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

THE BROMINATION OF CYCLOHEXANE, METHYLCYCLOHEXANE, AND ISOBUTANE

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Previous work (1) in this laboratory has shown that the side-chain bromination of toluene is favored by the presence of oxygen or peroxides, by low concentrations of bromine, and by the action of light. A chain mechanism involving bromine atoms was proposed to explain these effects. The present investigation was undertaken to determine whether or not similar factors control the bromination of aliphatic hydrocarbons. The hydrocarbons chosen for investigation were cyclohexane, methylcyclohexane, and isobutane. The present study makes possible a comparison of the relative reactivities of primary, secondary, and tertiary hydrogen atoms towards substitution by bromine atoms.

PREVIOUS WORK[2]

Markownikow (3) reported that cyclohexane reacts only slowly with bromine at 100°, and that at 110° an equimolecular mixture of the reactants gives chiefly polybromides and unchanged cyclohexane. Bodroux and Taboury (4) found that the bromination of boiling cyclohexane is accelerated by sunlight and ultraviolet light.

The photochemical vapor-phase bromination of cyclohexane has been studied by Pusch (5), Noddack (6), Wood and Rideal (7), and Jost (8). Both Pusch and Noddack employed radiation corresponding to the continuous absorption of bromine, worked at room temperature, and recorded no precautions to exclude oxygen. They agree that one molecule of bromine reacts per quantum of light absorbed.[3] Wood and Rideal employed glass apparatus at room temperature and used radiation corresponding to the band absorption of bromine. They observed a slow reaction in the dark. Because their reaction products consisted mostly of di- and

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[1] This paper is an abstract of a dissertation submitted by William Hered in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The University of Chicago, 1939.

[2] See Ref. 2 for references on the bromination of pure and impure hydrocarbons with and without metal catalysts.

[3] Pusch records that under the same conditions, the quantum yields in the bromination of toluene, hexane, and heptane exceed one and range as high as sixty.

tri-bromocyclohexanes, they suggested that cyclohexyl bromide was produced in an activated state such that it would easily react with molecular bromine. Jost worked with quartz apparatus at 73–106°, found no reaction in the dark, and concluded that the thermal reaction of Wood and Rideal must have been a wall reaction. He employed both types of radiation previously mentioned and found no difference between them. This was taken as an indication that an activated bromine molecule would eventually dissociate into atoms, even if not in a single step. Wood and Rideal and Jost are in agreement that the rate of the reaction in any single experiment is proportional to the light absorbed, and that the reaction is inhibited by oxygen. Jost records that in a series of experiments the rates of reaction also depend on the cyclohexane concentration. He states that in the absence of oxygen, the quantum yields varied from 12 to 37, in its presence, from 3 to 7. A temperature coefficient of about 2 for a range of 30° indicated that the quantum yield would have been about 2 at room temperature, in fair agreement with the work of Pusch and of Noddack. From the relations between the light absorbed and the extent of reaction and from the phenomenon of oxygen inhibition, Jost concludes that the vapor-phase photochemical bromination of cyclohexane is a chain reaction involving bromine atoms.

Markownikow (9) found that pure liquid methylcyclohexane does not react with bromine in diffused light. The reaction in sunlight is slow at 100°, moderate at 115°.

Isobutane and bromine in equimolecular quantities in daylight are reported by Butlerow (10) to give polybromides and unchanged isobutane.

The chlorination of isobutane and other paraffin hydrocarbons has been studied by Hass and co-workers, and some interesting generalizations have been reported (11). One of these is that the order of increasing activity of hydrogen atoms is primary, secondary, tertiary, and that their relative reactivities in the thermal vapor-phase chlorination at 300° are represented by the series 1.00, 3.25, 4.33. The series approaches 1, 1, 1 as the temperature increases, and is not affected by the presence of any catalysts investigated. The results of liquid-phase chlorination correspond to those obtained at a higher temperature in the vapor phase.

EXPERIMENTAL

A study has been made of the factors which influence the bromination of cyclohexane, methylcyclohexane, and isobutane in the liquid phase. Mixtures of bromine and of the hydrocarbon (containing no solvent) were allowed to react near room temperature in glass-stoppered or sealed containers. The progress of the reaction of cyclohexane or methylcyclohexane in sealed tubes was estimated with a precision of ±3% by comparison with standard solutions of bromine in carbon tetrachloride, and in stoppered tubes with a precision of better than 1% by titration with potassium iodide and sodium thiosulfate. Reactions in sealed tubes were usually allowed to proceed until the mixtures became colorless, when 100% reaction was assumed. The extent of the bromination of isobutane was determined by titration when the reaction did not reach completion.

Experiments in the dark were carried out in a large, stoppered, water-filled Dewar vessel maintained between 20° and 25°. Experiments in the light were usually carried out at a distance of 16 cm. (center to center) from a 300 watt incandescent lamp. The reaction vessel was suspended in a water-bath with a plane glass window. Tap water was circulated through this bath at a rate such that its temperature was maintained near 20°. In experiments lasting up to seven hours, the maximum variation was ±2°, in longer experiments, ±5°. To avoid any complications from a photochemical vapor-phase reaction, the reaction tubes were entirely screened from light above the level of their liquid contents.

Materials. Eastman Kodak Co. cyclohexane was washed with fuming sulfuric acid, dried over calcium chloride, fractionally distilled, and stored over sodium or phosphorus pentoxide. The fraction used has the following constants: m.p. 5.8°; b.p. 80.2–80.5° at 750 mm.; n_D^{20} 1.4256. The work of Seyer, Wright, and Bell (12) indicates that such material might contain a small amount of methylcyclohexane. Fractionation through a Podbielniak column yielded a fraction of m.p. 6.0° and n_D^{20} 1.4258 (recorded for cyclohexane (12), 6.47°, 1.42635) which was indistinguishable in bromination experiments from the material usually employed.

Methylcyclohexane and 99.5% isobutane were generously supplied by the Universal Oil Products Co. The methylcyclohexane was purified according to the procedure used for cyclohexane: b.p. 100.2–100.8° at 746 mm.; n_D^{20} 1.4231.

Procedure. Experiments with cyclohexane and methylcyclohexane in the presence of air were carried out in glass-stoppered vessels which were opened periodically for titration of samples. Isobutane experiments, usually employing 1.3 g. of hydrocarbon, were carried out according to the procedure described by Kharasch, Fineman, and Mayo (13) for cyclopropane, with provisions for admission of measured pressures of oxygen before the reaction tubes were sealed. The reported uncorrected oxygen pressures were measured while the reaction tubes were partially immersed in a bath at −80°.

Experiments with cyclohexane and methylcyclohexane in the absence of air, and with measured pressures of oxygen, were performed in much the same manner except that 5 cc. of the dry liquid hydrocarbon was introduced into the reaction tube with the aid of a pipette.

Analysis of products from isobutane and methylcyclohexane. The proportion of tertiary bromide in the bromination products was estimated from the extent of reaction with water at room temperature (14). The proportion of dibromide in the bromination products was estimated by removing the unsubstituted hydrocarbon and analyzing for bromine.

RESULTS

Effect of oxygen and light. The individual effects of light and oxygen on the bromination of cyclohexane, methylcyclohexane, and isobutane are shown in Table I. It is evident that in the absence of oxygen and light, all three hydrocarbons react only to the extent of 1% per month. In the dark, but in the presence of oxygen, cyclohexane and methylcyclohexane react much faster, about 10% per day. In the case of these two hydrocarbons, illumination in the absence of oxygen is approximately as effective in accelerating the reaction as oxygen in the absence of illumination, the factor being of the order of 500 in either case. The rate of bromination of isobutane (at a higher bromine concentration) is increased to a greater extent by light but to a lesser extent by oxygen.

The combined effects of oxygen and light are best illustrated with the cyclic hydrocarbons by experiments (Table II) in which the initial bromine concentration was 0.20 molar and the oxygen pressure was 5–15 cm. These data show that oxygen and light together cause the reaction to proceed several hundred times as fast as either agent alone. Their combined effect approximates the product, rather than the sum, of their individual effects. Experiments with 1.0 or 2.0 molar bromine solutions in isobutane indicate that the photochemical bromination of isobutane is accelerated by oxygen by a factor of only 20 to 25, depending on the bromine concentration.

TABLE I

EFFECT OF LIGHT AND OXYGEN ON BROMINATION OF HYDROCARBONS[a]

	INITIAL CONCENTRATION Br_2 (MOLES/LITER)	ABSENCE OF LIGHT		LIGHT PRESENT OXYGEN ABSENT
		Oxygen Absent	Oxygen Present	
Cyclohexane	0.05			40% in 70 hours (2)
	.20	5% in 8 months (2)	60% in 5 days[b] (2) 75% in 4 days[e] (2) 55% in 4 days[f] (2)	60% in 136 hours (2)
Methylcyclohexane	.05			100% in 2–3 hours (3)
	.20	8% in 6 months (3)	50% in 5 days[b] (2)	100% in 60–78 hours (3)
Isobutane	1.0			100% in 8 hours
	2.0	<2% in 2 months (2)	50% in 20 days[c] 70% in 20 days[d]	100% in 13–15 hours (2)
	5.0			100% in 35 hours

[a] Numbers in parentheses indicate total number of experiments in which substantially the same result was obtained.

[b] Air at 1 atmosphere pressure.

[c, d, e, f] Oxygen at 1, 10, 15 or 37 cm. (of mercury) pressure, respectively.

The accelerating effect of oxygen on the photochemical reaction varies with its pressure. Data on cyclohexane experiments at an initial bromine concentration of 0.20 molar in Table II are amplified in Figure 1. Similar data on methylcyclohexane are given in Table II and Figure 2. It is

TABLE II

Combined Effects of Light and Oxygen on Bromination of Hydrocarbons

	INITIAL CONCENTRATION Br_2	OXYGEN PRESSURE IN CM. MEASURED AT −80°						AIR AT 1 ATM.
		1	5	10	15	37	76	
Cyclohexane	0.05	90% in 10 min. (2)	85% in 10 min. (2)		80% in 10 min. (2)	70% in 10 min. (2)		85% in 1 hr. (3)
	.20	50% in 30 min. (4)	70% in 30 min. (4)		55% in 30 min. (2)	35% in 30 min. (4)	20% in 30 min. (2)	85% in 3 hrs. (5)
	1.0			100% in 7 hrs. (2)				85% in 5 hrs. (2)
	5.0							50% in 65 hrs. (2)
Methylcyclohexane	.05							85% in 5 min. (3)
	.20	80% in 5 min. (2)	90% in 5 min. (2)		80% in 5 min. (2)	70% in 5 min. (2)		85% in 15 min. (4)
	1.0			100% in 3 hrs. (2)				85% in 2 hrs. (2)
	5.0							50% in 48 hrs. (2)
Isobutane	1.0		100% in 20 min. (3)	100% in 20 min. (3)				
	2.0	90% in 4 hrs. (2)	90% in 45 min. (3)	90% in 45 min. (2)	90% in 45 min.	90% in 25 min. (2)		
	5.0			100% in 23 hrs. (3)				
Toluene	.20		100% in 2-4 sec. (2)		100% in 5-7 sec. (2)	100% in 10-12 sec. (2)	100% in 15-20 sec. (2)	
	1.0		100% in 20 sec. (2)		100% in 40 sec. (2)	100% in 2 min. (2)	100% in 3 min. (2)	

shown that oxygen exerts its maximum effect on the photochemical bromination of cyclohexane and methylcyclohexane at about 5 cm. pressure, and that higher oxygen pressures retard the reaction. The data indicate that the optimum oxygen pressure may be higher (with 2.0 molar bromine) for isobutane.

That oxygen retards as well as promotes the bromination of toluene had not been observed previously (1). The highest rate of bromination of toluene is obtained at low oxygen pressures (Table II).

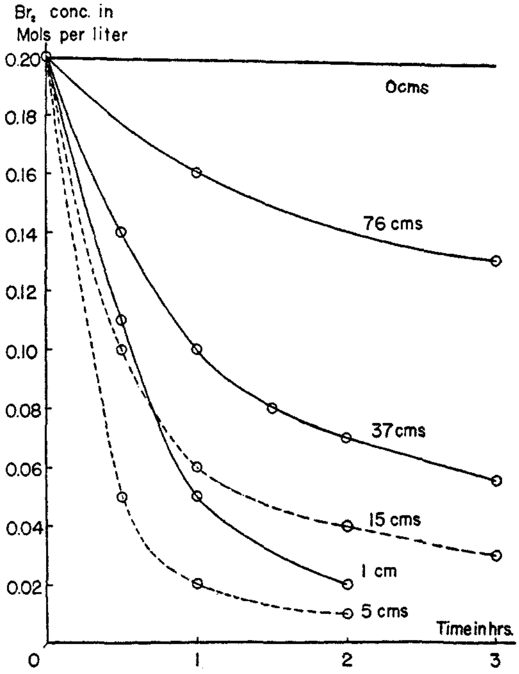

FIG. 1. PHOTOBROMINATION OF CYCLOHEXANE AT VARIOUS OXYGEN PRESSURES

On the basis of the data presented, valid comparison of the relative rates of bromination of cyclohexane, methylcyclohexane, and isobutane is possible only for the photochemical reaction with 10 cm. pressure of oxygen and an initial bromine concentration of 1.0 molar. The times required for complete reaction of bromine are in the approximate relationship: cyclohexane, 20; methylcyclohexane, 9; isobutane, 1.

Effect of bromine concentration. Comparative data on the effect of bromine concentration are available only for the photochemical reactions recorded in Tables I and II. Table I indicates that in the absence of oxygen, the proportion, but not the absolute amount, of bromine reacting with cyclohexane is greater in the more dilute solution. With methylcyclohexane under the same conditions, both the proportion and absolute amount of bromine reacting is greater in the more dilute solution. Isobutane was studied only at higher concentrations, and in the absence of oxygen the absolute amount of bromine reacting seems to be nearly independent of the initial bromine concentration, over the concentration range studied.

The most extensive study of the effect of bromine concentration was made in photochemical experiments in the presence of air, as shown in the last column of Table II. With both cyclohexane and methylcyclohexane, the time required for complete reaction decreases as the initial bromine concentration is decreased, and both the absolute amount and proportion of bromine reacting in a given time is lower at 5.0 than at 1.0 molar initial bromine concentration. Similar effects with both these hydrocarbons and isobutane are shown under various oxygen pressures in Table II. It is evident that bromination is actually retarded by high concentrations of bromine.

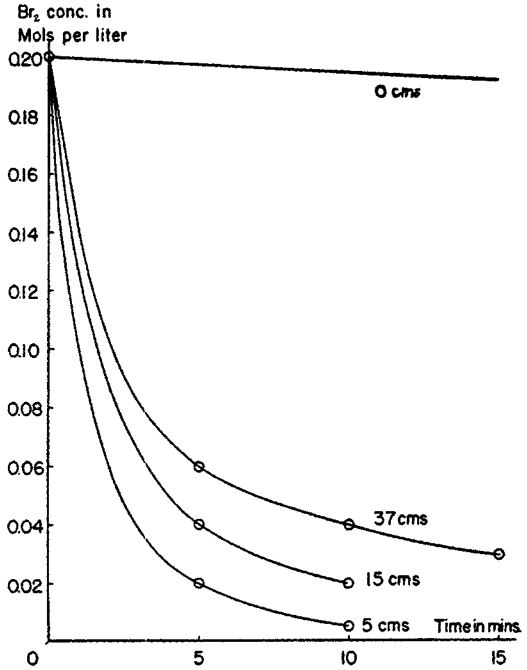

FIG. 2. PHOTOBROMINATION OF METHYLCYCLOHEXANE AT VARIOUS OXYGEN PRESSURES

Effect of peroxides. Although organic peroxides markedly increased the rate of side-chain bromination of toluene, no detectable acceleration was noted in the rate of bromination of the other three hydrocarbons employed in the present study. Experiments were carried out in the presence and absence of air and light, at initial bromine concentrations of 0.05 to 2.0 molar, using benzoyl peroxide, lauroyl peroxide, and ascaridole in proportions from 0.02 to 3 mole per cent per mole of bromine. The peroxides were added in one or in several portions to all three hydrocarbons. In a few experiments a slight retardation of the bromination was noted.

Effect of inhibitors. As in the case of toluene, the rate of bromination of these hydrocarbons can be retarded by small amounts of organic inhibitors (Table III). All of the experiments were carried out in the light, and 0.02 mole of the inhibitor per mole of bromine was employed. It is noteworthy that isoamyl nitrite inhibits the reaction nearly completely, and that thiophenol, ethanol, and diphenylamine are less effective inhibitors.

TABLE III

THE EFFECT OF INHIBITORS ON BROMINATION OF HYDROCARBONS

	INITIAL CONCENTRATION Br_2	OXYGEN PRESSURE	INHIBITOR	EXTENT OF REACTION
Cyclohexane	0.2	5 cm.	None (control)	90% in 1 hour
			diphenylamine	85% in 3 hours
			ethanol	60% in 3 hours
			thiophenol	80% in 14 hours
			isoamyl nitrite	<2%[a] in 74 hours
Methylcyclohexane	0.2	5 cm.	None (control)	100% in 15 min.
			isoamyl nitrite	<2%[a] in 60 hours
Isobutane	2.0	10 cm.	None (control)	100% in 1 hour
			isoamyl nitrite	<2%[a] in 50 hours

[a] Determined by titration of bromine.

Products of reaction. In the case of each hydrocarbon, several lots of reaction products were combined, fractionally distilled, and analyzed as described in the experimental part. Cyclohexane yielded only cyclohexyl bromide. Methylcyclohexane gave about 75% mono- and 25% dibromides. Isobutane gave a mixture of about 60% tertiary butyl bromide and 40% 1,2-dibromo-2-methylpropane. Because significant quantities of isobutyl bromide were not found it is thought that the dibromide may come from isobutene formed by loss of hydrogen bromide from tertiary butyl bromide.

Effect of reaction products. Figures 1 and 2, together with other data which cannot be economically presented in this paper, indicate that in the photochemical, oxygen-catalyzed brominations of cyclohexane and methylcyclohexane where the initial bromine concentration was 0.20 molar, the last quarter of the reaction was slower than in experiments where the initial bromine concentration was 0.05 molar. Tests indicated that cyclohexyl bromide and hydrogen bromide formed could have only a barely perceptible effect on the reaction, and it seemed likely that the product of the photochemical reaction of oxygen and cyclohexane produced an inhibitor for the bromination reaction. This was demonstrated by the following experiments. Cyclohexane with no previous treatment, or which had been previously illuminated in the absence of oxygen, reacted to the extent of 85% in 45 minutes. Cyclohexane which had been previously illuminated for four hours under one atmosphere pressure of oxygen required four hours for the same extent of reaction.[4] Accelerated formation of this inhibitor may explain the retarding effect of high oxygen pressures shown in Table II and Figures 1 and 2.

DISCUSSION OF RESULTS

The effects of visible light, oxygen, and inhibitors on the bromination of cyclohexane, methylcyclohexane, and isobutane, together with previous work on bromination reactions (1, 8) suggests that the reaction proceeds through a chain mechanism involving essentially the following steps:

$$\text{(a)}\quad Br_2 + h\nu \rightarrow 2Br\cdot$$
$$\text{(b)}\quad R\text{-}H + Br\cdot \rightarrow R\cdot + HBr$$
$$\text{(c)}\quad R\cdot + Br_2 \rightarrow R\text{-}Br + Br\cdot$$

Results of the present study indicate that tertiary hydrogen atoms are replaced in preference to the more numerous secondary hydrogen atoms of methylcyclohexane or primary hydrogen atoms of isobutane. The bromination of cyclohexane, which has no tertiary hydrogen atoms, is significantly slower than that of the other two hydrocarbons. The low reactivity of primary hydrogen atoms is further demonstrated in the unusually difficult bromination of neopentane (2,2-dimethylpropane) and trimethylacetic acid (15).

Thermal data indicate that reaction c is definitely exothermic, regardless of the variations in strength of the R–Br bonds formed. The results presented are wholly in agreement with the assumptions that the activation energy of reaction b is positive but small and that it varies with the strength of the carbon-to-hydrogen bond concerned. Tertiary and secondary

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[4] The initial bromine concentration was 0.20 molar and the oxygen pressure 5 cm. in these experiments.

carbon-to-hydrogen bonds are estimated to be weaker than primary carbon-to-hydrogen bonds by 4.4 and 2.5 kcal. per mole, respectively, while the corresponding carbon-to-bromine bonds are stronger than the primary bonds. Adding these differences has led to the estimate by Conn, Kistiakowsky, and Smith (16) that substitution of tertiary and secondary aliphatic hydrogen atoms by bromine is more exothermic by 5.5 and 3.1 kcal., respectively, than substitution of a primary hydrogen atom.

Differences in the activation energy of reaction b corresponding to those in the strength of carbon-to-hydrogen bonds may well be critical in limiting the chain length in bromination reactions at low temperature (0–25°), so that comparatively long chains can be formed if tertiary hydrogen atoms are present, only shorter chains in other cases. Capture of bromine atoms by bromine molecules may be one of the chain-terminating reactions and may account for the retardation of the reaction at high bromine concentrations (1).

The slow reaction of aliphatic hydrocarbons as compared with the side-chain bromination of toluene is apparently due to shorter chain lengths, not to the initiation of fewer chains. This interpretation is consistent with the failure of small quantities of peroxides to affect the bromination of the aliphatic hydrocarbons. Even if the peroxide is 100% efficient in producing free radicals in any manner, or bromine atoms from hydrogen bromide, a chain length of 5 or 10 would prevent 3 mole per cent of peroxide from exerting an effect greater than about 30% on the total reaction. If the efficiency is low, as is more likely, the effect would not be detectable in the present work. Similar reasoning leads to the conclusion that in the bromination of toluene, where small quantities of peroxides exert large effects, the chain lengths must be in the hundreds or thousands. Clearly the methyl group in toluene is more reactive than aliphatic methyl groups. A possible explanation is that since the benzyl radical formed in reaction b may be stabilized by resonance, less energy is required for separation of the hydrogen atom, and the activation energy of reaction b is, therefore, lower.

Consideration of a similar mechanism in the chlorination of aliphatic hydrocarbons shows that the reaction corresponding to b would be exothermic regardless of the nature of R. The activation energy for this step is probably so low that differences in the strength of the R–H bond are less important, particularly at high temperatures (11). Brominations at high temperatures, where bromine atoms could easily acquire the necessary activation energy, should show similar effects.

The inhibition of aliphatic-type chlorinations and of the vapor-phase bromination of cyclohexane (7, 8) by oxygen is well known. This paper shows that excess oxygen retards the liquid-phase bromination of cyclohexane, methylcyclohexane, isobutane, and toluene, but even at the highest oxygen pressures employed, the brominations are much faster than in the absence of all oxygen. Part of the retarding effect of oxygen is due to the formation of an oxidation product of cyclohexane but part may also be due to competition of oxygen and bromine molecules for the free radicals in step c, neither reaction having an appreciable activation energy. The latter explanation applies quantitatively to the vapor-phase bromination (7, 8) of cyclohexane.

The fact that the combined effects of light and oxygen on the bromination of cyclohexane, methylcyclohexane, and isobutane approximate the product, rather than the sum, of their individual effects leads to several tentative hypotheses. Of these, the most attractive is that light serves to initiate chains by dissociating bromine into atoms and that oxygen (but not peroxides) serves to increase the average length of the chains. Oxygen might protect the bromine atoms by formation of the unstable oxide BrO_2, or this oxide may decompose to give another oxide Br_2O (17) which serves as the brominating agent in a chain reaction. Some such explanation is also consistent with our observations that small quantities of peroxides are ineffective in aliphatic brominations.

We hope that further work will explain the combined effect of light and oxygen.

SUMMARY

1. Cyclohexane, methylcyclohexane, and isobutane react very slowly with bromine in the absence of light and oxygen.
2. The reactions are greatly accelerated by either light or oxygen, and the combined effects of light and oxygen are much greater than the sum of the individual effects.
3. The effects of bromine concentration, peroxides, and inhibitors have been studied.
4. An explanation for the phenomena observed is suggested.

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