The amount of iodine consumed upon oxidation of the new compound in dilute, faintly acid solution, by excess of 0.1 *N* iodine, was that required for conversion of the disulfoxide to cysteic acid. These facts, and the composition of the substance as shown by analysis, suggest that it is the disulfoxide corresponding to cystine. Further study of the compound is in progress.

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THE PHOTOCHEMISTRY OF PHOSGENE[1]

Sir:

Montgomery and Rollefson[2] have proposed the following mechanism for the photochemical reduction of phosgene

$$\mathrm{COCl_2} + h\nu = \mathrm{COCl} + \mathrm{Cl} \tag{1}$$
$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H} \tag{2}$$
$$\mathrm{H} + \mathrm{COCl_2} = \mathrm{CO} + \mathrm{Cl} + \mathrm{HCl} \tag{3}$$
$$\mathrm{CO} + \mathrm{Cl} + \mathrm{M} = \mathrm{COCl} + \mathrm{M} \tag{4}$$
$$2\mathrm{COCl} = \mathrm{COCl_2} + \mathrm{CO} \tag{5}$$
$$\mathrm{d(CO)}/\mathrm{d}t = I_{\mathrm{abs}}[1 + k_2(\mathrm{H_2})/k_4(\mathrm{CO})(\mathrm{M})] \tag{1}$$

In their derivation of (1) the rate of production of carbon monoxide in (5) erroneously is taken equal to the rate of consumption of COCl in this step; when this is corrected the 1 within the bracket drops out, and agreement with experiment is lost. It does not help to replace (5) by (5a) below, which must be followed by either (7) below or

$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl} \tag{6}$$

A number of other modifications have been examined; the most satisfactory consists of (1), (2), and (4), together with

$$\mathrm{H} + \mathrm{COCl_2} = \mathrm{HCl} + \mathrm{COCl} \tag{3a}$$
$$2\mathrm{COCl} = 2\mathrm{CO} + \mathrm{Cl_2} \tag{5a}$$
$$\mathrm{COCl} + \mathrm{Cl_2} = \mathrm{COCl_2} + \mathrm{Cl} \tag{7}$$
$$\mathrm{COCl} + \mathrm{H_2} = \mathrm{CO} + \mathrm{HCl} + \mathrm{H} \tag{8}$$
$$\mathrm{d(CO)}/\mathrm{d}t = \frac{2I_{\mathrm{abs}}k_2(\mathrm{H_2})}{k_2(\mathrm{H_2}) + k_4(\mathrm{CO})(\mathrm{M})} + k_8\sqrt{I_{\mathrm{abs}}/k_{6\mathrm{a}}(\mathrm{H_2})} \tag{2}$$

The second term here must be small, and the initial quantum yield accordingly cannot exceed 2.3–2.4, which is perhaps too low; the rate law is probably otherwise satisfactory.

The mechanism of Rollefson and Montgomery [Ref. 2, p. 4036] for the phosgene-sensitized oxidation of carbon monoxide, which is satisfactory only for low oxygen pressure, consists of (1) and (4) together with

$$\mathrm{COCl} + \mathrm{O_2} = \mathrm{CO_3Cl} \tag{9}$$
$$\mathrm{CO_3Cl} + \mathrm{CO} = 2\mathrm{CO_2} + \mathrm{Cl} \tag{10}$$
$$\mathrm{CO_3Cl} + \mathrm{COCl} = 2\mathrm{CO_2} + \mathrm{Cl_2} \tag{11}$$

By adding the further chain-breaking step

$$2\mathrm{CO_3Cl} + \mathrm{CO} = 3\mathrm{CO_2} + \mathrm{Cl_2O} \tag{12}$$

and making valid approximations one obtains the rate-law

$$\mathrm{d(CO)}/\mathrm{d}t = 2\sqrt{k_9k_{10}{}^2I_{\mathrm{abs}}(\mathrm{CO})(\mathrm{O_2})/[k_{10}k_{11} + k_9k_{12}(\mathrm{O_2})]} \tag{3}$$

which is in good agreement with experiment. The same result is obtained if $\mathrm{CO_3Cl}$ is replaced by $\mathrm{CO_2} + \mathrm{ClO}$. It can be shown that (12) is the only step that will give this result. A similar law can be derived for a mechanism based on the chain $\mathrm{Cl} + \mathrm{O_2} + \mathrm{M} = \mathrm{ClO_2} + \mathrm{M}$, $\mathrm{ClO_2} + \mathrm{CO} = \mathrm{ClO} + \mathrm{CO_2}$, $\mathrm{ClO} + \mathrm{CO} = \mathrm{Cl} + \mathrm{CO_2}$; this chain, however, is less plausible chemically than that of Rollefson and Montgomery. It seems unlikely that there is any other possible mechanism.

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[2] Montgomery and Rollefson, THIS JOURNAL, **55**, 4025 (1933).

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LOUIS S. KASSEL[3]

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THE STANDARD QUINHYDRONE ELECTRODE

Sir:

During an investigation into the effects of various electrolytes upon the potential of the cell $\mathrm{Pt/H_2}$, electrolyte, quinhydrone/Au, we have had need for a standard electrode. Both the 0.1 *N* and saturated calomel electrodes were found to have too great a lag when subject to temperature change.

In view of the above it was decided to investigate the possibility of using the standard quinhydrone electrode, first studied by Viebel [*J. Chem. Soc.*, **123**, 2203 (1923)] and now frequently employed. This involved a redetermination of the reproducibility of the potential difference between the hydrogen and quinhydrone electrodes in standard acid mixture, namely, 0.01 *N* HCl + 0.09 *N* KCl. Experimental details will be described in a later paper, but it may be said that no liquid junction is involved and readings are significant to 0.00001 volt. Measurements were made with two series of acid mixtures prepared (a) by mixing 1 part of 0.1 *N* HCl and 9 parts of 0.1 *N* KCl, and (b) by weighing out appropriate quantities of KCl and constant boiling HCl and diluting at 25°. These might be expected to