COMMUNICATIONS TO THE EDITOR

THE THERMAL REACTION BETWEEN FORMALDEHYDE AND CHLORINE

Sir:

Spence and Wild [*J. Chem. Soc.*, 1588 (1934)] report that the thermal reaction between chlorine and formaldehyde proceeds either by an explosion or by a relatively slow process, depending on temperature, pressure and the condition of the reaction vessel. They find further that any excess of formaldehyde present in an explosive mixture is decomposed into carbon monoxide and hydrogen; that the slow reaction is preceded by an induction period; that the rate of this latter reaction is somewhat affected by the walls of the reaction vessel; and that the amount of carbon monoxide produced in this reaction is apparently somewhat greater than the amount predicted from the observed pressure change. These observations accord well with results obtained for the photochemical reaction [Krauskopf and Rollefson, This Journal, **56**, 2542 (1934)] between the two gases, and it seems probable that the mechanism devised to account for the photochemical change may be applied successfully to the thermal process.

According to this mechanism, formyl chloride is produced from formaldehyde and chlorine: $CH_2O + Cl_2 \longrightarrow COHCl + HCl$, and decomposes subsequently into carbon monoxide and hydrogen chloride. The existence and comparative stability of the intermediate have been demonstrated in photochemical reaction mixtures; its lifetime would be considerably shortened by the higher temperatures used by Spence and Wild, but its presence in their reaction mixtures seems entirely reasonable. The formation of formyl chloride according to the above reaction involves no pressure change; the observed induction period, therefore, like the corresponding period in the photochemical reaction, can be explained as the time during which the intermediate is being produced faster than it decomposes. This first reaction is a highly exothermic chain process which under favorable conditions can become explosive. The second reaction is at least partially heterogeneous, since the pressure change in either the photochemical or the thermal process is more rapid immediately after the reaction vessel is cleaned. Whether increase of the surface–volume ratio produces any effect is doubtful. In the photochemical experiments an increase of surface appeared to increase the rate; but the increase may have been merely one of the erratic variations which occur so frequently in these experiments, or may have been due merely to the relative freshness of the added surface. Spence and Wild report a slight decrease of rate with increasing surface, but feel that the decrease is not significant.

Spence and Wild determined the amount of carbon monoxide formed by analysis of their gas mixtures. In every case, the amount of carbon monoxide indicated by analysis was greater than the amount calculated from the pressure change. This result they explain by assuming that the observed pressure increase is too small because of a concurrent chlorine-sensitized polymerization of formaldehyde. If formyl chloride is present, the discrepancy can be alternatively explained by supposing that during the process of analyzing the reaction mixture some formyl chloride decomposes, thus increasing the amount of carbon monoxide present.

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THE CHEMICAL BASIS FOR SOME BIOLOGICAL EFFECTS OF HEAVY WATER

Sir:

Empirical physiological effects of heavy water require chemical explanations [*cf.* Barnes and Jahn, *Quart. Rev. Biol.*, **9**, 292 (1934)]. We find the contractile vacuole of protozoa an excellent object for heavy water experiments. Thus in a race of *Paramecium caudatum* the contractile vacuole empties every 18.9 seconds in 30% D_2O compared to 11.3 seconds in controls (both at 18.8°). We have applied the Arrhenius equation: Velocity α $e^{-E/RT}$ to data on the rate of contraction at various temperatures and in ordinary water we find the following values of the constant E or energy of activation of the controlling catalyst: below 16° 24,000 calories; between 16 and 22° 17,000 calories and above 22° 14,000