irradiation, however, the total pressure reached a maximum value, while the partial pressure of NO_2 continued to decrease; from this we conclude that the ethylene had reacted at an appreciable rate after an induction period.

Nitric oxide was one of the final products, as shown by the absorption bands near 2260 Å. That ethylene oxide and acetaldehyde were among the final products was indicated by the pressure changes developed upon warming the freeze-out trap gradually from −195° to room temperature (after termination of irradiation and reaction). Additional oxidation products, besides the isomers of C_2H_4O, must have been formed since, although the original partial pressure of nitrogen dioxide was greater than that of ethylene, reaction proceeded to the exhaustion of the nitrogen dioxide.

Irradiation of ethylene–nitrogen dioxide mixtures with the shorter wave lengths of ultraviolet (270–220 mμ) also produced reaction. Preliminary experiments indicate a difference in behavior for this radiation than for the longer wave lengths of ultraviolet. Inasmuch as ethylene does not absorb the shorter wave length ultraviolet used, it should be ideal for the study outlined.

Conclusions

The two gases (carbon disulfide and ethylene) that were found to react with nitrogen dioxide when the gas mixtures were irradiated with ultraviolet light are known to react rapidly with oxygen atoms, while the two gases (carbon monoxide and methane) that did not react with nitrogen dioxide when the gas mixtures were irradiated, are known to react very slowly with oxygen atoms. Thus, Harteck and Kopsch[7] found that both carbon disulfide and ethylene reacted rapidly with the oxygen atoms obtained from a discharge tube, while methane and carbon monoxide reacted very slowly with oxygen atoms produced in this way. Our results show that oxygen atoms produced by the photolysis of nitrogen dioxide react with carbon disulfide and with ethylene at a rate comparable to the fast reaction of oxygen atoms and nitrogen dioxide.

Summary

Both methyl alcohol and hydrogen chloride react rapidly with nitrogen dioxide in the dark.

Neither carbon monoxide nor methane reacts with nitrogen dioxide in the dark or under the influence of ultraviolet radiation until the temperature of the gases is greater than 250°.

Neither carbon disulfide nor ethylene reacts with nitrogen dioxide in the dark at room temperature. Under the influence of ultraviolet radiation ($\lambda > 310$ mμ), however, each reacts with nitrogen dioxide at room temperature. The oxygen atoms produced in the photolysis of the nitrogen dioxide react rapidly with carbon disulfide and ethylene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Determination of α-Glycerophosphates in Aqueous Solutions by Means of Lead Tetraacetate

BY D. J. WORMITH AND J. J. RAE

Baer[1] finds that under certain conditions oxidations with lead tetraacetate can be performed in aqueous solutions. We have therefore utilized Carrara's[2] method employing this reagent to determine the percentage of calcium α-glycerophosphate in mixtures of the alpha and beta forms in aqueous solution.

Various factors have been found to affect the concordance and accuracy of these determinations. The presence of hydrochloric acid and of water is desirable to promote the solubility of the calcium or barium glycerophosphates, but too great a concentration of the acid or too much water causes loss of oxidizing power due apparently to hydrolysis of the tetraacetate. Again sufficient time must be given for the completion of the reaction, but treatment should not be continued too long, since under the conditions of analysis a spontaneous reduction of the tetraacetate takes place at the rate of 3% per day.

(1) E. Baer, M. J. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607 (1939).

(2) G. Carrara, *Giorn. Chim. ed. App.*, **14**, 236 (1932).

By systematic variations of the conditions the following preferred procedure was finally fixed upon.

To 0.2-g. samples of glycerophosphate, 25 cc. of water, 1.4 cc. of 0.1 *N* hydrochloric acid (0.003 *N*) and 20 cc. of 0.1 *N* lead tetraacetate (0.05 mole per liter) in glacial acetic acid are added and the solutions allowed to stand at room temperature for six hours. Controls containing 20 mg. of sodium dihydrogen phosphate, which prevents the hydrolysis of the lead tetraacetate without causing any reduction, in place of glycerophosphate, are allowed to stand the same length of time. Then 15 cc. of potassium iodide reagent, containing 500 g. of sodium acetate and 20 g. of potassium iodide per liter, is added and the iodine titrated with standard 0.1 *N* sodium thiosulfate solution.

Using this procedure the following results on a mixture of alpha and beta salts were obtained.

TABLE I

Glycerophosphate in sample, g. Calcium alpha	Sodium beta	% alpha	0.1 *N* lead tetraacetate reduced, cc. Found	Calcd.	% alpha calcd.
0	0.20	0	0.22	0	0
0.05	.15	25	4.57	4.38	25.3
.10	.10	50	8.82	8.76	50.2
.15	.05	75	13.04	13.14	74.6
.20	0	100	17.40	17.52	98.1

The advantages of lead tetraacetate over periodic acid are: (a) it is more easily available; (b) it gives a sharper end-point; (c) it does not continue to act as rapidly after the true end-point has been reached and (d) its blank test correction is smaller.

Summary

Lead tetraacetate can be used successfully for the quantitative determination of α-glycerphosphates in aqueous solutions according to the procedure outlined.

TORONTO, CANADA RECEIVED JUNE 23, 1941

NOTES

Sulfapyrazine, Sulfapyrimidine and "Sulfadiazine"*

BY RUDOLPH C. ELLINGSON

It is known that pyrazine monocarboxylic acid is of low toxicity in comparison with the α- and β-carboxylic acids of pyridine.[1] This and other considerations led me to synthesize the pyrazine analog of sulfapyridine, in the expectation that it would carry the desirable feature of low toxicity to the drug.

2-N⁴-Acetylsulfanilamidopyrazine, m. p. 250–252° (dec.), was obtained by allowing *p*-acetaminobenzenesulfonyl chloride to react with 2-aminopyrazine in pyridine. This compound was deacetylated by acid hydrolysis, giving 2-sulfanilamidopyrazine, m. p. 255–257° (dec.). Both compounds are colorless and tasteless. When the latter is suspended in ethanol and treated with sodium hydroxide, sodium 2-sulfanilamidopyrazine monohydrate is obtained.

TABLE I

Compound		C	H	N	S	Na	H_2O
2-N⁴-Acetylsulfanilamidopyrazine, $C_{12}H_{12}O_3N_4S$	Calcd.	49.3	4.1	19.2	11.0		
	Found	49.4	4.7	18.5	11.0		
2-Sulfanilamidopyrazine, $C_{10}H_{10}O_2N_4S$	Calcd.	48.0	4.0	22.4	12.8		
	Found	48.4	4.2	21.9	13.0		
Sodium 2-sulfanilamidopyrazine monohydrate, $C_{10}H_9O_2N_4SNa \cdot H_2O$	Calcd.			19.3		7.9	6.2
	Found			19.2		7.8	6.5

The solubilities of 2-sulfanilamidopyrazine and its acetyl derivative in 100 cc. of water at 37° are 5.2 and 5.6 mg., respectively. Thus 2-sulfanilamidopyrazine shares with its isomer, 2-sulfanilamidopyrimidine,[2] a pharmacologically desirable property,[3] not exhibited by most of the sulfa drugs in common use.

The *p*H of a 10% solution of sodium 2-sulfanilamidopyrazine monohydrate in physiological saline was 9.3 (glass electrode, corrected for sodium ion). Comparably, the sodium salts of sulfapyridine, sulfathiazole and sulfapyrimidine gave *p*H values of 10.7, 10.0 and 10.2, confirming Feinstone, *et al.*[4]

To avoid possible confusion between sulfapyridine and sulfapyrimidine, Roblin and co-workers[2] suggest that the latter be called sulfadiazine. Since our "sulfapyrazine" is also a sulfadiazine, it would seem that the use of these abbreviations, although convenient for physicians, is by no means ideal. In theory, there are six possible sulfadia-

* Original manuscript received March 18, 1941.

(1) Bills, McDonald and Spies, *Southern Med. J.*, **32**, 793 (1939).

(2) Roblin, Williams, Winnek and English, THIS JOURNAL, **62**, 2002 (1940).

(3) Northey, *Chem. Rev.*, **27**, 108 (1940).

(4) Feinstone, Williams, Wolff, Huntington and Crossley, *Bull Johns Hopkins Hosp.*, **67**, 430 (1940).