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Acidolytic Ozonolysis of Benzene and Some Homologues

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Benzene and eight of its methyl homologues have been ozonised in formic and acetic acids. The rate of reaction with ozone has been measured as well as the formation of active oxygen and peracids in the reaction mixtures.

The study of the ozonisation of benzene was initiated by Houzeau [1] in 1873 and by Renard [2] in 1895. Harries [3,4] placed these investigations on a more quantitative basis as he found that benzene could react with three molecules of ozone, giving a compound which he regarded as a triozonide, but whose structure never has been established. The well-known ozonolysis experiments of Levine and Cole [5] on *o*-xylene were re-interpreted by Wibaut [6] and later also discussed by Bailey.[7] It is to Wibaut and coworkers that we owe most of our quantitative knowledge of the ozonolysis of benzene and its homologues. Among other results they could demonstrate the following rate relationships: Hexamethylbenzene > mesitylene > xylene > toluene > benzene.[8] In these experiments, where non-participating solvents were used, Wibaut found that benzene was attacked about three times as rapidly in nitromethane as in chloroform. A large number of other, especially polycyclic, aromatics have been ozonised in participating solvents.[7,9–11] As such solvent methanol in particular has been used, giving rise to methoxy hydroperoxides as a part of the reaction mixtures.

Although the lower fatty acids have been used as solvents in ozonisation experiments for a number of years, it was only relatively recently noted [12,13] that especially formic acid was able to accept the active oxygen from ozonisation intermediates with the formation of performic acid. This reaction has now been applied to some aromatic hydrocarbons and the present authors wish to report on some experiments pertaining to benzene and some of its homologues. The investigation is only concerned with the formation of peracid and the rate of the reaction between the aromatic compound and ozone. Reaction products originating from the cleavage of the aromatic ring have not been investigated. The following substances have been ozonised: benzene, toluene,

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o-xylene, *m*-xylene, mesitylene, durene, isodurene, pentamethylbenzene, and hexamethylbenzene. Solvents were formic and acetic acids, the latter containing 0.2 % perchloric acid.

The formation of active oxygen and peracid in the solutions was followed iodometrically, while the disappearance of the aromatic compounds was followed spectroscopically. The following qualitative rate relationships were established: Hexamethylbenzene > pentamethylbenzene > durene, isodurene > mesitylene > *m*-xylene > *o*-xylene > toluene > benzene. The half-lives, as will be seen from Table 1, at 3—4°C in formic acid ranged from 15 min for benzene to 45 sec for hexamethylbenzene.

The reaction temperature is thus under the freezing points of the solvents, but with careful manipulation of the apparatus it was possible to keep the solutions undercooled. During the reaction the concentration of ozone was constant as the solvent was continuously kept saturated with the gas.

Under these conditions it is evident from our results that increased substitution with electron-donating methyl groups increases the rate of attack by ozone on the aromatic ring. This effect may partly be offset by some steric hindrance, but not seriously so.

Very roughly the reaction rate is doubled for each new methyl group which is introduced, although the increase is somewhat smaller among the higher members. The difference between formic and acetic acid is only pronounced in the case of benzene, where the reaction rate is about 50 % higher in the former solvent. Such an effect is not unexpected since formic acid has a higher dielectric constant than acetic acid.

After the ozonolysis the reaction mixtures contained active oxygen, some of which was peracid. A part of the titratable peracid could be isolated by distillation *in vacuo*. As a mean about 10 % of the titratable performic acid could be found in the distillate; for peracetic acid the figure was 38 % (see experimental part).

The content of active oxygen and peracid varied with time and reached a maximum value after an ozonisation time which became shorter as the substitution in the benzene ring increased. *E.g.* in the case of benzene maximum was reached after ozonising for 2 h, while hexamethylbenzene needed only

Table 1. Half-lives for various aromatic compounds during ozonolysis in formic and acetic acids.

Compound	$t_{0.5}$ in formic acid	$t_{0.5}$ in acetic acid
Benzene	15 min	22 min
Toluene	9 »	8.5 »
o-Xylene	5.5 »	3.5 »
m-Xylene	4.5 »	3 »
Mesitylene	3 »	3 »
Isodurene	1.5 »	1.5 »
Durene	1.5 »	1.5 »
Pentamethylbenzene	1 »	1 »
Hexamethylbenzene	45 sec	40 sec

Table 2. Maximum values for total active oxygen and peracids.

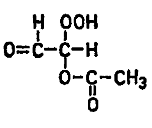
Compound	Formic acid as solvent		Acetic acid as solvent	
	Active oxygen	Performic acid	Active oxygen	Peracetic acid
Benzene	31.3	13.5	30.4	11.0
Toluene	55.0	26.0	62.4	29.8
o-Xylene	58.6	25.0	62.5	29.6
m-Xylene	45.2	18.7	54.1	21.1
Mesitylene	32.4	10.8	38.8	11.7
Isodurene	31.3	12.9	34.9	15.2
Durene	29.2	10.5	32.8	13.2
Pentamethylbenzene	37.8	11.7	41.1	12.8
Hexamethylbenzene	36.7	10.0	39.7	11.2

30 min. After the maximum was reached, the titration value decreased very slowly. The sequence in which the compounds produced maximum amounts of peroxidic material were roughly parallel to their reaction rates. The rates, however, were measured as the disappearance of the aromatic compound, *i.e.* the breaking-up of the aromatic system, while the formation of peroxidic compounds also is dependent upon ozonisation of the primarily formed unsaturated aliphatic entities. On the other hand, the latter process is so rapid compared to the attack on the aromatic ring, that it cannot influence the overall reaction rate.

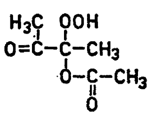
Further the maximum values themselves show another variation as will be evident from Table 2 where the yields of active oxygen and peracid are given in per cent of theoretical yield based on the uptake of three moles of ozone per mole of aromatic compound.

The general tendency is that the amount of active oxygen and peracid decreases from toluene to hexamethylbenzene, with a few local variations. This is not what would have been expected *a priori* as substitution of hydrogen with alkyl groups at the double bond often enhances the stability of ozonides and peroxidic intermediates. Probably anomalous ozonolysis, where no active compounds are produced, plays an increasing role with increasing substitution.

The primary intermediates will among the lower members of the series mainly be of the type (I), while the higher members mainly will produce (II).



(I)



(II)

There is no reason to expect that type (II) should be significantly less stable than type (I), which also is in accord with the fact that the content of active oxygen in the reaction mixtures after ozonolysis diminishes at about the same rate.

From the general trend in Table 2 it would have been expected that benzene should have shown the best yield of active compounds including peracid. That so is not the case can be explained by the very slow uptake of ozone by benzene. Thus during the ozonisation the active intermediates will decompose to such an extent that the yield curve is considerably flattened.

EXPERIMENTAL

Analytical methods. Benzene and toluene could be determined directly in formic and acetic acid by measurement of the extinction in ultraviolet at 2600 Å. The determination of the standard curves as well as the actual measurements were carried out under thermostatic control at 20° ± 0.02°. A certain absorption by the solvents at the chosen wavelength necessitated a correction, which was introduced by extrapolating the smooth curve occurring at lower wavelengths past our point of measurement.

For the higher hydrocarbons a modification of the simple procedure had to be introduced as the ozonolysis products interfered seriously with the spectroscopic determinations. The reaction mixtures were therefore extracted with a specified amount of heptane, which in turn was washed with aqueous sodium bicarbonate and dried, whereafter the determinations were performed on this extract. Standard curves were recorded after the same procedure and were not, as for benzene and toluene, straight lines but slightly curved. The measurements were carried out on a Beckman DK 2 recording spectrophotometer.

Total active oxygen was determined by running aliquots (usually 2 ml) of the ozonolysis mixtures into sodium iodide in glacial acetic acid, under a carbon dioxide atmosphere. The mixture was kept in the dark for 30 min and the liberated iodine titrated with standard thiosulphate.

Peracid was determined by running the aliquots into ice-cold aqueous potassium iodide and the liberated iodine titrated with thiosulphate within 30 sec. A peracid reacts instantaneously with iodide while other peroxidic species under these conditions react more slowly. The end-points were not absolutely sharp, presumably due to the presence of some reactive hydroperoxide, and the peracid values may therefore be slightly high.

Ozonisation procedure. The reaction was carried out in a gas-washing bottle with a fritted gas distributor. This vessel was placed in an ice-bath and the reaction mixtures

Table 3. Amounts of peracid recovered by distillation in % of the titrable peracid in the same reaction mixtures.

Compound	Performic acid %	Peracetic acid %
Benzene	10.0	31.9
Toluene	8.1	30.7
o-Xylene	12.0	26.6
m-Xylene	11.7	35.7
Mesitylene	10.0	38.2
Isodurene	12.8	34.2
Durene	7.4	37.8
Pentamethylbenzene	12.3	53.2
Hexamethylbenzene	11.4	50.0

attained a temperature of 3—4°C. At an oxygen flow of 30 l/h the delivery of ozone was about 2 g/h.

Materials. Benzene, toluene, and the xylenes were high-purity commercial products which were used directly. Mesitylene, durene, and isodurene were also commercial products, but they were purified in this laboratory. Pentamethyl- and hexamethylbenzene were prepared and purified in this laboratory.

Distillation of peracid. The samples for distillation were taken from the ozonolysis mixtures at their maximum content of active oxygen and titratable peracid. The distillation was carried out in a ground-glass apparatus at 17—18 mm Hg and at a temperature not above 40°C. The distillate was taken up directly in aqueous potassium iodide and the liberated iodine titrated with standard thiosulphate. In Table 3 are recorded the amounts of peracid recovered by distillation in per cent of the titratable peracid in the same reaction mixtures.

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