several concentrations of reactants and approaching equilibrium from synthesis and degradation is 12 $\times 10^{-3}$ (moles per liter) which corresponds to the constant 11 $\times 10^{-3}$ for the argininosuccinic acid reaction.[5]

Because of its relatively high absorption in the 280 mμ region, I may be readily determined in the presence of AMP and fumaric acid. Enzymatic synthesis and degradation of I is followed spectrophotometrically at this wave length and reversibility of the reaction is easily demonstrated.

Several metabolic consequences of the reaction described[1] are apparent. AMP-S may represent an intermediate in the mechanism for incorporating the amino group in purine nucleotides. Preliminary experiments which we have conducted with inosinic acid in pigeon liver preparations lend some support to this proposal. Should the analogy of reaction[1] with argininosuccinic acid metabolism be capable of extension, a role for carbamyl amino acid precursor or co-factor of both the amino group and the C-6 carbon of purines may be implicated.

The specificity of reaction (1) is limited at present to fumaric acid, adenosine 5′-phosphate, and adenine desoxyribosyl 5′-phosphate. The latter behaves in all respects like AMP. Similar reactions are being sought for other amino purine and pyrimidine nucleotides.

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RECEIVED NOVEMBER 26, 1954

APPLICATIONS OF FIELD IONIZATION TO MASS SPECTROMETRY

Sir:

The desorption of positive ions from surfaces by high electrostatic fields was first noted by E. W. Müller, who utilized the phenomenon in the field ion microscope.[1] In a recent publication from this laboratory preliminary mass spectrometric analyses of field produced ions from a few gases were reported,[2] and the mechanism of their formation discussed.[3] This work has now been extended, and, as a consideration of Table I will indicate, promises to have interesting applications:

(1) Analysis of gas mixtures. Table I shows that parent peaks predominate in almost all cases investigated. For example, no peaks over 0.1%, except the parent ion, were observed with acetone. By contrast electron impact ionization of this gas produces 19 peaks of comparable intensity. The extreme simplicity of the spectra often permits the use of isotopic peaks for the direct determination of chemical formulas.

(2) Determination of transient intermediates in photochemical, thermal or radiation processes. For example, we are currently looking for the presence of CH_3 radicals in the photodecomposition of acetone. This application is feasible through the unique property of the field ionization source mentioned above.

TABLE I

ION YIELDS FROM VARIOUS GASES WITH A TUNGSTEN FIELD IONIZATION SOURCE

Parent gas	Ions observed[a] (primary)	Ions observed[b] (secondary)
H_2	$H^+(0.5)$, $H_2^+(0.5)$	
D_2	$D^+(0.5)$, $D_2^+(0.5)$	
O_2	$O_2^+(1.000)$	
N_2	$N_2^+(1.000)$	
C_2H_6	$C_2H_6^+(0.8)$, CH_3 (or $C_2H_6^{++}$) (0.2)	$C_2H_5^+$, $C_2H_4^+$, $C_2H_2^+$
C_2H_4	$C_2H_4^+$ (1.000)	$C_2H_3^+$, $C_2H_2^+$, C_2H^+
CH_4	CH_4^+ (1.000)	CH_3^+, CH_2^+, CH^+, C^+
CH_3COCH_3	CH_3COCH_3 (1.000)	
CH_3OH	$CH_3OH^+(0.7)$, $CH_3O^+(0.3)$	

[a] For the sake of clarity this table does not list isotopic peaks. Their magnitudes are in accord with accepted natural abundances. [b] Ions listed as secondary result from collisional or vibrational breakup of primary ions as shown by pressure dependence, peak shape and apparent fractional mass.

(3) Information about fragmentation occurring on metal catalyst surfaces. We believe that the CH_3O^+ peak observed in the case of methanol represents a substrate produced fragment. This is borne out by the observation that the CH_3OH^+ peak broadens with increasing field while the CH_3O^+ peak does not. This indicates that CH_3O^+ ions can be formed only on the surface, since broadening corresponds to ion formation farther from the tip.

While substrate induced fragmentation interferes with the analytical applications indicated under (1) and (2), it is possible to suppress this phenomenon by suitable poisoning of the tip.

The use of pulsed fields should permit identification of ions produced in the chemisorbed layer, since the diffusion of gas to the vicinity of the tip can be made negligible in the time of a pulse. Variation of pulse repetition rates should permit the determination of sticking coefficients on individual crystal faces of the tip.

Our present experimental arrangement consists of a 12″ radius of curvature direction focussing mass spectrometer equipped with an electron multiplier type of ion detector, capable of measuring currents of 10^{-19} ampere. A 30-mil hole in the screen of a field emission microscope permits a portion of the ion beam to pass into this instrument, so that the detector "sees" an area of about 900 Å.^{2} of the tip surface. A focussing field ionization source for this mass spectrometer has been designed which should greatly increase the sensitivity of the method for analytical applications.

This work was supported in part by a grant from the National Science Foundation and in part by contract with the U.S. Air Force.

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RECEIVED DECEMBER 3, 1954

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(1) E. W. Müller, Feldemission, *Ergeb. d. Exakt. Naturwiss.*, **27**, 290 (1953).

(2) M. G. Inghram and R. Gomer, *J. Chem. Phys.*, **22**, 1279 (1954).

(3) It has recently come to our notice that similar conclusions regarding mechanism were reached by: F. Kirchner, *Naturwiss.* **6**, 136 (1954), on the basis of Müller's results[1] and field induced changes in field emission patterns.