TABLE I

MERCURY-SENSITIZED HYDROGENATIONS

Reactants	Vol. cc.[a]	Mol. act.[b]	Vol. cc.[a]	Mol. act.[b]	Vol. cc.[a]	Mol. act.[b]	Vol. cc.[a]	Mol. act.[b]
C_2H_2	15.2		23.4		26.2			
C_2H_4							25.5	
H_2	129	1.00	213	1.00	220	1.00	225	1.00
Products								
H_2	127	1.00	196	1.02	202	1.03	210	1.01
C_2H_2	13.0	0.022	5.1	0.21	3.5	0.32		
C_2H_6	0.25		1.0	0.88	1.3	0.97	2.45	0.76
C_4H_{10}	0.25		0.6	1.4	0.75	1.5	8.0	0.64
"C_6" + "C_8"			0.75	1.04	0.92	1.03	2.4	0.55

[a] Cc. of gas at S.T.P. [b] Relative tritium content per mole of compound; initial H_2 = 1.00.

will be produced in reaction 2, and tritium may be introduced into the product either by reactions of tritium atoms or by reactions of free radicals with the HT molecules. Reactions involving HT molecules will, in general, occur more slowly than those involving H_2; tritium atoms may react either more or less rapidly than protium atoms.[5]

The results of several experiments are summarized in Table I. The distributions of reaction products are similar to those found in other investigations[6] of these reactions, except that the formation of the C_6- and C_8-hydrocarbons has not been reported previously. In the reaction with ethylene no polymer formation was observed and material and activity balances are good. In the acetylene reaction, large amounts of polymer formed on the quartz tube; from material balances, the ratio of H_2 to C_2H_2 in this polymer is about 0.6.

Perhaps the most unexpected result is the slowness of the exchange between hydrogen gas and acetylene compared to the rates of hydrogenation and polymerization. After 87% of the acetylene has been consumed, the ratio of the molar activity of acetylene to that of hydrogen is only 0.32; at equilibrium[7] this ratio should be about 3. This is in marked contrast to the reaction[8] of acetylene with deuterium atoms from a discharge tube which leads to almost complete exchange with little loss of acetylene. This difference in behavior is undoubtedly attributable to the much higher hydrogen atom concentration produced in the discharge tube, which favors the reactions[8]

$$C_2H_2 + H \longrightarrow C_2H + H_2 \qquad (3)$$

$$C_2H + H \longrightarrow C_2H_2 \qquad (4)$$

or

$$C_2H_2 + H \longrightarrow C_2H_3 \qquad (5)$$

$$C_2H_3 + H \longrightarrow C_2H_2 + H_2 \qquad (6)$$

whereas in the mercury photosensitized reaction the hydrogen atom concentration is kept so low by reaction 3 or 5 that the C_2H or C_2H_3 radical first formed has an opportunity to react with molecular hydrogen or acetylene.

It is of interest that the tritium content per mole of the ethane produced both from ethylene and from acetylene is lower than that of the hydrogen in spite of the facts that the ethane from acetylene has incorporated two molecules of hydrogen, and that some of its tritium was introduced into the acetylene by exchange. The preferential incorporation of protium rather than tritium is in accord with expectation for reactions with molecular H_2 and HT; it might also result from a difference in the relative rate of production of protium and tritium atoms in reaction 2. Another point of interest is the ratio of the molar activity of butane to that of ethane. In the acetylene reaction this ratio is about 1.6, while in the ethylene reaction it is 0.8. From the postulate[9] that in both reactions the butane is formed by the recombination and the ethane by the disproportionation of ethyl radicals, it would be expected that these ratios would be the same, even though the molar activity of the ethyl radicals differed. The large difference between the observed ratios appears to be incompatible with such a postulate.

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[5] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[6] D. J. LeRoy and E. W. R. Steacie, *ibid.*, **12**, 369 (1944); W. J. Moore and H. S. Taylor, *ibid.*, **8**, 504 (1940).

[7] Estimated from vibration frequencies in F. Halverson, *ibid.*, **19**, 87 (1947); using the method of calculation in H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[8] K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B29**, 215 (1935).

[9] Reference 4, pp. 261, 265, 268.

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Nitric Oxide Interference in Nitrogen Isotope Analyses with the Mass Spectrometer[1,2]

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While conducting biological studies involving N^{15} as a tracer, an abnormally high mass 30 peak was often encountered in the mass spectrometer curves particularly when large samples were oxidized by the Dumas method.[3] Of the two equations which may be employed to compute atom per cent. N^{15}, erratic values were obtained using the direct method, while the indirect method yielded consistent results. The former requires experimental values for mass 30 as well as for masses 28 and 29; the latter represents mass 30 in terms of masses 28 and 29 based on the statistical occurrence of the $N^{15}N^{15}$ molecule. Both methods should yield the same results within the experimental limits of the spectrometer. However, the

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[1] This work was supported by a grant-in-aid from the Nutriton Foundation, Inc.

[2] Presented before the Regional Conclave, American Chemical Society, held in New Orleans, Louisiana, December, 1953.

[3] J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," John Wiley and Sons, Inc., New Yok., N. Y., 1938, p. 60

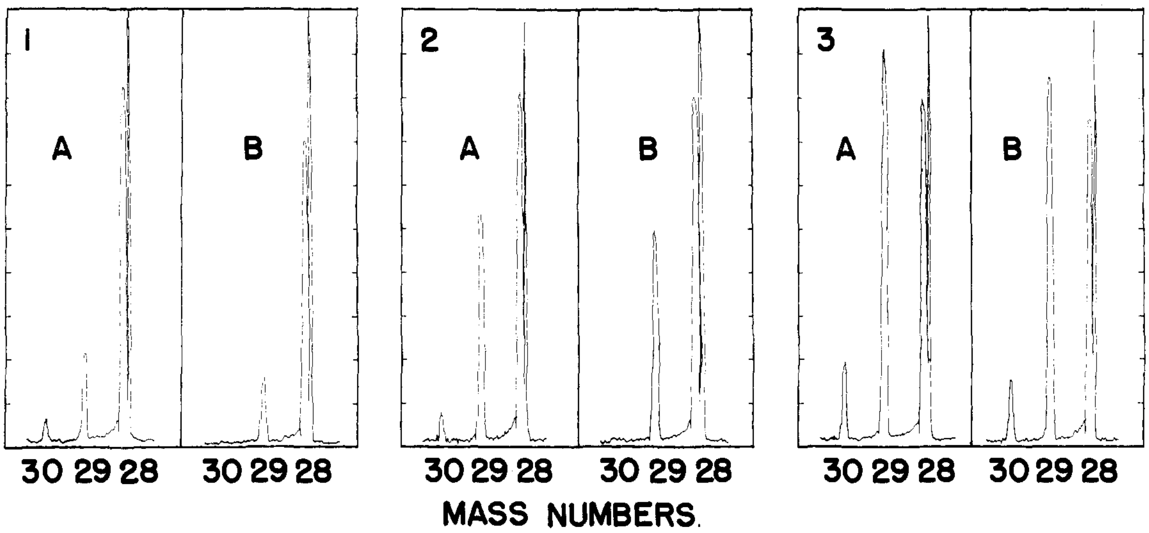

Fig. 1.—Mass spectrometer curves obtained in the analysis of nitrogen samples before and after treatment with alkaline potassium permanganate: 1, unlabeled arginine; 2 and 3, N^{15}-glutamine containing different amounts of N^{15}; Curves A, no further treatment; curves B, samples shaken in alkaline permanganate.

use of the former method resulted in consistently higher values. In the analysis of 48 samples of varying N^{15} content, the average deviation between results obtained by the two methods was 24%. It was brought to our attention that nitrogen samples from other institutions analyzed by the mass spectrometer also gave abnormally high mass 30 peaks.[4]

It appeared possible that some nitric oxide resulting from the combustion was escaping reduction and thus was contaminating the samples with a gas of mass 30. Since nitric oxide is easily removed from nitrogen samples by shaking in alkaline potassium permanganate, this principle was applied to the samples resulting from the Dumas method.

Experimental

Duplicate samples were oxidized in a Dumas combustion furnace. One sample of gas from each pair was analyzed by the mass spectrometer without further treatment, while the gas resulting from combustion of the other sample was drawn into a Van Slyke deaminization apparatus and shaken for two minutes in a solution containing 40 g. of potassium permanganate and 18 g. of sodium hydroxide per liter of water. Care was taken during the transfer of the samples to exclude all air.

Results and Discussion

The difference in the volume of the gas before and after the permanganate treatment was too small to be detected in the gas buret.

Figure 1 shows typical mass spectrometer curves which resulted from the analysis of nitrogen from unlabeled arginine and from N^{15}-glutamine prepared in this Laboratory.[5]

From these curves it appears evident that nitric oxide is the source of the erratic mass 30 peaks. Values for the atom per cent. N^{15} in the samples calculated from the measured peaks of these curves, listed in Table I, confirm this.

It is apparent that for samples which contain a large atom per cent. of N^{15} this abnormality should not seriously influence the results. However, for samples which contain a low atom per cent. of N^{15}, traces of nitric oxide may seriously influence the results obtained in calculating the absolute concentration of N^{15} present in a labeled sample.

TABLE I

ATOM PER CENT. N^{15} IN NITROGEN SAMPLES ANALYZED BY MASS SPECTROMETER CALCULATED BY BOTH METHODS

	No treatment		$KMnO_4$ treatment	
Nitrogen source	Direct method	Indirect method	Direct method	Indirect method
Unlabeled arginine	0.52	0.37	0.38[a]	0.38
N^{15}-Gutamine	1.91	1.75	1.78	1.78
N^{15}-Glutamine	7.92	7.85	8.14	8.08

[a] Mass 30 peak value is zero.

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[4] Private communication, Dr. Glen D. Hallmark.

[5] D. W. Hood and C. M. Lyman, *Arch. Biochem.*, **30**, 351 (1951).

The Ternary System Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°[1]

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In the course of preliminary study of possible solid solution formation between lithium alum[2] and soda alum, it was found contrary to a previous report[3] of the system Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 0° that soda alum does exist as a solid phase in stable equilibrium with saturated solutions at this temperature. Partial reinvestigation of this system was undertaken to determine the compositions of the isothermally invariant solutions. It revealed that although incongruently soluble the alum exists as a stable saturating phase over a considerable range

[1] The work reported in this note was supported in part by a grant from the National Science Foundation, Grant G159.

[2] H. A. Horan and J. J. Duane, THIS JOURNAL, **63**, 3533 (1941).

[3] J. T. Dobbins and J. A. Addleston, *J. Phys. Chem.*, **39**, 637 (1935).