Hydrogen Formation During Hydrazine Reduction of Oleic Acid[1]

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Abstract

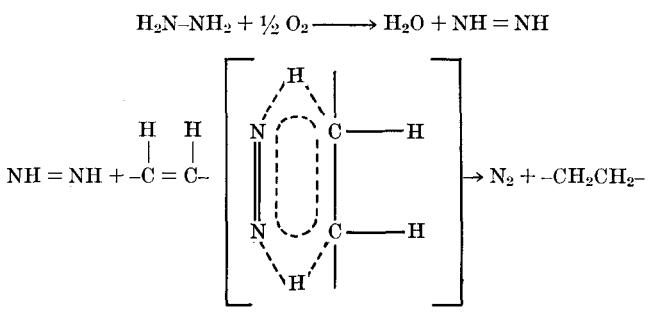
Hydrogen has been detected in the gas phase when oleic acid is reduced with hydrazine. The rate of hydrogen production has been followed during this reaction by coupling a gas chromatograph to an automated manometric system. The observation of hydrogen evolution alters prior concepts which assume that nitrogen is the only gas given off. Equations involving hydrazine autoxidation, hydrogen production, and reduction of double bonds have been postulated and their stoichiometry studied.

Introduction

IN STRUCTURAL STUDIES of hydrogenated fatty acids, hydrazine reduction has been employed to convert dienes to monoenes, since this reaction does not alter the position and geometric configurations of the residual bonds (11–13). An empirically determined choice of time, temperature, and oxygen flow is made so as to stop the reaction at a desired degree of reduction corresponding to maximum yield of monoenes. A continuous method is needed for following the progress of the reaction to the optimal point.

Reduction with hydrazine is accomplished, paradoxically, by autoxidation. It is postulated (8,10) that the unstable intermediate diimide (NH = NH) formed by oxidation reduces the double bond as follows:

$$H_2N\text{–}NH_2 + \tfrac{1}{2}\,O_2 \longrightarrow H_2O + NH{=}NH$$



The stoichiometry of these reactions would indicate that for each double bond reduced, ½ mole of oxygen would be consumed and 1 mole of nitrogen released—a net increase in volume of ½ mole. By following the increase in gas volume, the course of the reaction could be monitored.

Earlier research (2,3,8,10) indicated that nitrogen is the only gas liberated during the reaction; however, in the course of our work we discovered that hydrogen also evolves (6). Therefore, we can more accurately predict the progress of the reduction of the liquid phase by including hydrogen in the measurements for the changes in composition and volume of the gas phase.

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Experimental Procedures

All hydrogenations were performed in an automated manometric apparatus (5) modified from its previous use in heterogeneous catalytic reductions (7). Fig. 1 is a block diagram of the apparatus. The dry ice condenser, 6-way valve, electronic timer, and gas-liquid chromatograph (GLC) are additions to the earlier system (5). The condenser trap was necessary to prevent any solvent or water vapors from reaching and interfering with operation of the GLC column. Adding the 6-way valve and electronic timer permits automatic sampling of the gas phase (i.e., every 10 min). Each gas sample is analyzed by the GLC and recorded with one pen of the dual channel recorder. The second pen indicates volume change, which is followed with a pressure sensor and servo-driven syringe. A pump circulates the gases within the closed system. The reactor consists of a 10-ml flask with a magnetic stirrer and a small piece of capillary tubing extending into the reaction mixture. Capillary tubing allows the circulating gases to be bubbled through the reaction mixture at approximately 65 cc/min.

The procedure for each experiment consisted in filling the closed reaction system with oxygen and stabilizing accessory equipment, including electronics, dry ice–acetone condenser, and oil bath temperature (50C); then in the following order, 8.5 cc of 95% ethanol, 0.5 cc of oleic acid, and 1 cc of hydrazine hydrate were injected into the reaction flask at atmospheric pressure. The molecular ratio of hydrazine to oleic acid was 13:1. A high molecular ratio of hydrazine to oleic acid was used because previous studies indicated hydrazine is rapidly decomposed by autoxidation in the presence of pure oxygen (4). The GLC column was operated at room temperature and was packed with type 5A molecular sieve. Flow rate of argon gas in the column was 55 cc/min. Hydrogen was determined by comparison of peak heights with known amounts of injected hydrogen. Planimetric integration was used to determine oxygen and nitrogen.

Approximately 10 samples of the liquid reaction mixture were removed during the course of each experiment. In the first run, 50 μl samples were

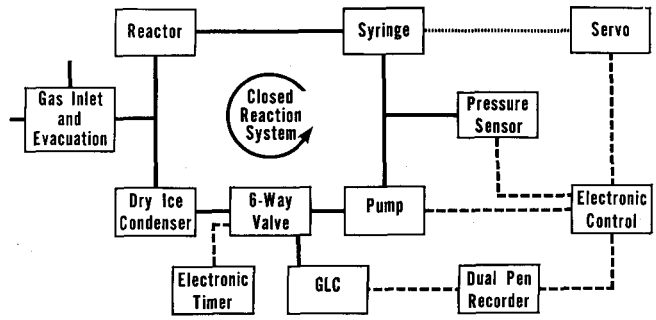

FIG. 1. Block diagram of automated manometric apparatus for hydrogenations. Dashed lines indicate electrical connections; dotted lines, mechanical connections; solid lines, tubing coupling.

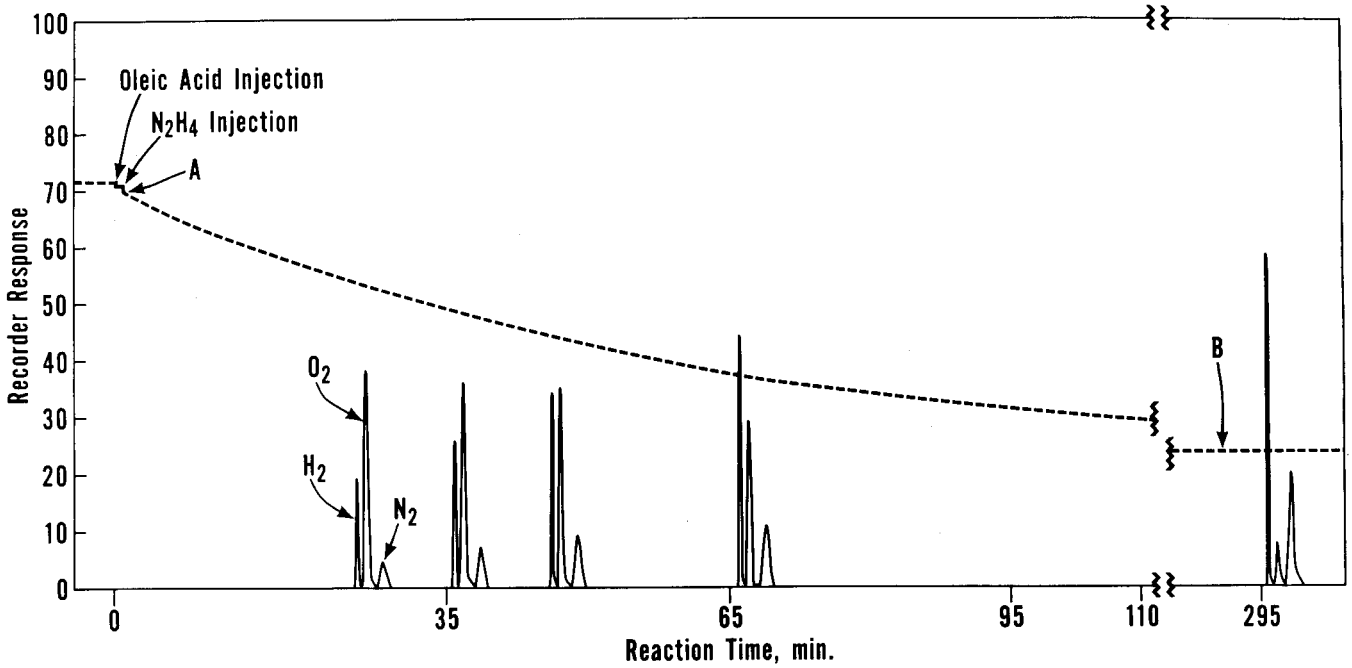

FIG. 2. Reproduction of recording made during a hydrazine—oleic acid reduction. Upper trace—volume change. Lower trace—GLC analyses. Point A—reaction initiation. Point B—end of reaction. Recorder response equivalent to 0–50 cc.

taken; during the second, 100 μl samples. Each sample was placed in recently boiled distilled water and titrated with 0.1 N HCl in a Beckman automatic titrator. The end point of pH 4.8 was selected after running a pH curve for hydrazine versus 0.1 N HCl. Comparisons were made of the titration of hydrazine alone and of hydrazine mixed with the appropriate amount of fatty acids. No measurable interference of fatty acids was observed. After titration, the samples were dissolved in pentane-hexane (PE), placed in separatory funnels, and washed with distilled water; the PE was evaporated from the sample over a steam bath under nitrogen. The acids were then converted to methyl esters by using diazomethane and analyzed on an Argon "Pye" chromatograph equipped with a 4 ft by ¼ in. glass column packed with 11% EGSS-X (Applied Science Laboratories).

Results

Fig. 2 shows the volume change and gas analyses as recorded during a hydrazine–oleic acid reduction. Since each division for the recorder response is equivalent to 0.5 cc of system volume (0 to 100 scale = 0 to 50 cc), the total volume change is easily determined as the difference between the points of injection of the hydrazine (A) and where the curve levels off near the end of the run (B); in this example, 23.5 cc. The lower trace is the GLC analyses of the gas samples taken approximately every 10 min. All samples are not shown, to keep the figure legible. Each series of three peaks as noted on the recording corresponds to hydrogen, oxygen, and nitrogen, in that order. As the reaction progresses, hydrogen and nitrogen increase in concentration while oxygen decreases.

A similar progression of the GLC analyses is noted during the autoxidation of hydrazine in ethanol when no oleic acid is present, except that little hydrogen is formed and the decrease in volume is small.

Fig. 3 compares the hydrazine consumed, nitrogen released, and oxygen reacted, respectively, when oleic acid is present and absent in the reaction mixture. Since the difference between the two curves of each figure is only slight, autoxidation of hydrazine is the primary reaction (2,4) and the reduction of double bonds, secondary.

A significant difference is apparent in the amount of hydrogen released in the presence and absence of oleic acid as shown in Fig. 4. In the presence of oleic acid, the hydrogen released is more than 10 times the amount when no oleic acid is present. An experiment was also performed in which only stearic acid was added to the reaction mixture. The hydrogen released was, within experimental error, the same as in the absence of oleic acid.

Discussion

To gain an integrated view of the hydrazine reaction, the analyses for one reduction of oleic acid are combined in Fig. 5. The gradual decrease in concentration of the reactants (oleic acid, hydrazine, and oxygen) and the gradual increase in gas volume, stearic acid, and nitrogen were as expected. What was unexpected was the release of hydrogen. As shown in Fig. 4, hydrogen increased to a concentration of 0.25 mmoles, or 4.5% of the gas phase.

Release of hydrogen was first postulated to explain discrepancies in the stoichiometry of the gas analyses. Mass spectrometric analysis of the gas phase during a reaction confirmed the presence of hydrogen gas. The hydrogen in the gas mixture went unnoticed previously by workers in the field, and it was not detected by us on a GLC column set up with helium as the carrier gas. By using heavier argon instead of helium as carrier gas a new peak preceding the oxygen peak was revealed and identified chromatographically as hydrogen.

The stoichiometry of the reduction of oleic acid with hydrazine has been studied extensively (1–4); however, the closed system experiments have not used GLC columns for gas monitoring, nor have they had

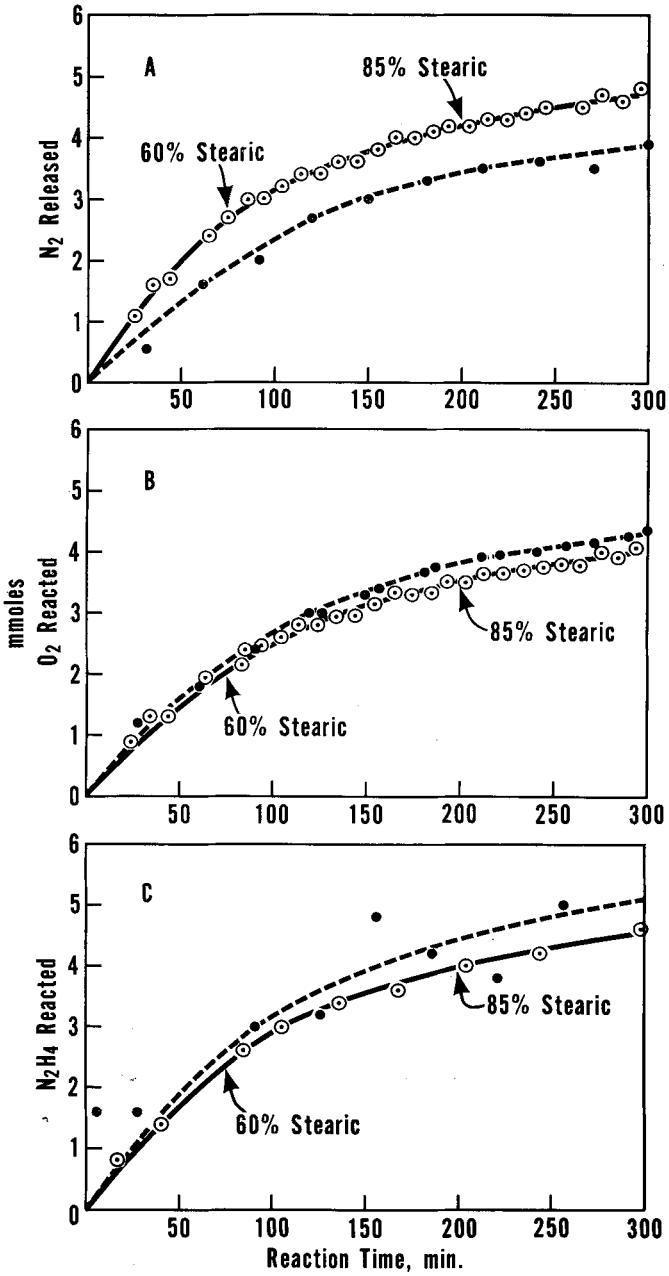

FIG. 3. Nitrogen (A), oxygen (B), and hydrazine (C) variations during hydrazine autoxidation without oleic (dashed lines) and hydrazine-oleic acid reduction (solid lines). Percentage of stearic acid indicates degree of reaction completion.

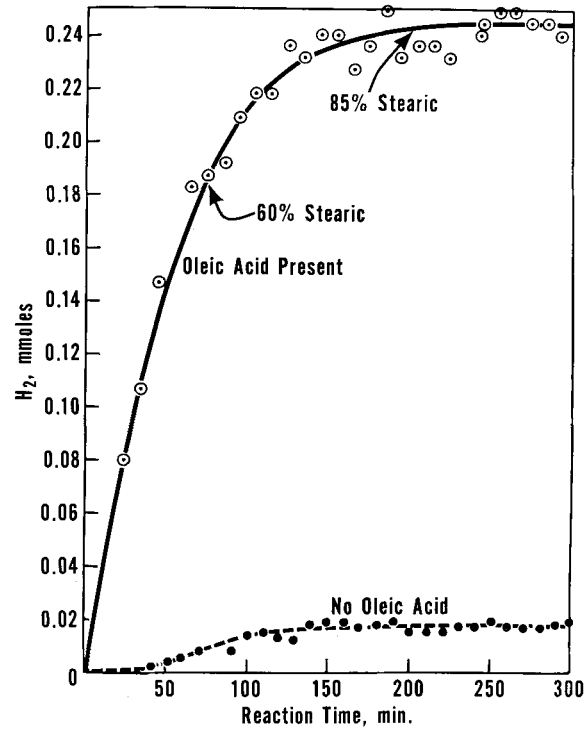

FIG. 4. Hydrogen release during hydrazine autoxidation (no oleic acid) and hydrazine oxidation-reduction (oleic acid present). Percentage of stearic acid indicates degree of reaction completion.

the convenience of an automated manometer apparatus. Earlier references give the following equation for the autoxidation of hydrazine (2–4):

$$N_2H_4 + O_2 \rightarrow 2\,H_2O + N_2 \qquad [1]$$

According to Equation 1, no gas volume change should occur during the course of the reaction.

When a double bond is reduced, it has been postulated that hydrazine reacts in the following manner:

$$\diagdown C = C \diagup + N_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow H_2O + N_2 + \underset{\vert\ \vert}{\overset{H\ H}{-C-C-}} \qquad [2]$$

Whereas for autoxidation of hydrazine (Equation 1) no gas volume change would be expected, i.e., N_2 release = O_2 uptake; for reduction, according to Equation 2, each 0.5 mole of oxygen absorbed should release 1 mole of nitrogen, or a net increase of 0.5 mole of gas. These anticipated simple relationships, however, were complicated by the discovery of hydrogen release as a concomitant reaction. Gas analysis on completion of reduction shows 4.5% to 5% of hydrogen. Thus, in the presence of a double bond, it is assumed a fraction of the hydrazine reacts to give free hydrogen and the equation becomes:

$$\vert\ \vert$$
$$-C = C- + N_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow$$
$$H_2O + N_2 + xH_2 + (1\text{-}x)\ \underset{\vert\ \vert}{\overset{H\ H}{-C-C-}} \qquad [3]$$

A possible intermediate in these reactions, as postulated by others (4,9), may be diimide (HN = NH). Evidence of such a molecule was obtained when mass spectrometer analyses of gas samples (taken directly above the reaction mixture) showed mass 30, which increased slightly during the reaction. Since the sensitivity of the mass spectrometer to this substance is not known and since other fragments, such as N^+ and O^+, would also give a mass 30 measurement, this evidence by itself is not conclusive.

It is apparent from Equation 1, or the autoxidation of hydrazine, that the difference between the volumes of oxygen absorbed and nitrogen released is zero; i.e., no net volume change occurs. From Equation 2, it may be deduced that mmoles of stearic acid formed = 2 (mmoles nitrogen evolved − mmoles oxygen absorbed).

If hydrogen release could be ignored, one could readily calculate the stearic acid formed by multiplying the observed gas volume increase in mmoles by 2.

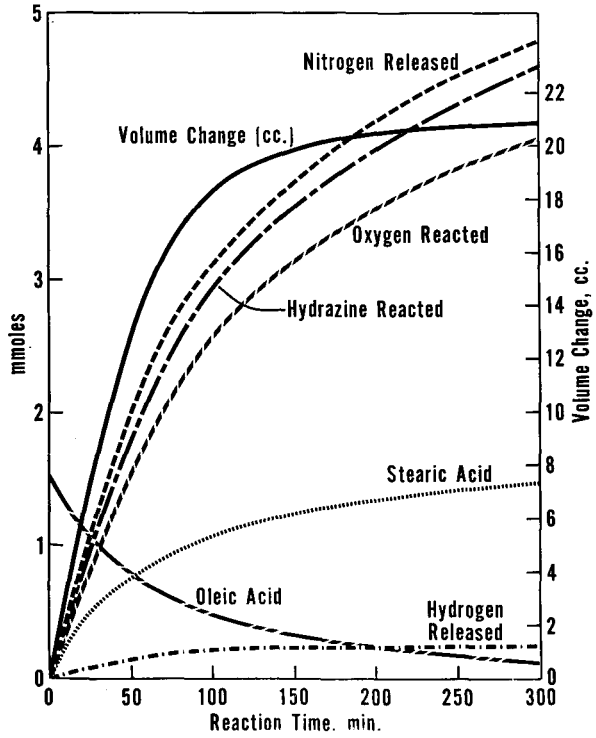

FIG. 5. Changing composition during a typical hydrazine–oleic acid reduction reaction.

Hydrogen is assumed to arise according to the following stoichiometry:

$$N_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow H_2O + N_2 + H_2 \qquad [4]$$

Thus, the correction for hydrogen release is included in Equation 5.

An attempt was made to compare the amount of double bond saturation calculated from gas analysis data with that determined by GLC analysis of the fatty acid mixtures. At any given time during the reaction, data are available from gas volume and analysis that permit calculation of mmoles of oxygen consumed, nitrogen released, and hydrogen released. An algebraic derivation was made using the simultaneous reactions shown as Equations 1, 2, and 4 to arrive at the following equation:

$$\text{mmoles stearic acid formed} = 2\,(\text{mmoles } N_2 \text{ released} - \text{mmoles } O_2 \text{ absorbed}) - \text{mmoles } H_2 \text{ released} \qquad [5]$$

The graph comparing the measured values of stearic acid with the calculated values based on Equation 5 is shown in Fig. 6. The differences observed between the two curves are not surprising when one considers the magnitude of cumulative errors of analysis involved and when one realizes that the calculation is based on the small differences between comparatively large values. Research is continuing on the practical application of this procedure for monitoring and calculating liquid-phase composition from gas-phase analyses.

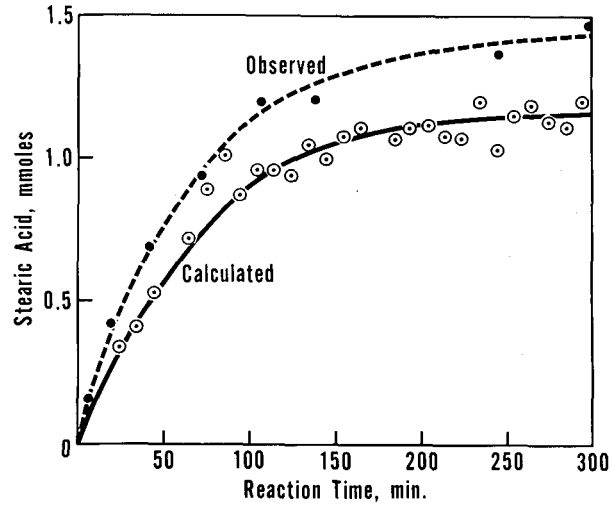

FIG. 6. Comparison of measured and theoretical degree of saturation when reducing oleic acid with hydrazine.

ACKNOWLEDGMENT

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