TABLE	III.	Ethane	OXIDATION,	SENSITIZATION	BY		
Di-tert-BUTYL PEROXIDE							

[Conditions: b; 240; HBr, 120; at inlet and (in	ath tempera contact tir carrier C ₂ H	ture, 210° C. me: approxim (s) at 0.26, 0.4	flows (cc./min ately 3 minutes. 8, and 0.70 of t	.): C ₂ H ₆ , 240; O ₂ , Sensitizer added he reactor length]			
	Unsensi- tized	1 Cc./Min. of Sensitizer at Inlet	1 Cc./Min. of Sensitizer at Inlet + Carrier, C2H6, at Injection Points	1 Cc./Min. of Sensitizer at Inlet + 1 Cc./Min. (in Carrier C2Hs) at All Injection Points			
Acetic acid produced, cc./min.	45	52	ŏ5	67			
TABLE IV. PHOTOSENSITIZATION OF ETHANE OXIDATION, CATALYZED BY HYDROGEN BROMIDE							
(S	tatic reactor	; 2:2:1 mixt	ure of C ₂ H ₆ :O ₂ :	HBr)			
Type	1	Cemp., ° C.	Reaction Time, Min.	Acetic Acid Formed, Me.			
Light Dark Light		195 195 170	$\begin{array}{c}10\\24\\27\end{array}$	$\begin{array}{c} 0.91 \\ 0.40 \\ 0.79 \end{array}$			

oxidation of propane was discussed and an interpretation was proposed. Ethyl bromide has the same effect on the ethane oxidation, as may be seen by reference to Table I. Substitution of 26 cc. per minute of ethyl bromide for 20 cc. per minute of ethane results in over a 10% increase in ethane consumption despite a 4° decrease in the operating temperature and a lowered catalyst input. Furthermore, it has been general experience that inclusion of ethyl bromide in a reacting mixture of ethane, oxygen, and hydrogen bromide lowers the temperature at which "cold flashing," or mild explosion of the mixture takes place.

Peroxide Sensitization. Di-tert-butyl peroxide also sensitizes ethane oxidation. As found previously with the propane oxidation, multiple injection of the sensitizer is advantageous. The effectiveness of the peroxide is demonstrated by results presented in Table III.

Photochemical Sensitization. The accelerating effect of ultraviolet light capable of dissociating hydrogen bromide has been demonstrated by the following:

All experiments were carried out in one of the static reactors equipped with a quartz thimble housing a 100-watt mercury arc (General Electric AH-4 type). A 2 to 2 to 1 mixture of ethane, oxygen, and hydrogen bromide, respectively, was used in most cases, and the total pressure was approximately 1 atmosphere. The effect of the light is best illustrated by a comparison of light and dark experiments at 195° and 170° C. (Table IV). The overall conversion of ethane to acetic acid is seen to be much more rapid in the photochemical reaction, even when this process is carried out at a considerably lower temperature than in the dark control experiment.

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RECEIVED August 17, 1948. Presented in part at the meeting of the Gordon Research Conferences of the American Association for the Advancement of Science, Colby Junior College, New London, N. H., June 1948.

(Oxidation of Hydrocarbons Catalyzed by Hydrogen Bromide)

OXIDATIONS OF AROMATIC COMPOUNDS

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The hydrogen bromide-catalyzed oxidations of aromatic hydrocarbons give the expected acids or ketones when primary or secondary hydrogen atoms on the side chain are attacked. These reactions are modified, however, by the scission of the postulated peroxide intermediates to yield phenol and aliphatic ketones or acids. When tertiary hydrogen atoms are attacked as, for example, in cumene, the scission reaction is dominant. Hydrogen bromide is also a catalyst for the oxidation of alkyl benzenes in liquid phase.

HE oxidations of aromatic compounds appear to conform to the general principles postulated regarding the mechanisms of oxidation in the presence of hydrogen bromide (3, 4,11, 12) as based upon the results obtained from aliphatic substances. However, the product distributions are more complex. and uniformity of reaction is less evident. Further, a large part of the input hydrocarbon appears to enter into transformations resulting in the formation of inseparable mixtures.

By-products from the oxidations of aromatic compounds, as from those of the paraffins, apparently result in some instances by easily interpreted reactions. Thus, halides are probably formed by direct brominations. Less important compounds are produced by competition of one type of hydrogen bromidecatalyzed oxidation with another-for example, propane, by reason of its primary carbon atoms, was converted to propionic acid in an amount equivalent to one tenth of the major product, acetone. A third and the most important classification of byproduct formation is that resulting from the condensation of primary reaction products-for example, of acetophenone resulting from the oxidation of ethylbenzene or cumene. A fourth group of reactions which leads to by-products is that of degradation or carbon chain rupture. Some of these are responsible for the presence of the small amounts of the carbon oxides and lower hydrocarbons found in some of the experiments. Of particular interest in the following discussions are those reactions which may be attributed to "peroxide degradation." In the case of ethylbenzene, acetophenone is the expected product; however, comparable amounts of phenols and of acetic acid, probably produced by splitting, are also formed. It will be recalled that such reactions also occurred in the cases of some of the paraffins. Thus, in the case of isopentane, acetone and acetic acid are produced (3). Similarly, the oxidation of 2,3dimethylbutane produces acetone and isopropyl alcohol (3). In passing to the oxidations of the individual aromatic compounds, it should be mentioned that experiments have shown that benzene is very resistant to hydrogen bromide-catalyzed oxidation; efforts to oxidize it at temperatures even as high as

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 $250\,^{\circ}$ C. yielded only a small amount of organic bromides, and apparently no oxygen entered into organic combination.

OXIDATION OF AROMATIC COMPOUNDS

Oxidation of Toluene. In the light of the experimental data obtained on oxidations of paraffins, the oxidation of toluene, by analogy with that of ethane, should yield benzoic acid. This is the case, as is to be seen by inspection of Table I. The temperature at which the experiment was conducted was lower (approximately 20° C.) and the amount of oxygen consumed considerably less (15%) than in an analogous experiment with ethane. This lower temperature was necessitated by the readiness of the system to "cold flash." However, despite the lower temperature, the product distribution from the oxidation of toluene is less clean-cut. Benzyl bromide is present in an amount equal to that of the acid, and there are other by-products which become of greater importance in the cases of the higher alkyl benzenes.

[Conditions: flows (co	./min.): C7H8, 2	77; O ₂ , 262; H	[Br, 131]
	Moles/	100 Moles Cons	umed of
Products	C_7H_8	O2	HBr
Benzoic acid	27.8	29.7	
Benzyl bromide	34.2		87.2
Phenol	Trace		
Bromophenol	2,5	2.7	6.5
Dibromophenol	1.3	1.4	3.2
Formic acid	Trace		
Benzene	Trace		
Carbon monoxide	5.0	5.4	
Carbon dioxide	3.8	4.1	
Ethylene	1.3		
Ethane	5.0		
Water		46.0	
Unidentified	17.7	23.0	0.0

The mechanism of the formation of the benzoic acid is undoubtedly parallel to that of acetic acid from ethane (4). However, the presence of phenol [for discussions of decomposition of hydroperoxides, see also (7) and (10)] and of brominated phenols suggests that peroxide degradation also plays a minor role in the reaction, thus:

or

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$$\begin{bmatrix} C_{6}H_{5}, & -C=O \end{bmatrix} \longrightarrow C_{6}H_{6}OH + CO_{2}$$
(1)
$$\begin{bmatrix} HO & -O \\ C_{6}H_{5}, & -CH_{2} \end{bmatrix} \longrightarrow C_{6}H_{5}OH + H_{6}CO$$
(2)

Formaldehyde would be easily oxidized to formic acid, of which a trace is found, or further to carbon oxides. This type of reaction seems to be of greater magnitude in the cases of the oxidations of ethylbenzene and of cumene; this will be discussed in the following pages. In the oxidation of ethane considerable quantities of free bromine were found. However, in the present instances such is not the case. This is not surprising in view of the ease of brominating toluene and phenol. It is seen from Table I that the bromophenols actually predominate over phenol itself.

The experimental procedure was that described under "Apparatus" in the second paper of this series (3). The condensable effluent product from toluene oxidation, as well as those from ethylbenzene and cumene, was worked up by first extracting with strong sodium hydroxide solution. The aqueous layer was saturated with carbon dioxide to "spring" the phenols, and after removal of these, the residual solution was made acid with 6 Nsulfuric acid to free the aromatic acids. The portion of the original organic layer which was insoluble in aqueous alkali was distilled under low pressure into several fractions; benzene was found by such distillation. Benzoic acid was identified by its equivalent weight (determined, 121; theoretical, 122) and melting point (determined, 120° to 121° C.; literature value, 121° C.; mixed melting point, 120° C.).

Benzyl bromide was identified by the following data: hydrolyzable bromine, 45.0% (theoretical, 46.8%); boiling point, 198° C. (literature value, 199° C.); tribenzylamine derivative, melting point, 91° C. (literature value, 92° C.).

(Interature value, 155° C.), the interative derivative, include, point, 91° C. (literature value, 92° C.). p-Bromophenol was identified by the following data: tribromo compound, melting point 92° C. (literature value, 92° C.), mixed, 92° C.; chloroacetic acid derivative, melting point 154° C. (literature value, 153° to 155° C.). That minor amounts of di- and tribromophenols are also present is indicated by a bromine content for the mixed phenols of 50%. Monobromophenols contain only 46% bromine. In the material balance polybromides are estimated as dibromophenols.

The oxidation of toluene is an essentially slow reaction. If at 199° C. the contact time in a 3-liter reactor is varied between 1.5 and 6.0 minutes, the gases being fed into the reactor in the proportion oxygen to hydrogen bromide to toluene equal to 2 to 1 to 2, the percentage of the input oxygen that reacts increases from 40 to 62%. Moreover, the reaction is inhibited by the accumulation of carbonaceous material on the walls of the reactor.

The reaction is also probably inhibited by the phenols formed in the oxidation. When 5% by weight of phenol (on the toluene input) was added to a feed in which 50.9% of the oxygen was being consumed, the latter value dropped to 36.7%. Even 1.5 hours after stopping the flow of phenol the proportion of the input oxygen reacted (40.8%) had not yet regained its original value.

At 199° C. the reaction is not sensibly accelerated by the addition of even as much as 11% by weight (on input toluene) of di-*tert*-butyl peroxide. If this amount of peroxide is added to a flow of 262 cc. per minute of oxygen, 262 of toluene, and 131 of hydrogen bromide, the percentage of the input oxygen reacted was increased by only about 3.7%. The exit gas contained higher than normal proportions of carbon oxides and methane, apparently owing to the decomposition of the added peroxide. At 150° C., however, the addition of 5% of the peroxide increased the oxygen consumption from 22.9 to 35.5% of the input oxygen without any appreciable change in the volume of exit gas. The peroxide is, therefore, a catalyst for the reaction under conditions where it is not too rapidly decomposed.

Oxidation of Ethylbenzene. The hydrogen bromide-catalyzed oxidation of ethylbenzene is more rapid under the same conditions than that of toluene and leads to a sensibly greater breakdown to gases. The major identified products are acetophenone, phenol, and acetic acid, but a large part of the reacted hydrocarbon appears as condensed inseparable material, possibly derivatives of methylphenyl carbinol or of acetophenone. Table II gives a partial material balance—that is, it takes account only of the isolated and identified products—for a run under the conditions indicated. The product mixture was worked up in the same manner as in the case of toluene.

In the oxidation of ethylbenzene, as in that of propane or higher straight-chain paraffins, competition is to be expected between

[Conditions: flows (co	./min.): C ₈ H ₁₀ , :	262; O ₂ , 262; H	[Br, 131]		
	Moles/100 Moles Consumed of				
Products	C_8H_{10}	O2	HBr		
Acetophenone	10.7	9,5			
Benzoic acid	0.6	0.5			
Phenol	7.0	6.2			
Bromophenol	3.3	2,9	10.0		
Benzene	2.0				
Acetic acid	18.6	16.7			
Carbon monoxide	17.8	15.9			
Carbon dioxide	10.9	9.7			
Methane	13.7				
Ethylene	1.6				
Unidentified	68.5	55.8	90.0		

TABLE III. CUMENE ON	XIDATION AT	r 195° C.«	
[Conditions: flows (cc./min.): C	H12, 254; O	a, 262; HB	r, 131]
	Moles/100	Moles Con	sumed of
Products	C_9H_{12}	O2	HBr
p-Cumylphenol Phenol Bromophenol Acetophenone Acetone Bromoacetone 2-Phenyl-1,2-dibromopropane Dimethylphenylcarbinol Benzoic acid Acetic acid Carbon monoxide Carbon monoxide Methane Unidentified	5.8 3.7 0.1 3.1 1.2 2.3 2.6 1.3 1.1 74.4	5.3 3.3 0.1 2.9 10.4 0.5 $2.90.21.92.41.282.0$	0.3 1.8 8.0 81.9
^a 49% hydrogen bromide recovered, oxygen consumed.	88% cumene	e consumed	, and 91%

the primary and secondary hydrogen atom types of hydrogen bromide-catalyzed oxidation; however, as in the oxidations of the paraffins, the reactions of the secondary hydrogen are much more rapid. Corresponding to the acetone formed in the oxidation of propane, ethylbenzene gives acetophenone. However, phenylacetic acid, which results from attack on the methyl group, was not found. In the case of ethylbenzene, as in that of toluene, no free bromine was found in the products, nor was the presence of organic peroxide demonstrated.

Acetophenone was determined quantitatively by the hydroxylamine method. It was identified by the following data: boiling point, 204° C. (literature value, 202° C.); 2,4-dinitrophenylhydrazone, melting point, 245° to 246° C. (literature value, 250° C.).

In the toluene oxidation the breaking of a carbon-carbon bond is a minor reaction, but with ethylbenzene such cleavage results in the formation of important products-acetic acid and phenolat rates comparable to that producing ketone. The high proportions of carbon oxides and methane indicate further breakdown of the side chain.

Phenol itself, obtained by a vacuum distillation of the phenolic fraction, is the major constituent of this fraction and was identified by the following data: boiling point, 180° to 183° C. (litera-ture value, 182° C.); molecular weight, 97 (theoretical, 94); acetyl value, equivalent per 100 grams, 0.98 (theoretical, 94); tribromo derivative, melting point, 90° to 91° C. (literature value, 92° C.), mixed, 89° to 92° C. Benzoic acid was identified, as for toluene oxidation, by its equivalent weight and melting point.

The remaining nongaseous products not included in Table II represent approximately 70% of the reacted hydrocarbon. The material was distilled under low pressure into three cuts and a residue; however, attempts to characterize the various fractions chemically by preparing derivatives and by subjecting to oxidation, reduction, etc., met with only partial success and were generally inconclusive. Discussion of the laborious details will be foregone.

In separate experiments conducted under the same conditions as for the oxidation of ethylbenzene, mixtures of only hydrogen bromide and acetophenone gave clearly defined, light-colored condensation products, on the whole apparently unlike those obtained in the ethylbenzene oxidation. On introducing oxygen, however, dark materials were produced, as in the oxidation of the hydrocarbon. Although the products of these control experiments were not closely studied, it seems reasonable that the condensed fractions from the ethylbenzene oxidation may be formed by hydrogen bromide-catalyzed condensation of acetophenone, followed by further complex changes (1, 5, 6).

Oxidation of Cumene. The hydrogen bromide-catalyzed oxidation of cumene is even more rapid than that of ethylbenzene. Cold flashes may occur at approximately 200° C., and it was found necessary to operate at 195° C. to obtain controllable reaction. The chief identified products are acetophenone, phenol, p-(α, α -dimethylbenzyl)phenol, (p-cumylphenol), and acetone. A large amount of the input materials is lost to condensation products similar to those obtained from ethylbenzene. No bromine appears and apparently no peroxides. A partial material balance for a typical run is given in Table III. The material was handled in the manner described previously.

The oxidation of cumene may be compared with that of isobutane, as each compound possesses a tertiary carbon-hydrogen bond which is the principal point of attack. However, the hydroperoxides formed apparently possess entirely different orders of stability. In the case of isobutane, tert-butyl hydroperoxide was the primary product, and ketone which might be expected from peroxide degradation was in quite minor amount $[(\mathcal{S}),$ Tables I and II]. In contrast no peroxide, as mentioned above, was isolated from the cumene oxidation, while acetone is the major identifiable component. The formation of the ketone may be explained as a consequence of decomposition of the hypothetical hydroperoxide:

$$\begin{bmatrix} HO - & -O \\ C_{6}H_{5} - & -C - CH_{3} \\ & CH_{3} \end{bmatrix} \longrightarrow C_{6}H_{5}OH + CH_{3}COCH_{3}$$
(3)

Phenol and phenol derivatives are important components of the reaction product. While reaction 3 is an acid-catalyzed decomposition of α, α -dimethylbenzyl hydroperoxide (7), reaction 4 is a purely thermal decomposition occurring simultaneously which leads to acetophenone thus:

$$\begin{bmatrix} O - & O \\ C_6H_5 - & C \\ CH_3 & CH_3 \end{bmatrix} \xrightarrow{O} C_6H_5CCH_3 + CH_3OH \\ CH_3 & C_1 \text{ compounds}$$
(4)

As in the ethylbenzene oxidation, small amounts of benzoic acid are formed, probably by a similar mechanism.

Owing to a rapid following reaction $p_{-(\alpha,\alpha-\text{dimethylbenzyl})}$ phenol, rather than phenol itself, is the chief phenolic material produced. It is probably formed by the reaction:



It is known that the reaction of phenol with the carbinol is accelerated by hydrohalide (8).

The dimethylphenylcarbinol found in the product probably results from reduction of some of the hydroperoxide (shown in Equation 4) by the hydrogen halide, a reaction which would also produce bromine. The halogen, however, reacts completely with phenols or with hydrocarbons, producing the several bromo compounds identified.

The dimethylbenzylphenol was readily isolated by vacuum the dimethyloenzylphenol was reachly isolated by vacuum distillation of the phenolic fraction. It was identified by the following data: melting point, 72.7 °C. (Eastman white label product, 73.1 °C.), mixed, 72.9 °C.; benzyl ether derivative, melt-ing point, 64.5 ° to 65.0 °C. (literature value, 65.0 °C.), mixed, 65.0 °C.; carbon, 84.4% (theoretical, 84.9); hydrogen, 7.6% (theoretical, 7.6). Phenol itself was identified by its boiling point, 81° c. (2000); C. (diterature value, 180° C.) and by a positive (theoretical, 7.6). Phenol itself was identified by its bound positive 181° to 183° C. (literature value, 182° C.) and by a positive Eegriew test (9). Benzoic acid was identified as before by its its Duclaux numbers as well as by melting point, acetic acid by its Duclaux numbers as well as by

the melting point of the acetanilide, 110.5 °C. (literature value, 114 °C.); mixed, 111 °C. Acetone was identified by the melting point of its 2,4-dinitrophenylhydrazone, 124 °to 125 °C. (literature value, 126 °C.) and acetophenone by the melting point of the same derivative, 249 °to 250 °C. (literature value, 250 °C.) mixed, 250 °C. Bromoacetone was identified in the low boiling fractions of the nonacidic organic fraction by its strong lachrymating power, and determined by hydrolyzing and titrating the bromine. The presence of α,β -dibromocumene was made probable by obtaining, in the vacuum distillation of the organic fraction boiling at 1.5 to 2 cm. at 87 ° to 151 °C. (literature value, 140 + °C.) and containing only traces of ketone. This appears to be the only bromine derivative of cumene possessing lachrymal power (2). The low ketone content of this cut seems to exclude the products of ethylbenzene oxidation. Dimethylphenylearbinol was identified by its boiling point, 204 °C. (literature value, 204 °C.), and acetyl value, 0.74 (theoretical 0.74).

As in the oxidation of ethylbenzene, a large portion of the reacted hydrocarbon appears in the products as condensed material. Tests performed on cuts made by low pressure fractionation of the residue indicated the probable presence of residual acetophenone, dimethylphenylcarbinol, and α,β -dibromocumene, especially in the first fraction. However, as the distillation temperature rises, less bromine appears in the product, and the higher fractions might appear to be a condensed carbinol. Since acetophenone is a product of cumene oxidation, the condensation products of this ketone would also be expected here.

DISCUSSION

Table IV shows that in passing from toluene to cumene, under comparable conditions, there is an increase in the over-all rate of the oxidation (as judged by oxygen consumption). This trend is to be expected from the present work on the lower paraffins, which demonstrated the greater ease of oxidizing compounds containing tertiary carbon-hydrogen bonds as compared with ones having secondary linkages. The latter in turn are considerably more readily attacked than are primary carbon-hydrogen bonds. Associated with the greater ease of oxidation of cumene is the larger proportionate conversion to condensed, high boiling material and to by-product bromides; these sets of comparative data are also presented in Table IV. However, all of these runs were made at the same comparatively high temperature, 195° C. Whereas isobutane was successfully oxidized at approximately 160° C., in the present study, cumene, which also possesses a tertiary carbon-hydrogen linkage, was reacted at 195°C. both to avoid condensation of product on the reactor walls and to furnish a basis of comparison. This high temperature undoubtedly contributes to the number and magnitude of the side reactions.

TABLE IV.	SUMMARY OF HYDROGEN BROMIDE-CATALYZEI	D
- Oz	IDATION OF AROMATIC HYDROCARBONS	

[Conditions: earbon,	temperature, 1 262; HBr, 131;	95° C.; flows contact time.	(cc./min.): O ₂ , approximately 3	262; hydro- minutes]
	7.4	Mole %		
	Mole % I	ole % Reacted nput Hydro-	Yield, Moles	/100 Moles

	Input	Hydro- e	earbon	Hydrocarbon Consumed		
Hydrocarbon	Ö2 Reacted	carbon Reacted	Con- densed ^a	Total phenols	Aceto- phenone	Benzoic acid
Toluene Ethylbenzene Cumene	44 74 91	45 66 88	18 68 74	3.8 10.3 9.6	10.7 3.1	$\substack{27.8\\0.6\\0.3}$
^a Higher mole	cular weig	ht unide	ntified pro	oducts.		

The relative yields of the phenol, acetophenone, and benzoic acid derived from the three aromatic hydrocarbons are also tabulated, and it may be seen that there is a progressive decrease in the yield of benzoic acid, while phenolic material increases from a very small amount in the case of toluene to become the major product from cumene. The work on the paraffins has shown that the character of the product as well as the ease of oxidation is determined by the type of carbon-hydrogen bond which is attached, and there is no need to enlarge upon the analogy with regard to the aromatics. Peroxide degradation, which explained certain by-products found in the oxidations of isopentane and 2,3-dimethylbutane, seems to be even more important in the cases of the alkyl benzenes. The accompanying chart serves to summarize peroxide degradation as it applies to the formation of phenolic material (Table V).



In the case of toluene, the reaction leading to phenol formation is of minor importance, the principal product being benzoic acid. In the case of ethylbenzene, acetophenone and its probable condensation products are the principal products, but acetic acid and phenol and its bromo derivatives also contribute substantially to the net result. Finally, the results of cumene oxidation indicate that none of the expected peroxide remains; apparently it undergoes scission and contributes the major identified products, phenols and acetone.

Liquid Phase Oxidations. The oxidation of benzyl bromide in liquid phase was carried out as follows: For 9.5 hours, 30 cc. per minute each of hydrogen bromide and oxygen were bubbled through the boiling liquid, which during the course of reaction increased in temperature from 194° C., the boiling point of the bromide, to 253° C. approximately the boiling point of benzoic acid. During the first 6 hours oxygen consumption averaged 7% and during the next three, 22%. On cooling, the product solidified and, despite the fact that it was mostly benzoic acid, had the odor of benzoyl bromide. The presence of the latter material was proved by its conversion to benzamide (melting point, 129° to 129.5° C.; literature value, 130° C.). The formation of this compound is significant in that it supports the idea that in alkyl bromide oxidations, the acids are formed via the hydrolysis of the acid bromide intermediates. Such an intermediate had not previously been isolated.

$$(C_{6}H_{\delta})CH_{2}Br + O_{2} \xrightarrow{HBr} (C_{6}H_{\delta})CBr + H_{2}O \xrightarrow{} (C_{6}H_{\delta})COOH + HBr \quad (9)$$

Benzyl alcohol was demonstrated to be an effective inhibitor for this oxidation.

From a similar liquid phase oxidation of mesitylene (sym. trimethylbenzene) at 165°C. (its boiling point), a small amount of mesitylenic acid was isolated (melting point, 163° to 164°C.). A bromide, probably 3,5-dimethylbenzyl bromide, and a trace of aldehyde were also present.

ACKNOWLEDGMENT

The authors express their thanks to H. de V. Finch for the results of his experiments on the hydrogen bromide-catalyzed oxidation of benzene.

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RECEIVED August 17, 1948. Presented in part at the meeting of the Gordon Research Conferences of the American Association for the Advancement of Science, Colby Junior College, New London, N. H., June 1948.

CORROSION-INHIBITED FUELS

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A survey is presented on already-known methods and recent advances in the field of corrosion prevention in pipe lines, storage containers, tanks, and other equipment in contact with fuels, even under severe conditions—e.g., in the presence of sea water. Of the three possibilities proper choice of corrosion-resistant construction materials, surface protection of metals or alloys in question by suitable treatment, and admixtures to the fuel in order to produce surface passivity—only the third method promises an extended technical application and sufficient endurance in practical use. Research in this field starting in the middle of the 1930's is reported, particularly with regard to prevention by use of fluoride cartridges of

HE phenomena of corrosion involve not only problems of applied chemistry and engineering but also interesting problems for basic research in different branches of science. The loss of material may be only a small percentage of the whole construction, but necessitates replacement of the entire equipment, when corrosion exceeds a certain point. Therefore, protection increases in importance the higher the ratio of cost of replacement to the loss of material by corrosion. Corrosion may be prevented by the choice of proper materials, such as special metals and alloys. In addition, two other principal ways exist. They are the protection of the surface of the construction material by proper treatment (the treatment varies according to the requirements of operation), and additions to the corroding medium to produce passivity. In producing passivity, there is the special task of diminishing the aggressiveness of fuels (5, 6, 9, 12, 13, 24, 29-33, 37, 40, 43, 49).

The use of fuels containing suitable inhibitors increases the security of storage and transportation as well as the safety of operation. For the following data, fuels such as alcohols and their mixtures with water are not considered, because additions for these fuels such as Akorol and pH-buffered alkali chromate, chlorate, and perchlorate mixtures have been known for several years (29, 31, 32). However, this report will deal with experiments concerning additions to fuels such as hydrocarbons, especially gasoline.

The problem of corrosion has been well known for a long time in the distribution of crude oil in pipe lines and pump stations. Many physical and chemical proposals were made in publications and patents—e.g., proper metals and alloys (2, 12, 13, 26, 36), dehydrating and desiccating (2, 9, 12, 17, 43, 51), sodium silicate (43, 46), sodium sulfite (43), sodium nitrite, proper pH value of the solution (11, 45, 49, 53, 54), aliphatic and aromatic amino compounds (1, 4, 7, 8, 23, 39, 41, 42, 50)—but no satisfactory solution was found. Either the procedure did not meet the requirements of prizeworthy and technically simple solution, or the dangerous corrosion by fuel containing tetraethyllead of light metal (magnesium) tanks in airplanes. Further development stimulated by extensive investigations on emulsifying agents led to the surprising result that, without regard to the construction materials used, even a small addition of Mepasin-sulfamido-acetic acid-sodium salt to the fuel prevents any corrosion (Mepasin refers to a certain fraction of hydrocarbons gained by the Fischer-Tropsch synthesis, chain length from about 12 to 18 carbon atoms). These results present a prospect of solving many corrosion problems, starting at the oil well and ending with the last fuel consumer, by the simple addition of the smallest amount of such chemicals.

protection, decreasing after a certain time, was not suitable for all construction materials. Finally, often the properties of the blended fuels did not meet the conditions required for motors. Also lacquering (27), electrolytic deposition and oxidation, metallization, ceramic (38) and plastic coatings (21), etc., were too expensive or not useful when in operation for any great period of time (9, 12). In many cases where construction was complex the usual methods gave less valuable protection than under normal conditions. In spite of partial success, it was recognized that a general solution of the problem could be reached only by treatment of the fuels, for by this means all parts of the construction could be protected.

The situation became urgent in 1936 when very serious corrosion phenomena were observed in magnesium alloy fuel tanks in airplanes serving the route from Rotterdam to Batavia. The tanks had been in service only a short time. Since a change of tank construction materials—connected with an unwelcome increase of weight—was undesirable, the best method was to try the second method mentioned above and search for "additions to the corroding medium to produce passivity" (3, 14, 15, 18–20, 22, 33, 47, 52).

After experimentation in the laboratory, special chemicals were put in fuel tanks. These agents contained mainly alkali fluorides and additional salts—e.g., magnesium carbonate—for buffering and maintaining a certain concentration range of hydrogen ions with pH above 7 (18-20, 22, 33). In this way, the problem could be solved relatively quickly. Important in the elaboration of this method is the fact that serious corrosion phenomena were observed only in the presence of water which was not dissolved in the fuel, but appeared as a second phase on the bottom of the tank. This water may have entered the tank either by injection with the fuel, by careless workmanship, or by precipitation from the air inside the tank in cooling. This corrosion is extremely serious in the presence of fuel containing tetraethyllead, for this