Therefore, convection cannot cause the observed values of D in the H_2O–D_2O experiments to stray appreciably outside the range from D_i to D_o. Thus we would have observed easily the enormous decrease of D reported by Adamson and Irani, and we must conclude that their measurements are erroneous.

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THE PREPARATION OF A CRYSTALLINE gem-DITHIOL UNDER MILD CONDITIONS

Sir:

We wish to report the synthesis in 80% yield of the first crystalline *gem*-dithiol, 2,2-dimercapto-1,3-diphenylpropane, m.p. 81.5–83°, by the combined action of hydrogen sulfide and hydrogen chloride upon dibenzyl ketone at atmospheric pressure. Since these conditions heretofore have been used for the preparation of thioketones and thioaldehydes (or their polymers) in variable yield,[1] we believe that previous investigators have failed to recognize that *gem*-dithiols are among the reaction products because the reaction mixtures have been worked up by the use of procedures which would have destroyed *gem*-dithiols. It seems likely that the formation of *gem*-dithiols from carbonyl compounds is of far greater generality than has been recognized up to the present time, and that their presence can explain some puzzling reaction products which have been observed. We are exploring the scope of the reaction, as well as the chemistry of *gem*-dithiols, broadly. The first previous synthesis[2] of *gem*-dithiols utilized pressures in the range of 35–8500 atmospheres without added catalysts, and yields were commonly 15 to 35%.

A solution of dibenzyl ketone (19.4 g., 0.0924 mole) in 50 ml. of ethanol was cooled in an ice-bath. Dry hydrogen chloride and dry hydrogen sulfide were simultaneously bubbled through the solution for a period of six hours. The reaction mixture was allowed to stand overnight in a refrigerator. The precipitate was filtered, washed with cold ethanol, and dried in air to yield 19.6 g. (80%) of colorless, granular crystals, m.p. 75–80°. Two recrystallizations from ethanol (at temperatures not exceeding 50°) yielded 15 g. of colorless needles, m.p. 81.5–83°. Infrared absorption at 2570 cm.$^{-1}$ showed the presence of the sulfhydryl group; carbonyl absorption was absent. Sodium nitroprusside gave a positive sulfhydryl test. Lead acetate produced a yellow precipitate which slowly turned black on standing, a behavior typical of *gem*-dithiols.[2] *Anal.* Calcd. for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.63. Found: C, 69.41; H, 6.31; S, 24.63.

The *gem*-dithiol yielded with 2,4-dinitrophenylhydrazine reagent the same orange crystalline 2,4-dinitrophenylhydrazone as dibenzyl ketone, m.p. 98.5–99.5° after recrystallization from ethanol. Identification was made by comparison of melting points (no depression on admixture) and infrared absorption spectra.

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(1) (a) A. Schönberg, p. 705 ff., in "Methoden der organischen Chemie," (Houben-Weyl), 4th ed. (ed. E. Müller). G. Thieme, Stuttgart. Vol. 9. 1955; (b) E. Campaigne. *Chem. Rev.*, **39**, 1 (1946).

(2) T. L. Cairns. G. L. Evans. A. W. Larcher and B. C. McKusick, THIS JOURNAL. **74**, 3982 (1952).

EXCHANGE RATES OF ACETYLENIC HYDROGENS IN AQUEOUS SOLUTIONS[1]

Sir:

Available studies on the exchange of acetylenic hydrogens with those of aqueous solutions do not establish definitely the details of the exchange process but do imply that the rate is only moderate, even when the aqueous phase contains one molar hydroxide ion.[2,3] In view of the acidic character of acetylenes,[4,5] this is surprisingly slow. We have consequently reinvestigated this exchange for phenylacetylene and for acetylene itself. For the first of these, $C_6H_5C_2D$ was prepared and aliquots were shaken with aqueous buffer solutions at 25°. Analysis was made with an infrared spectrometer on solutions of the phenylacetylene in carbon tetrachloride. In the second case, acetylene was shaken at 25° with buffers made up with water which contained 60 atom per cent. deuterium. Analysis of the C_2HD formed was made by gas phase infrared. In both cases the aqueous hydrogens were in large excess and only initial rates were measured so that reverse processes can be neglected. At *p*H values below ten the rate of exchange easily could be made independent of the degree of shaking, indicating that the slow step occurred in the aqueous phase. We therefore have used the observed half-times for exchange and the measured mole ratios and solubilities to calculate the listed values of the first order rate coefficients for the solution reaction. The relevant equation is $k_{\text{soln}} = 0.69A/V_B S t_{1/2}$, where A is total moles and S is aqueous solubility of the acetylene compound, V_B is volume of aqueous phase and $t_{1/2}$ is the observed half-time for the two-phase exchange.

Solution	*p*H	$10^6 k_{\text{soln.}}$, sec.$^{-1}$
Acetylene		
0.02 M total phosphate	8.60	2600
0.02 M total phosphate	9.04	6000
Phenylacetylene		
0.01 M HCl	2	no exchn.
0.04 M total acetate	5.03	2
0.02 M total phosphate	7.03	71
0.02 M total phosphate	7.91	510
0.02 M total phosphate	8.60	1300
0.05 M total phosphate	8.60	1500
0.014 M total borate	9.0	4600
0.012 M total borate	9.5	12000

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(2) L. H. Reyerson and S. Yuster. THIS JOURNAL, **56**, 1426 (1934); **57**, 779 (1935); see also L. H. Reyerson and B. Gillespie. *ibid.*, **57**, 2250 (1935); **58**, 282 (1936); and **59**, 901 (1937).

(3) R. P. Bell. *ibid.*, **57**, 778 (1935).

(4) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

(5) W. K. McEwen, *ibid.*, **58**, 1124 (1936).