950. *Photochemical Addition of Hydrogen Sulphide to C_2 Olefins.*

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The irradiation by ultraviolet light of hydrogen sulphide in the presence of ethylene, 1,1-difluoroethylene, and tetrafluoroethylene gives rise to addition products, RSH and R_2S. Examination of the secondary products has enabled a radical-chain mechanism to be postulated. Application of the reaction to synthesis is demonstrated through the production of polyfluoroalkylsulphur compounds from the fluoro-olefins.

Vaughan and Rust [1] first showed that when hydrogen sulphide is irradiated in the presence of olefins with light of wavelength less than 3000 Å alkanethiols and alkyl sulphides resulted. The secondary products were, however, not detected and no detailed mechanism was suggested. In an attempt to elucidate the reaction mechanism the products of the reaction of hydrogen sulphide with ethylene have been analysed. Broadly, the results can be explained in terms of initiation by photolysis of hydrogen sulphide to a hydrogen atom and a thiol radical: [2] $H_2S \longrightarrow \cdot H + \cdot SH$. Both species are able to attack

[1] Vaughan and Rust, *J. Org. Chem.*, 1942, **7**, 472; B.P. 581,775; U.S.P. 2,398,479, 2,398,480 2,398,481.

[2] Darwent and Roberts, *Proc. Roy. Soc.*, 1953, *A*, **216**, 352.

the π-bond of the olefin. The main chain-propagator is the thiol radical. The analytical pattern is similar for the fluoro-olefins, and this method provides a ready synthesis of polyfluoroalkylsulphur compounds.

Experimental

Materials.—Hydrogen sulphide, generated from ferrous sulphide and sulphuric acid, was fractionated through traps at −78°, −96°, −145°, and −196°, the fraction collecting at −145° being retained. Ethylene was obtained from a cylinder (C.I.G. brand) and fractionated as above, the last fraction being retained. Tetrafluoroethylene was prepared by pyrolysis of Teflon and fractionated as was ethylene. 1,1-Difluoroethylene was presented by Dupont de Nemours Company to whom we are extremely grateful. It was fractionated in a manner similar to that for the other olefins.

Apparatus.—A conventional high-vacuum apparatus was used. The products were fractionated through a series of traps, each of which was connected to a gas burette; the lead from this was to the gas-chromatography machine.

The reaction vessel was of silica, cylindrical, and with a volume of 130 ml. After being dosed with reactants, the vessel was placed in a thermostat-bath at 30°, and during irradiation was rotated at 30 r.p.m. Irradiation was by a Hanovia U.V.S. 500, medium-pressure mercury-arc lamp, unfiltered. The experimental arrangement is shown in Fig. 1.

Between runs the reaction vessel was washed with carbon disulphide, detergent, and water, then oven-dried and degassed under a vacuum.

Products were analysed by means of a Perkin-Elmer model 21 infrared spectrometer and a Perkin-Elmer model 154-C gas-chromatograph. The latter was fitted with either a 2-m. silica-gel column at 25°, or a 2-m. di-isodecyl phthalate column at 70°. Nitrogen or hydrogen was used as carrier gas.

Method of Analysis.—The volatile products from a run were fractionated through traps at −96° (A), −145° (B), −196° (C), and one containing charcoal at −196° (D), the last to absorb non-condensable products. Most of the hydrogen sulphide collected in B; the small amount going through into C was removed by absorption in a mixture of silver nitrate in ethylene glycol impregnated on firebrick. A fifth fraction, E, consisted of the involatile products remaining in the reaction vessel.

Results

Hydrogen Sulphide–Ethylene Reaction.—Identification of products. A series of runs at 30°, with total pressures of 500 mm., was carried out where the reactant ratio H_2S–C_2H_4 was varied between 10 and 6 to 1. The time of irradiation was in each case 8 hr. The various fractions described above were analysed by gas-chromatography.

Fraction A (−96°). Di-isodecyl phthalate, 2-m. column, 70°, hydrogen carrier. Two peaks were recorded, with retention characteristics the same as of standard samples of ethanethiol and ethyl sulphide.

Fraction B (−145°). Di-isodecyl phthalate column, 70°, hydrogen carrier. One peak was recorded with retention characteristics the same as of a standard sample of hydrogen sulphide.

Fraction C (−196°). Di-isodecyl phthalate column, 70°, hydrogen carrier. Two peaks were recorded, with retention characteristics the same as of standard samples of ethylene and hydrogen sulphide. On a silica gel column at 25° with hydrogen as carrier, two peaks were recorded with retention characteristics the same as of standard samples of ethylene and ethane. The small amount of hydrogen sulphide was absorbed by the silica gel.

Fraction D (charcoal trap, −196°). Silica gel column, 25°, hydrogen carrier. No peak was recorded. With nitrogen as carrier, a single peak was recorded with retention characteristics the same as those of hydrogen.

Fraction E (involatile). This consisted of a white deposit on the walls of the reaction vessel and a liquid residue. Both were soluble in carbon disulphide, and the liquid residue in carbon tetrachloride. The solution in carbon tetrachloride gave an infrared spectrum identical with that of diethyl disulphide. The carbon tetrachloride extract was tested for the presence of >S and SH groups by the very sensitive sodium nitroprusside test.[3] This proved to be negative.

[3] Colowick and Kaplan, "Methods of Enzymology," Academic Press, New York, 1957, Vol. III, p. 938.

The white deposit was presumed to be sulphur. It is concluded, therefore, that the products are (hydrogen sulphide, ethylene, *i.e.*, reactants) ethane, ethanethiol, ethyl sulphide, diethyl disulphide, hydrogen, and sulphur. No butanethiol was detected.

Variation of Product Concentrations with Time.—A series of runs at 30° was carried out with initial pressures of hydrogen sulphide 434 mm. and ethylene 71 mm., to give a reactant ratio $H_2S : C_2H_4 = 6{\cdot}1 : 1$. The time of irradiation was varied between 0 and 8 hr. The volumes

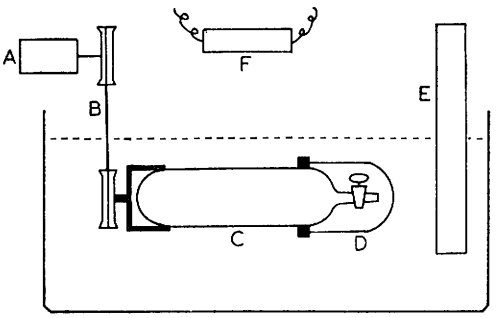


FIG. 1. Irradiation apparatus: A, Motor. B, Pulley drive. C, Reaction vessel. D, Water-tight cap. E, Temperature control. F, Lamp.

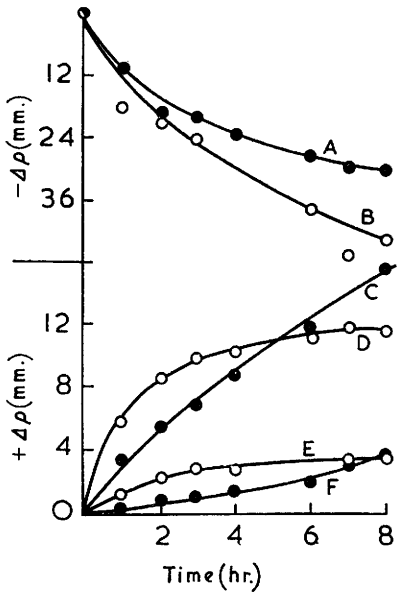
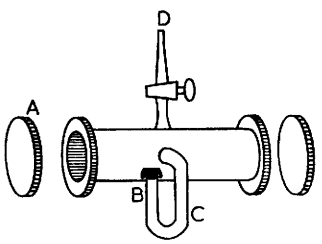


FIG. 2. Variation of reactant and product concentrations with time (H_2S–C_2H_4 reaction).

A = C_2H_4 (initial p 71 mm.).
B = H_2S (initial p 434 mm.).
C = H_2. D = $C_2H_5{\cdot}SH$.
E = C_2H_6. F = $(C_2H_5)_2S$.

FIG. 3. Combined fraction collector and infrared gas cell.

A, NaCl window. B, Rubber septum. C, Condensing tube packed with glass wool. D, B10 cone.
(The cell is connected to the gas-chromatograph by means of a hypodermic needle inserted through the rubber septum.)



of each of the volatile fractions were determined in the gas-burette, and the concentrations of the individual components in these fractions by gas-chromatography.

The results are shown in Fig. 2 (sulphur and diethyl disulphide were not determined quantitatively). They show that the yield of organosulphur compounds is reasonably high. While of no synthetic importance for these particular compounds, the method could possibly be used for the synthesis of substituted alkanethiols and alkyl sulphides. Accordingly some experiments were carried out where the ethylene was replaced by 1,1-difluoroethylene and tetrafluoroethylene.

Irradiation of Hydrogen Sulphide with 1,1-Difluoroethylene and Tetrafluoroethylene.—6 : 1 Mixtures of hydrogen sulphide with each olefin were irradiated for 8 hr. at 30°. The gas-chromatographic analytical patterns were then established for the various fractions. In each

case products analogous to those for the reaction of hydrogen sulphide and ethylene were obtained, namely, a thiol and a sulphide, together with a fluorocarbon and hydrogen. The infrared spectrum of each product from the chromatographic separation established the presence of the expected polyfluoroalkyl group. An infrared cell was constructed whereby individual components from the fractometer could be directly collected (Fig. 3), and small amounts of material were thus not subjected to handling losses.

It is interesting that in the case of 1,1-difluoroethylene the volatile organosulphur fraction contained only two products, whereas it is feasible that five products could be obtained in the addition reaction, *viz.*, $CH_3{\cdot}CF_2{\cdot}SH$, $CH_3{\cdot}CF_2{\cdot}S{\cdot}CF_2{\cdot}CH_3$, $CHF_2{\cdot}CH_2{\cdot}SH$, $CHF_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CHF_2$, $CHF_2{\cdot}CH_2{\cdot}S{\cdot}CF_2{\cdot}CH_3$. It has been shown [4] that photochemical addition of 1,1-difluoroethylene to trichlorosilane yields only trichloro-2,2-difluoroethylsilane, and in our analogous reaction we assume that the products are similarly constituted, namely, 2,2-difluoroethanethiol and bis-2,2-difluoroethyl sulphide.

The relative amounts of products formed are consistent with the statement that the photochemical method is well suited to the synthesis of polyfluoroalkanethiols and derived sulphides.

Discussion

As the reaction is a low-temperature photochemical one the mechanism is presumably free-radical in nature. The following mechanism accounts for all the products:

$$H_2S \xrightarrow{h\nu} {\cdot}H + {\cdot}SH \quad (1)$$

$${\cdot}H + H_2S \longrightarrow H_2 + {\cdot}SH \quad (2)$$

$${\cdot}H + C_2H_4 \longrightarrow {\cdot}CH_2{\cdot}CH_3 \quad (3)$$

$${\cdot}CH_2{\cdot}CH_3 + H_2S \longrightarrow C_2H_6 + {\cdot}SH \quad (4)$$

$${\cdot}SH + C_2H_4 \longrightarrow {\cdot}CH_2{\cdot}CH_2{\cdot}SH \quad (5)$$

$${\cdot}CH_2{\cdot}CH_2{\cdot}SH + H_2S \longrightarrow C_2H_5{\cdot}SH + {\cdot}SH \quad (6)$$

$$C_2H_5{\cdot}SH \xrightarrow{h\nu} C_2H_5{\cdot}S{\cdot} + H{\cdot} \quad 7)$$

$$C_2H_5{\cdot}SH + {\cdot}R \longrightarrow C_2H_5{\cdot}S{\cdot} + RH \quad (8)$$

$$C_2H_5{\cdot}S{\cdot} + C_2H_4 \longrightarrow C_2H_5{\cdot}S{\cdot}CH_2{\cdot}CH_2 \quad (9)$$

$$C_2H_5{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot} + H_2S \longrightarrow (C_2H_5)_2S + {\cdot}SH \quad (10)$$

$$C_2H_5{\cdot}S{\cdot} + C_2H_5{\cdot}S{\cdot} \longrightarrow C_2H_5{\cdot}S{\cdot}S{\cdot}C_2H_5 \quad (11)$$

$${\cdot}SH + {\cdot}SH \longrightarrow H_2S + \tfrac{1}{8}S \quad (12)$$

$${\cdot}SH + {\cdot}SH \longrightarrow H_2 + S_2 \quad (13)$$

[The species, R, in step (8), is a free radical.]

The polymerisation step

$${\cdot}CH_2{\cdot}CH_2{\cdot}SH + C_2H_4 \longrightarrow {\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SH \quad (14)$$

is discounted since no butanethiol was detected under our experimental conditions.

Steps 1, 2, 12, and 13 were proposed by Darwent and Roberts [2] to account for the photochemical decomposition of hydrogen sulphide at room temperature. Reactions 3—11 are of the normal type and they will be either exothermic or thermoneutral. It can be seen from Fig. 2 that the formation of ethyl sulphide is dependent on the formation of ethanethiol; this is accounted for in steps 7 and 8. The ready detection, and amounts, of hydrogen, ethane, and diethyl disulphide formed suggest that under the experimental conditions (gas-phase reaction at low temperature and pressure) the chains are short; this is in contrast to the results of Vaughan and Rust.[1]

If in the chain-termination steps 11—13 it is assumed that 13 is small [2] compared with 12, then initially, when 7 and 8 are negligible, steps 2—4 will account for all the hydrogen and ethane formed. In this case if we write R = Rate of formation, we have:

$$R_{\text{Hydrogen}}/R_{\text{Ethane}} = k_2[H_2S]/k_3[C_2H_4]. \quad (15)$$

Thus

$$k_2/k_3 = R_{\text{Hydrogen}}[C_2H_4]/R_{\text{Ethane}}[H_2S]. \quad (16)$$

[4] Bell and Haszeldine, unpublished work.

From the experimental results, k_2/k_3 from (16) is ~0·5. It must be stressed that this value is not very accurate owing to the difficulty in measuring small quantities of ethane in the presence of large amounts of ethylene.

Making the reasonable assumption that A_2/A_3 is of the order of 10, and using the above value for k_2/k_3, we find the energy of activation difference $E_2 - E_3$ to be 1·8 kcal. mole^{-1}. This order of magnitude is similar to the kinetic results obtained by Darwent and Roberts.[5]

The loss of hydrogen sulphide and ethylene is greater than can be accounted for in the formation of volatile products, which may be explained in terms of the formation of diethyl disulphide which was not measured. Hydrogen sulphide is also lost at a greater rate than ethylene; this is expected in that the photolysis of hydrogen sulphide, represented by steps 1, 2, and 12, is stoicheiometrically described by: $H_2S \longrightarrow H_2 + S$.

The synthetic aspects of this reaction have been discussed, and by suitably altering conditions to increase the chain length this method is of obvious significance.

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[5] Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, **14**, 55.