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
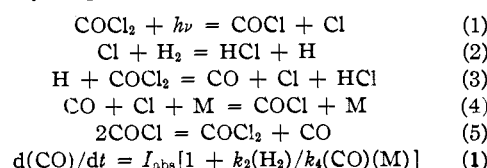LANKENAU HOSPITAL RESEARCH INSTITUTE
PHILADELPHIA, PENNSYLVANIA   E. C. WAGNER
RECEIVED NOVEMBER 9, 1933

THE PHOTOCHEMISTRY OF PHOSGENE[1]

Sir:

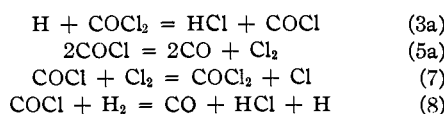Montgomery and Rollefson[2] have proposed the following mechanism for the photochemical reduction of phosgene

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

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

$$H + Cl_2 = HCl + Cl \tag{6}$$
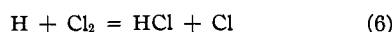
A number of other modifications have been examined; the most satisfactory consists of (1), (2), and (4), together with

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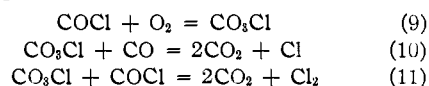$$2COCl = 2CO + Cl_2 \tag{5a}$$
$$COCl + Cl_2 = COCl_2 + Cl \tag{7}$$
$$COCl + H_2 = CO + HCl + H \tag{8}$$
$$d(CO)/dt = \frac{2I_{abs}k_2(H_2)}{k_2(H_2) + k_4(CO)(M)} + k_8\sqrt{I_{abs}/k_{6a}(H_2)} \tag{2}$$

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 satisfac-

(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).

tory only for low oxygen pressure, consists of (1) and (4) together with

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

By adding the further chain-breaking step

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

and making valid approximations one obtains the rate-law

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

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.

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PITTSBURGH, PA.   LOUIS S. KASSEL[3]
RECEIVED NOVEMBER 13, 1933

THE STANDARD QUINHYDRONE ELECTRODE

Sir:

During an investigation into the effects of various electrolytes upon the potential of the cell Pt/H₂, 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

differ slightly in hydrogen-ion concentration. However, since the difference in potential between the hydrogen and quinhydrone electrodes in the same solution is not a function of the hydrogen-ion concentration but of the total electrolyte present, little difference between the values in the two series would be expected. This proved to be the case. The mean values at 25 ± 0.01° were: for (a) 0.69903 ± 0.00002 volt, for (b) 0.69898 ± 0.00002 volt. When the quinhydrone electrode is part of a cell involving liquid junction 0.6990 volt should be used for both (a) and (b). Due to its reproducibility and constancy we are convinced that in all around qualifications this standard quinhydrone electrode excels either the 0.1 N or saturated calomel electrode.

The above potentials differ appreciably from the ideal value for the cell Pt/H_2, electrolyte, quinhydrone/Au because of the salt error. This will be considered in a later report.

MORLEY CHEMICAL LABORATORY   FRANK HOVORKA
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RECEIVED NOVEMBER 17, 1933

ADDITION OF HYDROGEN BROMIDE TO 4,4-DIMETHYLPENTENE-1

Sir:

The addition of halogen acids to substituted ethylenes has been under investigation in our laboratory for some time, particularly as regards the effects of peroxides and antioxidants on the direction of addition. For certain theoretical reasons these studies included the addition of halogen acids to 4,4-dimethylpentene-1.

In view of the recent publication of Whitmore and Homeyer [THIS JOURNAL, 55, 4555 (1933)] it appears desirable to publish some of our pertinent findings.

Our results indicate that the direction of addition of hydrogen bromide to 4,4-dimethylpentene-1 is governed by the peroxide content of the material or reagents. From that standpoint the compound 1-bromo-4,4-dimethylpentane, the product first isolated by Whitmore and Homeyer, is what we define the "abnormal" product of the reaction. This product is formed whenever the addition of halogen acid is carried out in air, or when the mixture contains peroxides. On the other hand, if the addition of hydrogen bromide is carried out *in vacuo* in the presence of good antioxidants, the isomeric 2-bromo-4,4-dimethyl-

pentane is obtained. It is this last product that we consider the "normal" product of the reaction.

In conformity with what we have just stated, we find that if the addition of hydrogen bromide to 4,4-dimethylpentene-1 is carried out *in vacuo* (instead of in air) 50% of the 2-bromo-4,4-dimethylpentane is obtained. The physical constants of the hitherto unknown 2-bromo-4,4-dimethylpentane are: b. p. 59.4° at 34 mm.; n_D^{20} 1.4463; while those of the 1-bromo-4,4-dimethylpentane under the same experimental conditions are: 68.8° and 1.4485. The table summarizes some of our results. The yields were excellent in all cases.

No.	Mole of olefin	Mole HBr	Reagent added, in mole
1	0.046	0.075	Ascaridole, 0.0012
2	.046	.075	None
3	.045	.079	Acetic acid, 0.075
4	.048	.077	p-Thiocresol, 0.0024
5	.049	.088	Diphenylamine, 0.0030

No.	Gas in bombs	n_D^{20}	2-Isomer, % ·· 10%
1	Air (R. T.)	1.4483	0
2	Vac. (0°)	1.4474	50
3	Vac. (0°)	1.4479	27
4	Vac. (R. T.)	1.4469	73
5	Vac. (R. T.)	1.4463	100

JONES CHEMICAL LABORATORY   M. S. KHARASCH
UNIVERSITY OF CHICAGO   CHESTER HANNUM
CHICAGO, ILLINOIS   M. GLADSTONE
RECEIVED NOVEMBER 20, 1933

THE RULE OF SHIFT (VERSCHIEBUNGSGESETZ)

Sir:

Efforts to discover an indirect method for the correlation of the configurations of structurally similar substances have led to the enunciation of several rules all of which may be classed under the general heading of the "Rules of Shift." The earliest of these is perhaps that of Tschugaeff[1] stating that in homologous series the rotations of individual members increase asymptotically to a maximum value. To the same group belong the "Lactone Rule" of Hudson,[2] the "Phenylhydrazide Rule" of Levene,[3] etc. In its most comprehensive form (presented by K. Freudenberg[4]) the rule states that in similar, configurationally-related substances an identical substitution on identical groups produces a shift of rotation in the

(1) Tschugaeff, Ber., 31, 360 (1898); Chem. Zentr., I, 93 (1905); Trans. Faraday Soc., 10, 70 (1914).
(2) Hudson, THIS JOURNAL, 40, 813 (1918); 40, 1141 (1919).
(3) Levene, J. Biol. Chem., 23, 145 (1915).
(4) Freudenberg, Ber., 66, 177 (1933).