

It is noted that a value of 3.7 kcal./mole for the methyl-methyl interaction gives a calculated energy difference of 5.5 kcal./mole (one methyl-methyl interaction plus two methyl-hydrogen interactions) between the diequatorial and diaxial forms of *cis*-1,3-dimethylcyclohexane, which is in perfect agreement with the value predicted by Beckett, Pitzer and Spitzer.⁷

When the C-H bonds of each methyl group are staggered relative to the bonds of the carbon atom to which the methyl is bound, keeping normal bond angles and bond lengths, the separation¹³ of one pair of hydrogens is 0.8 Å. The van der Waals repulsion at this distance is enormous (about 200 kcal.¹⁴) and the molecule does not remain in this exact conformational arrangement. If each methyl is rotated through an angle of 25°, the two hydrogens can be moved to a separation of 1.6 Å., but another pair has also come to this same distance, and one hydrogen on each methyl is now 1.75 Å. from the nearby axial hydrogen. The total of these repulsions is 8 kcal. However, the partial eclipsing costs 1.0 kcal. for each methyl, so the total energy of the methyl-methyl interaction is 10 kcal./mole. With this molecule bond angle deformation seems to be rather important. Widening one bond angle in this form (that of the ring carbon between those to which the methyls are attached) to 120° causes the van der Waals repulsion between the two methyls to entirely disappear, and the closest hydrogen on a methyl is 1.8 Å. from the axial ring hydrogen. This repulsion amounts to 1.6 kcal., and the 2.1 kcal. for partial eclipsing¹⁵ plus 2 kcal. for angle deformation¹⁵ gives a total energy of 5.7 kcal. It does not seem unreasonable that the total energy can be further reduced to the observed value by successive adjustment of these and similar quantities.

The value found for the energy of a 1,3-dimethyl interaction cannot be applied to systems

(13) Measured on Dreiding models.

(14) Estimated by the method outlined by N. L. Allinger, J. Allinger, L. A. Freiberg, R. Czaja and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

(15) N. L. Allinger, *ibid.*, **81**, 5727 (1959).

such as the perhydrophenanthrenes. Certainly, as pointed out by Dauben and Pitzer,⁶ in such a rigid system the deformations which so greatly lowered the energy in the above case cannot readily take place.

Experimental

cis- and *trans*-1,1,3,5-Tetramethylcyclohexane (I).—The hydrocarbons used in the present work were prepared starting from isophorone, which was reduced with hydrogen and a palladium-on-carbon catalyst to 3,3,5-trimethylcyclohexanone. Addition of methyl Grignard gave 1,3,3,5-tetramethylcyclohexanol, which was dehydrated to the olefin with formic acid. Hydrogenation with platinum in acetic acid yielded a mixture of *cis*- and *trans*-1,3,3,5-tetramethylcyclohexane in a 3:2 ratio. The pure isomers were obtained by preparative gas phase chromatography on a column of silicone on firebrick. After redistillation the isomers had the constants: *cis*, b.p. 144.5–145°, n_D^{20} 1.4288, d_{20}^{20} 0.7811; *trans*, b.p. 148.5–149°, n_D^{20} 1.4342, d_{20}^{20} 0.7913. The reported⁹ values are: *cis*, b.p. 152.4–152.5°, n_D^{20} 1.4319, d_{20}^{20} 0.7813; *trans*, b.p. 156.4–156.5°, n_D^{20} 1.4370, d_{20}^{20} 0.7929.

Equilibration of *cis*- and *trans*-1,1,3,5-Tetramethylcyclohexane.—For each run about 100 mg. of a pure isomer of I was sealed in a small tube with about 25 mg. of 10% palladium-on-carbon. Equilibrium was established by heating the tubes at various temperatures for the times specified in Table I. The analysis of the equilibrated mixtures was carried out with a column of γ -nitro- γ -methylpimelonitrile on firebrick at 70°. The area under the curves was measured with a disk chart integrator.

TABLE I
EQUILIBRATION DATA FOR COMPOUND I

| Temp., °C. | Time | K |
|------------|---------|-------|
| 247 | 5 days | 16.02 |
| 284 | 12 hr. | 11.87 |
| 297 | 20 hr. | 11.40 |
| 324 | 22 hr. | 10.16 |
| 358 | 3.5 hr. | 8.33 |

Each value of *K* in Table I was an average of at least three analyses on the equilibrated sample obtained from the *cis* isomer and three analyses on the equilibrated sample obtained from the *trans* isomer. The average deviation in *K* was about ± 0.25 .

The values for ΔH and ΔS of the reaction were calculated using the values found for *K*, and fitting a straight line to eq. 1 by the least squares method.

$$\ln K = - \left(\frac{1}{T} \right) \left(\frac{\Delta H}{R} \right) + \frac{\Delta S}{R} \quad (1)$$

[CONTRIBUTION FROM THE HOUSTON RESEARCH LABORATORY, SHELL OIL CO., DEER PARK, TEXAS]

Electrophilic Attack of the Aromatic Ring in the Chromic Acid Oxidation of Alkylbenzenes¹

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Ring oxidation is competitive with side-chain oxidation in the chromic acid oxidation of alkylbenzenes under Kuhn-Roth conditions. In the case of *t*-butylbenzene, oxidation proceeds exclusively by way of the ring, the reaction being first-order in hydrocarbon and exhibiting a linear $\log k-H_0$ relationship. Study of a series of methylbenzenes shows that ring oxidation is enhanced by increased substitution, and that the rate is a function of the σ -complex basicity of the hydrocarbon. These results suggest that ring oxidation occurs by electrophilic aromatic substitution.

Introduction

The mechanism of chromic acid oxidation of simpler organic molecules containing functional groups has been the subject of extensive investiga-

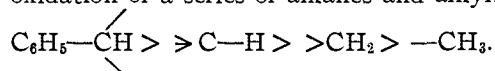
tion. An example is the very careful study of the system chromic acid-isopropyl alcohol by Westheimer and co-workers.² More recently, studies of chromic acid oxidation have been directed toward

(1) Presented in part before the Division of Organic Chemistry, 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(2) G. T. E. Graham and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952); and earlier papers.

hydrocarbon substrates, and have resulted in both qualitative and kinetic evidence regarding mechanism.

The current status of these findings is exemplified in the work of Wiberg and Evans, who reported a particularly thorough investigation of the chromic acid oxidation of diphenylmethane and its derivatives.³ It was concluded in this study that for diphenylmethane itself as well as for a number of substituted diphenylmethanes, the rate-determining step leading to the corresponding benzophenone involves homolytic cleavage of the α -carbon-hydrogen bond. It was pointed out, however, that introduction of a substituent with exceptional ability to stabilize an electron deficiency (e.g., the *p*-methoxy group) apparently causes a change in mechanism; hydride-ion abstraction was suggested as the mechanism in these cases. Other evidence for a hydride-abstraction mechanism in the chromic acid oxidation of hydrocarbons has been presented by Necsoiu and Nenitzescu.⁴ These workers found that the carbonium ions expected as intermediates in the oxidation of a series of substituted methanes, all containing tertiary hydrogen, could be trapped as the corresponding azides. Both the hydrogen-abstraction and hydride-abstraction mechanisms are consistent with the following order of reactivity reported by Foster and Hickenbottom⁵ in the chromic acid oxidation of a series of alkanes and alkylbenzenes:



A common feature of the observations outlined above is that they pertain only to oxidation at an extra-nuclear carbon atom, even in the case of alkylbenzenes. Although oxidation of substituted aromatics might conceivably involve a nuclear position as well as the side-chain, such an effect was not observed under the relatively mild conditions employed.³ Qualitative evidence for oxidation of the aromatic nucleus in alkylbenzenes was recently encountered, however, under the more vigorous conditions of the Kuhn-Roth C-methyl determination (130°, 3.3 *N* chromic acid, 6.0 *M* sulfuric acid).⁶ It was observed that toluene, ethylbenzene and isopropylbenzene, none of which would be expected to form acetic acid by side-chain oxidation, gave small yields of volatile acid. Ultraviolet examination of the product from toluene showed that no more than 30% was benzoic acid. Toluene thus yields a small but measurable amount of acetic acid *via* ring oxidation, as is presumably the case with ethylbenzene and isopropylbenzene. Even greater yields of acetic acid were similarly obtained from mesitylene and 6-methyltetralin. Prompted by these results, the present investigation is concerned with a systematic study of aromatic-ring oxidation in alkylbenzenes.

Results and Discussion

Ring Oxidation of *t*-Butylbenzene.—A study of the chromic acid oxidation of monoalkylbenzenes

(3) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

(4) I. Necsoiu and C. D. Nenitzescu, *Chemistry & Industry*, 377 (1960).

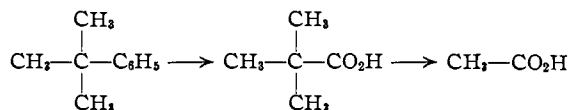
(5) G. Foster and W. J. Hickenbottom, *J. Chem. Soc.*, 680 (1960).

(6) S. G. Brandenberger, L. W. Maas and I. Dvoretzky, *Anal. Chem.*, **33**, 453 (1961).

under Kuhn-Roth conditions by Jurecek and co-workers⁷ indicates, on the basis of the longest-chain aliphatic acid which could be isolated, that side-chain cleavage occurs between the α - and β -carbon atoms. This conclusion was strengthened in the present study by the results of Table I for the oxidation of *sec*-butylbenzene in 0.75 *M* sulfuric acid. At this relatively low sulfuric acid concentration, benzoic acid is not as rapidly destroyed as in the case of higher acidities,⁶ and ultraviolet analysis of the total volatile acid shows that benzoic acid and acetic acid are formed in equal amounts. On the assumption that side-chain oxidation is initiated at an α -hydrogen atom, *t*-butylbenzene, which has no α -hydrogens, was investigated as a compound in which ring oxidation might be the predominant reaction. In this case, even were side-chain oxidation to occur, acetic acid would not be a likely product.

Oxidation of *t*-butylbenzene under the same conditions which yielded small amounts of acetic acid from toluene⁶ gave a 98% yield of acid, shown by ultraviolet analysis not to be benzoic acid. This result suggests that ring oxidation of *t*-butylbenzene is indeed the major reaction. However, the acid formed cannot be assumed to be acetic acid without further investigation. In particular, trimethylacetic acid might well be an intermediate product in the ring oxidation of *t*-butylbenzene. Eisenbraun, McElvain and Aycock⁸ have shown that trimethylacetic acid, under milder conditions than those adopted for the present work, is relatively stable and is not oxidized to acetic acid.

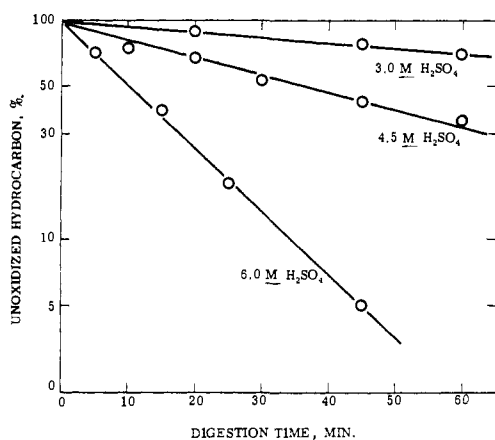
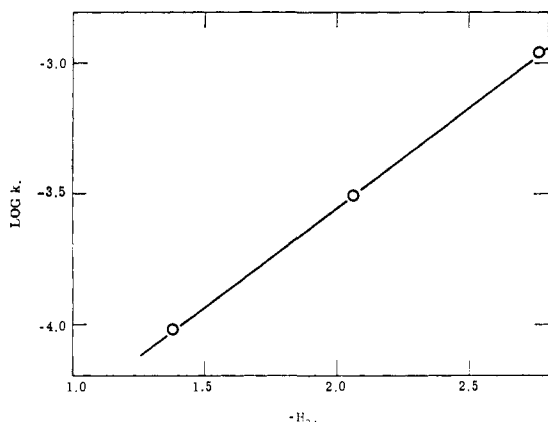
The total volatile acid obtained from *t*-butylbenzene was therefore separated by liquid-liquid partition chromatography, a control experiment establishing that acetic and trimethylacetic acids indeed could be separated by this procedure. The acid from the above oxidation of *t*-butylbenzene was thereby found to consist entirely of acetic acid. Correspondingly, the product from the digestion of trimethylacetic acid under the same conditions was found to be acetic acid. Finally, the product from the oxidation of *t*-butylbenzene during a fifteen-minute interval rather than the above three-hour interval was found to be a mixture of 10 mole % trimethylacetic acid and 90 mole % acetic acid. The oxidation of *t*-butylbenzene thus appears to follow the sequence



Effect of Acidity on the Rate of Oxidation of *t*-Butylbenzene.—The factors influencing ring oxidation were further investigated through the effect of sulfuric acid concentration on the rate of oxidation of *t*-butylbenzene. The results of rate studies at several acid concentrations are presented in Fig. 1. The amount of unreacted hydrocarbon present was calculated from the acid found on the

(7) M. Jurecek, M. Soncek, J. Churacek and J. Renger, *Z. Anal. Chem.*, **165**, 109 (1958).

(8) E. J. Eisenbraun, S. M. McElvain and B. F. Aycock, *J. Am. Chem. Soc.*, **76**, 607 (1954).

Fig. 1.—Oxidation of *t*-butylbenzene at 130°.Fig. 2.—Effect of acidity on the rate of oxidation of *t*-butylbenzene at 130°; H_0 values taken from ref. 9.

assumption that one mole of hydrocarbon yields one mole of acid, either acetic acid or trimethylacetic acid, and that there is no appreciable concentration of any intermediate other than trimethylacetic acid present during the course of the oxidation. At each acid concentration, the oxidation is first order with respect to hydrocarbon.

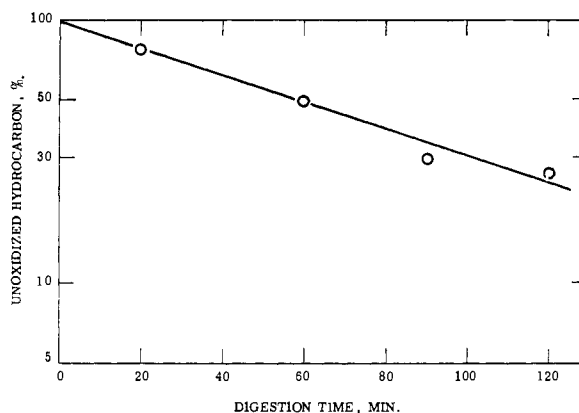
TABLE I

| Digestion time, min. | PRODUCTS FROM OXIDATION OF <i>sec</i> -BUTYL BENZENE | | |
|----------------------|--|--------------|--------------------------|
| | Yield of acid, moles/mole hydrocarbon | | |
| | Total acid | Benzoic acid | Acetic acid ^a |
| 20 | 0.50 | 0.22 | 0.28 |
| 60 | 1.05 | .52 | .53 |
| 90 | 1.42 | .72 | .70 |
| 120 | 1.47 | .74 | .73 |

^a Total acid minus benzoic acid.

The logarithm of the rate constant for the oxidation of *t*-butylbenzene is found to vary linearly with the Hammett acidity function (H_0) corresponding to the sulfuric acid concentration, the slope of the line being 0.78 (Fig. 2). Although such correlations ideally involve rate data and H_0 values determined at the same temperature, and are expected to have a unit slope, significant correlations have been found with rate determinations at temperatures from 0 to 140° referred to H_0 values in the region of 25°. These results ap-

(9) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1955).

Fig. 3.—Oxidation of *sec*-butylbenzene in 0.75 *M* H_2SO_4 at 130°.

pear reasonable in view of the finding that $d[H_0]_{30^\circ}/d[H_0]_{20^\circ}$ is constant and equal to 0.93 in the concentration range of 10 to 80% sulfuric acid.¹⁰ Accordingly, the slope of a linear $\log k-H_0$ relationship generally decreases for rate constants at higher temperatures referred to H_0 at 25°. It is of interest that a linear dependence of rate of oxidation by chromic acid on H_0 has also been observed for isopropyl alcohol¹¹ and aromatic aldehydes¹² as well as for diphenylmethane.³

The first-order dependence of the reaction on hydrocarbon in the case of *sec*-butylbenzene is illustrated by Fig. 3. Earlier work⁶ demonstrated that a quantitative yield of acetic acid can be obtained from *sec*-butylbenzene in 6.0 *M* sulfuric acid after only forty-five minutes. This result, in conjunction with the data of Table I and Fig. 3, demonstrates that side-chain oxidation of an alkylbenzene is also acid catalyzed. In addition, these data allow a comparison of the ease of ring and side-chain oxidation. Side-chain oxidation proceeds at a measurable rate even at sulfuric acid concentrations as low as 0.75 *M*. The first-order rate constant for *sec*-butylbenzene under these conditions is $1.19 \times 10^{-2} \text{ min.}^{-1}$, compared to a value of $5.58 \times 10^{-3} \text{ min.}^{-1}$ for *t*-butylbenzene in 3.0 *M* sulfuric acid. Indeed, the ring oxidation of *t*-butylbenzene at 130° in 0.75 *M* sulfuric acid is immeasurably slow.

The effect of sulfuric acid concentration on ring oxidation was briefly examined in terms of a poly-substituted alkylbenzene. Under the conditions used for the examples of Table II (6.0 *M* sulfuric acid), *m*-xylene gave 1.19 moles of volatile acid per mole of sample, of which only 0.01 mole was found by ultraviolet analysis to be *m*-toluic acid. The 1.18 moles of acetic acid corresponds to 59% of that which could be obtained by complete ring attack. When oxidized under the same conditions but in 0.75 *M* sulfuric acid, *m*-xylene gave 0.98 mole of acid per mole of sample, of which 0.19 mole was *m*-toluic acid. The remaining 0.79 mole of acetic acid corresponds to 40% of the maximum by ring oxidation. In contrast to the

(10) A. I. Gelbstein, G. G. Shcheglove and M. J. Temkin, *Doklady Akad. Nauk S.S.S.R.*, **107**, 108 (1956).

(11) J. Rocek and J. Krupicka, *Coll. Czechoslov. Chem. Commun.*, **23**, 2068 (1958).

(12) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

TABLE II
OXIDATION OF METHYLBENZENES

| Hydrocarbon | Yield of acetic acid, moles/mole hydrocarbon | Calcd. rate of ring oxidation, relative to <i>p</i> -xylene |
|------------------|--|---|
| Toluene | 0.17 | 0.18 |
| <i>o</i> -Xylene | 0.91 | 1.45 |
| <i>m</i> -Xylene | 1.18 | 2.50 |
| <i>p</i> -Xylene | 0.73 | 1.00 |
| Mesitylene | 2.15 | 6.60 |
| Durene | 2.33 | 4.85 |
| Prehnitene | 2.48 | 5.68 |
| Isodurene | 2.67 | 6.92 |

behavior of *t*-butylbenzene, the activating effect of a second alkyl group is such that even in 0.75 *M* sulfuric acid the ring is extensively attacked.

Oxidation of Methylbenzenes.—The ring oxidation of *t*-butylbenzene demonstrated above appears to be an effect of substituent type. Further evidence bearing on the mechanism of ring oxidation is provided by the effect of degree of substitution. To this end, a series of methylbenzenes was studied, the results being summarized in Table II. In terms of acetic acid yields alone, these data show that increased substitution greatly enhances ring oxidation, suggesting an electrophilic attack on the ring. This effect is further indicated by the relative rates of ring oxidation for the various methylbenzenes, calculated from the data of Table II and the considerations developed below.

It is reasonable to assume that once ring oxidation is initiated, further oxidation of the ring proceeds very rapidly relative to side-chain oxidation. For example, *p*-cresol, which can be regarded as a partially oxidized toluene, gives a 100% yield of acetic acid compared to a 17% yield obtained from toluene itself. Moreover, if oxidation is initiated on the side chain, ring oxidation should be inhibited by the deactivating influence of the resulting carboxyl group, and further oxidation should proceed *via* a side chain. This effect is shown by *m*-toluic acid, which gives a 16% yield of acetic acid, whereas a 59% yield is obtained from *m*-xylene. Thus, the ratio of the fraction of sample oxidized to acetic acid to the fraction oxidized to other products should be the ratio of the rate of ring oxidation to the rate of side-chain oxidation. For example, 72% of the theoretical yield of three moles of acetic acid per mole of sample was obtained from mesitylene. The ratio of the rates of ring and side-chain oxidation is then 72/28. If a statistical correction is made for the number of methyl groups present—in this case three—the ratio of the rate of ring oxidation to the rate of methyl group oxidation for mesitylene is 72/(28/3), or 7.71. Finally, if it is assumed that the rate of oxidation of a methyl group is constant for all the methylbenzenes, the value 7.71 can be taken as a measure of the rate of ring oxidation itself.

The assumption of a constant rate for the oxidation of a methyl group has been examined in some detail, and appears valid for the methylbenzene series in the event of either of the two mechanisms suggested by Wiberg and Evans³—hydrogen or hydride abstraction. Although the rate of oxidation was increased by methyl substitution

in the diphenylmethane series, this effect does not appear to hold in the methylbenzenes. For example, Kooyman¹³ observed that the rate of hydrogen abstraction per methyl group by the trichloromethyl radical was constant in the series toluene-xylene-mesitylene (Table III). This result in turn is in good agreement with the nearly constant carbon-hydrogen dissociation energies reported for these compounds.¹⁴ Thus, if methyl-group oxidation does proceed by a hydrogen abstraction, the rate would be expected to be independent of further methyl substitution on the ring. A similar conclusion can be reached regarding the hydride-abstraction mechanism by consideration of the corresponding radical ionization energies¹⁵ also shown in Table III. These values are again independent of degree of methyl substitution. Since the sum of the radical ionization energy and the carbon-hydrogen dissociation energy differs from that of hydride removal from the hydrocarbon in the gas phase by a constant value—namely, the electron affinity of the hydrogen atom—the rate of hydride removal in the methylbenzene series should also be independent of the degree of methyl substitution on the ring.

TABLE III
HYDROGEN-ATOM AND HYDRIDE-ION ABSTRACTIONS IN METHYLBENZENES

| Hydrocarbon | Rel. rate of hydrogen abstrn. by trichloromethyl radical, ¹³ per methyl group | Carbon-hydrogen disson. energy, ¹⁴ kcal./mole | Radical ioniz. energy, ¹⁵ ev. |
|------------------|--|--|--|
| Toluene | 0.42 | 77.5 | 7.73 |
| <i>o</i> -Xylene | .51 | 74.0 | 7.61 |
| <i>m</i> -Xylene | .43 | 77.2 | 7.65 |
| <i>p</i> -Xylene | .48 | 74.8 | 7.46 |
| Mesitylene | .43 | .. | .. |

Rates of ring oxidation calculated on the basis of the above considerations are given in Table II relative to *p*-xylene. The mechanistic significance of these rates can be inferred by reference to the work of Brown and Brady,¹⁶ who showed that the reaction of an aromatic hydrocarbon with hydrogen fluoride-boron trifluoride involves formation of a σ -complex similar to the transition state in electrophilic aromatic substitution. On this basis, there should be a linear relationship between the logarithm of the rate of aromatic substitution and the logarithm of the basicity of the hydrocarbon in question toward hydrogen fluoride-boron trifluoride. Such a relationship has been demonstrated previously by Condon¹⁷ and by Brown and Brady¹⁶ for rates of aromatic chlorination calculated from partial rate factors. Similarly, Mackor, Smit and van der Waals¹⁸ observed a linear relationship of unit slope between basicity and experimentally determined rates of

(13) E. C. Kooyman, *Disc. Faraday Soc.*, **10**, 163 (1951).

(14) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

(15) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

(16) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(17) F. E. Condon, *ibid.*, **74**, 2528 (1952).

(18) E. L. Mackor, P. J. Smit and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957).

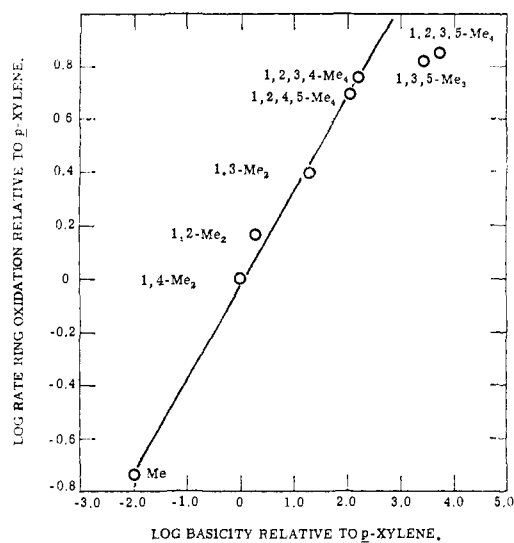


Fig. 4.—Effect of methyl groups on ring oxidation of methylbenzenes.

hydrogen-deuterium exchange for alkylbenzenes in trifluoroacetic acid-mineral acid.

Figure 4 illustrates the application of this criterion to the methylbenzenes of Table II, rates of ring oxidation and basicities both being expressed relative to *p*-xylene. An excellent linear relationship is exhibited by toluene, the xylenes, durene and prehnitene, the points for mesitylene and isodurene deviating somewhat in the direction of lower rates of ring oxidation. This deviation is highly suggestive of a steric effect. A common feature of mesitylene and isodurene is the absence of an unsubstituted ring position which is not *ortho* to two methyl groups. The unsubstituted ring positions in durene are similarly hindered. In accordance with these considerations, the points of Fig. 3 corresponding to durene, mesitylene and isodurene appear to lie on a second line of lesser slope than the line for those methylbenzenes which contain an unhindered ring position. These linear relationships for the two types of alkylbenzenes are a strong indication that ring oxidation involves electrophilic attack, and that it is subject to an *ortho* steric effect.

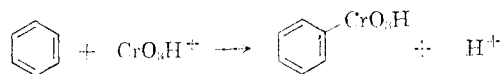
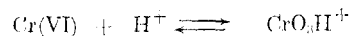
A similar effect is observed in the bromination of methylbenzenes,¹⁹ the experimental rates for mesitylene and isodurene being significantly lower than those calculated from partial rate factors. Brown and Stock¹⁹ attributed this difference either to a large steric factor or to the formation of stable π -complexes by the higher-methylated aromatics. The absence of deviation in hydrogen-deuterium exchange¹⁸ supports the former explanation. Further indication of the steric effect in question is provided by the partial rate factors for bromination and nitration of toluene and *t*-butylbenzene as discussed by de la Mare.²⁰ These data show a distinctly higher *ortho/para* reactivity ratio for bromination than for nitration, pointing to the greater steric requirements of the latter re-

(19) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957).

(20) P. B. D. de la Mare, in "Theoretical Organic Chemistry—the Kekulé Symposium," Butterworths, London, 1959, p. 223.

action. In accordance with this effect, a significant steric requirement for ring oxidation by chromic acid would appear reasonable.

Mechanism of Ring Oxidation.—The relative rates of oxidation in the above methylbenzene series indicate that ring oxidation involves an electrophilic attack on the aromatic system as the rate-determining step. This electrophilic character of the oxidation and the observed acid catalysis suggest that a protonated, positively-charged species of chromium(VI) is responsible for the attack on the benzene ring. Following this initial attack on the ring, the reaction could proceed by hydrolysis of the unstable substitution product to a phenol, which in turn would be rapidly oxidized to the final products. The over-all mechanism can be formulated as



It is interesting that the above mechanism is consistent with the analogy between oxidation reactions and electrophilic aromatic substitutions previously discussed by Levitt.²¹

Experimental

Oxidation of *t*-Butylbenzene.—The digestion and determination of volatile acid were carried out by procedures previously described.⁶ Sample size was 20–30 mg., and the oxidant consisted of 6.7 ml. of 5 *N* chromic acid and 3.3 ml. of 18 *M* sulfuric acid. The digestion was carried out at 130°.

Kinetic Studies.—The rate determinations with *t*-butylbenzene and *sec*-butylbenzene were made at 130 ± 1° with Phillips Pure Grade hydrocarbons (minimum purity of 99 mole %). Chromic acid concentration was 3.3 *N* and total volume of oxidant 10 ml. Rate determinations were made with *t*-butylbenzene at 6.0, 4.5 and 3.0 *M* sulfuric acid concentrations, and with *sec*-butylbenzene at 0.75 *M* sulfuric acid concentration. Separate samples of identical weight were oxidized for each time interval comprising the rate studies. For both hydrocarbons, the reaction mixtures were homogeneous at the temperature and sulfuric acid concentrations investigated. To prevent further oxidation during the distillation of the acidic products, excess chromic acid was destroyed with hydrazine before distillation.²²

Determination of Benzoic Acid.—The determination of benzoic acid was based on a calibration of benzoic acid concentration in water against absorbance in the region of the 2250 Å. absorption band of benzoic acid. The ultraviolet spectra of aliquots of the distillates were obtained with a Cary model-11 spectrophotometer.

Chromatographic Separation of Acids.—The volatile acid products from the oxidations of *t*-butylbenzene and trimethylacetic acid were separated by the liquid-liquid partition chromatographic method of Marvel and Rands.²³ The detailed modification of this procedure has been described previously.⁵

Oxidation of Methylbenzenes.—The methylbenzenes were oxidized for 3-hour periods at 130°. Sample size was 20–30 mg., and the oxidizing mixture consisted of 10 ml. of 5 *N* chromic acid and 5 ml. of 18 *M* sulfuric acid.

Acknowledgment.—The authors are indebted to J. M. Martin, Jr., for the ultraviolet analyses.

(21) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(22) F. Pregl and J. Grant, "Quantitative Organic Microanalysis," Fourth English Edition, The Blakiston Co., Philadelphia, Pa., 1946.

(23) C. S. Marvel and R. D. Rands, Jr., *J. Am. Chem. Soc.*, **72**, 2642 (1950).