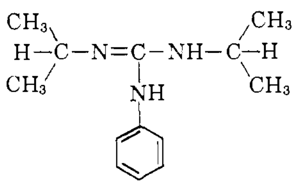
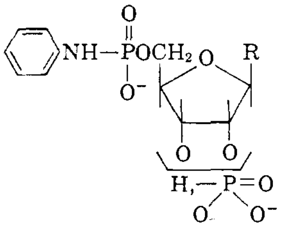
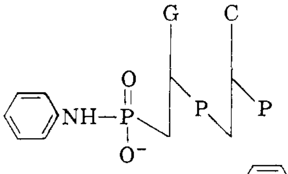


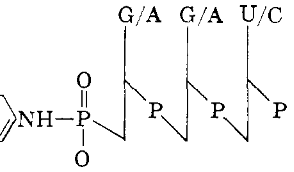
III



IV



V



VI

the 1M fraction (peak 7) probably higher homologs. Thus after alkaline hydrolysis, the guanosine compound IV (R = guanine) has been isolated from peaks 2, 3, 4, 6 and 7. The peak immediately after 2 and probably the peaks 4 and 5 as well gave the corresponding adenosine compound IV (R = adenine). The results show that at least two of the amino acid acceptor ribonucleic acid chains end in pA groups. The most significant results of this investigation have, therefore, been (1) that while predominantly the ribonucleic acid chains end in pG groups, a few probably end in pA and one or more also in pU[5] and (2) that there is hardly any common sequence after the nucleotide containing the phosphomonoester end group.

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OBSERVATION OF NH_4^+ IN THE DECOMPOSITION OF AMMONIUM ON PLATINUM

Sir:

Recent studies of catalyzed reactions in a mass spectrometer[1] have shown that this instrument is a powerful tool for the investigation of primary processes. With this instrument, direct observations may be made within a time of about one microsecond after formation of transient species such as positive and negative ions and free radicals evolving from the surface of the catalyst.

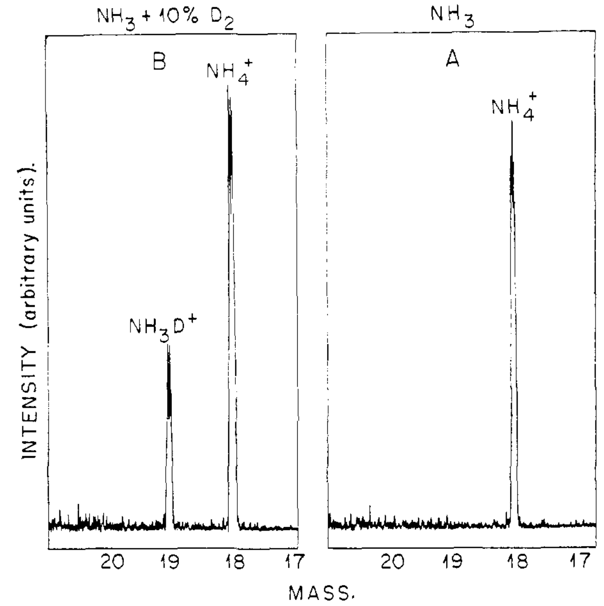

Fig. 1.—Ions released from a platinum catalyst in the catalytic decomposition of ammonia: the partial pressure of ammonia was 100 microns in both A and B and the temperature of the catalyst was 1200°. In B, 10% of deuterium was added to the system. No ionizing electrons were utilized in the production of these charged species.

We have now utilized the techniques previously discussed[1] to investigate the decomposition of ammonia on platinum in our high pressure research mass spectrometer. *The following observations were made with the hot platinum catalyst as the only source of ionization; consequently, the charged species observed must have evolved from the hot surface of the catalyst.* Ions appearing at mass 18 and believed to be NH_4^+ were observed as displayed in Fig. 1A. In order to confirm the identity of this unknown species, D_2 was added to the system and an additional species was observed at mass 19, NH_3D^+, as shown in Fig. 1B. Note that when D_2 was added to the system the NH_4^+ ion intensity remained essentially constant suggesting that the NH_3D^+ ion is formed on the catalytic surface by an independent reaction between NH_3 and D_2. Although the data in Figs. 1A and 1B were taken at a temperature of 1200°, the NH_4^+ ion was observed evolving from the catalyst at temperatures as low as 500°.

There appear to be two possible reactions of neutral species which would yield the NH_4^+ ion. One would be the reaction of an NH_3 molecule with another NH_3 molecule on the catalytic surface. If this were the source of NH_4^+, then the addition of D_2 to the system at constant NH_3 pressure (Fig. 1B) would not significantly change the total ion intensity. Since the data in Fig. 1B clearly show that more ions are formed when D_2 is added, we rule out this reaction. The second and much more likely source of NH_4^+ is the reaction of an ammonia molecule with a hydrogen molecule formed in the decomposition reaction (10 to 15% decomposition). Should this indeed be the reaction, then the addition of a small amount of D_2 to the system as is illustrated in Fig. 1B would not greatly change the rate of NH_3 decomposition and hence the H_2 concentration; therefore, the NH_4^+ ion intensity should not change greatly. This is in accord with the data. Furthermore, the D_2 would provide another neutral reactant to give rise to ions. As a further experimental test, we measured the NH_4^+ concentration as a function of H_2 pressure over a tenfold range with all other variables held constant. We found that the NH_4^+ ion intensity increased as a linear function of the H_2 pressure. Identical results were obtained for the concentration of NH_3D^+ when D_2 was substi-

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(1) Charles E. Melton, *J. Chem. Phys.*, 35, 1751 (1961).

tuted for H_2 in another experiment. Thus we believe that the reaction is between ammonia and hydrogen and gives some species of empirical composition NH_4. We observe this species as an ion, but this observation does not necessarily imply that the NH_4 species is adsorbed on the surface as an ion. Incidentally, it should be pointed out that the rate of NH_4^+ formation is dependent upon the first power of the H_2 pressure rather than $[H_2]^{1/2}$. This behavior suggests that ammonia reacts with H_2 molecules rather than atoms adsorbed on the surface.

The author is indebted to Drs. E. H. Taylor and Russell Baldock of this Laboratory and to Professor P. H. Emmett of Johns Hopkins University, a consultant to the Laboratory, for stimulating discussions during the course of this investigation.

(2) Operated for the U. S. Atomic Energy Commission by Union Carbide Corporation.

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RECEIVED FEBRUARY 3, 1962

TEMPERATURE DEPENDENCE OF PROTON HYPERFINE SPLITTINGS[1]

Sir:

We have found that the isotropic proton hyperfine splittings in the potassium toluenide electron spin resonance (e.s.r.) absorption spectrum are slightly temperature dependent in the temperature range 160 to 270° K. Although changes in individual splittings could not be followed over the whole temperature range, we have been able to estimate the change in the sum of the alkyl and para proton splittings as +1 gauss and in the sum of the meta and ortho proton splittings as −1 gauss. Proton hyperfine splittings were found to be temperature dependent in a similar degree in the case of other monoalkylbenzenides. The temperature dependence showed little variation with a change in size of the alkyl group. We have observed no such behavior of the proton splittings in the spectra of other free radical ions such as potassium benzenide, or naphthalenide.

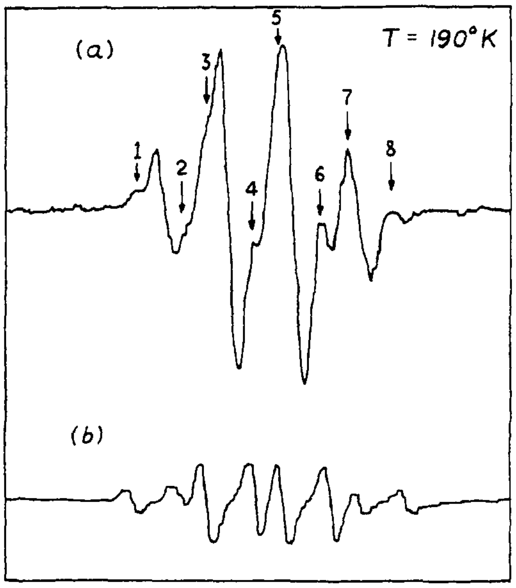

Fig. 1.—High field group of lines in the first derivative of the e.s.r. absorption spectra of (a) the 4:1 mixture of potassium *p*-deuteriotoluenide and undeuterated toluenide and (b) potassium toluenide alone. The positions of the eight lines from the toluenide are indicated by numbered arrows in (a); magnetic field decreases from left to right; solvent was 1:1 tetrahydrofuran to 1,2-dimethoxyethane.

The temperature dependence of these splittings may be understood on the basis of a thermally accessible electronic[2] excited state. Considering that transitions occur between these states at a rate rapid compared to frequency separations of hyperfine lines to be averaged, one expects to observe a spectrum which is a weighted average of the ground and excited state spectra. The supposition of a thermally accessible excited state is not unreasonable in view of the evidence for orbital degeneracy in the benzene anion.[3] Forming the indicated statistical average leads to the expression

$$\log\left(\frac{S_T - S_0}{S_1 - S_T}\right) = -\Delta E/RT \qquad (1)$$

for S_T, the value of the hyperfine splitting at temperature T. The corresponding splittings for the ground and excited states are denoted by S_0 and S_1, respectively, ΔE is the energy difference between the states and R the gas constant. The data for toluenide may be fit with ΔE between 1.5 and 2.0 kilocalories/mole and reasonable values for S_0 and S_1.

In addition to accounting for the temperature dependence of proton hyperfine splittings, equation (1) also indicates the possibility of a deuterium isotope effect resulting from differences in vibrational energies associated with the electronic states of interest in deuterated and undeuterated anions. Such an isotope effect has been observed in the case of *p*-deuteriotoluenide ion. Figure 1(a) shows the group of lines occurring at high field for a 4:1 mixture of deuterated to undeuterated toluenide.[4] The group as a whole is asymmetric indicating that the centers of the two sets of lines, one from the toluenide (indicated with numbered arrows in Fig. 1), the other from the *p*-deuteriotoluenide anion, are shifted with respect to each other. Figure 1(b) is the high field group of lines in the e.s.r. spectrum of potassium toluenide. A closer inspection of Fig. 1(a) reveals that the *p*-deuteriotoluenide lines are shifted toward high field compared to their expected positions. The complete spectrum of this mixture retains over-all inversion symmetry. The low field lines are asymmetric in the opposite sense to their counterparts at high fields and the center line has a center of inversion. Clearly, the sum of the ortho and meta

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(1) This work has been supported in part by the National Science Foundation.

(2) For simplicity the terms electronic and vibrational are used even though the Born-Oppenheimer separation may not apply.

(3) M. C. Townsend and S. I. Weissman, *J. Chem. Phys.*, **32**, 309 (1960).

(4) For an e.s.r. absorption spectrum of the toluenide ion see (a) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 498 (1961), or (b) V. V. Voevodskii, S. P. Solodovnikov and V. M. Chibrikin, *Doklady Akad. Nauk SSSR*, **129**, 1082 (1959).