[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Photobromination of Branched-chain Hydrocarbons; the Dark Reaction of Bromine with Tertiary Alkyl Bromides[1,2]

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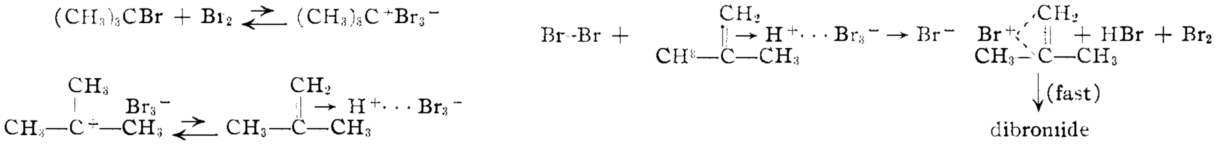
The photobromination of hydrocarbons in the liquid phase is highly selective and constitutes an excellent method for the preparation of tertiary bromides from hydrocarbons which contain only primary hydrogen atoms in addition to the tertiary hydrogen atom. The presence of secondary or an additional tertiary hydrogen atom in the adjacent position leads to the formation of considerable quantities of dibromides. It is proposed that these dibromides arise from an ionic or molecular reaction of bromine with the tertiary bromide formed in the initial photochemical reaction. The dark reaction of bromine with *t*-butyl bromide exhibits third-order kinetics. No evidence could be obtained of a measurable equilibrium between olefin and hydrogen halide in solutions of *t*-butyl chloride and *t*-butyl bromide in refluxing sulfur dioxide or of 2-bromo-2,3,3-trimethylbutane in carbon tetrachloride (76°). Yet bromine reacts rapidly with the tertiary halides under these conditions. These results are consistent with a reaction mechanism in which a bromine molecule brings about the ionization of the tertiary bromide, followed by reaction of a second bromine molecule with the high energy π-complex form of the carbonium ion



$$(CH_3)_3CBr + Br_2 \rightleftarrows (CH_3)_3C^+Br_3^-$$

It has been demonstrated previously that the liquid phase photobromination of aliphatic hydrocarbons involves a free radical chain reaction which proceeds readily only with relatively reactive carbon–hydrogen bonds, such as the tertiary hydrogen in isobutane.[3] Primary hydrogens, such as those present in neopentane, *t*-butylbenzene or trimethylacetic acid, are not attacked noticeably by bromine atoms even at temperatures as high as 80°.[4]

The formation of more than statistical amounts of dibromides in the photobromination of branched-chain hydrocarbons in the liquid phase has been observed upon several occasions.[3,5] These results are puzzling in view of observations that chlorine substituents tend to reduce the susceptibility of a hydrocarbon chain to further attack.[6]

Varying explanations have been proposed to account for the high yields of dibromides. Thus the formation of dibromides in the photobromination of isobutane at 25–30° has been attributed to the dehydrobromination of the tertiary bromides originally formed.[3] On the other hand, the production of 2,3-dibromo-2,3-dimethylbutane as the major product of the photobromination of 2,3-dimethylbutane at 25–30° has been attributed to an increased reactivity of a tertiary hydrogen atom toward bromine atoms after the introduction of the first bromine atom in the molecule.[5] Furthermore, the production of 1,2-dibromo-2-methylpropane in the reaction of *t*-butyl bromide with bromine at 0° in the presence of di-*t*-butyl peroxide has been interpreted as a peroxide-catalyzed (free radical) reaction.[7]

In the preceding paper of this series, it was shown that the attack of chlorine atoms along a chain tends to occur at a position remote from a chlorine substituent.[6] This result casts doubt upon explanations based upon the presumed high suceptibility toward attack by bromine atoms of carbon–hydrogen bonds immediately adjacent to a bromine substituent.[5,7] Since simple tertiary alkyl bromides exhibit considerable stability at ordinary temperatures, it also appeared doubtful that the large amounts of dibromides could be the result of a prior dissociation of the tertiary bromide into olefin and hydrogen bromide.[3]

In order to obtain further information on this question, we undertook a study of the photobromination of a number of hydrocarbons containing at least one tertiary carbon–hydrogen bond: cumene, 2-methylpentane, 2,2,3-trimethylbutane (triptane) and 2,3-dimethylbutane. Moreover, the reactions of bromine with *t*-butyl, *t*-amyl and triptyl bromides were studied in the hope of elucidating the mechanism responsible for the formation of dibromides. In the course of this work, procedures were developed which permit the conversion of the above hydrocarbons into the corresponding tertiary monobromides in excellent yield.

Results

The photobromination of triptane at 80° produced 2-bromo-2,3,3-trimethylbutane in nearly quantitative yields. No special precautions were necessary and the reaction could be carried out with 25 mole % bromine without measurable formation of higher brominated products.

Cumene also reacted readily to give the tertiary bromide, but in this case the formation of higher bromides was a factor. The yield (based on bromine) decreased from 94% for a 25 mole % bromination at 0° to 73% for a 50 mole % bromination at 60°. In the reaction of bromine with cumene at 0° under illumination, it was observed that bromine did not accumulate in the reaction flask until two moles of the halogen had been added per mole of cumene

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[1] Directive Effects in Aliphatic Substitutions. III.

[2] This paper is abstracted from a thesis submitted by Glen A. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] M. S. Kharasch, W. Hered and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941).

[4] M. S. Kharasch and M. Z. Fineman, THIS JOURNAL, **63**, 2776 (1941).

[5] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **8**, 438 (1943).

[6] H. C. Brown and A. B. Ash, THIS JOURNAL, **77**, 4019 (1955). This paper contains numerous references to the literature.

[7] N. A. Milas and C. N. Winnick, *ibid.*, **71**, 748 (1949).

treated. 1,2-Dibromo-2-phenylpropane was the major product of the reaction.

In this reaction it was observed that bromine was not consumed at the start of the reaction in the absence of radiation. However, after the reaction had proceeded part-way, bromine was consumed in the dark. This observation suggests that the reaction responsible for the formation of dibromides is not the same as the free radical chain reaction responsible for the formation of the tertiary bromide from the hydrocarbon.

The major product in the photobromination of 2,3-dimethylbutane with 25 mole % bromine at 55° was not 2-bromo-2,3-dimethylbutane. Instead, an 89% yield of 2,3-dibromo-2,3-dimethylbutane was obtained.[5] Bromination of 2-methylpentane under similar conditions resulted in the formation of 76% of 2-bromo-2-methylpentane together with 6.5% of secondary bromides and 17.5% of a dibromide fraction which is probably chiefly 2,3-dibromo-2-methylpentane.

In order to ascertain the possibility of forming the tertiary bromides, with as little interference from dibromide formation as possible, several photobrominations were carried out at 25°, using not more than 5 mole % bromine. The reaction products were analyzed for total bromine, and for tertiary bromide by solvolysis in aqueous alcohol. The data are summarized in Table I.

TABLE I

PHOTOBROMINATION OF BRANCHED-CHAIN HYDROCARBONS

Hydrocarbon	Bromine, mole %	Temp., °C.	Yield of *t*-bromide, %
Cumene	5	25.0	100
2,2,3-Trimethylbutane	5	25.0	96
2-Methylpentane	5	25.0	90
2,3-Dimethylbutane	5	25.0	<50[a]
2,3-Dimethylbutane	3.1	25.0	79
2,3-Dimethylbutane	3.8	0–2	86

[a] Some dibromide crystallized from the hydrocarbon toward the end of the bromination and was not included in the analysis.

These data clearly establish the very high selectivity of the photobromination reaction. Within the relatively narrow limits of error of the experimental procedure, only tertiary substitution occurred in the case of cumene and triptane. It is concluded that attack of a bromine atom on a primary hydrogen atom does not occur under the reaction conditions for any of the hydrocarbons under observation.[4]

If the 10% of unidentified bromides present in the product from 2-methylpentane are considered to be secondary bromides, the relative reactivity in this molecule of a tertiary to a secondary hydrogen atom toward attack by a bromine atom at 25° is 36:1. This must be considered only as a minimum value, since some dibromide formation probably occurred and the quantity of secondary bromides formed is probably smaller than the amount of non-solvolytic bromine determined in the analysis.

Although the formation of dibromides was relatively unimportant for the 5 mole % brominations of cumene, triptane and 2-methylpentane, it was the predominant reaction in the 5 mole % bromination of 2,3-dimethylbutane. To measure the tertiary bromide–dibromide ratio more accurately for 2,3-dibromobutane, brominations were performed using less than 5 mole % bromine and lower temperatures. The results of these experiments (Table I) indicate that the formation of dibromides in the bromination of 2,3-dimethylbutane is less pronounced at a lower temperature and at a lower bromine–hydrocarbon ratio. This temperature effect excludes the formation of the dibromide by a free radical mechanism as a result of increased hydrogen reactivity following the introduction of a bromine substituent in the molecule. Were this the case, bromine atoms would be expected to display even higher selectivity with a decrease in temperature with a resulting higher percentage of dibromides in the product at the lower temperature.

To test further this conclusion that the dibromides formed in the photobromination of branched-chain hydrocarbons do not arise from a free radical reaction,[5,7] 2-bromo-2,3,3-trimethylbutane and *t*-amyl bromide were treated with bromine in the dark in carbon tetrachloride solution at 25°. In 40 hours, 0.064 mole of 2-bromo-2,3,3-trimethylbutane reacted with 0.076 mole of bromine to produce 0.04 mole of dibromide and 0.01 mole of tribromide. Similarly, *t*-amyl bromide and an equivalent molar amount of bromine produced 59% dibromides and 11% tribromides.

That the reaction of bromine and *t*-butyl bromide at 0° is not catalyzed by di-*t*-butyl peroxide is demonstrated by the results shown in Fig. 1, where the disappearance of bromine in carbon tetrachloride solutions of bromine and *t*-butyl bromide, in the presence and absence of di-*t*-butyl peroxide, is plotted as a function of time.

The data show that the rate of disappearance of bromine actually was lower for the bromination performed in the presence of the peroxide. The lower rate of bromine disappearance in the presence of peroxide undoubtedly involves the reaction of hydrogen bromide and di-*t*-butyl peroxide. If sufficient peroxide is present, this reaction will regenerate one-fourth of the bromine which originally reacted with the tertiary bromide.[7]

$$Br_2 + (CH_3)_3CBr \longrightarrow (CH_3)_2CBrCH_2Br + HBr$$

$$4HBr + (CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CBr + 2H_2O + Br_2$$

Indeed, in Fig. 1, the initial rate of disappearance of bromine in the bromination of *t*-butyl bromide in the presence of the peroxide is approximately 75% of the initial rate of the peroxide-free reaction.

In the course of investigating the mechanism of the dark reaction of bromine with tertiary halides, we studied the kinetics of reaction of bromine with *t*-butyl bromide at 0° in carbon tetrachloride as well as the question of dehydrohalogenation of tertiary halides under conditions conducive for their reaction with bromine. It appears appropriate to defer reporting the results of these experiments to that portion of the Discussion of the mechanism to which the experiments are directly pertinent.

Discussion

The formation of dibromides in the photobromination of branched-chain hydrocarbons evidently occurs *via* reaction of molecular bromine with the tertiary bromide formed in the initial photochemical stage of the reaction. The process presumably is related to the reaction of bromine with *t*-amyl alcohol to produce trimethylethylene dibromide.[8]

It has long been recognized that alkyl halides react with bromine particularly in the presence of metal halides, such as ferric bromide, to produce mainly dibromides.[9] Bromine is now recognized to possess some of the characteristics of a Lewis acid, as evidenced by its ability to form complexes with aromatic hydrocarbons[10a] and with alkyl bromides[10b] and iodides,[10b] as well as with tertiary alcohols.[10c]

Consequently, the first step in the reaction of tertiary bromides with bromine may be considered to involve an ionization of the alkyl bromide under the catalytic influence of the halogen.

$$(CH_3)_3CBr + Br_2 \rightleftharpoons (CH_3)_3C^+Br_3^-$$

It has been shown that at elevated temperatures hydrogen bromide catalyzes the dehydrobromination of alkyl bromides.[11] However, the reaction of bromine with *t*-butyl bromide (Fig. 1) is not autocatalytic, so that the reaction is not catalyzed by hydrogen bromide. Moreover, we have observed that the reaction of 2,3-dimethyl-2-butanol with bromine proceeds at room temperature in carbon tetrachloride solution with the formation of 2,3-dibromo-2,3-dimethylbutane as major product. The presence of finely divided calcium carbonate slows down the reaction somewhat, but otherwise does not affect the nature of the reaction. This result indicates that hydrogen halide catalysis of the ionization stage is not an essential feature of the reactions under consideration.

In a medium with the non-polar characteristics of the hydrocarbons or carbon tetrachloride utilized in the present study, ionization presumably will occur only to an ion pair and further dissociation should not be significant. We therefore are faced with the question as to the processes involved in the reaction of the ion pair with bromine to form the dibromide.

One possibility worth considering is the conversion of the ion pair into the olefin, followed by reaction of the olefin with halogen. The reaction leading to the formation of the olefin then would bear a close resemblance to the iodine-catalyzed dehydration of tertiary alcohols[12] where the slow reaction of iodine with the olefin permits its isolation as such.

Indeed, the reaction of bromine with *t*-butyl chloride or α-phenylethyl bromide in the highly polar medium, liquid sulfur dioxide, has been considered to proceed through the spontaneous dehydrohalogenation of the alkyl halide.[13]

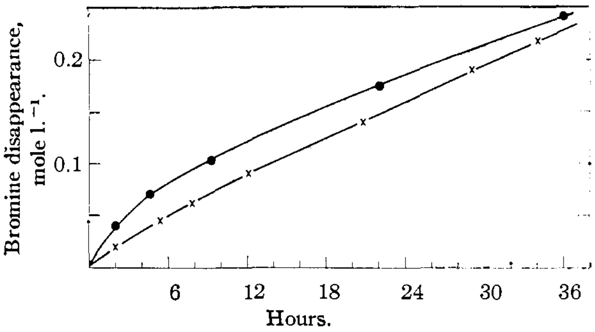

Fig. 1.—Reaction of bromine (1.2 *M*) and *t*-butyl bromide (1.2 *M*) in carbon tetrachloride at 0°: ●, peroxide free; ×, 2% by vol. of di-*t*-butyl peroxide.

$$RX \rightleftharpoons R^+X^-$$
$$R^+X^- \rightleftharpoons \text{olefin} + HX$$

However, the only evidence presented to support this proposed equilibrium between *t*-butyl chloride, isobutylene and hydrogen chloride in the sulfur dioxide medium was the reaction with bromine to produce the dibromide.[13]

The formation of the olefin as an intermediate also has been considered to be the reaction path for the reaction of *t*-butyl bromide or iodide with iodine monochloride.[14]

At first glance the formation of olefin as an intermediate in these reactions appears quite reasonable. The ionized halide need merely transfer a proton to bromide ion (in liquid sulfur dioxide), or to trihalide ion (in the halogen-catalyzed reaction).

$$(CH_3)_3C^+Br^- \rightleftharpoons (CH_3)_2C{=}CH_2 + HBr$$
$$(CH_3)_3C^+Br_3^- \rightleftharpoons (CH_3)_2C{=}CH_2 + [HBr_3]$$

We have attempted to obtain independent evidence for the equilibrium postulated by Hughes, Ingold and Scott[13] by rectification of sulfur dioxide solutions of *t*-butyl chloride and bromide in a 100-plate low-temperature column. Under total reflux, the temperature at the top of the column did not drop below that expected for pure sulfur dioxide. A sample of the distillate was then removed under high reflux ratio. No trace of hydrogen chloride or of hydrogen bromide could be detected by mass spectrographic analysis of these samples. The results permit an upper limit to be assigned to the rate of dehydrohalogenation of the tertiary halides under these experimental conditions. Since the rate of formation of dibromide from the reaction of bromine with *t*-butyl chloride in liquid sulfur dioxide occurs at a rate many magnitudes greater than the rate of spontaneous dehydrohalogenation of this alkyl halide, spontaneous conversion of the ionized alkyl halide into olefin and hydrogen halide cannot

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[8] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3557 (1953); F. C. Whitmore, W. L. Evers and H. S. Rothrock, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 408.

[9] E. Linermann, *Ann.*, **136**, 37 (1865); V. Meyer and F. Muller, *Ber.*, **24**, 4277 (1891); V. Meyer and P. Petrenko-Kritschenko, *ibid.*, **25**, 3304 (1892); A. D. Herzfelder, *ibid.*, **26**, 1257 (1893); A. Kronstein, *ibid.*, **54**, 1 (1921).

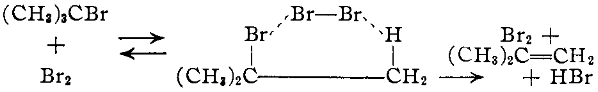
[10] (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **72**, 4677 (1950); (b) **74**, 1891 (1952); (c) **75**, 3561 (1953).

[11] F. R. Mayo and A. A. Dolnick, *ibid.*, **66**, 985 (1944).

[12] F. C. Whitmore and W. L. Evers, *ibid.*, **55**, 812 (1933); F. C. Whitmore and H. S. Rothrock, *ibid.*, **55**, 1106 (1933); M. L. Dhar, E. D. Hughes, C. K. Ingold, D. M. M. Mandour, G. A. More and L. S. Woolf, *J. Chem. Soc.*, 2093 (1948).

[13] E. D. Hughes, C. K. Ingold and A. D. Scott, *ibid.*, 1271 (1937).

[14] R. M. Keefer and L. S. Andrews, THIS JOURNAL, **75**, 543 (1953); **76**, 253 (1954). These authors also have considered the possibility that the olefin might arise through a cyclic transition state. As applied to the present problem this would be:



$$\begin{matrix}(CH_3)_3CBr\\+\\Br_2\end{matrix} \rightleftharpoons \begin{matrix} & Br{-}Br & \\ Br & & H\\ | & & |\\ (CH_3)_2C & \text{———} & CH_2\end{matrix} \longrightarrow \begin{matrix}Br_2 +\\(CH_3)_2C{=}CH_2\\+ HBr\end{matrix}$$

play any significant role in the observed reaction of bromine with the tertiary halide.[13]

Our failure to detect even slight traces of hydrogen halide above solutions of *t*-butyl chloride and bromide in liquid sulfur dioxide argues against any significant dissociation of the tertiary halides into olefin and hydrogen halide in these solutions.

Hydrogen bromide is an exceedingly strong acid.[15] Consequently, a low tendency for the transfer of a proton from the carbonium ion to the bromide ion would not be surprising. The species $HBr \cdot Br_2$ would be expected to possess an even greater proton transfer ability and the carbonium ion would therefore be expected to possess an even smaller tendency to transfer a proton to the Br_3^- ion.

Iodine possesses stronger Lewis acid characteristics than bromine.[10] If bromine were capable of the hydrohalogenation of tertiary alkyl bromides under conditions typical of those utilized for the formation of dibromide, it would be expected that iodine should be even more effective. Accordingly, an attempt was made to dehydrohalogenate *t*-amyl bromide at 25° in refluxing methylene chloride in the presence of molecular iodine.

However, here also we observed no significant dissociation into hydrogen bromide and olefin over a period of six hours. The sensitivity of the experimental method was such that for the entire reaction time we can set an upper limit to the dissociation of the *t*-amyl bromide of less than 0.001% of the material present in the reaction vessel.

All of these experiments and considerations argue strongly against the possibility that dissociation of the tertiary halides into the olefin plays any significant role in the formation of the dibromides. Of course, they do not completely exclude the possibility that exceedingly minute concentrations of olefin and hydrogen bromide exist in the reaction mixture, concentrations too small to be detected by our methods, and that the reaction might proceed through the very rapid replenishment of these minute concentrations under the catalytic influence of the halogen.

Kinetics appeared to provide a critical test of this possibility. If the formation of the olefin were involved in the rate-determining step, the rate should be first order in alkyl bromide and bromine. On the other hand, if the reaction of the olefin with bromine were the rate-determining step, the reaction should be first order in alkyl bromide and bromine and inversely proportional to the hydrogen bromide concentration.

Accordingly, we carried out a kinetic study of the reaction of bromine with an equimolar amount of *t*-butyl bromide in carbon tetrachloride solution at 0° in sealed ampules from which the hydrogen bromide formed in the reaction could not escape. The results are summarized in Table II.

The lack of constancy of the two second-order constants, k_2 and k_2', appears definitely to exclude the two alternative mechanisms based upon the formation of the olefin as a reaction intermediate.

TABLE II

REACTION OF BROMINE WITH *t*-BUTYL BROMIDE AT 0° IN CARBON TETRACHLORIDE SOLUTION[a]

Time, hr.	Bromine, mole liter^{-1}	Reaction, %	$k_2 \times 10^2$, l. mole^{-1} hr.$^{-1}$	$k_2' \times 10^3$ hr.$^{-1}$	$k_3 \times 10^2$, l.^{2} mole^{-2} hr.$^{-1}$
0	0.925	0			
23	.841	9.2	0.47	0.20	0.53
50	.768	17.5	.44	.35	.53
72	.719	22.8	.43	.50	.53
95	.676	27.0	.42	.58	.54
120	.646	30.2	.39	.61	.51
144	.615	33.6	.35	.67	.51
169	.586	36.7	.37	.72	.52
195	.564	39.1	.35	.74	.51
217	.542	41.5	.35	.80	.51
242	.525	43.8	.34	.81	.51

[a] The solution as originally prepared was 1.00 *M* in bromine and *t*-butyl bromide. The three rate constants in Table II were calculated from the integrated forms of the equations, $dx/dt = k_2(\alpha - x)^2$, $dx/dt = k_2'(\alpha - x)^2/x$ and $dx/dt = k_3(\alpha - x)^3$, where α is the concentration of bromine at zero time and $\alpha - x$ the concentration of bromine at a given time.

The relative constancy of the third-order rate constants suggests that the reaction may proceed through an attack by a bromine molecule on the alkyl bromide–bromine complex or the derived ion pair

$$Br_2 + (CH_3)_3C^+Br_3^- \longrightarrow (CH_3)_2CBrCH_2Br + HBr + Br_2$$

We therefore are faced with the question as to the process by which bromine can react with the tertiary carbonium ion to produce the dibromide.

In saturated aliphatic hydrocarbons and their derivatives, substitution of hydrogen does not occur at a significant rate at room temperature except under free radical conditions (illumination or peroxide catalysts). In the preceding paper it was pointed out that the presence of electron-attracting substituents greatly increases the difficulty of attack of carbon–hydrogen bonds by chlorine atoms. Consequently, the positive charge of the carbonium ion should reduce greatly the activity of carbon–hydrogen bonds toward attack by bromine atoms. For this and other reasons, a simple direct substitution process for the carbonium ion appears to be out of the question.

Both experimental data and theoretical considerations argue against the possibility that the olefin is an important intermediate in the formation of the dibromide. We have argued previously that a direct substitution reaction of the carbonium ion is improbable. As far as we can see, the only way out of this impasse appears to be the postulate of a reaction of bromine with the π-complex form of the carbonium ion.[16]

It is therefore proposed that, under the influence of the bromine, the tertiary bromide undergoes ionization to an ion-pair containing the more stable σ-form of the carbonium ion.[17] According to this interpretation, the σ-structure will be in equilibrium with a small amount of the higher energy π-struc-

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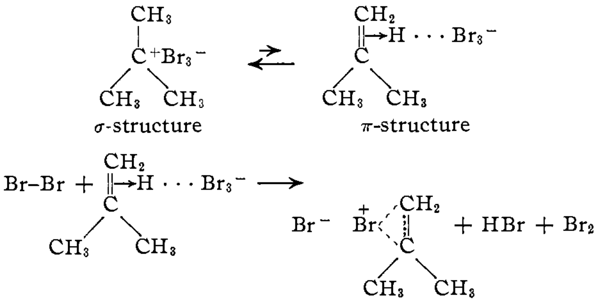
[15] It has been estimated to have an ionization constant of 10^{+8}. Private communication from R. P. Bell of Oxford University.

[16] The π-complex form of the carbonium ion has been presented as an intermediate in olefin hydration: R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952); J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *ibid.*, **75**, 1253 (1953).

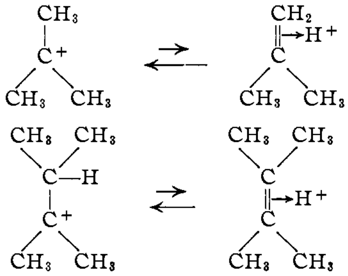
[17] H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

ture.[18] Bromine is then considered to react with the π-form, displacing a proton and forming the bromonium ion. This then reacts in the usual manner to form the dibromide.

$$(CH_3)_3CBr + Br_2 \rightleftarrows (CH_3)_3C^+Br_3^-$$



The results show that the ease of formation of dibromides from tertiary bromides increases with the nature of the hydrogen atom in the position adjacent to the halogen: primary < secondary < tertiary. This is attributed to a more favorable equilibrium for the π-form in the case of the ions containing secondary or tertiary hydrogens.



This mechanism is consistent with all of the experimental data now available for the reaction under discussion. Moreover, it also is consistent with the available data on the addition of halogen acids to olefins.[19,20] It is therefore proposed as a reasonable explanation for the rapid dark reactions of halogens with tertiary alkyl halides, both in non-polar media, as in the present study, and in highly polar media of low basicity, as in liquid sulfur dioxide.[13] The utility of this concept in interpreting other types of reactions of alkyl halides in media such as sulfur dioxide and nitromethane remains to be explored.

Experimental Part

Materials.—Research grade triptane, obtained from General Motors Corp., was passed over silica gel and rectified in a 50-plate column packed with stainless steel helices; b.p. 80.3° at 745 mm., n^{20}_{D} 1.3895. The cumene was rectified in the same column; b.p. 151.4–151.5° at 740 mm., n^{20}_{D} 1.4915. 2,3-Dimethylbutane (99 mole % minimum) and 2-methylpentane (99 mole % minimum), obtained from the Phillips Petroleum Co., were passed over silica gel before use. The hydrocarbons were dried thoroughly over calcium hydride under a nitrogen atmosphere prior to use.

Photobromination of Triptane.—Triptane (1 mole) was brominated at 80° with bromine (0.25 mole) over a period of 1.5 hours in a 500-ml. four-necked flask equipped with a Trubore stirrer, dropping funnel, thermometer and condenser fitted with a drying tube. During the addition of the bromine, the triptane was illuminated by a 150-watt, clear light bulb placed one inch from the flask. Hydrogen bromide was evolved steadily during the reaction and the triptane remained nearly colorless at all times. After distilling 25 g. of triptane, the flask was cooled to 0°, whereupon the contents froze to a nearly solid mass of crystals. From 57 g. of apparently dry crystals left by washing with 50 ml. of cold triptane, 36 g. of 2-bromo-2,3,3-trimethylbutane (80%), m.p. 149–150° (sealed tube), and 10 g. of triptane were obtained by vacuum sublimation at 80° (25 mm.). Concentration of the filtrate produced more 2-bromo-2,3,3-trimethylbutane, only slightly impure. Appreciable amounts of primary bromides or dibromides could not be isolated.

Photobromination of Cumene.—Cumene (1 mole) was brominated with Merck reagent grade bromine (0.5 mole) over a period of one-half hour at 60° in an apparatus similar to that used for the bromination of triptane. The cumene was colorless at all times during the reaction. After the reaction was complete, the flask was flushed with dry nitrogen to remove hydrogen bromide and the mixture of bromides was analyzed by determination of the fraction of the bromine which could be hydrolyzed in 80% ethanol at 25°. As the total bromine content of the product was 0.00322 mole per gram and the hydrolyzable bromine concentration was 0.00234 mole per gram, 73% of the bromine was present as the tertiary bromide.[21] When the bromination was repeated at 0° (0.25 mole of bromine per mole of cumene, reaction time 1.5 hours), 94% of the bromine was found to be present as the tertiary bromide. The tertiary bromide could not be crystallized from solution at −80° and attempts to rectify the reaction product at pressures below 1 mm. resulted in dehydrobromination.

Production of 1,2-Dibromo-2-phenylpropane by Bromination of Cumene.—Bromine was added under illumination to 0.5 mole of cumene in methylene chloride solution at 0°, until a bromine color persisted in solution for two minutes after the addition of a drop of bromine. Exactly one mole of bromine was required. Rectification of the product in a Vigreux column gave 111 g. of 1,2-dibromo-2-phenylpropane (74%), b.p. 120–120.5° (16 mm.).

Photobromination of 2,3-Dimethylbutane.—Bromine, 0.5 mole, was added to 2 moles of 2,3-dimethylbutane (n^{20}_{D} 1.3749) at 55° over a period of six hours. The addition was made at such a rate that the hydrocarbon remained colorless through the reaction. Upon cooling, 65 g. of crystals (m.p. 168–170°) were obtained. Sublimation at 95–100° (5 mm.) gave 54 g. of 2,3-dibromo-2,3-dimethylbutane (89%), m.p. 169–171° (sealed tube).

Photobromination of 2-Methylpentane.—Bromine, 0.5 mole, was added dropwise to 2 moles of 2-methylpentane (n^{20}_{D} 1.3714) at 60° over a period of eight hours at a rate such that the solution was nearly colorless at all times. Rectification of the product in a 20-inch modified Widmer column yielded 64 g. of material boiling at 79–79.5° (140 mm.) and 10 g. of material boiling at 92–92.5° (40 mm.). The first fraction contained 48.0% bromine (calcd. for monobromide, 48.4%) and by hydrolysis in 80% ethanol at 25° was found to contain 92% tertiary bromide. The lower boiling fraction thus was judged to be a mixture of 2-bromo-2-methylpentane (92%) and secondary bromides (8%) of 2-methylpentane. The second fraction contained 65.4%

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(18) There has been a great deal of discussion of the importance of the π-structure of carbonium ions. See M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 211–213. Present evidence favors the view that the π- or bridged structure must be less stable than the σ- or classical structure with the result that the π-structure ordinarily plays no significant role in the ionization of carbonium ion formation or in their subsequent reactions. See J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., THIS JOURNAL, **74**, 4283 (1952); H. C. Brown and R. B. Kornblum, *ibid.*, **76**, 4510 (1954). In the present instance the reaction conditions are unfavorable for the usual reactions of carbonium ions, forcing the reaction to proceed through the higher energy, less stable π-complex structure.

(19) M. Havill (Russell), Ph.D. Thesis, Purdue University, 1953.

(20) Independent evidence of the participation of the π-complex form of the carbonium ion in a related reaction has been obtained by Professor Henry Feuer and Dr. J. Bello of Purdue University in their study of the reaction between N-methylol-2,3-dibromoisobutyramide and bromine. This work was discussed at the 1954 Fall Meeting of the American Chemical Society and will be published in the near future.

(21) The analytical procedures based on selective hydrolysis were tested thoroughly on mixtures of primary, secondary and tertiary bromides and dibromides.

bromine (calcd. for dibromide, 65.5%) and was considered to be largely 2,3-dibromo-2-methylpentane.

Bromination of 2-Bromo-2,3,3-trimethylbutane.—2-Bromo-2,3,3-trimethylbutane (0.075 mole) was dissolved in 100 g. of carbon tetrachloride and reagent grade bromine (0.076 mole), freshly distilled from phosphorus pentoxide, was added. The flask was carefully shielded from light and protected from moisture. After 40 hours at 25°, the mixture was nearly colorless. After removal of the carbon tetrachloride, 2 g. of unreacted 2-bromo-2,3,3-trimethylbutane (0.011 mole) was sublimed from the flask under vacuum. The remaining material was rectified in a 20-inch modified Widmer column and 10.3 g. (63%) of dibromide (presumably 1,2-dibromo-2,3,3-trimethylbutane), b.p. 88.5–89.5° (10 mm.), and 3 g. of tribromide (14%), b.p. 107–110° (3 mm.), were collected. The dibromide fraction contained 61.6% bromine (calcd. 62.0%) and the higher-boiling fraction contained 70.7% bromine (calcd. for tribromide, 71.2%).

Bromination of *t*-Amyl Bromide.—Bromine, 0.25 mole, was added to freshly distilled *t*-amyl bromide, 0.25 mole, dissolved in 120 g. of carbon tetrachloride. After standing in the dark for 40 hours at 25° the reaction mixture was rectified in a 20-inch modified Widmer column. There were collected 34 g. of 2,3-dibromo-2-methylbutane (59%), b.p. 72.5–73° (30 mm.), n^{20}_{D} 1.5095, and 8.5 g. of tribromide (11%), b.p. 110–114° (15 mm.). The dibromide fraction contained 69.1% bromine (calcd. 69.5%) and the tribromide fraction 77.1% bromine (calcd. 77.6%).

Bromination of 2,3-Dimethyl-2-butanol.—2,3-Dimethyl-2-butanol (b.p. 65.5° (100 mm.), n^{20}_{D} 1.4182) and bromine were dissolved in sufficient carbon tetrachloride to make a solution 2 *M* in each component. After 60 hours in the dark, all of the bromine had been consumed. Crystallization and rectification of the product from 10.2 g. of 2,3-dimethyl-2-butanol yielded 18.2 g. of 2,3-dibromo-2,3-dimethylbutane (m.p. 168–169°), 2.1 g. of unreacted alcohol, 1 g. of tribromide fraction (b.p. 140–150° (25 mm.)), 74.3% Br (calcd. 72.5%) and traces of a lachrymator. When the reaction was repeated (16 g. bromine, 10.2 g. alcohol) in the presence of 10 g. of finely divided calcium carbonate, only 80% of the bromine had reacted in 72 hours. Crystallization and rectification of the product produced 10 g. of dibromide, 5 g. of unreacted alcohol, and 4 g. of a high-boiling material (presumably mainly the tribromide).

Bromination of *t*-Butyl Bromide.—*t*-Butyl bromide, 40 g., and an equivalent molar amount of bromine, 46 g., were allowed to stand in the absence of solvent for 42 hours at 0° in the dark. Rectification gave 43 g. (68%) of isobutylene dibromide (b.p. 146–149°) and 6 g. of higher boiling material (presumably mainly the tribromide). The data on the rate of reaction of bromine with *t*-butyl bromide in carbon tetrachloride solution at 0°, plotted in Fig. 1, was obtained by mixing at 0°, 15 ml. of a 4.0 *M* (at 0°) solution of bromine in carbon tetrachloride with 25 ml. of a 2.4 *M* (at 0°) solution of *t*-butyl bromide and diluting to 50 ml. with carbon tetrachloride. Samples were removed at appropriate intervals, added to 20 ml. of water containing the potassium iodide from 2 ml. of the saturated aqueous solution, and titrated with 0.1 *N* sodium thiosulfate solution.

The kinetic results summarized in Table II were obtained in similar manner. C.P. Bromine (15.984 g.) and freshly distilled *t*-butyl bromide (13.700 g.) were diluted to 100 ml. at 0° with reagent grade carbon tetrachloride. Samples of 5 ml. were sealed under vacuum in ampoules of about 8 ml. volume. The samples were stored in an ice-bath and 1-ml. aliquots titrated with standard sodium thiosulfate solution at appropriate intervals.

Five Mole Per Cent. Photobrominations at 25°.—Five mole per cent. brominations were performed at 25.0 ± 0.1° by immersing a 200-ml. three-necked flask, equipped with a Trubore stirrer, gas inlet tube, thermometer and condenser fitted with drying tube, in a water-bath containing a 150-watt, clear light bulb immersed in the thermostat one inch from the flask. After the hydrocarbon had been degassed by a stream of prepurified nitrogen, a weighed quantity of reagent grade bromine, freshly distilled from phosphorus pentoxide, was allowed to vaporize into a stream of nitrogen and to react with the hydrocarbon during a period of one hour. Hydrogen bromide was removed from the solution by a stream of nitrogen and total and hydrolyzable bromine analyses were performed directly on the reaction product.[22] Hydrolysis of the bromination products of 2-methylpentane and 2,3-dimethylbutane in ethanol at 25° did not give a constant sodium hydroxide titer after a few hours, as did the bromination products of triptane and cumene. Instead, the titer increased slowly, exhibiting a linear increase with time. The concentration of tertiary bromide was obtained in these cases by extrapolation of the linear portion of the hydrolysis curve to zero time.

The experimental data are summarized in Table III.

TABLE III

ANALYTICAL RESULTS OF BROMINATIONS[a]

Hydrocarbon[b] (°C.)	Bromine	Total bromide	Tertiary bromide
Cumene (25)	0.055	0.0541	0.0541
Triptane (25)	.050	.0486	.0457
2-Methylpentane (25)	.051	.0492	.0443
2,3-Dimethylbutane (25)[c]	.051		.0214
2,3-Dimethylbutane (25)	.031	.0302	.0238
2,3-Dimethylbutane (0)	.038	.0371	.0326

[a] All quantities in moles. [b] One mole of hydrocarbon used in all expts. [c] Some dibromide crystallized from solution during the bromination.

Experiments to Detect the Dehydrohalogenation of Tertiary Alkyl Halides.—Sulfur dioxide (15 ml.) was charged into a Podbielniak Hyd-Robot column (100 theoretical plates) and brought to reflux temperature at 737 mm. *t*-Butyl chloride (5 ml.) was added to the refluxing sulfur dioxide. The reflux temperature at total reflux remained at −12.5 ± 0.5° during the next six hours (pot temperature −6°). It is estimated that the formation of 0.5 ml. of hydrogen chloride vapor would have lowered the reflux temperature to that of hydrogen chloride. At the end of the experiment, 100 ml. of vapor under standard conditions was removed slowly at a high reflux ratio and analyzed by means of a mass spectrometer. Hydrogen chloride was not detected in this sample. From the sensitivity of the instrument, the amount present must have been less than 0.01%. From these data it is estimated that not more than 0.001% of the *t*-butyl chloride dehydrochlorinated during the six-hour period.

The above experiment was repeated using *t*-butyl bromide (5 ml.) in sulfur dioxide (25 ml.) at 722 mm. (reflux temperature −14 ± 0.5°, pot temperature −7°). Again no hydrogen bromide could be detected in a mass spectrometer after six hours of reflux. Consequently, less than 0.001% of the *t*-butyl bromide can have dehydrobrominated during this period.

To test the stability of 2-bromo-2,3,3-trimethylbutane toward spontaneous dehydrobromination, 500 ml. of a 0.2 *M* solution of the bromide in C.P. carbon tetrachloride was rectified at atmospheric pressure in a 50-cm. modified Widmer column. Over a 24-hour period 400 ml. of carbon tetrachloride was removed at a high reflux ratio. All gases evolved were passed into a sodium hydroxide solution. Extraction of the distillate by water indicated the complete absence of acidic materials or bromide ion in the distillate. The halide ion content of the sodium hydroxide solution did not increase during the rectification.

The following experiment established the failure of iodine to bring about dehydrohalogenation. *t*-Amyl bromide (5 ml.), methylene chloride (25 ml.) and 2 g. of iodine were placed in the pot of a Podbielniak Hyd-Robot column. The column was operated at a pressure such that the temperature of the pot remained at 25°. Distillate (100 ml. of vapor at standard conditions) was removed slowly from the column under a high reflux ratio during a six-hour period. The distillation temperature was 14° at 300 mm., the expected reflux temperature for pure methylene chloride. Analysis of the distillate by means of a mass spectrometer failed to detect hydrogen bromide (limit of detection, 0.01%). Thus, less than 0.001% of the *t*-amyl bromide dehydrobrominated during the six-hour period.

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(22) Total halogen analyses were performed by the Rauscher method: W. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).