

Our unavoidable conclusion is that benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.⁵

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
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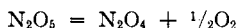
HENRY GILMAN
W. F. SCHULZ

COMMUNICATIONS TO THE EDITOR

THE STABILITY OF NITROGEN PENTOXIDE AT 1000 ATMOSPHERES OF OXYGEN IN THE PRESENCE OF NITROGEN TETROXIDE

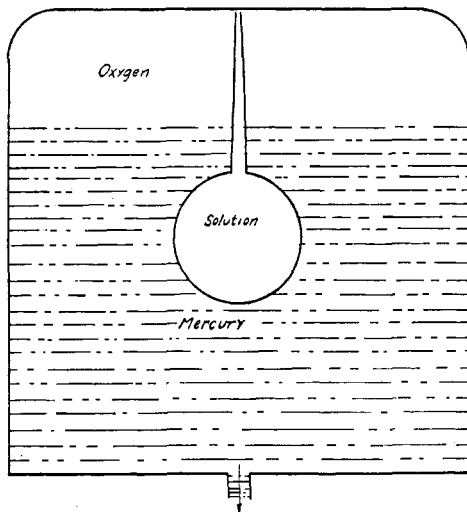
Sir:

The equilibrium



has been investigated at 1000 atmospheres' pressure of oxygen by dissolving nitrogen tetroxide and nitrogen pentoxide in carbon tetrachloride in an apparatus shown schematically in Fig. 1.

It was found that at this pressure of oxygen the reaction goes completely to the right. With the gas evolution apparatus used for analysis it was possible to detect as little as 0.5 cc. of oxygen, which, with the volumes of nitrogen pentoxide solution used, is equivalent to a partial pressure of 0.00155 atmosphere of nitrogen pentoxide at 25°. The partial pressure of nitrogen tetroxide in one of the runs was 0.710 atmosphere, so that the equilibrium constant in atmospheres is greater than 1.48×10^4 . The values given for the partial pressures depend on the assumption of a perfect solution of nitrogen tetroxide, nitrogen pentoxide and carbon tetrachloride and upon a solubility determination of nitrogen pentoxide in a solution of nitrogen tetroxide in carbon tetrachloride. This equilibrium constant gives a free energy change less



To pressure pump
and gage

Fig. 1.

⁵ Professor Rupe is in agreement with this conclusion, and he is now engaged in a further study of the constitution of the product obtained from citronellal and benzylmagnesium chloride.

than -5600 cal. Now, assuming that the entropy of nitrogen tetroxide is equal to or less than that of nitrogen pentoxide, then the total increase in entropy is equal to or less than 24 units, the entropy of $1/2\text{O}_2$. Using these values in the equation

$$\Delta F^\circ = \Delta H - T\Delta S^\circ$$

we obtain for ΔH a value equal to or less than 1600 calories.

The value given for ΔH in the "International Critical Tables" is 2690 cal. Either this value is too high or the entropy of nitrogen tetroxide is greater than that of nitrogen pentoxide, which would be surprising.

It was not feasible, with the apparatus used, to go higher than 1000 atmospheres' pressure.

DEPARTMENT OF CHEMISTRY
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LOUIS LEWON
HENRY EYRING

THE PHOTO-REACTION OF HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a recent communication [THIS JOURNAL, 52, 2793 (1930)] Rollefson and Lindquist criticize our conclusions [*Nature*, 127, 93 (1931)] regarding the photo-reaction of hydrogen and iodine monochloride, namely, that excited chlorine atoms *may* not be necessary for it to take place. They maintain that, as our hydrogen pressure was large compared with the pressure of iodine monochloride, the chlorine atoms (*excited to the 2P_1 state by collisions*) would have more chance of reacting with the hydrogen than with the iodine monochloride. Nevertheless, we have been able to bring about the reaction with hydrogen pressures (*circa* 70 mm.) comparable with the pressure of iodine monochloride.

We used Merck's crystalline iodine monochloride contained in a small glass tube which was subsequently broken in the reaction vessel. Hydrogen passing through a palladium tube was brought to the required pressure in the reaction vessel, which was then sealed up. The pressure was recorded on a glass spiral gage, and no contact with impurities, tap-grease, etc., was permitted [Ashley and West, *Nature*, 127, 308 (1931)]. The vessel was then irradiated with a mercury vapor lamp through a filter of quinine sulfate solution, and also through a filter of picric acid and cupric sulfate, transmitting only the 5461, 5764 and 5791 Å. lines. The reaction is slow but measurable, and the rate of iodine formation increases when the initial hydrogen pressure is increased. If the chain mechanism suggested is correct, the reaction, even under the most favorable conditions, could only have roughly 1/500,000 the speed of the hydrogen-chlorine reaction. Doubtless the reaction $\text{ICl} + \text{Cl} = \text{Cl}_2 + \text{I}$ takes

place as Rollefson and Lindquist suggest, but it would be unwise to infer from any of these experiments that the chlorine atom is unexcited.

Rollefson and Lindquist give only a few details of their experimental conditions, gas pressures, etc., but they mention one significant fact, namely, that their chlorine pressure was always large compared with the pressures of hydrogen and iodine monochloride. In these circumstances the iodine compound in the vapor phase may have been mainly iodine trichloride. This substance is of a lighter color than iodine monochloride, and must have an altogether different absorption spectrum. We have found that the vapors of iodine monochloride and chlorine react very readily, and, indeed, Rollefson and Lindquist themselves admit that they froze out iodine trichloride in the solid phase.

We do not wish to make any further statement until we have completed the study of the reaction kinetics.

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RECEIVED JUNE 2, 1931
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T. IREDALE
D. P. MELLOR

CATALYTIC REDUCTION OF MIXTURES OF PARA-NITRO- AND NITROSO-PHENOLS WITH KETONES

Sir:

It has recently been shown by the writer that *p-sec.*-alkylaminophenols are formed by the catalytic reduction of mixtures of *p*-nitro- or nitrosophenol and ketones at room temperatures [Major, THIS JOURNAL, 53, 1901 (1931)]. The suggestion was made that the reaction probably involved formation of *p*-hydroxy-phenylhydroxylamine as an active intermediate product of the reduction and that this compound condensed with the ketone and finally that the condensation product was reduced to the alkylaminophenol. Vavon and Krajićinović have reported that they have been able to make the condensation product between benzaldehyde and phenylhydroxylamine, $C_6H_5CH=N(O)C_6H_5$, by the catalytic reduction of a mixture of nitrobenzene and benzaldehyde [Vavon and Krajićinović, *Compt. rend.*, 187, 420 (1928)].

However, it was noted that heat was formed during the catalytic reduction of mixtures of *p*-nitro- and nitrosophenol and acetone. There remained, then, the possibility that the heat of the reaction between *p*-nitro- or nitrosophenol and hydrogen was sufficient to cause the *p*-aminophenol which formed to condense with the ketone. This condensation product would then be readily reduced to *p-sec.*-alkylaminophenol.

Evidence which apparently favored this point of view was obtained when a solution of 0.1 mole of *p*-aminophenol in acetone was heated to

the boiling point and then shaken with hydrogen in the usual way in the presence of a platinum oxide catalyst. Hydrogen was absorbed and 50% of the theoretical yield of *p*-isopropylaminophenol was recovered from the reaction mixture.

On the other hand, it was found that a mixture of 0.05 mole of *p*-aminophenol, 3.5 moles of acetone and 0.1 g. of Adams' platinum oxide catalyst did not absorb any more hydrogen than was necessary to reduce the platinum oxide when the temperature of the reaction mixture was kept at 4–5° or at 26–32.5°. The mixture was shaken at 4–5° for one hour and at 26–32.5° for two and three-quarter hours.

It was also found that in one and one-half hours very little *p*-isopropylaminophenol was formed during the reduction of a solution of 0.05 mole of *p*-nitrosophenol in 3.5 moles of acetone in the presence of the platinum oxide catalyst at 4–5°. On the other hand, in one hour at 16–32.5° the catalytic reduction of 0.05 mole of *p*-nitrosophenol in 3.5 moles of acetone gave a 60% yield of *p*-isopropylaminophenol.

It seems fairly evident, then, that while catalytic reduction of a mixture of *p*-aminophenol and acetone at elevated temperatures will produce *p*-isopropylaminophenol, this reduction does not occur to any appreciable extent during a few hours at room temperature. However, catalytic reduction of a mixture of *p*-nitrosophenol and acetone at room temperature does give *p*-isopropylaminophenol. Accordingly, it seems most likely that *p*-hydroxyphenylhydroxylamine is formed as an intermediate during the reduction and that due to its somewhat greater activity than *p*-aminophenol it condenses with the ketone and the condensation product is in turn reduced to *p*-*sec.*-alkylaminophenol.

LABORATORY FOR PURE RESEARCH
MERCER AND Co., INC.
RAHWAY, N. J.

RANDOLPH T. MAJOR

RECEIVED JUNE 11, 1931
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AN ADSORPTION METHOD FOR THE DETERMINATION OF THE AREA OF A POWDER

Sir:

The writers have devised a simple procedure which seems to give information that is more definite with respect to the area of a fine powder than that given by any earlier method.

The powder, titanitic oxide or silicon dioxide, for example, is dried in a high vacuum at as high a temperature as can be used without affecting the area of the crystals. The cool, dry powder is immersed in a solution of oleic acid, butyric acid or some other suitable acid, in very dry benzene, and the suspension is shaken until equilibrium is attained. After the

powder has settled, a sample of the supernatant liquid is drawn off. The benzene of this sample and of a sample of the initial solution is evaporated off, if oleic acid is the solute chosen, and the oleic acid left from each solution is dissolved in 95% ethyl alcohol. The alcohol solutions are then titrated with carbonate-free sodium hydroxide dissolved in water. The difference in concentration is considered to give the amount of acid adsorbed by the surface of the powder. Only air that is thoroughly dried by phosphorus pentoxide is allowed to enter the vessel in which the solution is prepared and the flasks in which the adsorption experiments are carried out.

Figure 1 shows how the amount of oleic acid adsorbed by the surface of one gram of powder varies with the concentration of the final or equilibrium solution of oleic acid in benzene. At concentrations above 0.01 to 0.02 mole per kilogram of benzene, the adsorption becomes practically constant, and the oleic acid on the surface of the grains of powder may be said to form a condensed film. There is some evidence which seems to indicate that this film is monomolecular.

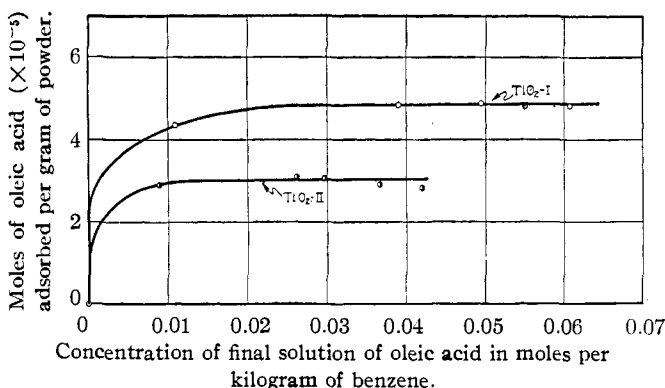


Fig. 1.

It may be assumed that the area occupied per molecule of oleic acid at the interface is 20.0 sq. Å., which is about the mean value for condensed films of the acid on water at a zero film pressure. On this basis, the area for TiO₂-I was calculated as 22.9 sq. m. per cc. of titanic oxide (3.89 grams), and for TiO₂-II as 14.4 sq. m. per cc. The ratio of these values is 1.59, while the ratio for the energy of immersion [Harkins and Dahlstrom, to be published] in ethyl acetate for the same two powders is 1.53, and the ratio of the weights of propyl alcohol adsorbed [Gans and Brooks, to be published] from the vapor per unit weight of these powders at a constant vapor pressure equal to one-half the saturation pressure at room temperature is 1.53.

The area of the powder TiO₂-II as determined for us by a microscopic

method [Dunn, *Ind. Eng. Chem., Anal. Ed.*, 2, 59 (1930)], applicable to crystalline powders, is 13.8 sq. m. per cc. of powder, on the assumption of a spherical shape for each particle. This is in good agreement with the value 14.4 obtained by the adsorption method. However, the closeness of the agreement is to some extent accidental, since the adsorption method includes the area of the colloidal part of the powder, which is not included by the microscopic method. Further comparisons with various other methods will be made later.

GEORGE HERBERT JONES LABORATORY
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WILLIAM D. HARKINS
DAVID M. GANS

RECEIVED JUNE 12, 1931
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CRYSTALLIZATION OF ANHYDROUS SODIUM ACETATE FROM AQUEOUS SOLUTION AT ROOM TEMPERATURE

Sir:

If the trihydrate of sodium acetate, $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$, is placed in a sealed tube and heated to 58° , it loses its water of crystallization and partially dissolves in this water. At 80° all the salt is dissolved. On cooling in the sealed tube, the writer, experimenting under the supervision of Professor Stuart Woodford Young, made the interesting and unexpected observation that the form crystallizing from this aqueous solution is anhydrous. This anhydrous form appears whether the solution be cooled rapidly or slowly, the only difference being in the appearance of the crystal. The slowly cooled solution will start crystallizing at only a few nuclei, from which there is a radial growth of thin needles. The rapidly cooled solution is immediately filled with small nuclei. Both of these are flattened and elongated orthorhombic crystals with the three indices of refraction lower than 1.45. This anhydrous form is shown by crystallographic observation, for which we are indebted to Professor A. F. Rogers, to be the same as the anhydride formed by direct dehydration, and the normal solubility curve is exhibited.

The crystals remain unaltered as long as the tube is kept sealed. Here, then, is a solution that is 2400% supersaturated and yet can be kept indefinitely in contact with the anhydrous form. Cooling below 0° has no effect, but cooling in liquid ammonia or liquid air brings about conversion to the stable trihydrate.

In 1904 and 1905 Dr. Young and W. E. Burke were able to form and identify ten new hydrates of sodium thiosulfate. At the beginning of the work on sodium acetate it was thought that some new hydrates might be produced, but so far none has been found.

This recent work of Dr. Young, who had been on the faculty of Stanford

University since 1892, was halted by his unexpected death on April 9, 1931, and is discontinued for the present.

DEPARTMENT OF CHEMISTRY
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WILLIAM W. CONNER

RECEIVED JUNE 15, 1931
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DISCONTINUITIES IN ADSORPTION ISOTHERMS

Sir:

In previous communications¹ we have shown that the adsorption of hydrogen by nickel and copper at low temperatures increases with pressure in a markedly discontinuous manner. Recently Allmand and Burrage² have reported a large number of isotherms for charcoal and silica gel which show discontinuities, and have suggested that the failure on the part of other investigators to detect this phenomenon is to be ascribed to an insufficient number of experimental points. In the course of an extended study, during the past four years, of the adsorption isotherms of hydrogen, nitrogen and carbon monoxide by nickel, copper and iron, at pressures up to one atmosphere and at temperatures which cover the range, -200 to $+200^{\circ}$, we have found a considerable number of discontinuous isotherms, and have studied them in some detail, particularly from the standpoint of the effects produced by temperature and the presence of poisons.

The evidence now available points clearly to the conclusion that a step-wise increase of adsorption with pressure is a general characteristic of the physical, or "secondary," type of adsorption. There is no evidence that discontinuities ever occur in "chemical" adsorption. The steps have been found under conditions which preclude the existence of liquid films or of multimolecular layers of gas; further, the phenomenon appears to have no direct relation to the "active spots" of catalytic theory.

We have been led to advance a new hypothesis of physical adsorption, according to which the observed steps represent the formation of concentric rows of adsorbed molecules, first at the edges of each crystal face, and building up successively toward the center. The evidence in support of this hypothesis rests primarily on the uniformity in the volumes corresponding to successive steps, and on the actual magnitude of the individual step. The mechanism by which adsorption can occur in successive rows may readily be derived on the assumptions that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules,

¹ Benton and White, *THIS JOURNAL*, **52**, 2325 (1930); also paper read at the Atlanta meeting of the American Chemical Society, April, 1930.

² Allmand and Burrage, *Proc. Roy. Soc. (London)*, **A130**, 610 (1931); *J. Phys. Chem.*, **35**, 1692 (1931).

and that physically adsorbed molecules possess mobility in the plane of the surface.

Details will follow shortly.

COBB CHEMICAL LABORATORY
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ARTHUR F. BENTON
T. A. WHITE

RECEIVED JUNE 18, 1931
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HAZARDS IN CATALYTIC HYDROGENATION AT ELEVATED TEMPERATURES AND PRESSURES

Sir:

T. S. Carswell [THIS JOURNAL, 53, 2417 (1931)] has reported an explosion which occurred while he was attempting to hydrogenate *o*-nitroanisole in the liquid phase with a nickel catalyst. He states that the purpose of his communication "is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale." There is no doubt that a warning is needed but in my opinion it should be against the procedure used by him and not against catalytic hydrogenation at elevated temperatures and pressures. This general method has been in successful use in this Laboratory for the past three years [THIS JOURNAL, 52, 4349, 5192 (1930); 53, 1091, 1095, 1402, 1425, 1868, 2012 (1931); *J. Phys. Chem.*, 35, 1684 (1931)] using a wide variety of compounds and dealing with quantities similar to those used by Dr. Carswell. The procedure used by him is, in my opinion, ill-advised in several respects. The bomb was inadequate and sufficient information was not available to him before the attempt was made to hydrogenate 400 g. of nitroanisole. A bomb for experimental purposes 15 cm. in diameter should have a wall thickness several times as great as that (5 mm.) used by Carswell. Our own bombs have a wall thickness of 2 to 2.5 cm. and are only 6 cm. in internal diameter. They were bored out of properly annealed rolls of nickel-chromium steel [*cf.* Ernst, *Ind. Eng. Chem.*, 18, 664 (1926)]. In order to control the rate of hydrogenation it is important that the bomb be provided with a thermometer or thermocouple well, so designed that there is little lag between the actual temperature of the liquid contents of the bomb and the reading of the temperature measuring device.

The temperature and amount of catalyst used by Carswell were excessively high for the compound to be hydrogenated, and apparently he made no attempt to control the rate of hydrogenation by control of the rate of shaking of the bomb. The reactions are quite exothermic and would result in local superheating if heat was being liberated more rapidly than it could be dissipated. In the hydrogenation of 100 g. of toluene with less than 0.5 g. of nickel, for example, we have observed a temperature rise of as much

as 150° within two or three minutes. In the hydrogenation of only 20 g. of nitrophenol at 100° with 0.3 g. of nickel a temperature rise of 100° was observed. It is not surprising that in the hydrogenation at 250° of 400 g. of nitroanisole in the presence of perhaps 50 g. of nickel, the temperature of the contents of the bomb rose so high that there resulted an explosive decomposition.

There is little doubt that after suitable investigation the catalytic hydrogenation of such compounds as nitroanisole can be carried out on a commercial scale in relatively light equipment. However, one is not justified, as Carswell has demonstrated, in attempting to hydrogenate even so small a quantity as a few hundred grams of material without preliminary study and without having available a properly designed bomb.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN

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HOMER ADKINS

POSITIVE ION CATALYSIS IN THE KNOEVENAGEL REACTION

Sir:

Dakin [*J. Biol. Chem.*, **7**, 49 (1909)] found that amino acids might be employed in place of the amines usually used to effect condensations of the Knoevenagel type. In the presence of amino acids, the velocity of the condensation of cinnamic aldehyde with malonic acid in 50% alcohol was found to increase with increase in the hydrogen-ion concentration of the solution [D. L. Klein, Master's Thesis, New York University, 1930]. This result suggested the amino acid cation to be a more active catalyst than the other ions derivable from the ampholyte. As is well known, secondary aliphatic amines are preferable to primary amines for the catalysis of reactions of this type. Since, as a rule, such secondary amines are stronger bases than the corresponding primary amines, it appeared that with such substances the amine ion is the active catalyst. In agreement with this concept various amines have been found to be more active catalysts in acid solutions.

Extremely weak bases such as urea do not ordinarily appear to catalyze condensations of the Knoevenagel type in aqueous or alcoholic solution. When, however, the solutions are made strongly acid, such weak bases display some catalytic activity. By taking advantage of the fact that weak bases dissolved in acetic acid appear to be highly dissociated, it was found that in this solvent urea and similar substances are extremely efficacious catalysts for the condensation of aldehydes with substances containing an "active" methylene group.

On the basis of these results, it is concluded that condensations of the

Knoevenagel type are instances of positive ion catalysis. The details of this investigation will shortly be submitted to THIS JOURNAL.

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RECEIVED JUNE 18, 1931
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KENNETH CLARK BLANCHARD
DAVID L. KLEIN
JOSEPH MACDONALD

THE SEPARATION OF COLUMBIUM AND TANTALUM

Sir:

When columbium is reduced in acid solution from a valence of five to a valence of three the solution becomes blue. In the course of a study of the electrolytic reduction of columbium, with a view to the separation of this element from tantalum, reduction in alkaline solution was attempted. Although no color change was obtained, the formation of an amalgam at the mercury cathode was noted. This suggested the possibility of obtaining metallic columbium in the form of an amalgam by reduction in alkaline solution. Shortly thereafter the writer's attention was called to the article of Fink and Jones,¹ where they show that tungsten can be plated from a saturated solution of sodium carbonate at elevated temperature and high current density. Since that time, the writer has found that, at a current density of approximately 3 amp./sq. dm. and a temperature of 103°, columbium may be plated from a saturated solution of sodium carbonate containing ignited columbium oxide (Cb₂O₅). A copper cathode was used. Tantalum will not plate out from a similar bath under identical conditions of temperature and current density. Further, it has been found that a metallic plate is obtained from a carbonate bath containing a mixture of the ignited oxides of columbium and tantalum using the same temperature and current density as that indicated above. It seems to be a fairly safe conclusion that only columbium may be plated from a saturated solution of sodium carbonate containing a mixture of the ignited oxides of tantalum and columbium.

At present further studies are being made concerning the nature of the plates obtained by this method.

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URBANA, ILLINOIS

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D. D. PEIRCE

¹ C. G. Fink and F. L. Jones, *Trans. Am. Electrochem. Soc.*, Preprint 59-27, 273 (1931).