

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

CONTRIBUTION FROM THE
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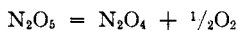
HENRY GILMAN
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COMMUNICATIONS TO THE EDITOR

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

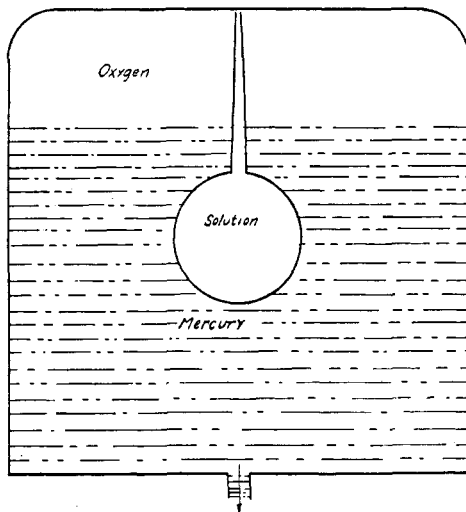
Sir:

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.

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LOUIS LEWON
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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