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MECHANISM OF AROMATIC OXYGENATION WITH BIS(3-NITROBENZENESULFONYL) PEROXIDE[1]

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Abstract—Oxygenation of toluene was investigated with bis(3-nitrobenzenesulfonyl) peroxide (NBSP) in the presence of salts known to affect radical (cupric, cuprous, and cobaltous chlorides, and sodium hexachloroiridate (IV)) and ionic (aluminium chloride) processes. The yield and orientation of the isomeric tolyl 3-nitrobenzenesulfonates, as well as a kinetic study, show that salts which bring about radical pathways do not catalyze oxygenation, although induced decomposition of peroxide is accomplished with formation of sulfonate salts. Aluminium chloride has a promoting effect on aromatic oxygenation at $AlCl_3$:NBSP $\cong$ 4:1, but at lower ratios rapid breakdown of the sulfonyl peroxide is effected in a competing reaction. The results are interpreted in terms of nucleophilic displacement by the aromatic nucleus at the peroxidic oxygen-oxygen bond in accord with the earlier proposal of Dannley and analogous to attack of stronger nucleophiles on aroyl peroxides.

A PRIORI, oxygenation of an aromatic compound by a sulfonyl peroxide can be regarded as occurring *via* a number of possible mechanistic pathways. One can consider initial homolytic cleavage of the O—O bond to give sulfonyloxy radicals, or heterolytic fission to sulfonyloxy cation- and anion-like entities. Attention should also be paid to routes involving induced decomposition of peroxide by the substrate. The concerted approach can be viewed as being in either the radical or ionic category.

Dannley *et al.*[4–6] have stated that the reaction of symmetrical bisarylsulfonyl peroxides with aromatic substrates, to give sulfonate ester products, follows an electrophilic pathway. Their conclusions were based on orientation, partial rate factors, the *rho* values of −4·75 to −6·4 in a Hammett–Brown treatment, and the absence of ESR signals. Other authors have advocated intervention of species from heterolysis for various reactions involving asymmetric peroxides.[7]

Consideration should also be given to participation of radical intermediates. Results from our laboratory[8] indicate that diisopropyl peroxydicarbonate (IPP) reacts with aromatics by way of an oxy radical possessing appreciable electrophilic character. For example, a Hammett–Brown treatment gave *rho* = −2·3, and catalysis is effected by copper salts. Hence, it would be expected that a sulfonyloxy radical generated from the corresponding peroxide should possess more electrophilic character than the analogous carbonate radical, and thereby might be involved as the attacking species in aromatic substitution. This approach possesses reasonable validity since claims have been made for homolytic cleavage of sulfonyl peroxides.[9,10] In particular, Haszeldine *et al.* postulated that aromatic oxygenation with dimethanesulfonyl peroxide occurs *via* homolysis,[9] and Crovatt and McKee[10] proposed that the similar process with bisbenzenesulfonyl peroxide is a radical reaction. Both groups based their proposals, in part, on the effective catalysis of polymerization by these peroxides.[9, 10] The absence of side-chain attack[5b] is not necessarily conclusive evidence against a homolytic mechanism, since certain radicals are much more prone to attack the nucleus than to abstract hydrogen.[8] Heterolytic breakdown would be more likely with asymmetrical peroxides. However, even acylsulfonyl peroxides have been used as radical sources, e.g., in sulfochlorination,[11] chlorination,[12] polymerization,[13] and for generation of various types of radicals.[14] The formation of *p*-toluenesulfonic anhydride, thought to come from *p*-tolylsulfonyloxy and *p*-toluenesulfonyl radicals, has also been described recently.[15]

Contributions from a variety of groups have resulted in considerable elucidation of the detailed aspects of aromatic oxygenation by hydrogen peroxide,[16] peracids,[17] and acyl-type peroxides.[8, 18] In contrast, information from sulfonyl peroxides in similar systems is meagre and the theoretical picture is clouded by conflicting claims and considerable uncertainty. Our objective was to clarify the mechanism of the sulfonyl peroxide-aromatic reaction. Attention was focused mainly on temperature effects and the influence of inorganic salts known to have a crucial impact on radical or ionic processes. Conclusions for the bis(3-nitrobenzenesulfonyl) peroxide–toluene system are derived mainly from isomer distributions, yield of esters, kinetic data, nature of the products, and response to alteration in conditions.

RESULTS AND DISCUSSION

Dannley *et al.*, who investigated the reaction of bis(3-nitrobenzenesulfonyl) peroxide (NBSP) with toluene, determined that tolyl 3-nitrobenzenesulfonates and 3-nitrobenzenesulfonic acid are generated.[4] They showed that this type of process is second order overall, first order in peroxide and first order in aromatic.[5a] This does not rule out a preliminary homolysis or heterolysis of peroxide as a fast initial step.

Under our standard conditions, the reaction of NBSP with toluene in acetonitrile gave a 91% yield of esters (Table 1). Orientations were determined after reductive cleavage of the isomeric esters by the naphthalene radical anion,[19] followed by direct glpc analysis of the cresols. The orientation (Table 1), accurate to *ca* 3%, was little influenced by added salt. The figures, *ortho*, 27%, *meta*, 6%, *para*, 67%, compare favourably with those obtained by Dannley and Corbett[4] ($o:p = 34:66$), as well as with the results ($o:m:p = 34:6:60$) from reaction of dimethanesulfonyl peroxide with toluene.[9] Attempts at isolation and identification of byproducts (<3% yield) were unsuccessful due to the paucity of material.

The rate of reaction with excess toluene in the absence of added salt showed good pseudo-first order dependence. The kinetic data for added salts are recorded in Tables 2 and 3.

Redox salt catalysts

Cupric chloride. This aspect of the study was undertaken because cupric chloride is known to catalyze oxygenation of toluene by IPP in a chain process.[8] The rate was found to be ten times that of the uncatalyzed case.[8b] When the reaction of NBSP with toluene was carried out under the standard conditions with a ratio of $CuCl_2$:NBSP $\cong 0{\cdot}1:1$, only minor change was noted. A slight reduction of ester yield, with essentially no change in isomer distribution and little, if any, alteration in the rate of peroxide disappearance occurred. The rate of NBSP decomposition could not be accurately determined due to interference by cupric salts in iodometric titration.[20]

TABLE 1. REACTIONS OF BIS(3-NITROBENZENESULFONYL) PEROXIDE WITH TOLUENE[a]

Salt	Mmole[b]	NBSP[b] mmole	Esters[b] %	Orientation[b]		
				o	*m*	*p*
none	—	0·95	91	27	5	68
none	—	1·01	92	26	7	67
$CuCl_2$	1·07	1·00	74	27	7	66
$CuCl_2$	0·10	0·98	87	27	7	66
$Cu(OAc)_2$[c]	0·10	1·00	85	28	8	65
$CuCl_2$ $CuCl$	0·30 0·32	1·00	54	28	3	69
CuCl	1·04	1·00	15[d]	26	6	68[e]
CuCl	0·60	0·93	40[f]	27	6	67
CuCl	0·30	1·05	69	27	7	66
CuCl	0·15	1·04	81	—	—	—
CuCl	0·10	1·01	81	27	6	69[e]
$CoCl_2$[g]	0·60	1·02	23[h]	29	4	67
$CoCl_2$[g]	0·30	0·99	74	28	7	65
$CoCl_2$[g]	0·10	1·00	79	27	6	66
$FeCl_3$	0·10	1·00	91	28	8	64
Na_2IrCl_6[g]	0·50	1·00	48	28	4	68
Na_2IrCl_6[g]	0·10	1·00	69	27	9	64
$AlCl_3$[i]	4·04	1·00	80	25	7	68
$AlCl_3$[i]	2·04	1·00	52	26	6	68
$AlCl_3$[i, j]	1·06	1·01	22	23	8	68
$AlCl_3$[i]	0·50	1·01	22	24	6	70
none[k]	—	1·01	53[l]	39	6	55
$CuCl_2$[k]	0·11	1·02	54[l]	35	5	60
$AlCl_3$[m]	1·02	1·02	55	31	4	65

[a] Toluene (4 ml, 37·6 mmole), acetonitrile (100 ml), 24 hr, room temp.

[b] Average of two or more runs.

[c] Dihydrate.

[d] 33% yield of copper(II) 3-nitrobenzenesulfonate dihydrate; <2% of benzyl chloride.

[e] One run.

[f] Benzyl chloride (*ca* 5%) and benzaldehyde (*ca* 10%) were detected (glpc with three columns, peak enhancement technique with authentic materials) in a mixture not exhaustively evaporated.

[g] Hexahydrate.

[h] 40% yield of cobalt(II) 3-nitrobenzenesulfonate hexahydrate.

[i] 2 hr, ice bath.

[j] In the absence of toluene, the precipitate was filtered, washed with acetonitrile, and examined spectrally (infrared).

[k] Toluene (100 ml), acetonitrile (50 ml), 80°, 0·5 hr.

[l] Benzyltoluenes (24%), ester : benzyltoluenes = 68 : 32.

[m] No acetonitrile, toluene (50 ml), ice bath, 1 hr.

Nearly all of the initial cupric ion was present at the end. Indeed, in the absence of toluene, little decomposition of sulfonyl peroxide was effected in the presence of cupric chloride. Changing the anion of the salt from chloride to acetate had negligible impact. Since cupric chloride appears to be an efficient oxidant in rearomatization of the *sigma* complex in radical oxygenation,[8] the negative results indicate the absence of such a pathway.

TABLE 2. KINETIC DATA FOR DECOMPOSITION OF BIS(3-NITROBENZENESULFONYL) PEROXIDE WITH COBALTOUS CHLORIDE

[NBSP] 10^2M	[S][a] 10^2M	[T][b] M	10^2k_{obs}[c] min^{-1}	10^6Rate[d] mole l.$^{-1}$ sec^{-1}	$10^6\text{Rate}_{\text{calcd}}$[e] mole l.$^{-1}$ sec^{-1}
1·00	0·0	0·376	1·77 ±0·05	2·93	2·93
0·89	0·10	0	0·48 ±0·09	0·72	0·77
0·95	0·25	0	0·94 ±0·09	1·50	1·28
1·03	0·50	0	1·15 ±0·09	1·98	2·00
0·94	0·75	0	1·38 ±0·05	2·16	2·22
0·95	1·00	0	1·75 ±0·05	2·77	2·58
0·50	1·00	0	1·47 ±0·05	1·22	1·37
1·02	0·10	0·376	2·53 ±0·05	4·31	3·87
0·96	0·10	0·376	2·53 ±0·05	4·05	3·95
0·93	0·25	0·376	2·65 ±0·03	4·11	4·00
0·96	0·50	0·376	3·00 ±0·05	4·80	4·67
0·76	0·50	0·376	2·97 ±0·03	3·76	3·68
0·95	0·75	0·376	3·22 ±0·03	5·10	5·07
0·93	1·00	0·376	3·43 ±0·05	5·22	5·25
0·72	1·00	0·376	3·47 ±0·09	4·16	4·07
0·71	1·25	0·376	3·68 ±0·09	4·35	4·30

[a] [S] = [salt].

[b] [T] = [toluene].

[c] All data exclusive of that with no salt are pseudo-first order rate constants extrapolated to zero time.

[d] The errors (%) in k_{obs} apply to these data also.

[e] Calculated on the basis of $k_1^T = (2{\cdot}93 \pm 0{\cdot}06) \times 10^{-4}$ sec^{-1} and $k_2 = (2{\cdot}72 \pm 0{\cdot}05) \times 10^{-3}$ l$^{1/2}$ mole$^{-1/2}$ sec^{-1} in Eq 9 (see text).

TABLE 3. KINETIC DATA FOR DECOMPOSITION OF BIS(3-NITROBENZENESULFONYL) PEROXIDE WITH SALTS

Salt	[S][a] 10^2M	[NBSP] 10^2M	[T][b] M	10^6Rate mole l.$^{-1}$ sec^{-1}
none	—	1·0	0·376	2·93 ±0·07[c]
$CuCl_2$	0·1	1·0	0	0·3[d]
$CuCl_2$	0·1	1·0	0·376	2·93 ±0·07[c]
CuCl	0·1	1·0	0·376	2·87 ±0·07[c]
$FeCl_3$	0·1	1·0	0·376	2·93 ±0·07[c]
Na_2IrCl_6[e]	0·1	1·0	0	2·4 ±0·1
Na_2IrCl_6[e]	0·1	1·0	0·376	4·27 ±0·11[f]
$AlCl_3$	4·3	1·0	0·376	5·7 ±0·5[g]
$AlCl_3$	2·4	1·0	0·376	52[d]
$AlCl_3$	2·0	1·0	0·376	27[d]
$AlCl_3$	1·2	1·0	0·376	150[d]
$AlCl_3$	0·7	1·0	0·376	140[d]
$AlCl_3$	0·5	1·0	0	180[d]

[a] [S] = [salt].

[b] [T] = [toluene].

[c] Average of two runs.

[d] Estimated.

[e] As the hexahydrate.

[f] After *ca* 15% decomposition, the slope of the first order plot reverts to that with no salt.

[g] Average of three runs; results with $AlCl_3$ were somewhat erratic.

Cuprous chloride. Under the standard conditions, varying the amount of cuprous chloride greatly influenced the yield of ester. The greater the amount of salt, the lower the quantity of principal product. The nearly linear relationship convincingly points to a competing reaction which proceeds at a comparable rate. In addition, the ester orientation was essentially unchanged, as was the rate of decomposition of NBSP. Again, the kinetics comprise an estimate since cuprous is oxidized to cupric which interferes with iodometry.[20] At high CuCl:NBSP ratios, a novel product was isolated as a water-soluble, light-green powder melting above 300°. Elemental analysis and the infrared spectrum indicate that the compound is copper (II) 3-nitrobenzenesulfonate dihydrate. Hydrates of this salt have previously been described.[21a]

Several routes can be visualized to account for the salt product. In one approach, induced decomposition of NBSP by cuprous chloride would give rise to $ArSO_2O\cdot$ and $ArSO_2OCuCl$. The analogous pathway for acyl-type peroxides is well documented.[8, 22] With the appropriate aromatic substrate, acyloxy radicals readily bring about aromatic substitution in the presence of an effective oxidant.[8] In our case there is no evidence of radical attack on the aromatic nucleus. Arylsulfonyloxy radicals may react with $ArSO_2OCuCl$ to give the observed cupric arylsulfonate and chlorine atoms. Alternatively, the mixed salt might dissociate to $Cu(OSO_2Ar)_2$ and cupric chloride. Ligand exchange between the mixed salt and $ArSO_3H$ bears literature analogy.[23] Finally, the induced breakdown of peroxide may proceed *via* a cyclic transition state with formation of the isolated salt and chlorine radicals.

Experimentally, benzyl chloride[8b] and benzaldehyde[8b] were detected, conceivably arising *via* benzyl radicals derived from toluene. Hydrogen abstraction might be effected by $ArSO_2O\cdot$ or chlorine atoms. On the assumption that benzal chloride is formed as an intermediate, about 50% of the chlorine may be accounted for. In reactions carried out at high CuCl:NBSP ratios, only meagre amounts of acidic, chlorine-containing effluent (nitrogen sweep) were detected; no bibenzyl or chlorotoluene was found.

In the presence of a mixture of cupric and cuprous chlorides, the yield of esters is lower than with either of the two salts separately. The reduction in yield is probably due to a summation of the effects of the two halides. These data furnish additional indication that a radical route does not pertain in oxygenation. In any event, the reaction differs drastically from that reported for acyl peroxides.

Cobaltous chloride. In general, the yield and orientation data with cobaltous chloride conform to those observed with cuprous chloride. The greater the amount of added salt, the lower the yield of ester; the orientation showed little deviation from that previously discussed. An additional product was also isolated from these reactions, in best yield at high $CoCl_2$:NBSP ratios, in the form of a water-soluble, pink-tinged solid of high m.p. (> 300°). Formulation of this substance as cobalt(II) 3-nitrobenzenesulfonate hexahydrate is supported by elemental analysis and an infrared spectrum similar to that of the copper(II) analog. We cannot be certain, as in the cuprous case, of its exact origin, nor do we know if cobalt(III) is involved. Similar salts of sulfonic acids are known, such as cobalt(II) benzenesulfonate hexahydrate.[21b]

Other salts. The influence of sodium hexachloroiridate(IV) hexahydrate and ferric chloride on the reaction course was also tested. In the case of the iridium compound, the greater the salt:NBSP ratio, the lower the yield of ester. At low salt:NBSP ratios, the rate of peroxide decomposition in the presence of toluene is fast until the colour change is complete, which occurs after *ca* 15% decomposition at 0·1 : 1 ratio. Thereafter, pseudo-first order kinetics pertain as in the case of the uncatalyzed reaction. The difference in initial rates in the presence and absence of toluene indicates that an independent reaction between salt and peroxide is causing the rate enhancement. We did not observe the separation of a salt product, although one is presumably present in solution.

With ferric chloride, no difference from the uncatalyzed reaction was detected. The yield of ester product was the same, and the rate of peroxide decomposition was unchanged.

Kinetic studies

A kinetic investigation was undertaken to ascertain whether or not a catalytic term is applicable to the rate equation for oxygenation. For this purpose the cobalt chloride system proved most amenable. A general rate equation (Eq 1), where [P] = [NBSP], [S] = [salt], [T] = toluene, $k_1^T = k_1[T]$, and $k_3^T = k_3[T]$, includes terms for the uncatalyzed reaction, the competing process, and catalysis of aromatic oxygenation. In

$$-d[P]/dt = k_1^T[P] + k_2[P]^x[S]^y + k_3^T[P]^w[S]^z \tag{1}$$

the absence of salt, Eq 1 reduces to Eq 2, describing a pseudo-first order reaction with k_1^T found to be $2\cdot93 \times 10^{-4}\ \text{sec}^{-1}$.

$$-d[P]/dt = k_1^T[P] \tag{2}$$

Two other types of conditions were employed. One set focused on the competing reaction, i.e., cobaltous chloride with peroxide in the absence of toluene at varying salt concentrations. Eliminating toluene dependent terms, one can then reduce the

$$-d[P]/dt = k_2[P]^x[S]^y \tag{3}$$

general rate expression (Eq 1) to Eq 3. The extrapolated rates to zero time (Table 2) fit Eq 4, where $k_2 = (2\cdot75 \pm 0\cdot21) \times 10^{-3}\ \text{mole}^{1/2}\ \text{l.}^{-1/2}\ \text{sec}^{-1}$.

$$-d[P]/dt = k_2[P][S]^{1/2} \tag{4}$$

The second category was directed toward a rate study in the presence of both salt and toluene. If no catalytic term is involved, the initial rates for these reactions should be given by an equation that includes the sum of the two terms in Eqs 2 and 4, giving

$$-d[P]/dt = k_1^T[P] + k_2[P][S]^{1/2} \tag{5}$$

Eq 5. The results are in accord with Eq 5 where $k_1^T = 2\cdot93 \times 10^{-4}\ \text{sec}^{-1}$ (± 8%) and $k_2 = 2\cdot68 \times 10^{-3}\ \text{mole}^{1/2}\ \text{l.}^{-1/2}\ \text{sec}^{-1}$ (± 4%).

Since the values for k_1^T and k_2 are in good agreement from the independent data sets, and the calculated initial rates agree with those determined by experiment (Table 2), we feel that no catalysis is in evidence for oxygenation, and that a completely independent competing reaction is involved. Although the origin of the half-power exponent in the rate expression (Eq 5) is not clear, it may be due to reversible association of cobaltous chloride with acetonitrile. Equilibration entailing various cobaltous-acetonitrile complexes has been shown with anhydrous cobaltous chloride.[24]

Aluminium chloride catalyst. The reactions with aluminium chloride were carried out to determine the effect on oxygenation of a strong Friedel–Crafts catalyst. At low aluminium chloride concentrations ($AlCl_3$:NBSP ≅ 0·5:1) the rate of peroxide decomposition was rapid, about 35 times that in the absence of salt, yet the yield of esters was only 22%. By altering the ratio to *ca* 1:1, the sulfonate yield remained low and the rate of decomposition of NBSP was again rapid. The reaction could not be interpreted in terms of simple first or second order kinetics. Increasing the ratio to about 2:1 afforded a 52% yield of esters and a decomposition rate only *ca* five times that of the uncatalyzed reaction. At $AlCl_3$:NBSP ≅ 4:1, the yield of esters was increased to 80% and the rate of decomposition (pseudo-first order) was still enhanced (double that of the reference reaction).

A possible explanation of these results takes into consideration the number of sites in the peroxide available for coordination. Apparently, formation of a symmetrical complex is necessary for catalysis by aluminium chloride in oxygenation. The results with less than four equivalents of Lewis acid suggest that a very fast, competing, degradative process involving aluminium chloride and NBSP is taking place. This view is supported by isolation of an acetonitrile-insoluble, salt-like product (not fully characterized) in the absence of toluene, whose infrared spectrum resembled those of the analogous cobalt and copper salts. Equilibrium association of catalyst with solvent is most likely occurring also.[25]

The detailed aspects of the competing pathway and the nature of the complexes remain to be elucidated. Promotion by Lewis acid with little change in ester orientation strongly suggests an ionic mechanism for the catalyzed and uncatalyzed reactions. Specificity in Lewis acid catalysis is demonstrated by the lack of rate enhancement on addition of arylsulfonic acid.[6]

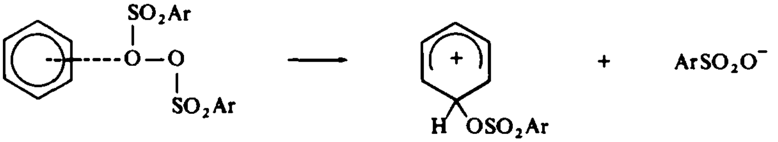
Temperature effects

Having reached the conclusion that aromatic oxygenation under standard conditions is most likely ionic in nature, we attempted to induce a radical reaction by thermal means. Trials, carried out at 80°, led to a novel product in addition to the one usually obtained. Sulfonate ester of somewhat different orientation was isolated in 54% yield. In all the high temperature reactions an increase in the proportion of *ortho* ester was noted. We regard this as a thermal effect, i.e., a reduction in selectivity under more energetic conditions.

Preparative gas chromatography furnished hydrocarbon material which was shown by spectral and gas chromatographic analyses to be a mixture of benzyltoluenes by comparison with an authentic mixture. The evidence revealed that little, if any, bibenzyl was present. The ester:hydrocarbon molar ratio was 68:32, with a hydrocarbon yield of 24%. Dannley and Corbett reported[4] a minor, unidentified byproduct which may well be the same hydrocarbon mixture. The benzyltoluenes can be considered to arise in an ionic fashion. The initial step would consist of hydride abstraction by onium type oxygen to give a benzyl cation and the sulfonic acid, followed by electrophilic aromatic substitution by the carbonium ion on another molecule of toluene. Proposals that hydride abstraction by positive oxygen can occur have been made.[26] A slightly modified route might involve the formation of benzyl 3-nitrobenzenesulfonate. This type of ester has been shown to undergo thermal decomposition in the presence of toluene to give benzyltoluenes.[27] Addition of cupric chloride caused no significant change in the proportion of the two products. Participation of benzyl radicals[8] seems unlikely, since little, or none, of the expected products, bibenzyl and benzyl chloride, was found (a speculative possibility would comprise induced decomposition of peroxide by benzyl radicals).

Mechanistic considerations

The results of our study confirm the earlier hypothesis that the reaction of bisarylsulfonyl peroxides with aromatic compounds proceeds by an ionic substitution pathway.[4–6] This is particularly significant when one considers that these peroxides are efficient initiators of radical polymerization,[9, 10] and that various attempts to force homolytic subsfitution ended in failure. These findings imply, in effect, that nucleophilic attack (Eq 6) of the aromatic on the peroxide must be the important step and that fast initial homolysis or heterolysis is unlikely.



(6)

Viewing the oxygenation procedure in this manner has precedent in earlier work. Benzoyl peroxide has been shown to undergo nucleophilic displacement quite readily by triphenylphosphine at the oxygen–oxygen bond.[28] Similar reactions with phenolic and amine substrates are reasonably interpreted as polar processes,[29] rather than homolytic.[30] Under certain conditions aromatic compounds can act as nucleophiles, *viz*, catalysis by Lewis acids, appropriate substitution in the benzoyl peroxide,[18b, d] and enhanced basicity associated with the aromatic substrate.[18d] This reaction, competing with peroxide rearrangement,[18b] has been suggested to occur by way of ionic[18d] or radical-cation species.[18b] Aromatic substitutions which might conceivably proceed by a radical-cation mechanism are usually characterized by the presence of biphenyl type products[18b, 31a, b] and ESR signals,[31b, c] which have not been observed with sulfonyl peroxides. The addition of bisarylsulfonyl peroxides to styrene and *trans*-stilbene has been reported.[32] The faster decomposition of peroxide in the presence of styrene,[9] and the formation of addition products can be rationalized either by the nucleophilic character of the alkene or by a radical sequence. The possibility of mixed homolytic/heterolytic breakdown has been suggested.[9, 33]

The ease of the proposed nucleophilic reaction requires further discussion. A first consideration is comparison of the ground states of aroyl and arylsulfonyl peroxides. Since the sulfonyl group appears to be more electronegative than the carbonyl functionality, the peroxidic oxygens of sulfonyl peroxides are expected to possess a lower electron density than those of acyl peroxides. Hence, nucleophilic attack should be more likely in the present case. A favourable driving force is release of a very stable leaving group, the sulfonyloxy anion. An S_N2 type displacement on the peroxidic linkage need not require a large buildup of onium character. Although positive charge would be destabilized inductively in both the carbon and sulfur cases, resonance delocalization by sulfonyl would probably be better than for carbonyl. Aluminium chloride catalysis apparently results in further decrease of electron density associated with the oxygen–oxygen region, thus nicely accounting for the observed increase in rate.

When isotopic studies were carried out with benzoyl peroxide–*carbonyl*-^{18}O and reagents which are alleged to effect nucleophilic displacement on peroxide oxygen, positional integrity of the label was maintained to the extent of 87–100%.[28, 29] In aromatic oxygenation by sulfonyl peroxide containing ^{18}O in the sulfonyl groups, 39% of the label appeared in the phenolic oxygen, indicating that 61% of the reaction occurred by direct attack at peroxide oxygen.[34] The minor route was ascribed to S_N2' mode of displacement, with possible scrambling in ion pair intermediates as a less likely possibility.

The general mechanistic proposal accounts quite satisfactorily for the results from the present work, as well as from related prior investigations, such as the *rho* value and second order kinetics. Although alternative interpretations can be advanced for certain of the individual experiments, the overall data are best correlated by the present approach.

EXPERIMENTAL

Materials. 3-Nitrobenzenesulfonyl chloride (Eastman) was recrystallized from CCl_4, m.p. 62–63°. Naphthalene (Mallinckrodt, purified), acetonitrile (Mallinckrodt, Nanograde), and toluene (Mallinckrodt, AR) were used as obtained. THF was dried at reflux over calcium hydride and used freshly distilled. 2-, 3-, and 4-Methylphenyl 3-nitrobenzenesulfonates, prepared by the method of Dannley and Corbett,[4] were characterized by melting point and NMR spectrum. Bis(3-nitrobenzenesulfonyl) peroxide was obtained by a previously described procedure[4] modified[5] by the use of a Waring blendor to mix the reagents. Material prepared in this fashion assayed 95–98% pure by iodometric titration.[35] Although reported to be stable,[4] the peroxide exploded on one occasion at room temp. The inorganic salts were commercial materials used without further purification.

General procedure

Low temperature. Bis(3-nitrobenzenesulfonyl) peroxide (*ca* 1 mmole) was added to a soln of acetonitrile (100 ml) and toluene (4 ml, 37·6 mmole) containing a salt in most cases. The resulting soln was stirred for the length of time specified. In all runs, except those with $AlCl_3$ (ice bath temp), the procedures were carried out at room temp. In certain experiments with cuprous chloride and cobaltous chloride, a ppt was noticed, which was filtered in a few instances (*vide infra*) before evaporation. The reaction mixture was concentrated to *ca* 20 ml under reduced press, ether (90 ml) was added, and the resulting mixture was extracted with water (three 20-ml portions). The ethereal soln was dried (Na_2SO_4), filtered, evaporated, and the residue was dried in a vacuum desiccator overnight. The weight of the product is reported as the crude yield of esters. Although various columns were tested, the isomeric esters could not be separated by GLPC. The analyses showed less than 3% impurity. Attempts at isolation of the minor products were unsuccessful.

High temperature. A soln of peroxide (1 mmole) in acetonitrile (50 ml) was added to stirred toluene (100 ml) at 85° over a period of 15 min during which time the temp fell to 80° (Table 1). After an additional 15 min at reflux, the mixture was cooled. A colourless crystalline material separated, presumably 3-nitrobenzenesulfonic acid which has been reported as a reaction product.[4] The mixture was evaporated to *ca* 20 ml under reduced press, diluted with ether (50 ml), washed with water (three 20-ml portions), dried (Na_2SO_4) and freed of solvent. The product, after standing in a vacuum desiccator overnight, was in the form of a semisolid, *ca* 0·26 g. Gas chromatography revealed the existence of a more volatile product, not observed at low temps, in addition to ester. Preparative GLPC indicated a mixture whose IR spectrum suggested the presence of isomeric benzyltoluenes containing little or no bibenzyl. In particular, the bibenzyl peak at $\sim 11{\cdot}1\mu$ was absent. The NMR and IR spectra were indistinguishable in peak positions from those of an authentic mixture synthesized by a known method.[36] In addition, GLPC on mixtures of the hydrocarbon fraction with authentic benzyltoluenes [200 ft by 0·01 in capillary (SE-30), 160°] showed no additional peaks. In one hydrocarbon mixture an extra, small peak was observed that could possibly be due to bibenzyl. It was obscured when GLPC of mixtures with bibenzyl, that displayed an additional peak, were carried out. Both the NMR and GLPC data provide evidence of a slightly different isomer distribution for our benzyltoluenes than is obtained from the toluene-benzyl chloride-aluminium chloride-nitromethane system at 25°.[36] The mole ratio of esters : hydrocarbon was 68 : 32 as determined by GLPC comparison with authentic mixtures. This ratio was independent of the presence of cupric chloride (0·1 mmole) during reaction.

Salt products. With cuprous chloride and cobaltous chloride at high salt concentration, solid products precipitated during the course of the reaction. These water-soluble substances, purified by washing with acetonitrile, did not melt below 300°. The IR spectra of the products showed λ_{max}(KBr) 6·24 (arom unsat),[37a] 6·57, 7·13 (NO_2),[37b] 8·42, 9·68, 15·1 (RSO_3^-),[37c] together with bands (~11·3 and ~12·4μ) indicative of *meta* substitution.[37a] The cobalt salt showed a stronger water band than did the copper analog. (Found: C, 28·78; H, 2·28; Cl, none or trace; Cu, 12·39; N, 5·49; O, 38·29; S, 12·74. Calc for $C_{12}H_8CuN_2O_{10}S_2 \cdot 2H_2O$: C, 28·59; H, 2·40; Cl, 0·00; Cu, 12·61; N, 5·56; O, 37·91; S, 12·72%; (Found: C, 25·46; H, 3·54; Cl, none or trace; Co, 10·33; N, 4·95; S, 11·31. Calc for $C_{12}H_8CoN_2O_{10}S_2 \cdot 6H_2O$: C, 25·20; H, 3·53; Cl, 0·00; Co, 10·31; N, 4·90; S, 11·22%).

Isomer distributions. Orientation of tolyl 3-nitrobenzenesulfonates was determined by conversion of the esters to cresols, followed by GLPC analysis. To obtain the cresols, 10–25 ml of the reagent, prepared by dissolving Na (0·7 g) in a soln of naphthalene (3·9 g) in dry THF (100 ml) under N_2 (stirred overnight), was added to a soln of the crude ester in dry THF (5–10 ml). After *ca* 3 hr the mixture was treated with water (1–3 ml), diluted with ether (50 ml), and extracted with 10% NaOH (three 20-ml portions). The basic soln was extracted with ether (two 50-ml portions) and acidified with conc HCl. The cresols were taken up in ether (three 20-ml portions), the ethereal soln was dried (Na_2SO_4), and then concentrated. GLPC analysis was carried out on a 15 ft by 0·25 in column, 10% Bentone 34 and 15% SF-96 on acid-washed Chromosorb W (45/60 mesh), 200°, flow rate: 60 ml/min He, bromobenzene as internal standard. The method was calibrated by transforming known mixtures of the esters to cresols; conversion to cresols was *ortho*, 85 ±3%; *meta*, 99 ±1%, *para*, 93 ±3%. The greatest error is in the data for the *meta* isomer due to the small areas present in the GLPC spectra. As a minimum, three traces were used for each analysis. Reactions were run in triplicate in most cases; two of the reaction mixtures were converted to cresols, whereas the third was used for GLPC analysis of the crude reaction mixture.

Rate studies. A soln of the salt (Tables 2 and 3) and toluene (4 ml) in acetonitrile (36 ml, 40 ml in runs with no toluene) at 1·0–1·5° was added to a soln of bis(3-nitrobenzenesulfonlyl) peroxide (generally *ca* 1 mmole) in acetonitrile (60 ml) at 1·0–1·5°. The resulting soln was stirred rapidly and left in an ice bath. At intervals, 5 ml aliquots were removed and added to a mixture of glacial AcOH (5 ml) and 10% NaI (5 ml). The liberated I_2 was titrated with 0·01N $Na_2S_2O_3$. In some cases blanks were necessary. In the absence of salt, the kinetic plot showed good first order dependence. When salts were present, deviations from first order were apparent. Where these deviations occurred with low salt concentrations, the plot became first order after reaction with the salt was complete. In all experiments with salt, the initial rates were estimated by extrapolation to zero time. The rates were also followed in the absence of toluene. At 0°, little decomposition of peroxide in acetonitrile was observed, *ca* 1% over the time interval (60–90 min, 2 half lives) usually followed. At low salt concentrations (no toluene) estimates of the initial rates are crude since the reaction stops after a relatively small amount of peroxide has undergone induced decomposition. In particular, this applies to $CoCl_2$:NBSP = 0·1:1 and 0·25:1.

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