

A similar calculation using the data in Table I yields 30.32, which is in closer agreement with the calculated value.

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## COMMUNICATIONS TO THE EDITOR

### THE 4-*n*-ALKYL-GUAIACOLS

*Sir:*

In a recent paper by Coulthard, Marshall and Pyman [*J. Chem. Soc.*, 280 (1931)] on the variation of phenol coefficients, a number of *n*-alkyl guaiacols were prepared and studied. In view of the fact that the latter compounds were under investigation in the authors' laboratory at a much earlier date [Master of Science Thesis submitted by Norine Hower Howells at the Oklahoma A. and M. College, 1929] and since the methods of synthesis were somewhat different, it appears worth while to report briefly the results of this earlier work.

The 4-*n*-alkyl guaiacols were prepared here by the reduction of the corresponding acyl guaiacols, which were obtained after the method of Howells, Little and Andersen [THIS JOURNAL, 52, 4077 (1930)] by the oxidation of the carbinols resulting through the reaction of the benzoate of vanillin with *n*-alkylmagnesium halides. Unlike the work of Coulthard, Marshall and Pyman, the readily formed solid benzoate ester and diphenyl urethan were selected as derivatives for characterizing the new phenols.

The 4-*n*-pentyl guaiacol (b. p. 156–158° at 20 mm.) which resulted in good yields when 4-*n*-valeryl guaiacol was reduced by the Clemmensen method, was found also to have the maximum phenol coefficient for the series, comparable to the findings of the above authors.

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## INTERMEDIATE PRODUCTS IN THE THERMAL DECOMPOSITION OF AMMONIA

*Sir:*

An attempt has been made to identify the molecule NH as an intermediate product in the thermal decomposition of ammonia, through a study of the absorption spectrum of the decomposing gas. The emission band at  $\lambda\lambda$  3360–70, long known from photographs of the ammonia-oxygen

<sup>5</sup> This note is taken from a portion of a thesis submitted by Charles M. Blair in partial fulfilment of the requirements for the degree of Master of Arts.

flame, has been ascribed to the NH molecule by Hulthen and Nakamura [*Nature*, **119**, 235 (1927)]. Gaviola and Wood [*Phil. Mag.*, [7] **6**, 1191 (1928)] obtained the band in fluorescence, by the action of excited mercury atoms on a mixture of nitrogen and hydrogen. Recently Bates and Lavin [*Proc. Nat. Acad. Sci.*, **16**, 804 (1930)] were unsuccessful in obtaining this band in absorption from the active products issuing from a discharge in ammonia. They concluded, however, from a chemical study that the gas contained either NH or NH<sub>2</sub>.

Since it is possible that NH molecules formed on a surface may be unable to leave as free radicals, the attempt was made to obtain light absorption by the molecules on the surface in the following way: continuous ultraviolet radiation from a hydrogen discharge was focused, at a slight angle, at the end of a highly polished platinum tube whose ends were sealed into soft glass tubes furnished with plane quartz windows. The light suffered multiple reflections within the tube, and that coming out was focused on the slit of a Hilger quartz spectrograph. Ammonia was passed at a slow rate through the tube at atmospheric pressure in some experiments; in others the tube was filled with ammonia at various pressures and the rate measured simultaneously in a static system. The temperatures used were from 800 to 1125°.

Absorption in the region 3360 Å. could not be found on any of the plates. The absorption bands of ammonia from 2260 Å. to about 1900 Å. appeared very strong in all photographs taken at temperatures below 800° even at 20 mm. pressure. Above 800° these gradually disappeared, until at 1125° no trace remained. A few new weak bands, not previously reported, appeared in the region 2300–2450 Å. but were not sufficiently intense for wave length determinations. These may be due, perhaps, to absorption by ammonia in some higher vibrational state. We infer from the weak intensity of ammonia bands and from reaction velocity measurements that almost complete decomposition must have resulted at the higher temperatures. The duration of the absorption measurements was usually one-half hour.

Failure to detect the NH band can be due neither to insufficient decomposition of NH<sub>3</sub> nor to a too short life of the NH molecule. In the gas phase it is reported to have a lifetime of 10<sup>-3</sup> seconds, which is longer than the usual lives of adsorbed molecules. Either the surface decomposition does not proceed according to the mechanism NH<sub>3</sub> = NH + H<sub>2</sub>, or due to a possibly low absorption coefficient our effective absorbing layer was too short.

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