suction, washed with water, and dried. In order to free the aminophthalhydrazide from sulfur, the crude mixture is stirred up with that amount of 5% sodium hydroxide solution which would just correspond to the assumption that the dry solid contained no sulfur. After stirring and very slight warming the solution is filtered from undissolved sulfur, cooled to 0°, and stirred and scratched. Presently precipitation of the monosodium salt[3] of 3-aminophthalhydrazide begins and increases for some time. Finally the solid is filtered with suction, pressed as dry as possible on the filter, then washed sparingly with absolute alcohol or ether. It may then be dried in the air if it is to be preserved as the sodium salt. If, however, it is desired to reconvert the substance to "Luminol," the original solid is not washed with alcohol but is redissolved in water and reprecipitated by adding a slight excess of glacial acetic acid. The voluminous flocculent precipitate is again filtered with suction, washed free from sodium acetate with water, and dried. The product so obtained is free from sulfur and melts at 319–320° uncorr. (using a 360° melting point thermometer in a Berl and Kuhlmann copper block). The color of the final 3-aminophthalhydrazide appears to vary according to the mode of precipitation from almost white to quite deep yellow.

Anal. Calcd. for $C_8H_7N_3O_2$: C, 54.22; H, 3.98; N, 23.73. Found: C, 54.20, 54.31; H, 4.48, 4.62; N, 24.20, 24.02. *Neut. equiv.* Calcd., 177. Found: 175.

CONTRIBUTION NO. 98 FROM THE
RESEARCH LAB. OF ORGANIC CHEM.
MASSACHUSETTS INST. OF TECH.
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[3] Samples of the sodium salt (dried to constant weight at 105°) were analyzed by igniting in porcelain crucibles and converting the ash to sodium sulfate. Calcd. for $C_8H_6N_3O_2Na$: Na, 11.55. Found: Na, 11.77, 11.99.

COMMUNICATIONS TO THE EDITOR

AN INTERMEDIATE OXIDATION PRODUCT OF CYSTINE

Sir:

Previous work, reported at the April, 1933, Meeting of the American Society of Biological Chemists by Toennies and Lavine, but not completely included in the abstract [*J. Biol. Chem.*, **100,** XCI (1933)], has shown that the oxidation of cystine in non-aqueous solution by perbenzoic acid at low temperature consumed a maximum of four atoms of oxygen per molecule of cystine. The first two atoms of oxygen reacted more rapidly than the second two, and following the first stage and during the further oxidation there separated a precipitate whose composition accorded with that of the disulfone ($+{}^1/_2\,HClO_4$). This product, after hydrolysis by 95% methyl alcohol containing hydrogen chloride, and addition of chloroform, yielded a crystalline precipitate, whose properties and analytical values were those of a mixture of cysteic acid and the corresponding sulfinic acid. To permit step by step study of the course of the oxidation there was developed an analytical method involving rapid removal of perbenzoic acid from the reaction mixture, and application of a semi-quantitative form of the cyanide–nitroprusside test following acid–iodide treatment. It was observed that response to this test reached a maximum during the first stage of the oxidation (between one and two atoms of oxygen consumed), becoming negative toward the end, thus indicating the test to be associated with an oxide, or oxides, lower than the trioxide [*cf. J. Biol. Chem.*, **100,** 464 (1933)].

On the basis of these studies experiments aimed at the isolation of such intermediate oxidation products of cystine have been made. When cystine was oxidized to the stage at which somewhat more than two atoms of oxygen were consumed (with formation of only a little of the insoluble final oxidation product, and with only traces of unoxidized cystine left), immediate neutralization of the filtered liquid by addition of pyridine produced a precipitate. Sparing extraction of the filtered precipitate with water left a white residue which crystallized in the manner of an ampholyte, and which responded neither to the direct cyanide-nitroprusside test for —S—S—, nor to the nitroprusside test for —SH. After reduction of this substance with a large excess of 3 *N* hydriodic acid, the cyanide–nitroprusside test was as strong as for an equal amount of cystine. The amount of iodine liberated during the acid–iodide treatment corresponded to the requirements for reduction of the disulfoxide to cystine. The optical rotation of the reduced solution indicated an almost quantitative regeneration of cystine, and by neutralization of the solution cystine was precipitated.

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.

DEPARTMENT OF CHEMISTRY T. F. LAVINE
UNIVERSITY OF PENNSYLVANIA G. TOENNIES
LANKENAU HOSPITAL RESEARCH INSTITUTE
PHILADELPHIA, PENNSYLVANIA E. C. WAGNER

RECEIVED NOVEMBER 9, 1933

THE PHOTOCHEMISTRY OF PHOSGENE[1]

Sir:

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

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

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

$$H + Cl_2 = HCl + Cl \qquad (6)$$

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

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

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

$$COCl + O_2 = CO_3Cl \qquad (9)$$
$$CO_3Cl + CO = 2CO_2 + Cl \qquad (10)$$
$$CO_3Cl + COCl = 2CO_2 + Cl_2 \qquad (11)$$

By adding the further chain-breaking step

$$2CO_3Cl + CO = 3CO_2 + Cl_2O \qquad (12)$$

and making valid approximations one obtains the rate-law

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

which is in good agreement with experiment. The same result is obtained if CO_3Cl is replaced by $CO_2 + ClO$. 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 $Cl + O_2 + M = ClO_2 + M$, $ClO_2 + CO = ClO + CO_2$, $ClO + CO = Cl + CO_2$; this chain, however, is less plausible chemically than that of Rollefson and Montgomery. It seems unlikely that there is any other possible mechanism.

PITTSBURGH, PA. LOUIS S. KASSEL[3]

RECEIVED NOVEMBER 13, 1933

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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

[3] Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

THE STANDARD QUINHYDRONE ELECTRODE

Sir:

During an investigation into the effects of various electrolytes upon the potential of the cell 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