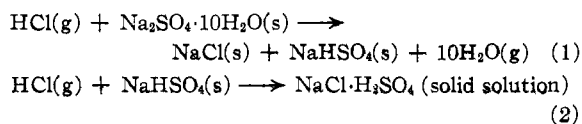


vapor we made two different types of measurements. In the first we measured the sorption of HCl gas on a $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - Na_2SO_4 mixture in the absence of protein.¹¹ We found in these experiments that the decahydrate reacted stoichiometrically and irreversibly at 25° with HCl and the sorption curves could be interpreted as corresponding to the consecutive reactions¹²



The first reaction occurs at constant pressure indicating the formation of a new phase, while the second takes place with rising pressure indicating solid solution. The region of constant-pressure sorption is very close to the pressure observed by C. and S. and it seems reasonable to thus interpret their results as arising from the reaction of HCl with the decahydrate rather than with the protein. This conclusion is not certain since C. and S. nowhere state their experimental method explicitly.

In order to then check further we performed an experiment in which the gelatin was first allowed to come to equilibrium with a constant vapor pressure of water. The side arm with decahydrate was then closed off and the sorption of HCl measured directly on this sample. The results of this experiment were similar to those found in the absence of H_2O and showed none of the characteristics reported by C. and S.

While the above experiments do not explain all of the features of the sorption processes observed by C. and S., in particular the results obtained with CO_2 and H_2S (similar to HCl) or the lengths of the isobars (with all gases) they do indicate that their results with HCl and gelatin are inconsistent with results obtained in these and other laboratories, and they indicate a probable source of the anomalies: namely, the reaction of HCl with the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - Na_2SO_4 mixtures introduced into the system to maintain constant vapor pressure of water.

(11) These experiments were done by weighing the sample *in situ* using as a balance a helical quartz spring.

(12) The H_2O in reaction 1 may be displaced as a vapor as indicated or may under some conditions be partially bound in the form of hydrates of the NaCl and/or NaHSO₄.

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Dielectric Measurement of Heptacosafuorotributylamine

BY FIELDING BROWN
RECEIVED JUNE 22, 1953

The dielectric constant and loss tangent of heptacosafuorotributylamine, $\text{C}_{12}\text{F}_{27}\text{N}$, has been measured over the temperature range of 140 to -52°. The measurements were carried out at frequencies of 60 cycles, 1000 cycles, 15 kc., 30 kc., 60 kc. and 100 kc., and the results are shown in the accompanying graph.

The liquid was measured in a cell originally

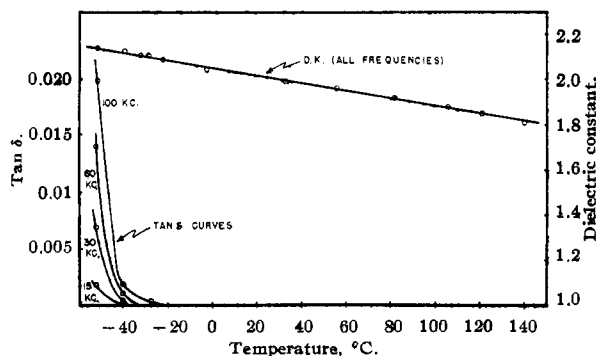


Fig. 1.—Dielectric properties of $\text{C}_{12}\text{F}_{27}\text{N}$.

described by Horsch and Berberich¹ and the values of capacity and power factor were determined by means of a General Radio 716-C bridge using generators and detectors appropriate to the frequencies in question. A General Radio 716-P2 guard circuit also was employed to balance the guard ring of the measuring cell.

The points on the dielectric constant curve are accurate to $\pm 4\%$ and those of the $\tan \delta$ curve to ± 0.00007 . As can be seen, the losses in the liquid are extremely small above -20° but rise sharply below that temperature. The values shown on the graph are further in approximate agreement with those given earlier.² Unfortunately it was not possible to carry the measurements low enough in temperature to calculate the electric moment of the molecule. Various members of this laboratory have assisted in performing the measurements.

(1) W. G. Horsch and L. J. Berberich, *Rev. Sci. Instr.*, **5**, 194 (1934).

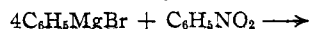
(2) Technical Report No. 57, Laboratory for Insulation Research, M. I. T.

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Reaction of Methyl *p*-Nitrobenzoate with Phenylmagnesium Bromide

BY DAVID Y. CURTIN AND JAMES C. KAUBER
RECEIVED JULY 6, 1953

Phenylmagnesium bromide has been shown to react readily with nitrobenzene to give diphenylamine as the principal product.¹



Newman and Smith,² however, have found that at -70° the reaction of *m*-nitrobenzaldehyde with phenylmagnesium bromide occurs preferentially at the carbonyl group to give *m*-nitrobenzhydrol in 77% yield.

In connection with other work, we have had occasion to examine the reaction of phenylmagnesium bromide with methyl *p*-nitrobenzoate at -70° and found it leads to *p*-carbomethoxydiphenylamine in a yield of 45% (based on Grignard reagent). None of the product to be expected from reaction at the ester carbonyl could be isolated.

(1) H. Gilman and R. McCracken, *THIS JOURNAL*, **51**, 821 (1929).

(2) M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).