

Blades¹⁶ in a later study of the thermal decomposition of vinyl isopropyl ether suggested that (A) is the correct configuration, since the products were acetaldehyde and propylene. Configuration (A)

(16) A. T. Blades, *Can. J. Chem.*, **31**, 418 (1953).

must also be the process leading to photodecomposition according to process II, since the photolysis of methyl vinyl ether does not yield ethylene, while the photolysis of *n*-butyl vinyl ether yields butene and acetaldehyde.¹⁷

In conclusion it may be mentioned that the effect of pressure on the rate of formation of ethylene in the presence of oxygen (Table I) seems to imply an excited state which may be deactivated by collisions. The scatter, however, does not allow an unambiguous decision.

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(17) E. Murad, unpublished results.

[CONTRIBUTION FROM WASHINGTON UNIVERSITY, SAINT LOUIS, MISSOURI]

Association Between Sodium and Naphthalenide Ions¹

BY N. M. ATHERTON AND S. I. WEISSMAN

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The electron spin resonance spectrum of the naphthalene negative ion in dimethoxyethane has been observed under very high resolution and improved values of the hyperfine coupling constants evaluated. It has been established that the more complex spectrum of the sodium derivative observed in tetrahydrofuran solution can be attributed to interaction with the sodium nucleus of spin 3/2. The sodium splitting is observed to be temperature dependent, and the existence of an ion-ion pair equilibrium is demonstrated. Sodium splittings were also measured in 2-methyltetrahydrofuran, tetrahydropyran and dioxane. Suggestions are made concerning a possible structure of the ion pair and the mechanism yielding spin density at the sodium nucleus.

Introduction

Over the past few years the electron spin resonance (e.s.r.) spectra of the negative ions of many aromatic compounds, formed by reaction of the compound with an alkali metal in a dry ether-type solvent, have been studied by several groups of workers. One of the most extensively studied radicals has been the naphthalene negative ion, and the interpretation of the spectrum is well established.^{2,3} The hyperfine pattern arises from interaction with the two sets of four equivalent protons, and of the 25 lines expected for such a system 17 have hitherto been resolved. The assignment of the lines was completed by measurements on α - and β -deuterated derivatives and the larger splitting shown to arise from nuclei in the α -position.^{2,3} This relatively simple pattern was obtained from the sodium, potassium and rubidium derivatives in dimethoxyethane (DME) solution and for the lithium and potassium derivatives in tetrahydrofuran (THF), but the spectrum from the sodium derivative in THF was anomalous, containing more lines than predicted for interaction with 8 protons, and the anomaly was not explained.⁴ An anomalous spectrum also was

reported for the sodium derivative in 2-methyltetrahydrofuran (Me-THF).

Recent improvements in spectrometer resolving power have made it possible to resolve all 25 lines in the "normal" spectrum and to re-measure the coupling constants. This improvement also suggested that some insight might be gained into the anomalous spectrum shown by the sodium derivative in THF and the present communication describes the results of this investigation and some analogous effects found in other solvents.

Experimental

The purification and storage of materials followed the lines already well established⁵ and the usual procedure for preparing the radical solutions was used. Absolute concentrations of radicals were determined using 1 cm. cells in a Cary recording spectrophotometer and a value of 2.20×10^3 for the extinction coefficient at 8000 Å.⁶ E.s.r. spectra were taken on a spectrometer designed by Professor J. Townsend of the Physics Department of this University. Low temperatures were achieved by boiling liquid nitrogen and streaming the cold gas past the sample tubes which were housed in a vacuum-jacketed quartz tube in the microwave cavity. The temperature was controlled by adjusting the boiling rate and, measured by a copper-constantan thermocouple, could be held constant to 1° over periods longer than that required to record a single spectrum.

Results and Discussion

Hyperfine Couplings in the Naphthalene Negative Ion.—In DME solution the sodium derivative

(1) This work has been supported in part by the U. S. Air Force under Contract and in part by an equipment loan contract with ONR. Acknowledgment is also made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

(2) S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

(3) T. R. Tuttle, R. I. Ward and S. I. Weissman, *J. Chem. Phys.*, **5**, 189 (1956).

(4) T. R. Tuttle, Ph.D. Thesis, Washington University, 1957.

(5) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(6) D. E. Paul, Ph.D. Thesis, Washington University, 1957.

has yielded a completely resolved 25-line spectrum, as expected for coupling to two sets of four equivalent protons (Fig. 1-a). Identical spectra were obtained from the potassium derivative in THF and dioxane solutions. The magnitudes of the cou-

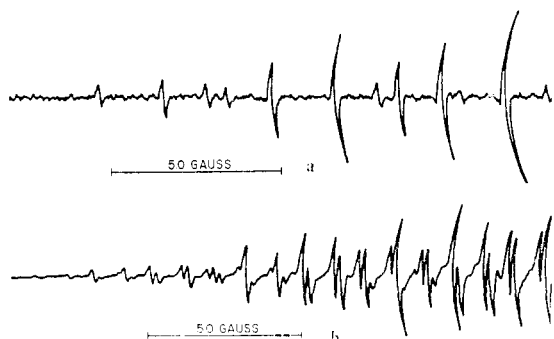


Fig. 1.—(a) dX''/dH vs. H for sodium naphthalenide in DME. (b) dX''/dH vs. H for sodium naphthalenide in THF at 295°K.

pling constants are 4.95 gauss for the α -protons and 1.865 gauss for the β , with an accuracy of $\pm 3\%$ for each. These values are in closer agreement with the ratio of the spin densities calculated from Hückel molecular orbital theory than those previously obtained.^{2,3} The spectra of naphthalenes deuterated in one α and one β position have also been measured, and it is found that the couplings to the deuterons are just those expected for spin densities corresponding to those above but multiplied by a factor of the ratio of the nuclear magnetic resonance frequencies of the deuteron to the proton.

The Spectrum of the Sodium Derivative in THF.—Fig. 1-b clearly shows that in THF at 22.5° each line of the naphthalene negative ion spectrum is further split into four lines of equal intensity, the magnitude of the splitting being 1.05 ± 0.03 gauss. Such a splitting can come only from an interaction with the sodium nucleus of spin 3/2. On cooling the solution the sodium splitting decreased, in the manner shown in Fig. 2, being less than one-third the total line width of the unsplit spectrum at -70° , at which temperature the spectrum corresponds exactly to that of Fig. 1-a, *i.e.*, the ion in DME. At intermediate temperatures the spectrum was a superposition of the "normal" and "split" forms, the contribution of the "normal" form increasing with decreasing temperature. This clearly indicates the existence of two distinct radical species in the solution. The species responsible for the split spectrum is certainly an ion pair, *i.e.*, it contains sodium, and the one responsible for the normal spectrum is probably the dissociated naphthalene ion. Measurements of electrical conductivity by Hoijtink⁷ and his collaborators are in accord with the latter assignment. All phenomena are reversible, the spectrum of a particular solution being dependent only on its concentration and temperature.

It is suggested, therefore, that there is in fact an equilibrium between a sodium ion-naphthalene

(7) G. J. Hoijtink, private communication.

negative ion-ion pair and a completely dissociated state, and from now on it will be convenient to talk of "ion-pairing."

Further evidence for the existence of such an equilibrium was found by successive dilution of a sample in THF at room temperature (22.5°) when, at concentrations less than $10^{-3} M$, the spectrum appears as a superposition of the two forms, the relative intensity of the unsplit component increasing with decreasing total concentration.

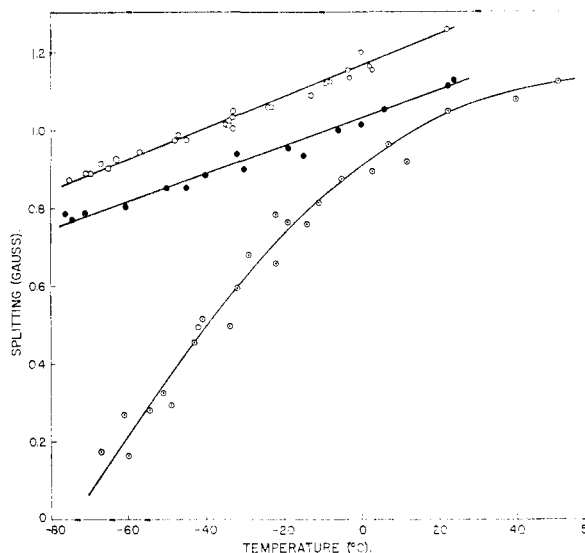


Fig. 2.—Hyperfine coupling constant with sodium versus temperature: open circles, in THP; solid circles, in MeTHF; dotted circles, in THF.

The variation of relative intensities with concentration was in agreement with the expectations for a simple dissociation process, but because of the limited range over which the measurements could be carried out, more complex equilibria cannot be excluded.

A series of measurements in mixtures of DME and THF again indicated that there existed a concentration dependent ion-ion pair equilibrium but that the sodium splitting varied with the mole fraction of THF. In general, the line widths appeared broader in such solutions, the effect being much stronger at high proportions of DME, so that spectra taken in that region were very ill-resolved. The decrease in splitting with decreasing mole-fraction of THF appears linear down to about 0.4 mole-fraction, but below this the broadening makes the splittings difficult to measure accurately, so that one cannot confidently extrapolate to zero sodium splitting for the ion pair in pure DME.

The breadths of the lines yield information concerning the rates of some of the processes in which the species might participate. Since the spectra of the ion pairs and the dissociated ions are distinct, the frequency of conversion of one to the other must be less than the changes in frequency of the e.s.r. lines which would accompany the conversion. In this region of "slow exchange" the breadths of the individual lines set lower limits on the life-

times of the species to which they belong: the mean lifetimes can be no shorter than the reciprocal of the breadths. In the spectra recorded here the line breadths are about 10^6 radians per second and the corresponding mean lifetimes are greater than 10^{-6} second. This estimate is unrealistic since it includes the possibility of the entire line breadth arising from the association-dissociation process. Since the lines are not significantly broader than those of similar radicals in which association does not occur, it is likely that the lifetimes are longer than 10^{-5} second.

It should be noted that each of the two species which is long-lived relative to conversion into the other may itself experience rapid processes which lead to sharply averaged spectra. An ion pair may undergo rapid transitions between various of its vibrational states to yield an averaged spectrum. The variation of sodium coupling constant with temperature will be ascribed to such averaging with mean lifetime of the individual vibrational states shorter than 10^{-9} second.

Spectra in other Solvents.—The sodium reduced naphthalene negative ion also was prepared in solution in tetrahydropyran (THP), 2-methyltetrahydrofuran (MeTHF) and dioxane, and all showed sodium splittings and ion-ion pair equilibria. The room temperature values of the splittings are shown in Table I, and the variations with temperature for THF, Me-THF and THP are included in Fig. 2. Owing to the high freezing point of dioxane the splitting could not be followed below 12° , but in the range 12 – 55° it was seen to be increasing slowly.

TABLE I
SUMMARY OF DATA

Solvent	Sodium coupling at 300°K . (gauss)	ΔH of dissociation (kcal. per mole)
THF	1.05 ± 0.03	-7.5 ± 1.5 -2.0
THP	$1.26 \pm .03$	-2.6 ± 1.5
Dioxane	$1.27 \pm .03$
MeTHF	$1.115 \pm .03$	4.7 ± 2.0
Proton splittings in $\text{C}_{10}\text{H}_8^-$	$\alpha = 4.95$ $\beta = 1.865$	$\pm 3\%$

No matter what variations of solvent or temperature were effected, the couplings to the α and β protons were always constant to within the limits of error already quoted.

There are two main features of the observations which require explanation, one of more chemical interest, the other perhaps of more physical. The former is the maintenance of an equilibrium between ion pairs and dissociated ions, the latter is the existence of spin density at the sodium nucleus in an ion pair. It is evident that solvation is a governing factor.

The concept of ion pairing is well established, and Warhurst⁸ has found direct evidence for its occurrence on systems similar to those considered here: dioxane solutions of aromatic ketyls. Work

in this Laboratory has uncovered e.s.r. evidence similar to that presented here for ion pairing in the ketyls, and Hoijtink,⁹ studying electron transfer reactions, finds evidence for ion pairing in THF but not in DME. Hoijtink discusses ion pair formation in relation to solvation and finds the former is reduced at lower temperatures.

Thermodynamic Quantities.—Estimates of the enthalpy of dissociation were made from the measurements of the dependence of relative concentrations on temperature. Under the assumption of a simple dissociation $\text{N}^-\text{Na}^+ = \text{N}^- + \text{Na}^+$, the ratio Γ of split (ion pair) to unsplit (dissociated ions) intensities is related to the equilibrium constant K and the total concentration A by $\Gamma^2 + \Gamma = A/K$. The variable Γ is useful since it is directly measured from the spectra. From plots of $\log(\Gamma^2 + \Gamma)$ against $1/T$ the enthalpy of dissociation may be obtained. Typical plots of $\log(\Gamma^2 + \Gamma)$ against $1/T$ for solution in THF and in MeTHF are shown in Figs. 3 and 4. The principal source of error in making the measurements is in estimating the relative intensities of the two types of spectra from the derivative curves, since there is often considerable overlap of the lines.

From such plots measurements of the ΔH values for solutions in THF, THP and Me-THF were made, and the mean values of several experiments are shown in Table I. An attempt was made to measure ΔH for dioxane solution in the range 12 – 55° , but at the higher temperatures the rate of decomposition of the radical was so rapid that the equilibrium was not maintained and the relative intensity measurements were vitiated. Data between 12° and room temperature indicated that ΔH was of the same order of magnitude as the others, and one expects that the over-all features are analogous in that solvent.

From the equilibrium measurements it is possible to estimate the remaining thermodynamic quantities involved. For example, for THF at 295.5°K . with $\log(\Gamma^2 + \Gamma) = 1.88$ at $A = 1.33 \times 10^{-4} M$ the dissociation constant is 1.74×10^{-6} , $\Delta F^\circ = 7960$ cal., with $\Delta H^\circ = -7500$ cal., $\Delta S^\circ = -51.6$ e.u. Similar values were obtained from other series of measurements, and while not too much emphasis can be placed on the absolute values, the orders of magnitude are of interest.

The principal quantity of interest is the high value of ΔS ; all the systems studied showed values similar to the example quoted above. While quite large ΔS values are not infrequent in ionic solutions, the values found here are surprisingly high, at first sight, although it appears that two effects can here combine. Firstly, insofar as the sodium ion in an ion pair may be considered to be in a potential well, then within such a well one expects that there will be a large number of close lying vibrational levels available to it. Such a multiplicity of states would result in a large contribution to the entropy. Secondly, in the dissociated state the solvation of a sodium ion results in some ordering of the solvent, which represents a decrease in entropy. Such a loss in solvent entropy has been discussed by Mathias and War-

(8) D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **57**, 1375 (1955).

(9) A. Aken, J. Dieleman, and G. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).

hurst¹⁰ rationalizing a decreased value of the pre-exponential factor for reaction of mono-sodium fluorene and methyl iodide. It can be seen that in the present case the two factors combine so that the large values of ΔS are not so unreasonable as may at first seem apparent.

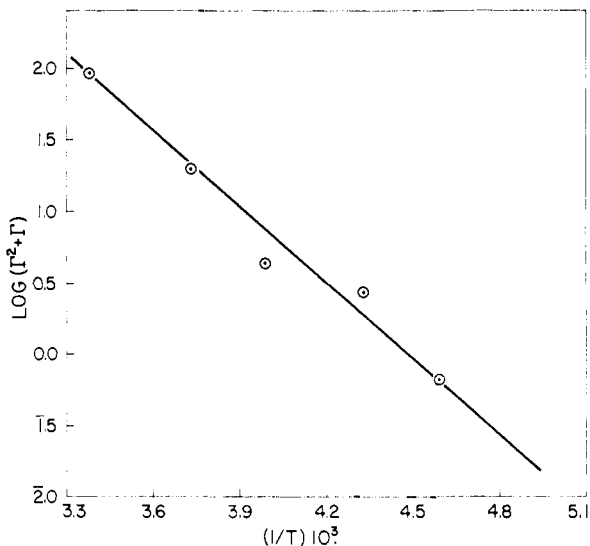


Fig. 3.— $\text{Log}(\Gamma^2 + \Gamma)$ vs. $1/T \times 10^3$ in THF.

Structure of the Ion Pair.—The observations described in the preceding pages have led us to some speculations concerning the structure of the ion pair. The term “ion pair” for the associated species is appropriate since most of its properties are well represented by the pair of weakly perturbed ions. The optical absorption spectrum and the spin distribution in the naphthalenide member of the pair are indistinguishable from those of the dissociated ion. The spin density at the sodium ion is only a few tenths of 1% of the value for a sodium atom and requires only a small departure from the unperturbed sodium ion.

We note first some of the mechanisms which could yield spin density at the sodium nucleus. A zeroth order wave function might be represented by the antisymmetrized configuration

$$(\sigma_1)^2 \dots (\sigma_n)^2 (\pi_1)^2 \dots (\pi_m)^2 \pi_{m+1} (1s)^2 (2s)^2 (2p)^6$$

where σ, \dots, σ_n are sigma orbitals of the naphthalenide ion, π_1, \dots, π_m its doubly occupied pi orbitals, π_{m+1} its singly occupied pi orbital; 1s, 2s and 2p are the orbitals of the sodium ion. The dominant term in the expectation value of the spin density

operator $\rho(r)$ is $[\pi_{m+1}(r)]^2$. At no point accessible to the sodium nucleus is the latter large enough to give the observed coupling. At places where $[\pi_{m+1}(r)]^2$ vanishes or is very small, other terms may become important. In particular, terms arising from non-orthogonality and exchange between and both 1s and 2s produce spin density at positions where the latter do not vanish.¹¹ The

(10) A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, **56**, 348 (1960).

(11) F. I. Adrian, *Phys. Rev.*, **106**, 1356 (1957)1

terms are of the form

$$\vec{S}(r_{Na}) \pi(r_{Na}) |s(r_{Na}), S^2(r_{Na})| |s(r_{Na})|^2$$

and similar ones for 2s. $S(r_{Na})$ is the overlap integral between π_{m+1} and is evaluated with the sodium nucleus at r_{Na} .

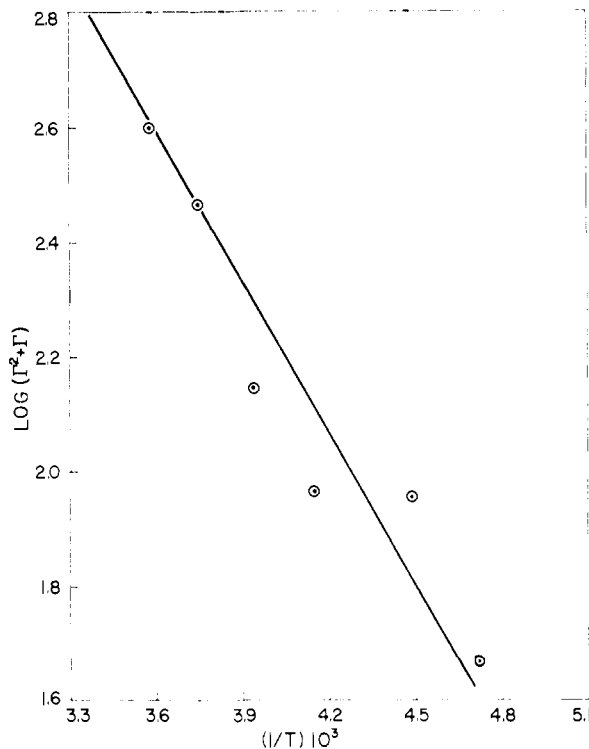


Fig. 4.— $\text{Log}(\Gamma^2 + \Gamma)$ vs. $1/T \times 10^3$ in MeTHF.

Another possible mechanism is the admixture of small amplitudes of sodium 3s function into the singly occupied orbital. (This mechanism amounts to inclusion of some covalent binding.) If the singly occupied orbital is of the form $\pi_{m+1} + \lambda(r_{Na})3s$ the new contributions to spin density $2\lambda(r_{Na})\pi(r_{Na})3s(r_{Na})$ and $\lambda^2(r_{Na})[3s(r_{Na})]^2$ have the same form as the non-orthogonality contributions.

Let $F(r_{Na})$ represent the spin density at r_{Na} arising from the mechanisms outlined above. For a state of vibrational motion of sodium relative to naphthalene represented by the wave function $\varphi_j(r_{Na})$ the contribution to spin density is

$$\rho_j = S |\varphi_j(r_{Na})|^2 F(r_{Na}) d\tau_{Na}$$

Since the observed spectra are sharp the total spin density is taken as a sharp average over ρ_j

$$\rho = \frac{\sum \rho_j \exp - \frac{W_j}{kT}}{\sum \exp - \frac{W_j}{kT}}$$

The use of this average implies rapid transitions between vibrational states. The lines are about 10^6 sec.^{-1} broad and the experiments show that the excursion in frequency is at least $5 \times 10^6 \text{ sec.}^{-1}$ per second. The frequency of exchange as esti-

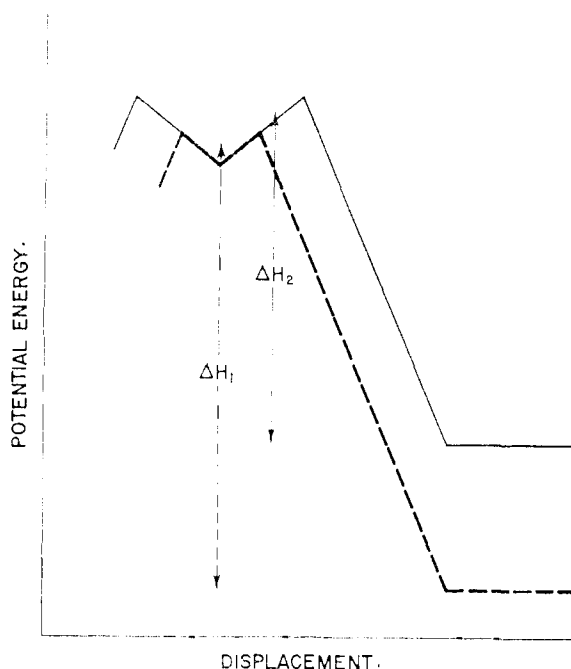


Fig. 5.—Idealized potential energy curve for displacement of sodium ion parallel to ring.

mated from the well-known formulas for exchange narrowing must be of the order 10^9 sec.^{-1} . The function $F(r_{\text{Na}})$ which gives the spin density for fixed positions of the sodium nucleus vanishes when r_{Na} lies in the plane P perpendicular to the naphthalene rings and passing through the 9 and 10 posi-

tions because of the antisymmetry of π_{m+1} relative to reflection in P . For positions of the sodium 2.5 Å. directly above the center of either of the rings numerical estimates suggest that the non-orthogonality mechanism alone provides spin density of the correct order of magnitude. Calculation of the dependence of coupling on temperature and properties of the solvent seems prohibitively difficult, but the highly idealized scheme shown in Fig. 5 seems to represent the qualitative features of the situation. The upper potential minimum corresponds to the equilibrium position of the sodium ion relative to the naphthalene in the ion pair. The displacement is parallel to the aromatic ring. The lower flat part corresponds to dissociation. For solvents in which ΔH of dissociation is large only a small range of excursion of sodium is permitted, while for those for which ΔH is small, large excursions are permitted. The diagram is thus in qualitative accord both with variations of coupling constants, with temperature, and with heat of dissociation.

The limiting value of the sodium coupling constant at low temperature in THF is very small and suggests that the equilibrium position of the sodium ion lies in the nodal plane P of the singly occupied orbital. In the other solvents it has not been possible to extend the measurements to low enough temperatures to obtain reliable limiting values of the coupling constant. The observed variations of coupling constant with temperature in the solvents other than THF is compatible either with a flat potential minimum or one displaced from the nodal plane.

The observations reported here reveal some of the potentialities of e.s.r. spectroscopy for direct demonstration of equilibria in solution. It is hoped that further work will lead to more detailed structural and kinetic information.

Acknowledgment.—Dr. R. E. Robertson carried out the computations of the sodium coupling constants. He will report his results in detail in a later publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH, PENNSYLVANIA]

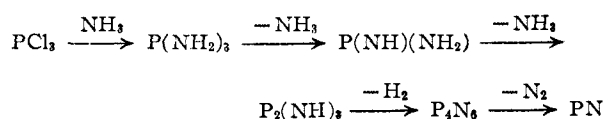
Phosphorus Nitrogen Chemistry. III. The Preparation and Properties of Phosphorus Tri-N-methylimide^{1,2}

BY ROBERT R. HOLMES

RECEIVED SEPTEMBER 6, 1960

The preparation of phosphorus tri-N-methylimide, $\text{P}_4\text{N}_6(\text{CH}_3)_6$, in high yield from the low temperature reaction of phosphorus trichloride and excess methylamine in the absence of solvent is reported, the product being the first member of a new class of phosphorus nitrogen compounds. Its reactions with methyl iodide, boron trichloride and oxygen are discussed. Physical properties indicate a cage structure analogous to phosphorus trioxide and is supported by chemical behavior. Its relation to other phosphorus nitrogen compounds is indicated.

Moureu and Wetroff³ summarized the reaction of phosphorus trichloride and ammonia by the set of equations



(1) Previous paper in the series: R. R. Holmes, *THIS JOURNAL*, **82**, 5285 (1960).

(2) Presented before the Inorganic Division at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; communication to the editor: **82**, 5509 (1960).

(3) H. Moureu and G. Wetroff, *Bull. soc. chim. (France)*, **4**, 918 (1937).