CCC.—*The Interaction of Sulphur Dioxide and Hydrogen Sulphide.*

By Ernest Matthews.

Interaction in the Gaseous State.

It has long been known that dry gaseous hydrogen sulphide and sulphur dioxide do not interact on mixing, but that they will react in the presence of water and certain other liquids. It has been suggested that there might be some relationship between the dielectric constant for a given substance and its ability or inability to cause the mutual decomposition of the two gases. Thus, Klein (*J. Physical Chem.*, 1911, **15**, 15) says: "While the dependence of chemical activity on the dielectric constant is not expressly stated by Baker in the Wilde Lecture for 1909, yet it is certainly implied." As a result of his own experiments and those of Kahlenberg and Schlundt (which proved that the Nernst-Thomson rule did not hold even qualitatively), he concludes that there is no such dependence. Klein's experiments have been repeated and extended but with substantially the same results.

The gases employed in the present experiments were dried by passage through a U-tube containing phosphorus pentoxide. The organic liquids were the purest obtainable and were dried and redistilled.

The results obtained are classified below; the dielectric constant is shown for each liquid, average values being given.

D.C.		Reaction.	*D.C.*		Reaction.
75	Water.	Immediate.	18	Methyl ethyl ketone.	After 2 mins.
56	Glycerol.	After 3 mins.	18	Benzaldehyde.	,, 8 ,,
55	Methyl sulphate.	,, 8 ,,	13	Benzyl alcohol.	Immediate.
39	Nitromethane.	,, 14 ,,	11	*tert.*-Butyl alcohol.	,,
39	Acetonitrile.	,, 3 ,,	6	Ethyl acetate.	After 8 mins.
34	Methyl alcohol.	Immediate.	5	Amyl acetate.	Immediate.
26	Ethyl alcohol.	,,	7	Aniline.	,,
24	*iso*Propyl alcohol.	,,	6	Methyl benzoate.	After 20 mins.
19	*iso*Butyl alcohol.	,,	5	Amyl benzoate.	,, 10 ,,
17	*tert.*-Amyl alcohol.	,,	5	Ethyl butyrate.	Immediate.
21	Acetone.	After 5 mins.	4	Ether.	After 8 mins.
21	Allyl alcohol.	Immediate.	—	Bornyl acetate.	Immediate.

No reaction occurred in the following solvents in 30 minutes: Nitrobenzene (36), phosphorus oxychloride (12), chlorobenzene (11), sulphuryl chloride (10), ethyl iodide (7), chloroform (5), carbon disulphide (3), carbon tetrachloride (2), benzene (2), and methyl salicylate (8).

Although the values of the dielectric constants are not known with accuracy, they serve to show that no rigid correspondence can hold between catalytic activity and dielectric constant.

In his work on the interaction of hydrogen sulphide and sulphur dioxide, Klein (*loc. cit.*) failed to differentiate between the action of liquid water and water vapour. Experiments have been carried out in which mixtures of these two gases, known to contain in the one case water vapour and in the other case ethyl alcohol vapour, were kept for more than 8 hours and 3 hours, respectively, before decomposition set in, and it was then due presumably to the formation of a liquid film on the surface of the glass. In each case addition of one drop of the liquid caused immediate separation of sulphur.

In view of this fact, the extreme precautions taken by Klein to dry both the gases and the reagents employed lose some of their significance, since the duration of his experiments rarely exceeded 2 hours.

Interaction in the Liquid State.

Quam (*J. Amer. Chem. Soc.*, 1925, **47**, 103) has asserted that sulphur dioxide reacts vigorously with liquid hydrogen sulphide, thus contradicting the earlier statement of Antony and Magri (*Gazzetta*, 1905, **35**, i, 206), who maintained that the liquefied gases require the presence of an ionising liquid to bring about reaction between them. In order to test this point, liquid hydrogen sulphide and liquid sulphur dioxide were mixed in the proportions of 2 : 1 in quantities of from 5—10 c.c., and in each case the mixture remained quite clear even when kept for 2 hours or more. The liquid on being warmed boiled away completely, leaving no residue except at the exit tube, where a deposit of sulphur was formed due to the presence of condensed water.

Experiments were then carried out with the liquid mixture of hydrogen sulphide and sulphur dioxide to determine under what conditions decomposition ensued. It was found that the addition of a little powdered sulphur had no effect, and also that ice was unable to cause the decomposition—a point of some interest.

The effect was then tried of the addition of 1—2 c.c. of the liquid mixture to small quantities of the most reactive organic liquids employed in the earlier experiments, when cooled to the temperature of solid carbon dioxide (— 78°). With ethyl alcohol, the decomposition was very vigorous, and almost equally so with amyl alcohol, amyl acetate, ether, ethyl acetate, acetone, and the other reactive substances which are liquid at this temperature. With ice, aniline, benzaldehyde, allyl alcohol, and glycerol, however, which were solid at this temperature, no decomposition occurred and the liquid remained clear (except for slight opalescence in the case of allyl alcohol, which did not increase on standing), although at the ordinary temperature, when liquid, they cause immediate decomposition.

Discussion.

It may be concluded that sulphur dioxide and hydrogen sulphide do not react with each other either in the gaseous state at the ordinary temperature or in the liquid state, except in the presence of a third substance in the liquid phase.

Further, the table on p. 2271 shows that the alcohols as a class are very active in effecting the decomposition. Moreover, it is found that ethyl alcohol is more effective even than water in bringing about decomposition. This would seem to be connected with the greater solubility of the two gases in alcohol than in water; thus 1 c.c. of alcohol at 16° dissolves 143 c.c. and 9 c.c. of sulphur dioxide and hydrogen sulphide, respectively, whereas 1 c.c. of water at 16° dissolves only 43 c.c. and 3 c.c., respectively.

It would seem desirable to investigate the rate of reaction in the presence of each of these two liquids, as it is possible that the ratio of the rates of reaction might be closely related to the ratio of their solubilities in alcohol and in water.

Klein takes the view that the substances effective in causing decomposition are those which are capable of forming unstable compounds with one or other of the two gases.

The failure of methyl salicylate to bring about decomposition, whilst other substances such as amyl acetate, amyl benzoate, etc., are capable of doing so, is difficult to explain on this basis, since, for instance, methyl salicylate would be expected to form addition compounds more readily than methyl benzoate.

Summary.

1. To bring about the decomposition of a mixture of sulphur dioxide and hydrogen sulphide in either the gaseous or the liquid state, the addition of a third substance is necessary, and it has been demonstrated that this third substance must be in the liquid phase.

2. There is no rigid relationship between the values of the dielectric constants of substances and their chemical activity as measured by their ability to bring about the interaction of hydrogen sulphide and sulphur dioxide.

3. The assertion that hydrogen sulphide and sulphur dioxide when in a liquid state react vigorously, even when dry, has been disproved.

4. It is suggested that the activity of a substance in causing decomposition is dependent on the solubility of the two gases in the substance when liquid, or on the solubility of the solids in the liquid mixture of the two gases.

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