Mechanism of the Reaction of $^3SO_2$ with Alkanes

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The aerosol formed in the photo-initiated reaction between butane (or 2-methylpropane) and sulphur dioxide has been treated with chlorine and the resultant products analysed. The products of the reaction between methyl radicals and sulphur dioxide have also been investigated. These studies show that the principal primary products of the photochemical reaction of sulphur dioxide with alkanes are sulphinic acids RSO_2H together with small yields of the disulphones $(RSO_2)_2$. On the addition of a solvent the sulphinic acids rearrange very quickly to a variety of secondary products. The sulphinic acids are formed in a non-chain radical sequence initiated by $^3SO_2$ which abstracts hydrogen from the alkanes to form an alkyl radical and $HSO_2\cdot$ (at 20 °C the primary : secondary : tertiary selectivity is 1 : 4 : 27). The resulting alkyl radical adds reversibly to ground state SO_2 and the sulphonyl radical $RSO_2\cdot$ radical either abstracts hydrogen from $HSO_2\cdot$ or combines with another sulphonyl radical.

THE photochemically initiated reaction between sulphur dioxide and alkanes was first investigated in detail by Dainton and Ivin.[1] These authors found an aerosol mist was formed and they showed that the products included sulphinic acids and that the quantum yield was appreciably less than unity. Subsequently other authors found further products and questioned Dainton and Ivin's conclusions that sulphinic acids were the main products.[2,3] These later authors also made further studies of the photochemical process and then in 1971 Calvert and his co-workers completed an exhaustive study of the primary photochemical process.[4] Their reaction mechanism can be summarised as in reactions (1)—(16).

The question of the chemical constitution of the final products remained unresolved. Dainton and Ivin established a reactant stoicheiometry (1 : 1 SO_2 : RH) when the alkane RH was in excess. Timmons found that when SO_2 was in excess, the reactant stoicheio-

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[1] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, 1950, **46**, 374, 382.

[2] R. B. Timmons, *Photochem. Photobiol.*, 1970, **12**, 219.

[3] H. S. Johnston and K. Dev Jain, *Science*, 1960, **12**, 1523.

[4] H. W. Sidebottom, C. C. Badcock, J. G. Calvert, G. W. Reinhardt, G. W. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, 1971, **93**, 2587 and previous papers in the series.

metry changed, more SO_2 being consumed than RH, and a variety of products was formed in addition to the sulphinic acids.[2] As Calvert and his co-workers comment however, Timmons' results in no way preclude the original suggestion of Dainton and Ivin that the primary products are the alkylsulphinic acids.

$$SO_2 + h\nu \xrightarrow{<320\ \mathrm{nm}} {}^1SO_2 \tag{1}$$

$$SO_2 + h\nu \xrightarrow{339\text{–}388\ \mathrm{nm}} {}^3SO_2 \tag{2}$$

$$^1SO_2 + SO_2 \longrightarrow 2SO_2 \tag{3}$$

$$\longrightarrow {}^3SO_2 + SO_2 \tag{4}$$

$$^1SO_2 + RH \longrightarrow SO_2 + RH \tag{5}$$

$$\longrightarrow {}^3SO_2 + RH \tag{6}$$

$$^1SO_2 \longrightarrow SO_2 + h\nu\ (\mathrm{f}) \tag{7}$$

$$\longrightarrow {}^3SO_2 \tag{8}$$

$$\longrightarrow SO_2 \tag{9}$$

$$^3SO_2 + RH \longrightarrow SO_2 + RH \tag{10}$$

$$\longrightarrow RSO_2H \tag{11}$$

$$\longrightarrow R\cdot + HSO_2\cdot \tag{12}$$

$$^3SO_2 \longrightarrow SO_2 + h\nu\ (\mathrm{p}) \tag{13}$$

$$\longrightarrow SO_2 \tag{14}$$

$$^3SO_2 + SO_2 \longrightarrow SO_3 + SO \tag{15}$$

$$\longrightarrow 2SO_2 \tag{16}$$

More recently Penzhorn and his co-workers re-investigated the reaction and made a very important advance.[5] They added an ether solution of diazomethane to the products. Diazomethane reacted with the acidic substances formed in the photolysis (especially the sulphinic acids) and these could then be analysed as relatively stable methyl esters. Previously the unstable nature of sulphinic acids had made it impossible to analyse the products satisfactorily, and this was the first study in which products were clearly identified. The major products observed by Penzhorn and his co-workers were sulphinic acids RSO_2H, sulphonic acids RSO_3H, and *S*-alkyl thiosulphonates RSO_2SR. They also observed small amounts of R_2S, RSO_2R, RSH, $(RSO_2)_2$, and RSSR.

Two problems remain unresolved. The first is to decide whether the wide variety of products are formed in the initial photochemical process or whether they are artefacts formed by rearrangement of sulphinic acids. The second problem is the mechanism of the reaction. Three mechanisms for the production of sulphinic acids have been suggested [reactions (17)—(23)].

(*a*) Direct insertion (*cf.* carbenes).

$$RH + {}^3SO_2 \longrightarrow RSO_2H \tag{17}$$

(*b*) Radical chain.

$$RH + {}^3SO_2 \longrightarrow R\cdot + SO_2H \tag{18}$$

$$R\cdot + SO_2 \rightleftharpoons RSO^{\cdot}_2 \tag{19}$$

$$RSO_2\cdot + RH \longrightarrow RSO_2H + R\cdot \tag{20}$$

(*c*) Radical non-chain.

$$RH + {}^3SO_2 \longrightarrow R\cdot + \dot{S}O_2H \tag{21}$$

$$R\cdot + SO_2 \rightleftharpoons RSO_2\cdot \tag{22}$$

$$RSO_2\cdot + \dot{S}O_2H \longrightarrow RSO_2H + SO_2 \tag{23}$$

The present study attempted to answer these two questions.

EXPERIMENTAL AND RESULTS

(a) *Photochemical Reactions of Sulphur Dioxide with n-Butane and 2-Methylpropane.*—The experiments were performed in a conventional vacuum line, using a Pyrex reaction vessel and the light source was a Hanovia U.V.S. 200 W lamp with a Pyrex filter. Sulphur dioxide (B.D.H.) was distilled off phosphorus pentaoxide to remove water, and chlorine (I.C.I.) was trap-to-trap distilled. The hydrocarbons n-butane and 2-methylpropane were Philips Research grade. Butanesulphonyl chloride was obtained commercially (Kodak), 1-methylpropane sulphonyl chloride was synthesised by the method of Truce *et al.* ($RBr \longrightarrow RSO_3Na \longrightarrow RSO_2Cl$),[6] bis-1-methylpropyl sulphone was synthesised by the method of Gilman and Beber ($R_2S \longrightarrow R_2SO_2$),[7] and bis-1-methylpropyl disulphone was synthesised by the method of Allen *et al.* ($RBr + Mg \xrightarrow{SO_2} RSO_2H \xrightarrow{H_2O_2} RSO_2SO_2R$).[8]

Sulphur dioxide and butane were irradiated for the required period and the aerosol then allowed to settle before unchanged butane and sulphur dioxide were pumped off. The products were treated in two different ways: (a) degassed carbon tetrachloride was distilled into the reaction vessel and (b) gaseous chlorine (Cl_2 concentration approximately equal to original SO_2 concentration) was added in the dark and after 5 min unchanged chlorine was pumped off, and carbon tetrachloride distilled into the vessel in its place.

The solutions prepared by these two processes were analysed by mass spectrometry and n.m.r. and i.r. spectroscopy. The major ions obtained from the mass spectra of the photochemical experiments are compared with the cracking patterns obtained from butanesulphonyl chloride, 1-methylpropane sulphonyl chloride, and bis-1-methylpropyl disulphone (Table 1). No parent ions were obtained from either sulphonyl chlorides, but bis-1-methylpropyl disulphone gave the parent ion which was also present in both the photochemical products. The identity of these ions was confirmed by high resolution spectra (see Table 1). The only other notable feature of the mass spectra results

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[5] R. D. Penzhorn, W. G. Filby, K. Günther, and L. Stieglitz, *Internat. J. Chem. Kinetics Symp.*, 1975, **1**, 611.

[6] W. E. Truce, R. W. Campbell, and G. D. Madding, *J. Org. Chem.*, 1967, **32**, 308.

[7] H. Gilman and N. J. Beber, *J. Amer. Chem. Soc.*, 1925, **47**, 1450.

[8] P. Allen, C. S. Krager, J. D. Haygood, and J. Sheuse, *J. Org. Chem.*, 1962, **27**, 93.

is that the cracking pattern of 1-methylpropanesulphonyl chloride resembles that of the chlorine treated product.

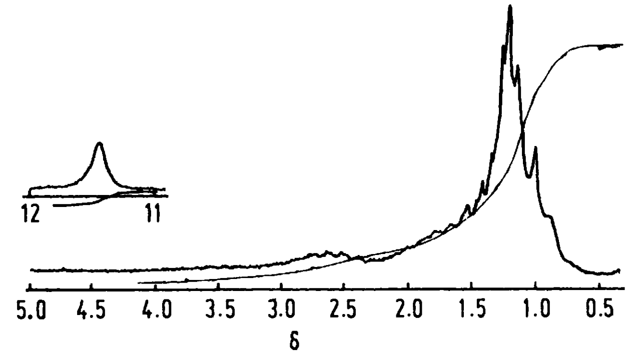


FIGURE 1 N.m.r. spectrum of unstabilised photochemical product of reaction of n-butane and sulphur dioxide dissolved in carbon tetrachloride

The i.r. spectra provided relatively little new information beyond confirming that both the chlorine-treated and the untreated products contained sulphonyl groups.

Figure 1 shows the n.m.r. spectrum of the unstabilised photochemical product dissolved in carbon tetrachloride. The spectrum shows a strongly acidic proton at δ 11.5 but the remainder of the spectrum shows no distinct bands, and in fact is characteristic of the spectra of complex mixtures containing a large number of fairly similar compounds. Figure 2 shows the n.m.r. spectra of the chlorine stabilised photochemical product, of butanesulphonyl chloride, and of 1-methylpropanesulphonyl chloride. The spectra of bis-1-methylpropyl disulphone in carbon tetrachloride and the chlorine treated product from the photochemical reaction with 2-methylpropane were also observed.

A referee has suggested that the apparent concentration of bis-1-methylpropyl disulphone in the chlorine stabilised product is so large that it should appear more clearly in the n.m.r. spectrum of the non-stabilised product if it is all a primary product. He has therefore suggested that some of the disulphone may be an artefact formed in the chlorination [$2RSO_2H + Cl \longrightarrow (RSO_2)_2 + 2HCl$ possibly in two steps].

The proportions of the two sulphonyl chlorides present in the chlorine treated product from reaction with n-butane were obtained by comparison of the n.m.r. spectrum of the treated products with those of mixtures of the pure sulphonyl chlorides of known concentration. The proportions of 1,1-dimethylethane- and 2-methylpropane-sulphonyl chlorides present in the chlorine stabilised product from 2-methylpropane was obtained directly from the n.m.r. spectrum of the product by comparing the integral for the singlet (from the 1,1-dimethylethane compound) with the triplet (from the 2-methylpropane compound).

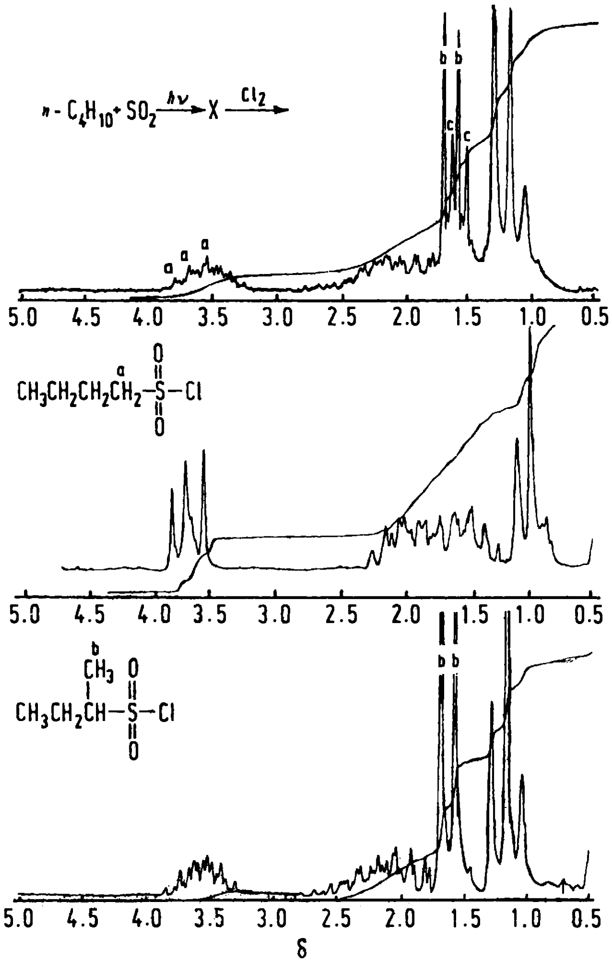


FIGURE 2 N.m.r. spectra of the chlorine stabilised product of reaction of n-butane and sulphur dioxide, of butanesulphonyl chloride, and of 1-methylpropanesulphonyl chloride

(b) *Interaction of Methyl Radicals with Sulphur Dioxide.*—Acetyl peroxide was synthesised by the method of Price

TABLE 1

Principal ions in mass spectra

Ion	*m/e*	% Of base peak Untreated product	Chlorine stabilised product	Butane-sulphonyl chloride	1-Methylpropane-sulphonyl chloride	Bis-1-methyl-propyl disulphone
$C_4H_9^+$	57	100	100	50	100	100
SO_2^+	64	50	40	20	27	90
$C_4H_9S^+$	89	6	5		5	3
$C_4H_9SH^+$	90	13	10		7	5
$C_4H_{10}SO_2^+$	122	17 *	5			3
$C_4H_{11}SO_2^+$	123	5	5			3
$(C_4H_9)_2SO^+$	178	1	1			1
$(C_4H_9SO)_2^+$	210	1 *	1			1
$(C_4H_9SO_2)_2^+$	242	1 *	1			1

* Found: *m/e* 242.061 679. $(C_4H_9SO_2)_2$ requires *M*, 242.064 630. Found: *m/e*, 210.075 862. $(C_4H_9SO)_2$ requires *M*, 210.074 822. Found: *m/e*, 122.025 354. $C_4H_{10}SO_2$ requires *M*, 122.040 147.

and Morita. Dimethyl sulphone was prepared by the oxidation of dimethyl sulphoxide with acidic hydrogen peroxide.

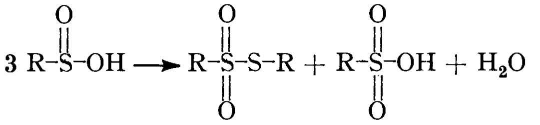
The experiments were performed in a conventional vacuum line. Sulphur dioxide and acetyl peroxide were condensed into the reaction vessel at known pressures and a pre-heated oven (95 °C) was then rapidly lifted round the vessel. After 1 h the gaseous products were distilled into a cold trap, before a solvent was added. The products included the expected decomposition products of acetyl peroxide including carbon dioxide, methane and ethane, but g.l.c. showed three products not attributable to the peroxide. Mass spectra showed these to be CH_3SSCH_3, $CH_3SO_2CH_3$, and $CH_3SO_2SCH_3$ by comparison with synthetic compounds and published spectra. In addition evaporation of the solvent left a solid, m.p. 157—161 °C (lit.,[9] for dimethyl disulphone, 167 °C) [Found: *m/e*, 157.971 40. Calc. for $C_2H_6O_4S_2$: *M*, 157.971 60], δ 3.6.

Examination of the mass and n.m.r. spectra of the product obtained from the solvent showed that from a reaction in which acetyl peroxide (14 mmHg) was treated with sulphur dioxide (6 mmHg) the principal products were dimethyl disulphone and dimethyl sulphone in the ratio 1.2 . 1. The other products are minor and their origin is uncertain.

Photolyses were carried out in which 2-methylpropane was added to the mixture of acetyl peroxide and sulphur dioxide. No evidence could be found for any attack on 2-methylpropane either by methyl radicals or methane sulphonyl radicals.

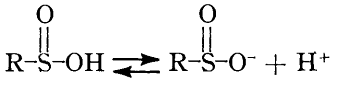
Bis-1-methylpropyl disulphone was recovered unchanged after treatment with a solution of chlorine in carbon tetrachloride in the dark.

DISCUSSION

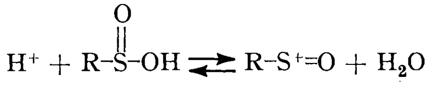


$$3\,\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \longrightarrow \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}S{-}R} + \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH} + H_2O \qquad (24)$$

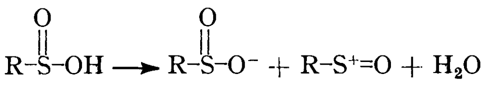
The great problem in studying the photochemical reaction between sulphur dioxide and alkanes has been the nature of the products. If the primary products are indeed sulphinic acids, it is well established that these are unstable substances which disproportionate [reaction (24)]. The mechanism of this reaction has been the subject of some speculation and one proposed scheme is as shown in reactions (25)—(29).[10] If this mechanism is correct it could go a long way to explaining the wide variety of products observed by Timmons and others.[2] The first attempt to avoid this difficulty by a chemical approach was that of Penzhorn and his co-workers, who treated their initial product with an ether solution of diazomethane [reaction (30)].[5]



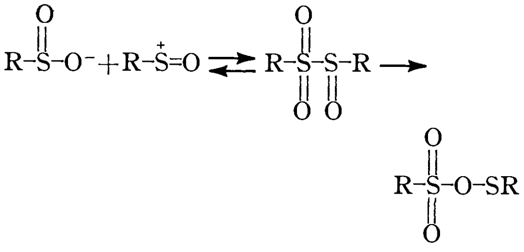
$$\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \rightleftharpoons \mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}O^-} + H^+ \qquad (25)$$



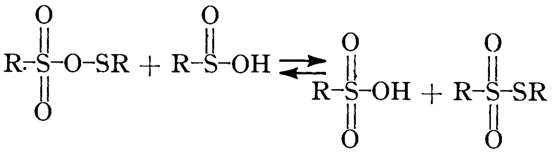
$$H^+ + \mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \rightleftharpoons \mathrm{R{-}S^+{=}O} + H_2O \qquad (26)$$



$$\textit{i.e.}\ 2\,\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}O^-} + \mathrm{R{-}S^+{=}O} + H_2O \qquad (27)$$



$$\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}O^-} + \mathrm{R{-}\overset{+}{S}{=}O} \rightleftharpoons \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}\underset{\underset{O}{\|}}{S}{-}R} \longrightarrow \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}SR} \qquad (28)$$



$$\mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}O{-}SR} + \mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \rightleftharpoons \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH} + \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}SR} \qquad (29)$$

$$RSO_2H + CH_2N_2 \longrightarrow RSO_2CH_3 + N_2 \qquad (30)$$

These workers found sulphinic acid esters but they also found sulphonic acid esters and a host of other products including RSO_2R, RSH, $(RSO_2)_2$, and $(RS)_2$. It remains uncertain whether these other products are formed in the photochemical reaction or whether they are formed by rearrangement of the initially formed sulphinic acids, either as the aerosol condenses or in the ether solution before they react with the diazomethane. We have sought to repeat Penzhorn's work but using a different method of stabilizing the initial product. We have simply added gaseous chlorine because sulphinic acids are known to react very rapidly to yield the relatively stable sulphonyl chlorides [reaction (31)].

$$RSO_2H + Cl_2 \longrightarrow RSO_2Cl + HCl \qquad (31)$$

Figure 1 shows the n.m.r. spectrum of the products from photochemical reaction of sulphur dioxide with n-butane which were collected by condensing carbon tetrachloride into the reaction vessel and washing out the products. It is clear that even this mild treatment yields a very complex mixture of products. However the first spectrum of Figure 2 shows the n.m.r. spectrum of similar products which have been treated with gaseous chlorine before the solvent was added. The first feature of this spectrum is the absence of any acidic proton. Although molecular chlorine reacts rapidly with sulphinic acids it does not react with the acid proton of a sulphonic acid, so no sulphonic acids are present in the initial product. The spectrum can be interpreted as the mixture of three compounds, 1-methylpropanesulphonyl chloride, butanesulphonyl chloride, and bis-1-methylpropyl disulphone. The triplet a, δ 3.38 (*J* 7 Hz) is due to the protons on carbon atom 1 in butanesulphonyl chloride. The strong doublet b, δ 1.58 (*J* 6.5 Hz), is due to the 1-methyl protons in 1-methylpropanesulphonyl chloride.

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[9] H. J. Backer, *Rec. Trav. chim.*, 1950, **69**, 1127; E. Block, M. D. Bently, F. A. Davis, I. B. Douglas, and J. A. Lacadie, *J. Org. Chem.*, 1975, **40**, 2770.

[10] J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, 1964, **84**, 605.

The weak doublet c, δ 1.51 (*J* 6.5 Hz), is due to the 1- and 1′-methyl protons in bis-1-methylpropyl disulphone. The terminal methyl group in 1-methylpropanesulphonyl chloride and bis-1-methylpropyl disulphone both absorb exactly at the same point, δ 1.14 (3 H, t, *J* 6.5 Hz).

The terminal methyl groups of all three compounds absorb in the same region, so that in order to determine the relative proportion of attack at the primary and secondary positions a series of known mixtures of the two sulphonyl chlorides were prepared and the ratio of the integrals for doublets in the δ 1.6 region and triplets in the δ 1.1 region was determined. The ratio of the peaks in the corresponding regions in the n.m.r. spectrum of the chlorine stabilised photochemical product was also obtained. The integral due to the doublet δ 1.51 was added to that of the doublet at δ 1.58 since both absorptions represented attack at the secondary position. The relative rates of attack at the primary and tertiary positions in 2-methylpropane by $^3SO_2$ were deduced from the n.m.r. spectrum of the chlorine stabilised product, by comparing the ratio of the singlet, δ 1.65 (9H) with the doublet, δ 3.58 (2H). The reactivity of the primary hydrogen atoms in 2-methylpropane will not be identical to those in n-butane, but there is ample evidence that the difference in their reactivity will be small. The precision of these ratios is not very great, but the agreement with other workers is within the possible experimental error. The data for t-butoxyl radicals is included in Table 2 because if the photochemical reaction with sulphur dioxide involves hydrogen abstraction by the triplet ($^3SO_2$), the transition state will resemble that of hydrogen abstraction by an alkoxyl radical since the unpaired spin is principally on the two oxygen atoms in $^3SO_2$.

TABLE 2

Relative selectivity of hydrogen abstraction by $^3SO_2$ from alkanes

Radical	Primary	Secondary	Tertiary	Reference
$^3SO_2$	1	4	27	This work
$^3SO_2$	1	5	23	11
$^3SO_2$	1	7	10	1
$^3SO_2$	1	11	82	5
$(CH_3)_3CO\cdot$	1	8	36	12

The data obtained by the study of the n.m.r. and mass spectra of the chlorine stabilised products are consistent with hydrogen abstraction by $^3SO_2$ followed by combination between the alkyl radical and sulphur dioxide [reactions (32) and (33)]. However the fate of

$$RH + {}^3SO_2 \longrightarrow R\cdot + HSO_2\cdot \qquad (32)$$

$$R\cdot + SO_2 \longrightarrow RSO_2\cdot \qquad (33)$$

alkanesulphonyl radical so formed is uncertain. The rate of reaction of butyl or 1-methylpropyl radicals has not been measured but the reaction of methyl radicals has been extensively studied. Full details of all the earlier work need not concern us here. The important

$$CH_3\cdot + SO_2 \rightleftharpoons CH_3SO_2\cdot \qquad (34)$$

fact is that the forward reaction is fast at room temperature (k_{298} 1.8 × 10^8 l mol^{-1} s^{-1}) [13] and the reaction is appreciably exothermic (ΔH −17 kcal mol^{-1}).[14] This means that at room temperature the equilibrium lies well to the right, although as the temperature rises so it will shift to the left until at *ca.* 160 °C the life time of the combined radical is very short.

In order to elucidate the mechanism of the photochemical reaction completely it was necessary to establish clearly the fate of the alkanesulphonyl radical formed by combination of an alkyl radical and sulphur dioxide, and in view of the earlier work methyl radicals were the obvious choice. Good and Thynne used azomethane as their source of methyl radicals,[13] but Calvert and his co-workers subsequently showed that azomethane reacted with sulphur dioxide.[13] We first attempted to use di-t-butyl peroxide, but this has two disadvantages. First it forms acetone as one of the products which can undergo further reaction and secondly a temperature approaching 120° was required to ensure rapid decomposition of the peroxide. The use of di-t-butyl peroxide was therefore abandoned and instead diacetyl peroxide was used. The two principal sulphur-containing products when diacetyl peroxide was decomposed in the presence of sulphur dioxide were dimethyl sulphone ($CH_3SO_2CH_3$) and dimethyl disulphone ($CH_3SO_2SO_2CH_3$). The formation of the sulphone can be explained on two counts. First the concentration of methyl radical in the thermal decomposition of diacetyl peroxide was much higher than the concentration of butyl radicals in the photochemical experiments. Secondly at the higher temperatures of the thermal reaction the equilibrium between methyl and sulphur dioxide is shifted to the left again increasing the concentration of methyl radicals and increasing the probability of the combination of a methyl with a methanesulphonyl radical. In the photochemical reaction at room temperature all the butyl radicals combine irreversibly with sulphur dioxide. When 2-methylpropane was added to the thermal decomposition of acetyl peroxide in an atmosphere of SO_2 no hydrogen abstraction took place and the two major products remained the same as when 2-methylpropane was omitted. This completely excludes a chain mechanism.

We are now in a position to write down a mechanism for the photochemical reaction of sulphur dioxide with alkanes. The first chemical step is hydrogen abstraction by $^3SO_2$ [reaction (35)]. The alkyl radicals so formed combine with sulphur dioxide; at room temperature and

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[11] F. B. Wampler and J. G. Calvert, *Internat. J. Chem. Kinetics*, *1973*, **5**, *669*.

[12] I. K. Stoddart, A. Nechvatal, and J. M. Tedder, *J.C.S. Perkin II*, 1974, 473.

[13] A. Good and J. C. J. Thyne, *Trans. Faraday Soc.*, 1967, **63**, 2708; J. G. Calvert, D. H. Slater, and J. W. Gall, 'Chemical Reactions in Urban Atmospheres,' Elsevier, New York, 1971; F. C. James, J. A. Ken, and J. P. Simons, *J.C.S. Faraday I*, 1973, 2124.

[14] W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1064; S. W. Benson, personal communication.

high SO_2 concentrations the reverse step can be neglected. The alkanesulphonyl radicals will not abstract hydrogen even from the very reactive tertiary site in 2-methylpropane.

$$RH + {}^3SO_2 \longrightarrow R\cdot + HSO_2\cdot \qquad (35)$$

$$R\cdot + SO_2 \rightleftharpoons RSO_2\cdot \qquad (36)$$

If the temperature is raised and the SO_2 concentration reduced the alkanesulphonyl radical will tend to decompose before it can react. The complete absence of sulphinic acid formation when methyl radicals react with sulphur dioxide in the presence of 2-methylpropane means that in the photochemical reaction the majority of the sulphinic acid is formed by disproportionation of an alkanesulphonyl radical and an $HSO_2\cdot$ radical. Some of the alkanesulphonyl radicals combine,

$$RSO_2\cdot + HSO_2\cdot \longrightarrow RSO_2H + SO_2 \qquad (37)$$

and under our conditions this was quite an important process. Confirmation that the dialkyl disulphone was

$$RSO_2\cdot + RSO_2\cdot \longrightarrow RSO_2SO_2R \qquad (38)$$

formed by combination of two alkanesulphonyl radicals and not by the two step process (39) and (40) was

$$RSO_2\cdot + SO_2 \rightleftharpoons RSO_2SO_2\cdot \qquad (39)$$

$$RSO_2SO_2\cdot + R\cdot \longrightarrow RSO_2SO_2R \qquad (40)$$

obtained by changing the sulphur dioxide concentration when diacetyl peroxide was decomposed. The proportion of sulphone RSO_2R to disulphone RSO_2SO_2R increased as the sulphur dioxide concentration was decreased. At high sulphur dioxide concentration no free alkyl radical would be present so that it could not combine with the radical $RSO_2SO_2\cdot$. The concentration of $RSO_2\cdot$ must always greatly exceed $RSO_2SO_2\cdot$ so that as the sulphur dioxide concentration falls the alkyl radicals are in sufficient concentration for some to be trapped by the $RSO_2\cdot$ radicals.

The complete sequence of chemical steps is thus (35)—(38). Under our conditions the complex range of other products including sulphonic acids are only formed in solution after the photochemical reaction is complete. It appears that even in the careful work of Penzhorn and his co-workers the disproportionation of the alkanesulphinic acids was occurring in the ether solution before they had a chance to combine with the diazomethane. This is not to say that no radical disproportionation occurs between alkanesulphonyl radicals in the gas phase, but under our conditions such processes were very unimportant and no sulphonic acids were formed. However if our photochemical product was dissolved in an inert solvent like carbon tetrachloride an extremely complex range of products including sulphonic acids was formed. We therefore believe that the principal primary products are alkane sulphinic acids as Dainton and Ivin originally suggested, but their disproportionation appears to be accelerated by other trace products of the photochemical reaction so that only a gaseous reagent like chlorine is able to react with them to form stable products before they rearrange.

The fact that light causes sulphur dioxide and alkanes to form an aerosol has attracted much attention in environmental studies. However the mechanism established here shows that these reactions are unlikely by themselves to form an aerosol in the atmosphere. The initial hydrogen abstraction by ${}^3SO_2$ may well take place where oil with a high sulphur content is being burnt. However there is almost no chance of the alkyl radical combining with sulphur dioxide in the atmosphere. It will have combined with atmospheric oxygen long before it gets a chance of reacting with SO_2 even in the most polluted atmospheres. The resultant alkylperoxyl radical is unreactive and it may live long enough to encounter a sulphur dioxide molecule. Interaction now would be expected to yield sulphur trioxide and an alkoxyl radical.

$$SO_2 + RH \longrightarrow HSO_2\cdot + R\cdot \qquad (41)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (42)$$

$$RO_2\cdot + SO_2 \longrightarrow RO\cdot + SO_3 \qquad (43)$$

This may be a minor route for the oxidation of atmospheric sulphur dioxide and to this extent the process is of interest. Further study of the photochemical reaction should now be made when oxygen is present.

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