

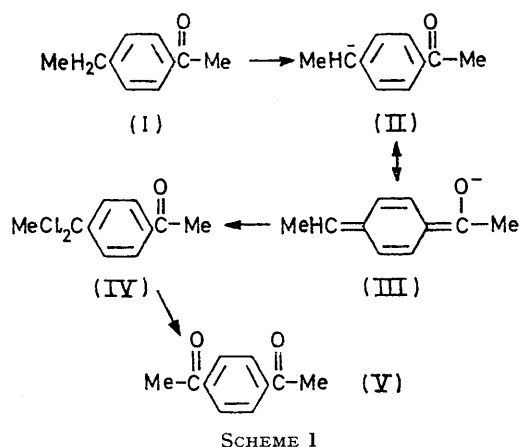
Sodium Hypochlorite as a Selective Oxidant for Organic Compounds

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A study of the reactions of sodium hypochlorite with a wide variety of compounds has been carried out. The data indicate that a structure capable of producing a carbanion stable enough to undergo halogenation is oxidized by sodium hypochlorite to a ketone or a carboxylic acid. How far the oxidation will proceed is determined by enolate-ion resonance stabilization and by inductive and steric effects of the activating group (e.g. $>CO$, $-NO_2$, $-CN$, or $-CO_2H$). Unactivated aromatic, hydroaromatic, alicyclic, and alkane systems are not oxidized. Heteroaromatic ring systems capable of undergoing azomethine-type addition can readily be cleaved, whereas benzenoid ring systems undergo no change. Oxidation of an activated alicyclic compound containing a tertiary sp^3 carbon system may result in loss of one, two, or three carbon atoms as CO_2 or $CHCl_3$ via 1,3- and 1,4-halogenation steps. Based on this investigation, a new methodology of oxidation has been developed for structural elucidation of complex materials such as coal.

THE advantages of hypohalide as a reagent for oxidation¹⁻⁴ of various ketones are well recognized, yet apparently little is known of the behaviour of various other compounds which undergo haloform-type reactions. The oxidation of methylene groups to carbonyl systems by hypohalite was first reported by Schiessler and Eldred,⁵ who obtained 9-oxofluorene-2-carboxylic acid as an 'anomalous' oxidation product from 2-acetylfluorene. The anomaly was resolved later by Neiswender *et al.*,⁶ who showed that methylene and methyl groups attached to an aromatic nucleus are selectively oxidized by sodium hypochlorite when the nucleus also contains an acetyl group.

Bartlett,⁷ from kinetic studies, established that the initial and rate-determining step of the haloform reaction is the enolization of the ketone. This mechanistic path was later confirmed from another set of kinetic data.⁸ The oxidation of active methylene and methyl groups⁶ seems to follow similar enolization steps (Scheme 1). The stabilization of the enolate ion [(II) \leftrightarrow (III)] by



acetyl groups facilitates its chlorination, and, in turn, favours further enolization. A second chlorination

results in (IV), which would be hydrolysed readily to the diketone (V). From this point on, a normal haloform reaction could occur. Mechanistically, the haloform reaction can therefore be applied to any structure which is acidic in character. In other words, a structure which can produce a carbanion stable enough to undergo halogenation would be oxidized by sodium hypohalite to a ketone or carboxylic acid. This hypothesis implies that hypohalite may act as a selective oxidant and thus be of use in structural studies.

We report here a series of experiments which establish the selective nature of hypohalite as an oxidant. An attempt is made to evaluate the advantages of this oxidation process in understanding structural features of a complex material such as coal.

Oxidation with 1.6N-Sodium Hypochlorite.—(a) *Simple aliphatic hydrocarbons and derivatives.* Simple hydrocarbons (cyclohexane, n-octane, and dodecane) were not reactive towards sodium hypochlorite. On the other hand, hydroxy-, nitro-, and halogeno-derivatives were oxidized readily. Except for acetonitrile, common solvents (methanol, ethanol, tetrahydrofuran, dioxan, nitromethane, methylene chloride, dimethoxyethane, and dimethylformamide) reacted readily. No attempt was made to determine the nature of the products. In many cases, solubility of the substrate in the reagent plays an important role in increasing the yield of products. The stability of acetonitrile in 1.6N-sodium hypochlorite makes it possible to use it as a solvent for hypohalite oxidations.

(b) *Unactivated aromatic carbocycles.* Schiessler and Eldred⁵ were unable to oxidize fluorene to fluorenone with hypohalite under the conditions used to oxidize acetylfluorene. The work by Neiswender *et al.*⁶ also revealed that an unactivated system (ethylbenzene) is unreactive towards hypohalite.

We attempted to oxidize n-butylbenzene, isopropylbenzene, bibenzyl, and tetralin. None of these (even in homogeneous solution in acetonitrile) was oxidized after

¹ R. C. Fuson and B. A. Bull, *Chem. Rev.*, 1934, **15**, 275.

² W. T. Smith and G. L. McLeod, *Org. Synth.*, Coll. Vol. IV, 1963, p. 345.

³ R. Levine and M. W. Farrar, *J. Amer. Chem. Soc.*, 1949, **71**, 1496.

⁴ R. Levine and J. R. Stephens, *J. Amer. Chem. Soc.*, 1950, **72**, 1642.

⁵ R. W. Schiessler and N. R. Eldred, *J. Amer. Chem. Soc.*, 1948, **70**, 3958.

⁶ D. D. Neiswender, jun., W. B. Moniz, and J. A. Dixon, *J. Amer. Chem. Soc.*, 1960, **82**, 2876.

⁷ P. D. Bartlett, *J. Amer. Chem. Soc.*, 1934, **56**, 967.

⁸ R. P. Bell and H. C. Longuett-Higgins, *J. Chem. Soc.*, 1946, 636.

treatment for 36 h at 60–70 °C. On the other hand, benzoic acid and benzil were oxidized to benzoic acid in 16 and 93% yield, respectively. Cleavage of diketones by sodium hypohalite was reported earlier; they were expected to be intermediate in the oxidation process.⁶

The stability of the aromatic ring itself was evident from the failure of attempts to oxidize naphthalene, anthracene, and phenanthrene. Since it is known that chloropicrin can be obtained by cleavage of picric acid with sodium hypohalite, *p*-nitrophenol, *m*-nitrophenol, and 2,4-dinitrophenol were treated similarly. The dinitro-derivative consumed a trace of hypohalite, but no identifiable product was isolated.

Anthraquinone and phenanthroquinone were stable under these oxidation conditions.

(c) *Activation by nitro-substituents.* Methylene and methyl groups activated by a ketonic function are known to be readily oxidizable by sodium hypohalite. The present work shows that nitro-groups have a similar effect. Nitro-derivatives of toluene, ethylbenzene, butylbenzene, and xylenes were readily oxidized to carboxylic acids. In the case of the nitrotoluenes, chloromethyl derivatives (8% from the *ortho*- and 20% from the *meta*-isomer) were also isolated.

Both methyl groups of nitro-derivatives of *o*-xylene and *m*-xylene can be oxidized. 3-Nitro-*o*-xylene was 75% oxidized and gave 2-methyl-3-nitrobenzoic acid, 2-methyl-6-nitrobenzoic acid, and 3-nitro-*o*-phthalic acid in molar ratio of 4:3:1. 4-Nitro-*o*-xylene similarly gave 2-methyl-5-nitrobenzoic acid, 2-methyl-4-nitrobenzoic acid, and 4-nitro-*o*-phthalic acid (5:5:1). 5-Nitro-*m*-xylene gave 3-methyl-5-nitrobenzoic acid and 5-nitroisophthalic acid (10:1) from 80% of the substrate.

p-Nitrobenzoic acid, propionic acid, and acetic acid were isolated as oxidation products of *p*-nitro-*n*-butylbenzene. Since propionic acid is not further oxidized by hypohalite, isolation of acetic acid seems to indicate that a diketone (PhCO·CH₂·COMe) or an α -triketone, (*p*-O₂N·C₆H₄·CO·CO·COMe) may be formed as intermediate when a long side chain is present.

Oxidation of *p*-nitrobiphenyl gave *p*-nitrobenzoic acid, benzoic acid, and *p*-nitrobenzil. The major product was the diketone, which on further oxidation was converted into *p*-nitrobenzoic acid and benzoic acid.

(d) *Activation by cyano-substituents.* *o*-Toluonitrile was oxidized to *o*-phthalic acid. It is not known whether nitrile hydrolysis precedes oxidation of the methyl group. No such hydrolysis was observed of the *para*- and *meta*-substrates, which gave cyanobenzoic acids, along with trace amounts of chloromethyl derivatives.

(e) *Activation by carboxy-substituents.* *o*-Toluic acid was oxidized to *o*-phthalic acid, along with an equimolar quantity of 2-(chloromethyl)benzoic acid. *p*-Toluic acid yielded terephthalic acid (6%) and 4-(chloromethyl)benzoic acid (43%). With a large excess of oxidant, the yield of terephthalic acid could be increased at the expense of chlorinated product. *m*-Toluic acid gave isophthalic acid (37.4%), 3-(chloromethyl)benzoic acid (21.4%), and 3-(hydroxymethyl)benzoic acid (11.8%).

Such hydrolysis of the chlorinated product was not observed in other cases.

The contribution of the inductive effect of the acetyl group to the oxidation of an alkyl side chain was reported by Neiswender *et al.*⁶ Similar yields of *meta*- and *para*-products and a lesser one of *ortho*-product from nitro-, cyano-, and carboxy-substrates seem to indicate that inductive and steric effects jointly predominate over that of enolate ion resonance stabilization.

(f) *Aromatic N-heterocycles.* Oxidative cleavage of an *N*-heterocycle usually requires drastic conditions; however, sodium hypohalite, though a mild oxidant, can cleave certain compounds of this type. Pyridine reacts very readily giving carbon dioxide and ammonia. No other product was characterized. Combined g.l.c.–mass spectral analysis of the rapidly quenched reaction mixture gave two peaks, one due to pyridine and the other to a minor component with parent peak at *m/e* 95, dipositive ion peaks at *m/e* 47.5, 47, and 46.5, and fragments at *m/e* 66 and 67 (loss of HCN) and 39 [loss of CO(?)]. The transitory formation of 2-pyridone is suspected.

The ring of 2-methylpyridine was cleaved also, but to an insignificant extent compared with oxidation of the methyl group. In the case of 2,6-dimethylpyridine, attack by the oxidant was confined to the 2-methyl group, to yield the 2-carboxylic acid along with traces of a chloromethyl product.

The heterocyclic ring of quinoline was cleaved to give isophthalic acid. Other products were a dichloroquinoline-2-one and a trichloroquinoline-2-one. However, isoquinoline gave no product except *o*-phthalic acid.

Thus a 2-unsubstituted *N*-heterocycle ring is not stable to hypohalite oxidation. Structures which can undergo an azomethine type of addition will be attacked by hypohalite on the unsubstituted carbon α to the hetero atom and thereby undergo ring cleavage. With α -alkyl derivatives oxidation takes the normal course, *i.e.* formation of a carbanion on the side-chain followed by further oxidation.

(g) *Saturated carbocycles.* Neiswender *et al.*⁶ reported that 6-acetyltetralin, oxidized with sodium hypochlorite, gave an 18% yield of the normal haloform reaction product, tetralin-6-carboxylic acid, along with 56% yield of a mixture of 3-(2,4-dicarboxyphenyl)propanoic acid and 3-(2,5-dicarboxyphenyl)propanoic acid, formed by cleavage of the alicyclic ring. Mechanistically, the reaction is comparable to that of *p*-nitrobiphenyl, nitro-xylene, or acetyl-*n*-butylbenzene. The cleavage of cyclohexanone to adipic acid, and of cyclopentene to glutaric acid follows the same path.

The present work provides further information about the fate of saturated carbocycles. A nitro-group on an alicyclic ring seems to be too labile to participate in activating an adjacent carbon–hydrogen bond for hypohalite oxidation. Nitrocyclohexane gave a mixture of chlorocyclohexane, chlorocyclohexene, and dichlorocyclohexane as products. Replacement of a nitro-group

by halogen has been reported⁹ for certain aromatic systems.

On the other hand, carboxy-substituents on an alicyclic system participate in oxidative cleavage of the ring. Cyclohexanecarboxylic acid gave a mixture of succinic, glutaric, and adipic acids as well as carbon dioxide ($C_4 > C_5 \gg C_6$ acid).

Cyclic ketones are known to undergo haloform-type reactions. Methyl substituents on such ketones were found to affect the nature and yield of cleavage products. From 2-methylcyclohexanone, a mixture of glutaric, adipic, succinic, 2-methyladipic, and 2-methylglutaric acid was obtained ($C_4 > C_6 \sim C_5 \gg \text{MeC}_5 \sim \text{MeC}_6$ acids). The relatively insignificant amount of methyl homologues of dicarboxylic acids in the present product mixture may indicate that chlorination of the methine carbon atom α to the ketonic function (*cf.* oxidation of cyclohexanecarboxylic acid) initiates the oxidation. For 3-methylcyclohexanone oxidation, dicarboxylic acids were formed in relative amounts $C_5 > C_4 > \text{MeC}_6$. Formation of both glutaric and succinic acids, and the predominance of the former over the others, again indicates the role of the methine carbon atom.

The reactivity of the saturated carbocyclic system towards hypohalite increases as the system becomes more complex. Cyclohexane is inert; norbornane is oxidized to norcamphor, but chloronorbornane and bicyclo-[2.2.1]hept-2-ene are the major products; and adamantane undergoes extensive chlorination, followed by ring cleavage to give carbon dioxide as the end product. Incorporating a hetero-group into a bridged carbocyclic system facilitates ring cleavage. Norcamphor was oxidized to cyclopentanedicarboxylic acid, succinic acid, and carbon dioxide. Adamantan-2-one gave cyclopentanedicarboxylic acid and carbon dioxide. Adamantan-1-carboxylic acid gave extensively chlorinated products and carbon dioxide. If the yield of carbon dioxide from different substrates undergoing oxidation under identical conditions can be taken as a measure of ring cleavage, the reactivity of these substrates is in the order adamantane < adamantan-2-one < norcamphor < adamantan-1-carboxylic acid. The ring cleavage shown in Scheme 2 may be envisaged. Incorporating a

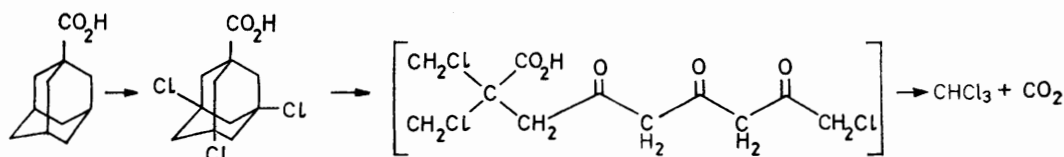
17,18-Hexahydrotribenzo[*a,e,i*]cyclododecene (*o*-xylene trimer) was non-reactive towards the oxidant and the nitro-derivative reacted very sluggishly. Extensive treatment with hypochlorite in the presence of large excess of alkali resulted in partial oxidation; two benzylic carbon atoms were oxidized to carbonyl groups in insignificant yield; the major product was mono-ketone. Such partial oxidation was only observed when the substrates were *p*-cresol-formaldehyde polymers or nitro-derivatives of styrene-divinylbenzene cross-polymer.

Coal, which is claimed to be a complex polymeric material, reacts with sodium hypochlorite like simple organic compounds. Consumption of oxidant by sub-bituminous coal (%C *ca.* 80%) is much faster than by bituminous coal (%C *ca.* 90%); as oxidation proceeds, complete dissolution of a sub-bituminous coal results in a light yellow solution, with <1% of the solid left in suspension. On the other hand, only 7–8% of bituminous coal goes into solution. However, if modified by nitration, bituminous coal becomes susceptible to hypochlorite oxidation and will then react as fast as sub-bituminous coal. The oxidation products of the nitro-coal are carbon dioxide, acetic acid, propionic acid, alkane- $\alpha\omega$ -dicarboxylic acids, and benzenepolycarboxylic acids.

Discussion.—The data presented demonstrate the selectivity of hypohalite as an oxidant. The vulnerability of a substrate depends on the presence and reactivity of electronegative elements. How far the oxidation will proceed is determined by enolate ion resonance stabilization, and inductive and steric effects of the activating groups; the latter two effects predominate over the former. The solubility of the substrate in the reagent has a role in determining the optimum yield of products.

Unactivated aromatic, hydroaromatic, alicyclic, and alkane systems are not oxidized (except for formation of epoxides or diols^{9,10} from unactivated double bonds). Heteroaromatic ring systems capable of undergoing azomethine-type addition can readily be cleaved, whereas benzenoid ring systems undergo no change.

Oxidation of activated alicyclic systems containing



SCHEME 2

benzene ring, on the other hand, decreases the reactivity of the system. Triptycene, only gave 9-chloro- and 9,10-dichloro-triptycene.

(h) *Polymeric material.* Polymeric materials having potential sites for hypohalite attack do not fall apart into simpler low molecular weight products. 5,6,11,12,-

tertiary sp^3 carbon centres may result in loss of one, two, or three carbon atoms as carbon dioxide or chloroform *via* 1,3- and 1,4-halogenation steps. Such shorten-

⁹ S. Marmar, *J. Org. Chem.*, 1963, **28**, 1656.

¹⁰ A. Kergomard, *Bull. Soc. chim. France*, 1961, 2360.

ing of chain length by oxidative decarboxylation of sugars and amino-acids has been reported.^{11,12}

Sodium hypochlorite oxidation is clean and devoid of side-reactions such as polymerization, rearrangements, etc. Oxidation sites end up as ketone or carboxylic acid systems. In some cases, halogenated products may be obtained owing to incomplete reaction, or as a result of replacement of nitro- or methoxy-groups.

The data on coal oxidation provide new information towards the understanding of coal structure. The reactivity of different coals was found to be related to the amount of oxygen of function in the substrate. Low-rank coal (sub-bituminous) has a higher percentage of oxygen and reacts vigorously with hypochlorite, whereas bituminous coal has to be activated by nitration or acylation to make it react (cf. bibenzyl, benzoic, and benzil; cyclohexane, cyclohexane carboxylic acid, and cyclohexanone, etc.).

Furthermore, the nature of the oxidation products allows inferences to be made concerning the chemical structure of coal. For example, the abundance of 'parent structural fragments' (or carbon distribution in structural types) in coal can be determined from the carbon distribution in the products. One such analysis based on the quantitative estimation of individual products obtained from one Western Canadian coal (theoretical model, C₂₉₃H₁₈₃N₅O₇; found: C, 90.4; H, 4.7%) is presented in Table I. The number of carbon

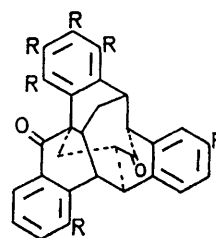
ment (or fragments) should be of *sp*³ carbon type, one has to assume a complex carbocyclic system containing

bridged tertiary carbon in the form $\geq\text{CH}$, $\text{H}-\text{C}-\text{C}-\text{CH}$,

and $\begin{array}{c} \text{H} \\ | \\ \geq\text{C}-\text{C}\leq \end{array}$. A three-dimensional network of the adamantane type is an approximation to this.

Similar analyses with other coals indicate that at least 50% of carbon in coal exists as complex bridged cycloalkane, about 10% as alkane chain or cycloalkane and about 26–30% as methine-substituted benzene ring. The questions remain as to whether these structural types exist independently or bound to each other, and, if the latter is true, how they are linked.

From knowledge of the oxidizability of methine-



(A)

benzene and adamantane systems, one can speculate that coal structure involves a combination of these two systems. A possible basic unit, in its simplest form, is shown (A), where the methylene carbon atoms of *o*-xylene trimer are bridged by CH·CH₂ groups. With R = H, such a component has C 86.5%, H : C 0.76 : 1, and O : C 0.07 : 1. Comparable figures for a coal having C 80–87% are H : C 0.76–0.73 : 1 and O : C 0.11–0.05 : 1. Thus coal may be considered conveniently as a mixture of component units of type (A), where R represents an adamantane-type substituent, which would yield five different benzenecarboxylic acids and carbon dioxide as major products of hypochlorite oxidation.

Comparative studies of the products formed from coal with different oxidants^{13–17} might be of value in substantiating such a hypothesis.

EXPERIMENTAL

Preliminary work revealed that best results were obtained at pH 12–13 with 1.5–1.6N-hypochlorite solution (determined by titration with sodium arsenate). As reaction proceeds, the pH of the mixture gradually decreases and at lower pH values, even between 9 and 10, autodecomposition of sodium hypochlorite is considerable. In order to maintain a high pH level, an excess of oxidant was therefore used. Molar ratios of substrate to oxidant varied from 1 : 5 to 1 : 20, depending on the nature of the substrate, its solubility, and the extent of oxidation required. The solubility of the

¹⁵ B. Juttner, *Brennstoff-Chem.*, 1956, **37**, 70.
¹⁶ R. Belcher, *J. Soc. Chem. Ind.*, 1948, **67**, 213, 265.
¹⁷ E. D. Holly and R. S. Montgomery, *Fuel*, 1956, **35**, 49, 56, 60; 1957, **36**, 63, 181, 497.

TABLE I

Carbon distribution in various structural fragments of coal

Oxidation products	Parent fragments	% Total carbon	C atom ^a	H atom ^a
C ₆ (CO ₂ H) ₆	C ₆ (CH) ₆	8.86	26	13
HC ₆ (CO ₂ H) ₅	HC ₆ (CH) ₅	5.81	17	9
H ₂ C ₆ (CO ₂ H) ₄ (1,2,3,4 and 1,2,4,5)	H ₂ C ₆ (CH) ₄	6.26	18	11
H ₃ C ₆ (CO ₂ H) ₃ (1,2,3, 1,2,4, and 1,3,5)	H ₃ C ₆ (CH) ₃	3.80	11	7
H ₄ C ₆ (CO ₂ H) ₂ (1,2)	H ₄ C ₆ (CH) ₂	1.43	4	3
Acetic, propionic, succinic, glutaric, and adipic acids	[CH ₂] _{2–6}	9.23	27	54
Mass ca. 700	?	13.30	39	19 ^b
CO ₂	Saturated polycycles	51.54	151	67 ^c

^a Number of atoms. ^b Calculated from the elemental analysis. ^c Computed as the difference between hydrogen input (183) and output (116) as products other than CO₂.

atoms which appeared in different products is calculated from the experimental data; but the number of hydrogen atoms presumably existing in the precursors are computed from the H/C ratios of the 'parent fragments'. This computation yields an H : C ratio for the fragments appearing as CO₂ of 0.44 : 1. Since this frag-

¹¹ R. L. Whistler and K. Yagi, *J. Org. Chem.*, 1961, **26**, 1050.
¹² H. L. Stahs, D. Taub, C. H. Kuo, and N. L. Wendler, *J. Org. Chem.*, 1964, **29**, 1424.

¹³ W. A. Bone, L. Horton, and S. G. Ward, *Proc. Roy. Soc., Ser. A*, 1930, **127**, 480.

¹⁴ J. Entel, *J. Amer. Chem. Soc.*, 1954, **76**, 3646; 1955, **77**, 611.

TABLE 2
Oxidation data for model compounds

Substrate	Molar ratio of substrate to hypochloride	Product	Yield (mole %)	Remarks
<i>o</i> -Nitrotoluene	1 : 22	<i>o</i> -Nitrobenzoic acid	60.7	
<i>p</i> -Nitrotoluene	1 : 22	1-Chloromethyl-2-nitrobenzene	8.9	M.p. 240—242° (isolated as solid)
		<i>p</i> -Nitrobenzoic acid	81.7	
<i>m</i> -Nitrotoluene	1 : 22	1-Chloromethyl-4-nitrobenzene	10.6	M.p. 141° (isolated as solid)
		<i>m</i> -Nitrobenzoic acid	70.0	
1-Ethyl-4-nitrobenzene	1 : 20	1-Chloromethyl-3-nitrobenzene	20.4	<i>m/e</i> 187, 185, 151, 150, 149, and 77; δ 5.0—5.35 (q) and 1.8—1.95 (d)
		<i>p</i> -Nitrobenzoic acid	90.0	
		1-(1-Chloroethyl)-4-nitrobenzene	7.3	
1-Butyl-4-nitrobenzene	1 : 20	1-(1-Hydroxyethyl)-4-nitrobenzene	Trace	} Identified by g.l.c.; no attempt made to determine the yield
		<i>p</i> -Nitrobenzoic acid	25.0	
		Acetic acid		
3-Nitro- <i>o</i> -xylene	1 : 20	Propionic acid		<i>m/e</i> 178, 163, and 89 (100%) <i>m/e</i> 195 and 91 (100%)
		2-Methyl-6-nitrobenzoic acid	33.2	
		2-Methyl-3-nitrobenzoic acid	43.1	
4-Nitro- <i>o</i> -xylene	1 : 20	3-Nitro- <i>o</i> -phthalic acid	11.0	} Identical mass spectra, but could be resolved by g.l.c.
		2-Methyl-5-nitrobenzoic acid	35.8	
		2-Methyl-3-nitrobenzoic acid	35.8	
5-Nitro- <i>m</i> -xylene	1 : 20	4-Nitro- <i>o</i> -phthalic acid	9.6	
		3-Methyl-5-nitrobenzoic acid	77.7	
		5-Nitroisophthalic acid	7.9	
<i>p</i> -Nitrobibenzyl	1 : 15	<i>p</i> -Nitrobenzil	72.0	<i>m/e</i> 255 (100%), 209, 180, 150, 133, 120, and 105; ν_{\max} 1620 cm ⁻¹
	1 : 25	<i>p</i> -Nitrobenzoic acid	62.0	
Benzil	1 : 4	Benzoic acid	63.3	
		Benzoic acid	138.0	
Benzoil	1 : 4	Benzoic acid	160.0	
<i>o</i> -Toluenitrile	1 : 20	<i>o</i> -Phthalic acid	21.0	
<i>p</i> -Toluenitrile	1 : 20	<i>p</i> -Cyanobenzoic acid	92.2	
		<i>p</i> -Chloromethylbenzonitrile	Trace	
<i>m</i> -Toluenitrile	1 : 20	<i>m</i> -Cyanobenzoic acid	72.6	<i>m/e</i> 151, 153, and 116; δ 4.1
		<i>m</i> -Chloromethylbenzonitrile	Trace	
<i>o</i> -Toluoic acid	1 : 15	<i>o</i> -Phthalic acid	36.0	<i>m/e</i> 186/184, 153/155 (100%), 125, 89, etc.
		<i>o</i> -Chloromethylbenzoic acid	33.8	
<i>p</i> -Toluoic acid	1 : 8	Terephthalic acid	6.4	
	1 : 16	<i>p</i> -Chloromethylbenzoic acid	43.5	
<i>m</i> -Toluoic acid	1 : 16	Terephthalic acid	32.6	
		<i>p</i> -Chloromethylbenzoic acid	11.1	
		Isophthalic acid	37.4	
		<i>m</i> -Chloromethylbenzoic acid	21.4	
		<i>m</i> -Hydroxymethylbenzoic acid	11.8	
2-Methylpyridine	1 : 7	Pyridine-2-carboxylic acid	57.9	
2,6-Dimethylpyridine	1 : 4	6-Methylpyridine-2-carboxylic acid	48.4	
		6-Chloromethylpyridine-2-carboxylic acid	7.0	
Quinoline	1 : 10	Other chloro-product (non-acidic)	Trace	Parent ions <i>m/e</i> 141 and 175
		Isophthalic acid	22.2	
		3,4-Dichloroquinoline-2-one	34.4	
Isoquinoline	1 : 10	Trichloroquinoline-2-one	39.0	<i>m/e</i> 217/215/213 (100%) (dipositive ions at <i>m/e</i> 106.5, 107.5, 94.5, 93.5, 92.5, etc.), 189/187/185 (<i>M</i> - 28), and 150/152/154 (<i>M</i> - 28 - 35) <i>m/e</i> 253/251/249/247 (100%) and 217/215/213 (<i>M</i> - Cl)
		<i>o</i> -Phthalic acid	58.3	
Nitrocyclohexane	1 : 10	Chlorocyclohexane		Solid m.p. 205—206° (from H ₂ O); identified as methyl ester by mass spectrum
		Chlorocyclohexene		
Cyclohexanecarboxylic acid	1 : 10	Dichlorocyclohexane		<i>m/e</i> 120/118 <i>m/e</i> 118/116 <i>m/e</i> 156/154/152 Yield not established
		Succinic acid		
2-Methylcyclohexane	1 : 10	Glutaric acid		} G.l.c. peak area showed C ₄ > C ₅ ≧ C ₆
		Adipic acid		
		Succinic acid		
3-Methylcyclohexanone	1 : 10	Glutaric acid		} C ₄ > C ₆ > C ₅
		Adipic acid		
		Succinic acid		
Norborane	1 : 10	Glutaric acid		} C ₅ > C ₄ > MeC ₆
		Methyladipic acid		
		Norcamphor		
Bicyclo[2.2.1]hept-2-ene	1 : 10	Chloronorboranes		<i>M</i> + C ₇ H ₁₀ O <i>M</i> + C ₇ H ₁₀ 45% of total product mixtures C ₇ H ₉ Cl; two-isomer
		Chloronorboranes		

TABLE 2 (Continued)

Substrate	Molar ratio of substrate to hypochlorite	Product	Yield (mole %)	Remarks
Norcamphor	1:10	Carbon dioxide	216	
		Succinic acid		
		Cyclopentanedicarboxylic acid		<i>m/e</i> 186 (C ₉ H ₁₄ O ₄) as methyl ester
		Chloropentanedicarboxylic acid		<i>m/e</i> 222/220 (C ₉ H ₁₃ ClO ₄) methyl ester
		Chloronorcamphor		<i>m/e</i> 146/144 (C ₇ H ₉ ClO)
Triptycene	1:10	Dichloronorcamphor	143	<i>m/e</i> 180/178 (C ₇ H ₉ Cl ₂ O)
		Monochlorinated		<i>m/e</i> 290/288
Adamantane	1:10	Dichlorinated	200	<i>m/e</i> 322/324/326
		Carbon dioxide		No other acidic product
		Monochloroadamantane		<i>m/e</i> 170, 172, 204, 206, 208, 238, 240, and 242
Dichloroadamantane				
Adamantan-2-one	1:10	Trichloroadamantane	200	
		Carbon dioxide		
		Succinic acid		C ₉ H ₁₃ ClO ₄
		Chlorocyclopentanedicarboxylic acid		C ₁₁ H ₁₆ O ₂ Cl ₂ (<i>m/e</i> 250) <i>m/e</i> 218 and 252

TABLE 3

Yields of products from coal oxidation (per g of organic matter in coal)

Product	Mmol	M equiv.	Product	Mmol	M equiv.
CO ₂	30.63		C ₈ H(CO ₂ H) ₅ (and NO ₂ deriv.)	0.31	1.55
AcOH	0.62	0.62	C ₆ (CO ₂ H) ₆	0.44	2.64
PrOH	0.22	0.22	<i>M</i> 750—600	0.28 ^a	1.12 ^a
C ₆ H ₄ (CO ₂ H) ₂ (1,2 and NO ₂ deriv.)	0.11	0.22	<i>M</i> 200—100	0.63 ^b	1.26 ^b
C ₆ H ₃ (CO ₂ H) ₃ (1,2,3, 1,2,4, and 1,3,5)	0.25	0.75	(succinic, glutaric, and adipic)		
C ₆ H ₂ (CO ₂ H) ₄ (1,2,3,4, 1,2,5,6, and NO ₂ deriv.)	0.37	1.48			

Yield of total acids other than CO₂: from chromatogram: 9.86 m equiv. g⁻¹; from direct titration: 10.35 m equiv. g⁻¹^a Based on assumed *M* 650 having 4 CO₂H groups. ^b Based on assumed *M* 160 (dimethyl glutarate).

substrate generally controls the extent of oxidation and yield of products. For insoluble substrate, the reaction time can be shortened by using acetonitrile (which was stable under the oxidation conditions used) as solvent, without any interference with the normal oxidation path, except that partial hydrolysis of acetonitrile to acetic acid occurred. The maximum temperature for the oxidation was 60–70 °C. Commercially available stabilized sodium hypochlorite solution was found to be suitable and was used for the present study.

General Procedure for Oxidation.—The substrate (1–2 g) was stirred under nitrogen at 60–70 °C for 3–5 h with 1.5–1.6*N*-sodium hypochlorite solution (pH 12–13; 100–300 ml). For insoluble substrates, acetonitrile was added in quantity just sufficient to keep the reactants in solution. In most cases, no excess of hypochlorite remained after reaction. Non-acidic materials were extracted with ether. The basic aqueous layer was acidified, concentrated by distillation (water-pump) and extracted with ether (if the acidic product was insoluble in ether, the reaction mixture after acidification, was dried under vacuum and extracted with methanol). Gases evolved from the reaction, swept out with nitrogen, were passed through barium hydroxide solution to trap any carbon dioxide. (Decrease in the pH of the solution causes the escape of carbon dioxide). For separation purposes, acidic products were completely methylated with diazomethane to form methyl esters.

The oxidation products were separated and characterized by g.l.c.–mass spectral analysis (Perkin-Elmer 270 double-focusing spectrophotometer). For chromatography, a 7 ft × $\frac{1}{8}$ in (o.d.) stainless steel column packed with 3% OV-17 on Chromosorb W (H.P.) was used. For steam-volatile acids (acetic, propionic, etc.) a 6 ft × $\frac{1}{8}$ in (o.d.)

stainless steel column packed with 5% FFAP on Porapak Q (50–80 mesh) was used. Most of the chromatographic analyses were performed with a Varian instrument equipped with a flame-ionization detector.

Products from each reaction were identified with the help of reference mass spectra of authentic compounds. Yields of products were calculated on the basis of the calibration curves made by peak-area measurement from the chromatographs of individual standard components. The oxidation data for model compounds are presented in Table 2.

Oxidation of pyridine. A vigorous reaction occurred when pyridine (1 g) was stirred with 50 ml 1.6*N*-sodium hypochlorite (50 ml). Carbon dioxide and ammonia were evolved. No identifiable product was recovered. A similar reaction with 0.5*N*-hypochlorite was quenched with sodium hydrogen sulphite. An ethereal extract was subjected to g.l.c.–mass spectral analysis [see text section (f)].

Nitration of Coal.—This was effected by suspending a freshly minuted sample of coal in acetonitrile or nitromethane and treating the suspension with nitronium tetrafluoroborate (6 mmol per g) at 10–20 °C for 2 h. Stirring was continued at 30–35 °C for another hour and the mixture was poured into ice-water and washed free of acid and solvents before being dried *in vacuo* (P₂O₅).

Oxidation of Coal.—G.l.c. analysis of the volatile acids was carried out on two columns: (1) 10.5% EGA, 1.75% H₃PO₄ on Anakrom ABS (100–110 mesh) and (2) 5% FFAP on Porapak Q (50–80 mesh). Column (2) was satisfactory for quantitative analysis. The non-volatile acids were separated as methyl esters. The analysis was done in Water's instrument, GPC/ALC 301, with a bank of five Styragel columns having polystyrene contour chain length exclusive values 800, 800, 100, 79 and 70 Å, and provided

with dual detector (8 μ l, 10 mm path length u.v. photometer set at 254 nm and 10 μ l differential refractometer in series). For quantitative work, the peak area, given by the refractometer, was used. The solvent was tetrahydrofuran, passed through at a flow rate of 2.0 ml min⁻¹. A 5 mg ($\frac{1}{4}$ w/v %) sample was taken for each run. Results of analysis of methyl esters, confirmed by g.l.c.-mass spectroscopy, are given in Table 3.

Preparation of o-Xylene Trimer.—Reaction of $\alpha\alpha'$ -dibromo-*o*-xylene with disodium tetraphenylethane-1,2-di-ide [$\phi_2\text{NaC}$]₂ in anhydrous tetrahydrofuran under nitrogen¹⁸ gave the trimer (16%), m.p. 184–185° (from EtOH), *m/e* 313–312, 207 (100%), 193, 178, 115, 105, 91, *etc.* δ_{OH} 2.7, δ_{CH_2} 6.9 (1 : 1).

Nitration of the trimer. Reaction with nitronium tetrafluoroborate (1 : 1 molar ratio in acetonitrile) gave *ca.* 30%

¹⁸ Ger.P. 1,067,816/1959.

mononitro-derivatives (ascertained by i.r. spectra). Some dinitro-derivatives were also formed.

Oxidation of the nitro-trimer. Oxidation with sodium hypochlorite by the standard procedure was unsuccessful. Treating the substrate with a large excess of sodium hypochlorite and added sodium hydroxide, and stirring at 60 °C for 3 days, gave a non-acidic product; a monoketone, *m/e* 371, from the mononitro-derivative, and a diketone, *m/e* 430, from the dinitro-derivative. The mass spectral fragmentation patterns are consistent with this structural assignment. I.r. spectra confirmed the presence of the ketonic functions.

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