitrite, to be effective inhibitors. The inhibition is not due merely to the binding or destruction of the peroxide by an equivalent quantity of inhibitor, for it also occurs in the photobromination. In the presence of a few mole per cent. of isoamyl nitrite the light-activated reaction is complete only after many hours, whereas it normally requires only a few minutes. Water, acetic acid, and nitrobenzene have no appreciable inhibitory effect when present in small concentrations (a few mole per cent. on the basis of the bromine present).

TABLE V

EFFECT OF INHIBITORS ON THE PEROXIDE-CATALYZED REACTION[c]

| EXPT. NO. | INHIBITOR | MOLES[a] INHIBITOR | MOLES ASCARIDOLE[a] | TIME, HOURS | YIELDS OF BROMIDES ISOLATED (%) | ESTIMATED[b] YIELDS, % | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Total Bromides | Benzyl Bromide | Bromo Toluenes |
| 8* | | None | 0 | 23 | 14 | 22 | 1 | 21 |
| 9* | | None | .03 | 23 | 67 | 94 | 85 | 9 |
| 10* | | None | .03 | 5 | 79 | 93 | 89 | 4 |
| 16 | $C_6H_5NO$ | .03 | 0 | 24 | 33 | 40 | 1 | 39 |
| 17* | $C_6H_5NO$ | .03 | .03 | 24 | 33 | 44 | 1 | 43 |
| 18 | $N_2O_4$ | .03 | .03 | 23 | 16 | 24 | 1 | 23 |
| 19 | $C_2H_5OH$ | 2.6 | 0 | 23 | 50 | 67 | 0.5 | 66 |
| 20* | $C_2H_5OH$ | .03 | .03 | 23 | 50 | 67 | 15 | 52 |
| 21 | $H_2O$ | .03 | 3 | 4 | 79 | 95 | 92 | 3 |
| 22 | AcOH | .03 | 3 | 24 | 78 | 94 | 82 | 12 |
| 23 | $C_6H_5NO_2$ | .03 | 3 | 24 | 83 | 98 | 85 | 13 |

*, [a], [b] Have the same significance as in Table III.

[c] The toluene/bromine ratio was 10:1 for all experiments.

*Solvents.*—The use of solvents in the peroxide-catalyzed reaction, as is shown in Table VI, merely confirms the observations already made.

Carbon tetrachloride is an inert diluent, and decreases the rate of side-chain and nuclear substitution. Acetic acid and nitrobenzene, however, strongly inhibit the peroxide-catalyzed chain reaction. It may be noted also that the rate of nuclear substitution is increased. This effect is con-

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[15] SWENSSON, *Z. wiss. Photochem.*, **20**, 206 (1921); *C. A.*, **15**, 2838 (1921).

sistent with the relatively high dielectric constants of these solvents as well as with the suppression of side-chain bromination. Experiment 29 shows that the solubility of hydrogen bromide in acetic acid cannot account for the catalysis of nuclear substitution. Also, the association theory of Lauer and Oda previously mentioned above is refuted by experiments 26 and 27, where the yield of benzyl bromide is not affected (within experimental error) by the change in concentration of the toluene.

*Light.*—In photobromination experiments at 10:1 dilution the yield of benzyl bromide is lowered by exclusion of oxygen. It is interesting to note that the rate of bromination is also markedly decreased (24 hours *in vacuo*, as compared with 20 minutes in air). In experiment 35 bromine atoms were apparently produced by the action of light on molecular bromine, for the product is principally benzyl bromide, yet the slow reaction indicates that the concentration of atoms thus produced is very small compared to that arising from peroxide action. A still more marked oxygen effect is observable in the 5:1 dilution experiments. Here the nuclear substitution predominates, because the high bromine concentration inhibits the chain reaction. In the absence of oxygen the yield of benzyl bromide is only 15 per cent., and the rate of reaction is extremely slow, while in the presence of air over 70 per cent. of benzyl bromide is formed in a few hours.

TABLE VI

EFFECT OF SOLVENTS ON THE PEROXIDE-CATALYZED REACTION

| EXPT. NO. | SOLVENT[c] | MOLES TOLUENE[a] | MOLES ASCARIDOLE[a] | TIME, HOURS | YIELD OF BROMIDES ISOLATED (%) | ESTIMATED[b] YIELDS,% | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Total Bromides | Benzyl Bromide | Bromo Toluenes |
| 8* | None | 10 | 0 | 23 | 14 | 22 | 1 | 21 |
| 9* | None | 10 | 3 | 23 | 67 | 94 | 85 | 9 |
| 24 | Carbon tetrachloride | 2 | 0 | 24 | 11 | 14 | 0.5 | 13 |
| 25* | Carbon tetrachloride | 2 | 3 | 23 | 26 | 33 | 25 | 8 |
| 26 | Acetic acid | 1 | 0 | 23 | 29 | 36 | 0.5 | 35 |
| 27 | Acetic acid | 2 | 0 | 23 | 32 | 42 | 0.4 | 42 |
| 28 | Acetic acid | 2 | 3 | 23 | 32 | 40 | 1 | 39 |
| 29 | Acetic acid | 2 | (0.97 mole HBr) | 23 | 15 | 19 | 0.2 | 19 |
| 30 | Nitrobenzene | 2 | 3 | 23 | 95 | 95 | 2 | 93 |

*, [a], [b] Have the same significance as in Table III.

[c] Sufficient solvent was added to bring the volume up to that of a 10:1 toluene-bromine solution.

These results invite reconsideration of the extent to which the direct photochemical dissociation of molecular bromine is actually involved in the so-called photobromination reaction. The materials used in these experiments were carefully degassed, and the degree of evacuation was high ($10^{-5}$ mm.). However, no attempt was made to remove the oxygen layer adsorbed on the glass, and traces of oxygen are necessarily present even after the best evacuation. The fact that under these conditions only 15 per cent. of benzyl bromide was formed after fifty-seven hours' illumination (experiment 33), suggests the possibility that if no oxygen were present light might be without effect on the reaction. The experimental data presented certainly do not prove this to be the case; on the other hand, *they cannot be taken as indicating unquestionably that light does have a direct effect on the reaction independent of the presence of oxygen.* It may be that in solutions of these concentrations light produces no bromine atoms whatsoever except through the activation of small amounts of oxygen.

TABLE VII

OXYGEN EFFECT IN PHOTOBROMINATION

| EXPT. NO. | MOLES TOLUENE[a] | AIR | ILLUMINATION[c] | MOLES ASCARIDOLE[a] | TIME, HOURS | YIELD OF BROMIDES ISOLATED (%) | ESTIMATED YIELDS[b], % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Total[d] Bromides | Benzyl Bromide | Bromo Toluenes |
| 31 | 5 | + | + | .03 | 0.3 | 83 | 100 | 90 | 10 |
| 32 | 5 | + | + | 0 | 2.5 | 84 | 100 | 75 | 25 |
| 33 | 5 | – | + | 0 | 57 | 79 | 95 | 15 | 80 |
| 11 | 10 | + | – | .03 | 0.06 | 73 | 90 | 87 | 3 |
| 34 | 10 | + | + | 0 | 0.3 | 94 | 100 | 90 | 10 |
| 35 | 10 | – | + | 0 | 24 | 95 | 100 | 68 | 32 |

[a], [b] Have the same significance as in Table III.

[c] 100-W. incandescent lamp at 30 cm. distance.

[d] Usually illuminated until bromine color disappeared.

TABLE VIII

PEROXIDE EFFECT IN THE BROMINATION OF ETHYLBENZENE

| MOLES ASCARIDOLE[a] | TIME, HOURS | YIELD BROMIDES ISOLATED (%) | |
|---|---|---|---|
| | | Nuclear | Side-chain[c] |
| 0 | 25 | 14 | 26 |
| 2 mole % | 1.5 | 6 | 91 |

[a] Has the same significance as in Table III.

[c] No analysis was made to determine whether this was the $\alpha$ or $\beta$ compound; by analogy with the photobromination of toluene it is probably the $\alpha$ isomer.

An alternative explanation of the oxygen effect is that oxygen combines with some "chain-breaker" which otherwise is free to inhibit the light-sensitized reaction.

As confirmatory evidence that the differences shown in these experiments are due to oxygen, it is noteworthy that in the reactions in which air is present, decolorization always starts at the surface and proceeds downward through the solution. On the other hand, in the vacuum experiments decolorization proceeds uniformly throughout the entire reaction mixture.

*Ethylbenzene.*—Several experiments were carried out with ethylbenzene. With this compound, at a 1:1 ratio of bromine to the hydrocarbon in the dark, only the nuclear substitution products are formed.[16] A strong peroxide effect was observed in this reaction at a dilution of 7:1; the results are recorded in Table VIII.

## EXPERIMENTAL

*Materials*—Mallinckrodt's "Analytical Reagent" toluene was distilled through an eight-ball Snyder column. The fraction boiling at 109.5°–110.3° at 749 mm. was stored over sodium and used directly. Commercial grade ethylbenzene was shaken with mercury for several days to remove sulfur, then dried and distilled; b.p. 134.8°–135.2° at 747 mm. Baker's C.P., bromine was used without further purification. One test experiment using bromine which had been carefully washed with alkali and permanganate, then dried and distilled from phosphorus pentoxide, gave exactly the same results as those obtained with the commercial C.P. product. Ascaridole, obtained from the Eastman Kodak Co., was used in all the recorded experiments. The solvents were of the best reagent grade and were distilled immediately prior to use.

*Apparatus*—Most of the experiments were carried out in a Pyrex 200-cc. four-necked flask equipped with two 50-cc. dropping funnels, a mercury-sealed stirrer, and a reflux condenser. This flask was equipped with ground glass joints throughout, and was partially immersed in a thermostat kept at 25°. The whole apparatus was covered with several layers of glazed black cloth which permitted the manipulation of the stopcocks without admission of light. On the rare occasions when it was necessary to examine the mixture during the course of the reaction this was done with the aid of a small flashlight.

*Procedure.*—The bromine and the ascaridole, the latter diluted with a few cubic centimeters of toluene or solvent, were admitted to the reaction mixture through the two dropping funnels. The bromine was added at once, while the peroxide solution was admitted intermittently over a period of five or ten minutes. The mixture was stirred during this period, and the hydrogen bromide evolved passed through the condenser into a water trap. The bromine was measured volumetrically, 0.040 or 0.080 moles being used. In some of the control experiments, in which the reaction was allowed to run several days, the reagents were merely mixed in a large open test-tube in the dark and kept at room temperature.

With the exception of the photobrominations, in which the solutions were illuminated at room temperature until colorless, the reaction was interrupted while bro-

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[16] SCHRAMM, *Ber.*, **18**, 606 (1885).

mine was still present. In most experiments a current of air was passed through the stirred solution for an hour at the end of the reaction to remove as much hydrogen bromide as possible and thus reduce the amount of washing necessary. The reduction of the remaining bromine was then accomplished with little or no exposure to light by pouring the reaction mixture into an excess of dilute sodium bisulfite solution in a covered separatory funnel. The organic phase was immediately washed with water until the washings no longer showed a precipitate with silver nitrate. In those experiments in which acetic acid was used as a solvent, carbon tetrachloride was employed to extract the product from the aqueous solution after the unchanged bromine had been destroyed. When the reaction was carried out in nitrobenzene, the extent of bromination was determined by titration of the residual bromine. Since the solvent and products could not be separated by fractionation in this case, the analysis for benzyl bromide was carried out on an aliquot sample according to the method described below.

The excess toluene was removed from the washed product by distillation under 20–30 mm. pressure. The products themselves were then distilled at the same pressure from a small Claisen flask with a long, indented neck. No effort was made to separate the bromotoluenes from the benzyl bromide. The boiling range of the products was from 70°–95° depending upon the composition and the exact pressure.

The yield of bromides isolated given in the various tables are those calculated from the weight of the distillate. However, there is necessarily a certain amount of loss in the washing by hydrolysis of benzyl bromide, and in the distillation. Material being carried over with the unchanged toluene would be principally the lower-boiling bromotoluenes. Conversely any hold-back in the distilling flask would be the side-chain substitution product. This last factor is negligible since the residue, except when ascaridole was used, was only 0.1–0.2 g. This fact also attests the absence of any higher bromination products.

The "estimated yields" were arrived at by a consideration of the yields obtained in the photobrominations which had gone to completion, and of the loss found in the treatment of artificial mixtures. Washing and distillation resulted in combined losses of 15–20%, as is indicated by experiments 32 and 33. In experiments in which the yield was very low the same loss by weight would be a much larger factor. However, the treatment of artificial mixtures indicated that the loss in purification of very small samples was only 25%, and was about equally divided between bromotoluene and benzyl bromide. A 1:1 mixture of benzyl bromide and bromotoluenes, weighing 2.0 g., lost 0.5 g. upon washing and distillation, and the remaining material was 53.0% benzyl bromide. Hence the net yields were estimated as actually being 10–25% too low, depending on the quantities of reagents used in the individual experiment. The precision of the "estimated yield" is ±10%.

In the analysis of benzyl bromide a small weighed sample of the product was treated with an excess of standard silver nitrate in alcohol solution. Then the excess silver nitrate was determined according to the method of Volhard. All analyses were carried out in duplicate. The yields of benzyl bromide and bromotoluene were calculated directly from the results of the analysis and the estimated yield. The precision of the *relative* yields of these products is ±1%.

Experiments which were carried out *in vacuo* were performed in the following manner. The toluene and bromine were placed in separate tubes, and these were joined by an inverted U-tube fastened to the vacuum line. To facilitate sealing there were constrictions in the tubing where the U-tube joined the line and the tube containing the toluene. Both tubes were chilled in liquid nitrogen, and the system was evacuated to a pressure of $10^{-5}$ mm. The yoke and tubes were temporarily closed off by means of a stop-cock above the constriction. Both reactants were warmed to their boiling points to permit escape of dissolved gases. They were then chilled once more, and the system was re-evacuated. This degassing process was repeated twice. The system was sealed off and removed from the line, and the bromine was distilled into the toluene by allowing it to warm to room temperature. The reaction tube was then sealed off and was ready for illumination. The control reaction in a sealed or open tube of the same diameter was carried out simultaneously.

## SUMMARY

1. The work of various investigators on the bromination of toluene has been summarized and few of the mechanisms they propose for the reactions involved have been discussed.

2. A strong oxygen effect, which influences the direction as well as the rate of the reaction, has been observed in the photobromination of toluene.

3. A number of inhibitors of the side-chain bromination of toluene have been discovered.

4. The side-chain bromination of ethylbenzene is influenced by oxygen and/or peroxides.

5. A chain reaction carried by bromine atoms has been proposed as a probable mechanism for side-chain bromination. It is in accord with the facts previously observed and is substantiated by the catalytic effects of oxygen and peroxides under various conditions.